A STUDY ON THE MICELLIZATION OF ANIONIC SURFACTANTS IN THE PRESENCE OF ELECTROLYTES CONTAINING DIFFERENT CO-IONS

ABSTRACT

By

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SUBMITTED
IN FULFILMENT OF THE REQUIREMENT
FOR THE DEGREE OF
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In chapter 1 a general introduction to the present study has been given along with the scope and objective of the work.

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In chapter 4 surface tension of aqueous solutions of sodium dodecyl sulfate (SDS) in the presence of sodium chloride, sodium acetate, sodium propionate and sodium butyrate was measured as a function of SDS and electrolyte concentration at 20, 25 and 30 °C. From the surface tension data the values of cmc, surface excess, counter ion binding constant, surface area covered per molecule at the air – solution interface, and standard free energies of micellization and adsorption for SDS in the presence of electrolytes were determined. At 25 °C the values of cmc and counter ion binding constant for SDS in the presence of the electrolytes were also determined by measuring conductance and EMF of the solutions. The cmc values obtained from the surface tension, conductance and EMF data are in agreement and the co-ions are found to have no effect on the cmc of SDS. However, co-ion has an influence on the surface activity behaviour of SDS since in sodium butyrate solution above ~ 0.15 mol kg^{-1} butyrate ion concentration the nature of variation of surface excess of SDS with electrolyte concentration is different from that in sodium chloride, sodium acetate and sodium propionate solutions.

Aggregation numbers of SDS in the presence of the four electrolytes were measured at 25 °C by using the steady-state fluorescence emission method with pyrene as the probe and cetylpyridinium chloride as the quencher. In the presence of butyrate ion having concentration ≥ 0.035 mol kg^{-1} the aggregation number of SDS is found to be lower than that in the presence of chloride, acetate and propionate ions. Surface potentials of SDS micelles in the presence of the electrolytes were computed by solving the non-linearized Poission–Boltzmann equation. With added electrolyte aggregation number of SDS micelle increases whereas its surface potential decreases.

In chapter 5 critical micelle concentrations of SDS and AOT were determined at 25 °C in aqueous medium as a function of sodium salicylate (NaSa) concentration by surface tension and EMF methods. In the case of SDS conductance method was also used. Salicylate ion does not affect the cmc values of SDS and AOT when the concentration of NaSa is less than 0.03 and 0.02 mol kg^{-1}, respectively. Above these respective concentration limits of NaSa, salicylate ion is found to affect the cmc's of SDS and AOT. The values of counter-ion binding constant (β) of SDS and AOT were determined from the CH plots and the EMF data. In the presence of NaSa β for AOT has a single value equal to 0.47. The higher value of β equal to 0.8 observed earlier for AOT in NaCl, NaAc, NaPr and NaBu solutions above 0.015 mol kg^{-1} of salt concentration has not been observed in NaSa solution. In NaSa solution β

for SDS is equal to 0.56. The observed trends in the values of cmc of SDS and AOT and in the value of β of AOT are attributed to mixed micelle formation of salicylate with SDS and AOT. It is considered that the salicylate ions reside just outside the Stern layer of the anionic micelles and form ion – pairs with the sodium ions bound to the micelles. Salicylate ion does not seem to have significant influence on the surface activity of SDS and AOT. Standard free energies of micellization and adsorption of SDS and AOT in the presence of NaSa were also evaluated.

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A HUMBLE DEDICATION TO

MY MOTHER

MRS. KRIA M. UMLONG

The North Eastern Hill University

Declaration

Month: July **Year: 2006**

I, Iohborlang M. Umlong, hereby declare that the subject matter of the thesis is the record of work done by me, that the contents of this thesis did not form basis of the award of any previous degree to me or to the best of my knowledge to anybody else, and that the thesis has not been submitted by me for any research degree in any other University / Institute.

This is being submitted to the North-Eastern Hill University for the award of degree of Doctor of Philosophy in Chemistry.

Prof. R. H. Duncan Lyngdoh	**Prof. K. Ismail**	**Iohborlang M. Umlong**
Head	**(Supervisor)**	**(Candidate)**
Department of Chemistry.		

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Shillong

Dated [illegible] July, 2006

IOHBORLANG M. UMLONG

CONTENTS

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CHAPTER 1

General Introduction

1.1 Surfactants

Surfactant molecules consist of a non-polar hydrophobic portion and a polar hydrophilic portion due to which they possess amphiphilic behaviour known as hydrophobic (or solvophobic) and hydrophilic (or solvophilic) behaviours. The polar hydrophilic part of a surfactant molecule is popularly known as head group and the hydrophobic part consisting of hydrocarbon chain with eight or more carbon atoms is called the tail. There are natural surfactants, which mostly occur in biological systems and hence are also called as bio-surfactants. Phospholipids, fatty acids and bile salts are some of the examples of naturally occurring surfactants. Surfactants used for domestic and industrial purposes are mostly synthetic. Soaps and detergents are formulations containing mainly synthetic surfactants as active components. Bio-surfactants and synthetic surfactants are classified further as anionic, cationic, nonionic and zwitterionic.[1]

Anionic surfactants have the general formula RA^-M^+, where R represents the hydrophobic chain with A^- head group and M^+ is the counter ion. These surfactants when dissolved in polar solvents dissociate to give negatively charged head group and on micellization form anionic micelles. Examples of anionic surfactants are $CH_3(CH_2)_{11}SO_4^-Na^+$ (sodium dodecyl sulfate; SDS) and $RC_6H_4SO_3^-Na^+$ (sodium alkyl benzene sulfonate).

Cationic surfactants carry a positive charge on the head group. In polar solvents cationic surfactants dissociate to give positively charged surfactant moiety and negatively charged counter ions. These surfactants have the general formula RX^+Y^-. Examples of cationic surfactants are $CH_3(CH_2)_{15}N^+(CH_3)_3Br^+$ (hexadecyl trimethylammonium bromide) and $C_{16}H_{33}C_5H_4N^+Cl^-$ (cetyl pyridinium chloride).

Nonionic surfactants do not carry any electrical charge and their aggregates do not have surface charge. Some of the examples of nonionic surfactants are polyoxyethylene (23) dodecanol [brij 35], polyoxyethylene (9-10) octyl phenol [Triton X–100] and polyoxyethylene (20) sorbitan monooleate [Tween 80].

Zwitterionic surfactants possess both anionic and cationic groups on the hydrophobic moiety and depending on the pH of the solution the surfactant can behave as either anionic, cationic or neutral species. The more common zwitterionic surfactants include N-alkyl and C-alkyl betaines, phosphatidyl amino alcohols and acids.

There are also surfactant molecules that contain two hydrophobic tails attached to one head group. Examples of such surfactants are dioctyl sulfosuccinate (anionic) and dioctadecyldimethylammonium chloride (cationic). Dioctyl sulfosuccinate is commonly known as Aerosol-OT or simply AOT. Triple-chained ionic surfactants are also known.[2]

Surfactant molecules containing two head groups and two hydrocarbon chains have also been synthesized. Such surfactants are called either gemini (or dimeric) surfactants if the spacer is between the two head groups or bolaforms if the spacer is between the hydrocarbon chains.[3]

Surfactants exhibit two very important properties due to their amphiphilic character. These are (i) surface activity or adsorption at an interface and (ii) self-organisation or aggregation. Due to surface activity, surfactants are able to lower the surface tension of a solution and form monolayer, film and multilayers. Self-organisation of surfactants is responsible for the formation of aggregates like micelles, vesicles and membranes.

1.2 Thermodynamics of Lowering of Surface Tension by Surfactants – Gibbs Adsorption Isotherm

Equilibrium exists between surfactant molecules at the interface and those in the bulk solution. The change in surface Gibbs function, dG_s at constant temperature and pressure is given as

$$dG_s = \gamma d\sigma + \sum_i \mu_i dn_{i\sigma} \tag{1.1}$$

where γ is the surface tension, $d\sigma$ is the change in the area of the surface, μ_i is the chemical potential of the ith component and $dn_{i\sigma}$ is the change in the amount of the ith component at the interface. In the light of the thermodynamic principles and by using the same approach that is used for deriving Gibbs – Duhem equation, we obtain the relation

$$d\gamma = -\sum_i \Gamma_i d\mu_i \tag{1.2}$$

where $d\gamma$ is the change in the surface or interfacial tension of the solvent and $d\mu_i$ is the change in chemical potential of the ith component. Γ_i is the surface excess of the ith component and is defined as

$$\Gamma_i = n_{i\sigma} / \sigma \tag{1.3}$$

$n_{i\sigma}$ and Γ_i can be positive or negative. Equation (1.2) is known as the Gibbs adsorption isotherm. For a two- component system at constant temperature and pressure equation (1.2) reduces to

$$d\gamma = -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 \qquad (1.4)$$

Subscripts 1 and 2 refer to solvent and solute, respectively. The location of the dividing surface of the two bulk phases is arbitrarily chosen such that the surface excess concentration of the solvent, Γ_1, becomes zero. This is, in fact, the most realistic position since we are considering a surface layer of adsorbed solute. Equation (1.4) now becomes

$$d\gamma = -\Gamma_2 d\mu_2 = -RT\Gamma_2 d\ln a_2 \qquad (1.5)$$

where a_2 is the activity of solute, R is the gas constant and T is the temperature. For dilute solutions Γ_2 can be written as

$$\Gamma_2 = -\left(\frac{1}{RT}\right)\left(\frac{d\gamma}{d\ln c_2}\right) \qquad (1.6)$$

where a_2 has been replaced by the concentration, c_2. Equation (1.6) is the modified form of Gibbs adsorption isotherm for solute by presuming the solution to be ideal. Since Γ_2 is positive for surfactants, $d\gamma/d\ln c_2$ must be negative. Therefore, accumulation of surfactants on the surface or interface lowers the surface tension. In surfactant solutions the surface tension initially decreases with increasing surfactant concentration and then attains generally a constant value above a critical concentration. Due to the ability of surfactants to lower interfacial tension, they are used as emulsifiers, foaming agents, etc.

1.3 Gibbs Adsorption Isotherm for Ionic Surfactants

Since in this thesis we have studied only anionic surfactants, Gibbs adsorption isotherm given by equation (1.2) has been looked into in more detail.[4] We consider here an anionic surfactant *RM* in aqueous medium in the presence of an added electrolyte *XM*. The dissociations of *RM* and *XM* in the bulk solution are given by

$$RM \rightarrow n_{-} R^{z-} + n_{+} M^{z+} \tag{1.7}$$

$$XM \rightarrow n_{-e} X^{s-} + n_{+e} M^{s+} \tag{1.8}$$

R^{z-} is the surfactant anion having charge z_{-} and M^{z+} is the counter ion having charge z_{+}. X^{s-} is an indifferent non-adsorbing co-ion and M^{s+} is the counter ion contributed by the added electrolyte, which is considered to be the same as the surfactant counter ion. n_{-} and n_{+} are the number of moles of surfactant ion and counter ion produced by the dissociation of one mole of surfactant, respectively. Similarly, n_{-e} and n_{+e} are the number of moles of X^{s-} and M^{s+} produced by the dissociation of one mole of electrolyte, respectively. Since the counter ion M^{z+} is the same, the charges $z_{+} = s_{+}$ and $n_{-} = n_{-e}$. Let c_M, c_R and c_X be the concentrations of the ionic species M^{z+}, R^{z-} and X^{s-} in the solution, respectively. The Gibbs adsorption isotherm given by equation (1.2) can now be written in the expanded form for the solution containing *RM* and *XM* as

$$d\gamma = -RT\,[\Gamma_M d\ln c_M + \Gamma_R d\ln c_R + \Gamma_X d\ln c_X] \tag{1.9}$$

where Γ_M, Γ_R and Γ_X are the surface excess of ionic species M^{z_+}, R^{z_-} and X^{s_-}, respectively. If c and c_e are the bulk concentrations of surfactant and electrolyte, respectively, then the ion concentrations are related to the known bulk concentrations as

$$c = \frac{c_R}{n_-}, \quad c_e = \frac{c_X}{n_{-e}} \tag{1.10}$$

If Γ and Γ_e are the surface excess of the surfactant and the electrolyte, then

$$\Gamma = \frac{\Gamma_R}{n_-}, \; \Gamma_e = \frac{\Gamma_X}{n_{-e}} \tag{1.11}$$

Electro-neutrality condition gives the following relations:

$$z_+ = \frac{n_- z_-}{n_+}, \quad s_+ = z_+ = \frac{n_{-e} s_-}{n_{+e}} \tag{1.12}$$

$$c_M = n_+ c + n_{+e} c_e \tag{1.13}$$

$$z_+ c_M = s_- c_X + z_- c_R = s_- n_{-e} c_e + z_- n_- c = n_{+e} z_+ c_e + n_+ z_+ c \tag{1.14}$$

$$z_+ \Gamma_M = z_- \Gamma_R + s_- \Gamma_X \tag{1.15}$$

Substituting equations (1.10) - (1.15) into equation (1.9) and by considering the surface excess of co-ion, Γ_X, to be zero, we get after rearrangement

$$d\gamma = -RT\Gamma d \ln[c_R^{n_-} (n_+ c + n_{+e} c_e)^{n_+}] \tag{1.16}$$

For a symmetric univalent surfactant and added electrolyte, equation (1.16) takes the form

$$d\gamma = -RT\Gamma[d \ln(c + c_e) + d \ln c] \tag{1.17}$$

In the absence of an electrolyte, for surface excess of a symmetric univalent surfactant one gets from equation (1.17) an expression of the type

$$\Gamma = -\left(\frac{1}{2RT}\right)\left(\frac{d\gamma}{d\ln c}\right) \tag{1.18}$$

Equation (1.16) on differentiation and further rearrangement yields an expression for the surface excess of a surfactant in the presence of a particular concentration of an electrolyte, which is of the form

$$\Gamma = -\left(\frac{1}{RT}\right)\left(\frac{1}{n_- + \dfrac{n_+^2 c}{n_+ c + n_{+e} c_e}}\right)\left(\frac{d\gamma}{d\ln c}\right)_{c_e} \tag{1.19}$$

Thus, from the above expressions the amount of an ionic surfactant adsorbed at the air – water or air – solution interface can be quantitatively estimated. If both the ionic surfactant and the added electrolyte are 1:1 type, then $n_- = n_+ = n_{+e} = 1$ and equation (1.19) becomes

$$\Gamma = -\left(\frac{1}{RT}\right)\left(\frac{1}{1 + \dfrac{c}{c + c_e}}\right)\left(\frac{d\gamma}{d\ln c}\right)_{c_e} \tag{1.20}$$

1.4 Micelle Formation

The second important property of a surfactant is its ability to undergo aggregation. Aggregation of a surfactant in solution is commonly known as micellization and the aggregates are called micelles.[5] Hydrophobic interaction is considered to be responsible for micellization of a surfactant. Water molecules become more ordered around the hydrocarbon tail of a surfactant. Transfer of hydrophobic tails of a surfactant from bulk water into micellar phase results in positive entropy change due to disordering of the ordered water molecules around the hydrocarbon tail. The entropy generated thus in the solvent medium drives the micellization process. Micelles formed in polar solvents are called normal micelles, whereas those formed in non-polar solvents are called reverse micelles.

1.5 Micellization Parameters

Micellization of surfactants in solution always begins at a particular critical concentration known as the critical micelle concentration (cmc). When micelle is formed a sudden change in several physical properties of surfactant solutions takes place enabling us to determine experimentally values of cmc of surfactants. Normally, changes in physical properties like surface tension, conductivity, viscosity, solubilization, osmotic pressure, etc, take place over a narrow concentration range. Therefore, a precise determination of the cmc is difficult and moreover values of cmc estimated from different experimental methods may also differ to a certain extent. Thus, numerous methods are available for determining the value of cmc.[6] Tensiometry, conductometry and fluorimetry are the widely used methods. Although calorimetry is also one of the best methods to estimate cmc and energetics of micellization, the cost of the instrument is relatively much higher. Critical micelle concentration is one of the important properties of a surfactant by which its micellization behaviour is characterized. Cmc depends on the structure of surfactant and on the concentration of added electrolytes. More about the factors affecting cmc are discussed in a latter section.

Aggregation number is another important fundamental parameter concerning a micelle. It gives an idea about the size of a micelle. Similar to cmc, aggregation number also shows dependence on the structure of a surfactant and on the amount of added electrolyte.[7-14] Marked changes in the aggregation number of surfactants indicate about changes in the micellar shape. Unlike cmc, aggregation number has dependence on the surfactant concentration.[15-18] In a particular surfactant solution micelles of different aggregation number can exist.[19] Such polydispersity is generally ignored for calculation purpose and only monodispersed micelles with single aggregation number are taken into account. Aggregation number is determined using experimental techniques like quasi-elastic light scattering, small-angle neutron scattering, steady-state fluorescence quenching and time-resolved fluorescence quenching.[7-9,13,14,16,20,21]

Other related micellization parameters are thermodynamic functions (Gibbs function, enthalpy and entropy) of micellization, counter ion binding constant of ionic surfactants and surface potential of ionic surfactants. Some other parameters/properties of surfactants that are related to their micellization are Kraft temperature, cloud point and solubilization.

1.6 Structure of Ionic Micelles

Micelles have regular structures and shapes. A general structure of a regular ionic micelle formed in polar solvents[22] is shown in Fig. 1.1. An ionic micelle consists of a liquid core or interior, which is oil like, formed by the associated hydrocarbon chains. The charged head groups project out into the water phase. Similar structure of micelles exists in polar non-aqueous solvents also. In non-polar solvents the structure of micelle gets reversed. The region immediately surrounding the core is the Stern layer which contains the ionic head groups and a part of counter ions (bound counter ions). The Stern layer constitutes the inner part of the electrical double layer surrounding the micelle. The outer layer, which is a diffuse layer contains the remaining counter ions (free counter ions) and is known as Gouy-Chapman layer. The shear layer lies between the Stern and the diffuse layers. Appreciable amount of water has been reported[23,24] to penetrate into the liquid-like hydrocarbon core.

1.7 Micellar Shape

Since micelles are in dynamic equilibrium with the surfactant monomers, considering them to have rigid structures with precise shapes may be unrealistic. Hartley[25] conceived a spherical shape to micelles. Small-angle neutron scattering experiments on micellar solutions,[8,16,20,26,27] dynamic light scattering experiments and phase diagram studies support the concept of micelles having regular shapes.[7-9,16,28,29] It is assumed that micelles at concentrations closed to the critical micelle concentration are roughly spherical. The radius of a micelle cannot be greater than the stretched-out length of the surfactant molecule. Typically micelles may have average radii of 1.2 – 3 nm and can contain 20 – 100 monomers. Other proposed structures include the rod-like micelle of Debye,[30] the lamellar model of Philippoff [31] and the disk or cylindrical model of Harkins.[32] Added electrolyte has great influence on the shape of ionic micelles. As the counter ion concentration is increased, the shape of ionic micelles changes in the sequence spherical – cylindrical – hexagonal – lamellar.[7,8,29,33-35] Some of the shapes of micelles are shown in Fig. 1.2. Geometrical parameters like surface area of the head group, alkyl chain length, molecular volume of the hydrocarbon chain, etc. control the shapes adopted by micelles.[11]

1.8 Thermodynamics of Micelle Formation

The two main approaches that are employed to understand the thermodynamics of the micellization process are (i) Phase - Separaton Model and (ii) Mass - Action Model. In the phase - separation approach the micelles are considered to form a separate phase at the cmc in equilibrium with the solution phase, while in the mass - action approach micelles and unassociated monomers are considered to be in association - dissociation equilibrium. The two models merge asymptotically with increasing aggregation number. Besides these two approaches thermodynamics of small systems developed by Hill[36] has also been applied to the aggregation of solutes. Application of mass-action law to small thermodynamic systems has been assessed by Blumenfeld et al.[37] and by Sokirko.[38] The phase - separation and the mass - action models are briefly discussed below.

1.8.1 Phase – Separation Model

In this approach the micelle is treated as a separate phase although there are problems associated with the application of the phase rule to micellar phase. In order to calculate the thermodynamic parameters of micellization, appropriate standard states are to be defined first. The hypothetical standard state for the surfactant in the aqueous phase is taken to be the solvated monomer at unit mole fraction with the properties of the infinitely dilute solution. For the surfactant in the micellar state, the micellar state itself is considered to be the standard state.[39,40]

If μ_s and μ_m are the chemical potential of the unassociated surfactant in the aqueous phase and of the associated surfactant in the micellar phase, respectively, and since the two phases are in equilibrium at and above the cmc

$$\mu_s = \mu_m \quad (1.21)$$

For a non-ionized surfactant

$$\mu_s = \mu_s^0 + RT \ln a_s \quad (1.22)$$

μ_s^0 corresponds to the chemical potential at the standard state. It is assumed that the concentration of free monomers is low and this permits one to replace the activity, a_s, of surfactant monomers by its mole fraction, x_s. The above equation (1.22) is therefore written as

$$\mu_s = \mu_s^0 + RT \ln x_s \quad (1.23)$$

Since micellar phase is treated as a separate hydrocarbon phase the mole fraction of the associated surfactant in this phase is equal to one and therefore

$$\mu_m = \mu_m^0 \quad (1.24)$$

If ΔG_m^0 is the standard free energy change for transfer of one mole of surfactant from solution to micellar phase, then

$$\Delta G_m^0 = \mu_m^0 - \mu_s^0 = \mu_m - \mu_s + RT\ln x_s = RT\ln x_s \qquad (1.25)$$

Assuming that the concentration of free surfactant in the presence of micelle is constant and equal to the critical micelle concentration, we get $x_s = x_{cmc}$. Equation (1.25) therefore becomes

$$\Delta G_m^0 = RT\ln x_{cmc} \qquad (1.26)$$

In the case of ionic surfactants, ΔG_m^0 must also include the free energy change for the transfer of β moles of counter ion from its standard state in the solution phase to the micellar phase. β is the number of moles of counter ion per mole of the associated monomer in the micellar phase and is known as the counter ion binding constant. If one mole of micelle consist of n mole of surfactant and m moles of counter ion, $\beta = m/n$. n is known as aggregation number. It is also considered that the free counter ions present in the solution phase are in equilibrium with the counter ions bound to the micelle. For ionic surfactants equation (1.26) therefore modifies to

$$\Delta G_m^0 = RT\ln x_{cmc} + \beta RT\ln x_M \qquad (1.27)$$

where x_M is the mole fraction of counter ion in the solution. At the cmc when the micellar phase is just formed, in the absence of added electrolyte it can be approximated that $x_c = x_{cmc}$ and equation (1.27) becomes

$$\Delta G_m^0 = (1+\beta)\mathrm{RT}\ln x_{cmc} \qquad (1.28)$$

1.8.2 Mass – Action Model

According to this model in the case of ionic surfactants micelles are assumed to be in equilibrium with the surfactant monomer ions and counter ions. Further, it is assumed that micelles are effectively monodispersed. The equilibrium is represented as

$$nR^- + mM^+ \square A^{(n-m)-} \qquad (1.29)$$

In the above equilibrium R^-, M^+ and $A^{(n-m)-}$ represent single detergent ion, counter ion and anionic micelle, respectively. Applying the mass-action law to the above equilibrium, the corresponding equilibrium constant, *K*, can be written as

$$K = \frac{a_A}{a_R^n a_M^m} \qquad (1.30)$$

a_A, a_R and a_M are activities of the surfactant monomer, counter ion and micelle, respectively. The standard free energy of micellization per mole of surfactant monomer is given by

$$\Delta G_m^0 = -\frac{RT}{n}\ln K \qquad (1.31)$$

Substituting the value of *K* from equation (1.30), we get

$$\frac{\Delta G_m^0}{RT} = -\left(\frac{1}{n}\right)\ln a_A + \ln a_R + \left(\frac{m}{n}\right)\ln a_M \qquad (1.32)$$

Equation (1.33) can be rearranged to the form

$$\ln a_R = \left[\frac{\Delta G_m^0}{RT} + \left(\frac{1}{n}\right)\ln a_A\right] - \left(\frac{m}{n}\right)\ln a_M \qquad (1.33)$$

Near the cmc, which generally falls in the low concentration region for most of the ionic surfactants activity terms can be approximated to concentration terms and equation (1.33) becomes

$$\ln c_R = \left[\frac{\Delta G_m^0}{RT} + \left(\frac{1}{n}\right)\ln c_A\right] - \left(\frac{m}{n}\right)\ln c_M \qquad (1.34)$$

Just above the cmc, we can approximate

$$c_R \approx c_0 \text{ and } \frac{\Delta G_m^0}{RT} + \left(\frac{1}{n}\right)\ln c_A \approx \frac{\Delta G_m^0}{RT} \qquad (1.35)$$

We have denoted cmc by c_0. Equation (1.34) now becomes

$$\ln c_0 = \frac{\Delta G_m^0}{RT} - \beta \ln c_M \qquad (1.36)$$

In mole fraction units equation (1.36) can be written as

$$\ln x_{cmc} = A - \beta \ln x_M \qquad (1.37)$$

where $\Delta G_m^0 / RT$ is represented by A. Equation (1.37) is similar to equation (1.27). Equations (1.27), (1.36) and (1.37) are the different forms of the Corrin – Harkins equation.[41]

1.9 Factors Affecting the CMC of Ionic Surfactants

As mentioned above cmc is an important property of a surfactant, which reflects on its micellization behaviour. As we have seen above, cmc is related to different other micellization parameters like Gibbs function and counter ion binding. Cmc of a surfactant is affected by several factors. Cmc is dependent on the number of carbon atoms in the hydrocarbon chain of the surfactant. As the number of carbon atoms increases cmc decreases. The dependence of cmc on the number of carbon atoms beyond 16 is not very significant. Branching of the hydrocarbon chain also affects the cmc. Nature of hydrophilic group is another factor on which cmc shows strong dependence. There is a pronounced difference between the cmc of ionic and nonionic surfactants with identical hydrophobic moieties indicating the influence of hydrophilic group on cmc. The lower cmc of the nonionic surfactants are a consequence of the lack of electrical work necessary in forming the micelles. Nature of counter ion, its radius and valence, also largely affects the value of cmc of ionic surfactants.[42-48] Cmc has interesting temperature dependence.[49-55] Most of the ionic surfactants exhibit at some temperature a minimum in the cmc.[49,50,56] This property of ionic surfactants is used in the differential scanning calorimetry technique for studying the micellization behaviour of ionic surfactants.[57] With increase in pressure cmc of ionic surfactants in water show a maximum.[58-65] Added electrolytes have significant effect on the cmc of both ionic and nonionic surfactants.[42-48,66,67] The addition of electrolytes also affects other properties of surfactants like cloud point,[68-70] free energy of micellization,[66] aggregation number,[7-14] etc. Non-electrolytes like urea, amides, alcohols, etc on addition produce both increase and decrease of cmc of surfactants.[71-73]

1.10 Scope and Objective of the Present Work

Aggregation behaviour of an ionic surfactant and characteristics of ionic micelle are quantified by determining the micellization parameters, such as cmc, aggregation number, shape of micelle, counter ion binding constant at the micellar surface, surface potential at the micellar surface, thermodynamic functions (free energy, enthalpy and entropy) of micellization, etc. Similarly, adsorption behaviour of an ionic surfactant is quantified by estimating the adsorption parameters like surface excess, surface area per adsorbed molecule, free energy of adsorption, adsorption coefficient, interaction parameter, counter ion binding constant at air – water interface, surface potential at the air – water interface, etc. Both micellization and adsorption parameters of an ionic surfactant are affected by the added electrolyte. Normally, the changes that occur in the values of micellization and adsorption parameters of an ionic surfactant due to the addition of electrolytes are attributed entirely to counter ion effect. Scattered works,[74-78] however, indicate that co-ions of added electrolytes can also have influence on the micellization and adsorption parameters of ionic surfactants depending on the nature and structure of co-ion and the surfactant. The role played by co-ions on the micellization and adsorption of ionic surfactants has not been addressed properly. It is, therefore, thought worthwhile to study the effect of electrolytes on micellization and adsorption of ionic surfactants by varying the co-ions. Two anionic surfactants are taken up for investigation in this thesis, which are dioctyl sulfosuccinate (AOT) and sodium dodecylsulfate (SDS). AOT is a double-chained anionic surfactant, while SDS is a single-chained anionic surfactant. The electrolytes used are sodium chloride, sodium acetate, sodium propionate, sodium butyrate, sodium salicylate and trisodium citrate. Surface tension, conductance, EMF and steady-state fluorescence quenching methods are used for determining some of the micellization and adsorption parameters. The experimental results are presented in chapters 3 - 6.

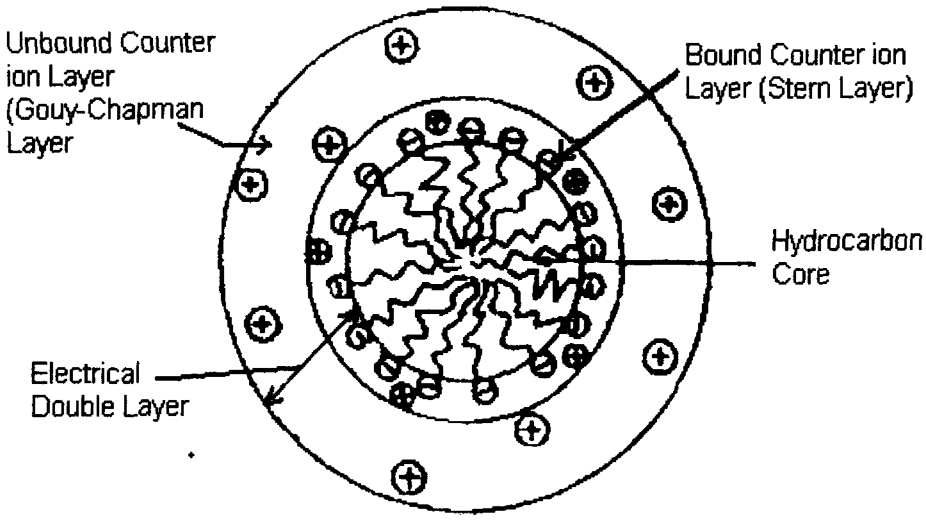

Figure 1.1 - A schematic representation of a spherical ionic micelle showing bound counter ions and the electrical double layer.

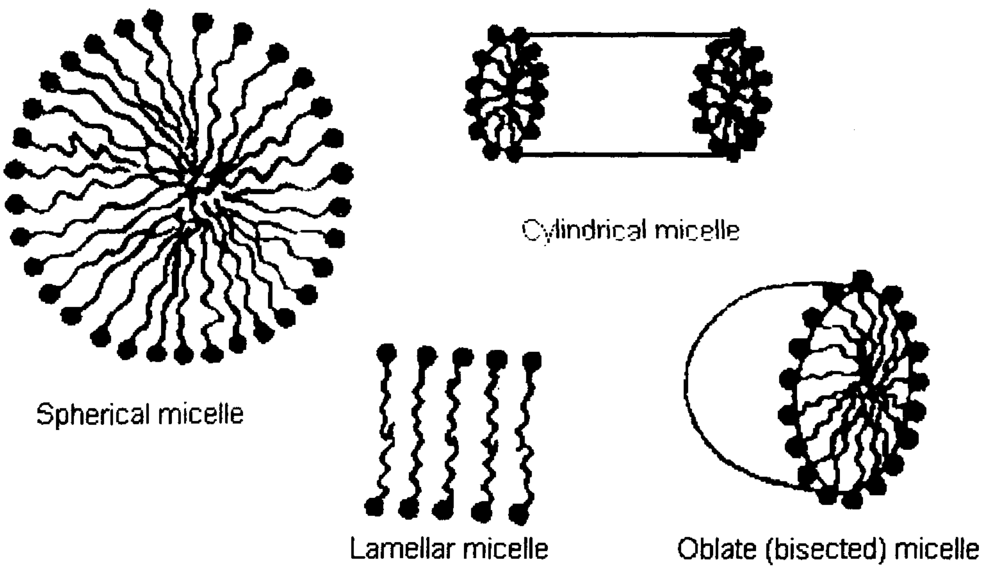

Figure 1.2 - Schematic representation of different shapes of micelles

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CHAPTER 2

Experimental Techniques

2.1 Surface Tension Measurement

Surface tension measurements were made using a K11 Krüss Tensiometer. This instrument determines the surface tension with the help of an optimally wettable probe suspended from a precision balance. The probe is either a ring or a plate. We used here a plate known as Wilhelmy plate method. A height-adjustable sample carrier is used to bring the liquid or solution in the sample vessel into contact with the plate. A force acts on the balance as soon as the plate touches the liquid surface. If the length of the plate is known, the force measured can be used to calculate the surface tension using the following relation

$$\gamma = \frac{F}{L\cos\theta} \tag{2.1}$$

where γ is the surface tension, F is the force acting on the balance, L is the wetted length of the plate and θ is the contact angle. The plate is made of roughened platinum and is optimally wetted so that the contact angle is virtually 0° such that $\cos\theta$ has a value of approximately 1. A schematic diagram of the Wilhelmy plate method is shown in Fig. 2.1. The K11 tensiometer is first calibrated using the prescribed method described in the instrument's manual. By calibrating the tensiometer, actually the force measuring balance is calibrated. For calibration the supplied 1g weight is used which gives an equivalent surface tension of 243.95 mN m^{-1} according to equation (2.1) since the length of the plate, $L = 0.0402$ m.

Before every use, the plate is first rinsed with acetone to remove any organic material sticking to the plate and thereafter washed with double-distilled water. Finally, the plate was heated to red hot with a Bunsen burner and then cooled.

The recommended sample vessel made up of Corning glass was used for holding the liquid or solution. This sample vessel is also cleaned thoroughly with acetone and water. The dry sample vessel is also flamed off with a Bunsen burner to make it free from any surface-active substance. The solution is taken in the cooled sample vessel up to the recommended height. The sample vessel containing the solution is then placed in the steel jacket of the tensiometer. The steel jacket is maintained at the required temperature using Haake DC 10 circulation bath. The supplied temperature sensor senses the temperature of the solution. The recommended immersion speed, search speed and immersion depth were selected. The entire operation of the tensiometer is controlled by the microprocessor. The instrument is attached to a PC and the surface tension values are displayed on the monitor screen. Ten surface tension values taken at an interval of 1 second and an average of these values were displayed on the screen. This particular tensiometer has a resolution of 0.01mN m^{-1}. The reproducibility of the measured surface tension values of the solutions was found to be within ±1 mN m^{-1}.

2.2 EMF Measurement

EMF of the test solutions were measured using Jenway 3345 Ion Meter and Jenway 924-329 combined ion-selective electrode reversible to sodium ion concentration in the solution. The principle of the Ion Meter is the same as that of a potentiometer. Before use the Ion Meter was calibrated using a standard solution of sodium chloride. This Ion Meter has a resolution of 0.1 mV and accuracy of ±0.2 mV.

2.3 Electrical Conductance Measurement

All conductance measurements were made at 1 kHz using Wayne Kerr B905 Automatic Precision Bridge. This LCR meter has 0.01 nS resolution and measures conductance with an accuracy of 0.05%. It has an averaging facility and averages 2 ('Average' 1) to 128 ('Average' 9) measurements in a time span of about 670 ms to 36 s, respectively. We have used throughout the 'Average' 9 option. The bridge works basically on the principle of Ohm's law. Matching currents are passed through the standard resistor and the solution under test. The corresponding two voltages produced, whose values depend upon the impedances at the standard resistor and the test solution, are measured, resolved and computed to give the desired information on the display. All functions of the instrument are under the direct control of a microprocessor. A dip-type conductivity cell having platinized platinum electrodes was used. The cell constant was determined using standard KCl solution.

2.4 Fluorescence Quenching Method for Aggregation Number Measurement

Pyrene has been used as a fluorescence probe and cetylpyridinium chloride as a quencher. In a homogeneous solution the Stern – Volmer equation relates the fluorescence emission intensity to the quencher concentration. Stern – Volmer equation is written as

$$\frac{I_0}{I_q} = 1 + K_{SV}[Q] \qquad (2.2)$$

I_0 and I_q are the intensities of fluorescence emission of pyrene in the absence and presence of the quencher, respectively. [Q] is the quencher concentration and K_{SV} is called Stern – Volmer constant.

In a micellar solution, pyrene and the quencher reside in the micellar phase. For quenching to take place quencher molecule and the probe molecule must reside in the same micelle. Selecting Poisson statistics to describe the distribution of probe and quencher among the micelles and assuming that intramicellar quenching rate is much faster than the rate of intramicellar fluorescence decay of the probe, in a micellar solution equation (2.2) takes the form

$$\frac{I_0}{I_q} = \exp\left\{\frac{[Q]}{[Micelle]}\right\} \qquad (2.3)$$

From equation (2.3) micelle concentration can be obtained. After obtaining micelle concentration, aggregation number, N_0, is calculated using the relation

$$N_0 = \frac{c - c_0}{[micelle]} \tag{2.4}$$

Here, steady-state fluorescence quenching is considered. The instrument used for recording fluorescence emission spectra is Hitachi F4500 FL spectrophotometer. The temperature of the sample was controlled by circulating water of required temperature from the circulation bath.

2.5 Density Measurement

Density of solutions whenever required to convert molal to molar concentration was measured using Anton Paar DMA 5000 Density Meter.

Mettler Toledo AG245 Electronic Balance was used for weighing.

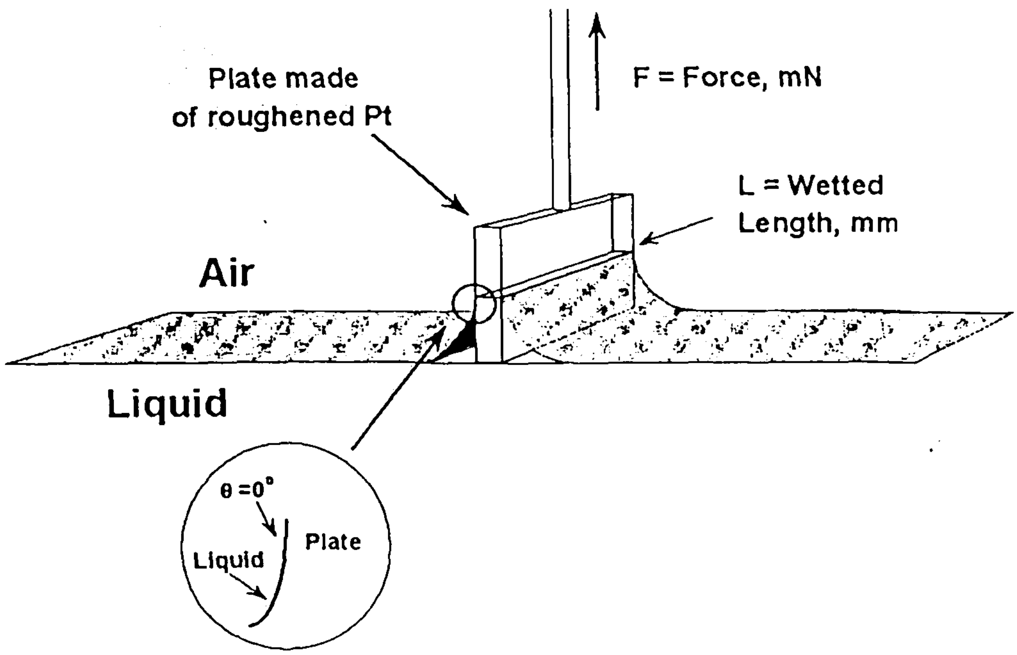

Figure 2.1 - Schematic diagram of Wilhelmy Plate

CHAPTER 3

Micellization of AOT in Aqueous Sodium Chloride, Sodium Acetate, Sodium Propionate and Sodium Butyrate Media.

3.1 Introduction

Micellization characteristics of a surfactant are understood by determining the values of its micellization parameters like critical micelle concentration (cmc), aggregation number, counter-ion binding constant, surface potential, free energy or enthalpy of micellization, etc. Micellization and hence micellization parameters are affected by several factors. One of the commonly studied factors that influence micellization of ionic surfactants is the concentration of added electrolyte. The effect of added electrolyte on micellization parameters is entirely attributed to counter-ion effect. However, scattered works do indicate that co-ion can also affect the micellization parameters. The first report on the effect of co-ion on cmc was made by Muller and Birkhahn[1]. They observed that the cmc values of the two fluorine-labeled surfactants, $CF_3(CH_2)_8COONa$ and $CF_3(CH_2)_{10}COONa$, in aqueous NaOH solution differed from their respective cmc values in NaCl solution. The effect of acetate and propionate ions on the cmc of SDS observed by us from conductance study[2] has, however, not been detected by tensiometry.[3] Ikeda et al.[4] reported that the molecular weight of sodium dodecyl sulfate micelles in aqueous solutions containing sodium salts changed in the order: NaSCN $<$ NaF $<$ NaCl $<$ NaBr $<$ NaI thereby envisaging the effect of co-ion on the aggregation number of ionic surfactants. The study made by Ranganathan et al.[5] on the dynamics of incorporation of organic co-ions into ionic micelles is indicative of co-ion – micelle interactions. Narita et al.[6] reported that the rate of cationic surfactant uptake by anionic polymer network is affected by the co-ions of the surfactant. Thus, co-ion, depending upon its nature, can produce perceivable changes in the values of micellization parameters and can also affect the solubilization process. The role played by co-ions on the micellization process of ionic surfactants has not been addressed properly and it is worthwhile to look into this aspect. Keeping this view in mind, we measured the surface tension of dioctyl sulfosuccinate (AOT) in aqueous solutions of sodium chloride, sodium acetate (NaAc), sodium propionate (NaPr), and sodium butyrate (NaBu).

6.2 Experimental

Dioctyl sulfosuccinate (Sigma ultra pure, 99 %), sodium chloride (E-Merck), sodium acetate (E-Merck), sodium propionate (Sigma), and sodium butyrate (E-Merck) were used as received. Doubly distilled water having conductance 2.1± 0.2 μS and surface tension 72 ± 0.1 mN m^{-1} at 25 °C was used throughout for making solutions. Surface tension measurements were made by Wilhelmy plate method using K11 Krüss Tensiometer. EMF measurements were made using Jenway 3345 Ion Meter and Jenway 924-329 sodium selective combined electrode. For making surface tension and EMF measurements as a function of AOT concentration, known amount of water or aqueous electrolytic solution of desired concentration was taken in the thermostated sample vessel and to this aliquots of stock solution of AOT in water or in the electrolytic solution of chosen concentration were added using a Finn pipette. After each addition of AOT solution and before recording the surface tension or EMF reading the solution mixture was stirred well and allowed to attain thermal equilibrium. Surface tension and EMF readings were found to be reproducible within ±1 mN m^{-1} and ±2 mV, respectively. It was observed that the solubility of AOT in electrolytic solution decreased as the electrolyte concentration increased. Moreover, the change in the EMF with increasing AOT concentration becomes less as the concentration of electrolyte increases. Aggregation numbers of AOT in water in the presence and absence of electrolytes were determined using the steady-state fluorescence quenching method. Pyrene (Fluka) was used as the fluorescent probe and cetylpyridinium chloride (CPC; Fluka) as the quencher. The excitation wavelength was 335 nm and the fluorescence emission intensities of pyrene were recorded at 373 and 384 nm using Hitachi F4500 FL spectrophotometer. The pyrene concentration was maintained in the range of ~1 x 10^{-6} mol dm^{-3} and the quencher concentration was varied in the range of 0 to ~8 x 10^{-6} mol dm^{-3}. All measurements were performed at 25 ± 0.1 °C using a Haake DC10 circulation bath. Density of the solutions whenever needed for converting molal concentrations to molar concentrations was measured using Anton Paar DMA 5000 density meter.

6.3 Results and Discussion

Surface tension, γ, values of AOT in the different electrolyte solutions at 25 °C are listed in Tables 3.1 – 3.4 and are also presented in Figs. 3.1 – 3.4 in the form of γ versus log$c$ plots, c is the concentration of AOT. The cmc values of AOT determined from these plots are given in Table 3.5. The variation of cmc with electrolyte concentration is depicted in Fig. 3.5. The cmc value of AOT in water is in agreement with the reported value.[7] From Table 3.5 and Fig. 3.5 it is clear that the co-ions chosen for study in this work do not have any effect on the cmc of AOT.

Surface excess values of AOT at the air-water interface near its cmc, Γ_{cmc}, in the presence of the four electrolytes were calculated from the respective surface tension data using the expression[8]

$$\Gamma_{cmc} = -\left[\frac{1}{RT}\right]\left[\frac{1}{1+\frac{c_0}{c_0+c_e}}\right]\left[\frac{d\gamma}{d\ln c}\right]_{at\ cmc} \tag{3.1}$$

where c_e, c_0, R and T represent the electrolyte concentration, cmc, gas constant, and absolute temperature, respectively. In the absence of electrolyte, i.e., for AOT in water, equation (3.1) becomes

$$\Gamma_{cmc} = -\left[\frac{1}{2RT}\right]\left[\frac{d\gamma}{d\ln c}\right]_{at\ cmc} \tag{3.2}$$

The computed values of Γ_{cmc} as a function of electrolyte concentration are given in Table 3.6. The variation of Γ_{cmc} with salt concentration is shown in Fig. 3.6. The value of Γ_{cmc} for AOT in water is found to be 1.63×10^{-6} mol m^{-2} and it is almost half the value of that reported for SDS.[9] The surface area, A_0, covered per molecule of AOT at the air-solution interface is calculated from the relation[10] $A_0 = 1/(N_A\Gamma_{cmc})$, where N_A represents the Avogadro number (Table

3.6). A_0 of AOT in the absence of electrolyte is found to be equal to 1.02 nm^2, which is nearly half the surface area covered per SDS molecule. This is expected because AOT is a double-chained surfactant. With increasing electrolyte concentration, Γ_{cmc} of AOT increases initially, reaches a maximum value, and thereafter shows a slight decreasing trend before becoming almost constant (Fig. 3.6). The maximum value of Γ_{cmc} of AOT in electrolyte solutions is found to be $(2.5 \pm 0.1) \times 10^{-6}$ mol m^{-2}. Added electrolyte thus enhances the adsorption of AOT at the air-water interface thereby decreasing the surface area coverage per molecule of AOT. Γ_{cmc} of AOT attains this maximum value at electrolyte concentrations that are equal to 0.06 ± 0.01 mol kg^{-1} of NaCl, and 0.03 ± 0.01 mol kg^{-1} of NaAc or NaPr or NaBu (Fig. 3.6). This indicates that the co-ions (anions in the present case) of electrolytes also play a role in enhancing the adsorption of AOT at the air-water interface. The effects of acetate, propionate and butyrate co-ions on Γ_{cmc} of AOT, however, appear to be almost similar. The influence of co-ions on Γ_{cmc} may be explained in the light of the fact that the enhancement of adsorption by electrolytes is due to their salting out effect and the co-ions of electrolytes due to their differential hydration, in turn, has an influence over this effect. Moreover, added electrolytes also tend to decrease the area per AOT molecule by better screening of electrostatic repulsion between the ionic heads as a result of increase in the number of counter ions in the Stern and diffuse layers.

From the cmc values of AOT in electrolyte solutions we determined the counter ion binding constant, β, by using the Corrin - Harkins (CH) equation[11]

$$\ln c_0 = A - \beta \ln [C] \qquad (3.3)$$

where $[C]$ is the concentration of the counter ion near the cmc and is taken as $c_0 + c_e$. Equation (3.3) can be derived from the mass action model for micellization.[12] The concentration terms in equation (3.3) are expressed in mole fraction / molal / molar unit. In the present case molal unit is used. The CH plot of $\ln c_0$ versus $\ln[C]$ is shown in Fig.3.7. From Fig. 3.7 it is obvious that the data lying below and above 0.015 mol kg^{-1} electrolyte concentration (c*) fall on two different straight lines thereby indicating two different β values for AOT. Since aggregation number increases with increase in the concentration of added electrolyte, β is expected to vary with $[C]$ resulting in nonlinearity of CH plot. The linearity of CH plot observed in a particular range of electrolyte concentration, however, envisages that in the presence of an added electrolyte both aggregation number and the amount of counter ion binding to the micelle increase in such a manner that β remains constant. The values of β for AOT in the four electrolyte solutions obtained from the least squares fit are listed in Table 3.7. In the light of the values given in Table 3.7, AOT can be assigned β values equal to 0.40 ± 0.04 and 0.82 ± 0.03 below and above c*, respectively. Moulik et al.[7] reported the cmc values of AOT in NaCl solution up to 0.015 mol dm^{-3} NaCl and obtained from the CH plot the value of β as 0.35, which is in given by the Nernst limit equal to 59.1 mV at 298K. a_{Na} in equation (3.5) represents the activity of sodium ion and is given by $c_{Na}\gamma_a$, c_{Na} is the concentration of sodium ion to which the ion-selective electrode responds and γ_a is its activity coefficient.

To determine the values of E_0 and $\log a_{Na}$ for AOT solution in water without the added electrolyte, two methods reported by Kale et al.[13] and Sasaki et al.[14] were used. The method of Kale et al.[13], however, did not provide acceptable values of a_{Na} above 0.001 mol kg^{-1} concentration of AOT. The method of Sasaki et al.[14] was, therefore, preferred here. In this method, the values of Λ term were first determined in the concentration region lying below 0.001 mol kg^{-1} AOT from the relation

$$\Lambda = [FE/(2.303RT)] - \log a_{Na} \qquad (3.6)$$

where F is the Faraday constant. Values of $\log a_{Na}$ required in equation (3.6) for computing Λ were obtained in the low concentration region of AOT (< 0.001 mol kg^{-1}) by using γ_a values of sodium ion calculated from the Debye-Hückel relation

$$\log\gamma_a = -0.5115I^{1/2}/[1+0.3291I^{1/2}] \qquad (3.7)$$

where I is the ionic strength of the solution and r is an ion-size parameter which we took as 5Å for sodium ion.[15] E_0 of equation (3.5) was then calculated as $[2.303RT/F]\lim_{c\to 0}\Lambda$ and its value was found to be 144.9 mV. Substituting this value of E_0 and the ideal value of N in equation (3.5) activity of sodium ion in the aqueous AOT solution in the entire experimental range of concentration was, in turn, evaluated using the expression

$$\log a_{Na} = (E - 144.9)/59.1 \qquad (3.8)$$

The values of $\log a_{Na}$ calculated in the above fashion are plotted against $\log c$ in Fig. 3.8. As in the case of E versus $\log c$ plot, $\log a_{Na}$ versus $\log c$ plot for AOT in water also exhibits change of slope at the cmc. The cmc value of AOT in water determined from Fig. 3.8 is equal to 2.75 mmol kg^{-1} which is in agreement with the value determined above from the surface tension measurement.

For determining the value of β for AOT we employed an approach similar to that reported by Gaillon et al.[16] According to this approach the experimental values of EMF for AOT solution in water can be represented by the expressions

$$E = A_1 + B_1 \log c \qquad \text{at } c < c_0 \qquad (3.9)$$

$$E = A_1 + B_1 \log[(1-\beta)c + \beta c_0] \qquad \text{at } c > c_0 \qquad (3.10)$$

From the empirical equation (3.4) we obtain the values of A_1 and B_1 as 138.3 and 57.8 mV, respectively. The value of β was then determined from equation (3.10) by using an iteration method and is found to be 0.42 for AOT in water, which is in agreement with the value derived from the CH plot.

To get the value of β for AOT in the presence of electrolytes, we measured the EMF of the solutions of AOT in the different electrolytes by choosing four concentrations of each electrolyte, two below and two above c* and these experimental values of E are given in Tables 3.9 – 3.12. The plots of EMF versus logc_t ($c_t = c + c_e$) in the four electrolytic solutions are shown in Figs. 3.9 and 3.10. The cmc values of AOT in the presence of electrolytes estimated from these plots (Figs. 3.9 and 3.10) are given in Table 3.13. Given in Table 3.13 are also the empirical values of the intercepts (A_1) and slopes (B_1) of equation (3.9) for AOT in the presence of electrolytes that were obtained by least squares fitting the E versus logc_t data lying below the respective cmc values. It is noticed that as the electrolyte concentration increases the value of B_1 also increases exhibiting more and more deviation from the Nernst limit. The values of β for AOT in the presence of electrolytes obtained from the EMF data using equation (3.10) are shown in Table 3.13. From the EMF measurements also it becomes clear that AOT has two different values of β below and above c*. For AOT in the presence of electrolytes additional breaks were observed in some of the E versus logc_t plots both below and above the cmc and at the moment it is not clear why such breaks other than that due to micellization occur.

The change in the value of β of AOT around c* may be attributed to a change in the shape of AOT micelle. This may be established by making a comparison with the β values of sodium dodecyl sulfate (SDS) in NaCl solution. Using the reported[4,17-19] values of the cmc of SDS in NaCl solutions, the CH plot was drawn and is shown in Fig. 3.11. From Fig. 3.11 it can be seen that SDS also has two values of β, 0.71 and 0.36 below and above ~0.45 mol dm^{-3} NaCl concentration, respectively. It was reported[18] that in NaCl solution above ~0.45 mol dm^{-3} concentration SDS undergoes a sphere to rod transition in the micellar shape. Thus, for SDS the β value is about 0.7 when the micelles have spherical shape and it becomes 0.36 when the micelles take up cylindrical shape. A change in the micellar shape can therefore lead to a marked and sudden shift in the value of β of a surfactant.

In order to have further insight into the change taking place in the value of β for AOT at c*, we measured the aggregation numbers, N_0, of AOT in the four electrolytic solutions by selecting 0.003, 0.009, 0.015, 0.035, and 0.065 mol kg^{-1} concentrations for each of the electrolyte. N_0 was determined using the relations[20]

$$\frac{I_0}{I_q} = \exp\left(\frac{[q]}{[micelle]}\right) \tag{3.11}$$

$$N_0 = \frac{(c - c_0)}{[micelle]} \tag{3.12}$$

I_0 and I_q are the intensities of fluorescence emission (at 373 or 384 nm) of pyrene in the absence and presence of the quencher, respectively. $[q]$ corresponds to the concentration of the quencher, which is cetylpyridinium ion. The measured values of I_0 and I_q as a function of CPC concentration are given in Tables 3.14 – 3.17. The plots of $\ln(I_0/I_q)$ versus $[q]$ for pyrene in AOT + water and in AOT + water + NaCl / NaAc / NaPr / NaBu media are presented in Figs. 3.12 –3.15. The aggregation number of AOT in water was found to be 22, which is in agreement with the reported value.[21,22] The N_0 values of AOT evaluated separately from I_0/I_q data at 373 and 384 nm were in agreement within ±1 in the absence of electrolyte and within ±5 in the presence of electrolyte. The values of N_0 of AOT obtained in the presence of electrolytes are given in Table 3.18. The main assumptions involved in this method of determining aggregation number are (i) the probe and quencher molecules follow Poisson distribution among micelles and (ii) intramicellar quenching rate is much faster than the rate of intramicellar probe fluorescence decay.[20] The intramicellar quenching rate is proportional to $(1/N_0)^p$, where p ≈ 1 for spherical micelles and >1 for elongated micelles.[20] Consequently, steady state fluorescence quenching technique is reported[23] to give lower values of N_0 especially when the micellar size becomes large (N_0 > ~100). In view of the above, although variations in the aggregation number of AOT are observed by changing the electrolyte, it is difficult to rationalize these variations as due to the effect of co-ions. Therefore, average aggregation numbers are assigned to AOT equal to 34 in the electrolyte concentration region ≤ ~0.015 mol kg^{-1} and 136 above this concentration limit. Thus, there is a clear indication of a sudden increase in the N_0 of AOT when the electrolyte concentration exceeds c*.

About the shape of AOT micelles there are conflicting reports. Sheu et al.[21] reported from SANS study that AOT forms spherical micelles near the cmc with N_0 equal to 15. By taking the radius of the sphere as equal to 12.6 Å which is the length of either of the 2-ethylhexyl succinate chains and the dry monomer tail volume as equal to 546 Å^3, Sheu et al.[21] also showed from geometric considerations that a spherical dry hydrophobic core can accommodate just 15 monomer tails of AOT. Furthermore, the study of Sheu et al.[21] revealed that N_0 of AOT increases from 20 to 31 as its concentration increases from ~0.004 to ~0.022 mol dm^{-3} and the micellar shape changes from spherical to oblate spheroid with continuously growing axial to polar radius ratio (1.15 at 0.004 to 1.64 at 0.022 mol dm^{-3} AOT). From NMR self-diffusion measurements Stilbs and Lindman[23] reported that the diffusion coefficient data for AOT micelles are not consistent with that of a spherical shaped micelle. The value of the packing parameter, $P = v/(a_0 l_c)$, for AOT is also not consistent with the value for spherical micelle.[24] In the expression for P, v is the molecular volume of the tail of a surfactant, a_0 the area of the surface of the hydrocarbon core at the micelle-solution interface (also taken as the area per head group[22]), and l_c the alkyl chain length. AOT in water is reported[22,25,26] to undergo several phase changes on increasing its concentration; from L_1 isotropic phase (< ~0.03 mol kg^{-1}) to lamellar phase to cubic phase to inverse hexagonal phase. On addition of NaCl (> ~0.26 mol kg^{-1}) an L_3 phase that is similar to a disordered cubic phase was also reported[26,27] for AOT in water.

In the light of the above information, AOT micelles in the electrolyte solutions of concentrations $\leq$ ~0.015 mol kg^{-1} may be considered to be of oblate spheroid shape. This can be substantiated by the geometrical considerations also. For instance, if we consider the axial (r_a) to polar (r_p) radius ratio as 1.5 and the polar radius as 12.6 Å, then the volume of an oblate hydrophobic core of AOT = $4\pi r_a^2 r_p/3$ = 18853 Å^3. Taking the dry monomer tail volume of AOT = 546 Å^3, we get N_0 = 35. If the ratio r_a/r_p becomes 2, then N_0 can grow up to 61. In our fluorescence spectral study, in the solution of AOT in 0.015 mol kg^{-1} electrolyte the effective sodium ion concentration ($c + c_e$) is 0.0191 mol kg^{-1} (Table 3.18) and the average N_0 corresponding to this concentration is 40 ± 7. If the effective sodium ion concentration in the AOT solutions is taken into consideration, then the aggregation numbers that are obtained in the present study for AOT in the electrolyte solutions having concentrations ≤ 0.015 mol kg^{-1} are comparable to the N_0 values obtained from SANS study by Sheu et al.[21] for AOT in water. Above c* the shape of the AOT micelles could not be established correctly based on the present work, although one expects as in the case of SDS micelles as cited above a shape change from oblate spheroid to some other non-spherical shape.

From the pyrene spectra the intensity ratio of peak 3 (384 nm) to peak 1 (373 nm), I_3/I_1, has been calculated and the values are given in Table 3.18. The term I_3/I_1 is a measure of polarity of the medium and is called the polarity index.[28,29] Above 0.015 mol kg^{-1} electrolyte concentration there is a sudden decrease in the value of the polarity index (Table 3.18), which indicates in this region of electrolyte concentration an increase in the polarity of the AOT micelle-solution interface.[28] This observation also envisages the presence of more counter ions at the interface above c*.

3.4 Conclusions

Critical micelle concentrations of AOT in water in the presence of sodium chloride, sodium acetate, sodium propionate, and sodium butyrate were determined at 25 °C from the surface tension method. The co-ions do not have any effect on the value of critical micelle concentration. The surface density of AOT at the air-water interface increases in the presence of added electrolyte and attains a maximum value of 2.5 ± 0.1 mol m^{-2} at a particular electrolyte concentration which is different for sodium chloride and the other three electrolytes. From the Corrin-Harkins plot it has been found that for AOT micelles the counter ion binding constant has values 0.40 and 0.82 below and above ~0.015 mol kg^{-1} electrolyte concentration (c*), respectively. Measurement of sodium ion activity from the EMF method has confirmed such a shift in the counter ion binding constant of AOT at c*. The higher value of counter ion binding constant for AOT has been reported for the first time. From fluorescence spectroscopy it has been found that the aggregation number of AOT is 22 in water and its average aggregation numbers in the presence of electrolytes are about 34 and 136 below and above c*, respectively. The increase by a factor of two in the counter ion binding constant is shown to be due to a change in the shape of the AOT micelles around c*. The shape of AOT micelles in the electrolyte concentration range ≤ c* is inferred to be oblate spheroid and a change from this shape appears to occur above c*. A sudden increase in the polarity of the micelle-solution interface is also observed above

3.5 References

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Table 3.1 - Surface Tension (γ) Values of AOT in Aqueous Sodium Chloride Medium at 25°C

[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}	[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}	[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0 mol kg^{-1}			
0.0123	65.0	0.9779	39.2	3.1996	30.4
0.0368	60.1	1.1700	38.8	3.3806	29.8
0.0612	57.3	1.3900	36.3	3.5703	30.1
0.0856	55.7	1.6099	34.9	3.7402	30.1
0.1100	54.1	1.8197	33.9	3.9201	29.6
0.1340	52.1	2.0300	32.9	4.0898	29.8
0.1820	50.4	2.2300	31.7	4.2599	29.3
0.2780	46.4	2.4300	31.4	4.4259	29.5
0.4210	45.3	2.6303	30.9	4.5899	29.5
0.6100	43.1	2.8197	30.6	4.7501	29.0
0.7951	41.1	3.0102	30.6	4.9797	29.4
		[NaCl] = 0.0012 mol kg^{-1}			
0.0500	53.5	1.1482	35.6	3.0488	29.7
0.1163	48.9	1.4485	34.3	3.2887	29.4
0.2483	46.3	1.7359	32.5	3.5223	29.1
0.3627	43.1	2.0148	31.3	3.7491	29.4
0.5246	40.7	2.2852	30.4	3.9703	29.3
0.6829	39.1	2.8433	29.7	4.1853	29.2
0.9031	37.4				
		[NaCl] = 0.0021 mol kg^{-1}			
0.0683	50.1	1.2343	33.9	2.6196	29.7
0.2042	44.3	1.4751	33.0	2.8283	29.4
0.3718	41.0	1.7093	32.2	3.0327	30.1
0.5363	39.0	1.9383	31.1	3.2317	29.7
0.7314	37.6	2.1614	30.2	3.4366	29.3
0.9873	35.7	2.4051	29.8	3.6168	29.5

Table 3.1 - Continued

[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}	[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}	[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0079 mol kg^{-1}			
0.0348	48.5	1.0659	31.0	2.0736	27.5
0.1043	43.2	1.3147	28.8	2.2409	27.5
0.2425	38.9	1.5572	28.3	2.4051	27.4
0.3784	36.5	1.7295	28.8	2.5664	27.5
0.5788	34.0	1.9034	28.2	2.7248	27.2
0.8088	32.2				
		[NaCl] = 0.0139 mol kg^{-1}			
0.0650	43.2	0.7235	30.4	1.4247	26.2
0.1619	38.0	0.9037	29.5	1.5088	26.8
0.2577	35.8	0.9925	29.1	1.5920	26.4
0.3526	34.3	1.0805	28.0	1.7641	26.3
0.4467	33.1	1.1677	27.5	1.8375	26.3
0.5398	32.2	1.3398	26.8	1.9179	26.2
0.6320	31.2				
		[NaCl] = 0.0197 mol kg^{-1}			
0.0691	41.1	0.6385	28.7	1.2068	26.3
0.1549	36.6	0.8359	27.4	1.2985	26.2
0.2441	34.7	0.9269	26.8	1.3891	26.1
0.3412	32.3	1.0213	26.7	1.4785	26.2
0.4413	31.1	1.1144	26.3	1.5676	26.1
0.5404	30.0				
		[NaCl] = 0.0292 mol kg^{-1}			
0.0530	41.1	0.5352	28.6	0.9641	25.7
0.1234	36.8	0.6710	27.3	1.0283	25.6
0.1933	34.3	0.7373	26.7	1.0920	25.8
0.2626	32.5	0.7690	26.4	1.1554	25.6
0.3303	31.6	0.8345	25.9	1.2182	25.4
0.4694	29.4				

Table 3.1 - Continued

[AOT] x10³/ mol kg⁻¹	γ/ mN m⁻¹	[AOT] x10³/ mol kg⁻¹	γ/ mN m⁻¹	[AOT] x10³/ mol kg⁻¹	γ/ mN m⁻¹
		[NaCl] = 0.0480 mol kg⁻¹			
0.0501	39.0	0.5059	26.6	0.8187	25.8
0.1165	35.0	0.5693	26.1	0.8803	25.6
0.1824	32.5	0.6322	25.9	0.9411	25.9
0.2480	30.6	0.6948	25.7	1.0017	25.8
0.3131	29.3	0.7571	25.7	1.0302	26.1
0.4434	27.3				
		[NaCl] = 0.0612 mol kg⁻¹			
0.0241	41.9	0.3092	28.3	0.6165	26.0
0.0561	37.7	0.3714	26.9	0.6978	25.6
0.1200	33.6	0.4332	25.3	0.7597	25.5
0.1835	31.3	0.4947	26.2	0.8223	25.8
0.2465	29.4	0.5558	25.5	0.8807	25.3
		[NaCl] = 0.0668 mol kg⁻¹			
0.0320	41.6	0.2851	28.3	0.5005	25.9
0.0640	38.0	0.3158	27.7	0.5311	25.6
0.0958	35.4	0.3468	27.1	0.5615	25.5
		[NaCl] = 0.0668 mol kg⁻¹			
0.1275	33.3	0.3778	27.3	0.5917	26.1
0.1592	32.1	0.4086	26.5	0.6219	25.5
0.1910	31.0	0.4446	26.1	0.7141	25.7
0.2221	30.1	0.4700	26.2		
		[NaCl] = 0.0788 mol kg⁻¹			
0.0158	43.9	0.1960	29.9	0.4718	25.7
0.0401	38.8	0.2584	28.4	0.5019	25.9
0.0710	35.6	0.3201	27.1	0.5081	25.7
0.1024	33.5	0.3813	25.6	0.5620	25.7
0.1337	32.9	0.4422	25.8	0.5916	25.6
0.1649	30.9				

Table 3.1 - Continued

[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}	[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}	[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0959 mol kg^{-1}			
0.0156	43.0	0.1937	28.9	0.3757	25.5
0.0390	36.2	0.2549	25.8	0.4057	25.9
0.0701	33.8	0.2849	26.1	0.4356	25.9
0.1011	32.1	0.3153	26.2	0.4350	26.1
0.1319	31.4	0.3455	26.1	0.4954	26.0
		[NaCl] = 0.1188 mol kg^{-1}			
0.0156	41.8	0.1933	28.0	0.3754	25.5
0.0389	36.4	0.2238	26.6	0.4054	25.9
0.0622	34.3	0.2544	26.2	0.4353	25.7
0.0855	33.1	0.2847	25.7	0.4652	25.6
0.1319	30.0	0.3150	25.9	0.5105	26.1
0.1626	28.9	0.3453	25.6	0.5246	25.8
		[NaCl] = 0.1869 mol kg^{-1}			
0.0026	53.4	0.1129	29.9	0.3335	25.9
0.0096	49.3	0.1448	28.5	0.3646	25.8
0.0169	45.0	0.1765	27.2	0.3957	25.6
0.0329	37.9	0.2081	26.8	0.4265	25.6
0.0489	35.3	0.2396	26.7	0.4573	25.5
0.0649	32.4	0.2710	26.4	0.4881	25.4
0.0809	31.5	0.3023	26.1		

Table 3.2 - Surface Tension (γ) Values of SDS in Aqueous Sodium Acetate Medium at 25 °C

[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}	[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}	[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}
		[NaAc] = 5.4 x 10^{-4} mol kg^{-1}			
0.0990	51.4	1.3419	36.0	3.0898	30.0
0.1961	48.8	1.6422	34.5	3.2842	30.3
0.2913	45.8	1.9228	33.4	3.4692	30.1
0.4810	43.5	2.1859	32.0	3.6444	29.5
0.6609	40.9	2.4324	31.3	3.8100	30.0
1.0198	38.5	2.8829	30.5	3.9685	29.8
		[NaAc] = 9.2 x 10^{-4} mol kg^{-1}			
0.1966	47.5	1.8430	33.1	3.0215	29.8
0.3858	43.8	2.1088	31.8	3.2190	29.9
0.5679	40.9	2.3579	30.7	3.4051	30.0
0.9293	38.2	2.5926	30.5	3.5820	29.8
1.2553	35.6	2.8134	30.2	3.7500	29.7
1.5589	34.1				
		[NaAc] = 0.0013 mol kg^{-1}			
0.0022	62.4	0.6542	39.0	3.1349	29.8
0.0134	59.1	0.8648	37.0	3.4732	29.1
0.0269	56.6	1.2751	34.8	3.8004	28.7
0.0447	53.2	1.6720	32.9	4.1184	29.0
0.0893	49.3	2.0556	31.4	4.4261	28.7
0.1779	46.7	2.4273	30.0	4.7263	28.7
0.2659	44.1	2.6081	29.8	5.2994	28.5
0.4400	41.2	2.7869	29.7		
		[NaAc] = 0.0016 mol kg^{-1}			
0.1825	45.5	1.4492	33.4	2.8140	30.2
0.3581	42.5	1.7137	32.1	2.9980	30.0
0.5274	39.3	1.9612	30.6	3.1727	29.9
0.6905	38.2	2.1940	30.2	3.3375	29.8
0.8479	37.1	2.4128	29.7	3.4948	29.8
1.1664	35.3	2.6190	29.9		

Table 3.2 - Continued

[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}	[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}	[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}
		[NaAc] = 0.0037 mol kg^{-1}			
0.0248	53.2	0.7036	36.0	2.2240	29.1
0.0577	49.2	0.8428	35.0	2.4045	29.0
0.1068	46.2	0.9769	34.1	2.5753	28.7
0.1552	44.3	1.2529	32.6	2.7367	28.8
0.2517	41.2	1.6358	30.4	2.8895	28.9
0.4094	39.1	1.8270	30.4	3.0341	28.9
0.5592	37.7	2.0316	29.2	3.1712	28.8
		[NaAc] = 0.0050 mol kg^{-1}			
0.0024	59.1	0.5979	35.4	2.1889	28.1
0.0094	54.7	0.6426	33.4	2.3830	28.2
0.0236	51.3	0.7760	32.3	2.5735	28.0
0.0471	48.4	0.9733	31.0	2.7608	27.6
0.0939	45.1	1.1672	30.4	2.9446	27.6
0.1406	42.9	1.3789	29.3	3.1256	27.8
0.2335	40.0	1.5868	28.6	3.3031	27.7
0.3256	38.9	1.7911	28.3	3.4788	27.5
0.4625	36.8	1.9917	28.0		
		[NaAc] = 0.0072 mol kg^{-1}			
0.0044	58.6	0.5246	34.4	1.8769	27.8
0.0176	52.5	0.6085	33.7	2.0264	27.6
0.0395	48.4	0.7745	32.4	2.1738	27.4
0.0745	45.1	0.9385	31.3	2.3197	27.4
0.1180	42.4	1.1001	30.3	2.4634	27.3
0.1831	40.0	1.2596	29.4	2.7455	27.3
0.2694	37.9	1.4169	28.4	3.0208	27.5
0.3550	36.6	1.5723	27.4	3.3553	27.5
0.4401	35.3	1.7256	27.6	3.6160	26.7
		[NaAc] = 0.0092 mol kg^{-1}			
0.0022	61.2	0.2648	36.6	1.6056	27.5
0.0044	58.3	0.3077	35.1	1.7584	27.2

Table 3.2 - Continued

[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}	[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}	[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}
		[NaAc] = 0.0092 mol kg^{-1}			
0.0132	53.1	0.3930	33.9	2.0579	26.9
0.0307	48.6	0.4777	32.8	2.2046	27.0
0.0569	45.9	0.6456	31.7	2.3498	27.1
0.0918	42.9	0.8108	30.7	2.6347	26.9
0.1353	41.0	1.1351	28.8	2.9122	26.9
0.1786	39.0	1.2940	27.0	3.0488	26.8
0.2218	37.8	1.4509	27.8	3.1829	26.7
		[NaAc] = 0.0124 mol kg^{-1}			
0.1550	39.6	0.9757	29.1	1.8537	26.9
0.3044	36.3	1.0966	28.5	2.0574	26.8
0.4484	33.0	1.2135	27.7	2.2342	26.4
0.5872	32.0	1.3269	27.4	2.4012	26.6
0.7212	31.2	1.4366	26.9	2.5593	26.5
0.8506	30.1	1.7484	27.1	3.1148	26.5
		[NaAc] = 0.0160 mol kg^{-1}			
0.0022	57.7	0.2836	33.4	1.4953	26.3
0.0065	54.1	0.3682	32.3	1.6479	26.2
0.0152	50.1	0.4523	31.7	1.7986	26.1
0.0282	47.2	0.6188	29.8	1.9477	25.9
0.0477	44.2	0.7421	29.0	2.0947	25.7
0.0737	42.0	0.8642	28.2	2.2394	25.7
0.0996	40.2	1.0250	27.0	2.3830	25.7
0.1340	38.8	1.1839	26.7	2.5943	25.8
0.1641	36.8	1.3407	26.5	2.8017	25.7
0.1983	35.5				
		[NaAc] = 0.0204 mol kg^{-1}			
0.0273	45.8	0.4398	31.4	1.1774	26.2
0.0722	41.3	0.5061	30.7	1.2801	26.2
0.1333	38.1	0.5690	30.0	1.3716	26.2
0.2176	35.6	0.7767	28.8	1.4536	26.2

Table 3.2 - Continued

[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}	[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}	[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}
		[NaAc] = 0.0204 mol kg^{-1}			
0.2959	34.3	0.9288	27.7	1.5277	26.1
0.3699	32.9	1.0613	27.0	1.5945	26.2
		[NaAc] = 0.022 mol kg^{-1}			
0.0023	59.3	0.2089	35.0	1.1154	26.2
0.0069	53.5	0.2493	34.0	1.2400	26.0
0.0092	51.9	0.3387	32.4	1.3637	25.8
0.0229	47.1	0.4275	30.8	1.4857	25.6
0.0594	42.3	0.5156	29.9	1.6067	25.5
0.0822	40.5	0.6032	29.0	1.7264	25.5
0.1049	39.0	0.7332	28.5	1.8447	25.4
0.1366	37.3	0.8621	28.0	1.9621	25.5
0.1683	36.0	0.9893	27.1		
		[NaAc] = 0.0740 mol kg^{-1}			
0.0024	53.2	0.1846	29.8	0.4599	25.6
0.0071	48.6	0.2309	28.6	0.5052	25.5
0.0165	43.8	0.2770	27.6	0.5502	25.5
0.0306	40.4	0.3230	26.6	0.5952	25.5
0.0540	36.8	0.3688	26.2	0.6399	25.5
0.0915	34.2	0.4144	25.8	0.6846	25.5
0.1381	31.2				
		[NaAc] = 0.1300 mol kg^{-1}			
0.0024	53.4	0.0556	34.9	0.3134	25.8
0.0073	47.3	0.0845	32.3	0.3606	25.6
0.0170	41.5	0.1230	30.0	0.4076	25.7
0.0242	39.8	0.1709	28.3	0.4544	25.6
0.0315	37.9	0.2186	26.6	0.5010	25.7
0.0436	36.5	0.2661	25.5		
		[NaAc] = 0.2000 mol kg^{-1}			
0.0024	51.4	0.0493	33.0	0.1799	25.7
0.0047	48.5	0.0587	31.3	0.1984	25.8

Table 3.2 - Continued

[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}	[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}	[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}
		[NaAc] = 0.2000 mol kg^{-1}			
0.0071	45.2	0.0728	30.0	0.2169	25.8
0.0118	42.6	0.0868	29.8	0.2354	25.7
0.0165	40.8	0.1054	28.7	0.2539	25.8
0.0212	39.6	0.1241	27.7	0.2769	25.7
0.0306	36.0	0.1427	27.1	0.2999	25.7
0.0400	34.8	0.1613	26.6		
		[NaAc] = 0.3000 mol kg^{-1}			
0.0024	51.6	0.0386	33.6	0.1057	26.9
0.0048	46.3	0.0434	32.8	0.1153	26.3
0.0097	41.7	0.0482	32.1	0.1248	25.8
0.0145	38.7	0.0578	31.0	0.1344	25.8
0.0193	37.7	0.0674	30.1	0.1439	25.9
0.0241	36.6	0.0770	29.3	0.1534	25.9
0.0289	35.5	0.0865	28.0	0.1630	25.9
0.0337	34.5				

Table 3.3 - Surface Tension (γ) Values of AOT in Aqueous Sodium Propionate Medium at 25°C

[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}	[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}	[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}
		[NaPr] = 7.9 x 10^{-4} mol kg^{-1}			
0.0095	64.9	0.6355	40.1	2.0928	31.9
0.0375	57.3	0.7009	39.6	2.2461	31.3
0.0925	52.1	0.8242	38.4	2.3764	30.8
0.1371	49.8	0.9385	37.6	2.4884	30.6
0.1807	48.3	1.0446	36.9	2.5854	30.5
0.2233	46.9	1.1435	36.3	2.6898	30.2
0.2650	46.1	1.3226	35.0	2.7793	30.1
0.3456	44.5	1.4802	33.9	2.8571	30.2
0.4227	43.4	1.6525	33.2	2.9250	30.2
0.4966	42.0	1.8019	32.4	2.9849	30.2
0.5676	40.8	1.9581	32.1		
		[NaPr] = 0.0018 mol kg^{-1}			
0.0024	65.1	0.9443	36.0	3.3322	29.4
0.0072	61.3	1.1637	34.9	3.5102	29.3
0.0144	57.4	1.3789	33.8	3.6841	29.1
0.0287	55.8	1.5905	32.9	4.0246	29.2
0.0478	53.1	1.7982	32.0	4.3544	29.2
0.1192	48.7	2.0018	31.2	4.6733	28.9
0.2138	45.9	2.2021	30.4	4.9822	28.2
0.3076	43.2	2.7818	30.0	5.2823	28.4
0.4469	41.2	2.9684	29.7	5.5722	28.3
0.5847	39.2	3.1523	29.6	5.8550	28.7
0.7658	37.5				
		[NaPr] = 0.0030 mol kg^{-1}			
0.0102	59.5	0.5511	37.1	2.1371	29.3
0.0204	56.5	0.6265	36.6	2.2281	29.2
0.0306	53.9	0.7681	36.2	2.3112	29.0
0.0507	51.7	0.8987	35.1	2.3503	28.9
0.0706	49.6	1.0196	34.2	2.3874	29.0
0.1388	46.1	1.1848	33.2	2.4907	29.0

Table 3.3 - Continued

[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}	[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}	[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}
		[NaPr] = 0.0030 mol kg^{-1}			
0.1862	44.6	1.3333	32.4	2.5818	28.9
0.2324	43.2	1.5095	31.8	2.6892	29.1
0.2864	42.2	1.6651	31.2	2.7825	28.7
0.3390	41.3	1.8027	30.5	2.8644	28.9
0.4069	39.4	1.9259	29.9	2.9365	28.5
0.4724	38.0	2.0372	29.6		
		[NaPr] = 0.0050 mol kg^{-1}			
0.0023	63.5	0.3588	38.6	1.7899	29.2
0.0069	59.2	0.4923	36.8	1.9473	29.0
0.0138	54.9	0.6244	35.3	2.2554	28.7
0.0276	52.2	0.7981	33.9	2.4062	28.6
0.0414	49.7	0.9692	32.7	2.5552	28.4
0.0873	46.3	1.1382	31.9	2.7023	28.5
0.1330	44.1	1.3045	31.0	2.8473	28.3
0.1785	42.3	1.4687	30.3	2.9904	28.2
0.2690	40.4	1.6305	29.6	3.1313	28.3
		[NaPr] = 0.0076 mol kg^{-1}			
0.0014	64.9	0.3511	36.8	1.4042	28.7
0.0055	58.7	0.4057	35.8	1.4782	28.4
0.0136	54.1	0.4586	35.0	1.5471	28.2
0.0271	50.2	0.5097	34.4	1.6119	28.1
0.0472	47.0	0.6072	33.2	1.6727	28.0
0.0735	45.3	0.6986	32.5	1.7299	27.9
0.0996	43.8	0.8259	31.5	1.7837	27.9
0.1252	42.3	0.9426	30.8	1.8346	27.6
0.1629	40.6	1.0499	30.4	1.8829	27.5
0.1998	39.5	1.1488	30.0	1.9285	27.4
0.2478	38.7	1.2403	29.5	1.9716	27.5
0.2945	37.9	1.3254	29.1	2.0125	27.4

Table 3.3 - Continued

[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}	[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}	[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}
		[NaPr] = 0.0104 mol kg^{-1}			
0.0013	64.5	0.2395	37.3	1.1388	28.8
0.0031	61.0	0.3054	36.1	1.1812	28.3
0.0066	56.5	0.4234	34.5	1.2660	28.1
0.0154	52.2	0.5495	33.1	1.3506	28.0
0.0327	48.2	0.6568	32.3	1.5203	28.0
0.0580	45.2	0.7828	31.1	1.6475	27.9
0.0908	42.4	0.8868	30.2	1.7743	27.5
0.1303	40.8	0.9859	29.5	1.9803	27.4
0.1682	40.1	1.0687	29.1		
		[NaPr] = 0.0273 mol kg^{-1}			
0.0003	62.6	0.1954	34.3	0.8495	26.2
0.0013	60.1	0.2456	32.9	0.8857	26.1
0.0032	56.0	0.2927	32.1	0.9193	26.0
0.0065	52.7	0.3371	31.2	0.9507	25.8
0.0116	49.8	0.4188	29.8	0.9799	26.0
0.0243	46.1	0.4920	29.0	1.0074	25.8
0.0368	43.8	0.5581	28.4	1.0331	25.8
0.0491	42.0	0.6180	27.8	1.0573	25.7
0.0673	40.0	0.6726	27.3	1.0801	25.6
0.0852	39.1	0.7225	26.9	1.1016	25.4
0.1141	37.1	0.7683	26.6	1.1411	25.7
0.1421	36.1	0.8105	26.4	1.1767	25.6
		[NaPr] = 0.0536 mol kg^{-1}			
0.0023	57.5	0.1450	33.1	0.5054	26.0
0.0069	51.3	0.1632	32.5	0.5408	25.8
0.0116	48.0	0.1861	31.6	0.5763	25.6
0.0162	45.9	0.2088	31.0	0.6114	25.6
0.0254	42.6	0.2315	30.5	0.6816	25.7
0.0347	41.7	0.2542	30.0	0.7166	25.7
0.0485	39.1	0.2904	29.7	0.7515	25.5

Table 3.3 - Continued

[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}	[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}	[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}
		[NaPr] = 0.0536 mol kg^{-1}			
0.0624	38.0	0.3265	28.5	0.7862	25.7
0.0762	36.0	0.3625	27.9	0.7776	25.5
0.0899	35.5	0.3984	27.3	0.8553	25.6
0.1083	34.2	0.4341	26.9	0.8897	25.5
0.1267	33.8	0.4698	26.5	0.9241	25.6
		[NaPr] = 0.0664 mol kg^{-1}			
0.0003	65.9	0.0686	36.5	0.3522	26.9
0.0010	58.8	0.0827	35.5	0.3729	26.7
0.0020	57.0	0.0964	34.9	0.3902	26.8
0.0040	52.0	0.1149	33.5	0.4076	26.5
0.0073	49.3	0.1326	32.5	0.4240	26.3
0.0105	46.9	0.1682	31.1	0.4394	26.1
0.0138	45.6	0.2009	30.5	0.4540	26.2
0.0202	43.0	0.2310	29.6	0.4678	26.2
0.0265	42.1	0.2589	28.9	0.4808	26.1
0.0358	40.2	0.2848	28.4	0.4932	26.3
0.0450	39.2	0.3088	28.0	0.5051	26.0
0.0569	37.2	0.3312	27.4	0.5163	26.1
		[NaPr] = 0.1129 mol kg^{-1}			
0.0024	54.6	0.0697	33.5	0.2267	26.8
0.0072	47.4	0.0840	32.5	0.2455	26.4
0.0120	44.8	0.1031	31.5	0.2832	25.6
0.0169	42.5	0.1127	30.6	0.3021	25.6
0.0217	41.0	0.1317	30.0	0.3209	25.6
0.0265	39.5	0.1413	29.4	0.3583	25.5
0.0361	38.1	0.1603	28.9	0.3957	25.5
0.0457	36.6	0.1698	28.5	0.4328	25.5
0.0553	35.5	0.1888	27.9	0.4700	26.6
0.0649	34.5	0.2077	27.4	0.5070	25.6

Table 3.3 - Continued

[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}	[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}	[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}
		[NaPr] = 0.1510 mol kg^{-1}			
0.0002	69.8	0.0455	35.3	0.2210	26.8
0.0005	64.5	0.0548	34.5	0.2320	26.4
0.0012	57.6	0.0745	32.6	0.2425	26.1
0.0024	53.8	0.0931	31.3	0.2525	26.0
0.0043	50.0	0.1106	30.2	0.2620	25.9
0.0067	47.4	0.1271	29.5	0.2712	25.9
0.0090	45.5	0.1427	28.0	0.2800	25.9
0.0113	44.2	0.1575	28.3	0.2884	25.8
0.0159	42.0	0.1715	27.8	0.2966	25.9
0.0205	40.7	0.1849	27.5	0.3043	25.7
		[NaPr] = 0.1985 mol kg^{-1}			
0.0023	51.0	0.0794	30.9	0.1998	25.6
0.0047	42.3	0.0887	30.0	0.2137	25.6
0.0141	41.2	0.0980	29.3	0.2274	25.9
0.0211	38.0	0.1073	29.0	0.2412	25.9
0.0281	36.9	0.1166	28.7	0.2550	25.8
0.0351	35.6	0.1305	27.2	0.2687	25.6
0.0421	34.8	0.1444	27.0	0.2825	25.9
0.0514	33.7	0.1583	26.4	0.3099	25.5
0.0608	32.6	0.1722	26.0	0.3373	25.6
0.0701	31.5	0.1860	25.8		
		[NaPr] = 0.2989 mol kg^{-1}			
0.0022	46.8	0.0401	32.3	0.1332	26.0
0.0045	44.3	0.0534	31.0	0.1464	25.8
0.0067	42.4	0.0668	29.8	0.1596	25.8
0.0112	40.1	0.0801	28.3	0.1728	25.8
0.0156	38.1	0.0934	26.9	0.1750	25.8
0.0223	36.2	0.1066	26.5	0.1816	26.0
0.0290	34.4	0.1199	26.1		

Table 3.4 - Surface Tension (γ) Values of AOT in Aqueous Sodium Butyrate Medium at 25°C

[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}	[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}	[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}
		[NaBu] = 5.1 x 10^{-4} mol kg^{-1}			
0.5319	41.5	2.4509	30.7	3.4517	29.7
1.2804	35.8	2.6310	30.3	3.6019	29.5
1.4549	34.4	2.8056	29.8	3.7474	29.4
1.9060	32.7	2.9746	30.1	3.8880	29.4
2.0727	31.9	3.1385	29.5	4.0256	29.3
2.2649	31.0	3.2978	29.7	4.1594	29.1
		[NaBu] = 0.0010 mol kg^{-1}			
0.0697	59.5	2.0774	31.2	4.2533	28.8
0.3475	48.5	2.4707	30.1	4.3815	29.1
0.5769	41.7	2.8519	28.9	4.5407	29.3
0.8917	37.7	3.2198	29.4	4.6615	29.0
1.2417	36.0	3.5754	30.0	4.7789	29.1
1.6693	33.6	3.9195	29.0	4.8924	29.0
		[NaBu] = 0.0017 mol kg^{-1}			
0.1136	47.8	1.7973	31.6	2.8578	29.0
0.2700	43.5	1.9635	30.8	2.9925	29.3
0.4666	40.8	2.1239	29.8	3.1227	29.1
0.8965	36.7	2.2800	30.1	3.2496	28.7
1.0768	35.1	2.4312	29.7	3.3731	28.8
1.0584	34.3	2.5777	29.3	3.4932	29.2
1.4492	32.9	2.7197	28.8	3.6102	29.1
1.6260	32.2				
		[NaBu] = 0.0033 mol kg^{-1}			
0.1026	46.6	0.8979	34.3	2.3385	28.8
0.2044	43.3	0.9941	33.7	2.5248	28.2
0.3055	41.4	1.1905	32.6	2.7104	28.3
0.4059	39.6	1.3824	31.4	2.8942	28.2
0.5058	38.1	1.6731	30.2	3.0770	28.0
0.6047	36.6	1.9617	29.2	3.2586	28.2
0.7031	35.9	2.1504	29.3	3.4390	28.1
0.8008	35.1				

Table 3.4 - Continued

[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}	[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}	[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}
		[NaBu] = 0.0052 mol kg^{-1}			
0.1221	43.4	1.4677	29.3	2.6744	27.6
0.3241	37.5	1.6483	28.7	2.8368	27.7
0.5223	34.8	1.8257	28.5	2.9973	28.0
0.7175	33.9	2.1728	28.1	3.1191	27.5
0.9096	32.7	2.3428	27.9	3.3100	27.6
1.0986	30.8	2.5097	27.9	3.4636	27.6
1.2845	30.0				
		[NaBu] = 0.0100 mol kg^{-1}			
0.3502	39.6	1.3531	28.4	2.1097	26.8
0.5300	35.2	1.4970	27.5	2.2534	26.7
0.7004	32.9	1.6631	27.0	2.3951	26.9
0.8678	31.4	1.8144	27.2	2.5347	26.7
1.0324	31.2	1.9630	27.1	2.6719	26.8
1.1944	29.4				
		[NaBu] = 0.0148 mol kg^{-1}			
0.1701	36.2	0.9791	27.4	1.7244	26.0
0.3374	33.1	1.1330	27.1	1.8665	26.0
0.5018	31.0	1.2845	26.6	2.0065	26.1
0.6635	29.7	1.4333	26.5	2.1440	25.9
0.8227	28.3	1.5799	26.0	2.2800	26.0
		[NaBu] = 0.0191 mol kg^{-1}			
0.1179	38.3	0.9054	27.1	1.6332	26.0
0.2343	34.6	1.0128	26.8	1.7323	25.8
0.3495	32.7	1.1193	26.5	1.7484	25.7
0.4633	30.9	1.2241	26.2	1.9281	25.7
0.5758	29.9	1.3281	26.1	2.0246	25.5
0.6870	28.9	1.4310	25.9	2.1195	25.4
0.7968	28.2	1.5326	25.8		

Table 3.4 - Continued

[AOT] x10³/ mol kg⁻¹	γ/ mN m⁻¹	[AOT] x10³/ mol kg⁻¹	γ/ mN m⁻¹	[AOT] x10³/ mol kg⁻¹	γ/ mN m⁻¹
		[NaBu] = 0.0245 mol kg⁻¹			
0.0851	38.8	0.5807	28.2	1.0523	25.6
0.1694	35.4	0.6609	27.8	1.1286	25.5
0.2531	33.2	0.7405	27.0	1.2046	25.0
0.3360	31.0	0.8195	26.2	1.2654	25.1
0.4183	30.3	0.8977	26.1	1.3544	25.2
0.4998	29.3	0.9753	25.5	1.4283	24.9
		[NaBu] = 0.0287 mol kg⁻¹			
0.0738	38.7	0.5754	28.1	1.0523	25.3
0.1470	35.2	0.6450	27.5	1.1185	25.8
0.2197	33.7	0.7141	26.9	1.1842	25.7
0.2918	31.3	0.7826	26.2	1.2498	25.4
0.3635	30.5	0.8508	25.5	1.3144	25.2
0.4346	29.4	0.9184	25.6	1.3789	25.5
0.5052	28.8	0.9864	25.4		
		[NaBu] = 0.0352 mol kg⁻¹			
0.0441	40.6	0.3048	30.7	0.7621	25.7
0.0881	37.9	0.3711	29.6	0.8395	25.6
0.1318	35.3	0.4464	28.1	0.9163	25.6
0.1754	33.2	0.5263	27.4	0.9923	25.6
0.2086	32.7	0.6055	26.2	1.0679	25.5
0.2619	32.1	0.6841	25.8		
		[NaBu] = 0.0635mol kg⁻¹			
0.0338	39.6	0.2340	29.3	0.4303	26.0
0.0674	35.9	0.2670	28.8	0.4626	25.4
0.1009	33.5	0.2999	27.3	0.4948	25.3
0.1344	32.0	0.3326	26.6	0.5269	25.6
0.1677	31.1	0.3653	26.4	0.5590	25.2
0.2009	30.3	0.3979	25.5	0.5909	25.4

Table 3.4 - Continued

[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}	[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}	[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}
		[NaBu] = 0.1659mol kg^{-1}			
0.0035	47.8	0.0928	30.2	0.2785	25.7
0.0104	42.4	0.1098	29.0	0.4814	25.5
0.0207	39.0	0.1267	28.6	0.5146	25.5
0.0311	36.4	0.1436	27.7	0.5474	25.4
0.0414	34.7	0.1775	26.6	0.5172	25.5
0.0586	32.2	0.2113	25.9	0.6131	25.4
0.0757	31.8	0.2449	25.9		
		[NaBu] = 0.2064 mol kg^{-1}			
0.0318	34.9	0.1724	25.7	0.2866	25.5
0.0555	31.7	0.1955	25.6	0.3091	25.5
0.0791	29.7	0.2184	25.8	0.3316	25.6
0.1026	28.2	0.2412	25.6	0.3539	25.4
0.1259	27.5	0.2640	25.6	0.3761	25.9
0.1492	26.6				
		[NaBu] = 0.3295 mol kg^{-1}			
0.0035	44.3	0.0743	28.5	0.1442	25.7
0.0082	39.9	0.0860	27.4	0.1557	25.4
0.0153	37.0	0.0977	26.0	0.1672	25.8
0.0272	33.7	0.1094	26.3	0.1787	25.5
0.0390	31.6	0.1210	25.7	0.1902	25.6
0.0508	30.5	0.1326	26.3	0.2017	25.4
0.0626	28.7				
		[NaBu] = 0.4987 mol kg^{-1}			
0.0018	46.2	0.0412	29.2	0.0944	26.4
0.0057	40.3	0.0590	28.3	0.1032	25.6
0.0136	35.5	0.0678	26.5	0.1120	26.5
0.0233	32.1	0.0767	26.6	0.1208	25.8
0.0322	30.6	0.0855	25.8	0.1295	26.1

Table 3.5 - Critical Micelle Concentrations (± 0.5 x 10^{-3} mol kg^{-1}) of AOT in Aqueous Electrolyte Solutions at 25 °C

[NaCl]/ mol kg^{-1}	c_0 x 10^3/ mol kg^{-1}	[NaAc]/ mol kg^{-1}	c_0 x 10^3/ mol kg^{-1}	[NaPr]/ mol kg^{-1}	c_0 x 10^3/ mol kg^{-1}	[NaBu]/ mol kg^{-1}	c_0 x 10^3/ mol kg^{-1}
0	2.66						
0.0012	2.51	5.4×10^{-4}	2.66	7.9×10^{-4}	2.59	5.1×10^{-4}	2.51
0.0021	2.29	9.2×10^{-4}	2.58	0.0018	2.44	0.0010	2.66
0.0079	1.86	0.0013	2.51	0.0030	2.18	0.0017	2.63
0.0139	1.38	0.0016	2.40	0.0050	1.88	0.0033	2.24
0.0197	1.07	0.0037	2.00	0.0076	1.73	0.0052	1.80
0.0292	0.85	0.0050	1.82	0.0104	1.33	0.0100	1.62
0.0480	0.60	0.0072	1.66	0.0273	0.95	0.0148	1.44
0.0612	0.47	0.0092	1.58	0.0536	0.55	0.0191	1.15
0.0668	0.43	0.0124	1.38	0.0664	0.42	0.0245	0.96
0.0788	0.41	0.0160	1.26	0.1129	0.31	0.0287	0.91
0.0959	0.29	0.0204	1.06	0.1510	0.24	0.0352	0.63
0.1188	0.28	0.0220	1.00	0.1985	0.16	0.0635	0.43
0.1869	0.20	0.0740	0.40	0.2989	0.12	0.1659	0.21
		0.1300	0.27			0.2064	0.17
		0.2000	0.18			0.3295	0.12
		0.3000	0.12			0.4987	0.08

Table 3.6 - Computed Values of Surface Excess (Γ_{cmc}) and Surface Area (A_0) per molecule of AOT near cmc in Different Electrolytes at 25 °C.

[NaCl] / mol kg^{-1}	Γ_{cmc} x 10^6 / mol m^{-2}	A_0 / nm^2	[NaAcl] / mol kg^{-1}	Γ_{cmc} x 10^6/ mol m^{-2}	A_0 / nm^2
	Electrolyte = NaCl			Electrolyte = NaAc	
0	1.63	1.02	5.4 x 10^{-4}	1.84	0.90
0.0012	1.93	0.86	9.2 x 10^{-4}	1.90	0.87
0.0021	1.80	0.92	0.0013	1.82	0.91
0.0079	1.85	0.90	0.0016	2.02	0.82
0.0139	2.06	0.81	0.0037	1.86	0.89
0.0197	2.15	0.77	0.0050	2.28	0.73
0.0292	2.38	0.70	0.0072	2.03	0.82
0.0480	2.40	0.69	0.0092	2.19	0.76
0.0612	2.52	0.66	0.0124	2.11	0.79
0.0668	2.49	0.67	0.0160	2.39	0.70
0.0788	2.52	0.66	0.0204	2.01	0.83
0.0959	2.21	0.75	0.0220	2.09	0.79
0.1188	2.41	0.69	0.0740	2.47	0.67
0.1869	2.30	0.72	0.1300	2.38	0.70
			0.2000	2.58	0.64
			0.3000	2.45	0.68

Table 3.6 – Continued

[NaPr] / mol kg^{-1}	Γ_{cmc} x 10^6/ mol m^{-2}	A_0 / nm^2	[NaBu] / mol kg^{-1}	Γ_{cmc} x 10^6/ mol m^{-2}	A_0 / nm^2
Electrolyte = NaPr			Electrolyte = NaBu		
0.0008	1.71	0.97	0.0005	1.75	0.95
0.0018	2.25	0.74	0.0010	2.13	0.78
0.0030	1.85	0.90	0.0017	1.70	0.98
0.0050	1.92	0.87	0.0033	1.80	0.92
0.0076	1.98	0.84	0.0052	1.80	0.92
0.0104	2.07	0.80	0.0100	2.08	0.80
0.0273	2.47	0.67	0.0148	1.80	0.92
0.0536	2.14	0.78	0.0191	2.05	0.81
0.0664	2.32	0.72	0.0245	2.23	0.74
0.1129	2.34	0.71	0.0287	2.22	0.75
0.1510	2.22	0.75	0.0352	2.58	0.64
0.1985	2.53	0.66	0.0635	2.45	0.68
0.2989	2.45	0.68	0.1659	2.40	0.69
			0.2064	2.17	0.77
			0.3295	2.24	0.74
			0.4987	2.12	0.78

Table 3.7 - Values of Counter Ion Binding Constant (β) for AOT Micelles in Aqueous Electrolyte Solutions at 25 °C Derived from Corrin-Harkins Plots ([C] represents Electrolyte Concentration in mol kg^{-1})

Electrolyte	β	
	$0 < [C] \leq 0.015$	$[C] > 0.015$
Sodium Chloride	0.39	0.82
Sodium Acetate	0.37	0.82
Sodium Propionate	0.44	0.80
Sodium Butyrate	0.38	0.85
Sodium Chloride[a]	0.35	-

[a] reported data at 20 °C [7]

Table 3.8 - EMF Values of Aqueous AOT Solution at 25°C

[AOT] x10^3/ mol kg^{-1}	EMF / mV	AOT] x10^3/ mol kg^{-1}	EMF / mV	[AOT] x10^3/ mol kg^{-1}	EMF / mV
0.1147	-88.0	1.9038	-19.7	6.7054	5.30
0.2846	-66.1	2.0962	-15.0	7.0457	6.60
0.5624	-52.2	2.2852	-14.0	7.6864	7.40
0.7797	-42.8	2.6529	-11.0	8.2779	8.10
0.8868	-38.3	3.0077	-8.80	8.8252	9.00
0.9930	-36.9	3.3506	-6.80	9.3330	9.90
1.0981	-33.2	3.8435	-3.60	10.105	10.9
1.2021	-30.3	4.3115	-1.60	10.793	11.8
1.3051	-27.0	4.7580	0.10	11.974	13.9
1.4074	-25.2	5.5902	2.00	12.946	15.0
1.5084	-23.6	5.9789	3.30	13.760	16.2
1.7082	-21.7	6.3493	4.00	23.058	24.0

Table 3.9 - EMF Values of AOT in Aqueous Sodium Chloride Medium at 25°C

[AOT] x10^3/ mol kg^{-1}	EMF / mV	[AOT] x10^3/ mol kg^{-1}	EMF / mV	[AOT] x10^3/ mol kg^{-1}	EMF / mV
		[NaCl] = 0.006 mol kg^{-1}			
6.1919	0.10	7.3101	5.10	8.3661	9.40
6.2291	0.40	7.4409	5.60	8.5001	9.70
6.2853	1.00	7.5687	6.10	8.6481	10.2
6.3595	1.30	7.6899	6.50	8.8109	10.4
6.4673	1.80	7.8095	7.10	9.0037	10.7
6.6088	2.40	7.9254	7.70	9.3588	11.2
6.7441	2.90	8.0375	8.10	9.9683	11.7
6.8932	3.40	8.1475	8.60	10.469	12.2
7.0376	4.00	8.2532	8.90	10.869	12.7
7.1767	4.60				
		[NaCl] = 0.010 mol kg^{-1}			
10.224	7.20	11.408	12.1	12.295	15.3
10.302	7.50	11.530	12.7	12.391	15.4
10.417	8.40	11.650	13.3	12.489	15.8
10.530	9.40	11.763	13.6	12.648	16.1
10.676	9.90	11.875	14.1	12.848	16.3
10.855	10.3	11.985	14.5	13.056	16.7
11.024	10.8	12.090	14.8	13.441	17.0
11.156	11.3	12.193	15.1	13.942	17.4
11.286	11.7				

Table 3.9 - Continued

[AOT] x10^3/ mol kg^{-1}	EMF / mV	[AOT] x10^3/ mol kg^{-1}	EMF / mV	[AOT] x10^3/ mol kg^{-1}	EMF / mV
		[NaCl] = 0.035 mol kg^{-1}			
35.190	42.9	35.720	45.5	36.384	46.9
35.238	43.5	35.795	45.6	36.552	47.2
35.295	43.8	35.861	45.8	36.908	47.4
35.360	44.1	35.927	46.0	37.344	47.6
35.426	44.4	35.993	46.3	37.820	47.9
35.499	44.7	36.059	46.6	38.302	48.1
35.581	45.0	36.142	46.8	38.620	48.3
35.655	45.3	36.251	46.8		
		[NaCl] = 0.065 mol kg^{-1}			
65.117	62.4	65.255	65.0	65.466	66.4
65.121	62.5	65.285	65.2	65.496	66.5
65.123	62.7	65.315	65.4	65.526	66.8
65.132	63.2	65.330	65.5	65.556	66.6
65.150	63.5	65.360	65.8	65.632	66.6
65.165	63.9	65.390	65.9	65.677	66.8
65.180	64.3	65.405	66.0	65.738	66.7
65.210	64.6	65.435	66.2	65.798	66.8
65.240	64.7				

Table 3.10 - EMF Values of AOT in Aqueous Sodium Acetate Medium at 25°C

[AOT] x10^3/ mol kg^{-1}	EMF / mV	[AOT] x10^3/ mol kg^{-1}	EMF / mV	[AOT] x10^3/ mol kg^{-1}	EMF / mV
		[NaAc] = 0.006 mol kg^{-1}			
5.7826	2.60	7.9932	10.4	10.4984	15.3
5.8321	2.80	8.1717	11.0	10.9024	15.8
5.9282	3.30	8.4144	11.6	11.3167	16.3
6.1238	3.90	8.6781	12.1	11.6983	16.8
6.3581	4.80	8.9376	12.5	12.2158	17.3
6.5845	5.80	9.1775	12.9	12.6760	17.8
6.8049	6.70	9.4107	13.3	13.2197	18.3
7.0182	7.40	9.6343	13.8	13.8013	18.8
7.2248	8.40	9.8519	14.3	14.3953	19.4
7.8091	9.80	10.109	14.8	14.8943	19.9
		[NaAc] = 0.010 mol kg^{-1}			
10.031	18.3	11.335	22.0	13.156	24.4
10.068	18.6	11.530	22.3	13.512	24.7
10.140	19.0	11.717	22.6	13.836	25.0
10.229	19.4	11.897	22.9	14.276	25.4
10.297	19.7	12.093	23.3	14.901	25.9
10.350	20.0	12.281	23.4	15.510	26.1
10.503	20.4	12.463	23.7	16.011	26.4
10.701	20.8	12.636	24.0	16.429	26.6
10.920	21.1	12.803	24.1	16.781	26.8
11.133	21.7	12.963	24.2		

Table 3.10 - Continued

[AOT] x10^3/ mol kg^{-1}	EMF / mV	[AOT] x10^3/ mol kg^{-1}	EMF / mV	[AOT] x10^3/ mol kg^{-1}	EMF / mV
		[NaAc] = 0.035 mol kg^{-1}			
35.052	42.9	35.861	44.7	37.001	46.3
35.077	43.1	35.985	44.8	37.146	46.4
35.101	43.4	36.109	45.2	37.335	46.5
35.149	43.6	36.226	45.3	37.533	46.6
35.230	43.8	36.359	45.5	37.750	46.7
35.328	44.0	36.485	45.9	37.968	46.8
35.450	44.3	36.611	46.0	38.275	46.9
35.597	44.4	36.747	46.1	38.629	47.1
35.729	44.6	36.874	46.2	39.005	47.2
		[NaAc] = 0.065 mol kg^{-1}			
65.090	59.3	65.556	61.8	66.361	62.9
65.105	59.6	65.647	62.1	66.499	63.1
65.135	59.7	65.768	62.3	66.637	63.2
65.180	60.4	65.874	62.5	66.913	63.3
65.240	60.7	65.995	62.5	67.269	63.3
65.300	61.1	66.117	62.7	67.673	63.3
65.375	61.4	66.239	62.8	68.504	63.3
65.466	61.7				

Table 3.11 - EMF Values of AOT in Aqueous Sodium Propionate Medium at 25°C

[AOT] x10^3/ mol kg^{-1}	EMF / mV	[AOT] x10^3/ mol kg^{-1}	EMF / mV	[AOT] x10^3/ mol kg^{-1}	EMF / mV
		[NaPr] = 0.006 mol kg^{-1}			
6.0635	-0.10	7.8654	7.40	9.4738	11.8
6.1748	0.40	8.0098	8.10	9.7751	12.4
6.3712	1.20	8.1964	8.70	10.184	12.8
6.5467	2.10	8.2932	9.00	10.681	13.4
6.7908	2.80	8.4318	9.40	11.302	13.9
7.0311	3.90	8.5688	9.80	12.154	14.4
7.2665	4.70	8.7041	10.2	13.281	15.4
7.4186	5.30	8.7584	10.6	14.987	16.5
7.5705	6.10	9.0328	10.9	16.797	17.8
7.7201	6.80	9.2241	11.4		
		[NaPr] = 0.010 mol kg^{-1}			
10.179	23.8	11.902	27.6	13.706	29.5
10.208	24.7	12.118	27.9	13.955	29.6
10.319	25.2	12.326	28.0	14.224	29.7
10.484	25.4	12.526	28.2	14.508	29.9
10.699	25.9	12.721	28.4	15.029	30.3
10.958	26.3	12.910	28.7	15.923	30.6
11.208	26.7	13.092	29.0	16.983	31.3
11.448	27.2	13.269	29.2	17.808	31.7
11.679	27.4	13.475	29.3		

Table 3.11 - Continued

[AOT] x10^3/ mol kg^{-1}	EMF / mV	[AOT] x10^3/ mol kg^{-1}	EMF / mV	[AOT] x10^3/ mol kg^{-1}	EMF / mV
		[NaPr] = 0.035 mol kg^{-1}			
35.012	42.2	35.993	45.4	37.292	47.1
35.044	42.5	36.151	45.6	37.447	47.2
35.093	42.9	36.301	45.9	37.594	47.3
35.182	43.3	36.452	46.1	37.733	47.5
35.271	43.9	36.595	46.4	37.872	47.6
35.385	44.4	36.738	46.5	38.003	47.8
35.515	44.6	36.874	46.6	38.134	48.1
35.663	44.9	37.001	46.8	38.266	48.1
35.827	45.3	37.138	46.9		
		[NaPr] = 0.065 mol kg^{-1}			
65.105	54.1	65.692	56.8	66.499	58.1
65.135	54.6	65.828	57.1	66.652	58.3
65.165	55.3	65.965	57.3	66.821	58.5
65.255	55.9	66.102	57.5	66.975	58.8
65.360	56.1	66.224	57.7	67.160	59.0
65.451	56.3	66.346	58.0	67.362	59.1
65.556	56.5				

Table 3.12 - EMF Values of AOT in Aqueous Sodium Butyrate Medium at 25°C

[AOT] x10^3/ mol kg^{-1}	EMF / mV	[AOT] x10^3/ mol kg^{-1}	EMF / mV	[AOT] x10^3/ mol kg^{-1}	EMF / mV
		[NaBu] = 0.006 mol kg^{-1}			
6.090	7.00	7.935	12.2	9.7481	15.1
6.192	7.20	8.127	12.5	10.109	15.4
6.269	7.80	8.316	13.0	10.549	15.8
6.454	8.40	8.502	13.3	11.187	16.3
6.681	9.10	8.682	13.5	12.015	17.1
6.901	9.40	8.860	13.8	13.092	17.8
7.117	10.2	9.035	13.9	14.296	18.2
7.329	10.9	9.260	14.1	15.060	18.8
7.536	11.4	9.480	14.5	15.730	19.6
7.736	11.9				
		[NaBu] = 0.010 mol kg^{-1}			
10.109	9.10	11.330	15.1	12.497	18.7
10.165	9.80	11.472	15.7	12.692	19.3
10.278	10.4	11.610	16.3	12.987	19.7
10.414	11.0	11.744	16.8	13.339	19.9
10.576	11.7	11.875	17.3	13.824	21.1
10.733	12.4	12.004	17.6	14.412	21.3
10.887	12.9	12.132	17.8	15.178	22.0
11.039	13.7	12.255	18.1	16.030	22.6
11.185	14.4	12.377	18.5	17.447	23.3

Table 3.12 - Continued

[AOT] x10^3/ mol kg^{-1}	EMF / mV	[AOT] x10^3/ mol kg^{-1}	EMF / mV	[AOT] x10^3/ mol kg^{-1}	EMF / mV
		[NaBu] = 0.035 mol kg^{-1}			
35.141	45.5	35.622	47.0	36.376	47.9
35.182	45.7	35.696	47.2	36.544	48.1
35.230	45.9	35.762	47.3	36.730	48.2
35.312	46.2	35.861	47.4	36.933	48.3
35.401	46.4	35.985	47.5	37.155	48.4
35.491	46.6	36.109	47.6	37.378	48.6
35.556	46.9	36.234	47.8		
		[NaBu] = 0.065 mol kg^{-1}			
64.910	58.7	65.210	60.9	65.798	61.8
64.940	59.4	65.315	61.2	65.965	61.9
64.970	60.0	65.375	61.3	66.056	62.1
65.030	60.2	65.451	61.5	66.178	62.2
65.075	60.4	65.586	61.6	66.300	62.2
65.120	60.5	65.722	61.7	66.422	62.2
65.165	60.7				

Table 3.13 - Values of Critical Micelle Concentration (± 0.05x10^{-3} mol kg^{-1}) and Counter Ion Binding Constant for AOT in Different Electrolyte Solutions Obtained from EMF Measurements and the Values of Intercept (A_1) and Slope (B_1) of Equation (3.9) at 25 °C

Salt	[Salt] / mol kg^{-1}	A_1 / mV	B_1/ mV	c_0 x 10^3/ mol kg^{-1}	β ± 0.02
NaCl	0.006	158.4	71.7	2.30	0.45
	0.010	157.5	72.9	1.78	0.45
	0.035	467.5	291.7	0.89	0.71
	0.065	1337.7	1073.7	0.38	0.73
NaAc	0.006	128.1	56.0	2.50	0.45
	0.010	117.7	49.2	2.00	0.39
	0.035	426.1	267.0	0.52	0.70
	0.065	883.3	693.9	0.46	0.71
NaPr	0.006	177.9	81.0	2.20	0.43
	0.010	109.9	42.7	1.81	0.37
	0.035	728.1	471.0	0.50	0.87
	0.065	2130.4	1750.0	0.31	0.90
NaBu	0.006	108.9	45.9	2.20	0.51
	0.010	232.4	111.7	1.88	0.49
	0.035	385.3	233.5	0.63	0.71
	0.065	691.6	531.9	0.37	0.83

Table 3.14 - Ratio of the Intensities of Fluorescence Emission of Pyrene in the Absence (I_o) And Presence (I_q) of the Quencher (CPC) at 373 nm in Aqueous AOT + NaCl Medium at 25°C

[Salt] / mol kg^{-1}	[AOT] / mol kg^{-1}	[CPC] x 10^5 / mol kg^{-1}	I_0 / I_q
0.0	*0.0077*	*0*	*1.0000*
		0.9800	1.6486
		1.9600	2.5090
		2.9300	3.6842
		4.8500	5.8644
0.003	0.0057	0	1.0000
		0.6879	1.0730
		0.0593	1.0076
		0.2369	1.0170
		0.3943	1.0373
		0.5902	1.0702
0.009	0.0040	0	1.0000
		0.1916	1.0164
		0.2641	1.0242
		0.3131	1.0287
0.015	0.0041	0	1.0000
		0.0872	1.0179
		0.1394	1.0269
		0.1916	1.0423
		0.2641	1.0497
		0.3131	1.0605
		0.3824	1.0700

Table 3.14 - Continued

[Salt] mol kg^{-1}	[AOT] / mol kg^{-1}	[CPC] x 10^5 / mol kg^{-1}	I_0 / I_q
0.035	0.0027	0	1.0000
		0.0523	1.0597
		0.0872	1.0785
		0.1394	1.1263
		0.1916	1.1851
		0.2641	1.2547
		0.3131	1.2905
		0.3824	1.3608
0.065	0.0013	0	1.0000
		0.0523	1.0607
		0.0872	1.1044
		0.1394	1.2144
		0.1916	1.2739
		0.2641	1.3837
		0.3131	1.4718
		0.3824	1.5692

Table 3.15 - Ratio of the Intensities of Fluorescence Emission of Pyrene in the Absence (I_o) And Presence (I_q) of the Quencher (CPC) at 373 nm in Aqueous AOT + NaAc Medium at 25°C

[Salt] mol kg^{-1}	[AOT] / mol kg^{-1}	[CPC] x 10^5 / mol kg^{-1}	I_0 / I_q
0.003	0.0057	0	1.0000
		0.1394	1.0109
		0.2616	1.0326
		0.4342	1.0476
0.009	0.0040	0	1.0000
		0.0436	1.0069
		0.1394	1.0097
		0.1916	1.0228
		0.3477	1.0639
0.015	0.0041	0	1.0000
		0.0523	1.0044
		0.0872	1.0082
		0.1916	1.0178
		0.2641	1.0298
		0.3131	1.0386
0.035	0.0027	0	1.0000
		0.0523	1.0602
		0.0872	1.1029
		0.1916	1.1732
		0.2641	1.2474
		0.3131	1.2988
		0.3824	1.3524
0.065	0.0013	0	1.0000
		0.1394	1.0109
		0.2616	1.0326
		0.4342	1.0476

Table 3.16 - Ratio of the Intensities of Fluorescence Emission of Pyrene in the Absence (I_o) and Presence (I_q) of the Quencher (CPC) at 373 nm in Aqueous AOT + NaPr Medium at 25°C

[Salt] / mol kg^{-1}	[AOT] / mol kg^{-1}	[CPC] x 10^5 / mol kg^{-1}	I_0 / I_q
0.003	0.0028	0	1.0000
		0.0793	1.0204
		0.1981	1.0812
		0.3168	1.1192
		0.4354	1.1560
		0.7901	1.2989
0.009	0.0040	0.0000	1.0000
		0.0436	1.0090
		0.0872	1.0160
		0.1394	1.0384
		0.2641	1.0513
		0.3477	1.0716
0.015	0.0041	0	1.0000
		0.0872	1.0076
		0.1394	1.0114
		0.1916	1.0117
		0.2611	1.0161
0.035	0.0027	0	1.0000
		0.0523	1.0524
		0.0872	1.0865
		0.1394	1.1380
		0.1916	1.1715
		0.2641	1.2473
		0.3131	1.3131
		0.3824	1.3414
0.065	0.0013	0	1.0000
		0.0397	1.0673
		0.0496	1.0867
		0.0991	1.1252
		0.1981	1.2507

Table 3.17 - Ratio of the Intensities of Fluorescence Emission of Pyrene in the Absence (I_o) And Presence (I_q) of the Quencher (CPC) at 373 nm in Aqueous AOT + NaBu Medium at 25°C

[Salt] / mol kg^{-1}	[AOT] / mol kg^{-1}	[CPC] x 10^5 / mol kg^{-1}	I_0 / I_q
0.003	0.0057	0	1.0000
		0.0872	1.0066
		0.1394	1.0094
		0.1916	1.0129
		0.2641	1.0205
		0.3824	1.0273
0.009	0.0040	0	1.0000
		0.0872	1.0191
		0.1916	1.0427
		0.3131	1.0598
		0.3824	1.0748
0.015	0.0041	0	1.0000
		0.0989	1.0316
		0.1975	1.0481
		0.2960	1.0571
		0.3942	1.0786
		0.4923	1.0873
		0.5902	1.1158

Table 3.17 - Continued

[Salt] / mol kg^{-1}	[AOT] / mol kg^{-1}	[CPC] x 10^5 / mol kg^{-1}	I_0 / I_q
0.035	0.0027	0	1.0000
		0.0872	1.0439
		0.1394	1.0712
		0.1916	1.1261
		0.2641	1.1935
		0.3131	1.1958
		0.3824	1.2359
0.065	0.0013	0	1.0000
		0.0523	1.0237
		0.0872	1.0938
		0.1394	1.1245
		0.1916	1.1891
		0.2641	1.2910
		0.3131	1.3381
		0.3824	1.4264

Table 3.18 - Aggregation Numbers of AOT and Values of Relative Intensity (I_3/I_1) of Peak 3 (at 384 nm) to Peak 1 (at 373 nm) of Pyrene in Water and Aqueous Electrolytes

[Electrolyte]/ mol kg^{-1}	[AOT]/ mol kg^{-1}	Water		Electrolyte							
				NaCl		NaAc		NaPr		NaBu	
		N_0	I_3/I_1*	N_0	I_3/I_1*	N_0	I_3/I_1*	N_0	I_3/I_1*	N_0	I_3/I_1*
0	0.0077	22	0.93								
0.003	0.0057[a]			36	0.93	37	0.92	21	0.93	25	0.94
0.009	0.0040			20	0.96	22	0.96	44	0.95	40	0.95
0.015	0.0041			46	0.99	32	0.98	34	0.97	47	0.91
0.035	0.0027			152	0.82	150	0.82	150	0.81	112	0.81
0.065	0.0013			152	0.82	127	0.79	155	0.80	86	0.80

[b] 0.0028 mol kg^{-1} in the case of NaPr, * $I_3/I_1 \pm 0.01$

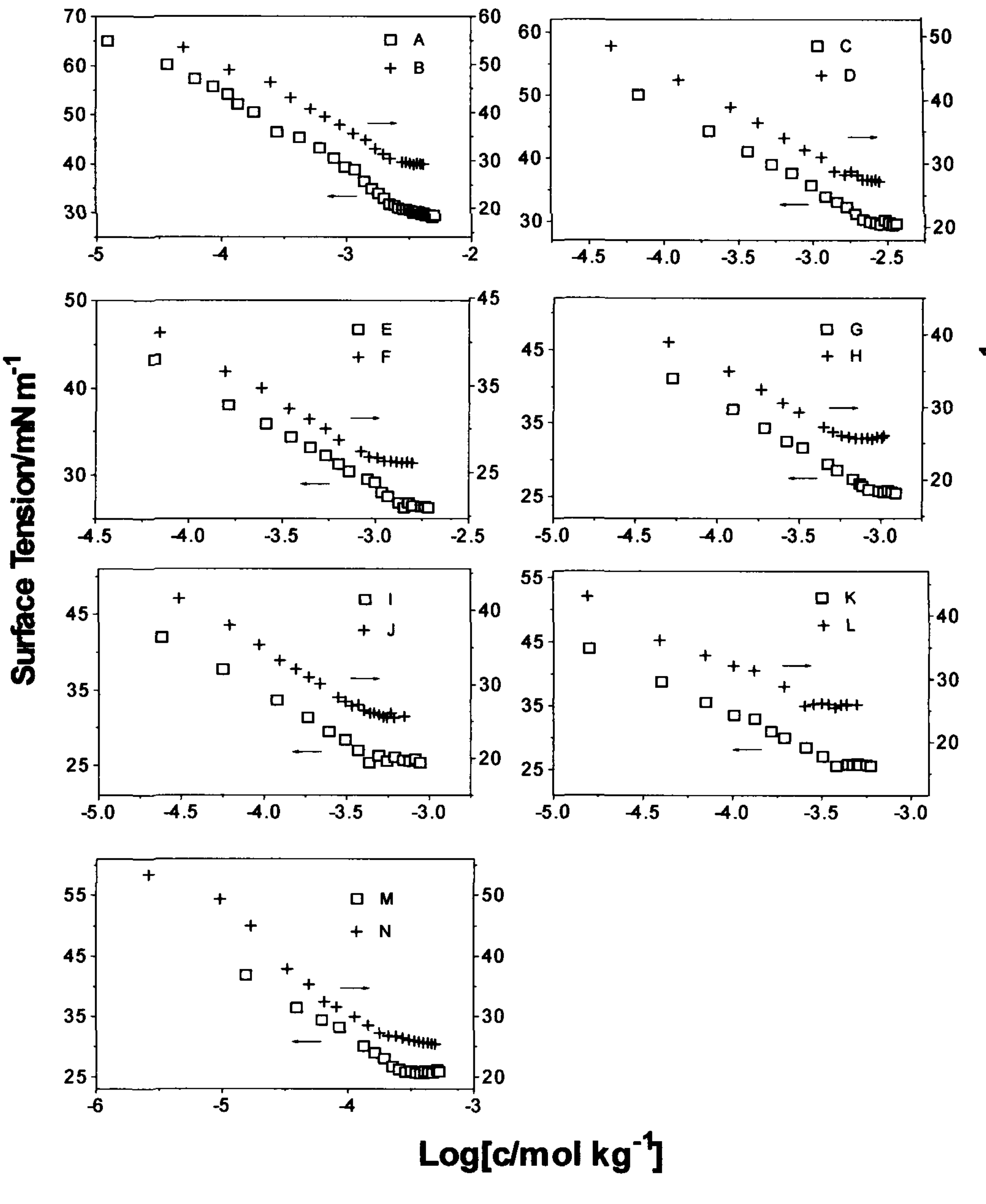

Figure 3.1 - Variation of surface tension with logarithm of AOT concentration in aqueous sodium chloride solutions. Sodium chloride concentrations in mol kg^{-1} are: 0.0012 (A), 0.0021 (B), 0.0079 (C), 0.0139 (D), 0.0197 (E), 0.0292 (F), 0.0480 (G), 0.0612 (H), 0.0668 (I), 0.0788 (J), 0.0959 (K), 0.1188 (L), and 0.1869 (M).

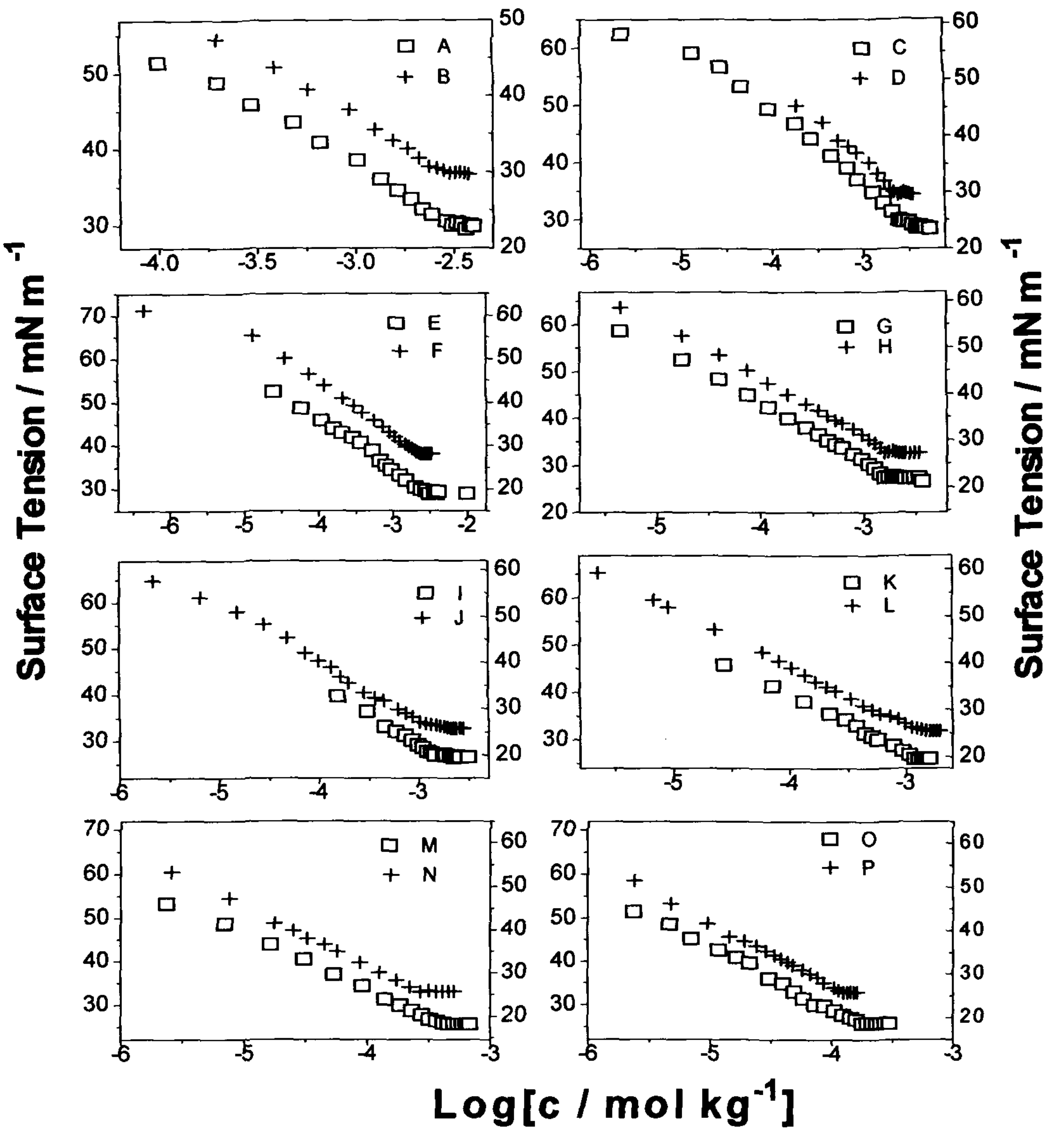

Figure 3.2 - Variation of surface tension with logarithm of AOT concentration in aqueous sodium acetate solutions. Sodium acetate concentrations in mol kg^{-1} are: 5.4×10^{-4} (A), 9.2×10^{-4} (B), 0.0013 (C), 0.0016 (D), 0.0037 (E), 0.0050 (F), 0.0072 (G), 0.0092 (H), 0.0124 (I), 0.0160 (J), 0.0204 (K), 0.0220 (L), 0.0740 (M), 0.1300 (N), 0.2000 (O) and 0.3000 (P).

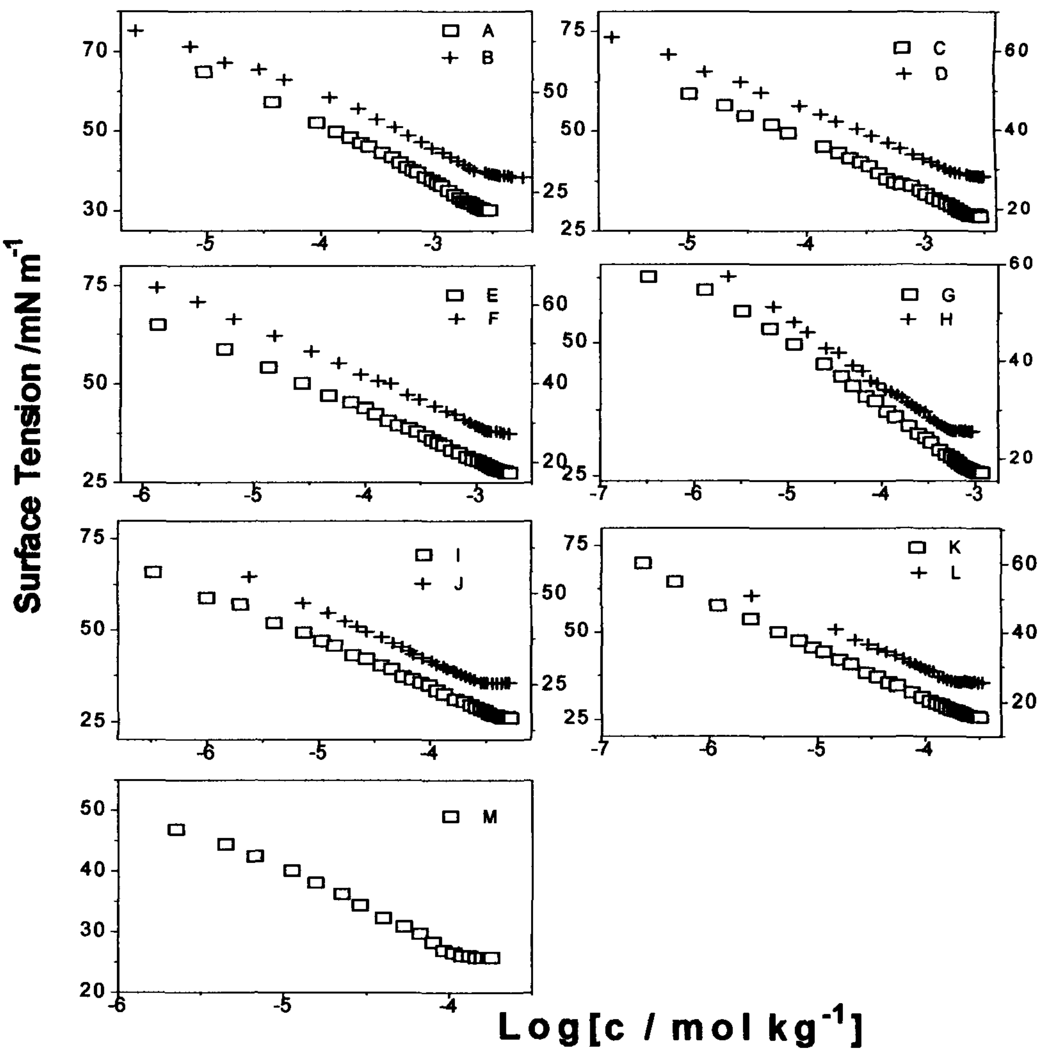

Figure 3.3 - Variation of surface tension with logarithm of AOT concentration in aqueous sodium propionate solutions. Sodium propionate concentrations in mol kg^{-1} are: 7.9x10^{-4} (A), 0.0018 (B), 0.0030 (C), 0.0050 (D), 0.0076 (E), 0.0104 (F), 0.0273 (G), 0.0536 (H), 0.0664 (I), 0.1129 (J), 0.1510 (K), 0.1985 (L), and 0.2989 (M).

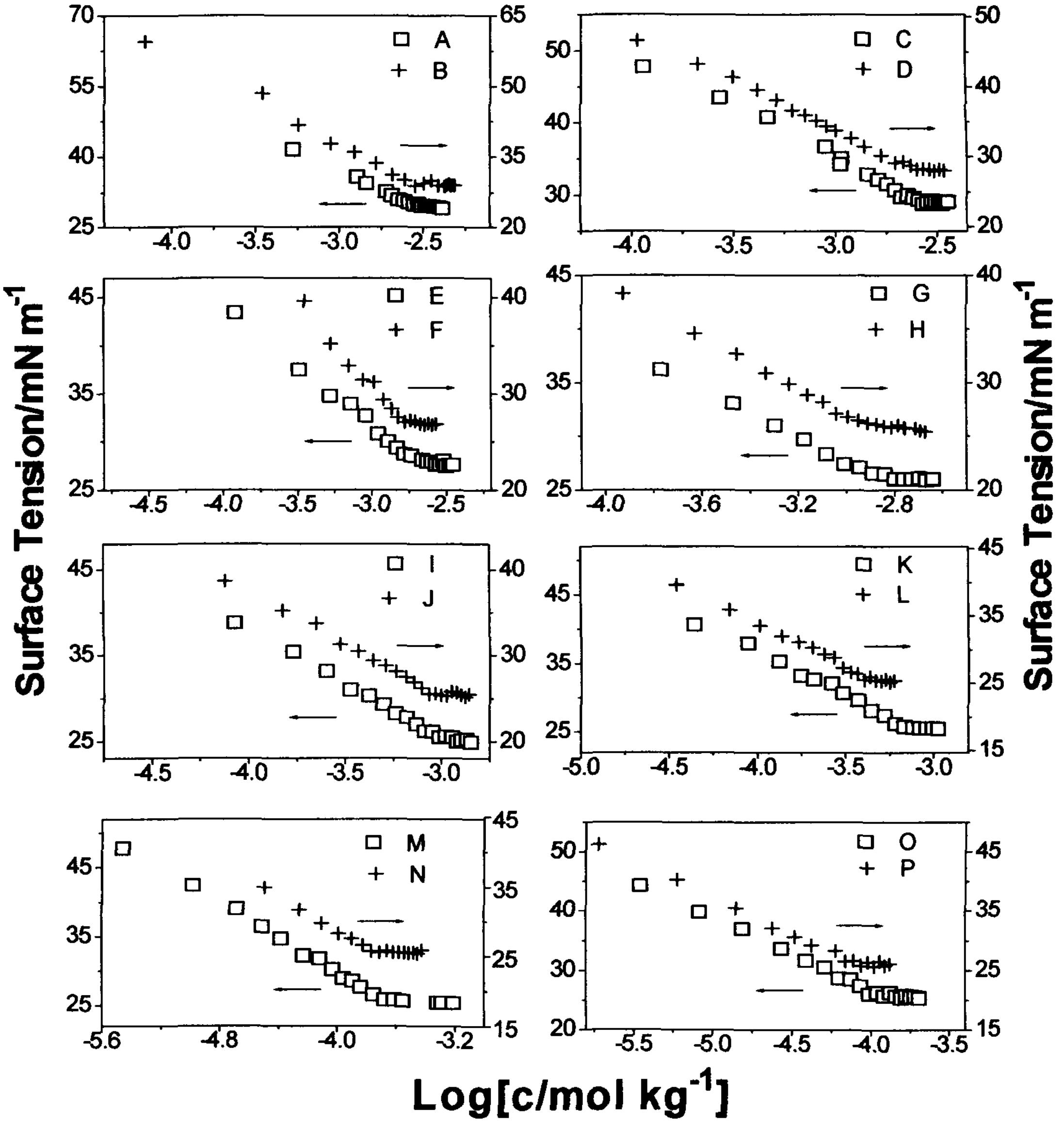

Figure 3.4 - Variation of surface tension with logarithm of AOT concentration in aqueous sodium butyrate solutions. Sodium butyrate concentrations in mol kg^{-1} are: 5.1x10^{-4} (A), 0.0010 (B), 0.0017 (C), 0.0033 (D), 0.0052 (E), 0.0100 (F), 0.0148 (G), 0.0191 (H), 0.0245 (I), 0.0287 (J), 0.0352 (K), 0.0635 (L), 0.1659 (M), 0.2064 (N), 0.3295 (O) and 0.4987 (P).

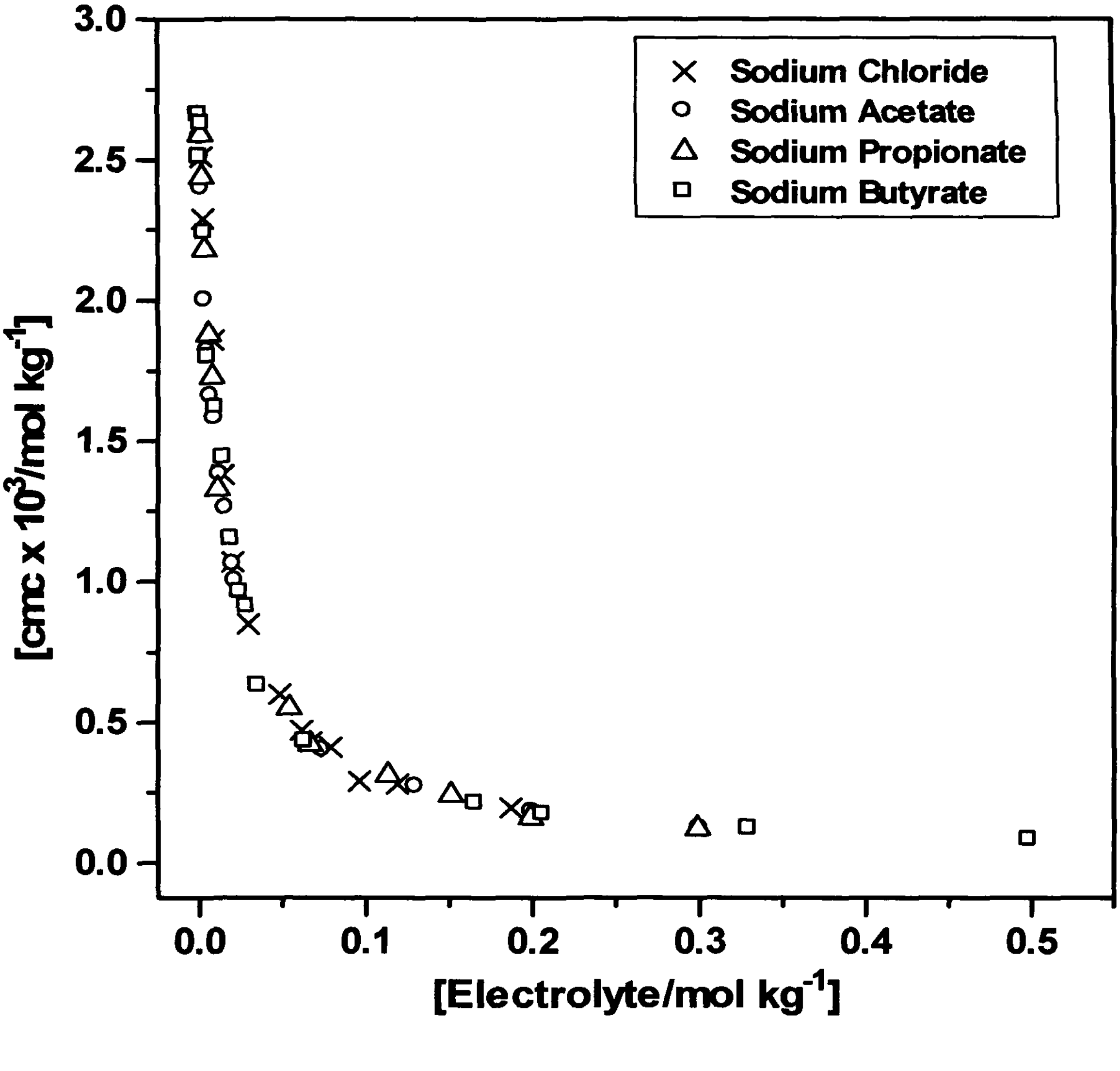

Figure 3.5 - Variation of cmc of AOT as a function of electrolyte concentration.

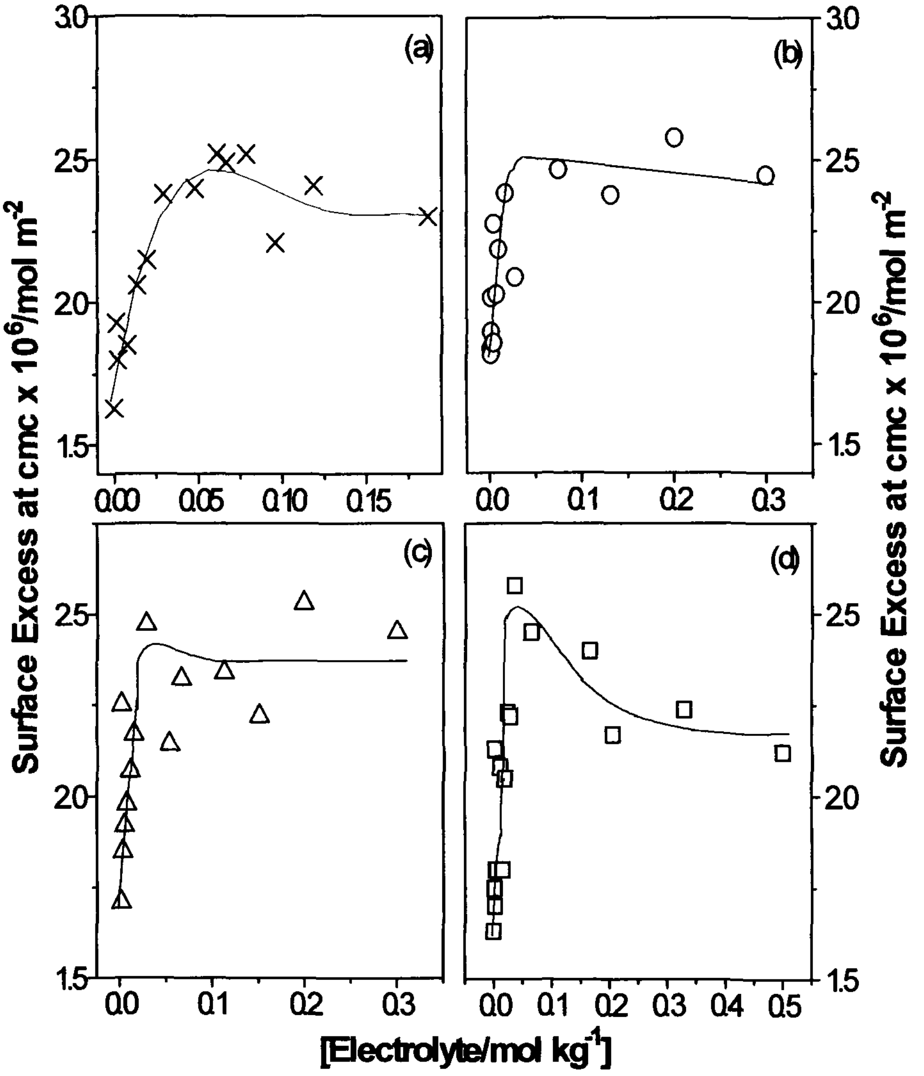

Figure 3.6 - Variation of surface excess of AOT at cmc with electrolyte concentration.

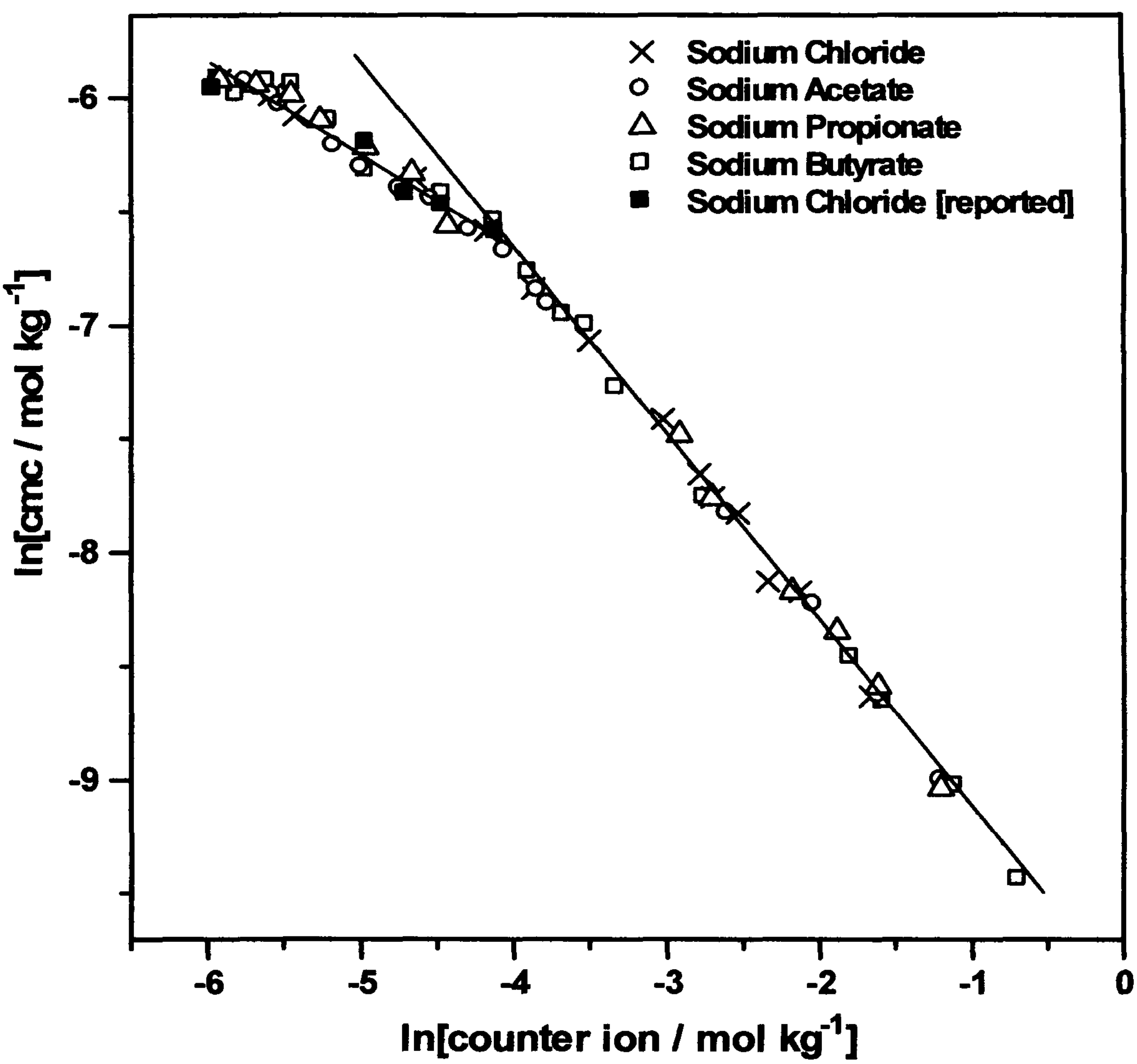

Figure 3.7 - Variation of logarithm of cmc of AOT with logarithm of counter ion concentration (■ : from ref. 7).

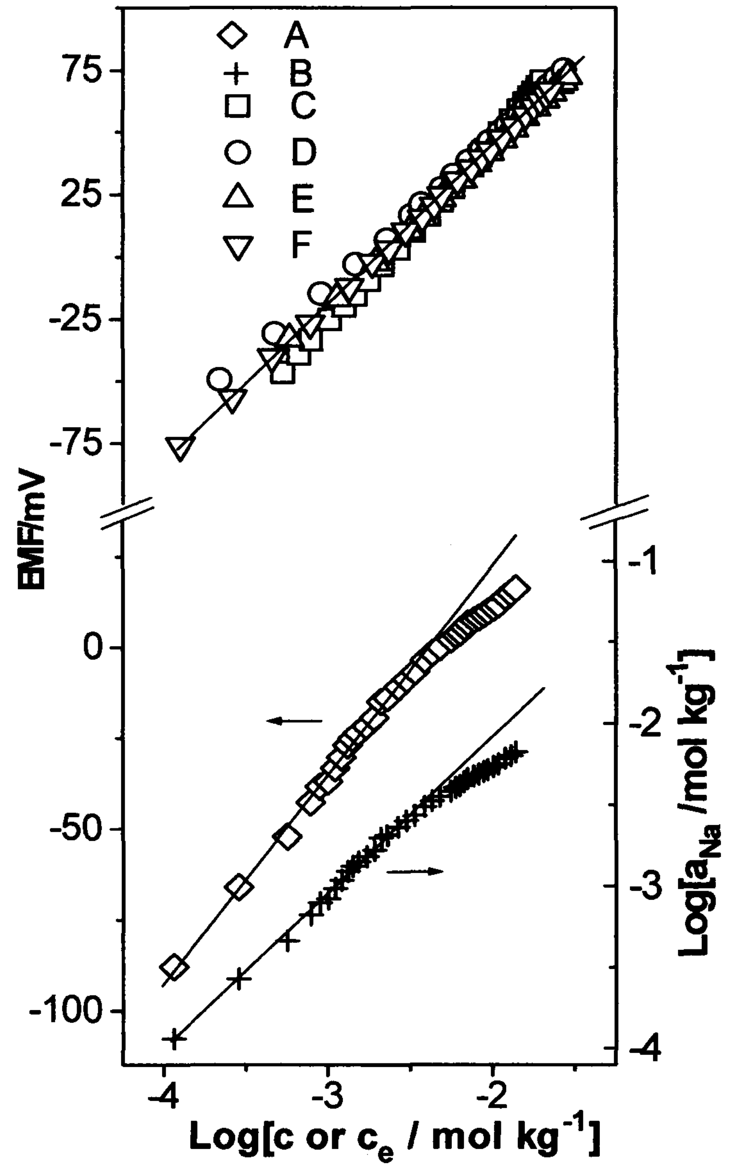

Figure 3.8 - Plots of ion meter response against logarithm of AOT or electrolyte concentration [A: AOT; C: NaCl; D: NaAc; E: NaPr; F: NaBu] and plot of logarithm of activity of sodium ion (B) in aqueous AOT solution against logarithm of AOT concentration.

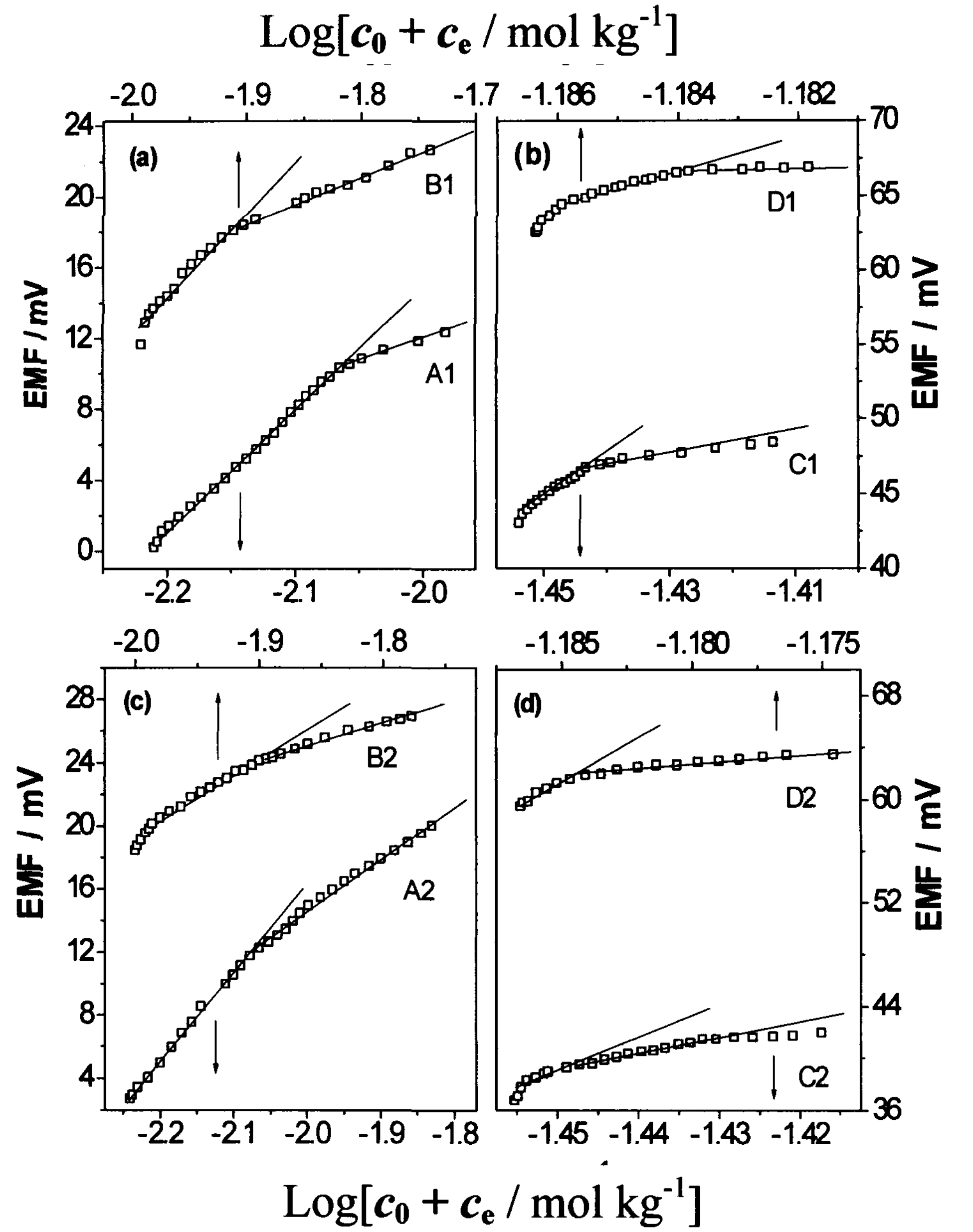

Figure 3.9 - Variation of ion meter response with the concentration of AOT in aqueous NaCl (A1 – D1) and NaAc (A2 – D2) solutions. The arrows indicate the abscissa scale used.

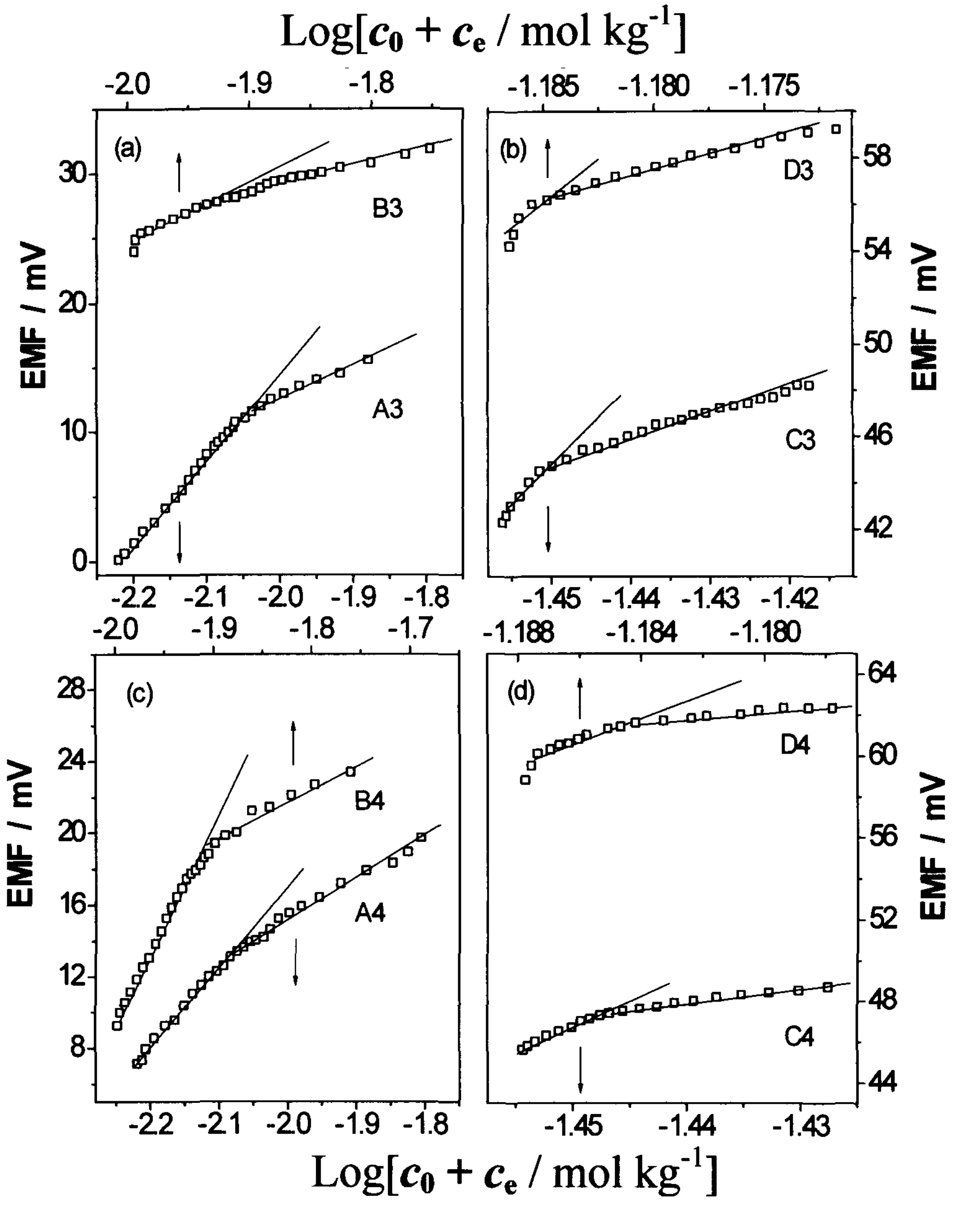

Figure 3.10 - Variation of ion meter response with the concentration of AOT in aqueous NaPr (A3 – D3) and NaBu (A4 – D4) solutions. The arrows indicate the abscissa scale used.

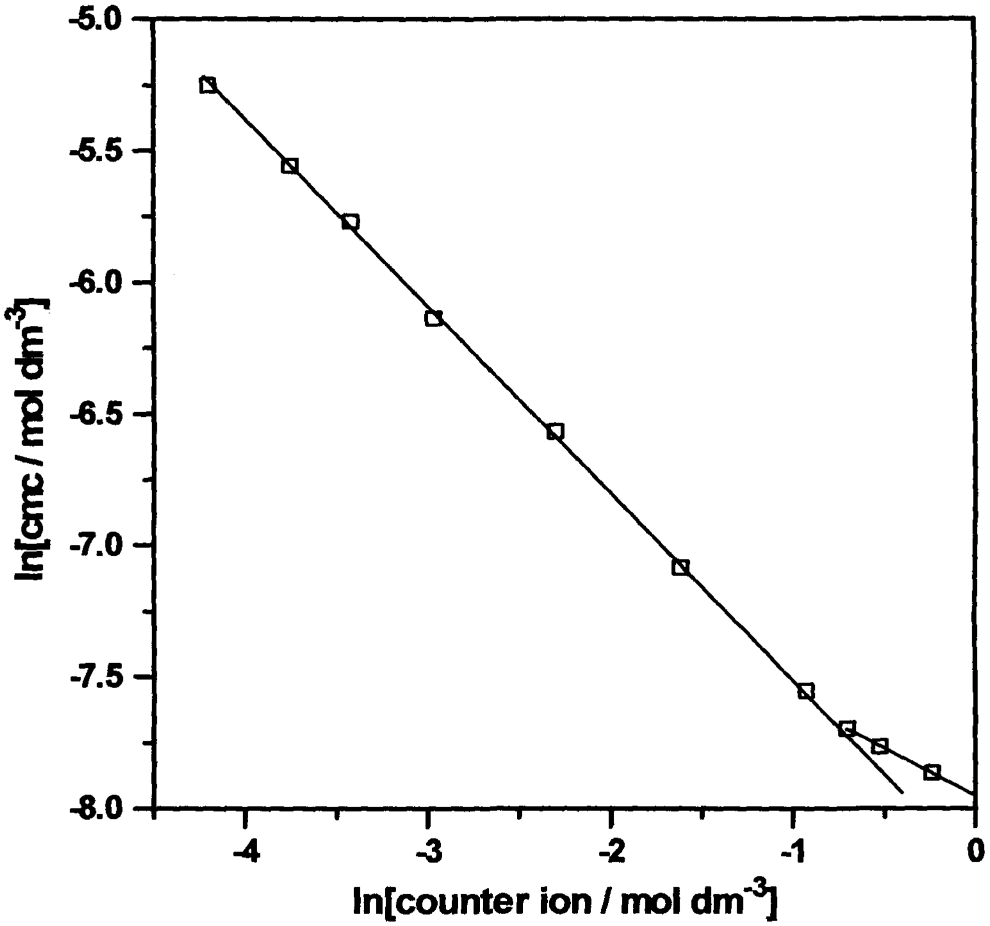

Figure 3.11 - Variation of logarithm of cmc of SDS with logarithm of counter ion concentration (cmc values from ref. 4, 16- 18).

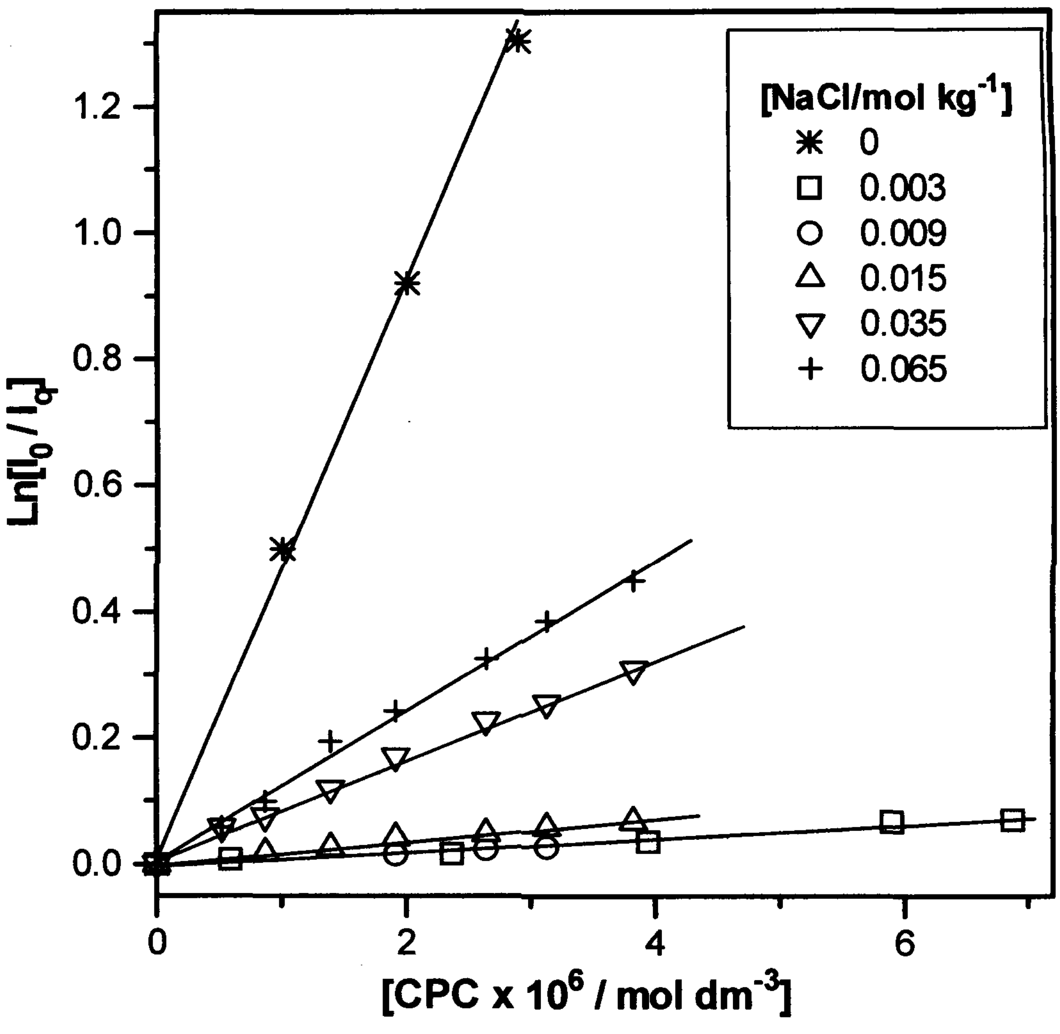

Figure 3.12 - Variation of ln[I_o/I_q] of pyrene at 373 nm with the concentration of the quencher in aqueous *AOT* solution containing NaCl.

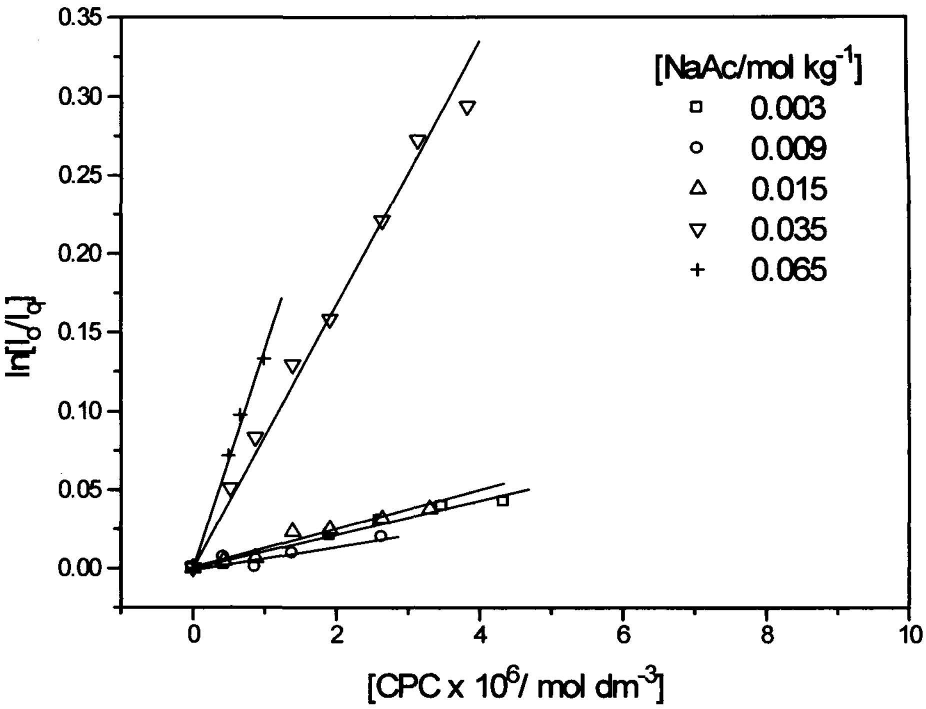

Figure 3.13 - Variation of $\ln[I_o/I_q]$ of pyrene at 373 nm with the concentration of the quencher in aqueous AOT solution containing NaAc.

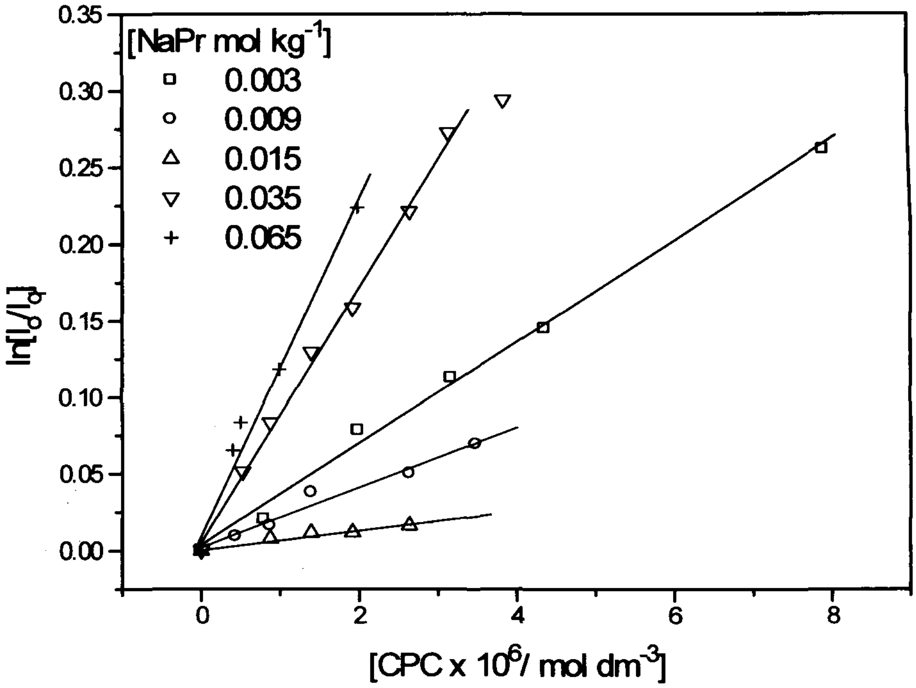

Figure 3.14 - Variation of $\ln[I_o/I_q]$ of pyrene at 373 nm with the concentration of the quencher in aqueous AOT solution containing NaPr

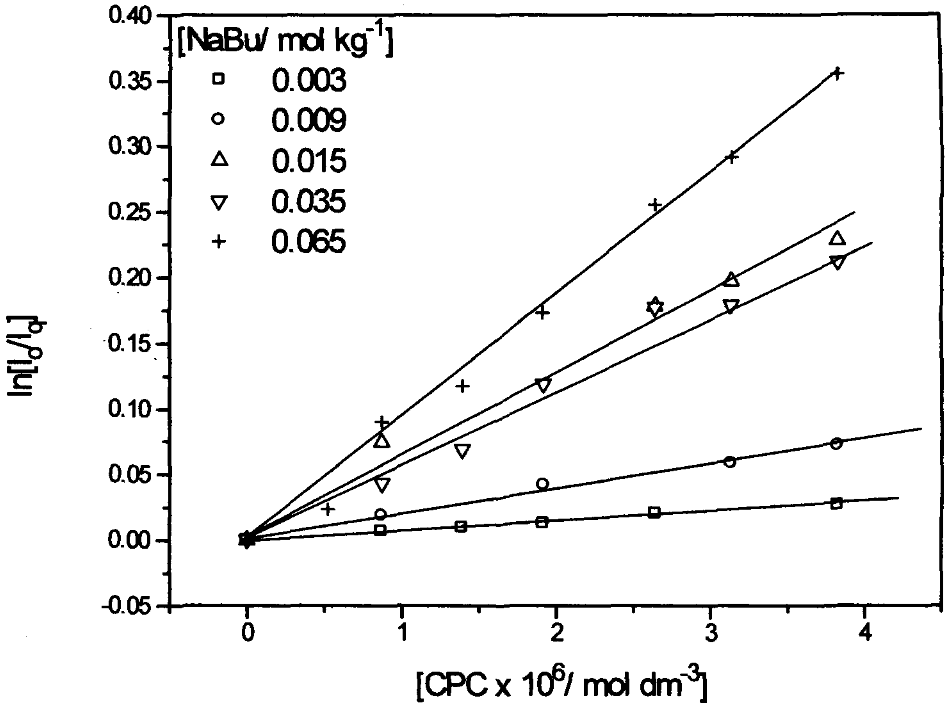

Figure 3.15 - Variation of $\ln[I_o/I_q]$ of pyrene at 373 nm with the concentration of the quencher in aqueous AOT solution containing NaBu.

CHAPTER 4

Micellization Behaviour of Sodium Dodecyl Sulfate in Different Electrolyte Media

4.1 Introduction

Added electrolytes are known to affect the aggregation behaviour of surfactants. In the case of ionic surfactants, the influence of added electrolytes on their micellization characteristics is attributed entirely to the counter ion effect. However, as mentioned in the previous chapter, scattered works reported in the literature[1-5] do indicate that a co-ion, depending upon its and surfactant's structures, can also affect the micellization phenomenon thereby producing perceivable changes in the micellization parameters of the chosen ionic surfactants. In the previous chapter we have observed that the chloride, acetate, propionate and butyrate co-ions do not have any effect on the micellization parameters of AOT, but these co-ions are found to have an influence on the adsorption behaviour of AOT.[6] Earlier, based on conductance data alone, it was reported[5] that chloride, acetate and propionate co-ions affect the cmc values of SDS in aqueous medium differently beyond some particular electrolyte concentrations. This observation has not yet been confirmed from other experimental techniques. With this view in mind, we first measured the cmc values of SDS in aqueous sodium butyrate medium using surface tension, conductance and EMF methods. Aggregation numbers of SDS in this electrolyte medium were also determined from the steady state fluorescence quenching method. Surprisingly, we observed that butyrate co-ion has no perceivable effect on the cmc or aggregation number of SDS. This prompted us to re-determine the cmc values of SDS in aqueous sodium chloride, sodium acetate and sodium propionate solutions using surface tension, conductance and emf methods. The results of the present work are presented in this chapter.

4.2 Experimental Section

Sodium dodecyl sulfate (Aldrich, 99+ %, Lot No. 13803DO) was used without purification as well as after purification. Purification of SDS was done first by keeping it in diethyl ether for ~ 24 hours (we have also tried refluxing SDS with ether for about 8 hours). The SDS obtained after filtering off the ether was then recrystallized from its solutions in water as well as in water + alcohol mixture. Sodium chloride (E-Merck), sodium acetate (E-Merck), sodium propionate (Sigma) and sodium butyrate (E-Merck) were used as received. Doubly distilled water having conductance 2.1 ± 0.2 μS and surface tension 72 ± 0.1 mN m^{-1} at 25 °C was used throughout for preparing solutions. Surface tension and EMF measurements were made as described in chapter 3. Fluorescence emission intensities of pyrene (Fluka) in the absence and presence of the quencher, cetylpyridinium chloride (CPC; Fluka), were also recorded as described in chapter 3. Conductance measurements were made as described in chapter 2.

4.3 Results and Discussion

Both the aqueous solutions of purified and unpurified samples of SDS exhibited minimum in the surface tension versus log$c$ plot (c = concentration of SDS). With the above purification method of SDS we could not get rid of the surface tension minimum. Hence, in the present investigation the Aldrich (99+ %, Lot No. 13803DO) sample of SDS has been used as received. Besides Aldrich

99+%, we observed that Fluka >99% (Analysis No. 304907/1 1291) sample of SDS also exhibited surface tension minimum.

The measured surface tension data of the solutions of SDS in aqueous sodium butyrate (NaBu), sodium acetate (NaAc), sodium propionate (NaPr) and sodium chloride solutions at 20, 25 and 30 °C are given in Tables 4.1 – 4.12. Some of the representative plots of surface tension (γ) versus log*c* at 25 °C are shown in Figs. 4.1 – 4.4.

The minimum in the plot of γ versus log*c* for SDS is considered to be caused by the presence of highly surface-active dodecyl alcohol molecules.[7] Dodecyl alcohol may be present as impurity in the supplied sample of SDS or it may be produced in the SDS solution by its hydrolysis. The rate constant for uncatalyzed hydrolysis of SDS, however, has a very low value (in the range of 10^{-8} s^{-1}) and the presence of acid enhances (rate constant is in the range of 10^{-3} to 10^{-4} s^{-1}) the rate of hydrolysis.[8] It is, therefore, unlikely that uncatalyzed hydrolysis of SDS causes surface tension minimum. Dodecyl alcohol due to its higher surface-activity lowers the surface tension below that of SDS. As the micelles start forming, the impurity gets solubilized in the micelles which results in the lowering of concentration of dodecyl alcohol in the bulk and, in turn, at the surface also. The surface tension therefore begins to increase and finally attains that of the pure SDS solution. This is how the occurrence of minimum in the plot of γ versus log*c* for SDS in the presence of impurity has been accounted for. The cmc of SDS is taken to be the concentration of SDS corresponding to the minimum in the plot of γ versus log$c$ and it is equal to 8.10 mmol kg^{-1} in the absence of any added electrolyte at 25 °C. This value is in good agreement with the cmc values of SDS obtained from conductance (8.10 mmol kg^{-1}) and EMF (7.94 mol kg^{-1}) methods (Figs. 4.5 and 4.6). Lin et al.[7] reported that the cmc of SDS (technical and laboratory grades) determined from conductance method matches not with the concentration corresponding to the minimum but with the concentration at which surface tension starts becoming almost constant after an increase from the minimum. Lin et al.[7] attributed the surface tension minimum to the formation of pre-micelles. The present study, however, shows that the SDS concentration at the minimum in the plot of γ versus log$c$ corresponds to cmc and hence to the formation of micelles. In the presence of added electrolytes also the concentration corresponding to the minimum is taken to be the cmc of SDS. With the addition of electrolyte the minimum is found to become smaller and around 0.2 mol kg^{-1} of electrolyte concentration the surface tension minimum disappears (Figs. 4.1 – 4.4). Added electrolyte is known to decrease the surface tension of surfactant solution by pushing more of surfactant molecules to the interface, whereas it does not seem to affect the depression in surface tension caused by the impurity like dodecyl alcohol. Due to this the surface tension minimum becomes smaller by the addition of electrolyte and eventually disappears (at ~ 0.2 mol kg^{-1} electrolyte). Suppression of surface tension of a surfactant leading to disappearance of the minimum by an added electrolyte, therefore, indicates that presence of no minimum in the plot of γ versus log$c$ does not ensure that the surfactant is free from impurity.

The values of cmc of SDS in the presence of NaBu, NaAc, NaPr, and NaCl determined from surface tension data are given in Table 4.13. The variation of cmc with electrolyte concentration is shown in Fig. 4.7. In these figures the reported[9-12] values of cmc of SDS in the presence of NaCl are also shown and a good agreement has been found between the present and reported values. The cmc values of SDS in all the four electrolytes are comparable and the cmc as usual decreases with increase in electrolyte concentration. The co-ions do not have any effect on the cmc of SDS as in the case of AOT (chapter 3). As mentioned in the introduction section above, using conductance method alone, it was earlier reported[5] that acetate and propionate co-ions affect the cmc of SDS by exhibiting an increase in the cmc instead of showing the usual decrease above 0.18 and 0.17 mol kg^{-1} concentrations of NaAc and NaPr, respectively at 25 °C. Such a co-ion effect on the cmc of SDS is not observed in the present investigation. We also measured the electrical conductance of SDS in NaAc, NaPr and NaBu solutions at 25 °C (Tables 4.14 – 4.16) and once again estimated the cmc values from the specific conductance (κ) versus surfactant concentration plots very carefully. Representative plots of κ versus c are shown in Figs. 4.5 and 4.8. The cmc values obtained from conductance data are given in Table 4.17 and are also shown in Fig. 4.7. From Fig. 4.7 it is evident that the cmc values estimated from surface tension and conductance methods are in agreement. Regarding estimation of cmc from the conductance data the following observations are made: (1) As the electrolyte concentration increases, determination of cmc from the conductance data becomes more uncertain. (2) The plot of κ versus surfactant concentration exhibits more than one inflexion out of which only one is due to micellization and the rest are due to ion – ion interaction. Due to the above reasons, conductance method sometimes may give erroneous cmc values particularly at higher electrolyte concentrations. For proper estimation of cmc from the conductance data, it is necessary to distinguish the inflexion in the plot of κ versus surfactant concentration as due to micellization or ion – ion interaction. Therefore, cmc values of ionic surfactants in the presence of electrolytes determined from conductance method need to be supported by other techniques. Binana-Limbele and Zana[13] had also highlighted regarding such a problem in the determination of cmc by using conductance method. In order to verify further the cmc values of SDS in the presence of chloride, acetate, propionate and butyrate co-ions, we also measured the cmc values using the EMF method. The measured EMF values of SDS solution in the absence and presence of the four different electrolytes at 25 °C are given in Table 4.18 -4.21and the plots of EMF versus log*c* are shown in Figs. 4.6 and 4.9 – 4.10. The values of cmc obtained from the EMF method are listed in Table 4.22, which are also found to be in agreement with the cmc values derived from surface tension and conductance data (Fig. 4.7). It is therefore concluded that there is no co-ion effect on the cmc of SDS by the acetate, propionate and butyrate ions and SDS is found to have similar values of cmc in the presence of NaCl, NaAc, NaPr, and NaBu.

The values of surface excess, Γ_{cmc}, for SDS at the air-water interface near its cmc in the presence of the electrolytes were calculated from the respective surface tension data using the expression given in the previous chapter, which is given by

$$\Gamma_{cmc} = -\left[\frac{1}{RT}\right]\left[\frac{1}{1+\dfrac{c_0}{c_0+c_e}}\right]\left[\frac{d\gamma}{d\ln c}\right]_{at\ cmc} \tag{4.1}$$

The terms c_0, c_e, R and T have the same meanings described in chapter 3. The calculated values of Γ_{cmc} for SDS are presented in Table 4.23. The variation of Γ_{cmc} with electrolyte concentration is shown in Fig. 4.11. The values of Γ_{cmc} for SDS in water and in aqueous NaCl solutions at 25 °C obtained in the present study are in agreement within ± 0.2 x 10^{-6} mol m^{-2} with the values reported by Tajima,[14] who measured Γ_{cmc} of SDS in NaCl solutions directly by using radiotracer technique. Therefore, the occurrence of surface tension minimum due to the presence of impurity in the sample of SDS used here has not affected the value of Γ_{cmc} significantly. Although for SDS in an electrolyte medium at a given temperature the computed values of Γ_{cmc} look scattered, a particular over-all trend in the variation of Γ_{cmc} with electrolyte concentration appears to exist as depicted in Fig. 4.11 by the solid lines. With the addition of electrolyte Γ_{cmc} of SDS initially increases as reported by others[14,15] and attains a maximum value. Added electrolyte is known to enhance the adsorption of ionic surfactants at the air-water interface causing Γ_{cmc} to increase. In NaCl, NaAc and NaPr solutions, Γ_{cmc} attains the maximum value in the region of 0.2 to 0.3 mol kg^{-1} electrolyte concentrations and thereafter Γ_{cmc} remains almost constant. In NaBu solution, Γ_{cmc} attains the maximum value at around 0.15 mol kg^{-1} electrolyte concentration and thereafter Γ_{cmc} decreases with further increase in NaBu concentration. The trends in the variation of Γ_{cmc} of SDS in NaCl, NaAc, NaPr and NaBu solutions are almost similar to that of AOT in these four respective electrolytes (chapter 3). However, values of Γ_{cmc} of SDS are about two times greater than that of AOT and the electrolyte concentrations at which Γ_{cmc} attains maximum are higher in the case of SDS compared to the case of AOT. As observed in the case of AOT, the co-ions appear to have an effect on the surface activity or surface excess of SDS also. The effect of chloride, acetate and propionate co-ions on Γ_{cmc} of SDS seems to be similar, whereas butyrate ion affects differently. As discussed in the previous chapter, added electrolytes influence the adsorption and hence Γ_{cmc} of an ionic surfactant due to their salting-out effect. Salting-out effect of electrolytes is, in turn, controlled by the hydration of ionic species of electrolytes and hence co-ions may be expected to affect Γ_{cmc} differently if their hydration numbers are considerably different. The dependence of Γ_{cmc} on temperature between 293 to 303 K range is found to be not significant.

The surface area, A_0, covered per molecule of SDS at the air-solution interface is estimated from the relation

$$A_0 = \frac{1}{N_A \Gamma_{cmc}} \quad (4.2)$$

where N_A is the Avogadro number. The computed values of A_0 are presented in Table 4.23. The value of A_0 for SDS is comparable with the reported[14] value. With the addition of electrolyte surface area covered per SDS molecule decreases. This is because firstly the added electrolyte pushes more surfactants to the interface as mentioned above and secondly due to the increase in the number of counter ions in the Stern and diffuse layers the electrostatic repulsion between the head groups are better screened on addition of electrolyte causing the adsorbed SDS molecules to come closer.

The counterion binding constant, β, has been calculated first by using the Corrin-Harkins (CH) equation

$$\ln X_{cmc} = A - \beta \ln X_c \quad (4.3)$$

where X_{cmc} and X_c represent cmc and total counter ion concentration in mole fraction unit, respectively. As it was done in the previous chapter, CH equation is also sometimes employed by expressing concentration terms in molar or molal unit.[12] The plots of $\ln X_{cmc}$ versus $\ln X_c$ are shown in Fig. 4.12. These CH plots were drawn using cmc values derived from surface tension data. The values of β obtained from the CH plots are given in Table 4.24, which are denoted by β_γ. These β_γ values are comparable to the reported values.[12,16,17] The values of β for

SDS in NaAc, NaPr and NaBu solutions were also calculated from the conductance data at 25 °C using the slope-ratio method and are listed in Table 4.24 as β_K. We also computed the values of β from the EMF data at 25 °C using the procedure described in the previous chapter. The experimental values of EMF, E, for solutions of SDS in water or electrolytic solution are represented by the expressions

$$E = A_1 + B_1 \log c_{Na} \quad \text{at} \quad c < c_0 \tag{4.4}$$

$$E = A_1 + B_1 \log[(1-\beta)c_{Na} + \beta c_0] \quad \text{at} \quad c > c_0 \tag{4.5}$$

where A_1 and B_1 are empirical constants and c_{Na} is the concentration of sodium ion in the solution. In the absence of electrolyte, c_{Na} is equal to the concentration of SDS and in the presence of electrolytes $c_{Na} = c + c_e$. By least - squares fitting the E versus concentration data to equation (4.4) empirical values of A_1 and B_1 were determined, which are displayed in Table 4.22 along with the cmc values. The values of B_1 differ from the Nernst limiting value of 59.1 mV and the deviation is more in the presence of added electrolyte because of increased ion-ion interaction. Since activity term is not used in Eq. (4.4) the non-ideality of the solution gets mostly absorbed in the B_1 term causing it to deviate from the limiting value. As in the case of AOT, for SDS also additional breaks other than that due to micellization were observed in some of the E versus log$c$ plots in the presence of electrolytes thus making the EMF method alone inadequate for the determination of cmc of ionic surfactants in the presence of electrolytes. The values of β were computed from equation (4.5) by the iteration method as described in the previous chapter. β derived from the EMF data is denoted as β_e and its values are listed in Table 4.22. It may be noted that from EMF and conductance data β can be estimated as a function of electrolyte concentration whereas the CH plot provides a single averaged value for β.

The standard free energy of micellization per mole of monomer was calculated from the relation,[12]

$$\Delta G_m^0 = (1+\beta)RT\ln X_{cmc} \tag{4.6}$$

The standard state refers to the hypothetical standard state of unit mole fraction. ΔG_m^0 was evaluated from the above equation (4.6) by using β_γ values. The values of ΔG_m^0 are given in Table 4.25. For calculating ΔG_m^0 of SDS in water without any salt, the β_γ values (= 0.72, 0.69 and 0.71 at 20, 25 and 30 °C, respectively) were taken to be the average of the β_γ values obtained in the presence of the four salts that are given in Table 4.24. The favouring of micellization by the added electrolyte is reflected in the values of ΔG_m^0. The values of ΔG_m^0 for SDS in NaCl solution are comparable to the values reported by Chatterjee et al.[12]

The standard free energy of adsorption, ΔG_{ad}^0, at the air – solution interface was calculated by using the equation[18]

$$\Delta G_{ad}^0 = \Delta G_m^0 - \frac{\pi_{cmc}}{\Gamma_{cmc}} \tag{4.7}$$

where the surface pressure, π_{cmc} = $\gamma_0 - \gamma_{cmc}$. γ_0 and γ_{cmc} refer to the surface tensions of solvent and the surfactant solution at the cmc, respectively. In SDS solutions that exhibit surface tension minimum, γ_{cmc} was taken to be the surface tension corresponding to the flat region after the minimum in the plot of γ versus log c. The calculated values of ΔG^0_{ad} for SDS in the presence of electrolytes at 20, 25 and 30 °C are listed in Table 4.25. On the addition of electrolyte, the value of ΔG^0_{ad} decreases and hence explains the observed increase in the surface activity of SDS.

The aggregation numbers, N_0, of SDS in the four electrolytic solutions at 25 °C were determined from the fluorescence quenching method by using the expressions[19]

$$\frac{I_0}{I_q} = \exp\left(\frac{[q]}{[micelle]}\right) \tag{4.8}$$

$$N_0 = \frac{(c - c_0)}{[micelle]} \tag{4.9}$$

where I_0 and I_q are the intensities of fluorescence emission at 374 nm of pyrene in the absence and presence of the quencher of concentration [q], respectively. A few characteristic fluorescence emission spectra of pyrene in aqueous solutions containing SDS and electrolyte are shown in Fig. 4.13. The values of I_0/I_q as a function of [q] for pyrene in aqueous SDS solutions containing the electrolytes are listed in Tables 4.26 - 4.29 and the plots of $\ln(I_0/I_q)$ versus [q] are shown in

Figs. 4.14 and 4.15. As $[q]$ becomes more and more the plot of $\ln(I_0 / I_q)$ versus $[q]$ is found to deviate from linearity and we have not included those data in Tables 4.26 - 4.29. Aggregation number of ionic surfactants is reported[20-26] to increase with increase in concentration of either surfactant or electrolyte. Accordingly, in the presence of an electrolyte N_0 of SDS increases if the electrolyte concentration increases and at a fixed electrolyte concentration N_0 increases if the SDS concentration is increased. Therefore, while comparing the aggregation number of a surfactant in the absence or presence of electrolytes it is necessary to take note of the surfactant concentration. For SDS in the absence of electrolyte we obtained $N_0 = 44$ and 70 when [SDS] = 0.01 and 0.1 mol kg^{-1}, respectively. The value of $N_0 = 70$ obtained here for SDS at [SDS] = 0.1 mol kg^{-1} is in good agreement with the value reported by Alargova et al.[19] Since cmc changes with the addition of electrolyte, we maintained almost constant ratio (2.6 ± 0.8) of [SDS] to cmc instead of keeping constant SDS concentration during the measurement of aggregation number in the presence of electrolytes. However, at a particular electrolyte concentration the concentration of SDS was the same in the case of all the four electrolytes. Measured values of the aggregation number of SDS in the presence of different concentrations of electrolytes are given in Table 4.30. The value of N_0 tends to increase with increasing electrolyte concentration and it has almost same value in all the four electrolytes. At high electrolyte concentration co-ions like F^-, Cl^-, Br^-, I^- and SCN^- are reported to have an effect on N_0 of SDS.[2,24,25] In the presence of butyrate ion having concentration in the range 0.035 to 0.097 mol kg^{-1} the aggregation number of SDS is found to be lower than that in the presence of chloride, acetate and propionate ions.

Using the values of cmc, counter ion binding constant and aggregation number obtained above we then computed surface potential, Ψ, of SDS micelle in the presence of electrolytes by solving numerically the non-linearized Poission – Boltzmann (PB) equation in spherical symmetry since in the range of electrolytic concentration covered in this study SDS micelles are known to have spherical shape.[11] The algorithm used for the computation is similar to that reported by Drummond et al.[27] In this computational method as an approximation the micelle concentration is presumed to be infinitely low. The PB equation is written as

$$\frac{d^2y}{dx^2} = \frac{(e^y - e^{-y})}{2x^4} \tag{4.10}$$

The different terms of equation (4.10) are defined as

$$y = \frac{e_0 \Psi_r}{k_B T} \tag{4.11}$$

$$x = \frac{1}{Br} \tag{4.12}$$

$$B = \left[\frac{8\pi N_A e_0^2 c_0}{10^3 \varepsilon k_B T}\right]^{1/2} \tag{4.13}$$

Ψ_r is the electrostatic potential at a distance r from the centre of the spherical micelle. The boundary conditions used are

$$y \to 0 \text{ as } x \to 0 \tag{4.14}$$

$$\frac{dy}{dx} = \frac{4\pi\rho_r e_0}{\varepsilon B k_B T x^2} \quad \text{at } r = r_n \tag{4.15}$$

r_n is the radius of the micelle and ρ_r is the surface charge density at a distance r from the centre of the reference micelle. The radius of the micelle r_n was calculated from the relation[28]

$$r_n = \left[\left(\frac{3N_0}{4\pi}\right)(27.4 + 26.9n_c)\right]^{1/3} \tag{4.16}$$

In equation (4.16) the term 27.4 + 26.9n_c gives[27] the volume of the hydrocarbon chain with carbon atoms equal to n_c and for SDS n_c=12. The micellar surface charge density was estimated using the expression

$$\rho_{r_n} = \frac{e_o N_o (1-\beta)}{4\pi r_n^2} \tag{4.17}$$

Equation (4.10) was solved using the fourth–order Runge – Kutta method and an iteration procedure. Arbitrary values of x and dy/dx were fed initially to start the computation which get changed iteratively in the subsequent cycles of computation. The computed values of surface potential at 25 °C are given in Table 4.31. Surface potentials were computed using β_e and β_γ values given in Tables 4.22 and 4.24, respectively. In the case of SDS in water we computed surface potential using two values of aggregation number given in Table 4.30. As the concentration of the added electrolyte increases surface potential of the SDS micelle decreases when constant β value is used for computation in spite of an increase in aggregation number.

4.4 Conclusion

Surface tension of aqueous solutions of SDS in the presence of sodium chloride, sodium acetate, sodium propionate and sodium butyrate was measured as functions of SDS and electrolyte concentration at 20, 25 and 30 °C. From the surface tension data the values of cmc, surface excess, counter ion binding constant, surface area covered per molecule at the air – solution interface, and standard free energies of micellization and adsorption for SDS in the presence of electrolytes were determined. At 25 °C the values of cmc and counter ion binding constant for SDS in the presence of the electrolytes were also determined by measuring conductance and EMF of the solutions. The cmc values obtained from the surface tension, conductance and EMF data are in agreement and the co-ions are found to have no effect on the cmc of SDS. However, co-ion has an influence on the surface activity behaviour of SDS since in sodium butyrate solution above ~ 0.15 mol kg^{-1} butyrate ion concentration the nature of variation of surface excess of SDS with electrolyte concentration is different from that in sodium chloride, sodium acetate and sodium propionate solutions. Aggregation numbers of SDS in the presence of the four electrolytes were measured at 25 °C by using the steady-state fluorescence emission method with pyrene as the probe and cetyl pyridinium chloride as the quencher. In the presence of butyrate ion having concentration $\geq$ 0.035 mol kg^{-1} the aggregation number of SDS is found to be lower than that in the presence of chloride, acetate and propionate ions. Surface potentials of SDS micelles in the presence of the electrolytes were computed by solving the non-linearized Poission–Boltzmann equation. With added electrolyte aggregation number of SDS micelle increases whereas its surface potential decreases.

4.5 References

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Table 4.1 - Surface Tension (γ) Values of SDS in Aqueous Sodium Butyrate Medium at 20 °C

[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaBu] = 0.0 mol kg^{-1}			
0	72.2	5.8452	38.8	8.6944	37.1
0.1293	72.0	6.1368	37.8	8.9712	37.9
0.3228	71.1	6.4269	36.4	9.2468	38.0
0.6439	68.0	6.7154	35.3	9.5209	38.4
0.9632	66.4	7.0025	34.6	10.065	38.6
1.4389	62.7	7.2882	33.8	10.604	38.9
1.9108	59.2	7.5722	33.5	11.137	38.6
2.5340	55.4	7.8549	33.8	11.665	38.6
3.1505	51.4	7.9958	34.4	12.188	38.7
3.7605	48.7	8.1362	35.1	12.706	38.6
4.3640	45.8	8.2762	35.8	13.218	38.6
4.9611	42.8	8.4159	36.6	14.229	38.5
5.5520	40.0				
		[NaBu] = 0.0260 mol kg^{-1}			
0.1573	61.3	1.6605	40.3	3.9557	35.8
0.3088	57.0	2.1904	38.8	4.2474	36.5
0.5651	51.8	2.6973	36.2	4.4394	35.9
0.7749	48.8	3.4137	36.3	4.5564	36.2
1.0079	46.8	3.7284	35.9	4.7954	36.3
1.3401	44.0				
		[NaBu] = 0. 0355 mol kg^{-1}			
0.1399	58.8	1.8743	38.1	3.5459	36.1
0.3777	51.5	2.2591	36.7	3.7551	36.5
0.5386	48.7	2.5878	35.0	4.6294	36.1
0.7763	45.8	2.7831	34.9	4.9788	36.0
1.0630	43.1	3.0000	35.7	5.1680	36.4
1.3078	41.1	3.2872	36.1	5.7204	36.2
1.5806	39.2				

Table 4.1 - Continued

[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaBu] = 0.0627mol kg^{-1}			
0.1756	54.2	1.3269	37.0	3.0572	34.9
0.3773	49.0	1.5026	36.1	3.2978	34.8
0.6244	44.6	1.7367	34.7	3.7916	34.8
0.7935	42.2	2.1401	34.7	3.8898	34.9
1.0082	39.8	2.4782	34.8	4.0778	34.9
1.1512	38.0	2.8095	34.9		
		[NaBu] = 0.0898 mol kg^{-1}			
0.3029	45.8	0.9323	38.5	2.6738	34.2
0.4253	43.7	1.0718	37.0	3.0699	34.2
0.5185	42.8	1.2001	35.7	3.4082	34.0
0.6117	41.5	1.4333	34.1	3.7284	34.1
0.7049	40.1	2.1849	33.6	4.1422	34.2
0.8097	39.4	2.4296	34.0	4.2996	34.0
		[NaBu] = 0.1231 mol kg^{-1}			
0.0912	51.0	0.7470	34.8	1.9500	33.5
0.1654	48.4	0.8838	33.6	2.4290	33.4
0.2281	46.0	1.0550	33.7	2.7998	33.7
0.3250	44.1	1.3287	33.2	3.0278	33.5
0.4619	40.3	1.4826	33.4	3.3926	33.5
0.5246	38.9	1.6536	33.5	3.6268	33.4
0.6444	36.1				
		[NaBu] = 0.2035 mol kg^{-1}			
0.0356	52.0	0.4034	37.1	1.1093	32.3
0.0712	49.9	0.4390	36.3	1.2101	32.7
0.1186	47.8	0.4864	34.2	1.4000	32.4
0.2017	43.4	0.6526	33.3	1.6847	32.8
0.2729	41.0	0.7356	32.8	1.8329	32.9

Table 4.1 - Continued

[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaBu] = 0.2984 mol kg^{-1}			
0.3559	38.6	0.9966	32.2	2.0111	32.7
0.0241	52.1	0.3784	34.1	0.7270	31.2
0.0549	48.1	0.4144	33.2	0.7664	31.5
0.0558	44.2	0.4652	32.4	0.8058	31.5
0.1407	41.9	0.5073	31.9	0.8448	31.6
0.1936	39.3	0.5492	31.5	0.9690	31.5
0.2463	37.7	0.5908	31.5	1.0818	31.7
0.3061	35.5	0.6320	31.5	1.1911	32.1
0.3419	34.9	0.6800	31.4		
		[NaBu] = 0.4011 mol kg^{-1}			
0.0262	50.2	0.3100	33.2	0.6309	30.5
0.0653	45.5	0.3403	31.9	0.6643	30.8
0.1008	42.0	0.4016	30.6	0.4859	30.7
0.1165	41.5	0.4301	31.0	0.7982	30.5
0.1421	39.6	0.4944	30.6	0.8619	30.6
0.1674	37.8	0.5289	30.5	0.9246	31.2
0.2182	36.6	0.5632	30.5	1.0557	30.8
0.2806	34.4	0.5972	30.5		

Table 4.2 - Surface Tension (γ) Values of SDS in Aqueous Sodium Butyrate Medium at 25 °C

[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaBu] = 0.0 mol kg^{-1}			
0	72.0				
0.1642	70.7	4.3354	42.7	8.1403	35.0
0.4367	69.1	4.5834	41.5	8.2537	35.9
0.7075	66.2	4.8300	40.5	8.3670	36.5
0.9767	63.6	5.0752	39.7	8.4799	37.6
1.2442	61.4	5.3190	38.7	8.5925	37.8
1.5102	59.4	5.5615	38.1	8.8168	38.2
1.7746	57.5	5.8024	37.4	9.0398	38.6
2.0375	55.4	6.0421	36.7	9.2617	38.5
2.2988	53.6	6.2806	35.9	9.4824	38.5
2.5586	51.6	6.5175	35.4	9.7018	38.5
2.8169	49.8	6.7532	34.9	9.9202	38.6
3.0736	48.2	6.9876	34.5	10.137	38.6
3.3289	47.0	7.2207	34.1	10.353	38.6
3.5827	45.9	7.4525	33.9	10.568	38.6
3.8350	45.2	7.6830	33.5	10.782	38.5
4.0859	43.9	7.9123	33.4	10.994	38.6
		[NaBu] = 0.0013 mol kg^{-1}			
0.5061	63.1	4.2838	41.1	11.072	37.7
0.7170	61.8	5.1042	36.8	12.123	37.7
1.3376	55.8	5.7534	36.1	14.412	38.8
1.7471	53.3	7.5322	36.2	15.923	38.5
2.0727	50.8	8.5472	38.9	18.286	38.3
2.4822	47.8	9.6632	38.6	19.312	38.1
2.8017	46.1	10.436	37.6	20.064	38.0
3.3676	43.2				

Table 4.2 - Continued

[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaBu] = 0.0053 mol kg^{-1}			
0.1965	67.9	4.3785	37.3	11.650	37.8
0.8045	58.2	5.0353	35.1	12.910	37.7
1.3509	53.0	6.3186	36.9	13.916	37.8
1.9285	47.8	7.3574	37.9	14.529	37.9
3.1012	41.1	8.5610	37.9	20.555	37.8
3.4019	39.8	9.2432	38.2	16.944	38.5
3.5985	39.5	10.151	38.0		
		[NaBu] = 0.0103 mol kg^{-1}			
0.7088	53.9	2.7837	41.4	9.1290	36.9
0.9798	51.3	3.5443	37.7	10.149	37.2
1.2160	49.2	4.0628	35.6	10.783	37.2
1.6137	46.0	5.2267	35.9	11.739	37.3
1.9712	44.1	7.0766	37.3	12.727	37.2
2.2721	42.1	8.4669	37.0	13.481	37.1
		[NaBu] = 0.0209 mol kg^{-1}			
0.2119	58.8	1.7809	40.6	7.0880	36.4
0.3893	54.7	1.6988	39.2	7.4942	36.1
0.6127	51.2	2.3358	37.9	7.8329	35.9
0.7902	48.4	4.8320	35.9	8.2039	36.1
1.2710	44.1	5.6173	36.1	8.6282	36.2
1.4943	42.5	6.2463	36.4		
		[NaBu] = 0.0355 mol kg^{-1}			
0.1073	59.4	1.1070	42.1	3.5809	35.6
0.2259	55.6	1.2652	41.0	3.9932	35.7
0.3954	51.7	1.5250	39.3	4.2078	35.9
0.6156	47.8	2.4569	35.7	4.6032	36.1
0.7230	46.0	3.0556	35.2	5.3256	35.9
0.8585	44.6	3.2255	35.7		

Table 4.2 - Continued

[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaBu] = 0.0627 mol kg^{-1}			
0.1320	56.8	1.3030	36.5	3.4788	34.8
0.2526	51.4	1.4007	35.2	3.9494	34.9
0.3445	49.3	1.5443	34.8	4.3564	34.9
0.5625	44.1	1.6878	34.1	4.8621	35.0
0.7979	41.5	2.0032	35.1	5.4932	34.9
0.9701	39.1	2.6177	34.8	5.7866	34.7
1.1080	37.8	3.0194	34.9		
		[NaBu] = 0.075 mol kg^{-1}			
0.0627	59.4	1.0950	37.3	3.3475	34.6
0.1312	55.6	1.4542	34.0	3.5418	34.4
0.1939	53.0	1.5683	32.9	3.7181	34.7
0.3935	47.8	1.8764	34.1	4.0432	34.6
0.5076	45.0	2.1844	34.5	4.2769	34.5
0.6673	42.8	2.5376	34.3	4.6819	34.6
0.8498	39.8	2.9541	34.6		
		[NaBu] = 0.1002 mol kg^{-1}			
0.1637	51.9	0.6789	36.7	2.7455	33.5
0.2303	48.7	0.7940	35.4	3.1822	33.9
0.3152	46.3	1.1213	33.2	3.5516	34.2
0.3819	44.6	1.5397	34.1	4.9094	33.5
0.4546	41.9	1.8851	34.1	5.1823	33.7
0.5576	38.8	2.2910	33.8	5.5940	34.1
		[NaBu] = 0.1900 mol kg^{-1}			
0.0729	53.4	0.6196	33.9	3.3345	32.6
0.1761	45.9	0.7531	33.7	3.5590	32.8
0.2247	43.8	0.9535	31.6	3.7716	32.7

Table 4.2 - Continued

[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaBu] = 0.1900 mol kg^{-1}			
0.2673	42.3	1.2573	32.4	3.9357	32.5
0.3158	40.3	1.6096	32.5	4.2455	32.6
0.3948	38.1	2.0288	33.0	4.4333	32.8
0.5345	35.5	2.8969	32.9		
		[NaBu] = 0.2984 mol kg^{-1}			
0.0335	51.8	0.3468	35.0	0.6453	31.2
0.0830	46.6	0.3855	34.0	0.6815	31.2
0.1487	42.5	0.4240	33.6	0.7174	31.3
0.1886	40.6	0.4621	33.0	0.7529	31.3
0.2287	39.1	0.5077	32.5	0.7882	31.2
0.2684	37.5	0.5368	31.7	0.9606	31.7
0.3078	36.1	0.6138	31.3	0.9943	31.3
		[NaBu] = 0.3903 mol kg^{-1}			
0.0215	50.3	0.2474	36.0	0.6562	31.1
0.0646	45.8	0.2958	34.2	0.7100	30.6
0.0914	44.3	0.3443	32.8	0.8016	31.1
0.1237	40.7	0.4034	31.8	0.9252	31.2
0.1506	39.7	0.4680	31.5	0.9736	31.0
0.2098	37.2	0.5487	31.3	1.0542	31.1
		[NaBu] = 0.4279 mol kg^{-1}			
0.0213	46.7	0.3294	32.7	0.7013	30.8
0.0850	43.3	0.4091	31.3	0.8395	31.2
0.1116	41.1	0.4676	30.3	0.8979	31.1
0.1275	40.0	0.5473	31.2	0.9617	30.9
0.1966	39.0	0.6164	31.0	1.0307	31.3
0.2710	34.6				

Table 4.3 - Surface Tension (γ) Values of SDS in Aqueous Sodium Butyrate Medium at 30 °C

[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaBu] = 0.0 mol kg^{-1}			
0	71.4	4.3640	44.2	8.4159	37.1
0.0970	70.6	4.9611	42.0	8.6944	37.4
0.2584	69.9	5.5520	40.0	8.9712	37.9
0.4836	68.7	5.8452	39.1	9.2468	38.3
0.6439	68.0	6.1368	38.2	9.5209	38.3
0.9632	65.4	6.7154	36.9	9.7938	38.5
1.4389	61.6	7.0025	36.1	10.065	38.5
1.9108	57.5	7.2882	35.6	10.335	38.6
2.5340	53.8	7.5722	35.3	10.604	38.5
3.1505	50.3	7.8549	36.2	10.871	38.6
3.7605	47.2	8.1362	36.5	11.137	38.5
		[NaBu] = 0.0260 mol kg^{-1}			
0.2941	55.2	1.7702	39.1	4.5272	35.6
0.4411	51.8	2.0703	37.7	4.6369	35.6
0.6125	50.1	2.3830	36.1	4.8398	36.0
0.8332	46.6	2.8114	34.1	5.1206	36.2
1.2007	42.9	3.4796	34.7	5.4579	35.6
1.4884	40.8	4.1165	36.0	5.8254	35.8
		[NaBu] = 0.0355 mol kg^{-1}			
0.1046	60.4	1.9241	37.0	4.2201	35.6
0.2325	55.4	2.2900	34.2	4.5922	35.3
0.6568	47.3	2.8716	33.2	4.8879	35.4
0.9241	44.1	3.1734	35.6	5.2484	35.6
1.1162	41.7	3.5804	35.5	5.4957	35.5
1.4182	39.1	3.8773	35.5	5.8415	35.4
		[NaBu] = 0.0627mol kg^{-1}			
0.1656	51.5	1.5676	32.5	4.1051	34.3
0.3372	45.8	1.9343	31.7	4.3424	34.1

Table 4.3 - Continued

[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaBu] = 0.0627mol kg^{-1}			
0.6508	40.4	2.3368	33.8	4.7383	34.5
0.8163	38.6	2.8218	33.8	5.2050	33.9
0.9760	36.9	3.1234	34.2	5.4428	34.2
1.1949	35.2	3.6739	34.8	5.6614	34.3
1.2777	34.7				
		[NaBu] = 0.0898 mol kg^{-1}			
0.1582	49.3	1.0783	35.2	2.4787	33.3
0.3692	44.8	1.2012	34.3	2.6603	33.1
0.5801	39.3	1.3187	33.5	2.9473	33.5
0.6857	37.8	1.6056	32.7	3.1234	33.7
0.7853	36.7	1.8986	33.6	3.2406	34.0
0.8967	36.2	2.1391	33.4	3.4517	33.7
		[NaBu] = 0.1231 mol kg^{-1}			
0.0628	52.2	0.9241	33.8	2.1504	33.0
0.1426	47.8	1.0838	32.3	2.3218	33.0
0.2225	45.7	1.1979	32.0	2.5670	33.0
0.3081	42.5	1.5060	32.4	2.8063	32.9
0.4450	41.1	1.6601	32.8	3.1371	33.0
0.6903	37.3	1.8652	33.0	3.4740	33.1
		[NaBu] = 0.2035 mol kg^{-1}			
0.0749	46.7	0.5300	34.0	1.4806	32.4
0.1210	43.7	0.5991	33.2	1.6589	32.3
0.1843	41.7	0.6855	32.6	1.8838	32.1
0.2477	39.8	0.8411	31.8	2.0565	32.2
0.3284	38.4	1.1359	31.3	2.2984	32.1
0.3802	37.0	1.2845	32.2	2.5866	32.1
0.4435	35.5	1.3942	32.4		

Table 4.3 - Continued

[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaBu] = 0.2984 mol kg^{-1}			
0.0341	57.7	0.3465	36.3	0.9771	31.0
0.0511	55.2	0.3807	35.9	1.2157	31.9
0.0682	53.0	0.4318	34.6	1.3974	31.8
0.0966	49.9	0.5795	32.1	1.5454	32.0
0.1363	46.9	0.6476	32.6	1.7042	32.0
0.1761	44.2	0.7842	31.4	1.8236	31.9
0.2329	40.9	0.8634	31.1	1.9599	32.0
		[NaBu] = 0.4011 mol kg^{-1}			
0.0398	48.8	0.3868	32.9	1.0410	30.6
0.1024	42.0	0.4494	31.4	1.1093	30.1
0.1365	40.1	0.5234	29.8	1.2060	30.6
0.1707	37.8	0.6258	30.1	1.3141	30.3
0.2048	36.4	0.7225	30.0	1.3767	30.5
0.2560	35.4	0.8135	30.3	1.4562	30.7
0.3242	33.3	0.9500	30.6		

Table 4.4 - Surface Tension (γ) Values of SDS in Aqueous Sodium Acetate Medium at 20 °C

[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaAc] = 0.0169 mol kg^{-1}			
0.1818	61.6	2.3192	39.9	5.2207	36.4
0.3628	57.5	2.6671	38.3	5.8793	36.4
0.5434	53.4	3.0125	37	6.5287	36.4
0.9041	49.9	3.3561	35.6	7.5115	36.3
1.2614	46.2	3.8728	34.6	8.4533	36.6
1.6163	44.1	4.5544	35.9	9.3805	36.5
1.9689	41.5				
		[NaAc] = 0.0489 mol kg^{-1}			
0.0884	62.8	1.1372	41.3	3.0084	35.5
0.2647	55.3	1.3096	39.3	3.3399	34.7
0.4405	51.2	1.6559	37.5	3.6705	35.1
0.6155	47.7	1.9977	36.4	3.9979	35.6
0.7900	45.5	2.3369	35.3	4.3234	36.6
0.9637	43.2	2.6738	35.5	4.6465	35.8
		[NaAc] = 0.0971 mol kg^{-1}			
0.1010	53.4	1.0426	35.8	2.1475	34.0
0.2014	50.7	1.1883	34.5	2.3293	34.1
0.3017	47.1	1.3827	33.8	2.5144	34.0
0.4516	43.9	1.5748	34.9	2.6985	33.8
0.6005	40.8	1.7653	34.1	2.8816	34.0
0.7486	39.5	1.9545	34.2	3.0629	34.0
0.8961	37.3				
		[NaAc] = 0.1446 mol kg^{-1}			
0.0379	60.1	0.6354	37.6	1.2160	34.1
0.1136	53.1	0.7088	36.6	1.3609	34.0
0.1889	49.8	0.7820	35.9	1.5026	33.9
0.2640	46.4	0.8549	35.0	1.6434	33.8
0.3388	43.9	0.9278	34.2	1.7833	33.8

Table 4.4 - Continued

[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaAc] = 0.1446 mol kg^{-1}			
0.4134	41.3	1.0001	33.0	2.0669	33.9
0.4877	40.0	1.0723	33.3	2.3406	33.6
0.5617	38.7	1.1443	33.7		
		[NaAC] = 0.2016 mol kg^{-1}			
0.1248	1.2840	1.0876	1.2892	3.1202	1.2939
0.1783	1.2848	1.5330	1.2903	3.6195	1.2944
0.2674	1.2854	1.8365	1.2909	4.2970	1.2952
0.3922	1.2864	2.1217	1.2915	4.9032	1.2960
0.6775	1.2879	2.5675	1.2930	5.7060	1.2967
		[NaAC] = 0.3016 mol kg^{-1}			
0.0412	56.5	0.3660	37.5	0.8362	32.3
0.0822	52.4	0.4458	35.5	0.9127	32.4
0.1231	48.1	0.5250	33.9	0.9886	32.2
0.1638	45.7	0.6036	32.4	1.0640	32.2
0.2045	43.2	0.6818	31.9	1.1390	32.0
0.2449	41.3	0.7592	32.2	1.2135	32.1
0.2852	39.5	0.8362	32.3		
		[NaAc] = 0.4127 mol kg^{-1}			
0.0305	56.0	0.4230	32.2	0.8054	31.2
0.0915	47.3	0.5123	1.2	0.8636	31.1
0.1522	33.2	0.5710	31.0	0.9216	31.3
0.2127	39.0	0.6300	31.1	0.9793	31.8
0.2729	36.6	0.6887	31.1	1.2146	31.2
0.3330	34.7	0.7472	31.1	1.4310	31.5

Table 4.5 - Surface Tension (γ) Values of SDS in Aqueous Sodium Acetate Medium at 25 °C

[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaAc] = 0.0048 mol kg^{-1}			
0.5638	62.9	3.4271	42.6	7.8239	38.3
1.3846	53.8	3.9339	39.3	8.4377	38.3
1.8545	49.5	4.2095	38.5	9.0829	38.3
2.0674	48.9	5.1811	35.1	9.8929	38.3
2.4747	46.2	5.7072	34.4	10.593	38.3
2.7191	44.7	6.6088	37.1	11.208	38.2
3.0007	43.5	7.1109	38.0	11.902	38.3
		[NaAc] = 0.0099 mol kg^{-1}			
0.2677	60.9	2.5609	42.0	6.7746	37.6
0.7566	54.4	3.3000	38.7	7.2228	37.3
1.0127	51.7	3.9402	36.2	8.2058	37.4
1.3327	48.2	5.5756	37.2	8.8329	37.5
1.5365	47.2	5.9307	37.1	9.4281	37.4
1.8973	44.8	6.3089	37.7	9.9580	37.4
2.1476	43.7				
		[NaAc] = 0.0172mol kg^{-1}			
0.4825	55.4	2.1089	41.3	5.7428	36.7
0.7149	52.4	2.3829	40.0	6.1422	36.8
0.8757	50.6	2.6985	38.0	6.3624	36.5
1.1140	48.7	3.3777	37.7	6.8806	36.8
1.3344	46.3	4.1641	35.6	7.5478	36.7
1.6085	44.1	4.6113	35.5	6.1819	36.8
1.8825	42.7	5.1768	36.8	8.7221	36.5
		[NaAc] = 0.0246 mol kg^{-1}			
0.1270	63.5	1.9599	39.3	5.3410	36.4
0.6654	50.5	2.2502	37.5	5.6496	36.2
0.8045	48.3	2.4862	36.6	5.8442	36.3
1.0283	46.5	3.5930	35.6	6.0915	36.4

Table 4.5 - Continued

[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaAc] = 0.0246 mol kg^{-1}			
1.2099	44.6	4.3125	36.0	6.2062	36.3
1.5365	42.0	4.6879	36.3	6.5512	36.5
1.7179	40.6	5.1716	36.2	6.8600	36.1
		[NaAc]= 0.0497 mol kg^{-1}			
0.3247	51.5	1.7416	37.2	4.3214	35.3
0.4959	48.4	2.4385	34.8	4.4805	35.4
0.6494	45.7	3.1763	35.2	4.6819	35.5
0.8561	43.5	3.7843	35.4	4.8054	35.4
1.0038	41.6	4.0321	35.4	4.9536	35.3
1.2338	40.4	4.1795	35.3	5.1419	35.6
1.4465	37.7				
		[NaAc] = 0.0967 mol kg^{-1}			
0.1933	53.0	1.0017	36.4	2.0330	33.6
0.2578	50.7	1.1482	34.5	2.4488	34.2
0.4277	45.4	1.3475	33.2	3.1693	33.6
0.6211	41.4	1.4412	33.7	3.8724	33.9
0.7968	38.6	1.6697	34.0	4.3997	34.0
0.8730	38.0				
		[NaAc] = 0.1466 mol kg^{-1}			
0.1862	48.3	0.9041	34.9	3.3669	34.0
0.2447	46.4	1.0052	33.1	4.7921	34.4
0.3085	44.9	1.2287	32.8	6.8285	33.9
0.4149	41.6	1.4042	33.3	9.4302	33.3
0.5107	40.5	1.7715	33.4	10.165	33.7
0.6436	37.2	2.4577	33.5	11.930	33.6
0.7606	36.0				

Table 4.5 - Continued

[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaAc] = 0.2006 mol kg^{-1}			
0.1133	51.6	0.6741	35.0	1.7560	32.9
0.1586	49.0	0.8498	33.1	1.8413	32.9
0.1926	48.2	1.0082	32.8	2.0222	32.9
0.2776	44.5	1.1839	33.0	2.1302	33.0
0.3625	42.0	1.1249	32.9	2.1978	32.9
0.4475	40.1	1.6030	32.9	2.1978	32.9
0.5834	36.4				
		[NaAc] = 0.2500 mol kg^{-1}			
0.2065	44.8	0.4588	37.0	1.3281	32.7
0.2351	43.8	0.5333	35.5	1.5828	32.4
0.2656	42.6	0.7054	32.9	1.7204	32.4
0.3326	40.2	0.7915	32.3	1.9498	32.5
0.3786	38.7	1.0324	32.2	2.2425	32.4
0.4031	38.3	1.2444	32.6		
		[NaAc] = 0.3015 mol kg^{-1}			
0.0382	59.9	0.3659	38.9	0.9611	32.2
0.0546	57.8	0.4315	36.5	1.1226	32.0
0.0819	54.4	0.4860	35.1	1.2124	32.1
0.1311	49.9	0.5516	33.5	1.3217	32.3
0.1748	46.8	0.5953	32.9	1.4690	32.0
0.2348	43.4	0.6881	32.2	1.5019	32.1
0.3059	40.7	0.7973	32.3		

Table 4.5 - Continued

[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaAc] = 0.3698 mol kg^{-1}			
0.0072	63.5	0.2905	37.7	0.7386	31.5
0.0215	58.5	0.3566	35.0	0.7900	31.6
0.0357	6.0	0.4216	33.0	1.0630	31.5
0.0570	52.5	0.4856	31.9	0.9052	31.8
0.0852	49.3	0.5484	31.9	0.9612	31.7
0.1271	45.2	0.6103	31.7	1.0168	31.8
0.1686	42.9	0.6712	31.8	1.0711	31.8
0.2232	40.0				
		[NaAc] = 0.4127 mol kg^{-1}			
0.0305	56.0	0.4230	32.2	0.8054	31.2
0.0915	47.3	0.5123	31.2	0.8636	31.1
0.1522	43.2	0.5710	31.0	0.9216	31.3
0.2127	39.0	0.6300	31.1	0.9793	31.8
0.2729	36.6	0.6887	31.1	1.2146	31.2
0.3330	34.7	0.7472	31.1	1.4310	31.5

Table 4.6 - Surface Tension (γ) Values of SDS in Aqueous Sodium Acetate Medium at 30 °C

[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaAc] = 0.0169 mol kg^{-1}			
0.0939	63.6	2.3112	39.1	5.2982	36.6
0.2817	57.4	2.8505	37.0	5.8080	36.6
0.4686	54.5	3.3848	34.8	6.6684	36.6
0.6550	51.7	3.9140	33.9	7.1421	36.7
0.9342	49.0	4.2562	36.0	7.9840	36.6
1.2110	46.3	4.7833	36.6	8.7907	36.7
1.7658	42.7				
		[NaAc] = 0.0489 mol kg^{-1}			
0.0841	63.3	1.5774	36.6	3.9685	34.7
0.2520	53.8	2.0684	34.2	4.2788	34.9
0.4193	48.6	2.3874	34.3	4.5870	35.4
0.5861	47.1	2.7079	34.2	4.8924	34.6
0.7522	44.7	3.0264	34.1	5.1967	35.0
0.9178	42.3	3.3422	34.5	5.4983	35.6
1.2495	39.5	3.6562	35.5	6.2751	35.1
		[NaAc] = 0.0971 mol kg^{-1}			
0.0509	60.6	0.7564	39.3	1.9250	34.0
0.1526	53.2	0.9546	36.5	2.1151	34.1
0.2540	49.9	1.1514	34.7	2.3037	34.0
0.3549	46.1	1.3469	33.2	2.4913	33.6
0.4556	43.9	1.5411	32.8	2.6769	34.0
0.5557	41.9	1.7339	33.9	2.8617	34.0
		[NaAc] = 0.1446 mol kg^{-1}			
0.0746	46.6	0.5166	38.9	1.5147	33.0
0.1489	45.3	0.6630	35.6	1.6532	32.9
0.2230	44.0	0.8073	34.5	1.7907	33.2
0.2968	42.9	0.9509	33.6	1.9272	33.3

Table 4.6 - Continued

[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaAc] = 0.1446 mol kg^{-1}			
0.3703	42.2	1.2346	33.3	2.1342	32.7
0.4435	40.6	1.3751	33.6	2.3352	32.9
		[NaAc] = 0.2016 mol kg^{-1}			
0.0577	55.2	0.5402	36.0	0.9531	32.2
0.1152	51.0	0.6238	33.9	1.0635	32.3
0.1724	46.5	0.6788	32.7	1.1712	32.2
0.2295	44.3	0.7341	31.3	1.2783	32.2
0.2864	41.9	0.7891	32.0	1.3846	32.5
0.3716	40.0	0.8440	32.7	1.6008	32.2
0.4561	38.0	0.8987	32.5	1.8090	31.7
		[NaAc] = 0.3016 mol kg^{-1}			
0.0406	53.8	0.2814	41.2	0.7099	31.3
0.0811	50.5	0.3211	38.1	0.7861	31.0
0.1215	49.7	0.3999	35.8	0.8618	31.2
0.1617	47.9	0.4782	33.4	0.9369	31.7
0.2017	47.1	0.5560	32.3	1.0115	31.5
0.2417	45.0	0.6332	31.2	1.0856	31.6
		[NaAc] = 0.4127 mol kg^{-1}			
0.0309	53.3	0.4875	30.4	1.0788	30.6
0.0925	47.3	0.5438	31.0	1.1944	30.4
0.1847	39.6	0.6071	31.6	1.3090	31.0
0.2762	36.3	0.7270	30.5	1.4231	30.6
0.3672	32.9	0.8451	30.9	1.5361	30.6
0.4272	32.0	0.9623	30.7		

Table 4.7 - Surface Tension (γ) Values of SDS in Aqueous Sodium Propionate Medium at 20 °C

[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaPr] = 0.0036 mol kg^{-1}			
0.2668	65.5	3.5944	44.3	9.6343	38.2
0.5337	62.4	4.5638	40.9	10.506	38.2
0.9476	57.0	5.3153	38.6	11.343	37.9
1.4052	53.1	6.2795	35.8	12.118	38.5
1.7645	52.0	7.2765	37.3	12.584	38.5
2.1839	49.5	7.7112	36.6	12.966	38.7
2.7285	47.2	8.1026	37.1	13.376	38.3
3.2102	45.9	8.8986	37.9		
		[NaPr] = 0.0104 mol kg^{-1}			
0.1708	61.9	3.5582	38.4	8.0283	37.3
0.5831	55.1	3.8997	36.0	8.3699	37.2
1.0662	48.3	4.4888	34.5	8.7705	37.2
1.2018	47.1	5.4316	36.3	9.1542	37.1
1.6494	43.7	6.2262	37.2	9.7841	37.2
2.0914	42.0	7.0978	37.5	10.467	37.1
2.4679	40.9	7.5984	37.5	11.110	37.2
3.1516	38.0				
		[NaPr] = 0.0267 mol kg^{-1}			
0.2745	55.1	1.9753	37.8	4.2848	35.7
0.5312	50.2	2.2317	37.1	4.6486	36.2
0.7937	46.8	2.5658	36.3	5.0064	35.6
1.1338	43.2	2.9419	35.4	5.4366	36.4
1.4205	41.3	3.4074	35.6	5.8901	35.3
1.6532	39.2	3.9923	35.6	6.4332	35.6
		[NaPr] = 0.0525 mol kg^{-1}			
0.0577	65.8	1.8223	34.2	3.9276	35.5
0.1846	57.4	2.0358	34.9	4.1872	35.0
0.3807	52.2	2.3764	35.9	4.5386	35.2

Table 4.7 - Continued

[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaPr] = 0.0525 mol kg^{-1}			
0.6229	46.7	2.6936	35.3	4.9026	34.9
0.8823	44.2	3.1895	35.5	5.3459	34.9
1.3958	39.1	3.5639	35.0		
		[NaPr] = 0.0735 mol kg^{-1}			
0.0594	61.9	1.2301	37.2	2.5842	34.9
0.1457	56.7	1.4406	36.0	2.9082	34.7
0.2374	52.7	1.7319	34.7	3.2153	35.2
0.3831	48.5	1.9803	34.6	3.3933	34.8
0.5287	45.4	2.2337	34.6	3.6093	34.9
0.7013	42.9	2.4696	34.6	4.3916	34.9
0.8956	40.0				
		[NaPr] = 0.1103 mol kg^{-1}			
0.0886	57.1	1.0012	35.7	2.2163	34.4
0.2190	51.2	1.1211	35.1	2.3309	34.4
0.3650	45.6	1.2880	34.3	2.5652	34.3
0.5319	42.0	1.4895	34.1	2.7793	34.4
0.6727	38.9	1.7050	34.4	2.9616	34.6
0.8135	38.9	1.9817	34.1	3.8373	34.5
		[NaPr] = 0.1750 mol kg^{-1}			
0.0957	53.1	0.9485	33.1	1.5098	33.2
0.2866	43.7	1.0429	33.2	1.6030	33.2
0.4768	39.7	1.1364	33.0	1.7899	33.2
0.6551	35.9	1.2301	33.0	1.8812	33.2
0.7602	34.6	1.3235	33.1	1.9735	33.2
0.8545	33.6	1.4169	33.6	2.0655	33.6

Table 4.7 - Continued

[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaPr] = 0.2665 mol kg^{-1}			
0.0414	54.0	0.4919	33.8	0.9730	32.0
0.0827	49.8	0.5728	33.0	1.0523	31.6
0.1239	47.2	0.6535	32.4	1.1312	32.1
0.1650	44.6	0.7337	32.0	1.2099	32.3
0.2459	41.6	0.8138	32.1	1.2880	32.2
0.3292	38.3	0.8917	32.1	1.3663	32.2
0.4107	36.4				
		[NaPr] = 0.3806 mol kg^{-1}			
0.0347	56.7	0.4467	32.8	0.8502	31.8
0.1040	47.5	0.5146	32.0	0.9165	31.9
0.1730	43.5	0.5822	32.0	0.9827	32.1
0.2418	39.4	0.6494	32.0	1.0487	31.9
0.3103	36.6	0.7167	31.8	1.1146	32.0
0.3787	33.9	0.7835	32.0		
		[NaPr] = 0.4714 mol kg^{-1}			
0.0126	59.6	0.2845	34.5	0.5924	31.2
0.0377	52.8	0.3575	31.9	0.6386	31.4
0.0627	49.9	0.4046	31.1	0.6844	31.1
0.0877	46.4	0.4521	31.2	0.7299	31.1
0.1376	42.1	0.4992	31.1	0.8227	31.2
0.1869	39.2	0.5459	30.9	0.9119	31.6
0.2359	36.9				
		[NaPr] = 0.5780 mol kg^{-1}			
0.0040	63.3	0.0800	45.8	0.3147	31.3
0.0101	61.8	0.1201	43.0	0.3528	30.8
0.0201	57.4	0.1595	39.4	0.3906	31.2
0.0302	54.3	0.1987	38.0	0.4282	31.2
0.0402	51.1	0.2377	34.4	0.4655	31.3
0.0602	48.6	0.2763	32.5	0.5026	30.9

Table 4.8 - Surface Tension (γ) Values of SDS in Aqueous Sodium Propionate Medium at 25 °C

[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaPr] = 0.0042 mol kg^{-1}			
0.2970	64.7	3.6410	39.4	8.6243	38.0
0.6026	60.6	4.0451	38.2	9.3094	38.1
0.9502	56.6	4.6326	36.4	10.352	37.7
1.1878	53.9	5.2146	34.6	10.827	38.1
1.6751	50.6	5.5415	35.0	11.351	38.2
2.1205	48.0	6.3434	35.4	11.856	37.7
2.6196	45.3	7.4426	37.6	12.343	38.0
3.1184	42.5	8.1493	38.2		
		[NaPr] = 0.0104 mol kg^{-1}			
0.4240	50.8	2.9562	38.1	6.0510	36.8
0.7735	48.5	3.3230	36.5	6.3771	37.3
1.1744	46.0	3.7812	35.5	6.7955	36.9
1.5012	44.0	4.3715	34.5	7.1899	37.1
1.8851	42.3	5.1561	36.8	7.8437	36.9
2.3951	40.1	5.7640	36.7	8.2153	36.9
		[NaPr] = 0.0267 mol kg^{-1}			
0.4658	51.2	2.3541	36.2	4.9354	35.7
0.7960	46.8	2.7298	35.8	5.3830	36.0
1.0271	43.5	3.3553	35.9	5.8200	35.7
1.4566	41.4	3.9914	36.0	6.1976	36.0
1.7335	39.3	4.4343	35.9	6.6930	35.3
2.1107	37.4				
		[NaPr] = 0.0519 mol kg^{-1}			
0.1515	55.4	1.2174	39.2	2.8309	34.9
0.2214	54.9	1.4970	37.3	3.1516	35.0
0.4078	49.4	1.7125	36.0	3.4310	35.3
0.5651	46.6	2.0447	34.5	3.6994	35.1
0.8040	43.5	2.2601	34.8	4.0544	35.0

Table 4.8 - Continued

[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaPr] = 0.0519 mol kg^{-1}			
1.0659	40.6	2.5458	35.0	4.6251	35.4
		[NaPr] = 0.0735 mol kg^{-1}			
0.1607	57.9	1.0694	38.0	2.2664	34.6
0.3269	50.2	1.2301	37.8	2.6598	34.7
0.4654	47.0	1.6178	35.0	2.8538	34.6
0.6094	44.1	1.4353	34.3	3.2473	34.9
0.7592	41.2	1.7953	34.2	3.7405	34.6
0.9087	39.1	2.0986	34.6		
		[NaPr] = 0.1103 mol kg^{-1}			
0.1713	50.7	1.1270	34.3	1.8507	33.7
0.2818	45.3	1.2985	33.8	2.5470	34.1
0.4365	43.2	1.5471	33.7	2.9671	34.1
0.5690	40.7	1.7625	33.3	3.2925	34.0
0.7569	37.9	1.9170	33.6	3.6579	34.0
0.9338	36.2	2.1935	33.7		
		[NaPr] = 0.1750 mol kg^{-1}			
0.0959	52.7	0.7618	34.8	1.3875	33.3
0.1914	47.9	0.8563	33.5	1.5130	33.4
0.2870	44.4	0.9505	33.1	1.6063	33.5
0.3822	42.1	1.0448	33.3	1.6991	33.5
0.4773	39.7	1.1388	33.2	1.7924	33.5
0.5723	37.9	1.2326	33.6	1.9794	33.4
0.6672	36.3	1.3263	33.4	2.1639	33.4
		[NaPr] = 0.2665 mol kg^{-1}			
0.0385	57.1	0.5328	33.8	1.0533	32.3
0.0768	52.2	0.6079	33.4	1.1265	33.0
0.1535	46.5	0.6827	33.0	1.1996	32.2

Table 4.8 - Continued

[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaPr] = 0.2665 mol kg^{-1}			
0.2300	43.0	0.7574	31.8	1.2724	32.0
0.3061	40.0	0.8316	32.5	1.3450	32.2
0.3819	37.5	0.9058	32.3	1.4175	32.2
0.4574	35.6	0.9796	32.2		
		[NaPr] = 0.3806 mol kg^{-1}			
0.0353	55.5	0.3848	33.8	0.7960	31.4
0.0705	51.5	0.4540	32.6	0.8638	31.5
0.1056	46.8	0.5228	31.6	0.9312	31.5
0.1758	42.8	0.5915	31.4	0.9985	30.7
0.2457	38.8	0.6598	31.3	1.0654	31.5
0.3086	37.0	0.7282	31.6	1.1322	31.3
		[NaPr] = 0.4714 mol kg^{-1}			
0.0239	52.0	0.3289	31.9	0.5976	31.1
0.0478	49.6	0.3740	31.7	0.6416	30.0
0.0716	47.2	0.4193	31.2	0.7307	30.9
0.1191	43.9	0.4643	30.9	0.8166	31.2
0.1666	40.8	0.5090	30.6	0.9014	31.3
0.2129	37.3	0.5535	31.4	0.9852	31.3
0.2843	33.7				
		NaPr] = 0.5780 mol kg^{-1}			
0.0215	55.0	0.2113	35.6	0.4560	30.7
0.0429	50.9	0.2533	33.7	0.4956	30.0
0.0643	47.9	0.3155	31.5	0.5350	30.5
0.0855	44.9	0.3556	30.6	0.5740	30.6
0.1067	42.7	0.3855	30.4	0.6128	30.7
0.1279	40.7	0.4157	30.8	0.6514	30.7
0.1702	37.4				

Table 4.9 - Surface Tension (γ) Values of SDS in Aqueous Sodium Propionate Medium at 30 °C

[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaPr] = 0.0104 mol kg^{-1}			
0.2777	57.1	3.2361	38.3	6.9203	37.0
0.8575	51.6	3.6528	36.5	7.4511	37.0
1.2029	48.0	4.2328	35.0	7.8365	36.9
1.6302	45.1	4.7514	34.6	8.3738	37.0
2.1614	42.6	6.1948	36.9	9.2198	37.0
2.5394	40.8	6.5633	37.1	9.9271	36.6
2.9042	39.1				
		[NaPr] = 0.0267 mol kg^{-1}			
0.2370	53.9	1.9021	38.1	3.9932	35.8
0.5045	50.9	2.2669	36.2	4.5219	35.8
0.7900	47.3	2.5647	34.9	5.0924	36.0
1.0271	43.9	3.0509	35.3	5.4881	35.6
1.3917	42.0	3.3669	35.6	5.9132	35.8
1.6407	40.1	3.9539	35.4	6.2780	35.6
		[NaPr] = 0.0519 mol kg^{-1}			
0.1849	49.6	1.4908	35.4	3.5541	34.6
0.3872	45.8	1.7188	33.7	3.9530	34.8
0.5894	42.0	1.9771	32.6	4.1670	34.7
0.7743	39.7	2.6177	34.3	4.3115	34.8
0.9766	38.6	3.0222	34.5	4.7274	34.7
1.1559	36.4	3.3054	34.8	5.7441	35.1
1.3177	36.2				
		[NaPr] = 0.0735 mol kg^{-1}			
0.2284	47.8	1.3078	35.1	2.4902	34.2
0.3884	45.0	1.4162	34.4	2.6670	34.1
0.5882	42.1	1.7078	33.7	2.8611	33.7
0.7938	40.0	1.9991	34.0	3.0784	34.2

Table 4.9 - Continued

[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaPr] = 0.0735 mol kg^{-1}			
0.9537	38.3	2.1703	34.0	3.3692	34.1
1.1080	36.9	2.3417	33.9		
		[NaPr] = 0.1750 mol kg^{-1}			
0.0979	51.5	0.7776	34.4	1.3537	33.1
0.1955	47.2	0.8740	33.1	1.4492	32.8
0.2930	43.6	0.9704	33.0	1.6411	33.1
0.3902	42.8	1.0664	32.9	1.8308	33.1
0.4873	39.2	1.1623	33.0	2.0199	33.2
0.5842	37.4	1.2581	33.1	2.2087	33.1
0.6811	35.5				
		[NaPr] = 0.2665 mol kg^{-1}			
0.0776	51.1	0.6134	32.4	1.1364	32.3
0.1549	45.1	0.6887	31.8	1.2101	31.9
0.2320	42.0	0.7641	32.0	1.2836	32.2
0.3088	39.7	0.8389	31.7	1.3568	32.2
0.3852	37.4	0.9138	32.2	1.4297	32.3
0.4616	35.6	0.9882	32.2	1.5026	32.6
0.5376	33.6	1.0623	32.4		
		[NaPr] = 0.3806 mol kg^{-1}			
0.0345	54.3	0.4443	32.5	0.8455	31.0
0.0690	50.6	0.5113	31.2	0.9115	30.9
0.1039	46.8	0.5789	31.1	0.9773	31.0
0.1720	43.0	0.6459	31.1	1.2830	31.1
0.2404	39.0	0.7126	31.0	1.1085	31.1
0.3020	36.5	0.7792	31.8	1.1736	31.1
0.3766	33.7				

Table 4.9 - Continued

[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaPr] = 0.4714 mol kg^{-1}			
0.0254	53.9	0.2989	33.9	0.6816	30.5
0.0507	49.4	0.3481	31.6	0.7735	30.6
0.1264	44.5	0.3964	31.4	0.8642	30.9
0.1765	40.7	0.4444	31.1	0.9535	30.7
0.2258	38.2	0.4920	30.7	1.1364	30.6
0.2750	35.9	0.5883	30.6	1.4013	30.6
		[NaPr] = 0.5780 mol kg^{-1}			
0.0201	57.6	0.2367	34.9	0.5191	30.0
0.0401	52.2	0.2751	33.4	0.5556	30.2
0.0600	49.1	0.3134	31.7	0.5919	30.2
0.0798	46.1	0.3709	31.0	0.6280	30.5
0.1196	42.5	0.4078	30.4	0.6638	30.3
0.1589	39.1	0.4452	30.3	0.6994	30.4
0.1979	36.9	0.4822	30.2		

Table 4.10 - Surface Tension (γ) Values of SDS in Aqueous Sodium Chloride Medium at 20 °C

[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaCl] = 0.0152 mol kg^{-1}			
0.2343	54.6	3.1807	36.8	6.1464	37.4
0.4673	52.4	3.6177	35.4	6.5543	36.8
0.6215	51.4	4.0497	34.2	6.9570	36.9
0.9307	49.0	4.4774	34.7	7.3574	36.9
1.3597	45.1	4.9003	36.2	7.7522	36.9
1.8456	42.6	5.3202	36.4	8.1456	36.9
2.2952	40.6	5.7349	36.8	8.5334	37.0
2.7405	39.0				
		[NaCl] = 0.0797 mol kg^{-1}			
0.0784	52.1	1.1634	35.8	2.2224	34.1
0.2346	47.6	1.3162	34.0	2.4273	34.0
0.3902	45.0	1.4687	33.0	2.5207	34.2
0.5454	42.4	1.6204	33.4	2.6689	34.1
0.7002	40.5	1.7715	33.8	2.8166	34.2
0.8543	38.9	1.9223	34.0	3.1162	34.1
1.0098	37.5	2.0727	34.1		
		[NaCl] = 0.1006 mol kg^{-1}			
0.0467	59.7	1.0487	36.0	2.2513	34.5
0.1277	53.1	1.2007	34.3	2.3990	34.4
0.2800	48.2	1.5060	33.1	2.5464	34.2
0.4347	44.0	1.6540	34.5	2.6936	34.5
0.5890	41.1	1.8040	4.5	2.8401	34.5
0.7427	39.2	1.9536	34.5	2.9863	34.4
0.8961	37.7	2.1025	34.4	3.1320	34.6
		[NaCl] = 0.1849 mol kg^{-1}			
0.0343	59.8	0.4413	39.7	1.1647	33.3
0.0685	56.0	0.5082	38.0	1.2292	33.3
0.1026	52.0	0.5750	36.7	1.2925	33.3

Table 4.10 - Continued

[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaCl] = 0.1849 mol kg^{-1}			
0.1710	48.5	0.7090	34.6	1.3575	33.2
0.2389	45.8	0.8411	33.7	1.4211	33.3
0.3066	43.1	0.9721	33.4	1.4847	33.3
0.3739	41.3	1.1021	33.5	1.5479	33.3
		[NaCl] = 0.2525 mol kg^{-1}			
0.0443	53.4	0.5699	33.7	1.1696	32.6
0.0884	49.9	0.6567	32.6	1.2386	32.3
0.1326	46.0	0.7429	32.7	1.3382	32.0
0.2208	42.6	0.8288	32.0	1.4221	32.0
0.3086	39.0	0.9144	32.6	1.5920	32.9
0.3960	36.3	0.9998	32.4	1.7580	32.7
0.4832	35.1	1.0848	32.6		
		[NaCl] = 0.3471 mol kg^{-1}			
0.0296	55.1	0.3804	34.4	0.8930	32.0
0.0590	51.0	0.4381	33.5	0.9489	32.0
0.0885	47.7	0.4956	32.5	1.0117	32.0
0.1473	44.1	0.5530	32.1	1.0603	32.0
0.2059	41.0	0.6682	31.4	1.1159	32.0
0.2643	38.4	0.7804	31.7	1.1709	32.2
0.3224	36.1	0.8366	32.2		
		[NaCl] = 0.5021 mol kg^{-1}			
0.0147	57.6	0.2185	37.0	0.5572	31.3
0.0442	51.5	0.2473	35.5	0.5838	31.2
0.0735	47.9	0.2758	34.6	0.6111	30.9
0.1027	44.3	0.3333	32.6	0.6385	31.2
0.1318	42.0	0.3899	31.7	0.6656	31.2
0.1609	40.8	0.4461	31.2	0.6927	31.1
0.1898	38.9	0.5018	31.2		

Table 4.11 - Surface Tension (γ) Values of SDS in Aqueous Sodium Chloride Medium at 25 °C

[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaCl] = 0.0152 mol kg^{-1}			
0.0707	62.2	2.8290	37.2	5.8348	36.9
0.2353	56.6	3.2714	35.9	6.2463	36.8
0.5482	52.1	3.7096	34.8	6.6562	36.9
1.0147	47.6	4.1431	34.1	6.9155	36.8
1.4755	44.5	4.5722	35.6	7.1833	37.1
1.9312	41.6	4.9972	36.3	7.5932	36.8
2.3825	39.3	5.3116	37.2	7.9850	36.9
		[NaCl] = 0.0797 mol kg^{-1}			
0.0798	53.9	1.1842	35.0	2.1097	34.2
0.2393	48.1	1.3401	34.2	2.2622	34.1
0.3982	44.9	1.4950	34.1	2.4140	34.3
0.5566	42.6	1.6494	34.0	2.5652	34.2
0.7142	40.5	1.8036	33.7	2.7160	34.6
0.8716	38.0	1.9567	34.1	2.8663	34.4
1.0281	37.2				
		[NaCl] = 0.1006 mol kg^{-1}			
0.0793	53.3	1.1769	33.8	2.2477	33.9
0.1585	50.0	1.3315	32.8	2.3984	34.0
0.2378	47.1	1.4854	33.1	2.5488	34.5
0.3958	44.0	1.6388	33.4	2.6985	34.2
0.5530	41.0	1.7920	33.6	2.9966	34.0
0.8660	36.7	1.9441	33.8	3.1450	34.0
1.0217	35.4	2.0962	33.8		
		[NaCl] = 0.1849 mol kg^{-1}			
0.0303	58.8	0.4495	39.1	1.1469	32.9
0.0605	56.8	0.5087	38.2	1.2037	33.0
0.0907	52.1	0.6274	35.6	1.2605	33.0
0.1574	48.0	0.7444	33.9	1.3171	33.0

Table 4.11 - Continued

[SDS] x10³ / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10³ / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10³ / mol kg^{-1}	γ / mN m^{-1}
		[NaCl] = 0.1849 mol kg^{-1}			
0.2111	45.4	0.8609	32.4	1.3735	33.0
0.3307	42.1	1.0324	33.0	1.4297	33.2
0.3902	40.0	1.0898	33.0	1.6023	33.1
		[NaCl] = 0.2525 mol kg^{-1}			
0.0431	53.7	0.6301	32.9	1.1377	32.1
0.0860	50.9	0.7225	32.2	1.2199	32.4
0.1289	47.7	0.8060	32.0	1.3021	32.3
0.2147	43.1	0.8895	32.2	1.3837	32.3
0.3004	40.7	0.9724	32.1	1.4650	32.7
0.3851	38.0	1.0552	32.1	1.6298	32.6
0.4698	36.0				
		[NaCl] = 0.3471 mol kg^{-1}			
0.0291	52.8	0.3741	34.6	0.9060	31.7
0.0580	50.0	0.4596	32.8	0.9610	31.9
0.0870	47.1	0.5444	31.7	1.0159	31.8
0.1449	43.5	0.6287	31.5	1.0706	31.7
0.2025	40.9	0.7412	31.6	1.1249	31.7
0.2599	38.2	0.7955	31.7	1.1793	32.2
0.3171	36.0	0.8508	31.9		
		[NaCl] = 0.5021 mol kg^{-1}			
0.0294	52.8	0.3033	32.9	0.5125	31.3
0.0586	49.1	0.3457	31.4	0.5402	30.9
0.0882	45.0	0.3735	30.8	0.5817	31.2
0.1314	42.0	0.4015	31.2	0.6226	30.6
0.1747	39.0	0.4295	31.2	0.6635	31.2
0.2178	36.1	0.4573	31.1	0.7039	31.3
0.2606	34.4	0.4850	31.6		

Table 4.12 - Surface Tension (γ) Values of SDS in Aqueous Sodium Chloride Medium at 30 °C

[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaCl] = 0.0152 mol kg^{-1}			
0.0824	58.2	2.1804	39.6	5.2243	36.5
0.2471	53.2	2.6554	37.4	5.5173	36.7
0.4111	51.3	3.1212	36.2	5.8080	36.5
0.5744	49.5	3.5828	34.9	6.0971	36.5
0.9012	47.0	4.0395	33.7	6.5377	36.7
1.2244	44.4	4.3334	34.7	6.9634	36.5
1.5454	42.6	4.6326	35.6	7.3862	36.9
1.8639	40.6	4.9298	36.5	7.8041	36.6
		[NaCl] = 0.0797 mol kg^{-1}			
0.1628	47.4	1.4445	33.5	2.5365	34.0
0.3250	44.0	1.6023	32.7	2.6905	34.1
0.4867	41.2	1.7593	33.4	2.8433	34.0
0.6476	39.6	1.9157	33.6	2.9966	33.9
0.8082	38.1	2.0717	33.9	3.1487	34.2
0.9681	36.8	2.2270	33.8	3.3001	34.0
1.1275	35.2	2.3825	34.0	3.4517	34.2
1.2863	34.6				
		[NaCl] = 0.1006 mol kg^{-1}			
0.0782	53.7	1.1605	33.4	2.2163	33.7
0.1563	50.2	1.3126	32.3	2.3650	33.6
0.2344	46.7	1.4646	32.9	2.5138	33.7
0.3902	43.8	1.6160	33.1	2.6658	33.6
0.5452	40.6	1.7670	33.7	2.9602	33.8
0.6999	38.6	1.9175	33.9	3.2533	33.6
0.8540	36.4	2.0669	33.7	3.6943	33.9
1.0075	34.9				

Table 4.12 Continued

[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaCl] = 0.1849 mol kg^{-1}			
0.0335	59.2	0.4964	38.1	1.2640	32.8
0.0669	55.7	0.6277	36.0	1.3266	32.8
0.1002	52.4	0.7571	33.8	1.3888	32.9
0.1670	49.0	0.8858	32.4	1.4509	32.8
0.2333	45.0	1.0019	32.6	1.5126	32.6
0.2994	43.6	1.1401	32.6	1.7031	32.9
0.3654	41.2	1.2012	32.8	1.9500	32.8
0.4310	39.1				
		[NaCl] = 0.2525 mol kg^{-1}			
0.0450	53.9	0.5349	34.5	1.1445	31.9
0.0899	48.8	0.6228	32.5	1.2304	32.1
0.1346	46.7	0.7106	31.6	1.3159	32.0
0.1794	44.7	0.7979	31.9	1.4013	32.2
0.2689	41.6	0.8850	31.8	1.4857	32.2
0.3578	38.4	0.9719	32.0	1.5708	32.2
0.4465	36.5	1.0584	31.9	1.6547	32.4
		[NaCl] = 0.3471 mol kg^{-1}			
0.0295	51.9	0.3799	34.5	0.8357	31.1
0.0589	48.8	0.4376	33.3	0.8917	31.1
0.0884	45.0	0.4950	31.9	0.9476	31.2
0.1471	43.4	0.5522	31.6	1.0035	31.1
0.2056	40.5	0.6093	31.0	1.0591	31.3
0.2639	37.7	0.7242	31.3	1.1144	31.2
0.3201	36.1	0.7794	31.1	1.2979	31.7
		[NaCl] = 0.5021 mol kg^{-1}			
0.0287	54.9	0.2266	36.5	0.5016	31.0
0.0572	48.9	0.2686	34.1	0.5419	31.0

Table 4.12 - Continued

[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaCl] = 0.5021 mol kg^{-1}			
0.0857	46.6	0.3103	33.6	0.5585	30.8
0.1141	43.1	0.3516	32.2	0.6221	31.1
0.1424	41.0	0.3928	31.0	0.6617	31.1
0.1706	39.5	0.4194	30.6	0.7703	31.1
0.1986	38.0	0.4609	30.9		

Table 4.13 - Critical Micelle Concentration Values (± 0.05 x 10^{-3} mol kg^{-1}) of SDS in Aqueous Electrolyte Solutions at Different Temperatures from Surface Tension Data

[NaCl]/ mol kg^{-1}	Cmc x 10^{-3} / mol kg^{-1}	[NaAc]/ mol kg^{-1}	Cmc x 10^{-3} / mol kg^{-1}	[NaPr]/ mol kg^{-1}	Cmc x 10^{-3} / mol kg^{-1}	[NaBu]/ mol kg^{-1}	Cmc x 10^{-3} / mol kg^{-1}
Temperature = 293K							
0	7.76	0.0169	3.89	0.0036	6.49	0.0260	3.30
0.0152	3.98	0.0489	2.37	0.0104	4.47	0.0355	2.76
0.0797	1.49	0.0971	1.44	0.0267	2.98	0.0627	1.88
0.1006	1.38	0.1446	1.07	0.0525	1.88	0.0898	1.66
0.1849	0.79	0.2016	0.84	0.0735	1.73	0.1231	1.26
0.2525	0.69	0.3016	0.66	0.1103	1.19	0.2035	0.75
0.3471	0.56	0.4127	0.50	0.1750	0.94	0.2984	0.55
0.5021	0.40			0.2665	0.67	0.4011	0.47
				0.3806	0.50		
				0.4714	0.40		
				0.5780	0.32		
Temperature = 298K							
0	8.10	0.0048	5.75	0.0042	5.30	0.0013	6.31
0.0152	4.10	0.0099	4.47	0.0104	4.34	0.0053	5.01
0.0797	1.58	0.0172	3.98	0.0267	2.51	0.0103	4.50
0.1010	1.33	0.0246	3.16	0.0519	2.00	0.0209	3.35
0.1849	0.82	0.0497	2.29	0.0735	1.41	0.0355	2.66
0.2525	0.69	0.0967	1.35	0.1103	1.15	0.0627	1.68
0.3471	0.52	0.1466	1.15	0.1750	0.89	0.0750	1.58
0.5021	0.36	0.2006	0.87	0.2665	0.55	0.1002	1.18
		0.3015	0.63	0.3806	0.50	0.1900	0.95
		0.3698	0.50	0.4714	0.37	0.2980	0.55
		0.4127	0.47	0.5780	0.33	0.3903	0.48
						0.4279	0.42

Table 4.13 - Continued

[NaCl]/ mol kg^{-1}	Cmc x 10^3 / mol kg^{-1}	[NaAc]/ mol kg^{-1}	Cmc x 10^3 / mol kg^{-1}	[NaPr]/ mol kg^{-1}	Cmc x 10^3 / mol kg^{-1}	[NaBu]/ mol kg^{-1}	Cmc x 10^3 / mol kg^{-1}
			Temperature = 303K				
0	7.59	0.0169	3.89	0.0104	4.73	0.0260	3.00
0.0152	4.07	0.0489	2.14	0.0267	2.63	0.0355	2.66
0.0797	1.58	0.0971	1.55	0.0519	2.00	0.0627	1.84
0.1010	1.33	0.1446	1.06	0.0735	1.58	0.0862	1.43
0.1849	0.85	0.2016	0.75	0.1750	0.87	0.1231	1.17
0.2525	0.71	0.3016	0.63	0.2665	0.66	0.2035	0.79
0.3471	0.56	0.4127	0.53	0.3806	0.50	0.2984	0.66
0.5021	0.40			0.4714	0.38	0.4011	0.54
				0.5780	0.35		

Table 4.14 - Specific Conductance (κ) Values of SDS in Aqueous Sodium Acetate Medium at 25 °C

[SDS] x10^3 / mol kg^{-1}	κ / S m^{-1}	[SDS] x 10^3 / mol kg^{-1}	κ / S m^{-1}	[SDS] x10^3 / mol kg^{-1}	κ / S m^{-1}
		[NaAc] = 0.0 mol kg^{-1}			
0	0.0120x10^{-2}	6.6043	0.0489	11.386	0.0685
0.5204	0.0041	6.8325	0.0505	11.797	0.0701
1.0354	0.0080	7.0597	0.0522	12.204	0.0711
1.5453	0.0118	7.2858	0.0539	12.608	0.0727
2.0501	0.0156	7.5108	0.0556	13.008	0.0732
2.5498	0.0192	7.7347	0.0571	13.405	0.0749
3.0446	0.0230	7.9576	0.0583	13.798	0.0753
3.5345	0.0265	8.1794	0.0594	14.187	0.0769
4.0195	0.0301	8.4002	0.0603	14.573	0.0775
4.4998	0.0329	8.6200	0.0612	14.956	0.0786
4.9755	0.0366	8.8387	0.0617	15.335	0.0795
5.2115	0.0384	9.0564	0.0626	15.712	0.0801
5.4465	0.0401	9.2731	0.0635	16.084	0.0812
5.6803	0.0417	9.7035	0.0645	16.454	0.0821
5.9130	0.0438	10.130	0.0656	16.821	0.0825
6.1445	0.0453	10.552	0.0667	17.184	0.0835
6.3750	0.0471	10.971	0.0677		
		[NaAc] = 0.0011 mol kg^{-1}			
0.7100	0.0140	5.5800	0.0466	10.530	0.0690
1.5600	0.0196	6.4000	0.0519	10.790	0.0697
2.1200	0.0234	7.5800	0.0596	11.460	0.0714
2.9900	0.0290	8.5000	0.0633	12.330	0.0735
3.9700	0.0361	9.3400	0.0659	12.690	0.0744
4.7900	0.0414	9.7900	0.0671	13.090	0.0753
		[NaAc] = 0.0071 mol kg^{-1}			
0.1000	0.0611	1.6700	0.0717	12.110	0.1153
0.1600	0.0615	2.3100	0.0768	13.560	0.1199

Table 4.14 - Continued

[SDS] x10^3 / mol kg^{-1}	κ / S m^{-1}	[SDS] x 10^3 / mol kg^{-1}	κ / S m^{-1}	[SDS] x10^3 / mol kg^{-1}	κ / S m^{-1}
		[NaAc] = 0.0071 mol kg^{-1}			
0.2400	0.0621	3.2300	0.0822	15.320	0.1252
0.4300	0.0642	5.1800	0.0960	16.940	0.1303
0.6300	0.0647	7.3600	0.1030	17.640	0.1332
1.0700	0.0685	9.6600	0.1100		
		[NaAc] = 0.0137 mol kg^{-1}			
0.2100	0.1182	3.2200	0.1385	8.7300	0.1574
0.6100	0.1213	5.2600	0.1468	9.9900	0.1605
1.3800	0.1255	6.8000	0.1531	11.200	0.1630
2.2600	0.1325	7.8900	0.1554	12.450	0.1674
2.8900	0.1343				
		[NaAc] = 0.0246 mol kg^{-1}			
0.6700	0.2060	2.5400	0.2182	7.1100	0.2317
1.0000	0.2106	2.6600	0.2187	9.0500	0.2381
1.6200	0.2121	3.9900	0.2262	11.190	0.2425
2.2300	0.2161	5.4900	0.2288	12.370	0.2480
2.3100	0.2164	5.9100	0.2298		
		[NaAc] = 0.0309 mol kg^{-1}			
0.2700	0.2533	2.6100	0.2666	7.1500	0.2799
0.4800	0.2546	3.6800	0.2698	7.6800	0.2817
0.8200	0.2570	4.2400	0.2728	8.9200	0.2846
1.3200	0.2595	5.5400	0.2767	9.4400	0.2864
1.5000	0.2612	6.4500	0.2782		
		[NaAc] = 0.0539 mol kg^{-1}			
0.1800	0.4125	2.3700	0.4248	4.5200	0.4300
0.7000	0.4152	2.7800	0.4259	5.1700	0.4310
0.9900	0.4177	3.3500	0.4266	5.6100	0.4326
1.6200	0.4216	3.9500	0.4279	6.2900	0.4339
1.9900	0.4239				

Table 4.14 - Continued

[SDS] x10³ / mol kg⁻¹	κ / S m⁻¹	[SDS] x 10³ / mol kg⁻¹	κ / S m⁻¹	[SDS] x10³ / mol kg⁻¹	κ / S m⁻¹
		[NaAc] = 0.2017 mol kg⁻¹			
0.1200	1.2839	1.4500	1.2900	3.0800	1.2956
0.2000	1.2846	1.6200	1.2909	3.3800	1.2968
0.3800	1.2854	2.1200	1.2928	3.6400	1.2977
0.8100	1.2873	2.3900	1.2931	3.9800	1.2988
1.3000	1.2884	2.7900	1.2946	4.3000	1.2998
		[NaAc] = 0.3080 mol kg⁻¹			
0.1100	1.9734	0.6100	1.9869	2.0800	2.0067
0.2200	1.9740	0.7100	1.9869	2.5900	2.0093
0.2800	1.9741	0.9200	1.9923	2.7900	2.0126
0.3300	1.9745	1.1400	1.9951	3.0000	2.0136
0.3800	1.9765	1.3500	1.9987	3.1800	2.0146
0.4400	1.9794	1.4500	1.9997	3.3800	2.0160
0.4900	1.9816	1.5600	1.9998	3.5700	2.0172
0.5500	1.9831	1.8200	2.0044		
		[NaAc] = 0.3698 mol kg⁻¹			
0.0400	2.0285	0.2100	2.0338	0.5600	2.0402
0.0700	2.0300	0.2300	2.0347	0.6000	2.0408
0.0900	2.0311	0.2600	2.0348	0.6500	2.0410
0.1100	2.0312	0.3000	2.0353	0.7000	2.0417
0.1300	2.0313	0.3300	2.0364	0.7400	2.0421
0.1500	2.0325	0.3800	2.0374	0.8500	2.0427
0.1600	2.0331	0.4300	2.0383	0.9100	2.0442
0.1800	2.0326	0.4800	2.0395		

Table 4.15 - Specific Conductance (κ) Values of SDS in Aqueous Sodium Propionate Medium at 25°C

[SDS] x10^3 / mol kg^{-1}	κ / S m^{-1}	[SDS] x 10^3 / mol kg^{-1}	κ / S m^{-1}	[SDS] x10^3 / mol kg^{-1}	κ / S m^{-1}
		[NaPr] = 0.0042 mol kg^{-1}			
0	0.0361	5.9800	0.0759	12.570	0.0981
0.6200	0.0404	7.1200	0.0838	13.610	0.1018
1.2300	0.0447	8.2400	0.0864	14.630	0.1036
1.8400	0.0488	9.3500	0.0893	15.640	0.1055
2.4500	0.0530	10.440	0.0919	16.640	0.1078
3.6400	0.0605	11.510	0.0946	17.620	0.1101
4.8200	0.0682				
		[NaPr] = 0.0090 mol kg^{-1}			
0	0.0807	2.8100	0.0994	7.0000	0.1207
0.3200	0.0833	3.6500	0.1048	7.8300	0.1229
0.6400	0.0854	4.2600	0.1086	8.4500	0.1244
1.0700	0.0882	4.8900	0.1124	9.0600	0.1258
1.4100	0.0904	5.2100	0.1143	9.7200	0.1275
1.8400	0.0932	6.0300	0.1179	10.120	0.1282
2.2800	0.0960	6.5100	0.1194		
		[NaPr] = 0.0268 mol kg^{-1}			
1.1600	0.2244	2.6100	0.2313	4.2800	0.2376
1.3500	0.2250	2.9500	0.2329	4.5900	0.2384
1.5300	0.2263	3.2900	0.2342	4.9000	0.2391
1.9000	0.2280	3.6300	0.2359	5.2100	0.2403
2.2600	0.2299	3.9500	0.2368	5.5100	0.2415
		[NaPr] = 0. 0506mol kg^{-1}			
0	0.3745	3.1000	0.3889	8.2300	0.4016
0.1700	0.3751	4.0800	0.3915	9.1100	0.4039
0.3800	0.3764	4.8900	0.3934	10.280	0.4068
0.7300	0.3785	5.4700	0.3945	10.740	0.4078

Table 4.15 Continued

[SDS] x10³ / mol kg⁻¹	*κ* / S m⁻¹	*[SDS] x 10³ /* mol kg⁻¹	*κ* / S m⁻¹	*[SDS] x10³ /* mol kg⁻¹	*κ* / S m⁻¹
		[NaPr] = 0. 0506mol kg⁻¹			
1.0400	0.3799	5.8100	0.3951	12.370	0.4120
1.5500	0.3826	6.6300	0.3977	12.990	0.4134
2.0100	0.3854	7.3600	0.3994	13.690	0.4150
2.4200	0.3873				
		[NaPr] = 0. 0732mol kg⁻¹			
0.4300	0.5392	0.9900	0.5435	1.8100	0.5489
0.5000	0.5395	1.1300	0.5444	1.9400	0.5491
0.5700	0.5401	1.2700	0.5454	2.0700	0.5496
0.6400	0.5411	1.4000	0.5463	2.2100	0.5500
0.7100	0.5425	1.5400	0.5470	2.3400	0.5505
0.7800	0.5426	1.6700	0.5481	2.4700	0.5510
0.8500	0.5428				
		[NaPr] = 0.1733 mol kg⁻¹			
0	1.1239	0.4500	1.1311	1.2500	1.1400
0.0700	1.1255	0.5700	1.1334	1.3500	1.1412
0.1300	1.1267	0.6900	1.1351	1.4500	1.1420
0.2000	1.1279	0.8100	1.1373	1.5500	1.1424
0.2600	1.1282	0.9200	1.1379	1.6500	1.1430
0.3300	1.1300	1.0300	1.1387		
		[NaPr] = 0.2685 mol kg⁻¹			
0	1.6059	0.5400	1.6105	1.2400	1.6141
0.0900	1.6070	0.6300	1.6120	1.4100	1.6148
0.1800	1.6075	0.7200	1.6125	1.5700	1.6148
0.2800	1.6086	0.9000	1.6129	1.7400	1.6158
0.3700	1.6094	0.9800	1.6133	1.9000	1.6161
0.4600	1.6100	1.0700	1.6136	2.0600	1.6168

Table 4.16 - Specific Conductance (κ) Values of SDS in Aqueous Sodium Butyrate Medium at 25°C

[SDS] x10^3 / mol kg^{-1}	κ / S m^{-1}	[SDS] x 10^3 / mol kg^{-1}	κ / S m^{-1}	[SDS] x10^3 / mol kg^{-1}	κ / S m^{-1}
		[NaBu] = 0.0250 mol kg^{-1}			
0.9200	0.1997	3.5600	0.2143	6.5000	0.2215
1.4000	0.2024	4.0200	0.2155	6.8100	0.2222
1.8300	0.2049	4.6400	0.2171	7.4800	0.2238
2.3400	0.2078	5.2700	0.2189	8.7800	0.2270
2.8900	0.2108	5.7800	0.2201	9.9700	0.2294
3.3900	0.2137	6.1600	0.2209	11.870	0.2343
		[NaBu] = 0.0358 mol kg^{-1}			
0.3100	0.2591	3.5200	0.2758	6.3700	0.2829
0.7400	0.2617	4.3500	0.2783	6.7300	0.2835
1.3500	0.2656	5.0500	0.2800	7.8100	0.2864
1.7000	0.2668	5.5800	0.2807	8.7300	0.2882
2.0200	0.2694	5.9900	0.2820	9.9600	0.2935
2.8900	0.2736				
		[NaBu] = 0.0626 mol kg^{-1}			
0.2300	0.4321	1.7200	0.4410	3.8300	0.4460
0.4100	0.4331	1.9700	0.4419	4.2600	0.4472
0.6100	0.4339	2.3500	0.4430	4.5900	0.4478
1.0500	0.4367	2.6900	0.4437	5.0000	0.4489
1.3300	0.4368	2.9400	0.4449	5.4900	0.4500
1.5000	0.4384	3.4900	0.4449	6.1500	0.4508
		[NaBu] = 0.0887 mol kg^{-1}			
0.1300	0.5920	1.0500	0.5978	2.8900	0.6034
0.2600	0.5923	1.2800	0.5988	3.4700	0.6046
0.3400	0.5929	1.4900	0.5998	3.7600	0.6049
0.5300	0.5942	1.8900	0.6009	3.9700	0.6060
0.6600	0.5953	2.1500	0.6020	4.2300	0.6074
0.8200	0.5962	2.5200	0.6025		

Table 4.16 - Continued

[SDS] x10³ / mol kg⁻¹	κ / S m⁻¹	[SDS] x 10³ / mol kg⁻¹	κ / S m⁻¹	[SDS] x10³ / mol kg⁻¹	κ / S m⁻¹
		[NaBu] = 0.1097 mol kg⁻¹			
0.0400	0.7167	0.6800	0.7221	1.3800	0.7244
0.1000	0.7183	0.7800	0.7229	1.4800	0.7248
0.1600	0.7189	0.8800	0.7234	1.6800	0.7251
0.2700	0.7193	0.9800	0.7239	1.9700	0.7256
0.3700	0.7200	1.0800	0.7239	1.9700	0.7256
0.4700	0.7207	1.1800	0.7243	2.1600	0.7264
0.5800	0.7212				
		[NaBu] = 0.1507 mol kg⁻¹			
0.0700	0.9368	0.6700	0.9398	1.6300	0.9427
0.1400	0.9348	0.7700	0.9402	1.7900	0.9431
0.2100	0.9358	0.9100	0.9415	1.9600	0.9439
0.2800	0.9365	1.0500	0.9416	2.1300	0.9450
0.3500	0.9377	1.1900	0.9420	2.4600	0.9457
0.4600	0.9383	1.3200	0.9422	2.7800	0.9466
0.5600	0.9388	1.4600	0.9425		
		[NaBu] = 0.2034 mol kg⁻¹			
0.0200	1.2167	0.2600	1.2183	0.9500	1.2213
0.0400	1.2169	0.4100	1.2191	1.1000	1.2216
0.0700	1.2170	0.5400	1.2198	1.3300	1.2219
0.1200	1.2174	0.6300	1.2203	1.5600	1.2223
0.1600	1.2177	0.7100	1.2207	1.6100	1.2224
0.2100	1.2178	0.7900	1.2210		
		[NaBu] = 0.2915 mol kg⁻¹			
0.0400	1.6226	0.2900	1.6243	0.6200	1.6262
0.0800	1.6230	0.3300	1.6246	0.7200	1.6265
0.1300	1.6234	0.3800	1.6248	0.7300	1.6267

Table 4.16 - Continued

[SDS] x10^3 / mol kg^{-1}	κ / S m^{-1}	[SDS] x 10^3 / mol kg^{-1}	κ / S m^{-1}	[SDS] x10^3 / mol kg^{-1}	κ / S m^{-1}
		[NaBu] = 0.2915 mol kg^{-1}			
0.1700	1.6236	0.4600	1.6252	0.9300	1.6270
0.2100	1.6237	0.5400	1.6260	1.0200	1.6274
0.2500	1.6240				

Table 4.17 - Critical Micelle Concentration Values (± 0.05 x 10^{-3} mol kg^{-1}) of SDS in Aqueous Electrolyte Solutions at 25 °C from Conductance Data

[NaAc] / mol kg^{-1}	Cmc x 10^3 / mol kg^{-1}	[NaPr] / mol kg^{-1}	Cmc x 10^3 / mol kg^{-1}	[NaBu] / mol kg^{-1}	Cmc x 10^3 / mol kg^{-1}
0	8.10	0.0042	7.30	0.0250	3.75
0.0011	7.80	0.0090	5.40	0.0358	2.70
0.0071	5.25	0.0268	3.80	0.0626	2.10
0.0137	4.60	0.0506	2.40	0.0887	1.25
0.0246	4.00	0.0732	1.68	0.1097	1.00
0.0309	3.20	0.1733	0.90	0.1507	0.86
0.0539	2.00	0.2685	0.68	0.2034	0.71
0.2017	0.85			0.2915	0.54
0.3080	0.65				
0.3698	0.45				

Table 4.18 - EMF Values of SDS in Aqueous Sodium Chloride Medium at 25 °C

[SDS] x10^3/ mol kg^{-1}	EMF / mV	[SDS] x10^3/ mol kg^{-1}	EMF / mV	[SDS] x10^3/ mol kg^{-1}	EMF / mV
		[NaCl] = 0.0 mol kg^{-1}			
0.3030	-64.0	4.0380	0.3	9.8430	17.3
0.8080	-40.8	5.0480	5.2	15.143	20.0
1.0100	-34.4	5.6180	10.8	49.971	31.9
2.0190	-18.8	7.8240	14.9	79.752	42.0
2.9840	-07.7	8.5810	15.5	100.95	46.3
		[NaCl] = 0.0059 mol kg^{-1}			
0	5.3	5.9441	19.1	8.6706	23.2
3.6127	14.2	6.5054	20.1	9.1926	23.9
4.2088	15.4	7.0586	21.6	9.7073	24.3
4.7960	16.7	7.6037	22.0	10.466	25.3
5.3743	17.9	8.1410	22.6	11.695	25.6
		[NaCl] = 0.0148 mol kg^{-1}			
0	32.9	3.5248	37.6	6.0742	40.3
1.1066	34.3	4.1064	38.6	6.8867	40.8
1.7253	35.1	4.6792	39.1	7.6816	41.1
2.3345	36.2	5.2435	39.6	8.4595	41.4
2.9342	37.0				
		[NaCl] = 0.0356 mol kg^{-1}			
0	53.6	2.3458	56.6	4.6893	58.4
0.3320	54.2	2.7513	57.1	5.1335	58.6
0.6600	54.7	3.1506	57.6	5.4253	58.8
1.0914	55.1	3.5439	57.8	5.7854	59.3
1.5160	55.5	3.9314	58.0	6.1404	59.5
1.9341	56.0	4.3131	58.2		
		[NaCl] = 0.0600 mol kg^{-1}			
0	61.7	1.7406	65.0	3.0129	67.4
0.2987	62.2	1.9265	65.5	3.3643	67.4

Table 4.18 - Continued

[SDS] x10^3/ mol kg^{-1}	EMF / mV	[SDS] x10^3/ mol kg^{-1}	EMF / mV	[SDS] x10^3/ mol kg^{-1}	EMF / mV
		[NaCl] = 0.0600 mol kg^{-1}			
0.5940	62.8	2.1111	65.7	3.8815	67.6
0.7888	63.1	2.2942	65.9	4.5536	68.1
0.9822	63.5	2.4759	66.4	5.3668	68.4
1.1740	63.9	2.6563	66.9	6.3050	68.8
1.3643	64.4	2.8353	67.3	7.4965	69.3
1.5532	64.7				
		[NaCl] = 0.0900 mol kg^{-1}			
0	71.7	0.4193	75.3	0.9382	77.4
0.0444	72.0	0.4792	75.7	1.0600	77.6
0.0887	72.7	0.5387	75.9	1.2203	77.8
0.1328	73.2	0.5979	76.1	1.4563	78.0
0.1767	73.8	0.6567	76.3	1.7628	78.4
0.2378	74.1	0.7153	76.6	2.1334	78.9
0.2987	74.6	0.7735	76.9	2.5609	79.3
0.3592	75.0	0.8562	77.1	2.9706	79.8
		[NaCl] = 0.1998 mol kg^{-1}			
0.0155	99.8	0.1257	101.4	0.4987	101.7
0.0310	100.6	0.1557	101.5	0.6327	101.8
0.0495	100.9	0.3025	101.6	0.7871	101.8
0.0710	101.2	0.3879	101.7	0.9829	101.8
0.0985	101.3				

Table 4.19 - EMF Values of SDS in Aqueous Sodium Acetate Medium at 25 °C

[SDS] x10^3/ mol kg^{-1}	EMF / mV	[SDS] x10^3/ mol kg^{-1}	EMF / mV	[SDS] x10^3/ mol kg^{-1}	EMF / mV
		[NaAc] = 0.0059 mol kg^{-1}			
0	7.5	4.3541	20.1	9.1847	27.6
0.2757	9.2	5.0257	21.7	9.7113	28.0
0.6381	10.7	5.6761	23.1	10.223	28.3
1.1713	12.3	6.3064	24.4	10.775	28.6
1.6921	13.6	6.9173	25.2	11.416	28.9
2.2846	15.1	7.5098	25.9	12.135	29.4
2.9428	16.6	8.0847	26.3	12.920	29.7
3.6601	18.7	8.6428	27.0		
		[NaAc] = 0.0149 mol kg^{-1}			
0	33.0	3.2437	37.5	6.2500	40.3
0.3558	33.8	3.7016	38.0	6.6443	40.6
0.7927	34.5	4.1494	38.6	7.0307	40.9
1.3057	35.0	4.5876	39.1	7.4093	41.2
1.8070	35.5	5.0165	39.5	7.9025	41.5
2.2968	36.2	5.4363	39.8	8.5010	41.8
2.7756	36.7	5.8474	40.0	9.3070	42.2
		[NaAc] = 0.0349 mol kg^{-1}			
0	50.7	1.2175	53.6	3.2807	55.8
0.1054	51.1	1.4590	53.8	3.6462	55.9
0.2095	51.6	1.7223	54.1	3.9935	56.1
0.3465	52.1	2.0051	54.5	4.3241	56.2
0.5479	52.5	2.3048	54.8	4.6390	56.3
0.7771	52.8	2.6189	55.1	4.9395	56.4
1.0002	53.2	2.9450	55.4	5.2263	56.5
		[NaAc] =0.0601 mol kg^{-1}			
0	58.8	1.2081	60.9	2.8859	62.1
0.2015	59.3	1.4263	61.0	3.4126	62.1

Table 4.19 - Continued

[SDS] x10^3/ mol kg^{-1}	EMF mV	[SDS] x10^3/ mol kg^{-1}	EMF mV	[SDS] x10^3/ mol kg^{-1}	EMF mV
		[NaAc] = 0.0601 mol kg^{-1}			
0.4010	59.9	1.6420	61.3	4.0496	62.2
0.5984	60.1	1.8694	61.5	4.7846	62.3
0.7939	60.4	2.1497	61.7	5.6038	62.4
0.9873	60.7	2.4943	61.9		
		[NaAc] = 0.0900 mol kg^{-1}			
0	68.7	0.4193	72.3	0.9382	74.6
0.0444	69.6	0.4792	72.6	1.0600	74.7
0.0887	70.3	0.5387	73.0	1.2203	74.9
0.1328	70.7	0.5979	73.3	1.4563	75.1
0.1767	71.1	0.6567	73.6	1.7628	75.4
0.2378	71.5	0.7153	73.7	2.1334	75.6
0.2987	71.7	0.7735	74.0	2.5609	75.8
0.3592	72.1	0.8562	74.4		
		[NaAc] =0.1998 mol kg^{-1}			
0	89.4	0.2640	92.3	0.9300	93.6
0.0200	90.2	0.3073	92.6	1.1003	93.7
0.0400	90.6	0.3506	92.7	1.3074	93.8
0.0599	90.8	0.4108	92.9	1.5723	93.9
0.0798	91.2	0.4792	93.1	1.8754	94.0
0.1062	91.7	0.5556	93.2	2.2420	94.1
0.1325	91.9	0.6400	93.3	2.9371	94.3
0.1653	92.1	0.7652	93.4		

Table 4.20 - EMF Values of SDS in Aqueous Sodium Propionate Medium at 25 °C

[SDS] x10^3/ mol kg^{-1}	EMF / mV	[SDS] x10^3/ mol kg^{-1}	EMF / mV	[SDS] x10^3/ mol kg^{-1}	EMF / mV
		[NaPr] = 0.0063 mol kg^{-1}			
0	4.9	4.1982	16.7	8.3275	23.5
0.2754	6.0	4.8001	18.1	8.9381	23.8
0.6376	7.4	5.3849	19.6	9.5292	24.2
1.0823	8.8	5.9535	20.6	10.102	24.6
1.6047	10.4	6.5065	21.3	10.766	24.9
2.2827	12.2	7.0444	22.0	11.510	25.6
2.9403	14.0	7.6967	22.9	12.324	26.3
3.5785	15.4				
		[NaPr] = 0.0149 mol kg^{-1}			
0	28.7	2.8588	33.0	6.3261	35.8
0.2678	29.5	3.4793	33.7	6.8492	36.3
0.6199	30.2	4.0818	34.3	7.3582	36.4
1.0523	31.0	4.6670	34.8	7.9757	36.8
1.5602	31.6	5.2357	35.0	8.6903	37.0
2.2194	32.3	5.7885	35.4	9.4899	37.5
		[NaPr] = 0.0360 mol kg^{-1}			
0	47.8	1.3093	50.4	3.0467	52.1
0.1443	48.2	1.4948	50.7	3.3416	52.2
0.3074	48.6	1.7679	50.9	3.6520	52.4
0.4883	49.1	2.0350	51.2	3.9539	52.5
0.6864	49.4	2.2962	51.5	4.3200	52.7
0.9296	49.8	2.5518	51.8	4.7435	52.8
1.1209	50.1	2.8019	51.9	5.2171	52.9
		[NaPr] = 0.0612 mol kg^{-1}			
0	59.1	1.0353	61.4	2.4771	62.8
0.1463	59.3	1.1919	61.6	2.9395	63.1
0.2911	59.7	1.3569	61.8	3.4730	63.4

Table 4.20 Continued

[SDS] x10^3/ mol kg^{-1}	EMF / mV	[SDS] x10^3/ mol kg^{-1}	EMF / mV	[SDS] x10^3/ mol kg^{-1}	EMF / mV
		[NaPr] =0.0612 mol kg^{-1}			
0.4344	60.2	1.5604	62.1	4.0677	63.7
0.5762	60.4	1.8105	62.3	4.5552	63.9
0.7166	60.6	2.0948	62.4	5.0997	64.5
0.8769	61.1				
		[NaPr] = 0.0902 mol kg^{-1}			
0	66.6	0.3080	69.6	1.0003	71.0
0.0314	66.9	0.3981	69.9	1.1637	71.2
0.0626	67.3	0.4871	70.1	1.3236	71.3
0.1061	67.7	0.5751	70.4	1.5313	71.5
0.1494	68.4	0.6621	70.5	1.7827	71.7
0.1924	69.0	0.7481	70.6	2.0728	71.8
0.2474	69.4	0.8612	70.8	2.4414	72.1
		[NaPr] = 0.1999 mol kg^{-1}			
0	87.1	0.1740	89.5	0.5405	90.5
0.0188	87.3	0.2102	89.6	0.6070	90.6
0.0376	87.8	0.2461	89.8	0.6888	90.7
0.0562	88.0	0.2818	89.9	0.8166	90.8
0.0748	88.4	0.3171	90.1	0.9711	90.9
0.0934	88.7	0.3522	90.2	1.1494	90.9
0.1118	88.9	0.4043	90.2	1.4843	91.2
0.1375	89.2	0.4729	90.4	1.8908	91.4

Table 4.21 - EMF Values of SDS in Aqueous Sodium Butyrate Medium at 25 °C

[SDS] x10^3/ mol kg^{-1}	EMF / mV	[SDS] x10^3/ mol kg^{-1}	EMF / mV	[SDS] x10^3/ mol kg^{-1}	EMF / mV
		[NaBu] = 0.0061 mol kg^{-1}			
0	0.1	3.1954	9.7	7.1592	17.4
0.2698	0.9	3.8114	11.2	7.6652	18.1
0.6246	1.9	4.4097	12.7	8.1580	18.6
0.9739	2.8	4.9909	14.0	8.7561	19.1
1.3177	4.1	5.5558	15.1	9.4489	19.6
1.6562	5.4	6.1051	16.1	10.225	20.3
2.0721	6.6	6.6393	17.0	11.071	20.7
2.5608	8.0				
		[NaBu] = 0.0153 mol kg^{-1}			
0	26.7	2.0810	29.9	6.1497	33.8
0.2194	27.3	2.5360	30.3	6.7594	34.1
0.4365	27.7	2.9808	30.9	7.3488	34.3
0.7335	28.2	3.5588	31.3	8.0309	34.9
1.0586	28.6	4.1890	31.9	8.9002	34.9
1.3787	29.3	4.8657	32.7	9.8270	35.6
1.6938	29.5	5.5189	33.5	10.799	36.0
		[NaBu] = 0.0366 mol kg^{-1}			
0	26.7	1.8995	47.5	4.8874	48.9
0.1995	45.6	2.4058	47.8	5.5154	49.0
0.4247	45.9	2.8972	48.1	6.1185	49.1
0.7024	46.5	3.3743	48.4	6.7924	49.4
1.0433	46.8	3.8379	48.6	7.4365	49.5
1.4438	47.2	4.3437	48.8	8.1384	49.7
		[NaBu] = 0.0601 mol kg^{-1}			
0	56.0	0.8629	57.0	3.3318	57.6
0.0555	56.3	1.3756	57.3	4.0843	57.7
0.1660	56.6	1.8692	57.4	4.7919	57.8
0.4383	56.8	2.5300	57.5		

Table 4.21 - Continued

[SDS] x10^3/ mol kg^{-1}	EMF / mV	[SDS] x10^3/ mol kg^{-1}	EMF / mV	[SDS] x10^3/ mol kg^{-1}	EMF / mV
		[NaBu] = 0.0900 mol kg^{-1}			
0	62.0	0.4633	64.1	1.2857	65.5
0.0376	62.3	0.5348	64.4	1.6070	65.7
0.0975	62.6	0.6057	64.5	2.0196	65.9
0.1718	62.8	0.6761	64.7	2.5438	66.1
0.2456	63.0	0.8152	65.0	3.0891	66.3
0.3187	63.5	1.0199	65.3	4.0773	66.8
0.3913	63.8				
		[NaBu] = 0.1998 mol kg^{-1}			
0	88.2	0.0174	90.6	0.0607	91.9
0.0019	88.5	0.0210	90.7	0.0688	91.9
0.0038	88.9	0.0246	90.9	0.0816	92.0
0.0056	89.2	0.0317	91.3	0.0971	92.1
0.0075	89.5	0.0352	91.4	0.1149	92.2
0.0093	89.9	0.0404	91.6	0.1483	92.4
0.0112	90.1	0.0473	91.7	0.1890	92.5
0.0137	90.3	0.0540	91.8	0.2343	92.6

Table 4.22 - Values of Critical Micelle Concentration and Counter Ion Binding Constant (β_c) for SDS in Different Aqueous Electrolyte Solutions from EMF Data at 25 ° C and the Values of Intercept (A_1) and Slope (B_1) of Eq. (4.4)

Electrolyte	[Electrolyte] / mol kg^{-1}	A_1/ mV	B_1/ mV	cmc ± 0.05 x 10^3 / mol kg^{-1}	β_c ± 0.02
NaCl	0.0	134.4	56.4	7.94	0.80
	0.0059	127.4	56.2	7.03	0.52
	0.0148	131.7	54.2	5.61	0.59
	0.0356	201.3	101.8	3.13	0.52
	0.0600	400.8	276.5	2.23	0.78
	0.0909	911.2	801.0	1.03	0.73
	0.1998	398.7	425.4	0.69	0.74
NaAc	0.0059	126.2	52.7	6.69	0.50
	0.0149	124.4	49.9	5.40	0.52
	0.0349	179.1	87.0	3.32	0.61
	0.0601	214.6	126.8	2.27	0.78
	0.0900	1094.0	979.3	1.01	0.87
	0.1998	557.3	664.4	0.74	0.76
NaPr	0.0063	121.1	52.7	7.19	0.56
	0.0149	115.0	46.9	5.05	0.52
	0.0360	179.7	90.9	3.44	0.63
	0.0612	205.6	119.1	1.90	0.52
	0.0902	489.3	402.0	1.02	0.73
	0.1999	571.5	689.1	0.69	0.68
NaBu	0.0061	121.9	55.3	6.63	0.52
	0.0153	127.2	55.7	5.47	0.58
	0.0366	135.4	62.2	3.30	0.60
	0.0601	197.7	114.8	1.84	0.69
	0.0900	453.7	373.1	1.10	0.78
	0.1998	569.8	684.8	0.74	0.76

Table 4.23 - Computed Values of Surface Excess (Γ_{cmc}) and Surface Area (A_0) per Molecule of SDS near cmc at Different Temperatures in Presence of Electrolytes

[Electrolyte]/ mol kg^{-1}	Γ_{cmc} (± 0.5) x 10^6/ mol m^{-2}			A_0/ nm^2		
	Temperature					
	293 K	298 K	303 K	293 K	298 K	303 K
			Electrolyte = NaCl			
0	2.97	3.46	2.98	0.56	0.48	0.56
0.0152	4.29	3.70	3.25	0.39	0.45	0.51
0.0797	4.39	4.25	3.37	0.38	0.39	0.49
0.1006	4.19	4.18	4.12	0.40	0.40	0.40
0.1849	4.04	4.30	4.43	0.41	0.39	0.37
0.2525	4.35	4.82	4.36	0.38	0.34	0.38
0.3471	4.69	4.60	4.26	0.35	0.36	0.39
0.5021	4.78	5.01	4.23	0.35	0.33	0.39
			Electrolyte = NaAc			
0.0048	--	4.29	--	--	0.39	--
0.0099	--	4.15	--	--	0.40	--
0.0169	4.13	--	4.16	0.40	--	0.40
0.0172	--	3.72	--	--	0.45	--
0.0246	--	4.43	--	--	0.37	--
0.0489	4.25	--	3.87	0.39	--	0.43
0.0497	--	3.75	--	--	0.44	--
0.0971	3.88	4.51	4.50	0.43	0.37	0.37
0.1446	4.50	4.41	4.55	0.37	0.38	0.37
0.2006	--	4.91	--	--	0.34	--
0.2016	4.56	--	4.70	0.36	--	0.35
0.3016	4.61	5.14	4.89	0.36	0.32	0.34
0.3698	--	4.88	--	--	0.34	--
0.4127	4.73	4.61	4.90	0.35	0.36	0.34

Table 4.23 - Continued

[Electrolyte]/ mol kg^{-1}	Γ_{cmc} (± 0.5)x 10^6/ mol m^{-2}			A_0/ nm^2		
	Temperature					
	293 K	298 K	303 K	293 K	298 K	303 K
	Electrolyte = NaPr					
0.0036	3.40	--	--	0.49	--	--
0.0042	--	4.39	--	--	0.38	--
0.0104	3.43	3.81	3.99	0.48	0.44	0.42
0.0267	3.97	3.65	4.71	0.42	0.46	0.35
0.0519	4.36	--	3.30	0.38	--	0.50
0.0525	--	4.31	--	--	0.39	--
0.0735	4.22	4.61	4.19	0.39	0.36	0.40
0.1103	4.41	3.79	4.77	0.38	0.44	0.35
0.1750	4.18	4.62	--	0.40	0.36	--
0.2665	4.73	4.66	4.93	0.35	0.36	0.34
0.3806	5.01	4.88	4.84	0.33	0.34	0.34
0.4714	4.98	5.25	5.21	0.33	0.32	0.32
0.5780	5.14	4.90	4.76	0.32	0.34	0.35

Table 4.23 - Continued

[Electrolyte]/ mol kg^{-1}	Γ_{cmc} ($\pm$ 0.5) x 10^6/ mol m^{-2}			A_0/ nm^2		
	Temperature					
	293 K	298 K	303 K	293 K	298 K	303 K
			Electrolyte = NaBu			
0.0013	--	3.89	--	--	0.43	--
0.0053	--	4.28	--	--	0.39	--
0.0103	--	4.68	--	--	0.35	--
0.0209	--	4.43	--	--	0.37	--
0.0260	4.38	--	4.13	0.38	--	0.40
0.0355	3.56	3.82	3.93	0.47	0.43	0.42
0.0627	4.32	4.00	3.22	0.38	0.42	0.52
0.0750	--	4.27	--	--	0.39	--
0.0898	4.27	--	3.21	0.39	--	0.52
0.1002	--	4.96	--	--	0.33	--
0.1231	5.40	--	4.33	0.31	--	0.38
0.1900	--	4.25	--	--	0.39	--
0.2035	5.00	--	3.54	0.33	--	0.47
0.2984	3.59	3.99	3.64	0.46	0.42	0.46
0.3903	--	3.75	--	--	0.44	--
0.4011	3.89	--	2.94	0.43	--	0.57
0.4279	--	4.01	--	--	0.41	--

Table 4.24 - Value of Counter Ion Binding Constant for SDS in Different Electrolyte Solutions Derived From Corrin-Harkins Plots (β_γ) and Slope-Ratio Method (β_κ)

Electrolyte	β_γ (From Surface Tension Data) Temperature 293 K	298 K	303 K	β_κ at 298K [NaAc] mol kg^{-1}	β_κ	[NaPr] mol kg^{-1}	β_κ	[NaBu] mol kg^{-1}	β_κ
NaCl	0.70	0.74	0.71	0.0	0.64				
NaAc	0.72	0.68	0.72	0.0011	0.61	0.0042	0.61	0.0250	0.58
NaPr	0.71	0.68	0.71	0.0071	0.58	0.0090	0.61	0.0358	0.55
NaBu	0.76	0.67	0.70	0.0137	0.58	0.0268	0.37	0.0626	0.62
				0.0246	0.53	0.0506	0.53	0.0887	0.61
				0.0309	0.53	0.0732	0.54	0.1097	0.71
				0.0539	0.63	0.1733	0.54	0.1507	0.63
				0.2017	0.62	0.2685	0.64	0.2034	0.74
				0.3080	0.65			0.2915	0.57
				0.3698	0.53				

Table 4.25 - Values of ΔG^{o}_{m} and ΔG^{o}_{ad} of SDS in Aqueous Electrolyte Solutions at Different Temperatures

[Electrolyte] mol kg^{-1}	$-\Delta G^{o}_{m} \pm 0.5$ / kJ mol^{-1} ($-\Delta G^{o}_{ad} \pm 0.5$ / kJ mol^{-1})# Temperature					
	293 K		298 K		303 K	
			Electrolyte = NaCl			
0	37.19	(48.50)	36.98	(46.70)	38.33	(49.60)
0.0152	39.52	(47.73)	41.02	(50.50)	41.02	(51.94)
0.0797	43.60	(52.23)	45.13	(54.03)	45.10	(56.37)
0.1010	43.92	(52.87)	45.88	(54.97)	45.84	(55.14)
0.1849	46.23	(55.79)	47.97	(57.04)	47.78	(56.63)
0.2525	46.80	(55.86)	48.72	(57.00)	48.56	(57.82)
0.3471	47.67	(56.18)	49.94	(58.70)	49.59	(59.12)
0.5021	49.08	(57.51)	51.54	(59.76)	51.05	(60.76)
			Electrolyte = NaAc			
0.0048	--	--	38.19	(45.85)	--	--
0.0099	--	--	39.24	(47.58)	--	--
0.0169	40.09	(48.71)	--	--	41.45	(49.96)
0.0172	--	--	39.73	(49.22)	--	--
0.0246	--	--	40.69	(48.77)	--	--
0.0489	41.44	(50.02)	--	--	43.10	(52.82)
0.0497	--	--	41.65	(51.41)	--	--
0.0971	44.26	(54.02)	44.23	(52.66)	45.45	(53.89)
0.1446	45.50	(53.99)	44.9	(53.59)	47.10	(55.62)
0.2006	--	--	46.07	(54.05)	--	--
0.2016	46.52	(55.27)	--	--	48.60	(57.07)
0.3016	47.54	(56.24)	47.42	(55.16)	49.36	(57.71)
0.3698	--	--	48.39	(56.60)	--	--
0.4127	48.71	(57.34)	48.65	(57.50)	50.12	(58.49)

All the Values in the parentheses denote ΔG^{o}_{ad}

Table 4.25 - Continued

[Electrolyte] mol kg^{-1}	$-\Delta G^{o}_{m} \pm 0.5$ / kJ mol^{-1} ($-\Delta G^{o}_{ad} \pm 0.5$ / kJ mol^{-1})#					
	Temperature					
	293 K		298 K		303 K	
	Electrolyte = NaPr					
0.0036	37.72	(47.66)	--	--	--	--
0.0042	--	--	38.53	(46.28)	--	--
0.0104	39.27	(49.42)	39.37	(48.55)	40.37	(49.14)
0.0267	40.96	(50.13)	41.65	(51.56)	42.90	(50.61)
0.0519	--	--	42.59	(51.18)	44.08	(55.38)
0.0525	42.88	(51.37)	--	--	--	--
0.0735	43.23	(52.07)	44.05	(52.16)	45.10	(54.17)
0.1103	44.79	(53.32)	44.90	(54.93)	--	--
0.1750	45.78	(55.06)	45.97	(54.33)	47.68	(55.83)
0.2665	47.20	(55.57)	47.98	(56.65)	48.87	(57.03)
0.3806	48.43	(56.41)	48.39	(56.71)	50.08	(58.51)
0.4714	49.36	(57.57)	49.65	(57.42)	51.27	(59.06)
0.5780	50.30	(58.22)	50.13	(58.40)	51.63	(60.24)

All the Values in the parentheses denote ΔG^{o}_{ad}

Table 4.25 - Continued

[Electrolyte] mol kg^{-1}	$-\Delta G^o_m \pm 0.5$ / kJ mol^{-1} ($-\Delta G^o_{ad} \pm 0.5$ / kJ mol^{-1})#					
	Temperature					
	293 K		298 K		303 K	
	Electrolyte = NaBu					
0.0013	--	--	37.58	(46.19)	--	--
0.0053	--	--	38.54	(46.53)	--	--
0.0103	--	--	38.98	(46.42)	--	--
0.0209	--	--	40.20	(48.31)	--	--
0.0260	41.72	(49.92)	--	--	42.08	(50.90)
0.0355	42.49	(52.60)	41.16	(50.61)	42.60	(51.91)
0.0627	44.14	(52.75)	43.06	(52.36)	44.18	(55.89)
0.0750	--	--	43.32	(52.08)	--	--
0.0898	44.67	(53.55)	--	--	45.26	(57.23)
0.1002	--	--	44.53	(52.23)	--	--
0.1231	45.86	(52.90)	--	--	46.12	(55.13)
0.1900	--	--	45.43	(54.70)	--	--
0.2035	48.09	(55.79)	--	--	47.81	(59.06)
0.2984	49.43	(60.71)	47.70	(57.85)	48.59	(59.55)
0.3903	--	--	48.27	(59.07)	--	--
0.4011	50.11	(60.75)	--	--	49.46	(63.74)
0.4279	--	--	48.82	(58.97)		

All the Values in the parentheses denote ΔG^o_{ad}

Table 4.26 - Ratio of the Intensities (I_o/I_q) of Fluorescence Emission of Pyrene in the Absence (I_o) and Presence (I_q) of the Quencher (CPC) at 374 nm in Aqueous SDS + NaCl Medium at 25 °C

[NaCl] / mol kg^{-1}	[SDS] / mol kg^{-1}	[CPC] x 10^5 / mol kg^{-1}	$\frac{I_0}{I_q}$
0.0	0.1000	0	1.0000
		1.7643	1.1823
		5.8004	1.4797
		6.9333	1.6770
		8.0574	1.8132
		9.1727	1.9085
		9.6710	2.1556
		10.280	2.2800
0.006	0.0180	0	1.0000
		0.9424	1.0489
		1.7886	1.0989
		2.6803	1.1231
0.015	0.0120	0	1.0000
		0.9424	1.1057
		1.7886	1.2213
		2.6803	1.3593
		3.5701	1.4560
		4.4582	1.6053
0.035	0.0099	0	1.0000
		0.9424	1.0950
		1.7886	1.2644
		2.6803	1.4508
		3.5701	1.6129
		4.4582	1.7359
		5.5345	2.0074

Table. 4.26 - Continued

[NaCl] mol kg^{-1}	[SDS] mol kg^{-1}	[CPC] x 10^5 mol kg^{-1}	$\frac{I_0}{I_q}$
0.060	0.0033	0	1.0000
		0.9424	2.6600
		1.7886	4.1671
		2.6803	6.2328
0.097	0.0021	0	1.0000
		0.5373	1.9711
		1.0740	2.9431

Table 4.27 - Ratio of the Intensities (I_o/I_q) of Fluorescence Emission of Pyrene in the Absence (I_o) and Presence (I_q) of the Quencher (CPC) at 374 nm in Aqueous SDS + NaAc Medium at 25 °C

[NaAc] mol kg^{-1}	[SDS] mol kg^{-1}	[CPC] x 10^5 mol kg^{-1}	$\frac{I_0}{I_q}$
0.006	0.0180	0	1.0000
		0.8952	1.0320
		1.4315	1.0472
		1.7886	1.0627
		2.1455	1.0922
0.015	0.0120	0	1.0000
		0.8952	1.0872
		1.4315	1.1325
		1.7886	1.1796
		2.1455	1.2169
0.035	0.0100	0	1.0000
		0.8952	1.1203
		1.4315	1.1942
		1.7886	1.2254
		2.1455	1.2638
0.060	0.0033	0	1.0000
		1.0740	2.1252
		1.6101	2.8058
		2.1455	3.4627
		2.6803	4.7990
		3.2144	5.8851

Table 4.27 - Continued

[NaAc] mol kg^{-1}	[SDS] mol kg^{-1}	[CPC] x 10^5 mol kg^{-1}	$\frac{I_0}{I_q}$
0.097	0.0021	0	1.0000
		1.6101	2.4717
		2.1455	2.8369
		2.6803	3.5909
		3.2144	5.3372
0.200	0.0021	0	1.0000
		1.6101	1.8931
		2.1455	2.8936
		2.6803	3.5282
		3.2144	3.9444
0.300	0.0016	0	1.0000
		1.6101	2.4356
		2.1455	3.4384
		2.6803	4.4723
		3.2144	5.7013
0.400	0.0012	0	1.0000
		1.6101	3.3341
		2.1455	5.2698
		2.6803	6.0364

Table 4.28 - Ratio of the Intensities (I_o/I_q) of Fluorescence Emission of Pyrene in the Absence (I_o) and Presence (I_q) of the Quencher (CPC) at 374 nm in Aqueous SDS + NaPr Medium at 25 °C

[NaPr] mol kg^{-1}	[SDS] mol kg^{-1}	[CPC] x 10^5 mol kg^{-1}	$\frac{I_0}{I_q}$
0.006	0.0180	0	1.0000
		0.9042	1.0322
		1.7886	1.0949
		2.6803	1.1429
		3.5701	1.2077
		4.4582	1.2610
		5.3445	1.3118
0.015	0.0120	0	1.0000
		0.9042	1.1382
		1.7886	1.1931
		2.6803	1.3311
		3.5701	1.4521
		4.4582	1.5909
		5.3445	1.7393
0.035	0.0100	0	1.0000
		0.9042	1.1226
		1.7886	1.2076
		2.6803	1.3862
		3.5701	1.5364
		4.4582	1.7280
		5.3445	1.8873

Table 4.28 - Continued

[NaPr] mol kg^{-1}	[SDS] mol kg^{-1}	[CPC] x 10^5 mol kg^{-1}	$\frac{I_0}{I_q}$
0.060	0.0033	0	1.0000
		1.7886	4.5697
		2.6803	6.1873
0.090	0.0021	0	1.0000
		0.5373	1.5791
		1.0740	2.1025

Table 4.29 - Ratio of the Intensities (I_o/I_q) of Flourescence Emission of Pyrene in the Absence (I_o) and Presence (I_q) of the Quencher (CPC) at 374 nm in Aqueous SDS + NaBu Medium at 25 °C

[NaBu] mol kg^{-1}	[SDS] mol kg^{-1}	[CPC] x 10^5 mol kg^{-1}	$\frac{I_0}{I_q}$
0.006	0.0180	0	1.0000
		0.7163	1.0093
		1.0740	1.0492
		1.6101	1.0559
		2.1455	1.0865
		2.6803	1.1023
		3.2144	1.1622
0.015	0.0120	0	1.0000
		0.7163	1.0565
		1.0740	1.1083
		1.6101	1.1594
		2.1455	1.1980
		2.6803	1.2699
		3.2144	1.3523
0.035	0.0100	0	1.0000
		0.7163	1.0800
		1.0740	1.1295
		1.6101	1.1762
		2.1455	1.2057
		2.6803	1.2748
		3.2144	1.3824

Table 4.29 - Continued

[NaBu] mol kg^{-1}	[SDS] mol kg^{-1}	[CPC] x 10^5 mol kg^{-1}	$\frac{I_0}{I_q}$
0.060	0.0033	0	1.0000
		0.7163	1.4779
		1.0740	2.0016
		1.6101	2.5625
		2.1455	3.0413
		2.6803	3.9409
		3.2144	5.0181
0.090	0.0023	0	1.0000
		0.7163	1.7225
		1.0740	2.6505
		1.6101	3.3726
		2.1455	4.5132
		2.6803	5.5069
		3.2144	6.3490

Table 4.30 - Aggregation Numbers of SDS in Aqueous Electrolyte Media at 25 °C

[Electrolyte] / mol kg^{-1}	N_0				
	Medium				
	Water	H_2O + NaBu	H_2O + NaAc	H_2O + NaPr	H_2O + NaCl
0.0	70[a] (44)[b]	--	--	--	--
0.006		44	44	59	50
0.015		63	62	69	72
0.035		67	79	86	93
0.060		69	101	98	94
0.097		70	80	94	90
0.200			92		
0.300			84		
0.400			82		

[a] Aggregation number of SDS when [SDS] = 0.10 mol kg^{-1}
[b] Aggregation number of SDS when [SDS] = 0.01 mol kg^{-1}

Table 4.31 – Values of Surface Potential of SDS micelle in Aqueous Electrolyte Media at 25 °C

[Electrolyte]/ mol kg^{-1}	Medium								
	Water			H_2O + NaBu			H_2O + NaPr		
	N_0	β	Ψ /mV	N_0	β	Ψ /mV	N_0	β	Ψ /mV
0.0	70	0.67	-120.4						
		0.74	-103.3						
		0.80	-85.7						
	44	0.67	-103.7						
		0.74	-86.9						
		0.80	-70.4						
0.006				44	0.67	-95.3	59	0.68	-102.9
					0.52	-121.6		0.56	-124.9
0.015				63	0.67	-98.3	69	0.68	-98.9
					0.58	-114.0		0.58	-116.6
0.035				67	0.67	-87.3	86	0.68	-92.2
					0.60	-98.9		0.58	-108.6
0.060				69	0.67	-79.9	98	0.68	-85.1
					0.69	-75.5		0.52	-108.5
0.097				70	0.67	-70.0	94	0.68	-74.9
					0.78	-51.1		0.73	-66.2

Table 4.31 – Continued

[Electrolyte]/ mol kg^{-1}	Medium					
	H_2O + NaAc			H_2O + NaCl		
	N_0	β	Ψ /mV	N_0	β	Ψ /mV
0.006	44	0.67	-95.4	50	0.74	-83.8
		0.50	-124.5		0.52	-125.7
0.015	62	0.67	-97.9	72	0.74	-87.1
		0.52	-122.4		0.59	-116.3
0.035	79	0.67	-91.5	93	0.74	-82.1
		0.61	-101.9		0.52	-118.7
0.060	101	0.67	-87.6	94	0.74	-72.9
		0.78	-65.8		0.78	-64.3
0.097	80	0.67	-72.9	90	0.74	-63.4
		0.53	-92.0		0.73	-65.2
0.200	92	0.67	-61.8			
		0.76	-48.2			
0.300	84	0.67	-53.1			
0.400	82	0.67	-47.9			

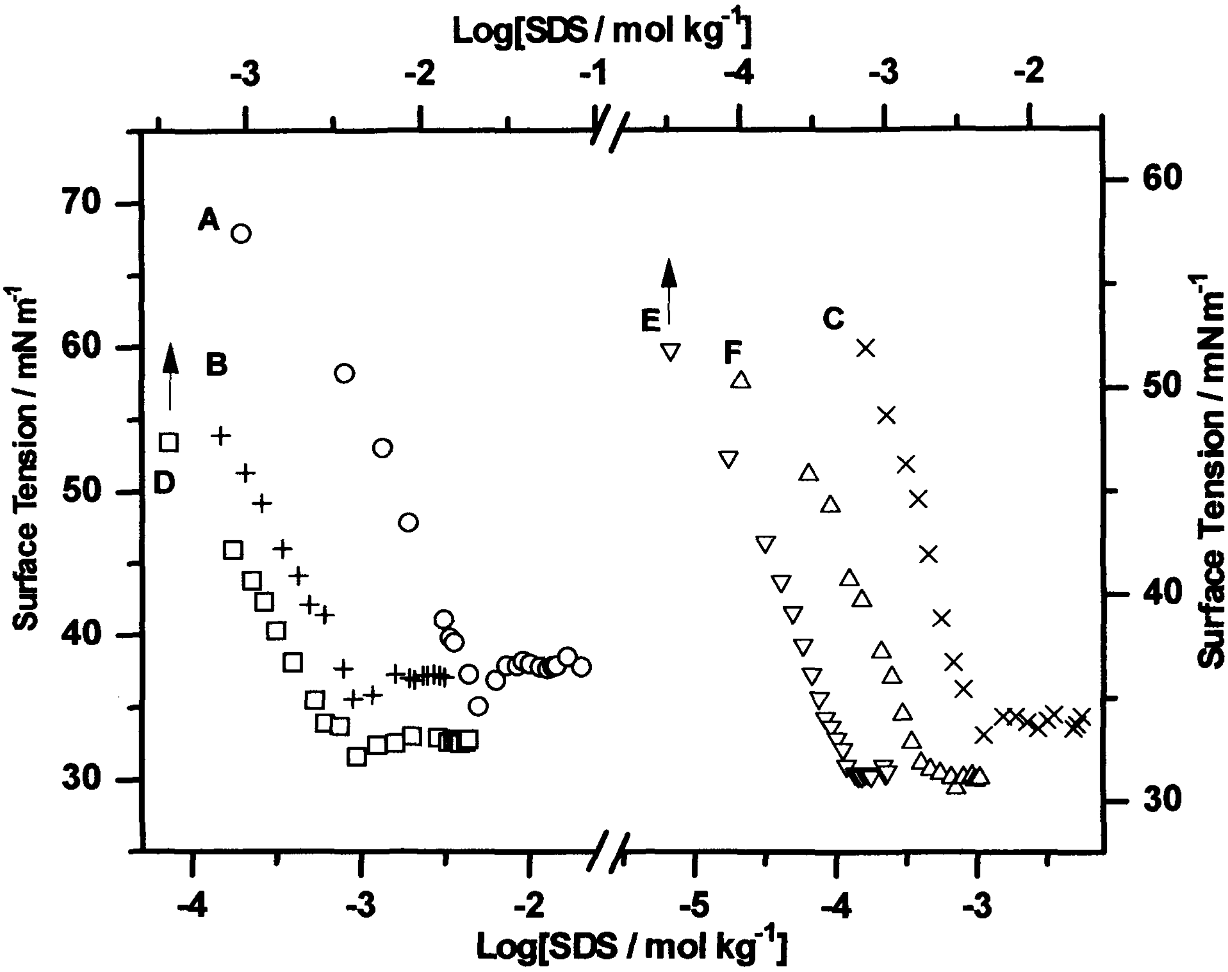

Figure 4.1 – A few representative plots of surface tension versus log[SDS] in aqueous NaBu solution at 25 °C. Concentrations (mol kg^{-1}) of NaBu are equal to 0.0052 (A), 0.0103 (B), 0.1002 (C), 0.1900 (D), 0.2904 (E) and 0.3903 (F).

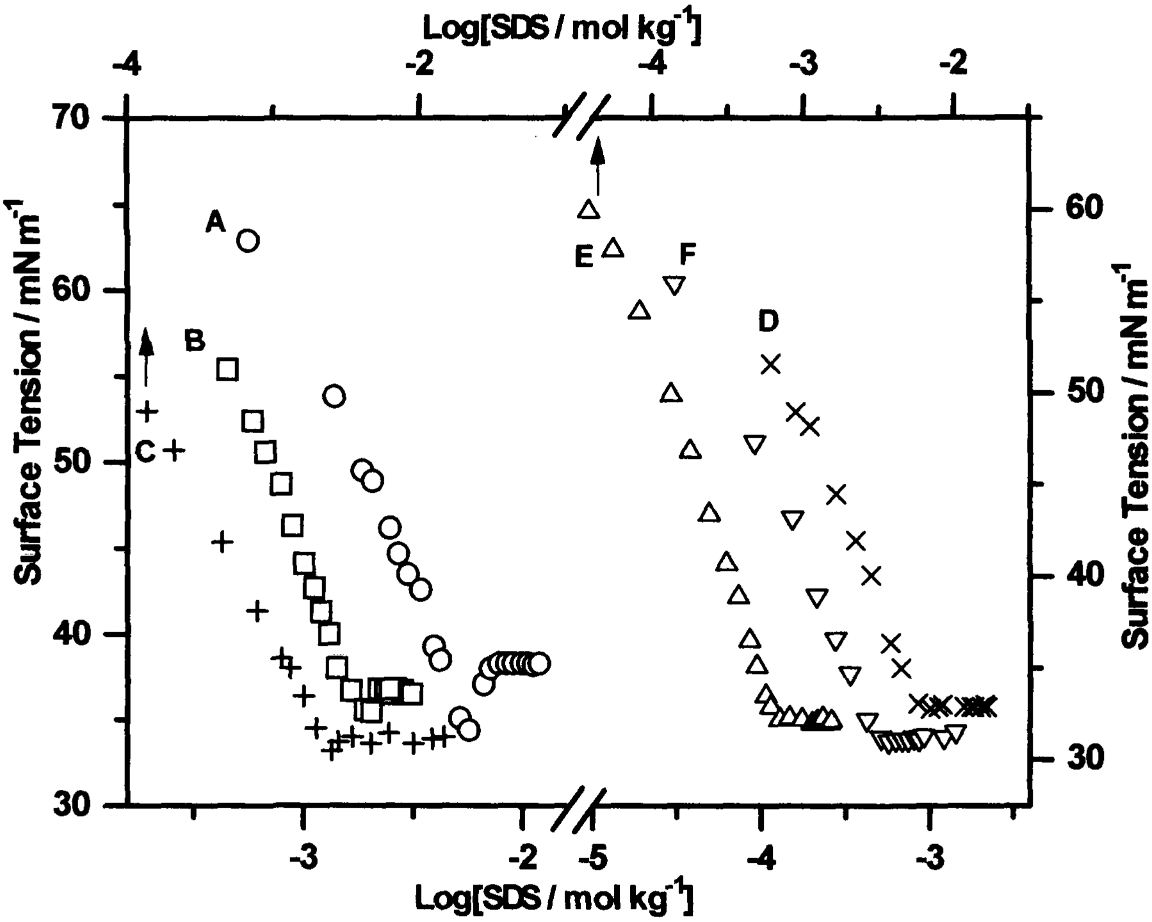

Figure 4.2 – A few representative plots of surface tension versus log[SDS] in aqueous NaAc solution at 25 °C. Concentrations (mol kg^{-1}) of NaAc are equal to 0.0048 (A), 0.0172 (B), 0.0967 (C), 0.2006 (D), 0.3015(E) and 0.4127 (F).

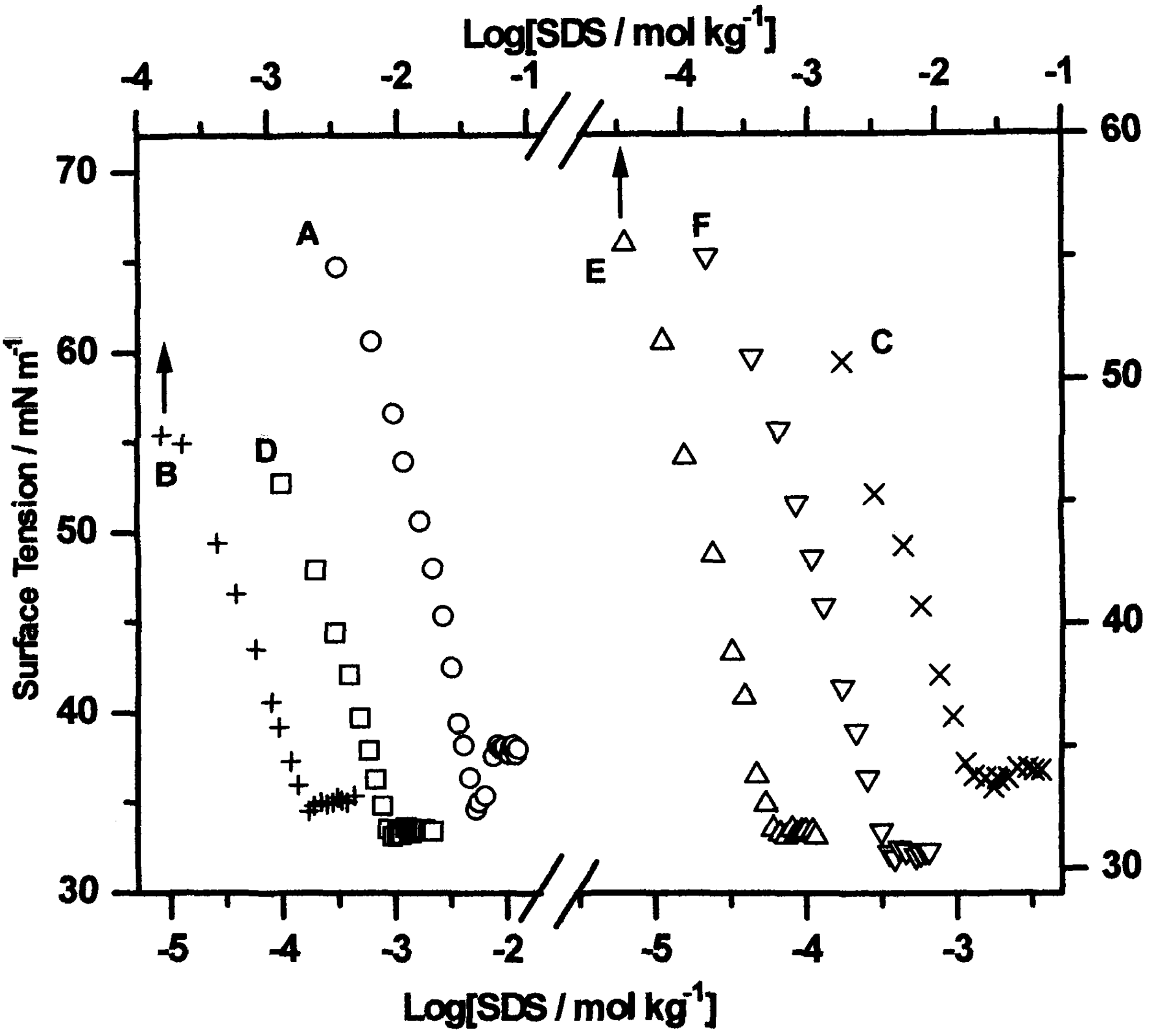

Figure 4.3 – A few representative plots of surface tension versus log[SDS] in aqueous NaPr solution at 25 °C. Concentrations (mol kg^{-1}) of NaPr are equal to 0.0042 (A), 0.0519 (B), 0.1103 (C), 0.1750 (D), 0.3806 (E) and 0.5780 (F).

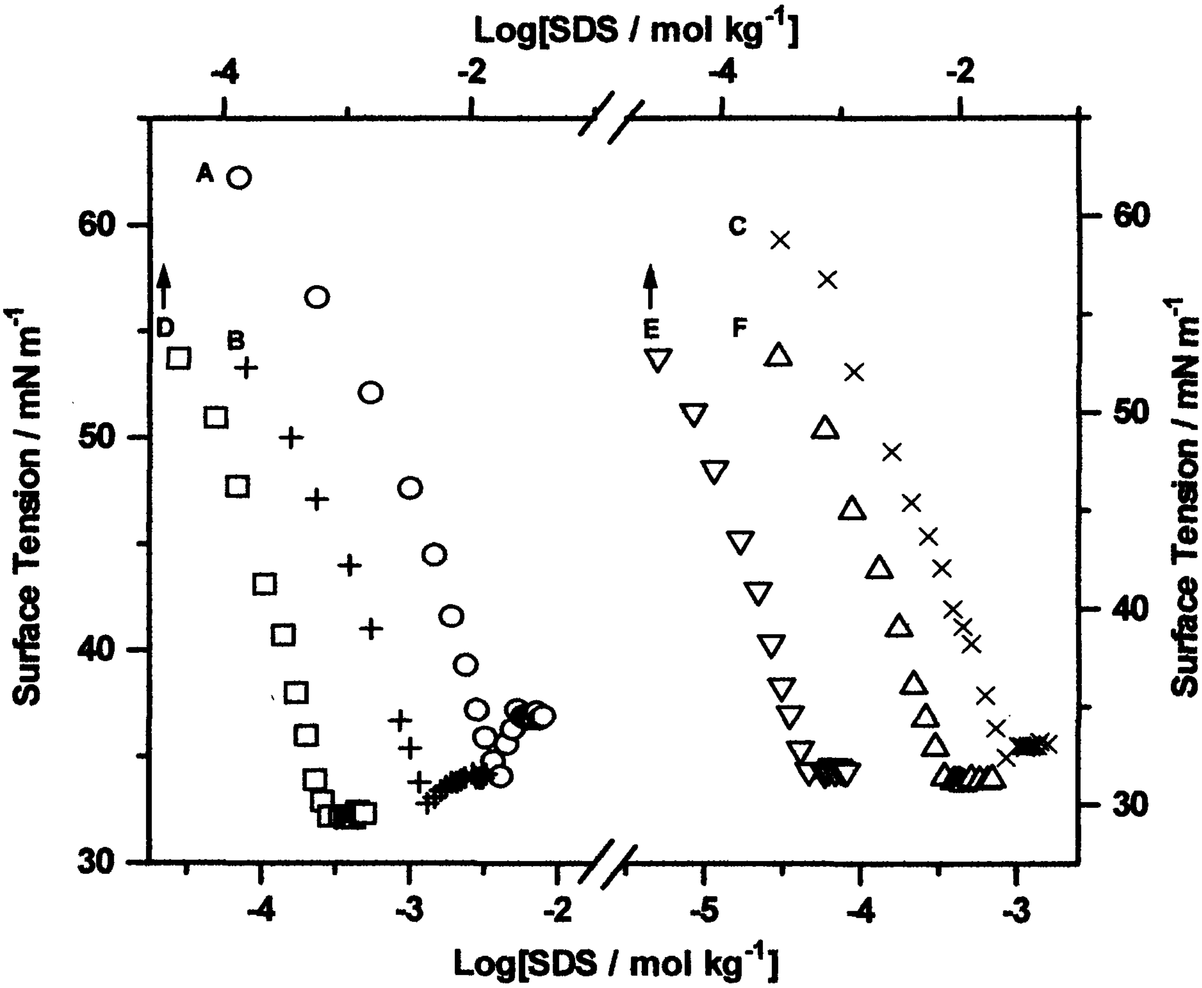

Figure 4.4 – A few representative plots of surface tension versus log[SDS] in aqueous NaCl solution at 25 °C. Concentrations (mol kg^{-1}) of NaCl are equal to 0.0152 (A), 0.1006 (B), 0.1849 (C), 0.2525 (D), 0.3471(E) and 0.5021 (F).

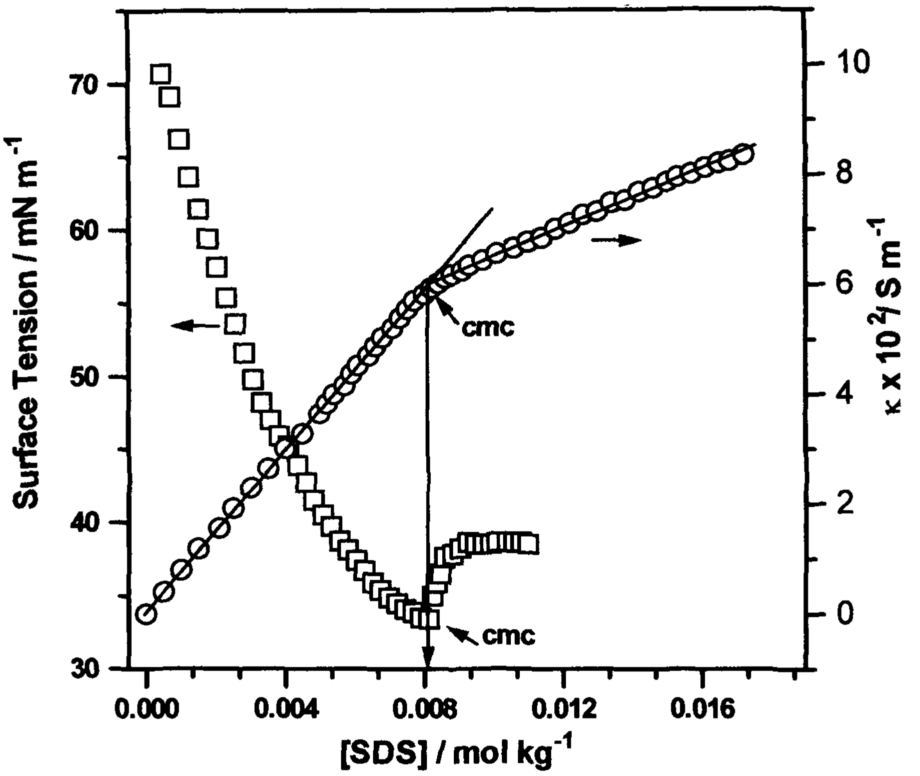

Figure 4.5 – Plots of surface tension and specific conductance of aqueous solution of SDS at 25 °C as a function of SDS concentration.

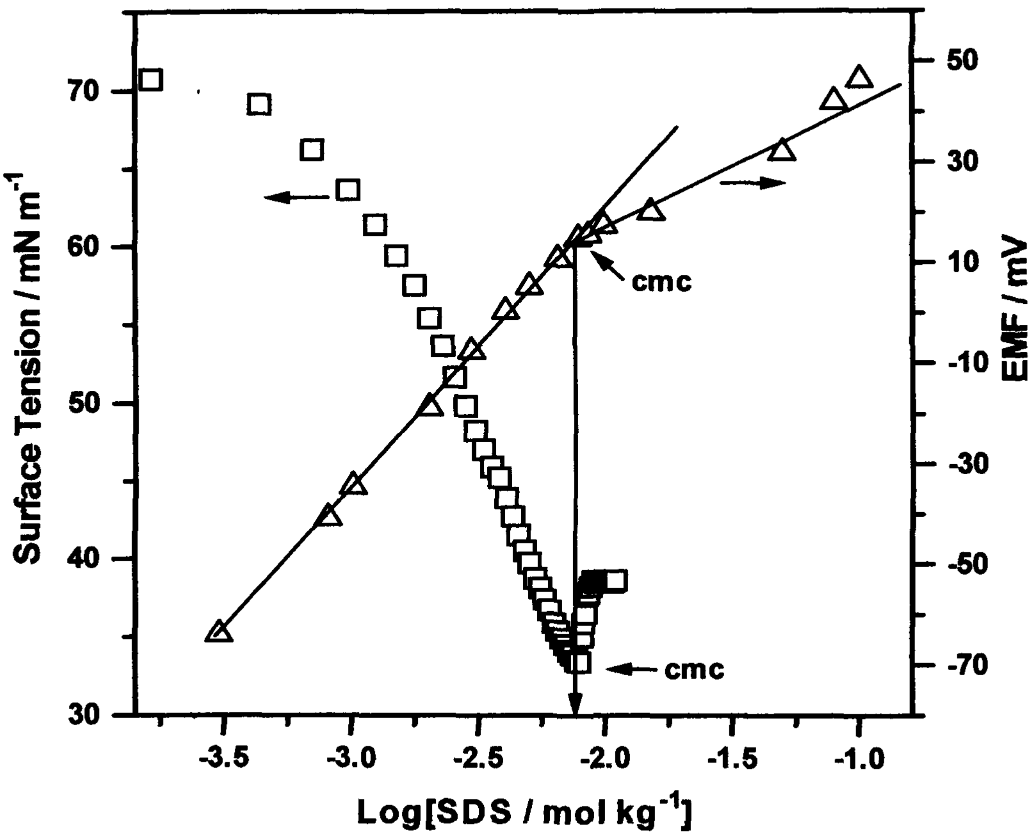

Figure 4.6 – Plots of surface tension and EMF of aqueous solution of SDS at 25 °C as a function of logarithm of SDS concentration.

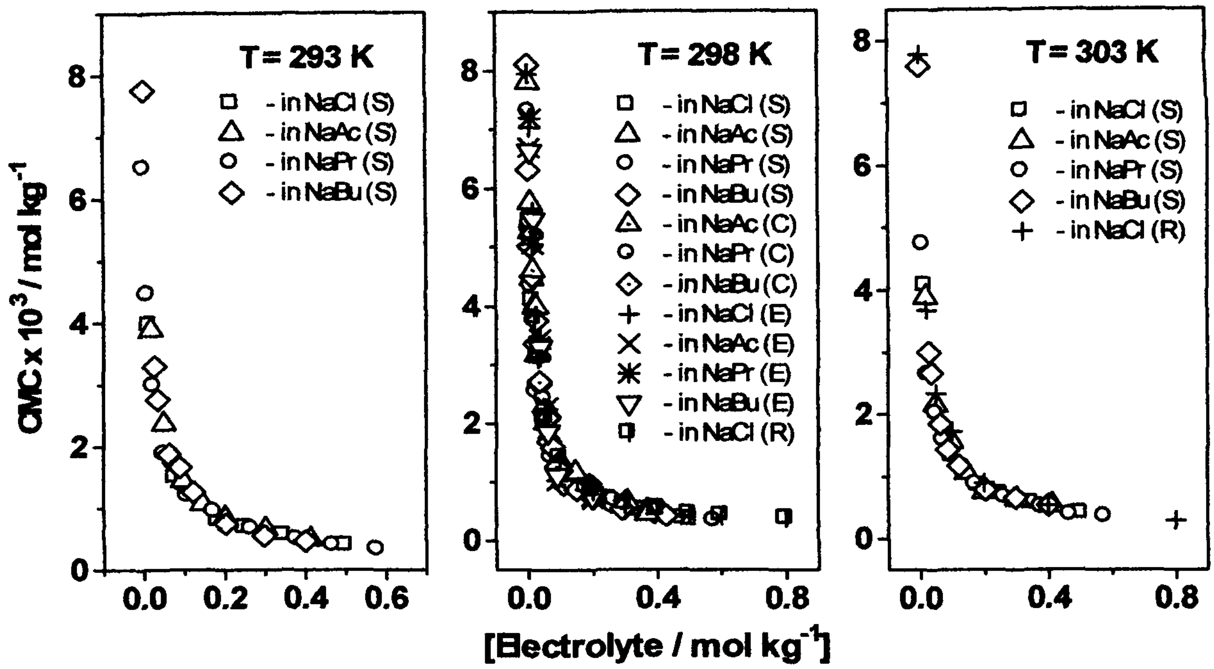

Figure 4.7 – Variation of cmc of SDS with electrolyte concentration at 20, 25 and 30 °C. S, C, E and R letters given in the parentheses indicate that cmc is from surface tension, conductance, emf and reported data, respectively. Reported cmc values are from references 9, 10 and 11 at 25 °C and from reference 12 at 30 °C.

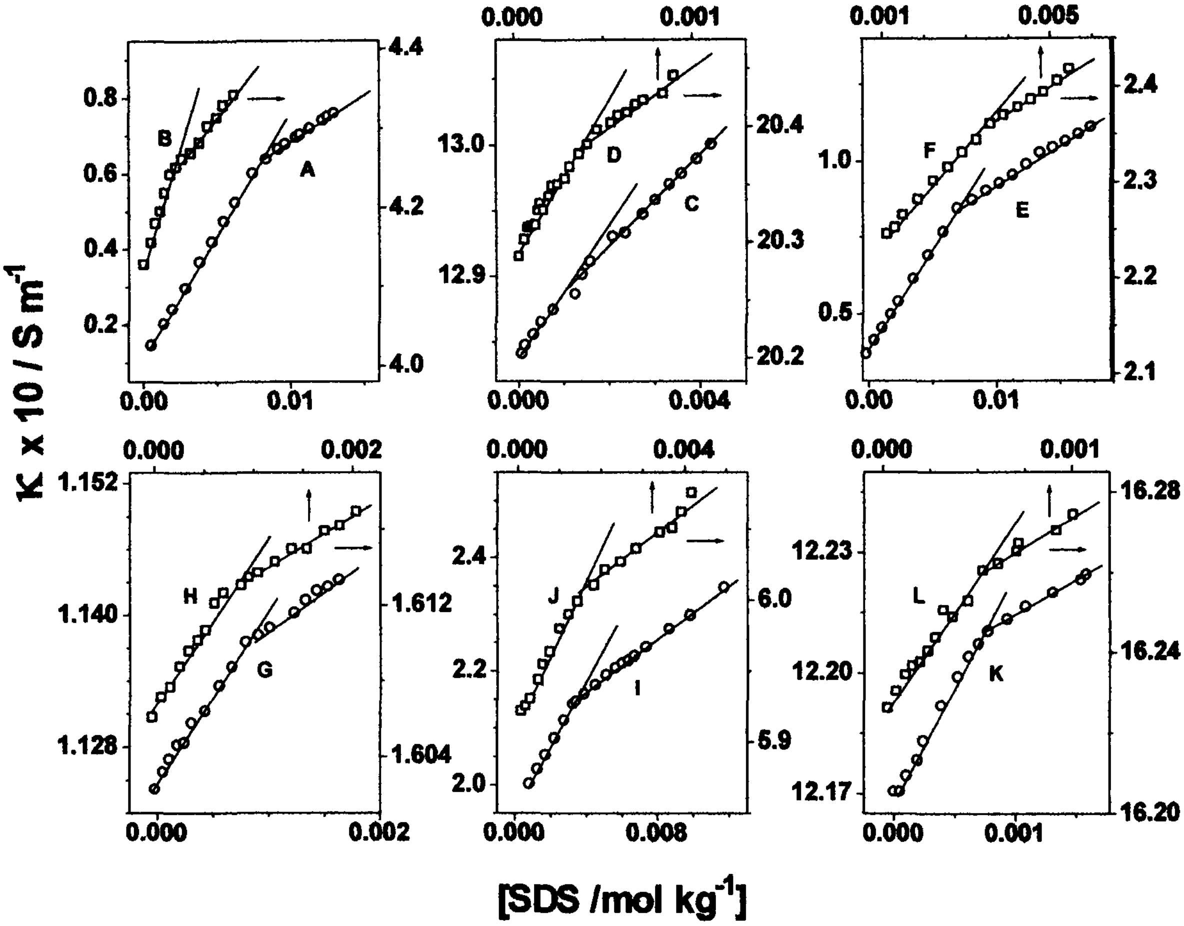

Figure 4.8 – Plots of specific conductance of aqueous solutions of SDS in the presence of NaAc (A – D), NaPr (E – H) and NaBu (I – L) as a function of concentration of SDS at 25 °C. Electrolyte concentrations in mol kg^{-1} are 0.0011 (A), 0.0539 (B), 0.2017 (C), 0.3698 (D), 0.0042 (E), 0.0268 (F), 0.1733 (G), 0.2685 (H), 0.0250 (I), 0.0887 (J), 0.2034 (K), and 0.2915 (L). [Left and right ordinates represent κ x 10/S m^{-1}. Top and bottom abscissa represent SDS concentration in mol kg^{-1}].

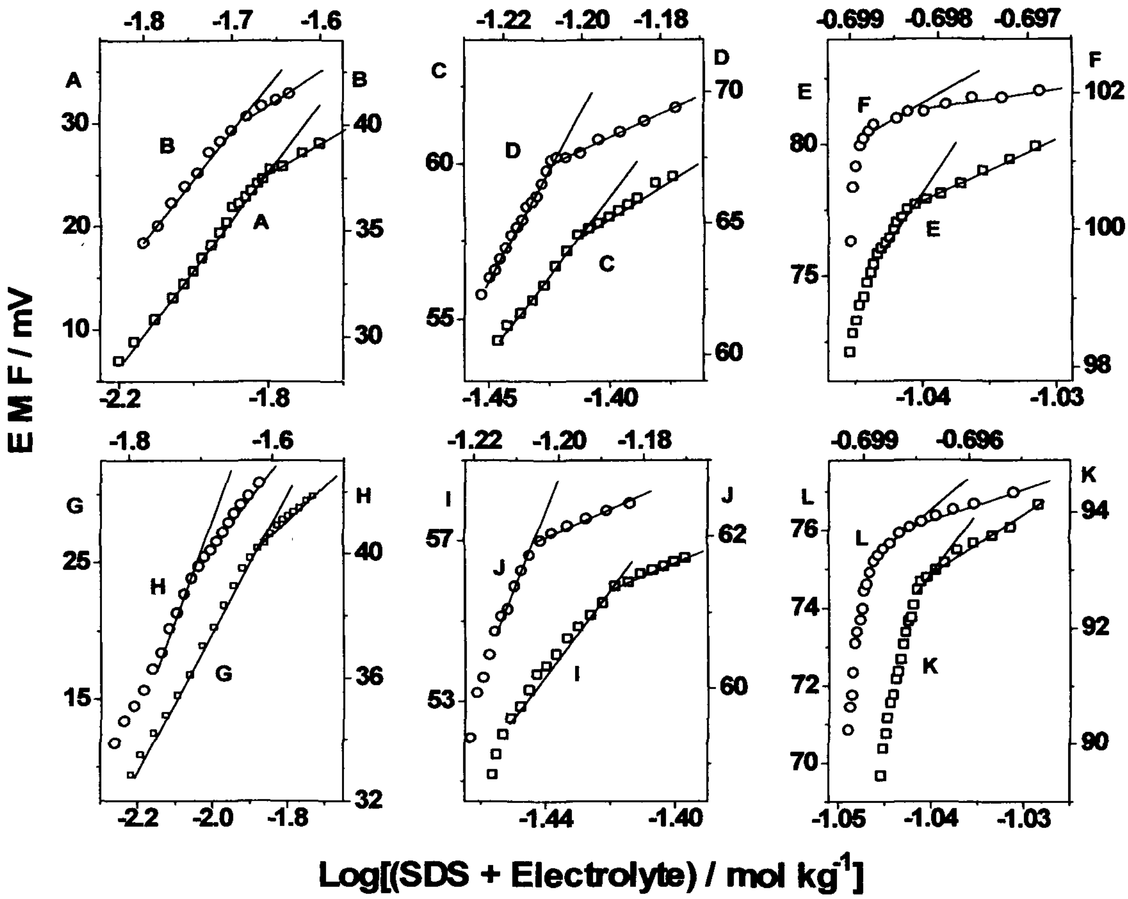

Figure 4.9 – Plots of EMF of aqueous solutions of SDS in the presence of electrolytes as a function of logarithm of counterion concentration. NaCl concentrations in mol kg^{-1} are (top row) 0.0059 (A), 0.0148 (B), 0.0356 (C), 0.0600 (D), 0.0909 (E) and 0.1998 (F). NaAc concentrations in mol kg^{-1} are (bottom row) 0.0059 (A), .0149 (B), 0.0349 (C), 0.0601 (D), 0.0900 (E) and 0.1998 (F). [Left and right ordinates represent EMF/mV. Top and bottom abscissa represent Log[(SDS + Electrolyte)/mol kg^{-1}].

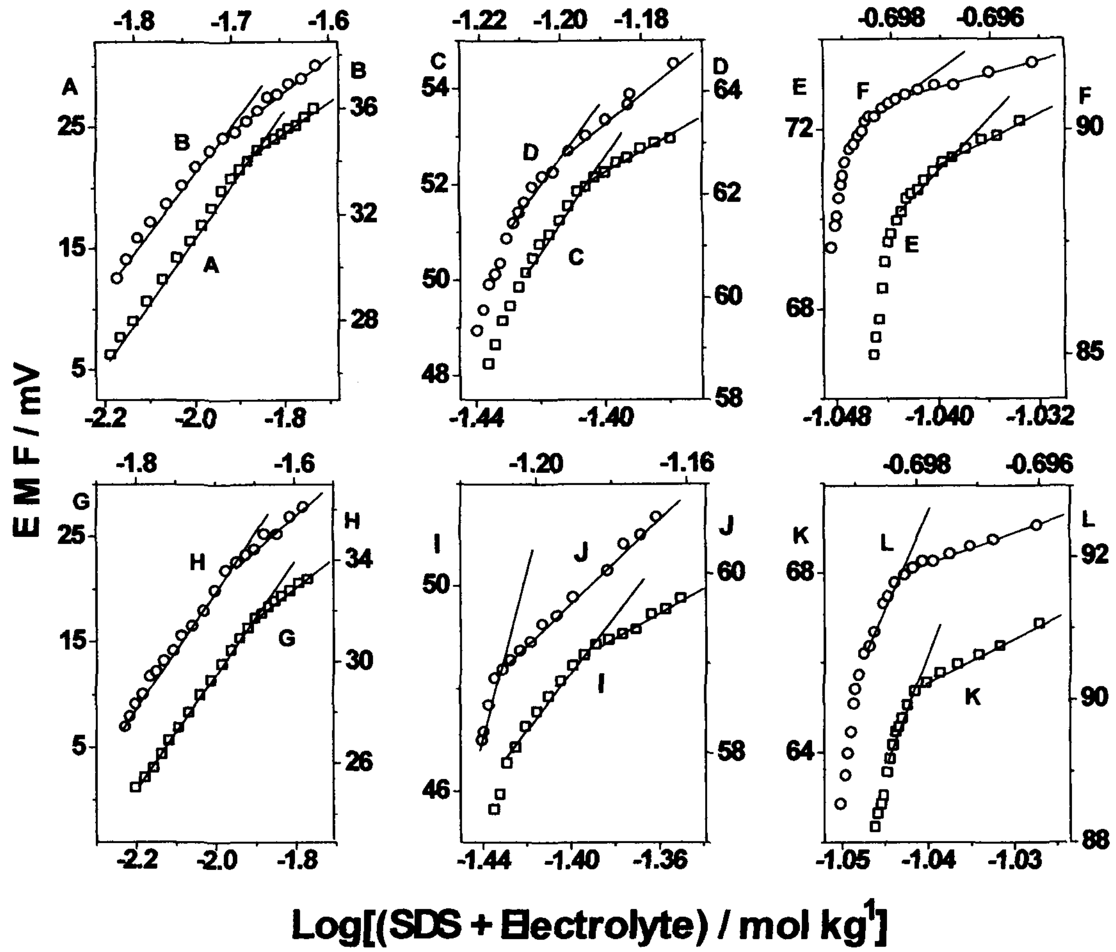

Figure 4.10 - Plots of EMF of aqueous solutions of SDS in the presence of electrolytes as a function of logarithm of counterion concentration. NaPr concentrations in mol kg^{-1} are (top row) 0.0063 (A), 0.0149 (B), 0.0360 (C), 0.0612 (D), 0.0902 (E) and 0.1999 (F). NaBu concentrations in mol kg^{-1} are (bottom row) 0.0061 (A), 0.0153 (B), 0.0366 (C), 0.0601 (D), 0.0900 (E) and 0.1998 (F). [Left and right ordinates represent EMF/mV. Top and bottom abscissa represent Log[(SDS + Electrolyte)/mol kg^{-1}].

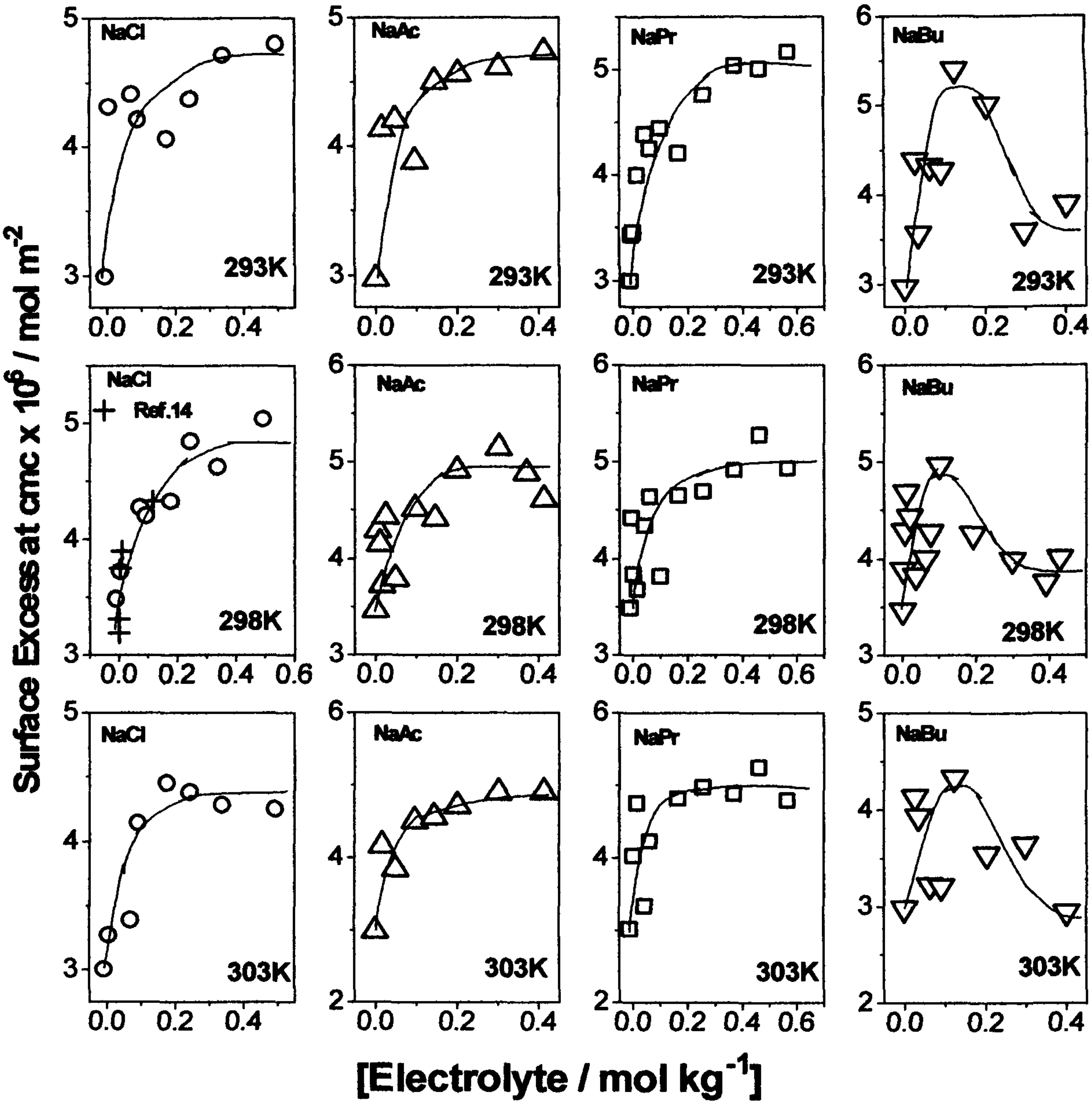

Figure 4.11 - Variation of surface excess of SDS at cmc with electrolyte concentration.

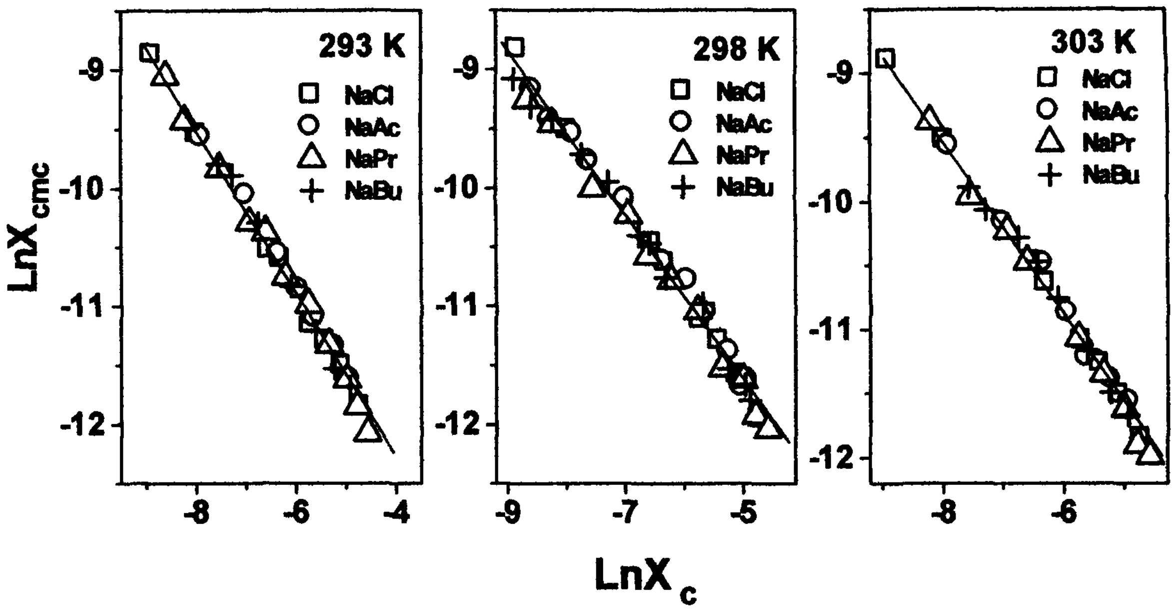

Figure 4.12 - Variation of ln X_{cmc} with ln X_c for solutions of SDS in different electrolytes [cmc values are from Table 4.13].

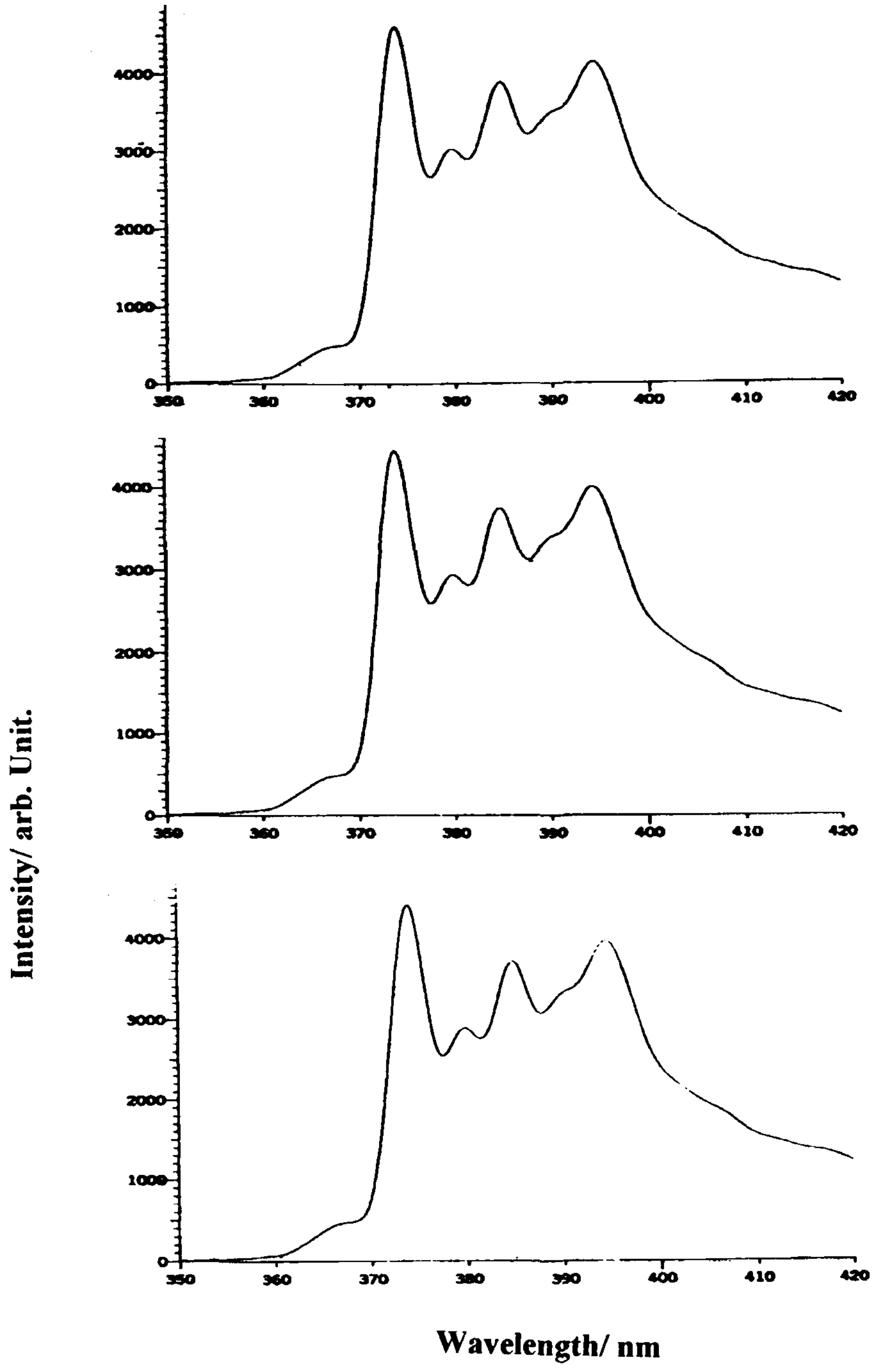

Figure 4.13 – Few characteristic fluorescence emission spectra of pyrene in aqueous SDS (Conc. = 0.019 mol kg^{-1}) in NaAc medium (Conc. = 0.0060 mol kg^{-1}). Top row contains no quencher, middle row, quencher conc.= 0.89 x10^{-5} and bottom row quencher conc=1.4 x 10^{-5}.

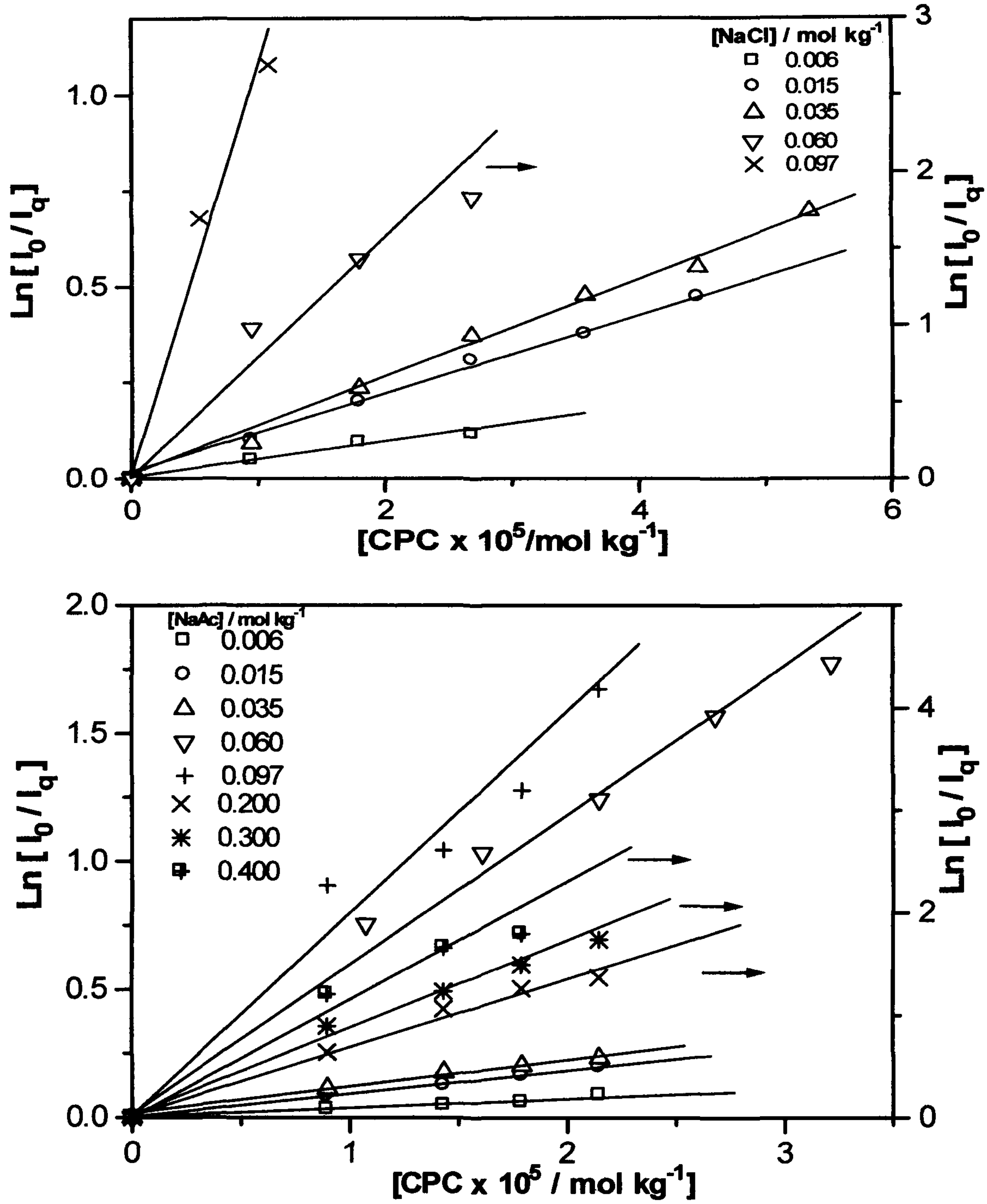

Figure 4.14 - Variation of ln [I_o/I_q] of pyrene with quencher concentration in aqueous SDS + NaCl (top) and SDS + NaAc (bottom) solutions at 25 °C.

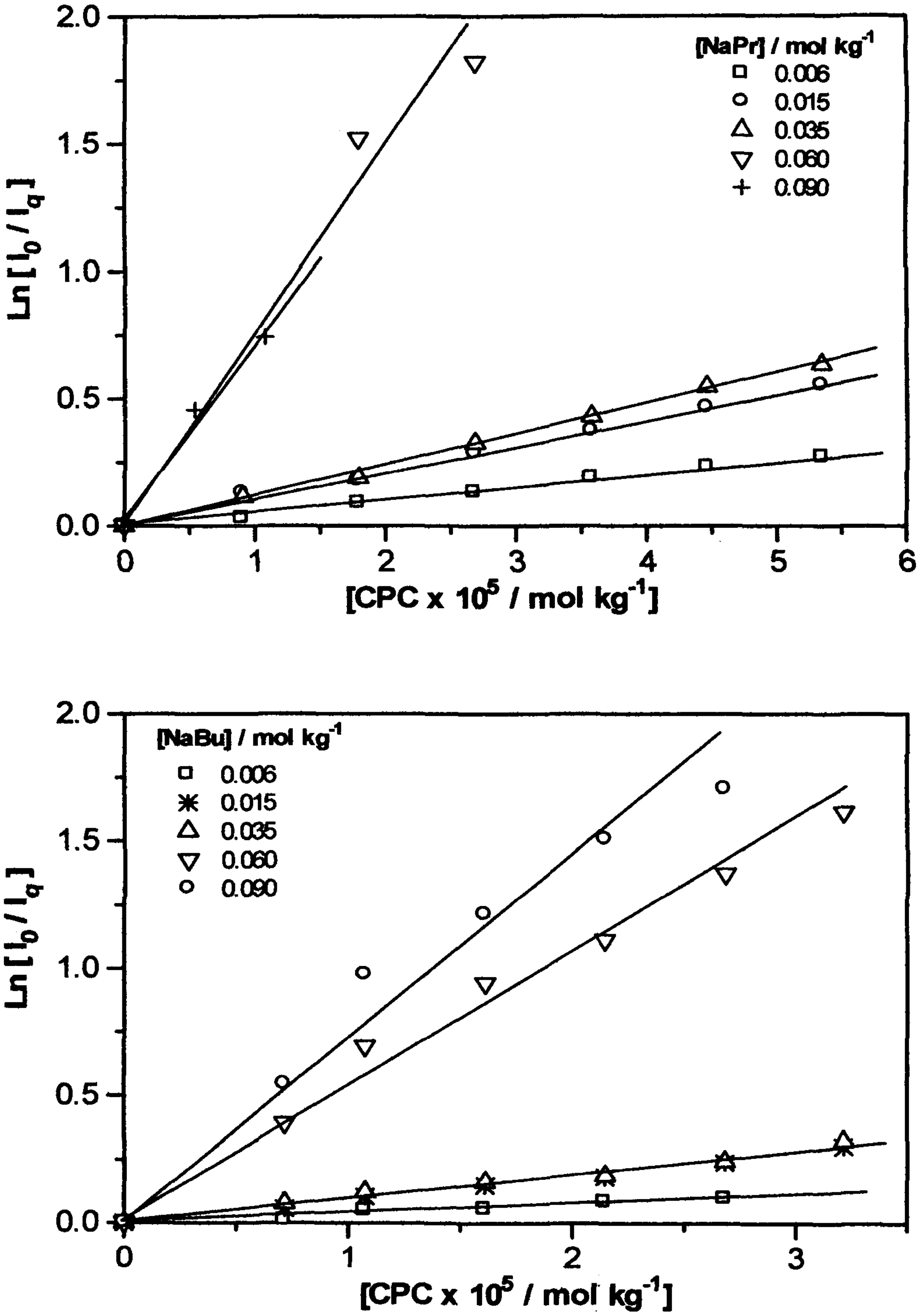

Figure 4.15 - Variation of ln $[I_o/I_q]$ of pyrene with quencher concentration in aqueous SDS + NaPr (top) and SDS + NaBu (bottom) solutions at 25 °C.

Micellization Behaviour of Dioctyl Sulfosuccinate and Sodium Dodecyl Sulfate in the Presence of a Hydrotrope

5.1 Introduction

In the previous chapters (chapters 3 and 4) we studied the micellization behaviour of AOT and SDS in aqueous medium in the presence of four electrolytes having same counter ion (Na^+) but different co-ions, viz., chloride, acetate, propionate and butyrate. In this chapter we have taken up the study of micellization behaviour of AOT and SDS in aqueous medium in the presence of a hydrotrope.

Hydrotropes are organic compounds capable of increasing the solubility of the organic species in water or aqueous salt solutions.[1] They have been widely used in the formulation of surfactant systems for detergency. The solubilizing power of hydrotropes has also been employed in drug formulation and several other industrial applications. Hydrotrope action or hydrotropy is considered to be similar to solubilization and sometimes it is also considered different from solubilization. Balasubramaniam et al.[2] reported that hydrotropy is a collective molecular phenomenon which is different from salting-in behaviour. Some of the examples of hydrotropes are sodium benzoate, sodium salicylate, sodium p-toluene sulfonate, resorcinol and pyrogallol.[2-4]

We have chosen here sodium salicylate as the hydrotrope for our study and this belongs to the class of anionic hydrotropes. Sodium salicylate on addition to CPC or CTAB shows strong viscoelastic property.[5-12] Thus, salicylate ion has a strong effect on the micellar structure of cationic surfactants mainly due to mixed micelle formation. In respect to cationic surfactants salicylate ion is a counter ion and the opposite charges of the cationic surfactant and hydrotrope ion favour mixed micelle formation. We viewed that it would be worthwhile to investigate whether salicylate ion due to its hydrotropic property has any effect on the micellization of anionic surfactants. Micellization parameters of AOT and SDS are therefore determined in the presence of sodium salicylate using different methods.

5.2 Experimental Section

Surface tension, conductance and EMF methods were used to determine the critical micelle concentrations. These methods are described in the previous chapters. AOT (Sigma, 99%), SDS (Aldrich, 99+ %, Lot No. 13803DO) and sodium salicylate (NaSa; Fluka, > 99.5%) were used without further purification.

5.3 Results and Discussion

Measured surface tension values of SDS and AOT at 25 °C in aqueous sodium salicylate solutions of varying concentrations are presented in Tables 5.1 and 5.2, respectively. Plots of surface tension versus log*c* (*c* denotes surfactant concentration) are shown in Figs. 5.1 and 5.2. From Fig. 5.1 it is apparent that in the presence of NaSa the aqueous solutions of the SDS sample used in this study exhibit surface tension minimum up to ~ 0.3 mol kg^{-1} of NaSa, whereas the same sample of SDS exhibited surface tension minimum in the presence of NaCl, NaAc, NaPr and NaBu up to ~ 0.2 mol kg^{-1} of electrolyte as pointed out in chapter 4. The cmc is taken to be the surfactant concentration corresponding to the minimum. We also measured electrical conductance and EMF of SDS in NaSa solutions at 25 °C and these data are given in Tables 5.3 and 5.4, respectively. For SDS in NaSa solutions the variations of conductance with c and EMF with log$c$ are shown in Figs. 5.3 and 5.4, respectively. In the case of AOT conductance method does not give correct cmc values and hence we measured only EMF of AOT + NaSa solutions in addition to their surface tension measurements. The experimental values of EMF of AOT in NaSa solutions are given in Table 5.5 and the variations of EMF with logc are shown in Fig. 5.5. The values of cmc of SDS and AOT in the presence of NaSa determined from the different methods are listed in Tables 5.6 and 5.7, respectively. In the cases of both SDS (Fig. 5.6) and AOT (Fig. 5.7), similar type of variations of cmc with the concentration of NaSa has been observed. The cmc values of SDS in the presence of NaSa determined in the present study from three different methods are compared in Fig. 5.6 with the values reported by Treiner et al.[13] based on conductance method. The present values of cmc are in good agreement with the reported[13] values up to 0.1 mol kg^{-1} of NaSa. In Figs. 5.6 and 5.7 we have also compared the cmc values of SDS + NaSa and AOT + NaSa systems with the cmc values of SDS and AOT in the presence of other electrolytes that are given in chapters 3 and 4. It can be seen from Figs. 5.6 and 5.7 that in the cases of both SDS and AOT the cmc values in the presence of NaSa are in agreement with those in the presence of other electrolytes up to certain concentrations only, which are estimated to be about 0.03 and 0.02 mol kg^{-1} NaSa for SDS and

AOT, respectively. Above these concentrations of NaSa, the cmc values of SDS and AOT are higher than the values in NaCl, NaAc, NaPr or NaBu solutions. Up to 0.03 mol kg^{-1} NaSa in the case of SDS and up to 0.02 mol kg^{-1} NaSa in the case of AOT the decrease in their cmc values can be attributed fully to the counter ion effect. Above these particular concentrations of NaSa an additional effect besides the counter ion effect seems to operate in aqueous solutions of SDS and AOT causing their cmc values in the presence of NaSa to become eventually higher than the corresponding cmc values in NaCl or NaAc or NaPr or NaBu solution.

The cmc values of AOT in NaSa solutions determined from the surface tension and EMF data nicely fit into the Corrin-Harkins (CH) relation

$$\ln X_{cmc} = A - \beta \ln X_c \qquad (5.1)$$

with $\beta = 0.46$ and $A = -14.44$. The terms of equation (5.1) are defined in the previous chapter. The CH plot for AOT in NaSa is shown in Fig. 5.8. The CH plots for AOT in NaCl and NaBu (from chapter 3) are redrawn in Fig. 5.8 for the sake of comparison. In the presence of NaCl, NaAc, NaPr, and NaBu the value of counter ion binding constant, β, for AOT below 0.015 mol kg^{-1} electrolyte concentration is nearly 0.4 and it becomes double above 0.015 mol kg^{-1} electrolyte concentration (cf. chapter 3). Therefore, above 0.015 mol kg^{-1} of NaCl / NaAc / NaPr / NaBu two times more counter ions condense into the AOT micellar surface than the amount of counter ions bound to the micelle below this particular electrolyte concentration. Although the exact cause for this sudden change in the β value is not yet clear, we proposed in the previous work that this could be due to the change in the micellar shape. Surprisingly, such a transition in the value of β does not take place in the presence of NaSa. The values of β of AOT in the presence of NaSa were also computed by least - squares fitting the EMF (E) data to equations

$$E = A_1 + B_1 \log c_{Na} \qquad \text{at } c < c_0 \qquad (5.2)$$

$$E = A_1 + B_1 \log[(1-\beta)c_{Na} + \beta c_0] \qquad \text{at } c > c_0 \qquad (5.3)$$

where the terms c_0 and c_{Na} represent the cmc and concentration of sodium ion, respectively. A_1 and B_1 are empirical constants. In the absence of electrolyte, c_{Na} is equal to the concentration of surfactant and in the presence of electrolytes $c_{Na} = c + c_e$, where c_e is the electrolyte concentration. The method of calculating β from EMF data using equations (5.2) and (5.3) are described in chapters 3 and 4 and the values of β thus obtained are listed in Table 5.7. The average of the concentration dependent values of β of AOT estimated from the EMF data is found to be 0.47.

In the case of SDS, its cmc values in the presence of NaSa determined from the surface tension, conductance and emf data fit into the CH relation with $\beta = 0.56$ and A = -13.85 (Fig. 5.8). This value of β is about 0.1 unit less than the values of β obtained from CH plots for SDS in the presence of NaCl or NaAc or NaPr or NaBu (cf. chapter 4). The values of β of SDS in the presence of NaSa computed from the EMF data (Table 5.4) by using equations (5.2) and (5.3) are listed in Table 5.6. The average value of β for SDS obtained from the EMF data is found to be 0.58. In the light of the variations observed in the value of β determined from CH plots, EMF data and conductance data (cf. chapter 4), the value of β for SDS in NaSa solution can be considered as comparable to the values in NaCl, NaAc, NaPr and NaBu solutions. It is reported[9] that NaSa reduces the counter ion binding constant value of cationic surfactant due to mixed micelle formation which is expected because of the charge neutralization on formation of mixed micelle between species of opposite charges. Higher degree of counter ion binding of salicylate to cationic micelles than chloride ion is also reported since salicylate ion is reported to interact with cationic micelles both electrostatically and hydrophobically.[14] On the basis of the β value obtained for SDS in NaSa solution it is evident that salicylate as a co-ion does not exhibit significant effect on the binding of sodium ions to SDS micelles.

The above observations reveal that salicylate co-ion influences the cmc values of both SDS and AOT and also β value of AOT unlike chloride, acetate, propionate and butyrate co-ions. As mentioned above NaSa is a hydrotrope and hence is expected to show influence on the micellization of surfactants differently from that of NaCl or NaAc or NaPr or NaBu. Hydrotropes are reported to undergo self-aggregation[2-4,15] and to form mixed micelles with cationic surfactants.[3,5-12] The present study indicate that above 0.02 mol kg^{-1} NaSa concentration salicylate ion may be forming mixed micelle with AOT thereby causing an increase in its cmc value. Similarly, salicylate may be forming mixed micelle with SDS above 0.03 mol kg^{-1} NaSa. Treiner et al.[13] also reported possibility of mixed micelle formation between

SDS and salicylate in order to account for the differences observed in the partition coefficient values of 1-pentanol in SDS micellar solutions in the presence of NaCl and NaSa. Mixed micelle formation between surfactants of same charge is known to take place due to hydrophobic interaction instead of electrostatic interaction.[16] In such mixed micelles the second component is considered to approach the surface of the first micelle from its hydrophobic end. Interaction of anionic dyes with anionic micelles also occurs in a similar manner.[17,18] Although increase in cmc may be explained as due to mixed micelle formation between anionic surfactant (SDS or AOT) and salicylate, it cannot simultaneously explain the decrease in β of AOT in the presence of NaSa (above 0.02 mol kg^{-1} NaSa). To account for the decrease in β of anionic surfactants by the addition of NaSa it is necessary that the salicylate ion neutralizes some of the counter-ion charges after formation of mixed micelle with AOT. Mixed micelles formed between SDS or AOT and salicylic acid ($pK_a = 3.03 \pm 0.07$ at 25 °C)[19,20] produced by the hydrolysis of salicylate ion is considered to be negligible here. Imae and Kohasaka[21] proposed a two-site model of salicylate binding to cationic micelles in order to explain (i) the transformation of cylindrical alkyltrimethylammonium micelles into spherical micelles as the concentration of added salicylate increases and (ii) the reversal of charge on the cationic micelles at high concentration of salicylate ion. The two sites of salicylate binding are (1) locations between the surfactant head groups and (2) exterior surface of micelles. Such a two - site binding gives rise to intercalated and surface-bound salicylate ions.[19,20] The two-site model of salicylate binding to alkyltrimethylammonium-type cationic micelles has been further supported by the surface potential study made by Cassidy and Warr[19] on tetradecyltrimethylammonium bromide + NaSa systems. In the light of the two-site model of salicylate binding to cationic micelles, it is visualized that in the case of anionic micelles salicylate ions will not choose the sites between the head groups due to electrostatic repulsion, but they can still choose the second site around the exterior surface of anionic micelles, i.e., between the Stern layer and the shear surface. The salicylate ions residing just outside the Stern layer may now be considered to form ion - pairs with the sodium counter ions present in the Stern layer. This type of ion-pair formation at the interface is favoured due to the fact that the dielectric constant at the micelle – solution interface is less than that in the bulk. In fact, at the SDS micelle – solution interface dielectric constant of about 55 ± 10 has been reported.[17] Thus, salicylate ion is considered to form mixed micelles with anionic surfactants by going to the surface of the anionic micelle and then forming ion pairs with the bound counter-ions. This is schematically shown in Fig. 5.9. Such ion – pair formation between the salicylate ions and sodium ions at the micellar surface appears to be significant only in the case of AOT when NaSa concentration is more than 0.02 mol kg^{-1} since β of AOT does not become equal to 0.8 as it happens in other electrolytes.

The values of surface excess, Γ_{cmc}, were calculated as in the previous chapters using the relation

Table 5.1 - Continued

[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaSa] = 0.2000 mol kg^{-1}			
0.0143	59.1	0.5637	38.1	1.6347	32.7
0.0285	57.0	0.6470	37.1	1.8320	32.5
0.0570	54.1	0.7300	36.1	2.0274	32.6
0.0997	51.2	0.7988	35.0	2.2847	32.7
0.1423	48.3	0.8948	34.1	2.5394	32.8
0.1990	46.0	0.9905	33.3	2.7902	32.8
0.2555	43.7	1.0993	32.4	3.0383	32.8
0.3259	42.1	1.2343	32.2	3.2834	32.9
0.3962	40.7	1.3688	32.3	3.5255	32.7
0.4801	39.4	1.5022	32.5		
		[NaSa] = 0.3001 mol kg^{-1}			
0.0173	59.0	0.5652	36.6	1.3984	32.2
0.0519	53.0	0.6328	35.9	1.4966	31.9
0.0864	50.5	0.7003	35.1	1.6594	32.1
0.1209	48.1	0.7677	34.3	1.8211	32.1
0.1726	45.8	0.8348	33.7	1.9818	32.3
0.2241	43.6	0.9017	33.2	2.1415	32.2
0.2927	41.9	1.0018	32.2	2.4578	32.3
0.3611	40.3	1.1016	31.2	2.7701	32.4
0.4293	38.9	1.2009	31.4	3.0785	32.4
0.4973	37.5	1.2999	31.5	3.3830	32.3
		[NaSa] = 0.4009 mol kg^{-1}			
0.0185	52.2	0.3313	38.0	1.4429	30.8
0.0370	50.5	0.4409	36.3	1.6181	31.1
0.0555	48.9	0.5500	34.7	1.9649	30.9
0.0740	47.3	0.6587	33.2	2.3073	30.9
0.1109	45.1	0.7670	32.4	2.6454	31.1
0.1478	42.8	0.8749	31.3	2.9792	31.0
0.1846	41.7	0.9823	30.4	3.3088	31.0
0.2213	40.6	1.1249	30.6	3.6343	30.9
0.2764	39.3	1.2667	30.6		

Table 5.2 - Surface Tension (γ) Values of AOT in Aqueous Sodium Salicylate Solution at 25 °C

[AOT] x10³ / mol kg⁻¹	γ / mN m⁻¹	[AOT] x10³ / mol kg⁻¹	γ / mN m⁻¹	[AOT] x10³ / mol kg⁻¹	γ / mN m⁻¹
		[NaSa] = 0.0012 mol kg⁻¹			
0.0063	61.6	0.4017	40.0	2.6008	28.9
0.0189	56.6	0.4923	39.8	2.7933	29.0
0.0252	55.4	0.6415	38.2	3.1668	29.3
0.0314	54.3	0.7886	36.9	3.3479	29.2
0.0440	53.3	0.9624	35.1	3.5255	28.9
0.0565	51.6	1.1333	34.5	3.6996	28.9
0.0816	49.5	1.3568	33.2	3.8704	28.7
0.1065	48.1	1.5755	32.3	4.0379	28.7
0.1563	46.4	1.7894	31.6	4.2023	28.8
0.1873	44.7	1.9987	30.9	4.3636	28.7
0.2490	43.4	2.2037	30.4	4.5218	28.6
0.3103	42.0	2.4043	29.5		
		[NaSa] = 0.0048 mol kg⁻¹			
0.0093	55.7	0.7451	36.1	2.6775	28.2
0.0186	52.4	0.9376	34.4	2.9055	28.1
0.0340	49.8	1.1218	33.0	3.1184	28.0
0.2741	42.0	1.3550	31.7	3.3176	28.0
0.3322	41.0	1.5752	30.5	3.5045	28.1
0.4038	39.0	1.8838	29.5	3.7362	27.9
0.4742	38.8	2.1683	28.7	3.9503	28.0
0.6117	37.0	2.4324	28.5		
		[NaSa] = 0.0066 mol kg⁻¹			
0.0058	56.8	0.4897	35.3	1.8580	27.9
0.0173	52.1	0.5987	34.0	1.9973	27.7
0.0346	49.0	0.7331	32.7	2.1796	27.4
0.0634	46.2	0.8655	31.5	2.3579	27.1
0.0978	43.7	0.9959	30.7	2.5324	27.0
0.1263	42.5	1.1245	30.2	2.7032	27.3
0.1548	41.8	1.2762	29.4	2.8704	27.0
0.2115	40.0	1.4254	28.8	3.0342	26.9

Table 5.2 - Continued

[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}	[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}	[AOT] x10^3/ mol kg^{-1}	γ/ mN m^{-1}
		[NaSa] = 0.0066 mol kg^{-1}			
0.2678	38.8	1.5721	28.4	3.1945	26.9
0.3238	37.6	1.7162	28.1	3.3516	27.0
0.3795	36.7				
		[NaSa] = 0.0101 mol kg^{-1}			
0.0038	57.7	0.3703	34.6	1.4228	27.4
0.0100	53.2	0.5136	33.1	1.5154	27.3
0.0224	49.2	0.6503	31.4	1.6011	27.2
0.0470	45.5	0.8127	30.4	1.6805	27.2
0.0833	42.7	0.9588	29.5	1.7544	27.2
0.1189	41.0	1.0913	28.7	1.8232	27.3
0.1538	39.2	1.2118	27.9	1.8873	27.1
0.2654	36.8	1.3217	27.6		
		[NaSa] = 0.0150 mol kg^{-1}			
0.0010	63.7	0.1338	39.5	1.2475	27.4
0.0030	58.7	0.1905	38.0	1.3694	27.1
0.0070	53.8	0.2462	36.6	1.5411	26.8
0.0130	51.0	0.3008	35.5	1.7007	26.6
0.0209	49.0	0.3544	34.4	1.8964	26.5
0.0288	47.0	0.4414	33.1	2.0751	26.4
0.0387	45.7	0.5258	32.0	2.2384	26.4
0.0486	44.5	0.6871	30.7	2.2968	26.3
0.0623	43.4	0.8393	29.5	2.5277	26.2
0.0759	42.4	0.9830	28.5	2.6609	25.9
0.1050	40.8	1.1187	27.8	2.8869	26.0
		[NaSa] = 0.0196 mol kg^{-1}			
0.0038	56.0	0.1545	38.7	0.9056	27.6
0.0114	53.0	0.1731	38.3	1.0031	27.3
0.0191	51.0	0.2101	37.2	1.0990	26.9
0.0267	49.2	0.2468	36.4	1.1933	26.7
0.0361	47.8	0.3016	35.3	1.2860	26.4

Table 5.2 - Continued

[AOT] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[AOT] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[AOT] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaSa] = 0.0196 mol kg^{-1}			
0.0456	46.6	0.3558	34.3	1.3772	26.2
0.0570	45.2	0.4452	32.8	1.4669	25.9
0.0683	44.0	0.5332	31.6	1.5552	25.9
0.0834	42.8	0.6199	30.4	1.6420	25.8
0.0984	41.8	0.7054	29.5	1.7275	25.7
0.1172	40.3	0.8063	28.5	1.8116	25.8
0.1359	39.4				
		[NaSa] = 0.0350 mol kg^{-1}			
0.0031	55.9	0.1415	36.6	1.0191	26.0
0.0062	52.4	0.1717	35.6	1.2129	25.7
0.0125	48.5	0.2167	34.4	1.3981	25.4
0.0218	46.0	0.2612	33.2	1.5748	25.3
0.0280	45.1	0.3488	31.5	1.7443	25.5
0.0404	42.9	0.4349	29.9	1.8665	25.5
0.0559	41.4	0.5193	28.8	2.0232	25.3
0.0713	40.1	0.6022	27.9	2.1738	25.6
0.0913	38.8	0.7103	27.0	2.3181	25.5
0.1111	37.7	0.8157	26.4	2.4229	25.2
		[NaSa] = 0.0650 mol kg^{-1}			
0.0025	55.0	0.2160	31.6	1.0875	25.6
0.0075	49.9	0.2629	30.7	1.2651	25.5
0.0150	46.4	0.3091	29.8	1.4333	25.7
0.0249	43.3	0.3999	28.5	1.5927	25.5
0.0472	40.3	0.4884	27.1	1.7435	25.6
0.0840	37.5	0.5958	26.5	1.8868	25.6
0.1205	35.0	0.7001	26.1	2.0236	25.5
0.1686	33.3	0.8996	25.8		

Table 5.2 - Continued

[AOT] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[AOT] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[AOT] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaSa] = 0.0970 mol kg^{-1}			
0.0013	56.4	0.1713	31.4	0.6475	25.4
0.0038	50.5	0.2165	30.2	0.7314	25.8
0.0088	46.5	0.2605	29.1	0.8107	25.5
0.0162	43.7	0.3141	28.3	0.8858	25.3
0.0287	41.2	0.3660	27.4	0.9575	25.3
0.0532	37.9	0.4164	26.7	1.0255	25.4
0.1014	34.5	0.4653	26.0	1.0905	25.2
0.1367	32.9	0.5540	25.6	1.1522	25.1
		[NaSa] = 0.2000 mol kg^{-1}			
0.0017	54.3	0.1251	32.4	0.4365	26.0
0.0050	49.1	0.1721	30.7	0.4777	25.9
0.0116	46.6	0.2183	28.8	0.5580	25.8
0.0187	43.5	0.2636	27.7	0.8755	25.8
0.0282	40.6	0.3080	26.8	0.9424	25.7
0.0446	38.6	0.3516	26.3	1.0070	25.5
0.0609	36.6	0.3944	26.0	1.0596	25.6
0.0932	34.3				
		[NaSa] = 0.3000 mol kg^{-1}			
0.0014	55.5	0.0498	36.9	0.3170	26.1
0.0042	50.1	0.0621	35.7	0.3875	25.9
0.0098	46.0	0.0756	33.7	0.4554	25.8
0.0153	43.6	0.0890	32.0	0.5423	25.8
0.0209	41.4	0.1420	30.3	0.6252	25.8
0.0374	39.8	0.1936	28.6	0.7046	25.8
0.0374	38.2	0.2562	27.3	0.7804	25.7

Table 5.2 - Continued

[AOT] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[AOT] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[AOT] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaSa] = 0.3880 mol kg^{-1}			
0.0013	55.5	0.0937	32.4	0.2870	26.5
0.0040	50.0	0.1190	31.6	0.3098	26.1
0.0093	45.6	0.1439	30.6	0.3324	25.9
0.0159	43.0	0.1685	29.7	0.3766	25.9
0.0225	41.4	0.1928	28.7	0.4199	26.1
0.0291	39.8	0.2168	28.0	0.4621	25.9
0.0422	36.5	0.2405	27.5	0.5033	26.0
0.0681	34.4	0.2639	26.9	0.5435	25.8

Table 5.3 - Specific Conductance (κ) Values of SDS in Aqueous Sodium Salicylate Solution at 25 °C

[SDS] x10^3 / mol kg^{-1}	κ / S m^{-1}	[SDS] x10^3 / mol kg^{-1}	κ / S m^{-1}	[SDS] x10^3 / mol kg^{-1}	κ / S m^{-1}
		[NaSa] = 0.0055 mol kg^{-1}			
0	0.0431	0.9703	0.0503	3.6159	0.0684
0.0433	0.0439	1.1741	0.0520	3.9603	0.0702
0.0866	0.0442	1.3755	0.0535	5.2651	0.0793
0.1297	0.0446	1.5744	0.0550	6.1732	0.0842
0.1727	0.0450	1.7710	0.0563	7.0271	0.0890
0.2157	0.0456	1.9653	0.0576	7.8313	0.0913
0.3012	0.0459	2.1573	0.0590	8.5902	0.0935
0.3863	0.0462	2.3470	0.0603	9.3074	0.0954
0.5131	0.0474	2.5346	0.0615	9.9863	0.0974
0.6390	0.0486	2.9033	0.0641	10.630	0.0989
0.8055	0.0495	3.2636	0.0665	11.241	0.1006
		[NaSa] = 0.0499 mol kg^{-1}			
0	0.3373	1.5800	0.3464	3.3500	0.3535
0.3200	0.3390	1.8800	0.3479	3.6300	0.3541
0.6400	0.3420	2.1800	0.3489	4.1900	0.3557
0.9600	0.3435	2.4800	0.3501	4.7300	0.3572
1.2700	0.3453	3.0600	0.3513	5.2700	0.3581
		[NaSa] = 0.1016 mol kg^{-1}			
0	0.6288	0.4300	0.6409	1.8900	0.6490
0.0400	0.6337	0.6800	0.6422	2.0800	0.4498
0.0900	0.6362	0.9300	0.6435	2.2700	0.6506
0.1300	0.6364	1.1700	0.6455	2.4600	0.6510
0.1700	0.6373	1.4200	0.6471	2.6500	0.6518
0.2200	0.6391	1.6500	0.6484		

Table 5.3 – Continued

[SDS] x10³ / mol kg⁻¹	κ / S m⁻¹	[SDS] x10³ / mol kg⁻¹	κ / S m⁻¹	[SDS] x10³ / mol kg⁻¹	κ / S m⁻¹
		[NaSa] = 0.1996 mol kg⁻¹			
0	1.2129	0.4800	1.2155	1.5700	1.2183
0.0300	1.2111	0.6800	1.2165	1.8800	1.2185
0.0700	1.2130	0.9400	1.2170	2.1800	1.2190
0.1400	1.2145	1.2600	1.2179	2.4700	1.2196
0.2800	1.2147				
		[NaSa] = 0.3003 mol kg⁻¹			
0.2400	1.6425	1.0500	1.6495	2.0300	1.6567
0.3600	1.6436	1.1600	1.6500	2.1600	1.6575
0.4800	1.6445	1.2700	1.6513	2.6500	1.6605
0.5900	1.6457	1.3800	1.6517		
0.8200	1.6477	1.6400	1.6540		
0.9300	1.6488	1.7700	1.6543		
		[NaSa] = 0.4000 mol kg⁻¹			
0.5800	2.0628	0.8700	2.0738	1.0600	2.0759
0.6800	2.0669	0.9700	2.0744	1.1600	2.0765
0.7800	2.0700				

Table 5.4 - EMF Values of SDS in Aqueous Sodium Salicylate Solution at 25 °C

[SDS] x10^3 / mol kg^{-1}	EMF / mV	[SDS] x10^3 / mol kg^{-1}	EMF / mV	[SDS] x10^3 / mol kg^{-1}	EMF / mV
		[NaSa] = 0.0052 mol kg^{-1}			
0	7.2	4.1667	15.6	12.265	22.3
0.3388	8.1	4.7353	16.6	13.038	22.4
0.4396	8.8	5.2903	17.0	13.781	22.8
0.7726	9.5	6.8784	19.3	14.495	23.3
1.1013	10.1	7.3836	20.0	15.182	23.6
1.4257	10.8	7.8774	20.4	15.845	24.0
1.7460	11.6	8.8324	21.1		
2.3742	12.6	9.7461	21.4		
2.9867	13.6	10.621	21.8		
3.5841	14.7	11.460	22.1		
		[NaSa] = 0.1000 mol kg^{-1}			
0	56.2	0.9076	61.4	2.3994	63.8
0.0308	56.9	1.0260	61.7	2.5927	63.9
0.0616	57.5	1.1437	61.9	2.7844	64.2
0.1231	57.9	1.2608	62.2	3.0553	64.5
0.2150	58.6	1.4353	62.5	3.3228	65.0
0.3066	59.4	1.6085	62.6	3.5870	65.1
0.4280	60.0	1.8089	62.8	3.8481	65.2
0.5489	60.6	2.0075	63.0	4.1059	65.3
0.6691	60.8	2.2043	63.3	4.3607	65.4
0.7887	61.1				
		[NaSa] = 0.2000 mol kg^{-1}			
0	77.0				
0.0285	77.3	0.6470	79.9	1.7268	81.6
0.0570	77.9	0.7850	80.2	1.8579	81.9
0.0855	78.1	0.9222	80.4	2.1176	81.9
0.1139	78.3	1.0585	80.6	2.3740	81.8
0.1707	78.6	1.1939	80.7	2.6272	81.9
0.2555	79.0	1.3284	80.8	2.8773	81.9
0.3681	79.3	1.4620	81.0	3.3683	81.8
0.5080	79.7	1.5948	81.3	3.8473	81.9

Table 5.4 – Continued

[SDS] x10^3 / mol kg^{-1}	EMF / mV	[SDS] x10^3 / mol kg^{-1}	EMF / mV	[SDS] x10^3 / mol kg^{-1}	EMF / mV
		[NaSa] = 0.3001 mol kg^{-1}			
0	82.6	0.5821	56.7	1.3162	87.8
0.0692	84.3	0.6834	86.9	1.5780	87.9
0.1726	84.9	0.7844	87.1	1.8049	88.0
0.2755	85.4	0.9184	87.3	2.1254	82.2
0.3781	85.7	1.0517	87.5	2.4419	88.4
0.4803	86.3	1.1843	87.6	2.7544	88.5
		[NaSa] = 0.4009 mol kg^{-1}			
0	91.1	0.4409	93.0	1.3020	93.6
0.0370	92.0	0.5500	93.1	1.4780	93.7
0.0740	92.2	0.6587	93.2	1.6528	94.1
0.1477	92.4	0.7670	93.3	1.8266	94.0
0.2213	92.6	0.8748	93.4	2.1708	94.2
0.2947	92.9	1.0892	93.5		

Table 5.5 - EMF Values of AOT in Aqueous Sodium Salicylate Solution at 25 °C

[AOT] x10^3 / mol kg^{-1}	EMF / mV	[AOT] x10^3 / mol kg^{-1}	EMF / mV	[AOT] x10^3 / mol kg^{-1}	EMF / mV
		[NaSa] = 0.0048 mol kg^{-1}			
0	4.5	1.3707	10.6	3.4884	15.4
0.0186	4.8	1.7977	11.7	3.7214	16.0
0.0555	5.7	2.1811	12.4	3.9364	16.7
0.1164	6.1	2.4270	13.2	4.1354	16.9
0.2359	6.4	2.6565	13.7	4.3203	17.0
0.4657	7.6	2.9591	14.0	4.4923	17.3
0.8922	9.3	3.2353	14.4		
		[NaSa] = 0.0101 mol kg^{-1}			
0	22.1	0.1880	24.0	1.1346	25.3
0.0075	22.7	0.2975	24.3	1.3373	25.4
0.0224	22.9	0.4204	24.4	1.4176	25.5
0.0470	23.2	0.6417	24.7	1.4273	25.5
0.0952	23.9	0.8949	25.1		
		[NaSa] = 0.0150 mol kg^{-1}			
0	21.6	0.1708	25.7	0.9821	27.3
0.0120	22.1	0.2083	25.9	1.1180	27.5
0.0239	22.4	0.2452	26.1	1.2467	27.6
0.0357	22.9	0.2818	26.3	1.4159	27.7
0.0476	23.8	0.3534	26.5	1.5734	27.8
0.0593	24.0	0.4233	26.7	1.7805	27.9
0.0711	24.0	0.5249	26.8	1.9691	28.0
0.0866	24.9	0.6229	26.9	2.1415	28.1
0.1060	25.2	0.8679	27.2	2.2997	28.2
0.1328	25.6				
		[NaSa] = 0.0350 mol kg^{-1}			
0	39.4	0.1536	44.0	0.4178	45.5
0.0062	40.4	0.1717	44.2	0.4519	45.6
0.0125	41.3	0.1897	44.3	0.4857	45.7
0.0187	41.9	0.2077	44.6	0.5193	45.7
0.0311	42.2	0.2256	44.7	0.5637	46.0

Table 5.5 - Continued

[AOT] x10^3 / mol kg^{-1}	EMF / mV	[AOT] x10^3 / mol kg^{-1}	EMF / mV	[AOT] x10^3 / mol kg^{-1}	EMF / MV
		[NaSa] = 0.0350 mol kg^{-1}			
0.0435	43.0	0.2434	44.8	0.6185	46.0
0.0621	43.6	0.2788	45.1	0.7262	46.2
0.0805	43.7	0.3140	45.2	0.8312	46.3
0.0989	43.8	0.3489	45.3	1.0338	46.2
0.1355	43.8	0.3835	45.7	1.2270	46.4
		[NaSa] = 0.0650 mol kg^{-1}			
0	48.9	0.1757	54.1	1.3182	56.5
0.0150	49.9	0.2231	54.7	1.5783	56.8
0.0299	50.7	0.2930	55.1	1.8175	57.0
0.0496	51.6	0.3751	55.4	2.0380	57.1
0.0742	52.4	0.5079	55.8	2.2421	57.2
0.1035	52.9	0.7226	56.1	2.4315	57.3
0.1374	53.8	1.0341	56.2	2.6077	57.4
		[NaSa] = 0.0970 mol kg^{-1}			
0	58.4	0.0834	62.8	0.6517	65.4
0.0050	60.3	0.1308	63.1	0.8144	65.9
0.0150	60.8	0.1997	63.5	0.9609	66.0
0.0274	61.3	0.2875	63.8	1.0935	66.1
0.0422	61.8	0.3913	64.4	1.2142	66.7
0.0593	62.3	0.5081	65.0	1.3244	66.8
		[NaSa] = 0.2000 mol kg^{-1}			
0	71.8	0.2380	78.0	0.8560	81.4
0.0067	72.4	0.3124	78.6	0.9235	81.6
0.0199	73.1	0.3845	79.3	0.9889	81.9
0.0331	73.6	0.4544	79.8	1.0522	82.0
0.0527	74.4	0.5619	80.2	1.1135	82.1
0.0819	75.3	0.6393	80.7	1.1730	82.2
0.1140	76.1	0.7140	80.9	1.2307	82.5
0.1456	76.8	0.7862	81.1	1.2866	82.5
0.2076	77.2				

Table 5.5 - Continued

[AOT] x10^3 / mol kg^{-1}	EMF / mV	[AOT] x10^3 / mol kg^{-1}	EMF / mV	[AOT] x10^3 / mol kg^{-1}	EMF / MV
		[NaSa] = 0.3000 mol kg^{-1}			
0	84.2	0.1249	86.0	0.8234	87.7
0.0056	84.6	0.2024	86.6	0.9950	88.0
0.0167	85.1	0.3253	86.8	1.1501	87.9
0.0388	85.6	0.5069	87.3	1.2908	88.0
0.0715	85.7	0.6722	87.7		
		[NaSa] = 0.3880 mol kg^{-1}			
0	86.3	0.1064	90.9	0.3211	92.3
0.0027	87.0	0.1315	91.3	0.3657	92.3
0.0080	87.7	0.1562	91.5	0.4091	92.3
0.0186	88.6	0.1807	91.8	0.4516	92.4
0.0396	89.3	0.2287	92.0	0.4930	92.4
0.0604	89.9	0.2755	92.3	0.5335	92.6
0.0810	90.5				

Table 5.6 - Values of Critical Micelle Concentration (± 0.05 x 10^{-3} mol kg^{-1}) of SDS in Aqueous NaSa Solution Obtained by Different Methods and the Values of Intercept (A_1) and Slope (B_1) of Eq (5.2) at 25 °C

Surface Tension		Conductance		EMF				
[NaSa]/ mol kg^{-1}	Cmc x 10^3 mol kg^{-1}	[NaSa]/ mol kg^{-1}	Cmc x 10^3 mol kg^{-1}	[NaSa]/ mol kg^{-1}	Cmc x 10^3 mol kg^{-1}	A_1 / mV	B_1 / mV	β ± 0.02
0.0052	5.90	0.0055	6.00	0.0052	7.40	80.49	31.98	0.47
0.0503	2.40	0.0499	2.00	0.0500	2.60	250.8	155.4	0.50
0.1000	1.80	0.1016	1.65	0.1000	1.50	591.1	531.9	0.57
0.2000	1.20	0.1996	1.20	0.2000	1.10	671.7	848.4	0.56
0.3001	1.10	0.3003	1.05	0.3001	1.06	739.7	1251	0.68
0.4009	0.98	0.4004	0.88	0.4009	0.98	428.9	847.2	0.68

Table 5.7 - Values of Critical Micelle Concentration (± 0.05 x 10^{-3} mol kg^{-1}) of AOT in Aqueous NaSa Solution Obtained by Different Methods and the Values of Intercept (A_1) and Slope (B_1) of Eq (5.2) at 25 °C

Surface Tension		EMF				
[NaSa] / mol kg^{-1}	Cmc x 10^3 mol kg^{-1}	[NaSa] / mol kg^{-1}	Cmc x 10^3 mol kg^{-1}	A_1 / mV	B_1 / mV	$\beta \pm$ 0.02
0.0012	2.60	0.0048	2.00	116.8	48.00	0.36
0.0048	2.11	0.0101	1.29	86.94	31.62	0.61
0.0066	1.66	0.0150	1.28	101.0	41.04	0.51
0.0101	1.41	0.0349	0.90	186.6	97.10	0.35
0.0150	1.32	0.0650	0.67	309.3	214.3	0.47
0.0196	1.15	0.0970	0.60	1172	1095	0.48
0.0350	0.91	0.2000	0.38	2794	3888	0.56
0.0651	0.70	0.3000	0.33	1726	3138	0.53
0.0970	0.53	0.3880	0.28	1943	4505	0.40
0.2000	0.36					
0.3000	0.34					
0.3880	0.32					

Table 5.8 - Computed Values of Surface Excess (Γ_{cmc}) and Surface Area per Molecule (A_0) of SDS and AOT near cmc at 25 ° C in Presence of NaSa

Surfactant : SDS			Surfactant : AOT		
[NaSa] mol kg^{-1}	(Γ_{cmc} ± 0.5) x 10^6 / mol m^{-2}	A_0 / nm^2	[NaSa] mol kg^{-1}	(Γ_{cmc} ± 0.5) x 10^6 / mol m^{-2}	A_0/ nm^2
0.0	3.46[a]	0.48	0.0	1.63[b]	1.02
0.0052	3.03	0.58	0.0012	1.58	1.05
0.0503	3.05	0.62	0.0048	1.94	0.86
0.1000	4.10	0.41	0.0066	1.96	0.85
0.2000	3.79	0.44	0.0101	2.00	0.83
0.3001	3.45	0.48	0.0150	2.14	0.78
0.4009	2.92	0.57	0.0196	2.34	0.71
			0.0350	2.37	0.70
			0.0651	2.38	0.70
			0.0970	2.23	0.74
			0.2000	2.38	0.70
			0.3000	2.35	0.71
			0.3880	2.22	0.75

a) Value taken from chapter 4; b) Value taken from chapter 3.

Table 5.9 - Values of ΔG°_{m} and ΔG°_{ad} of SDS and AOT in Aqueous NaSa Solution at 25 °C

Surfactant : SDS			Surfactant : AOT		
[NaSa] mol kg^{-1}	$-\Delta G^{\circ}_{m}$/ kJ mol^{-1}	$-\Delta G^{\circ}_{ad}$/ kJ mol^{-1}	[NaSa] mol kg^{-1}	$-\Delta G^{\circ}_{m}$/ kJ mol^{-1}	$-\Delta G^{\circ}_{ad}$/ kJ mol^{-1}
0.0052	35.37	47.71	0.0012	36.31	54.54
0.0503	38.85	50.32	0.0048	37.07	51.55
0.1000	39.96	48.30	0.0066	37.94	51.77
0.2000	41.53	50.18	0.0101	38.54	52.14
0.3001	41.88	51.24	0.0150	38.78	51.12
0.4009	42.33	52.95	0.0196	39.28	50.35
			0.0350	40.14	50.9
			0.0651	41.09	51.8
			0.0970	42.14	53.48
			0.2000	43.49	54.29
			0.3000	43.66	54.64
			0.3880	44.01	55.72

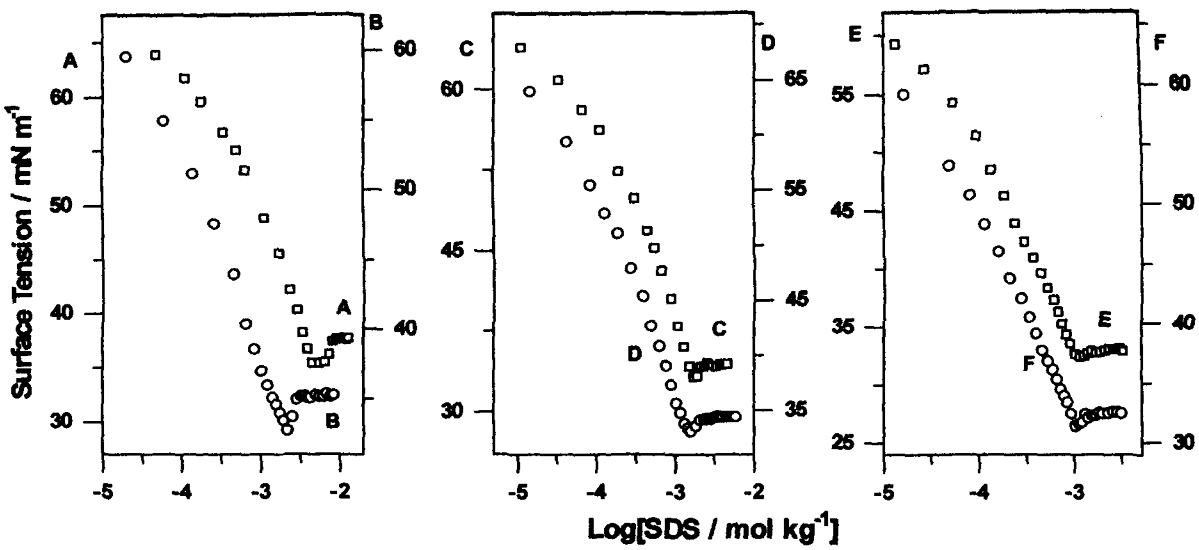

Figure 5.1 - Variation of surface tension of aqueous solution of SDS in the presence of NaSa with log[SDS]. The concentrations of NaSa in mol kg^{-1} are 0.0052 (A), 0.0503 (B), 0.1000 (C), 0.2000 (D), 0.3001 (E) and 0.4009 (F).

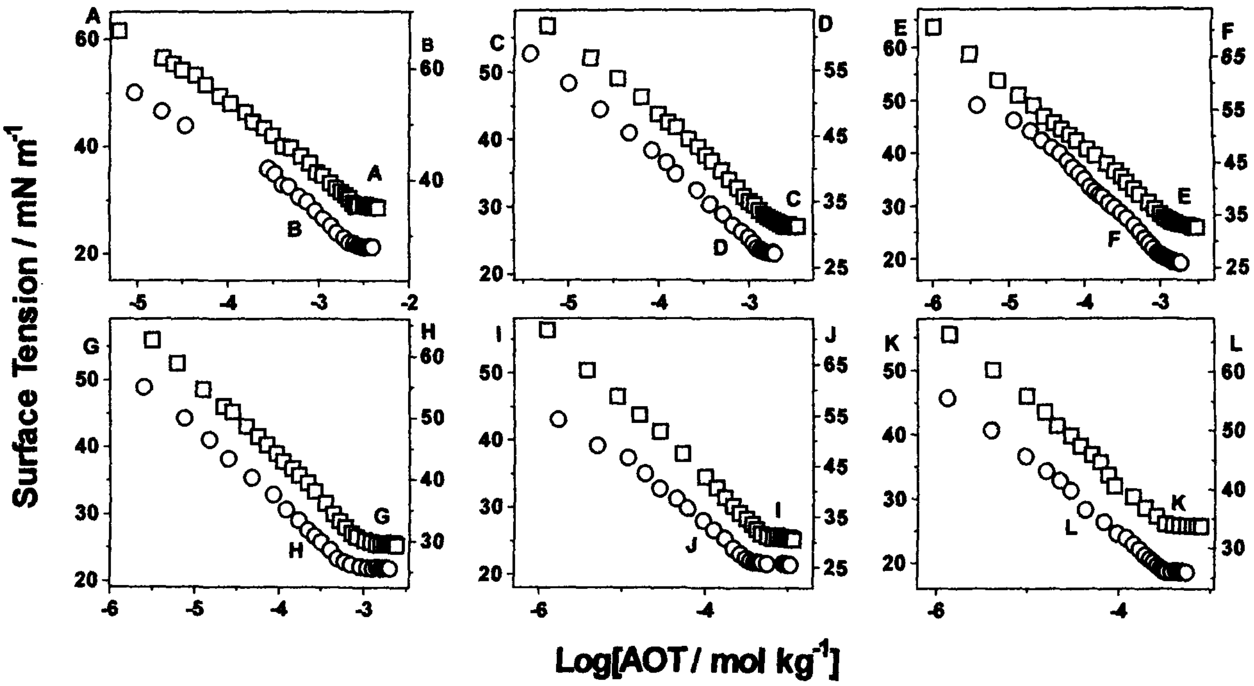

Figure 5.2 Variation of surface tension of aqueous solution of AOT in the presence of NaSa with log[AOT]. The concentrations of NaSa in mol kg^{-1} are 0.0012 (A), 0.0048 (B), 0.0066 (C), 0.0.0101 (D), 0.0150 (E), 0.0196 (F), 0.0350 (G), 0.0651 (H), 0.0970 (I), 0.2000 (J), 0.3000 (K), and 0.3880 (L).

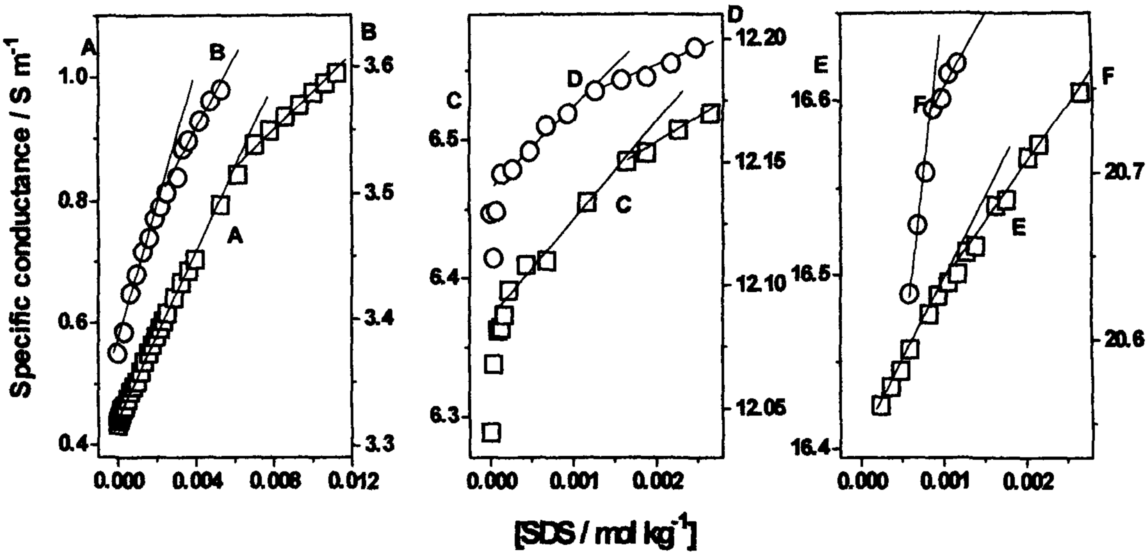

Figure 5.3 - Variation of specific conductance of aqueous solution of SDS in the presence of NaSa with [SDS]. The concentrations of NaSa in mol kg^{-1} are 0.0055 (A), 0.0499 (B), 0.1016 (C), 0.1996 (D), 0.3003 (E) and 0.4004 (F).

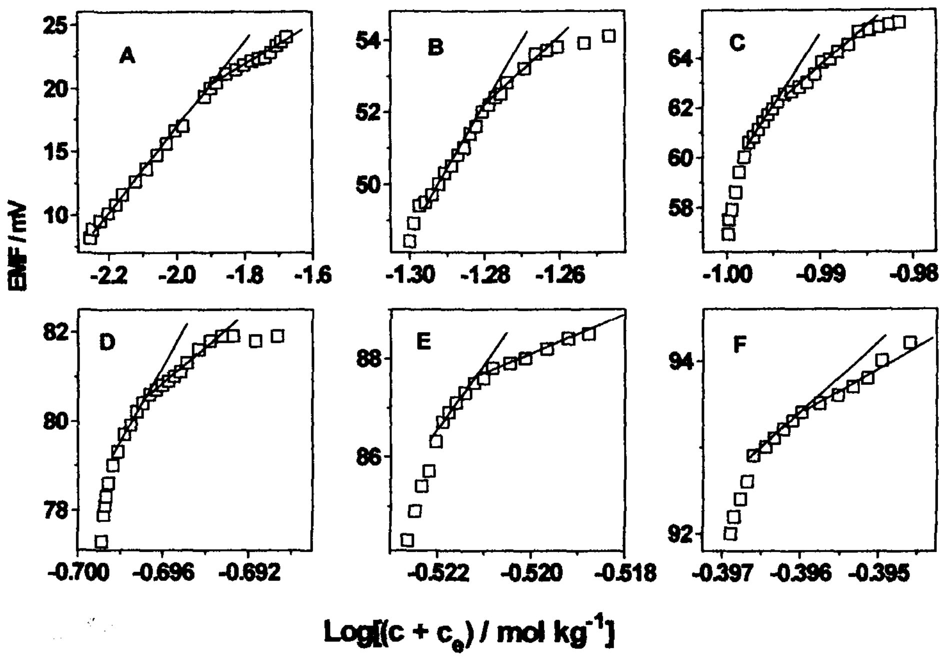

Figure-5.4 - Variation of EMF of aqueous solution of SDS in the presence of NaSa with Log[Na^+]. The concentrations of NaSa in mol kg^{-1} are 0.0052 (A), 0.0500 (B), 0.1000 (C), 0.2000 (D), 0.3001 (E) and 0.4009 (F).

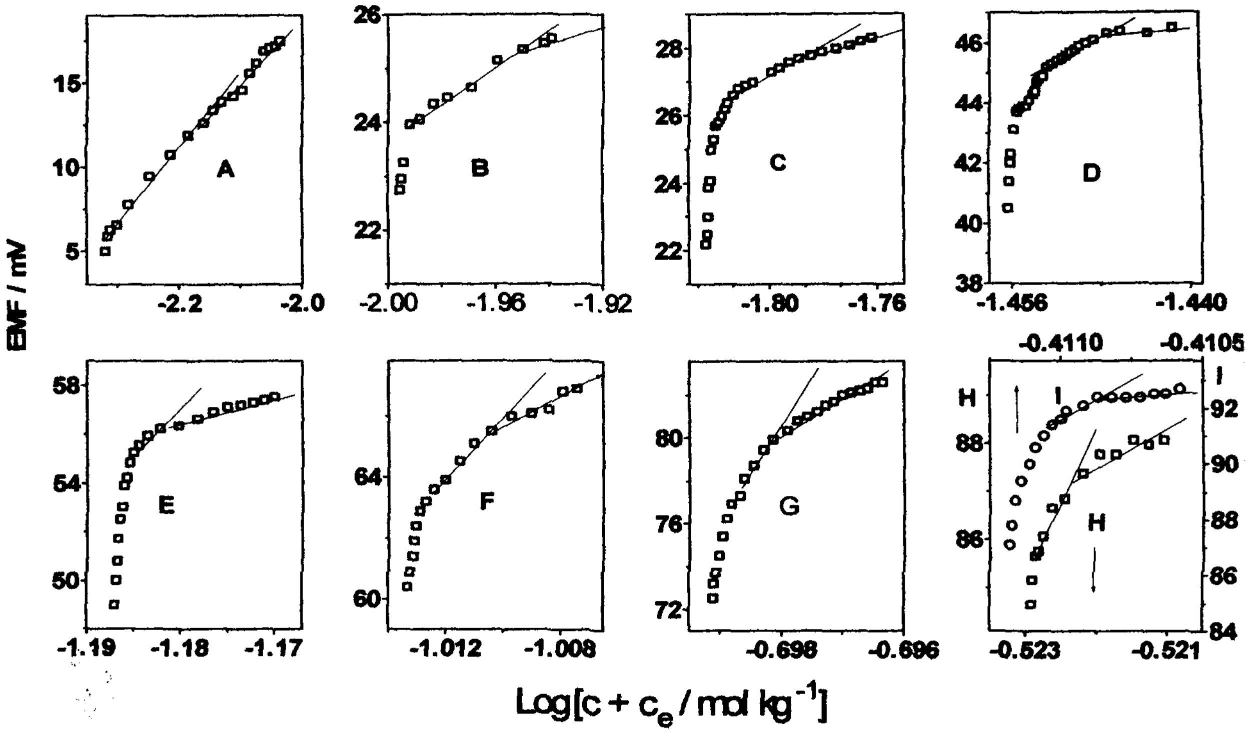

Figure 5.5 Variation of EMF of aqueous solution of AOT in the presence of NaSa with log[Na^+]. The concentrations of NaSa in mol kg^{-1} are 0.0048 (A), 0.0101 (B), 0.0150 (C), 0.0349 (D), 0.0650 (E), 0.0970 (F), 0.2000 (G), 0.3000 (H) and 0.3880 (I).

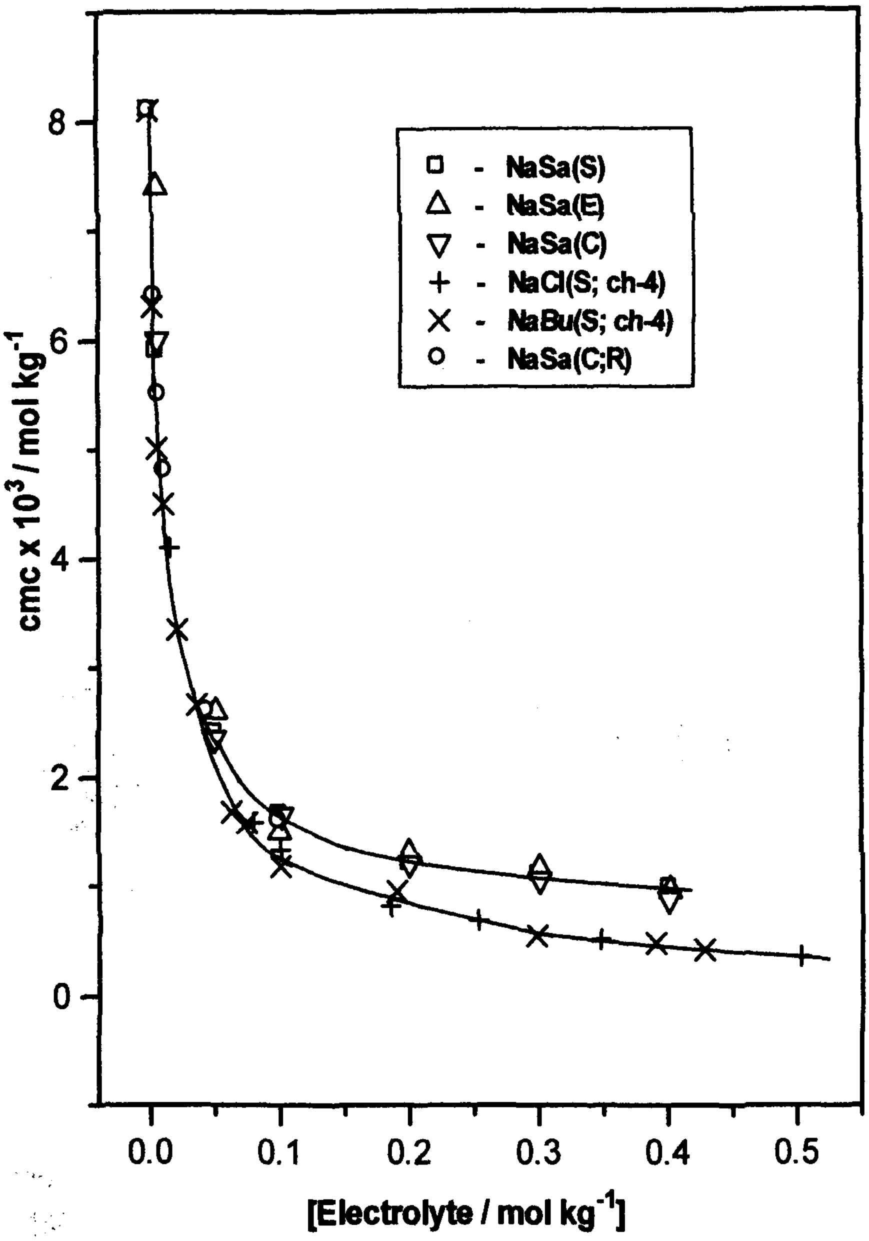

Figure 5.6 - Variation of cmc of SDS with NaSa concentration. S, C, E and R letters given in the parentheses indicate that cmc is from surface tension, conductance, emf and reported data, respectively. Reported cmc values are from reference 13. Cmc values of SDS in NaCl and NaBu solutions are taken from chapter 4.

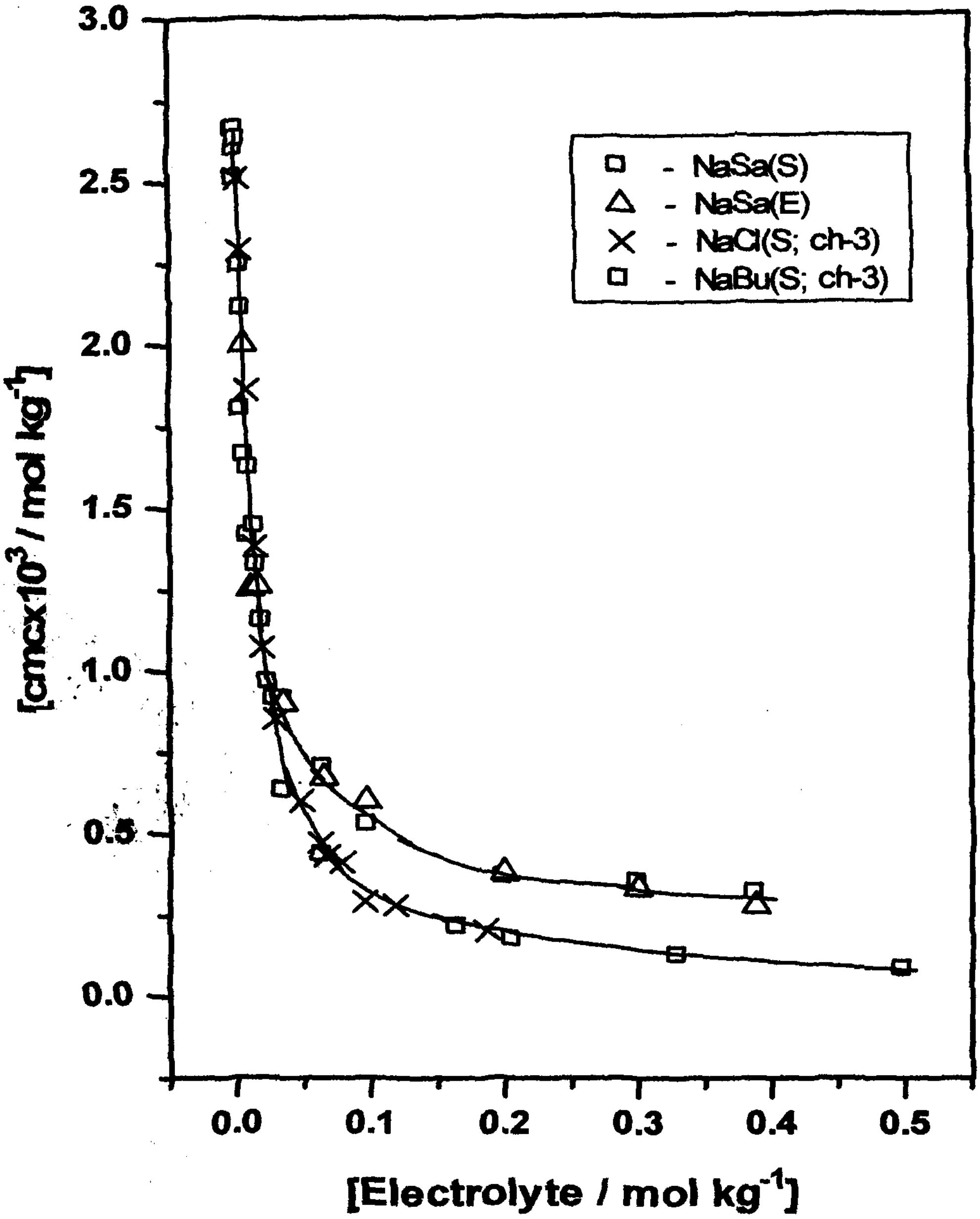

Figure 5.7 – Variation of cmc of AOT with NaSa concentration. S and E letters given in the parentheses indicate that cmc is from surface tension and emf, respectively. Cmc values of AOT in NaCl and NaBu solutions are taken from chapter 3.

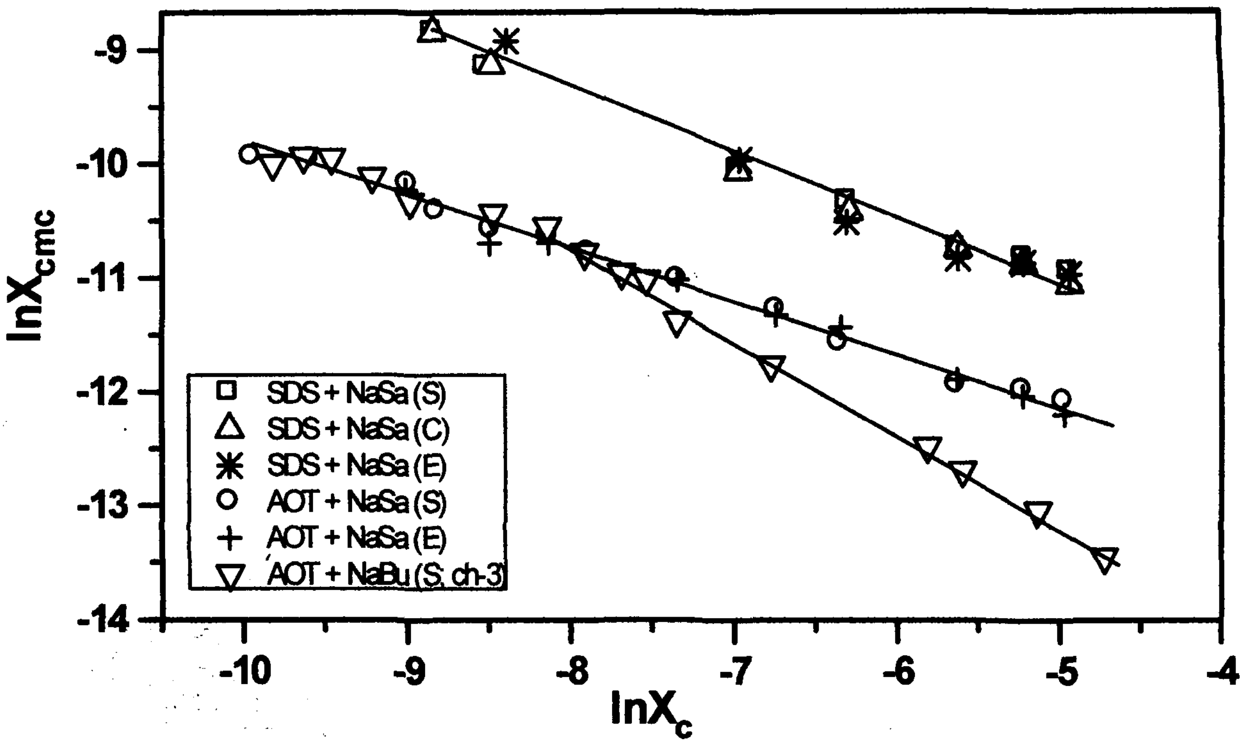

Figure 5.8 – Variation of ln X_{cmc} with ln X_c of AOT as well as SDS in NaSa solution. , C and E letters given in the parentheses indicate that cmc is from surface tension, conductance and emf data, respectively. Data for AOT in NaBu solution taken from chapter 3.

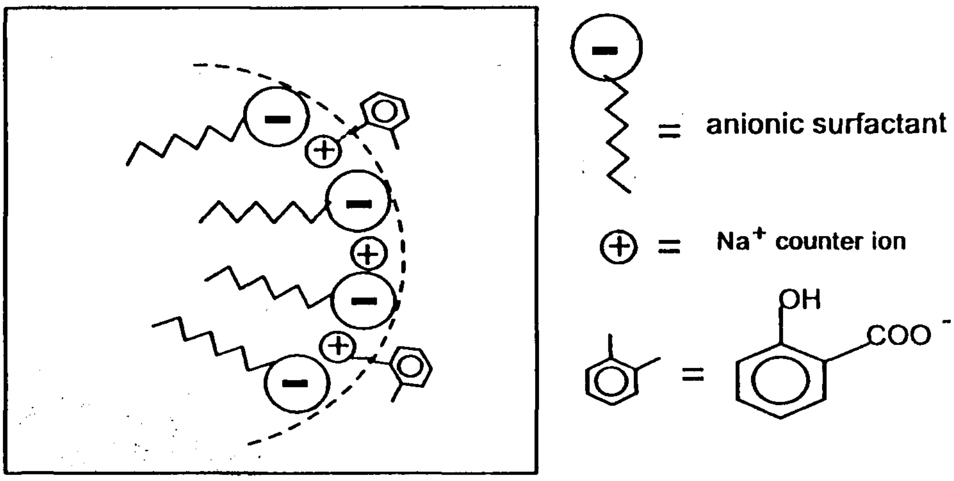

Figure 5.9 – Schematic representation of binding of salicylate ion to anionic micelle through ion – pair formation with counter ion

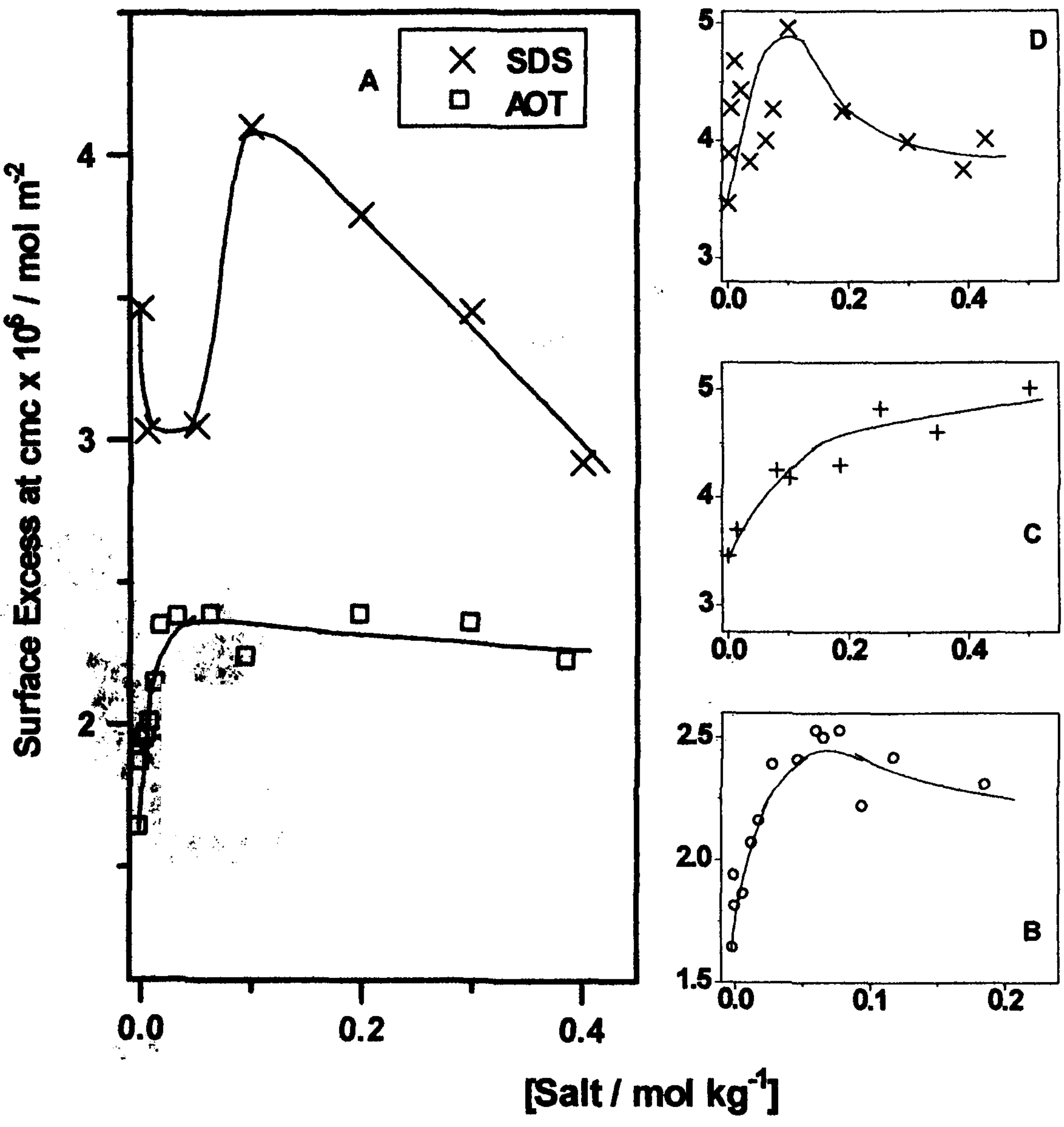

Figure 5.10 – Variation of surface excess at cmc of SDS and AOT with NaSa concentration (A). Variations of surface excess at cmc of AOT (data from chapter 3) with NaCl concentration (B) and of SDS (data from chapter 4) with NaCl (C) and NaBu (D) concentrations are also shown.

CHAPTER 6

Micellization Behaviour of Dioctyl Sulfosuccinate and Sodium Dodecyl Sulfate in the Presence of Sodium Citrate

6.1 Introduction

In the previous chapters (chapters 3, 4 and 5) we have studied the micellization behaviours of AOT and SDS in aqueous medium in the presence of five electrolytes having same counter ion (Na^+) but different co-ions, viz., chloride, acetate, propionate, butyrate and salicylate. In continuation of our investigation on the micellization and adsorption behaviours of anionic surfactants in the presence of added salts containing different co-ions, in this chapter we have evaluated the various micellization parameters of AOT and SDS in aqueous sodium citrate solution by using surface tension, EMF, conductance and fluorescence emission methods. The purpose of undertaking this study is to find out how an unsymmetrical electrolyte influences the micellization and adsorption characteristics of anionic surfactants in comparison to 1:1 electrolytes that were chosen for study in the previous chapters. Sodium citrate, which is a 3:1 electrolyte, has therefore been chosen. The other reasons to choose sodium citrate are (i) it is used as an anticoagulant in haemodialysis[1] and (ii) citrate buffer is a commonly used buffer medium for various physicochemical, biochemical and pathological studies. It is therefore thought to be worthwhile to investigate the aggregation and adsorption behaviours of surfactants in aqueous sodium citrate medium.

6.2 Experimental Section

Details of surface tension, conductance, EMF and fluorescence emission methods used for determining the micellization parameters are given in the previous chapters. AOT (Sigma, 99%), SDS (Aldrich, 99+ %) and trisodium citrate (NaCit; Qualigens, 99 % assay, Excelar grade) were used without further purification.

6.3 Results and Discussion

Experimental values of surface tension of SDS at 20, 25 and 30 °C in aqueous NaCit solutions of varying concentrations are presented in Tables 6.1-6.3 and those of AOT are given in Tables 6.4 – 6.6. Plots of surface tension of SDS and AOT versus log*c* (*c* denotes surfactant concentration) are shown in Figs. 6.1 - 6.6. From Figs. 6.1 – 6.3 it is apparent that the SDS sample used in this study exhibits surface tension minimum in the presence of NaCit. The difficulty in purifying SDS so as to eliminate the surface tension minimum has been discussed in chapter 4. The cmc is taken to be the surfactant concentration corresponding to the minimum. The measured electrical conductance values of SDS in NaCit solutions at 20, 25 and 30 °C are given in Tables 6.7 – 6.9. The EMF values of SDS and AOT in NaCit solutions at 25 °C are listed in Tables 6.10 and 6.11, respectively. Plots showing the variations of conductance of SDS with *c* are illustrated in Figs. 6.7 – 6.9. In Figs. 6.10 and 6.11 plots of EMF versus log*c* are shown for solutions of SDS and AOT, respectively. The values of cmc of SDS and AOT in the presence of NaCit determined from the different methods are listed in Tables 6.12 - 6.14.

In Figs. 6.12 and 6.13 we have shown the variation of cmc of SDS and AOT with Na^+ ion concentration. The present values of cmc of SDS and AOT in NaCit solutions become comparable with their corresponding cmc values in NaCl, NaAc, NaPr and NaBu solutions if the NaCit concentrations are increased by 3 times to account for the added Na^+ concentration. This clearly shows that the cmc values of SDS and AOT in NaCit solution are not influenced by the citrate co-ion. The change in the values of cmc of both SDS and AOT caused by the addition of NaCit is hence attributable fully to counter ion effect.

The cmc values of SDS in NaCit solutions determined from the surface tension, conductance and emf data were least – squares fitted to the Corrin-Harkins (CH) relation

$$\ln X_{cmc} = A - \beta \ln X_c \quad (6.1)$$

The computed values of A and the counter ion binding constant, β, at 20, 25 and 30 °C are given in Table 6.15. The CH plots of SDS in NaCit solution are shown in Fig. 6.14. The values of β of SDS in NaCit solution are found to be [illegible]Cl, NaAc, NaPr, NaBu and NaSa solutions (cf. chapters 4 and 5). By least – squares fitting the cmc data obtained only from surface tension data to Eq. (6.1) also provided higher value of β for SDS in NaCit solution than that in the other five electrolytes. The triply charged citrate co-ion therefore appears to push more counter ions to the micellar surface relative to singly charged co-ions. To confirm this observation more studies on similar systems is, however, required.

The CH plots for AOT in NaCit solution are shown in Fig. 6.15 and the least-squares fitted values of A and β are listed in Table 6.15. It is interesting to note that the counter ion binding feature of AOT in NaCit solution is similar to that in NaCl, NaAc, NaPr, and NaBu solutions (cf. chapter 3). The value of β for AOT below 0.02 mol kg^{-1} of Na^+ concentration (≈ 0.007 mol kg^{-1} of NaCit) is in the range of 0.3 to 0.4 and above this concentration limit the value of β increases by more than two times (Table 6.15). The transition from lower to higher value of β of AOT is controlled by the sodium ion concentration in the solution and the chloride, acetate, propionate, butyrate (cf. chapter 3) and citrate co-ions do not show any significant influence on this phenomenon. However, salicylate ion suppresses this phenomenon, which has been discussed in chapter 5.

The values of β of SDS and AOT at 25 °C in the presence of NaCit were also computed by least - squares fitting the EMF (E) data to equations[2]

$$E = A_1 + B_1 \log c_{Na} \qquad \text{at } c < c_0 \qquad (6.2)$$

$$E = A_1 + B_1 \log[(1-\beta)c_{Na} + \beta c_0] \qquad \text{at } c > c_0 \qquad (6.3)$$

where the terms c_0 and c_{Na} represent the cmc and concentration of sodium ion, respectively, A_1 and B_1 are empirical constants. In the absence of electrolyte, c_{Na} is equal to the concentration of surfactant and in the presence of electrolytes $c_{Na} = c + 3c_e$, where c_e refers to the concentration of NaCit. The method of calculating β from EMF data using equations (6.2) and (6.3) are described in the previous chapters and the values of β thus obtained are listed in Tables 6.13 and 6.14. The average of the concentration dependent values of β of SDS at 25 °C estimated from the EMF data is found to be 0.83 and is in agreement with the value 0.84 (Table 6.15) obtained from the CH plot. In the case of AOT the values of β calculated from the EMF data (Table 6.14) using the above equations (6.2) and (6.3) also reveal that in the Na^+ ion concentration range lying below 0.02 mol kg^{-1} β has low value equal to 0.44 (average value) and above this concentration limit it has a higher value equal to 0.78 (average value). This trend in the value of β of AOT in NaCit solution is similar to that observed from the EMF data of AOT in NaCl, NaAc, NaPr and NaBu solutions. Therefore, in NaCit solution also some structural change of AOT micelles is expected to take place when the added Na^+ ion concentration exceeds 0.02 mol kg^{-1}.

To calculate the surface excess, Γ_{cmc}, of SDS and AOT in NaCit solution the equation used in the case of 1:1 electrolyte media (equations (3.1) or (4.1) or (5.4)) needs modification. As shown in chapter 1, a general expression for Γ_{cmc} is of the form[3]

$$\Gamma_{cmc} = -\left[\frac{1}{RT}\right]\left[\frac{1}{n_- + \dfrac{n_+^2 c_0}{(n_+ c_0 + n_{+e} c_e)}}\right]\left[\frac{d\gamma}{d\ln c}\right]_{at\ cmc} \tag{6.4}$$

In equation (6.4), n_- and n_+ are the number of moles of anionic surfactant monomer and counter ions produced by the dissociation of one mole of the surfactant, respectively. For SDS and AOT, $n_- = 1$ and $n_+ = 1$. n_{+e} is the number of moles of positive ions produced by the dissociation of one mole of the added electrolyte. In the present case of NaCit, $n_{+e} = 3$. The other terms of equation (6.4) have the same meanings defined in the previous chapters. Therefore, for SDS + NaCit and AOT + NaCit systems equation (6.4) takes the form

$$\Gamma_{cmc} = -\left[\frac{1}{RT}\right]\left[\frac{1}{1+\frac{c_0}{(c_0+3c_e)}}\right]\left[\frac{d\gamma}{d\ln c}\right]_{at\ cmc} \qquad (6.5)$$

The values of Γ_{cmc} calculated from equation (6.5) are given in Table 6.16 and are plotted in Figs. 6.16 and 6.17 as a function of salt concentration for SDS and AOT, respectively. The values of Γ_{cmc} of SDS and AOT increase initially by the addition of NaCit similar to the behaviour observed by the addition of NaCl or NaAc or NaPr or NaBu (cf. chapters 4 and 5). In the presence of NaCit, Γ_{cmc} of SDS reaches a maximum value after the initial increase and starts decreasing beyond a particular concentration of NaCit (Fig. 6.16), which is similar to the trend observed for SDS in NaBu solution (cf. chapter 4). The added Na^+ ion concentration at which Γ_{cmc} attains maximum value lies in the region of 0.2 – 0.3 mol kg^{-1} (~ 0.06 – 0.1 mol kg^{-1} of NaCit). Surface excess of AOT in NaCit solution also attains a maximum value, but appears to remain almost constant at this maximum value without showing a decreasing trend. This type of surface activity behaviour of AOT in NaCit solution is almost similar to that of AOT in NaCl, NaAc and NaPr solutions (cf. chapter 3). Thus, similar to the inference made in the previous chapters, it appears that co-ion exhibits some influence on the surface activity behaviour of SDS and AOT at higher concentration range of the added electrolyte. As pointed out in chapter 3, salting – out effect of electrolytes is one of the reasons for their influence on the surface excess of surfactants.[2] Salting – out effect of an electrolyte is controlled by the hydration of its ionic species and therefore it is visualized that co-ions because of their hydration can exhibit influence on surface activity of surfactants. AOT, in the absence and presence of added salts, always has lower values of surface excess than SDS, which is because of its double-chained structure. In Table 6.16 we have also included the values of the area, A_0, covered per molecule of AOT or SDS at the air – solution interface in the presence of NaCit, which were evaluated by using the relation $A_0 = (N_A \Gamma_{cmc})^{-1}$.

Having evaluated the values of β and Γ_{cmc}, we then estimated for SDS and AOT in the presence of NaCit the values of the standard free energy of micellization per mole of monomer (ΔG^0_m) and the standard free energy of adsorption at the air – solution interface (ΔG^0_{ad}) by using the relations,[4-6]

$$\Delta G^0_m = (1+\beta)RT\ln X_{cmc} \quad (6.6)$$

$$\Delta G^0_{ad} = \Delta G^0_m - \frac{\pi_{cmc}}{\Gamma_{cmc}} \quad (6.7)$$

The different terms of equations (6.6) and (6.7) have the same meanings defined in chapters 4 and 5. In equation (6.6) for evaluating ΔG^0_m we used the values of β obtained from the CH plots (Table 6.15). The calculated values of ΔG^0_m and ΔG^0_{ad} are given in Table 6.17 for SDS and in Table 6.18 for AOT. The variation of ΔG^0_m with the concentration of added sodium ion at 25 °C is shown in Fig. 6.18. The values of ΔG^0_m for SDS in NaCit are lower than in other electrolytes, which is obviously due to relatively higher values of β for SDS in NaCit. Thus, Fig. 6.18 reveals that the added co-ion has an effect on ΔG^0_m of

SDS. On the other hand, the values of ΔG_m^0 for AOT in NaCit are similar to that in NaCl (Fig. 6.18) below as well as above 0.02 mol kg^{-1} of sodium ion concentration. A sudden jump in the value of ΔG_m^0 for AOT around 0.02 mol kg^{-1} of sodium ion concentration can be seen clearly from Fig. 6.18 which is due to the shift occurring in the value of β at this concentration of added sodium ion. In the presence of NaSa there is no sudden shift in the value of β for AOT (cf. chapter 5) and hence the value of ΔG_m^0 for AOT continuously decreases as the concentration of NaSa increases (Fig. 6.18). Therefore, in the case of AOT the effect of co-ion other than salicylate on ΔG_m^0 is negligible.

regular dependence of cmc and other derived micellization parameters on temperature in the range from 293 to 303 K has been found.

As described in chapters 3 and 4, the aggregation numbers, N_0, of SDS and AOT in the presence of NaCit at 25 °C were determined from the fluorescence quenching method by using the expressions[7]

$$\frac{I_0}{I_q} = \exp\left(\frac{[q]}{[micelle]}\right) \tag{6.8}$$

$$N_0 = \frac{(c - c_0)}{[micelle]} \tag{6.9}$$

where I_0 and I_q are the intensities of fluorescence emission of pyrene at 374 nm in the absence and presence of the quencher of concentration $[q]$, respectively. A few characteristic fluorescence emission spectra of pyrene in aqueous solutions containing surfactant and NaCit are shown in Fig. 6.19. The values of I_0/I_q for pyrene as a function of [q] in aqueous SDS and AOT solutions containing NaCit are listed in Tables 6.19 and 6.20, respectively and the corresponding plots of $\ln(I_0/I_q)$ versus [q] are shown in Figs. 6.20 and 6.21. Values of N_0 of SDS in the presence of different concentrations of NaCit are calculated by least-squares fitting the I_0/I_q data at different concentrations of CPC to equation (6.8). The values of N_0 obtained thus are given in Table 6.19 and the variation of N_0 with the concentration of added sodium ion is illustrated in Fig. 6.20. For comparison sake we have also indicated in Fig. 6.20 the N_0 values of SDS in NaCl, NaAc, NaPr and NaBu solutions (cf. chapter 4). In NaCit solution the aggregation number of SDS initially increases continuously with increase in sodium ion concentration and appears to attain a constant value equal to 100 ± 5 when the NaCit concentration exceeds 0.2 mol kg^{-1}. For ionic surfactants increase in aggregation number with increase in concentration of either surfactant or electrolyte is known to be a general trend.[8-14] From the emission spectra of pyrene in solutions of SDS in the presence of NaCit, the ratio of the intensity of the third peak at 384 nm to that of the first peak at 374 nm, I_3/I_1, was calculated and its values as a function of NaCit concentration are given in Table 6.19. The value of the term I_3/I_1, which is also known as polarity index, reflects on the polarity of the medium around the pyrene molecule.[15,16] The values of I_3/I_1 of pyrene in aqueous NaCit solutions containing SDS micelles (Table 6.19) are in agreement with the value 0.88 reported[15] for pyrene in aqueous solution of SDS micelles without any added electrolyte. For AOT, the values of N_0 as a function of NaCit concentration calculated by using equation (6.7) are given in Table 6.20. Aggregation numbers of AOT are relatively lower than that of SDS and this is due to the two hydrocarbon tails present in an AOT molecule, which cause more geometric strains during aggregation. The values of I_3/I_1 of pyrene in solutions of AOT containing NaCit are given in Table 6.20. In the case of AOT as can be seen from Fig. 6.22, N_0 and I_3/I_1 have interesting dependences on NaCit concentration. The sudden change in N_0 of AOT between 0.007 and 0.008 mol kg^{-1} of NaCit is similar to the change observed in the value of β of AOT. In the concentration range of NaCit where β and N_0 have lower values, I_3/I_1 has values greater than one and hence in this region intensity of the third peak (at 384 nm) of pyrene is more than that of the first peak (at 374 nm). In aqueous AOT solution in the absence of any added electrolyte I_3/I_1 is, however, equal to less than one (= 0.93; cf. chapter 3). I_3/I_1>1 has been reported[15] in hydrocarbon solvents, 1-pentanol and isopropanol. The value of I_3/I_1 becomes less than one in the NaCit concentration range (> 0.007 mol kg^{-1}) where β and N_0 have higher values. The sudden change in the value of I_3/I_1 from >1 to <1 indicates that the polarity of the medium experienced by pyrene in the two concentration regions of NaCit are different. In fact, due to the sudden increase in the number of counter ions bound to AOT micelles a change in the dielectric constant of the micelle – solution interface can be expected to take place at ~ 0.007 mol kg^{-1} of NaCit. The sudden increase in N_0 of AOT around 0.007 mol kg^{-1} of NaCit may also be due to the increase in the value of β since presence of more counter ions decreases the repulsion between the head groups thereby facilitating the assembly of more monomers. However, at the moment it is not known exactly what is the driving force for the sudden enhancement in the value of β of AOT when the contribution of sodium ions from the added electrolytes like NaCl, NaAc, NaPr, NaBu (cf. chapter 3) and NaCit exceeds 0.02 mol kg^{-1}.

6.4 Conclusion

Critical micelle concentrations of SDS and AOT were determined in aqueous medium as a function of NaCit concentration by surface tension and EMF methods. In the case of SDS conductance method was also used. Surface tension and conductance measurements were made at 20, 25 and 30 °C, whereas EMF measurement was made at 25 °C. The cmc values of SDS and AOT in NaCit solution are in agreement with the corresponding cmc values in NaCl, NaAc, NaPr and NaBu solutions. Cmc of SDS and AOT in NaCit solution is completely controlled by the Na^+ ion concentration and the citrate co- ion does not have any effect on the cmc. The values of counter-ion binding constant of SDS and AOT were determined from the CH plots and the EMF data. The counter ion binding constant of SDS in NaCit solution is relatively higher than that in other electrolytes. The triply charged citrate co-ion therefore appears to push more counter ions to the micellar surface of SDS compared to singly charged co-ions. Binding behaviour of sodium counter ion to the AOT micelles in NaCit solution is similar to that in NaCl, NaAc, NaPr and NaBu solutions. AOT has two different values of β below and above 0.007 mol kg^{-1} of NaCit. Citrate co-ion has been found to produce slight changes in the surface activity behaviour of SDS and AOT. Standard free energies of micellization and adsorption of SDS and AOT in the presence of

NaCit were also evaluated. In NaCit solution, the value of standard free energy of micellization of SDS is lower than the values in other electrolytes and that of AOT is found to be comparable to the values in NaCl, NaAc, NaPr and NaBu. Aggregation number of SDS and AOT increases with the addition of NaCit. In the case of AOT, corresponding to the concentration of NaCit where a sudden increase in counter ion binding constant occurs it has been observed that the aggregation number increases and polarity index decreases abruptly. The basic reason for the sudden increase in the value of the counter ion binding constant of AOT when the concentration of the added sodium ion exceeds 0.02 mol kg^{-1} is not known at the moment.

6.5 References

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Table 6.1 - Surface Tension (γ) Values of SDS in Aqueous Sodium Citrate Solution at 20 °C

[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaCit] = 0.0052 mol kg^{-1}			
0.0550	66.6	2.0013	42.6	4.4379	35.4
0.1644	62.2	2.1911	41.0	4.7508	36.4
0.2729	58.5	2.3783	40.0	5.0918	36.9
0.3806	56.8	2.5630	39.3	5.3534	37.3
0.5937	53.0	2.7451	38.6	5.6437	37.4
0.8036	51.1	2.9247	38.0	5.9269	37.3
1.0105	49.0	3.1019	37.3	6.2035	37.3
1.2144	47.9	3.2767	36.4	6.4737	37.4
1.4154	45.9	3.4493	35.7	6.7375	37.8
1.6134	44.4	3.7875	34.9	6.9952	37.3
1.8087	43.2	4.1473	34.6	7.2470	37.3
		[NaCit] = 0.0150 mol kg^{-1}			
0.0411	66.0	0.8376	45.1	2.1550	34.7
0.0822	62.7	0.9529	43.6	2.4293	34.8
0.1230	60.7	1.0671	42.2	2.6974	35.7
0.2044	57.3	1.1803	41.1	3.0884	36.0
0.2853	54.5	1.2925	40.1	3.4665	36.4
0.3657	52.9	1.4406	39.0	3.8325	36.3
0.4455	51.0	1.5868	38.2	4.1867	36.3
0.5249	49.4	1.7314	37.2	4.5299	36.4
0.6038	48.2	1.8742	36.2	4.8625	36.3
0.6822	47.2	2.0154	35.4	5.1850	36.4
0.7601	46.1				
		[NaCit] = 0.0314 mol kg^{-1}			
0.0325	63.4	0.8725	39.7	2.7103	35.0
0.0649	60.2	0.9911	38.4	2.9040	35.0
0.0972	58.0	1.2240	35.9	3.0935	34.9
0.1615	54.5	1.4514	34.2	3.2790	35.0
0.2253	52.0	1.6735	34.3	3.5499	35.1
0.2888	49.8	1.8904	34.4	3.8124	35.0
0.3833	47.4	2.1024	34.6	4.1499	35.3

Table 6.1 - Continued

[SDS] x10³ / mol kg⁻¹	γ / mN m⁻¹	[SDS] x10³ / mol kg⁻¹	γ / mN m⁻¹	[SDS] x10³ / mol kg⁻¹	γ / mN m⁻¹
		[NaCit] = 0.0314 mol kg⁻¹			
0.5079	45.0	2.3096	35.0	4.4740	35.0
0.7524	41.0	2.5122	34.9		
		[NaCit] = 0.0568 mol kg⁻¹			
0.0099	66.6	0.4582	41.1	1.1914	34.1
0.0263	62.3	0.5184	39.8	1.2953	34.1
0.0492	59.0	0.5780	38.6	1.3970	33.9
0.0818	56.1	0.6369	37.4	1.4967	34.1
0.1142	53.3	0.6951	36.6	1.5943	34.2
0.1464	50.9	0.7527	35.6	1.6900	34.2
0.2102	48.1	0.8660	34.2	1.7837	34.1
0.2733	46.0	0.9768	33.6	1.8756	34.0
0.3356	44.1	1.0853	34.0	1.9657	34.2
0.3973	42.4				
		[NaCit] = 0.0855 mol kg⁻¹			
0.0214	61.2	0.3569	38.8	0.8244	33.3
0.0427	57.3	0.3954	37.1	0.8741	33.5
0.0744	53.2	0.4522	35.9	0.9230	33.6
0.1162	49.9	0.5081	34.7	0.9712	33.4
0.1576	46.8	0.5631	33.9	1.0186	33.5
0.1984	44.8	0.6171	33.1	1.0652	33.5
0.2387	43.1	0.6702	33.0	1.1111	33.6
0.2786	41.8	0.7225	32.9	1.1563	33.5
0.3180	40.6	0.7739	33.0	1.2008	33.4
		[NaCit] = 0.1016 mol kg⁻¹			
0.0123	64.4	0.2742	40.9	0.7683	33.2
0.0369	57.9	0.3200	39.3	0.8280	33.1
0.0613	54.2	0.3651	37.8	0.8866	33.2
0.0856	51.7	0.4097	36.8	0.9443	33.3
0.1097	49.7	0.4538	35.8	1.0010	33.2
0.1336	48.0	0.5190	34.4	1.0568	33.1
0.1574	46.4	0.5829	33.2	1.1116	33.0
0.1811	45.0	0.6458	33.1	1.1656	33.1

Table 6.1 - Continued

[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaCit] = 0.1982 mol kg^{-1}			
0.0087	60.0	0.2727	32.8	0.7838	31.5
0.0260	53.7	0.3040	32.3	0.8345	31.9
0.0431	49.4	0.3349	31.8	0.8841	31.6
0.0602	46.7	0.3956	31.1	0.9328	31.5
0.0771	44.9	0.4548	31.2	0.9804	31.5
0.0940	43.0	0.5128	31.3	1.0270	31.8
0.1439	38.8	0.5694	31.2	1.0728	31.7
0.1767	37.0	0.6248	31.2	1.1175	31.7
0.2091	35.4	0.6789	31.5	1.2045	31.5
0.2411	34.1	0.7319	31.4		
		[NaCit] = 0.3033 mol kg^{-1}			
0.0060	54.7	0.0742	37.8	0.2230	30.0
0.0119	52.7	0.1011	36.2	0.2452	29.7
0.0177	50.1	0.1271	34.1	0.2667	29.8
0.0236	47.6	0.1522	31.9	0.2876	29.6
0.0351	44.3	0.1765	31.2	0.3275	29.6
0.0521	42.0	0.2001	30.3		
		[NaCit] = 0.4116 mol kg^{-1}			
0.0014	62.6	0.0522	37.7	0.1419	30.4
0.0038	57.8	0.0598	36.5	0.1659	30.3
0.0061	54.8	0.0674	35.4	0.1847	30.4
0.0089	52.1	0.0747	34.6	0.2025	30.4
0.0146	48.9	0.0820	33.9	0.2195	30.3
0.0201	46.0	0.0891	33.3	0.2357	30.5
0.0284	43.2	0.1030	32.5	0.2511	30.7
0.0365	41.1	0.1164	31.7	0.2659	30.4
0.0444	39.0	0.1294	31.0		

Table 6.2- Surface Tension (γ) Values of SDS in Aqueous Sodium Citrate Solution at 25 °C

[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaCit] = 0.0052 mol kg^{-1}			
0.1037	64.1	4.0358	34.0	7.3271	36.9
0.3089	58.7	4.5654	35.8	7.7282	36.9
0.6114	53.0	5.0732	36.4	8.1150	37.0
1.1016	47.8	5.5603	37.6	8.4879	37.0
1.6682	43.6	6.0284	37.1	8.8479	37.1
2.3009	39.2	6.4780	37.3	9.1956	36.9
2.9052	36.8	6.9107	37.0	9.5317	37.0
3.4830	34.5				
		[NaCit] = 0.0150 mol kg^{-1}			
0.0411	65.6	0.9131	44.9	2.0856	35.3
0.1228	60.3	1.0275	43.8	2.2206	34.8
0.2848	57.2	1.1408	42.7	2.3577	34.7
0.3650	54.8	1.2532	41.5	2.4930	34.6
0.4448	52.4	1.3646	40.3	2.7592	35.7
0.5240	51.0	1.5115	39.1	2.9550	36.0
0.6028	49.6	1.6566	38.1	3.1475	35.9
0.6811	48.4	1.8002	37.0	3.3369	36.0
0.7589	47.2	1.9420	35.9	3.5231	36.0
0.8362	46.0				
		[NaCit] = 0.0314 mol kg^{-1}			
0.0130	69.0	0.8126	39.5	2.4620	34.8
0.0455	63.7	0.9320	37.9	2.6611	34.7
0.0778	60.7	1.0498	36.5	2.8559	34.9
0.1294	57.7	1.1663	35.5	3.0465	34.9
0.1935	54.7	1.3951	34.1	3.2330	34.8
0.3204	50.0	1.6185	34.3	3.4155	35.0
0.4458	45.6	1.8367	34.5	3.5943	34.8
0.5696	43.3	2.0499	34.7	3.7692	34.7
0.6919	41.2	2.2582	35.0	3.9406	34.8

Table 6.2 - Continued

[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaCit] = 0.0568 mol kg^{-1}			
0.0172	62.8	0.3818	42.1	1.0995	33.2
0.0513	56.9	0.4455	40.5	1.2099	33.7
0.0853	53.9	0.5085	39.0	1.3178	33.5
0.1191	51.6	0.5707	37.7	1.4234	33.8
0.1526	49.4	0.6323	36.5	1.5268	33.9
0.1859	48.2	0.6930	35.6	1.6279	33.9
0.2191	47.2	0.7531	34.8	1.7270	34.0
0.2520	45.9	0.8712	33.6	1.8240	33.9
0.2848	44.7	0.9867	33.0	1.9189	34.1
0.3335	43.3				
		[NaCit] = 0.0855 mol kg^{-1}			
0.0227	62.6	0.4171	37.6	0.9185	33.0
0.0452	58.0	0.4769	36.1	1.0196	33.0
0.0676	53.7	0.5356	34.9	1.1175	32.9
0.0843	53.3	0.5932	34.1	1.2121	33.0
0.1666	47.0	0.6498	33.2	1.3038	33.1
0.2310	43.7	0.7054	32.9	1.3926	33.0
0.2942	41.5	0.8138	33.0	1.4786	33.1
0.3562	39.5				
		[NaCit] = 0.1016 mol kg^{-1}			
0.0125	64.3	0.2700	40.3	0.8693	32.9
0.0311	58.6	0.3163	38.7	0.9472	33.0
0.0533	55.0	0.3620	37.3	1.0233	33.2
0.0791	52.2	0.4071	36.0	1.0996	33.0
0.1035	49.9	0.4517	34.7	1.1706	33.1
0.1278	47.8	0.5175	33.3	1.2418	33.0
0.1638	45.7	0.6247	32.8	1.3115	32.8
0.1996	43.7	0.7081	32.8	1.3797	32.9
0.2350	42.0	0.7897	33.0	1.4465	32.8

Table 6.2 - Continued

[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaCit] = 0.1982 mol kg^{-1}			
0.0089	61.2	0.2433	33.4	0.6351	31.6
0.0230	54.6	0.2757	32.3	0.6903	31.5
0.0406	50.3	0.3076	31.5	0.7443	31.7
0.0581	47.4	0.3392	31.0	0.7971	31.6
0.0755	45.1	0.3704	30.9	0.8487	31.6
0.1013	42.6	0.4012	30.8	0.8992	31.6
0.1303	40.3	0.4467	31.2	0.9487	31.5
0.1523	38.3	0.4915	31.6	0.9971	31.7
0.1775	36.3	0.5355	31.5	1.0445	31.8
0.2106	34.8	0.5787	31.3		
		[NaCit] = 0.3033 mol kg^{-1}			
0.0065	56.5	0.1431	31.5	0.4354	30.8
0.0129	52.5	0.1646	30.3	0.4704	31.0
0.0193	49.0	0.2060	29.4	0.5034	30.9
0.0320	44.7	0.2451	30.4	0.5348	31.0
0.0505	40.9	0.2822	30.4	0.5645	30.8
0.0747	37.8	0.3175	30.5	0.5927	30.9
0.0982	35.2	0.3592	30.6	0.6195	31.0
0.1210	33.1	0.3984	30.7	0.6451	30.9
		[NaCit] = 0.4116 mol kg^{-1}			
0.0028	54.3	0.0979	31.3	0.2029	29.6
0.0056	51.9	0.1111	30.4	0.2129	29.8
0.0111	48.1	0.1239	30.0	0.2226	30.0
0.0166	45.8	0.1363	29.7	0.2321	29.7
0.0247	42.5	0.1483	29.5	0.2413	29.9
0.0352	39.5	0.1599	29.3	0.2502	30.0
0.0455	37.8	0.1711	29.1	0.2589	29.6
0.0555	36.7	0.1820	29.4	0.2674	29.8
0.0701	34.4	0.1926	29.6	0.2756	29.6
0.0843	32.4				

Table 6.3 - Surface Tension (γ) Values of SDS in Aqueous Sodium Citrate Solution at 30 °C

[SDS] x10³ / mol kg⁻¹	γ / mN m⁻¹	[SDS] x10³ / mol kg⁻¹	γ / mN m⁻¹	[SDS] x10³ / mol kg⁻¹	γ / mN m⁻¹
		[NaCit] = 0.0052 mol kg⁻¹			
0.1117	64.5	1.6897	44.3	6.0438	37.2
0.2225	61.0	2.0819	41.7	6.4591	37.2
0.3324	58.0	2.3689	40.4	6.8596	37.2
0.4416	56.7	2.6498	39.0	7.2464	37.2
0.5499	55.0	3.1943	36.7	7.6199	37.4
0.6574	53.5	3.7170	35.2	7.9811	37.2
0.8700	51.2	4.7018	36.4	8.3303	37.3
1.0795	48.9	5.1661	37.0	8.6680	37.1
1.2858	47.3	5.6131	37.1	8.9952	37.1
1.4892	45.8				
		[NaCit] = 0.0150 mol kg⁻¹			
0.0408	64.6	1.0957	42.0	3.4093	35.9
0.0814	61.9	1.2447	40.7	3.5930	35.8
0.1422	58.6	1.4650	39.0	3.7738	35.8
0.2826	56.4	1.6815	37.5	3.9518	36.0
0.3227	52.9	1.8941	36.4	4.1269	35.8
0.4811	49.9	2.1031	35.3	4.2992	35.6
0.6376	47.4	2.5104	35.3	4.4689	35.9
0.7921	45.3	2.8395	35.4	4.6360	35.7
0.9448	43.4	3.2225	35.8	4.8005	35.8
		[NaCit] = 0.0314 mol kg⁻¹			
0.0321	59.4	0.4398	44.3	1.3771	33.7
0.0640	56.6	0.5010	43.1	1.5979	33.5
0.0959	54.7	0.5923	42.5	1.8136	34.2
0.1276	53.1	0.6827	40.3	2.0245	34.6
0.1593	51.7	0.8019	38.9	2.2813	34.6
0.1908	50.5	0.9197	37.6	2.4321	34.6
0.2223	49.3	1.0361	36.6	2.5803	34.6
0.2536	48.3	1.1511	35.6	2.7742	34.6
0.3161	46.8	1.2648	34.6	2.9639	34.8
0.3781	45.6				

Table 6.3 - Continued

[SDS] x10[3] / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10[3] / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10[3] / mol kg^{-1}	γ / mN m^{-1}
		[NaCit] = 0.0568 mol kg^{-1}			
0.0343	60.2	0.4928	39.3	1.3577	33.8
0.0683	56.1	0.5553	38.2	1.4624	34.0
0.1022	53.1	0.6169	37.0	1.5650	34.0
0.1359	51.2	0.6779	35.8	1.6653	33.9
0.1693	49.2	0.7977	34.5	1.7636	34.0
0.2025	47.8	0.9148	32.9	1.8598	34.1
0.2356	46.6	1.0293	33.1	1.9541	33.9
0.3011	44.3	1.1412	33.2	2.0464	34.0
0.3658	42.3	1.2506	33.4	2.1369	33.8
0.4297	40.5				
		[NaCit] = 0.0855 mol kg^{-1}			
0.0192	60.3	0.3120	40.3	0.9030	32.7
0.0382	56.8	0.3642	38.8	1.0173	33.3
0.0572	54.6	0.4155	37.4	1.0728	33.2
0.0760	52.5	0.4828	35.8	1.1273	33.2
0.0948	50.8	0.5487	34.2	1.1808	33.2
0.1134	49.3	0.6133	33.4	1.2333	33.1
0.1412	47.6	0.6765	32.7	1.2849	33.1
0.1687	46.1	0.7232	32.3	1.3355	33.2
0.2051	44.1	0.7843	32.4	1.3853	33.1
0.2411	42.5	0.8442	32.6	1.4342	33.1
0.2767	41.4				
		[NaCit] = 0.1016 mol kg^{-1}			
0.0121	60.5	0.2854	38.6	0.6903	32.1
0.0290	56.6	0.3191	37.5	0.7502	32.3
0.0531	52.6	0.3524	36.6	0.8671	32.9
0.0770	50.1	0.3854	35.4	0.9241	33.2
0.1007	47.9	0.4182	34.4	0.9802	33.0
0.1243	46.1	0.4614	33.5	1.0353	32.9
0.1477	44.7	0.5041	32.6	1.0896	33.2
0.1826	42.7	0.5463	32.1	1.1954	32.0

Table 6.3 - Continued

[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDS] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaCit] = 0.1016 mol kg^{-1}			
0.2172	41.0	0.5881	32.0	1.2980	32.9
0.2515	39.8	0.6293	31.9		
		[NaCit] = 0.1982 mol kg^{-1}			
0.0088	60.8	0.1803	36.2	0.5694	31.3
0.0219	54.8	0.2048	35.0	0.6115	31.3
0.0367	50.9	0.2292	33.8	0.6665	31.2
0.0540	47.6	0.2533	32.7	0.7204	31.4
0.0711	45.1	0.3009	31.0	0.7730	31.3
0.0882	43.3	0.3630	30.3	0.8245	31.3
0.1052	41.5	0.4237	30.8	0.9964	31.3
0.1304	39.4	0.4683	31.1	1.0891	31.6
0.1555	37.5	0.5266	31.3		
		[NaCit] = 0.3033 mol kg^{-1}			
0.0057	54.4	0.1309	32.0	0.3255	30.0
0.0169	47.8	0.1500	30.4	0.3545	30.2
0.0334	43.4	0.1686	29.3	0.3823	30.0
0.0496	40.0	0.1958	29.1	0.4090	29.5
0.0707	37.1	0.2305	29.7	0.4346	30.1
0.0913	35.1	0.2636	29.9	0.4592	30.0
0.1114	33.6	0.2952	30.0		
		[NaCit] = 0.4116 mol kg^{-1}			
0.0029	56.3	0.0689	33.8	0.1641	29.1
0.0057	52.7	0.0785	32.6	0.1755	29.0
0.0113	48.5	0.0880	31.6	0.1864	29.4
0.0196	44.7	0.0972	30.7	0.1971	29.1
0.0278	41.7	0.1062	30.4	0.2074	29.0
0.0384	39.0	0.1151	30.0	0.2175	29.3
0.0488	37.1	0.1404	29.0	0.2272	29.2
0.0590	35.1	0.1524	29.3	0.2367	29.4

Table 6.4 - Surface Tension (γ) Values of AOT in Aqueous Sodium Citrate Solution at 20 °C

[AOT] x10³ / mol kg⁻¹	γ / mN m⁻¹	[AOT] x10³ / mol kg⁻¹	γ / mN m⁻¹	[AOT] x10³ / mol kg⁻¹	γ / mN m⁻¹
		[NaCit] = 0.0 mol kg⁻¹			
0	72.5	0.4653	47.1	3.0474	31.9
0.0149	66.4	0.5783	45.3	3.4707	31.2
0.0208	64.6	0.8008	43.1	3.8744	30.9
0.0356	63.8	1.0184	41.2	4.6280	30.2
0.0593	61.0	1.2839	39.1	5.3176	29.8
0.1006	57.9	1.4398	37.9	5.9509	29.4
0.1477	54.8	1.8929	35.7	6.8096	29.0
0.2120	52.6	2.2310	34.3	7.5747	28.6
0.3509	49.2	2.6029	33.0	8.2608	28.4
		[NaCit] = 0.0010 mol kg⁻¹			
0.0122	58.2	0.6281	37.9	1.8479	30.6
0.0365	53.0	0.7493	36.7	2.3563	29.6
0.0727	49.5	0.8664	35.7	2.7815	29.1
0.1204	46.6	1.0163	34.6	3.1424	29.0
0.1675	45.0	1.1597	33.6	3.4525	29.0
0.2140	43.7	1.3633	32.8	3.7220	28.9
0.3052	42.5	1.5544	32.0	3.9579	29.0
0.3722	41.4	1.7048	31.3	4.1666	28.7
0.5024	39.7				
		[NaCit] = 0.0069 mol kg⁻¹			
0.0139	50.6	0.3732	33.2	1.6104	26.3
0.0277	47.8	0.4744	32.1	1.7600	26.4
0.0552	43.7	0.5734	31.0	1.9040	26.3
0.1097	40.3	0.7650	29.1	2.0426	26.2
0.1637	38.0	0.9484	27.8	2.1762	26.2
0.2169	36.4	1.1242	26.7	2.3051	26.3
0.2696	35.2	1.2929	26.8	2.4294	26.2
0.3217	34.1	1.4548	26.5		

Table 6.4 - Continued

[AOT] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[AOT] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[AOT] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaCit] = 0.0116 mol kg^{-1}			
0.0017	61.5	0.1741	35.3	0.7338	27.6
0.0050	54.0	0.2180	34.1	0.8056	27.0
0.0104	50.3	0.2595	32.9	0.9235	26.6
0.0213	45.9	0.3178	31.6	1.0364	26.4
0.0373	43.5	0.3718	30.4	1.0824	26.0
0.0583	41.0	0.4380	29.6	1.1232	25.9
0.0787	39.5	0.4983	28.8	1.1596	26.0
0.0987	38.3	0.5793	28.2	1.1922	25.9
0.1373	36.8	0.6507		1.2216	
		[Nacit] = 0.0277 mol kg^{-1}			
0.0015	59.8	0.1100	34.8	0.4874	26.8
0.0045	54.6	0.1539	33.2	0.5170	26.5
0.0104	50.0	0.1932	31.7	0.5427	26.2
0.0163	45.8	0.2450	30.4	0.5651	26.1
0.0249	43.5	0.2946	29.4	0.5849	26.1
0.0334	41.8	0.3288	28.6	0.6025	26.1
0.0472	40.1	0.3632	28.0	0.61[illegible]3	26.0
0.0605	38.4	0.4121	27.5	0.6241	26.2
0.0860	36.6	0.4529	27.1		
		[NaCit] = 0.0720 mol kg^{-1}			
0.0018	52.7	0.0639	34.0	0.3513	26.4
0.0037	50.6	0.0892	32.2	0.3962	26.1
0.0055	48.5	0.1132	30.7	0.4356	26.3
0.0109	45.2	0.1415	29.5	0.4811	26.0
0.0163	41.9	0.1681	28.5	0.5202	25.9
0.0269	39.1	0.2052	28.0	0.5541	25.9
0.0373	36.8	0.2392	27.0	0.5838	25.9
0.0508	35.0	0.2995	26.7		

Table 6.4 - Continued

[AOT] x10³ / mol kg⁻¹	γ / mN m⁻¹	[AOT] x10³ / mol kg⁻¹	γ / mN m⁻¹	[AOT] x10³ / mol kg⁻¹	γ / mN m⁻¹
		[NaCit] = 0.0986 mol kg⁻¹			
0.0014	56.5	0.0878	30.1	0.2941	26.0
0.0042	49.5	0.1143	28.8	0.3282	26.4
0.0098	42.5	0.1389	27.6	0.3584	26.1
0.0181	39.3	0.1675	27.2	0.3853	25.9
0.0288	36.4	0.1939	26.9	0.4094	26.0
0.0393	34.7	0.2260	26.0	0.4311	25.9
0.0495	33.1	0.2552	26.5	0.4508	25.9
0.0691	31.6				
		[NaCit] = 0.1895 mol kg⁻¹			
0.0009	57.5	0.0765	28.6	0.2122	26.2
0.0027	50.8	0.0950	27.3	0.2291	26.2
0.0062	44.1	0.1172	26.8	0.2441	26.2
0.0131	38.9	0.1371	26.4	0.2576	26.1
0.0263	34.5	0.1551	26.3	0.2697	26.1
0.0418	32.2	0.1714	26.2	0.2807	26.2
0.0563	29.9	0.1932	26.3		
		[NaCit] = 0.3261 mol kg⁻¹			
0.0005	53.9	0.0328	28.4	0.1111	26.3
0.0015	49.0	0.0402	27.0	0.1211	26.3
0.0034	44.4	0.0473	27.0	0.1300	26.3
0.0063	38.2	0.0570	26.8	0.1379	26.3
0.0109	35.0	0.0660	26.4	0.1450	26.2
0.0154	33.1	0.0769	26.3	0.1514	26.3
0.0198	31.1	0.0867	26.2	0.1572	26.2
0.0264	29.7	0.0998	26.3		
		[NaCit] = 0.4335 mol kg⁻¹			
0.0002	55.8	0.0222	30.9	0.0596	25.4
0.0007	50.1	0.0255	28.9	0.0641	25.3
0.0014	45.4	0.0316	27.1	0.0682	25.4
0.0024	40.7	0.0371	26.6	0.0752	25.4
0.0077	37.0	0.0420	26.0	0.0782	25.3
0.0110	34.8	0.0487	25.5	0.0809	25.6
0.0150	32.7	0.0545	25.4	0.0835	25.5

Table 6.5 - Surface Tension (γ) Values of AOT in Aqueous Sodium Citrate Solution at 25 °C

[AOT] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[AOT] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[AOT] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaCit] = 0.0010 mol kg^{-1}			
0.0120	58.7	0.7152	36.3	2.4226	29.1
0.0357	53.0	0.8687	35.2	2.7338	29.0
0.0711	49.6	1.0154	34.0	3.0093	28.9
0.1178	47.0	1.1899	33.1	3.2551	28.6
0.2095	43.5	1.3554	32.3	3.4756	28.5
0.2989	41.8	1.6618	31.0	3.6745	28.4
0.3862	40.4	1.9393	29.9	3.8550	28.6
0.5546	38.3	2.1918	29.5	3.9662	28.5
		[NaCit] = 0.0069 mol kg^{-1}			
0.0059	54.6	0.7199	29.0	2.0750	25.3
0.0205	48.8	0.9161	27.7	2.2152	25.4
0.0439	44.4	1.1036	26.7	2.3502	25.4
0.0730	42.0	1.2830	26.2	2.4802	25.3
0.1305	39.0	1.4548	25.9	2.6055	25.5
0.2436	34.9	1.6195	25.4	2.7260	25.4
0.4081	32.2	1.7775	25.6	2.8429	25.6
0.5667	30.5	1.9292	25.5		
		[NaCit] = 0.0116 mol kg^{-1}			
0.0029	59.2	0.2078	33.6	0.7343	26.6
0.0057	52.8	0.2429	32.7	0.8086	26.0
0.0170	47.1	0.2764	31.9	0.8731	25.8
0.0393	42.6	0.3164	30.9	0.9296	25.8
0.0609	40.6	0.3542	30.5	0.9912	25.9
0.0821	38.9	0.4245	29.6	1.0446	25.8
0.1078	37.4	0.4881	28.8	1.0913	25.7
0.1327	36.0	0.5732	27.9	1.1325	25.9
0.1712	34.6	0.6479	26.9	1.1692	25.8

Table 6.5 - Continued

[AOT] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[AOT] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[AOT] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[Nacit] = 0.0277 mol kg^{-1}			
0.0016	58.8	0.2209	29.4	0.5094	25.6
0.0112	49.7	0.2723	28.2	0.5326	25.6
0.0268	42.9	0.3299	27.5	0.5532	25.7
0.3138	39.7	0.3778	26.8	0.5716	25.7
0.0606	36.4	0.4183	26.2	0.5882	25.7
0.1136	33.6	0.4504	25.7	0.6031	25.5
0.1604	30.9	0.4831	25.6		
		[NaCit] = 0.0720 mol kg^{-1}			
0.0018	51.1	0.0516	34.9	0.2825	26.5
0.0036	48.7	0.0660	33.3	0.3357	26.0
0.0054	46.8	0.0937	31.4	0.3818	25.7
0.0107	43.6	0.1199	29.7	0.4223	25.7
0.0160	40.7	0.1731	27.9	0.4689	25.7
0.0264	38.0	0.2205	26.8	0.5090	25.8
0.0366	36.6				
		[NaCit] = 0.0986 mol kg^{-1}			
0.0028	52.7	0.0962	29.2	0.2884	25.4
0.0083	45.0	0.1133	28.4	0.3117	25.5
0.0190	39.1	0.1434	27.4	0.0333	25.7
0.0295	36.8	0.1711	26.6	0.3711	25.7
0.0398	34.6	0.2048	26.2	0.4040	25.7
0.0595	32.0	0.2353	26.0	0.4326	25.6
0.0783	30.2	0.2631	25.7		
		[NaCit] = 0.1895 mol kg^{-1}			
0.0009	55.4	0.0414	31.4	0.1899	25.7
0.0017	52.6	0.0555	29.7	0.2088	25.8
0.0051	48.0	0.0688	28.0	0.2256	25.7
0.0085	42.2	0.0874	27.4	0.2405	25.7
0.0110	40.4	0.1044	26.8	0.2539	25.9
0.0135	38.6	0.1250	26.5	0.2660	25.7
0.0184	36.5	0.1436	25.9	0.2770	25.6
0.0232	34.5	0.1683	25.9	0.2870	25.4
0.0324	32.9				

Table 6.5 - Continued

[AOT] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[AOT] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[AOT] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaCit] = 0.3261 mol kg^{-1}			
0.0005	56.8	0.0176	31.4	0.0847	26.0
0.0014	49.0	0.0256	29.5	0.0933	25.9
0.0028	45.3	0.0331	27.6	0.1012	25.7
0.0046	41.8	0.0435	26.8	0.1084	25.6
0.0073	38.5	0.0531	26.2	0.1182	25.8
0.0100	35.3	0.0647	26.1	0.1269	25.7
0.0138	33.2	0.0752	26.1		
		[NaCit] = 0.4335 mol kg^{-1}			
0.0005	62.1	0.0178	30.8	0.0602	26.5
0.0010	56.4	0.0249	29.1	0.0648	26.4
0.0015	53.0	0.0313	27.3	0.0689	26.4
0.0034	44.4	0.0370	26.8	0.0727	26.4
0.0062	37.7	0.0421	26.6	0.0760	26.5
0.0097	34.2	0.0490	26.5	0.0790	26.5
0.0139	32.6	0.0549	26.5		

Table 6.6 - Surface Tension (γ) Values of AOT in Aqueous Sodium Citrate Solution at 30 °C

[AOT] x10³ / mol kg⁻¹	γ / mN m⁻¹	[AOT] x10³ / mol kg⁻¹	γ / mN m⁻¹	[AOT] x10³ / mol kg⁻¹	γ / mN m⁻¹
		[NaCit] = 0.0 mol kg⁻¹			
0	71.5	0.2838	48.0	3.2126	30.3
0.0029	69.1	0.3508	46.5	3.4562	30.0
0.0058	67.6	0.4504	44.8	3.7708	29.7
0.0115	65.8	0.5600	43.5	4.1483	29.4
0.0172	64.0	0.6684	41.7	4.5096	29.2
0.0230	63.0	0.8817	39.7	5.1871	28.8
0.0287	62.8	1.0906	37.8	5.8107	28.6
0.0459	60.5	1.2952	36.5	6.6582	28.3
0.0574	59.7	1.7404	34.9	7.4153	28.2
0.0974	55.9	2.0260	33.2	8.5123	28.3
0.1145	55.0	2.3033	32.1	9.4436	28.2
0.1429	53.2	2.5282	30.8	10.244	28.0
0.1712	52.0	2.7477	30.8	10.940	27.8
0.1995	50.5	2.9620	30.4	12.091	27.3
0.2277	49.4				
		[NaCit] = 0.0010 mol kg⁻¹			
0.0133	57.8	1.0445	33.9	2.8874	28.6
0.0398	51.7	1.2364	32.6	3.0821	28.5
0.0921	47.9	1.5883	31.1	3.2612	28.6
0.1947	43.8	1.9029	29.8	3.4265	28.9
0.3433	41.1	2.1861	28.8	3.5796	28.5
0.4861	38.5	2.4422	28.5	3.7217	28.7
0.6678	36.9	2.6749	28.5	3.8539	28.6
0.8405	35.3				
		[NaCit] = 0.0069 mol kg⁻¹			
0.0060	55.1	0.6859	28.8	2.0072	25.6
0.0211	48.6	0.8389	27.8	2.1537	25.5
0.0451	44.2	0.9866	26.8	2.2945	25.3
0.0749	41.6	1.1758	26.2	2.4300	25.4
0.1340	38.4	1.3567	25.7	2.5604	25.3
0.2499	35.2	1.5298	25.5	2.6860	25.6
0.3629	32.4	1.6956	25.5	2.8070	25.5
0.5273	30.6	1.8546	25.5	2.9239	25.5

Table 6.6 - Continued

[AOT] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[AOT] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[AOT] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaCit] = 0.0116 mol kg^{-1}			
0.0058	53.2	0.2727	31.4	0.9357	25.4
0.0174	47.2	0.3523	30.2	0.9976	25.2
0.0400	42.7	0.4241	29.2	1.0511	25.3
0.0729	39.9	0.5192	28.3	1.0979	25.3
0.1046	37.3	0.6019	27.4	1.1391	25.3
0.1451	35.8	0.6968	26.9	1.1757	25.2
0.1837	34.3	0.7777	26.3	1.2084	25.4
0.2295	32.8	0.8634	26.0		
		[Nacit] = 0.0277 mol kg^{-1}			
0.0031	53.2	0.1290	32.0	0.4765	25.4
0.0091	48.4	0.1716	30.6	0.5022	25.5
0.0151	43.6	0.2098	29.5	0.5249	25.4
0.0268	40.8	0.2753	28.2	0.5452	25.4
0.0382	38.6	0.3295	26.9	0.5634	25.4
0.0602	36.4	0.3750	26.3	0.5798	25.5
0.0811	34.3	0.4138	25.8	0.5947	25.3
0.1058	33.1	0.4473	25.5	0.6083	25.4
		[NaCit] = 0.0720 mol kg^{-1}			
0.0036	50.0	0.1283	28.9	0.3543	25.6
0.0106	43.2	0.1549	27.5	0.3838	25.3
0.0244	38.5	0.2036	26.5	0.4235	25.1
0.0379	36.0	0.2473	25.7	0.4587	25.1
0.0509	33.7	0.2865	25.0	0.5044	25.0
0.0761	32.1	0.3220	25.6	0.5433	24.8
0.1000	30.4				
		[NaCit] = 0.0986 mol kg^{-1}			
0.0029	48.3	0.0812	29.8	0.4079	25.2
0.0086	43.3	0.1258	28.0	0.3350	25.1
0.0142	40.8	0.1655	26.4	0.3554	25.2
0.0198	38.6	0.2011	26.0	0.3742	25.3
0.0307	36.0	0.2332	25.6	0.3999	25.1

Table 6.6 - Continued

[AOT] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[AOT] x10^3 / mol kg^{-1}	γ / mN m^{-1}	[AOT] x10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaCit] = 0.0986 mol kg^{-1}			
0.0413	33.8	0.2622	25.0	0.4230	25.1
0.0618	31.8	0.2887	25.4	0.4438	25.1
		[NaCit] = 0.1895 mol kg^{-1}			
0.0009	54.3	0.0368	31.4	0.1655	25.4
0.0026	49.0	0.0511	29.5	0.1804	25.2
0.0051	43.1	0.0647	27.6	0.2003	25.2
0.0085	40.2	0.0894	26.7	0.2180	25.2
0.0134	37.7	0.1115	25.7	0.3385	25.1
0.0183	35.2	0.1313	25.5	0.2563	24.8
0.0277	33.2	0.1492	25.4		
		[NaCit] = 0.3261 mol kg^{-1}			
0.0005	55.8	0.0196	30.9	0.0647	25.4
0.0014	50.1	0.0261	28.9	0.0701	25.3
0.0028	45.4	0.0322	27.1	0.0803	25.4
0.0047	40.7	0.0395	26.6	0.0895	25.4
0.0075	37.0	0.0463	26.0	0.1018	25.3
0.0102	34.8	0.0528	25.5	0.1126	25.6
0.0128	32.7	0.0589	25.4	0.1221	25.5
0.0016	31.8				
		[NaCit] = 0.4335 mol kg^{-1}			
0.0005	55.8	0.0246	28.8	0.0597	25.9
0.0015	48.5	0.0309	27.2	0.0643	26.0
0.0029	43.3	0.0366	26.6	0.0684	25.9
0.0052	39.0	0.0417	26.1	0.0721	25.7
0.0096	34.2	0.0485	26.0	0.0765	25.7
0.0137	32.0	0.0544	26.0	0.0804	25.7
0.0175	30.2				

Table 6.7 - Specific Conductance (κ) Values of SDS in Aqueous Sodium Citrate Solution at 20 °C

[SDS] x10^3 / mol kg^{-1}	κ / S m^{-1}	[SDS] x10^3 / mol kg^{-1}	κ / S m^{-1}	[SDS] x10^3 / mol kg^{-1}	κ / S m^{-1}
		[NaCit] = 0.0052 mol kg^{-1}			
0	0.1377	1.4200	0.1455	4.1900	0.1595
0.0800	0.1381	1.7100	0.1471	4.4200	0.1602
0.2000	0.1391	1.8500	0.1485	4.6500	0.1607
0.3500	0.1397	2.1300	0.1498	4.9900	0.1618
0.5100	0.1411	2.4000	0.1510	5.3200	0.1630
0.6600	0.1417	2.6700	0.1522	5.6400	0.1639
0.8200	0.1423	3.2000	0.1552	6.0500	0.1648
0.9700	0.1432	3.7000	0.1574	6.3500	0.1655
1.1200	0.1441	3.9500	0.1584	6.6500	0.1660
		[NaCit] = 0.0150 mol kg^{-1}			
0.1600	0.3411	1.2600	0.3468	3.7000	0.3532
0.3300	0.3420	1.4100	0.3463	4.1800	0.3550
0.4900	0.3434	1.5600	0.3460	4.6400	0.3559
0.6500	0.3443	1.8500	0.3487	5.0800	0.3567
0.8000	0.3451	2.1300	0.3500	5.9000	0.3586
0.9600	0.3452	2.6800	0.3520	6.6700	0.3601
1.1100	0.3457	3.2000	0.3531		
		[NaCit] = 0.0568 mol kg^{-1}			
0.0400	1.0031	0.6200	1.0107	2.0400	1.0172
0.0700	1.0037	0.7300	1.0121	2.2000	1.0170
0.1100	1.0054	0.9400	1.0117	2.3500	1.0176
0.1700	1.0077	1.1400	1.0137	2.5000	1.0187
0.2900	1.0085	1.3400	1.0142	2.7900	1.0196
0.4000	1.0088	1.5200	1.0149	3.0500	1.0206
0.5100	1.0097	1.7000	1.0162		

Table 6.7 – Continued

[SDS] x10^3 / mol kg^{-1}	κ / S m^{-1}	[SDS] x10^3 / mol kg^{-1}	κ / S m^{-1}	[SDS] x10^3 / mol kg^{-1}	κ / S m^{-1}
		[NaCit] = 0.0855 mol kg^{-1}			
0.0200	1.3075	0.5700	1.3115	1.9100	1.3136
0.0600	1.3091	0.6800	1.3119	2.1600	1.3151
0.1100	1.3106	0.8900	1.3122	2.3900	1.3153
0.1700	1.3095	1.0900	1.3124	2.6100	1.3168
0.2300	1.3105	1.3800	1.3129	2.8200	1.3168
0.3400	1.3108	1.6500	1.3147	3.5600	1.3201
0.4600	1.3119				
		[NaCit] = 0.1016 mol kg^{-1}			
0.0300	1.4957	0.2800	1.4978	0.7400	1.5015
0.1100	1.4973	0.4400	1.4995	0.8900	1.5020
0.2000	1.4971	0.6000	1.5012	1.0200	1.5025
		[Nacit] = 0.1982 mol kg^{-1}			
0.0200	2.4267	0.3200	2.4336	0.8700	2.4362
0.0400	2.4297	0.3800	2.4342	0.9700	2.4370
0.0600	2.4305	0.3800	2.4342	1.0600	2.4365
0.1000	2.4310	0.5000	2.4342	1.1500	2.4374
0.1300	2.4318	0.5600	2.4350	1.2400	2.4385
0.1900	2.4325	0.6700	2.4355	1.3200	2.4381
0.2600	2.4332	0.7700	2.4378		

Table 6.8 - Specific Conductance (κ) Values of SDS in Aqueous Sodium Citrate Solution at 25 °C

[SDS] x10³ / mol kg⁻¹	κ / S m⁻¹	[SDS] x10³ / mol kg⁻¹	κ / S m⁻¹	[SDS] x10³ / mol kg⁻¹	κ / S m⁻¹
		[NaCit] = 0.0052 mol kg⁻¹			
0.1500	0.1538	1.6100	0.1625	3.7700	0.1753
0.3100	0.1558	1.7400	0.1639	4.0000	0.1767
0.4600	0.1571	1.8800	0.1648	4.2300	0.1777
0.6100	0.1571	2.0100	0.1656	4.4500	0.1787
0.7500	0.1581	2.2800	0.1664	4.6700	0.1796
0.9000	0.1591	2.5400	0.1672	4.8900	0.1804
1.0400	0.1599	2.8000	0.1693	5.1000	0.1813
1.1900	0.1606	3.0500	0.1714	5.3100	0.1822
1.3300	0.1611	3.2900	0.1726	5.7200	0.1833
1.3300	0.1611	3.5300	0.1738		
		[NaCit] = 0.0150 mol kg⁻¹			
0	0.3814	1.1500	0.3894	3.4800	0.3982
0.0700	0.3823	1.1500	0.3894	3.9000	0.3992
0.1400	0.3836	1.6500	0.3910	4.3000	0.4007
0.2100	0.3843	1.9000	0.3919	4.6900	0.4017
0.3500	0.3849	2.1400	0.3928	5.0600	0.4026
0.4800	0.3858	2.6000	0.3947	5.4200	0.4039
0.6200	0.3866	3.0500	0.3973	5.9400	0.4048
0.8900	0.3875				
		[NaCit] = 0.0568 mol kg⁻¹			
0.1100	1.1195	1.6400	1.1227	5.8500	1.1262
0.2300	1.1199	1.9900	1.1230	6.3700	1.1266
0.3800	1.1205	1.9900	1.1230	6.8600	1.1275
0.5700	1.1209	2.3200	1.1241	7.3300	1.1274
0.9300	1.1220	4.7700	1.1255	7.7900	1.1277
1.2900	1.1223	5.3200	1.1262		

Table 6.8 – Continued

[SDS] x10^3 / mol kg^{-1}	κ / S m^{-1}	[SDS] x10^3 / mol kg^{-1}	κ / S m^{-1}	[SDS] x10^3 / mol kg^{-1}	κ / S m^{-1}
		[NaCit] = 0.0855 mol kg^{-1}			
0	1.5165	0.3000	1.5286	0.5700	1.5309
0.0300	1.5230	0.3700	1.5276	0.6300	1.5319
0.0600	1.5241	0.4400	1.5287	0.7600	1.5333
0.0900	1.5256	0.4400	1.5287	0.8800	1.5337
0.1500	1.5273	0.5000	1.5305	1.1100	1.5345
0.2300	1.5274				
		[NaCit] = 0.1016 mol kg^{-1}			
0	1.6726	0.2000	1.6757	0.8000	1.6790
0.0200	1.6742	0.3200	1.6764	0.8500	1.6791
0.0400	1.6747	0.4300	1.6778	0.9500	1.6793
0.0800	1.6747	0.4300	1.6778	1.1400	1.6794
0.1200	1.6749	0.5400	1.6784	1.3100	1.6795
0.1600	1.6753	0.7000	1.6787	1.4800	1.6803
		[Nacit] = 0.1982 mol kg^{-1}			
0	2.6963	0.1400	2.7009	0.5600	2.7058
0.0200	2.6978	0.3600	2.7051	0.6500	2.7062
0.0400	2.6983	0.4600	2.7054	0.7800	2.7064
0.0500	2.6988	0.5600	2.7058	0.9100	2.7068
0.0800	2.6999				

Table 6.9 - Specific Conductance (κ) Values of SDS in Aqueous Sodium Citrate Solution at 30 °C

[SDS] x10^3 / mol kg^{-1}	κ / S m^{-1}	[SDS] x10^3 / mol kg^{-1}	κ / S m^{-1}	[SDS] x10^3 / mol kg^{-1}	κ / S m^{-1}
		[NaCit] = 0.0052 mol kg^{-1}			
0	0.1685	1.4100	0.1774	3.4200	0.1922
0.1800	0.1702	1.5700	0.1797	3.7100	0.1946
0.3600	0.1724	1.9000	0.1827	3.9900	0.1963
0.5400	0.1734	2.2200	0.1829	4.2600	0.1977
0.7200	0.1737	2.5300	0.1840	4.5300	0.1986
0.9000	0.1758	2.8400	0.1881	5.0400	0.1996
1.0700	0.1759	3.1300	0.1899	5.5400	0.2015
1.2400	0.1762				
		[NaCit] = 0.0150 mol kg^{-1}			
0	0.4212	1.4400	0.4312	3.9600	0.4424
0.0500	0.4229	1.8200	0.4333	4.4200	0.4434
0.1100	0.4236	2.1900	0.4358	4.8600	0.4450
0.2200	0.4241	2.6400	0.4368	5.4300	0.4466
0.4300	0.4257	2.9800	0.4385	5.9600	0.4483
0.6400	0.4269	3.4900	0.4404	6.4600	0.4502
1.0400	0.4291				
		[NaCit] = 0.0568 mol kg^{-1}			
0.0400	1.2363	0.5300	1.2388	1.3200	1.2399
0.0800	1.2373	0.6500	1.2392	1.5200	1.2397
0.1500	1.2378	0.8800	1.2397	1.7200	1.2398
0.2800	1.2381	1.1000	1.2398	1.9100	1.2399
0.4000	1.2383				
		[NaCit] = 0.0855 mol kg^{-1}			
0.0400	1.6909	0.4500	1.6946	1.0300	1.6982
0.1100	1.6912	0.5100	1.6950	1.1300	1.6985
0.1800	1.6917	0.5700	1.6956	1.2300	1.6995
0.2500	1.6925	0.6900	1.6971	1.4300	1.6997
0.3100	1.6931	0.8100	1.6976	6.4600	0.4502
0.3800	1.6941				

Table 6.9 - Continued

[SDS] x10^3 / mol kg^{-1}	κ / S m^{-1}	[SDS] x10^3 / mol kg^{-1}	κ / S m^{-1}	[SDS] x10^3 / mol kg^{-1}	κ / S m^{-1}
		[NaCit] = 0.1016 mol kg^{-1}			
0.0400	1.8450	0.4200	1.8484	1.2500	1.8526
0.0900	1.8455	0.5700	1.8492	1.4900	1.8532
0.2500	1.8467	0.7200	1.8501	1.7100	1.8540
0.2500	1.8467	0.9900	1.8512	1.9200	1.8551
0.3400	1.8475				
		[Nacit] = 0.1982 mol kg^{-1}			
0	2.9974	0.1700	3.0004	0.5900	3.0054
0.0600	2.9990	0.2800	3.0021	0.7800	3.0074
0.1700	3.0004	0.3900	3.0035	0.9500	3.0083

Table 6.10 - EMF Values of SDS in Aqueous Sodium Citrate Solution at 25 °C

[SDS] x10^3 / mol kg^{-1}	EMF / mV	[SDS] x10^3 / mol kg^{-1}	EMF / mV	[SDS] x10^3 / mol kg^{-1}	EMF / mV
		[NaCit] = 0.0151 mol kg^{-1}			
0	45.9	1.5228	49.6	4.3083	50.6
0.1541	46.4	1.8972	49.5	5.7205	51.1
0.3078	47.2	2.2692	49.9	7.0973	51.4
0.5376	47.8	2.7860	50.1	7.7729	51.5
0.8425	48.5	3.2980	50.4	8.4401	51.6
1.1458	49.0				
		[NaCit] = 0.0355 mol kg^{-1}			
0	62.6	0.6740	64.0	1.6965	65.3
0.0617	62.9	0.7955	64.2	1.8746	65.4
0.1233	63.1	0.9166	64.3	2.0520	65.5
0.1848	63.3	1.0375	64.5	2.2287	65.7
0.3076	63.4	1.1580	64.7	2.5216	65.8
0.4300	63.6	1.3382	64.9	2.8127	65.9
0.5522	63.8	1.5177	65.1		
		[NaCit] = 0.0649 mol kg^{-1}			
0	74.0	0.4599	76.0	1.2725	76.9
0.0463	74.4	0.5511	76.1	1.4504	77.0
0.0925	74.7	0.6421	76.3	1.6275	77.1
0.1386	74.9	0.7329	76.6	1.8475	77.2
0.1847	75.3	0.8234	76.7	2.0661	77.2
0.2307	75.6	0.9137	76.8	2.7563	77.2
0.2767	75.7	1.0935	76.8	3.4324	77.3
0.3684	76.1				
		[NaCit] = 0.1000 mol kg^{-1}			
0	82.9	0.2351	85.2	0.8913	85.9
0.0393	83.3	0.2741	85.3	1.0436	86.0
0.0786	83.7	0.3520	85.5	1.2705	86.0
0.1178	84.1	0.4297	85.6	1.4956	86.1
0.1570	84.3	0.5844	85.9	1.7931	86.1
0.1961	84.9	0.7382	86.0	2.0875	86.3

Table 6.10 - Continued

[SDS] x10^3 / mol kg^{-1}	EMF / mV	[SDS] x10^3 / mol kg^{-1}	EMF / mV	[SDS] x10^3 / mol kg^{-1}	EMF / mV
		[NaCit] = 0.2004 mol kg^{-1}			
0	93.3	0.2789	95.6	0.5926	96.4
0.0349	93.6	0.3137	95.6	0.6623	96.5
0.0697	93.9	0.3486	95.8	0.8018	96.6
0.1046	94.1	0.3835	95.9	1.0807	96.7
0.1394	94.4	0.4532	96.1	1.3595	96.7
0.2092	95.1	0.5229	96.3	1.6384	96.8
0.2440	95.3				
		[NaCit] = 0.3014 mol kg^{-1}			
0	101.1	0.0923	102.3	0.1839	103.2
0.0185	101.6	0.1106	102.6	0.2204	103.3
0.0370	101.8	0.1290	102.7	0.2931	103.4
0.0554	101.9	0.1473	102.9	0.4014	103.5
0.0739	102.1	0.1656	103.1	0.6155	103.8

Table 6.11 - EMF Values of AOT in Aqueous Sodium Citrate Solution at 25 °C

[AOT] x10^3 / mol kg^{-1}	EMF / mV	[AOT] x10^3 / mol kg^{-1}	EMF / mV	[AOT] x10^3 / mol kg^{-1}	EMF / mV
		[NaCit] = 0.0053 mol kg^{-1}			
0	21.7	0.4863	25.4	2.0644	28.3
0.0092	22.1	0.5711	25.6	2.2597	28.4
0.0183	22.6	0.6548	25.9	2.4486	28.6
0.0366	23.1	0.7374	26.3	2.6910	28.7
0.0820	23.6	0.9791	26.9	2.9232	28.8
0.1451	23.8	1.2120	27.1	3.1459	29.1
0.2254	24.4	1.4366	27.4	3.3596	29.6
0.3135	24.7	1.6532	27.7	3.5143	29.8
0.4005	25.2	1.8624	28.0	3.7135	29.9
		[NaCit] = 0.0116 mol kg^{-1}			
0	32.3	0.1052	36.6	0.5612	39.4
0.0025	32.8	0.1290	36.8	0.8554	39.6
0.0075	33.2	0.1526	37.0	0.9559	39.9
0.0125	33.6	0.1876	37.2	1.0517	40.5
0.0174	34.2	0.2221	37.4	1.1430	40.7
0.0249	34.5	0.2673	37.8	1.2302	40.9
0.0323	34.9	0.3116	38.2	1.3135	41.1
0.0446	35.2	0.4399	38.6	1.3932	41.6
0.0568	35.6	0.5415	38.9	1.4943	41.8
0.0811	36.2	0.6386	39.2	1.5899	42.1
		[NaCit] = 0.0149 mol kg^{-1}			
0	43.2	0.1279	45.6	0.6266	46.8
0.0029	44.1	0.1547	45.7	0.6883	46.9
0.0086	44.3	0.1811	45.8	0.7479	47.1
0.0171	44.6	0.2073	45.9	0.8977	47.2
0.0256	44.9	0.2585	46.0	1.0353	47.2
0.0369	45.0	0.3085	45.9	1.1159	47.3
0.0482	45.1	0.3573	46.2	1.1925	47.4
0.0607	45.2	0.4049	46.3	1.3352	47.4
0.0732	45.3	0.4513	46.4	1.4654	47.5
0.0870	45.4	0.4967	46.6	1.6942	47.8
0.1007	45.5	0.5628	46.7		

Table 6.11 - Continued

[AOT] x10^3 / mol kg^{-1}	EMF / mV	[AOT] x10^3 / mol kg^{-1}	EMF / mV	[AOT] x10^3 / mol kg^{-1}	EMF / MV
		[NaCit] = 0.0355 mol kg^{-1}			
0	58.4	0.0461	61.8	0.3051	62.9
0.0022	58.8	0.0590	61.9	0.3592	63.0
0.0067	59.4	0.0718	62.1	0.4928	63.1
0.0111	59.7	0.0909	62.2	0.6164	63.2
0.0155	60.2	0.1097	62.3	0.7486	63.3
0.0199	60.7	0.1406	62.5	0.9911	63.4
0.0287	61.1	0.1709	62.6	1.1920	63.6
0.0330	61.6	0.2105	62.7	0.9911	63.8
0.0396	61.7	0.2490	62.8		
		[NaCit] = 0.0656 mol kg^{-1}			
0	64.7	0.0613	67.8	0.1582	69.5
0.0021	65.1	0.0692	68.0	0.1861	69.6
0.0042	65.9	0.0772	68.1	0.2134	69.7
0.0083	66.1	0.0851	68.2	0.2492	69.8
0.0145	66.4	0.0930	68.3	0.2840	69.9
0.0207	66.7	0.1008	68.5	0.3347	70.0
0.0289	66.8	0.1105	68.7	0.3836	70.1
0.0370	67.0	0.1202	69.0	0.4615	70.2
0.0452	67.3	0.1393	69.3	0.5350	70.4
0.0532	67.5				
		[NaCit] = 0.1000 mol kg^{-1}			
0	77.1	0.0198	79.3	0.1444	80.4
0.0017	77.6	0.0264	79.6	0.2021	80.6
0.0033	77.9	0.0329	79.7	0.2571	80.9
0.0050	78.1	0.0426	79.9	0.3095	81.2
0.0066	78.4	0.0522	80.1	0.3594	81.3
0.0083	78.9	0.0681	80.2	0.4072	81.4
0.0100	79.0	0.0837	80.3	0.4529	81.6
0.0133	79.1	0.1145	80.4	0.4966	81.6

Table 6.11 - Continued

[AOT] x10^3 / mol kg^{-1}	EMF / mV	[AOT] x10^3 / mol kg^{-1}	EMF / mV	[AOT] x10^3 / mol kg^{-1}	EMF / MV
		[NaCit] = 0.2003 mol kg^{-1}			
0	90.5	0.0106	92.9	0.0289	94.1
0.0013	90.8	0.0132	93.6	0.0315	94.2
0.0027	91.1	0.0159	93.7	0.0418	94.3
0.0040	91.3	0.0185	93.7	0.0570	94.3
0.0053	91.6	0.0198	93.8	0.0867	94.5
0.0066	91.9	0.0211	93.9	0.1108	94.4
0.0080	92.2	0.0237	94.0	0.1343	94.4
0.0093	92.6	0.0263	94.1		
		[NaCit] = 0.2996 mol kg^{-1}			
0	98.0	0.0132	98.9	0.0781	99.7
0.0008	98.2	0.0181	99.1	0.1067	99.8
0.0017	98.3	0.0245	99.2	0.1470	99.9
0.0033	98.5	0.0325	99.4	0.1846	100.0
0.0007	98.6	0.0481	99.6	0.2197	100.1
0.0099	98.8				

Table 6.12 - Values of Critical Micelle Concentration (± 0.05 x 10^{-3} mol kg^{-1}) of SDS in Aqueous NaCit Solution Obtained by Surface Tension and Conductance Methods

[NaCit]/ mol kg^{-1}	[Na^+]/ mol kg^{-1}	Surface Tension Cmc x 10^3 / mol kg^{-1}			Conductance Cmc x 10^3 / mol kg^{-1}		
		293 K	298 K	303 K	293 K	298 K	303 K
0.0052	0.0156	4.10	3.98	3.76	3.60	4.40	4.30
0.0150	0.0450	2.40	2.40	2.24	2.60	3.10	2.20
0.0314	0.0942	1.58	1.50	1.59	-	-	-
0.0568	0.1704	1.05	1.00	0.94	1.15	1.00	0.85
0.0855	0.2565	0.71	0.69	0.75	0.70	0.76	0.70
0.1016	0.3048	0.59	0.55	0.63	0.60	0.55	0.65
0.1982	0.5946	0.36	0.34	0.37	0.44	0.32	0.35
0.3033	0.9099	0.22	0.21	0.20	-	-	-
0.4116	1.2348	0.14	0.15	0.14	-	-	-

Table 6.13 - Values of Critical Micelle Concentration (± 0.05 x 10^{-3} mol kg^{-1}) of SDS in Aqueous NaCit Solution Obtained by EMF Method and the Values of Intercept (A_1) and Slope (B_1) of Equation (6.2) at 25 °C

[NaCit] / mol kg^{-1}	[Na^+] / mol kg^{-1}	Cmc x 10^3 mol kg^{-1}	A_1 / mV	B_1 / mV	β ± 0.02
0.0151	0.0453	2.30	179.64	98.037	0.69
0.0355	0.1065	1.44	415.65	362.41	0.60
0.0649	0.1947	0.91	655.67	816.85	0.90
0.1000	0.3000	0.62	787.16	1343.3	0.96
0.2004	0.6009	0.33	2625.7	11456	0.92
0.3014	0.9042	0.18	990.27	20323	0.91

Table 6.14 - Values of Critical Micelle Concentration (± 0.05 x 10^{-3} mol kg^{-1}) of AOT in Aqueous NaCit Solution Obtained by Surface Tension and EMF Methods

$[Na^+]$/ mol kg^{-1}	Surface Tension Cmc x 10^3 / mol kg^{-1}			$[Na^+]$/ mol kg^{-1}	EMF (at 298 K)			
	293 K	298 K	303 K		Cmc x 10^3 mol kg^{-1}	A_1 / mV	B_1 / mV	β ± 0.02
0	2.69	2.66	2.75	0	2.51	138.30	57.800	0.42
0.0030	2.45	2.24	2.24	0.0159	1.38	140.12	65.070	0.45
0.0207	1.20	1.41	1.41	0.0348	1.01	332.80	203.64	0.67
0.0348	0.93	0.89	0.98	0.0447	0.75	220.86	130.20	0.63
0.0831	0.50	0.45	0.45	0.1065	0.39	680.98	636.68	0.77
0.2160	0.27	0.22	0.25	0.1968	0.22	3124.6	4332.5	0.80
0.2958	0.17	0.18	0.20	0.3000	0.19	2528.7	4685.5	0.89
0.5685	0.11	0.09	0.10	0.6009	0.10	5654.2	25161	0.92
0.9783	0.05	0.05	0.05	0.8988	0.05	1865.4	38177	0.75
1.3005	0.04	0.04	0.04					

Table 6.15 – Least-Squares Fitted Values of the Parameters of Equation (6.1)

Surfactant	Conc. Range of added Na^+ in mol kg^{-1}	293 K		298 K		303 K	
		A	*β*	*A*	*β*	*A*	*β*
SDS	0 – 1.2348	-15.36	0.75	-15.95	0.84	-15.64	0.78
AOT	0 – 0.02	-13.86	0.40	-13.19	0.33	-13.10	0.32
	> 0.02	-17.27	0.86	-17.47	0.89	-17.28	0.87

Table 6.16 - Computed Values of Surface Excess (Γ_{cm}) and Surface Area per Molecule (A_0) of SDS and AOT Near CMC in Presence of NaCit

[NaCit] mol kg^{-1}	($\Gamma_{cmc} \pm 0.5$) x 10^6 / mol m^{-2}			A_0 / nm^2		
	293 K	298 K	303 K	293 K	298 K	303 K
			Surfactant = SDS			
0	2.97	3.48	2.98	0.56	0.48	0.56
0.0052	4.00	3.98	3.99	0.42	0.42	0.42
0.0150	4.29	4.34	4.03	0.39	0.38	0.41
0.0314	4.26	4.26	4.13	0.39	0.39	0.40
0.0568	4.38	4.26	4.22	0.38	0.39	0.39
0.0855	4.29	4.33	4.29	0.39	0.38	0.39
0.1016	4.16	4.45	4.32	0.40	0.37	0.38
0.1982	3.80	4.21	4.10	0.44	0.39	0.41
0.3033	3.51	3.99	3.70	0.47	0.42	0.45
0.4116	3.26	3.78	3.62	0.51	0.44	0.46
			Surfactant = AOT			
0	1.80	1.63	1.63	0.92	1.02	1.02
0.0010	2.04	1.82	1.95	0.81	0.91	0.85
0.0069	2.14	2.02	2.11	0.78	0.82	0.79
0.0116	1.99	2.13	2.08	0.83	0.78	0.80
0.0277	2.04	1.94	2.25	0.81	0.86	0.74
0.0720	2.26	2.21	2.25	0.73	0.75	0.74
0.0986	2.25	2.28	2.29	0.74	0.73	0.73
0.1895	2.32	2.58	2.32	0.72	0.64	0.72
0.3261	2.52	2.51	2.41	0.66	0.66	0.69
0.4335	2.55	2.54	2.39	0.65	0.65	0.69

Table. 6.17 - Values of ΔG_m^o and ΔG_{ad}^0 of SDS in Aqueous NaCit Solution.

$[Na^+]$ mol kg^{-1}	$-\Delta G_m^o \pm 0.5$ / kJ mol^{-1}			$-\Delta G_{ad}^0 \pm 0.5$ / kJ mol^{-1}		
	293 K	298 K	303 K	293 K	298 K	303 K
0.0156	40.56	43.51	42.34	49.24	52.33	50.99
0.0450	42.85	45.82	44.62	51.17	54.13	53.61
0.0942	44.63	47.96	46.14	53.32	56.69	55.19
0.1704	46.38	49.82	48.45	55.03	58.75	57.46
0.2565	48.05	51.52	49.45	57.03	60.51	58.52
0.3048	48.85	52.56	50.22	58.17	61.30	59.25
0.5946	50.97	54.77	52.57	61.63	64.33	62.50
0.9099	53.10	56.99	55.29	65.18	67.26	66.64
1.2348	55.05	58.55	56.87	67.81	69.67	68.70

Table 6.18 - Values of ΔG_m^o and ΔG_{ad}^0 of AOT in Aqueous NaCit Solution

$[Na^+]$ mol kg^{-1}	$-\Delta G_m^o \pm 0.5$ / kJ mol^{-1}			$-\Delta G_{ad}^0 \pm 0.5$ / kJ mol^{-1}		
	293 K	298 K	303 K	293 K	298 K	303 K
0	33.88	32.78	31.88	55.83	57.93	58.24
0.0031	34.20	33.34	32.54	55.04	56.41	54.84
0.0207	36.64	34.87	34.03	57.90	57.30	56.06
0.0348	49.83	51.71	49.86	72.95	72.67	72.22
0.0831	52.65	54.90	53.41	74.95	77.69	74.07
0.2160	55.45	58.27	56.09	75.00	77.64	76.62
0.2958	57.55	59.21	57.11	77.54	78.16	77.41
0.5685	59.55	62.48	60.27	79.13	78.84	80.19
0.9783	63.15	65.27	63.44	81.36	82.37	82.73
1.3005	64.19	66.34	64.47	81.57	83.19	83.71

Table 6.19 - Ratio of the Intensities (I_o/I_q) of Fluorescence Emission of Pyrene in the Absence (I_o) and Presence (I_q) of the Quencher (CPC) at 374 nm in Aqueous SDS + NaCit Medium at 25 °C

[NaCit] / mol kg^{-1}	$(c-c_0)$ / mol kg^{-1}	$N_0 \pm 5$	[CPC] x 10^5 / mol kg^{-1}	$\frac{I_0}{I_q}$	$\frac{I_3}{I_1} \pm 0.01$
0.001	0.003	55	0	1.0000	0.84
			0.14	1.0372	
			0.28	1.0585	
0.005	0.002	74	0	1.0000	0.83
			0.10	1.0408	
			0.30	1.1004	
			0.40	1.1579	
			0.50	1.2180	
0.035	0.009	89	0	1.0000	0.87
			0.89	1.1011	
			1.43	1.1673	
			1.79	1.2229	
			2.15	1.2329	
0.097	0.002	100	0	1.0000	0.88
			0.89	1.8245	
			1.43	2.4558	
			1.79	3.0161	
			2.15	3.4675	
0.200	0.002	106	0	1.0000	0.91
			0.89	1.7374	
			1.43	2.4028	
			1.79	2.9867	
			2.15	3.5365	

Table 6.19 - Continued

[NaCit] / mol kg^{-1}	$(c - c_0)$ / mol kg^{-1}	$N_0 \pm 5$	[CPC] x 10^5 / mol kg^{-1}	$\frac{I_0}{I_q}$	$\frac{I_3}{I_1} \pm 0.01$
0.304	0.001	99	0	1.0000	0.92
			1.43	3.7618	
			1.79	6.2110	
			2.15	6.8519	
0.396	0.001	106	0	1.0000	0.83
			0.89	2.3921	
			1.43	4.6790	
			1.79	5.8025	
			2.15	8.1764	

Table 6.20 - Ratio of the Intensities (I_o/I_q) of Fluorescence Emission of Pyrene in the Absence (I_o) and Presence (I_q) of the Quencher (CPC) at 374 nm in Aqueous AOT + NaCit Medium at 25 °C

[NaCit] / mol kg^{-1}	$(c-c_0)$ / mol kg^{-1}	$N_0 \pm 5$	[CPC] x 10^5 / mol kg^{-1}	$\frac{I_0}{I_q}$	$\frac{I_3}{I_1} \pm 0.01$
0.001	0.005	24	0	1.0000	1.01
			1.40	1.0724	
			1.60	1.0853	
			1.80	1.1024	
			2.00	1.1111	
0.002	0.005	28	0	1.0000	1.03
			0.20	1.0083	
			0.60	1.0403	
			0.80	1.0389	
			1.00	1.0611	
0.004	0.005	41	0	1.0000	1.04
			2.00	1.1368	
			4.00	1.4882	
			6.00	1.6718	
			8.00	1.8276	
0.006	0.005	38	0	1.0000	1.03
			2.00	1.2049	
			4.00	1.3683	
			6.00	1.4888	
			8.00	1.6401	
0.007	0.002	37	0	1.0000	1.02
			0.10	1.0395	
			0.20	1.0579	
			0.30	1.0785	
			0.40	1.0954	

Table 6.20 - Continued

[NaCit] / mol kg^{-1}	$(c - c_0)$ / mol kg^{-1}	$N_0 \pm 5$	[CPC] x 10^5 / mol kg^{-1}	$\frac{I_0}{I_q}$	$\frac{I_3}{I_1} \pm 0.01$
0.008	0.002	71	0	1.0000	0.97
			0.10	1.0338	
			0.15	1.0627	
			0.20	1.0805	
			0.25	1.1148	
0.010	0.004	81	0	1.0000	0.89
			0.20	1.1123	
			0.40	1.1705	
			0.60	1.2850	
			0.80	1.4236	
0.05	0.002	75	0	1.0000	0.88
			0.20	1.1003	
			0.40	1.2345	
			0.60	1.2890	
0.10	0.002	82	0	1.0000	0.90
			0.10	1.0159	
			0.20	1.0674	
			0.30	1.1458	
			0.40	1.1775	

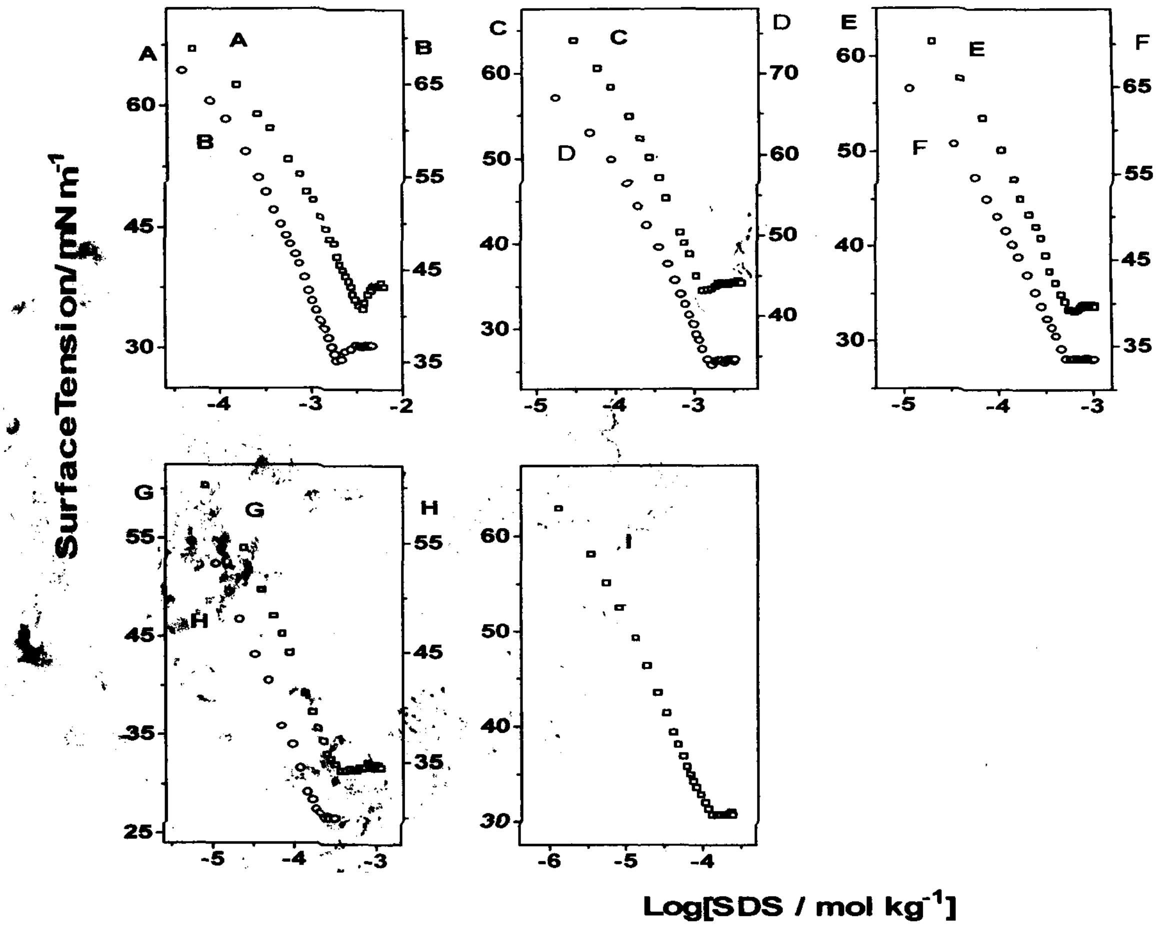

Figure 6.1 - Variation of surface tension of aqueous solution of SDS in the presence of NaCit with log[SDS] at 20 °C. The concentrations of NaCit in mol kg^{-1} are 0.0052 (A), 0.0150 (B), 0.0314 (C), 0.0568 (D), 0.0855 (E), 0.1016 (F), 0.1982 (G), 0.3033 (H) and 0.4116 (I).

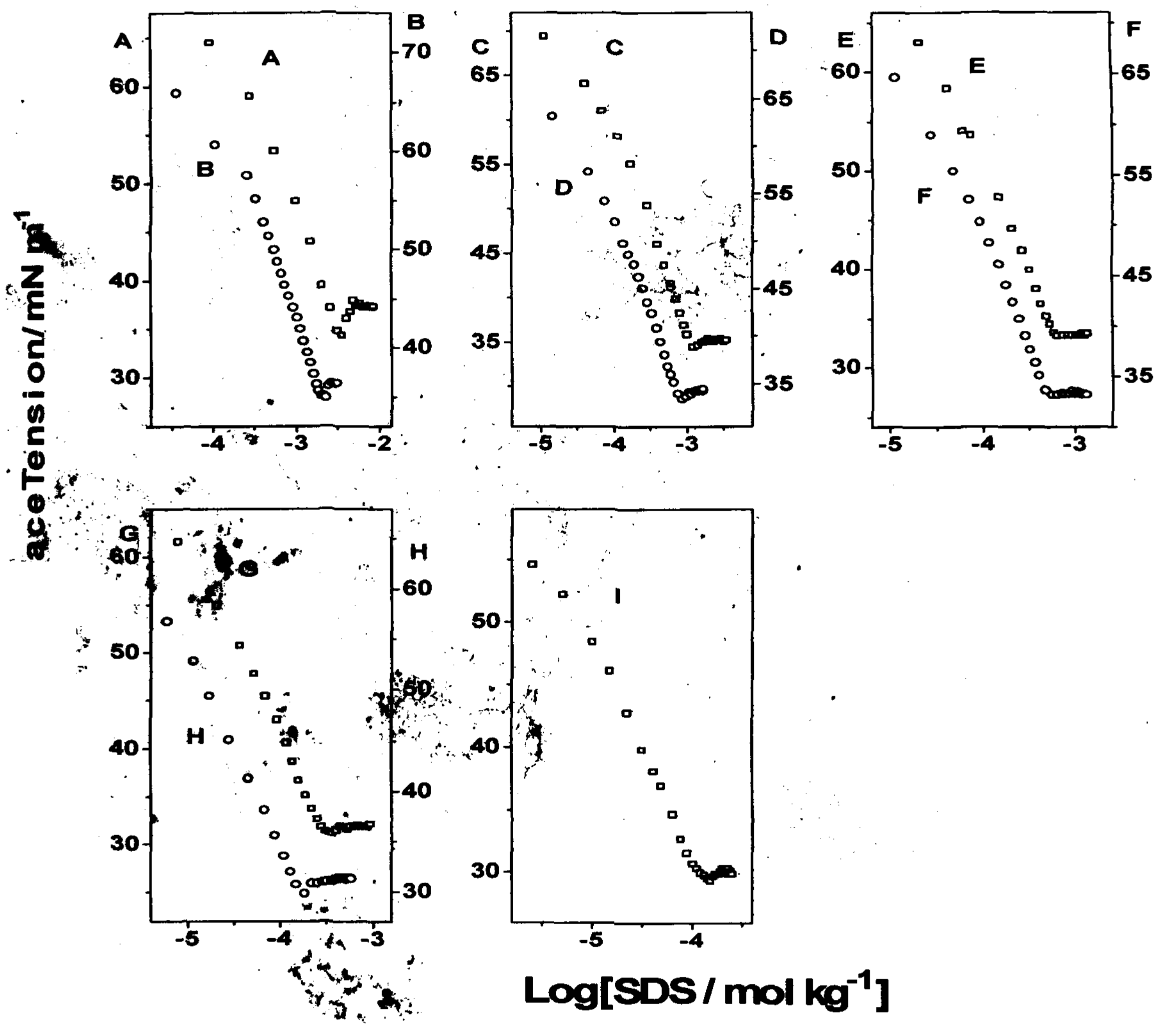

Figure 6.2 - Variation of surface tension of aqueous solution of SDS in the presence of NaCit with log[SDS] at 25 °C. The concentrations of NaCit in mol kg^{-1} are 0.0052 (A), 0.0150 (B), 0.0314 (C), 0.0568 (D), 0.0855 (E), 0.1016 (F), 0.1982 (G), 0.3033 (H) and 0.4116 (I).

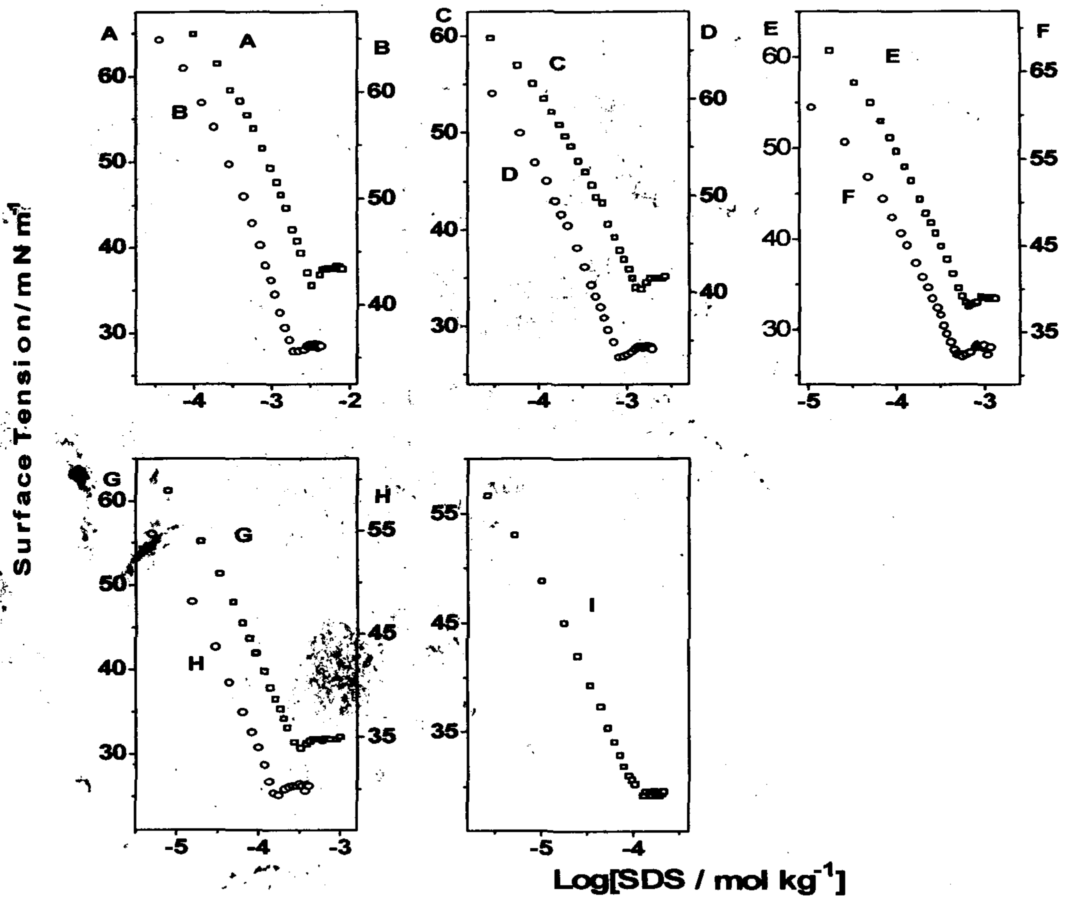

Figure 6.3 - Variation of surface tension of aqueous solution of SDS in the presence of NaCit with log[SDS] at 30 °C. The concentrations of NaCit in mol kg^{-1} are 0.0052 (A), 0.0150 (B), 0.0314 (C), 0.0568 (D), 0.0855 (E), 0.1016 (F), 0.1982 (G), 0.3033 (H) and 0.4116 (I).

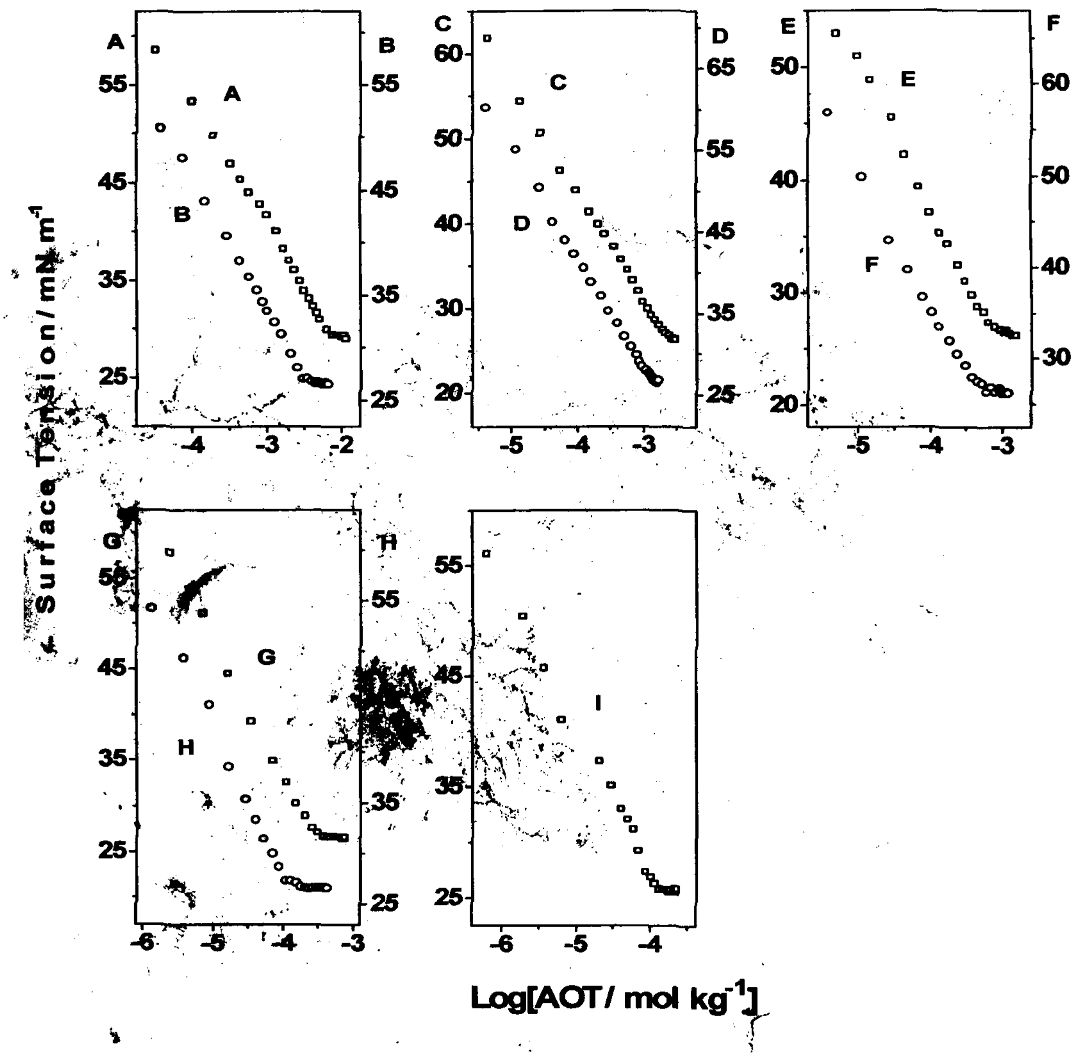

Figure 6.4 - Variation of surface tension of aqueous solution of AOT in the presence of NaCit with log[AOT] at 20 °C. The concentrations of NaCit in mol kg^{-1} are 0.0010 (A), 0.0069 (B), 0.0116 (C), 0.0277 (D), 0.0720 (E), 0.0986 (F), 0.1895 (G), 0.3261 (H) and 0.4335 (I).

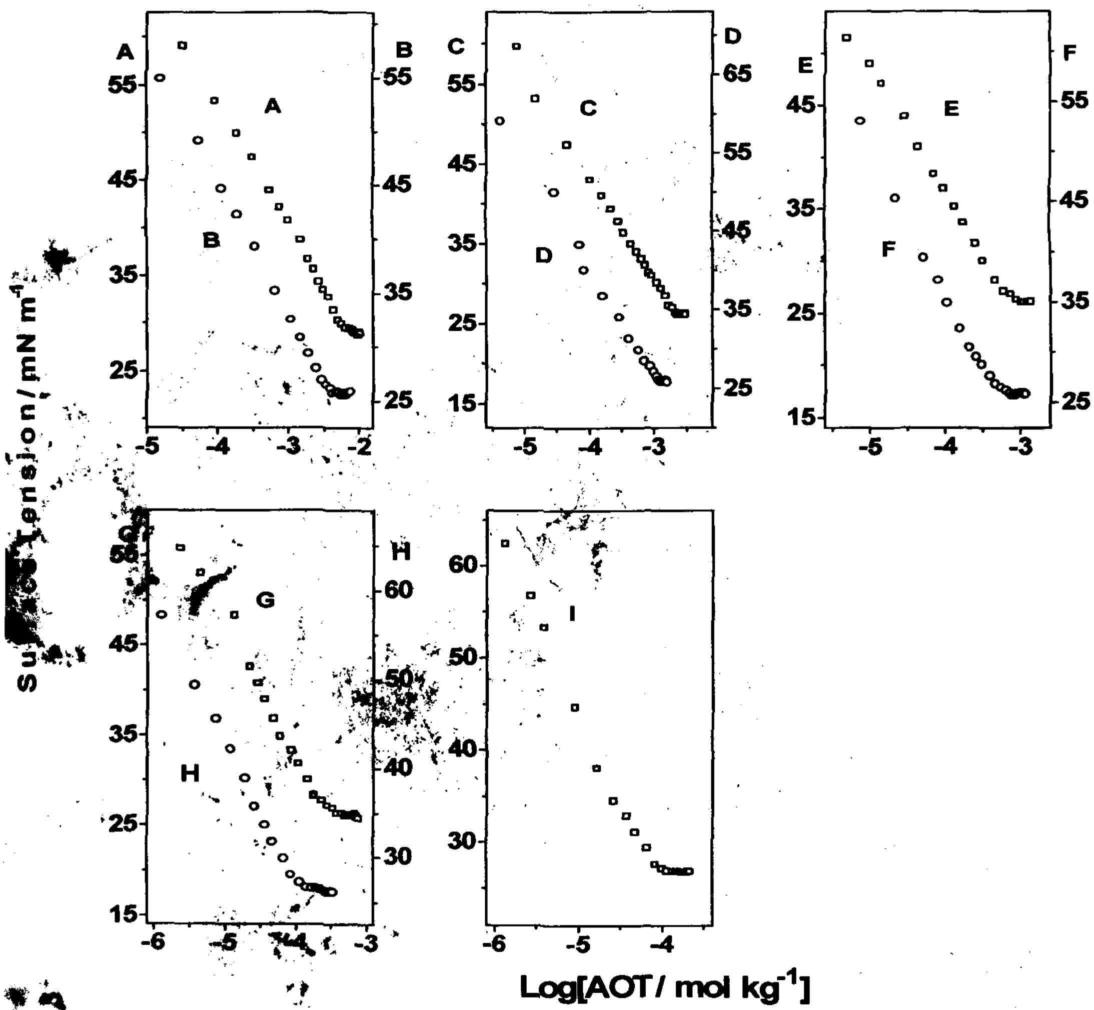

Figure 6.5 - Variation of surface tension of aqueous solution of AOT in the presence of NaCit with log[AOT] at 25 °C. The concentrations of NaCit in mol kg^{-1} are 0.0010 (A), 0.0069 (B), 0.0116 (C), 0.0277 (D), 0.0720 (E), 0.0986 (F), 0.1895 (G), 0.3261 (H) and 0.4335 (I).

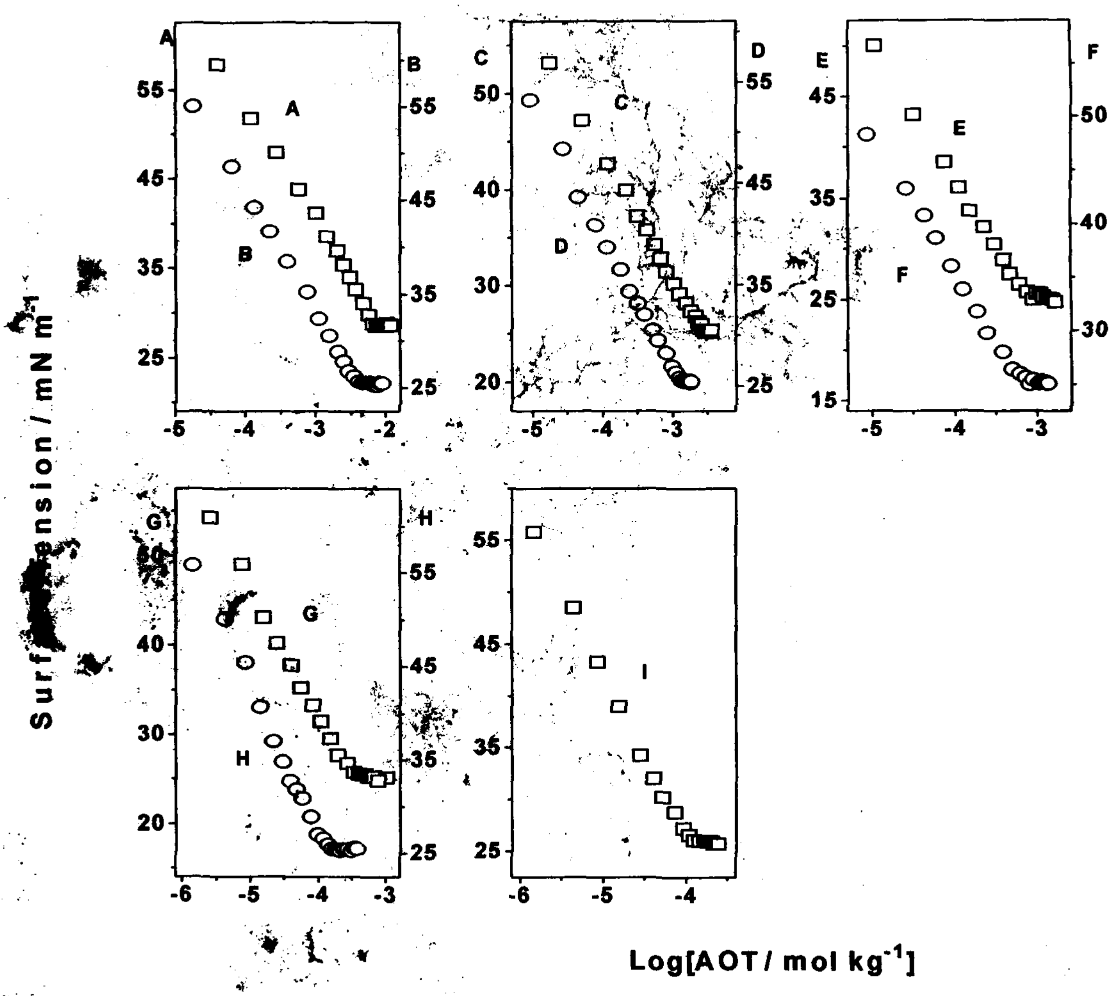

Figure 6.6 - Variation of surface tension of aqueous solution of AOT in the presence of NaCit with log[AOT] at 30 °C. The concentrations of NaCit in mol kg^{-1} are 0.0010 (A), 0.0069 (B), 0.0116 (C), 0.0277 (D), 0.0720 (E), 0.0986 (F), 0.1895 (G), 0.3261 (H) and 0.4335 (I).

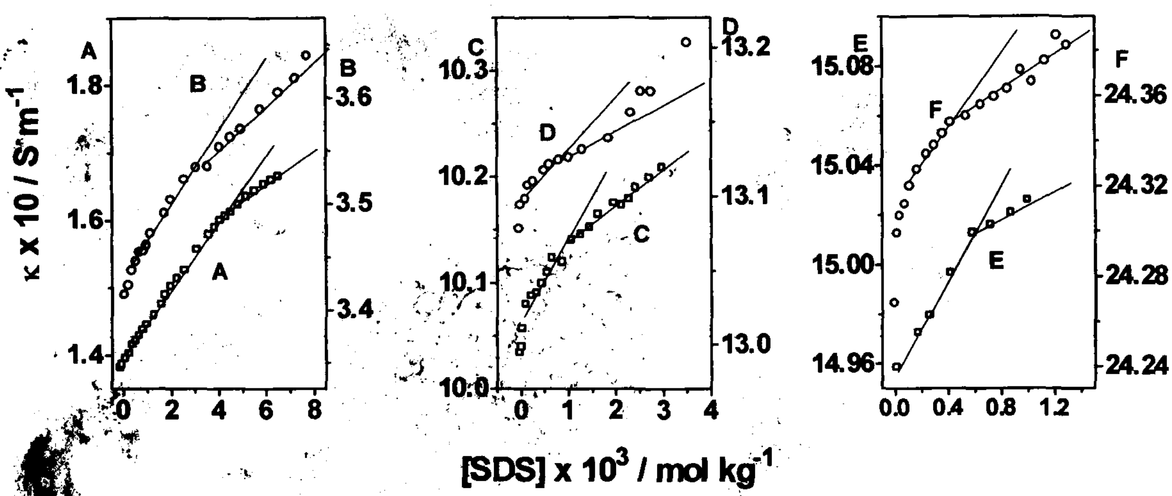

Figure 6.7 - Variation of specific conductance of aqueous solution of SDS in t presence of NaCit with concentration of SDS at 20 °C. The concentrations of NaCit in mol kg^{-1} are 0.0052 (A), 0.0150 (B), 0.0568 (C), 0.0855 (D), 0.1016 (E) and 0.1982 (F).

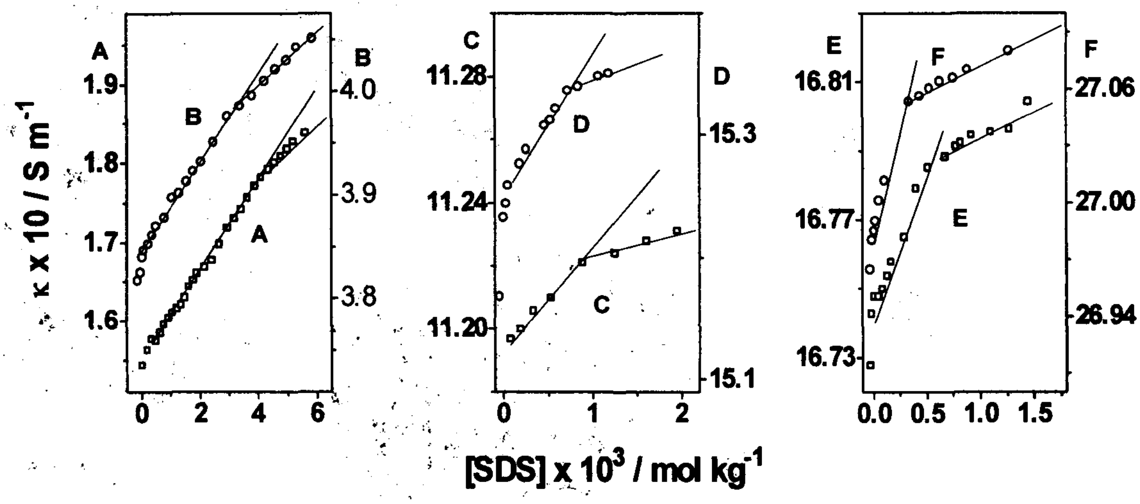

Figure 6.8 - Variation of specific conductance of aqueous solution of SDS in the presence of NaCit with concentration of SDS at 25 °C. The concentrations of NaCit in mol kg^{-1} are 0.0052 (A), 0.0150 (B), 0.0568 (C), 0.0855 (D), 0.1016 (E) and 0.1982 (F).

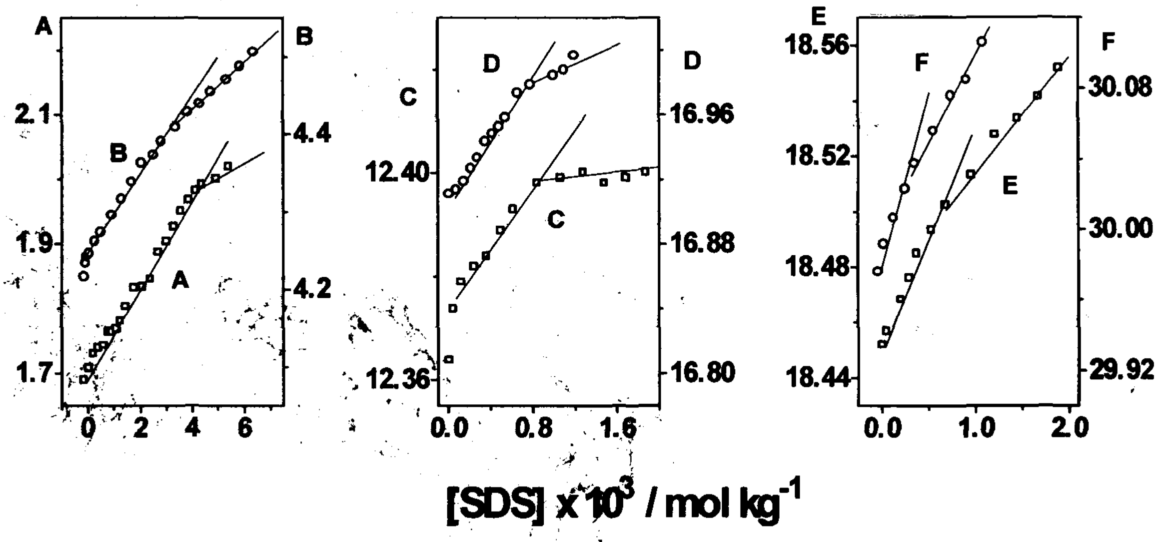

Figure 6.9 - Variation of specific conductance of aqueous solution of SDS in the presence of NaCit with concentration of SDS at 30 °C. The concentrations of NaCit in mol kg^{-1} are 0.0052 (A), 0.0150 (B), 0.0568 (C), 0.0855 (D), 0.1016 (E) and 0.1982 (F).

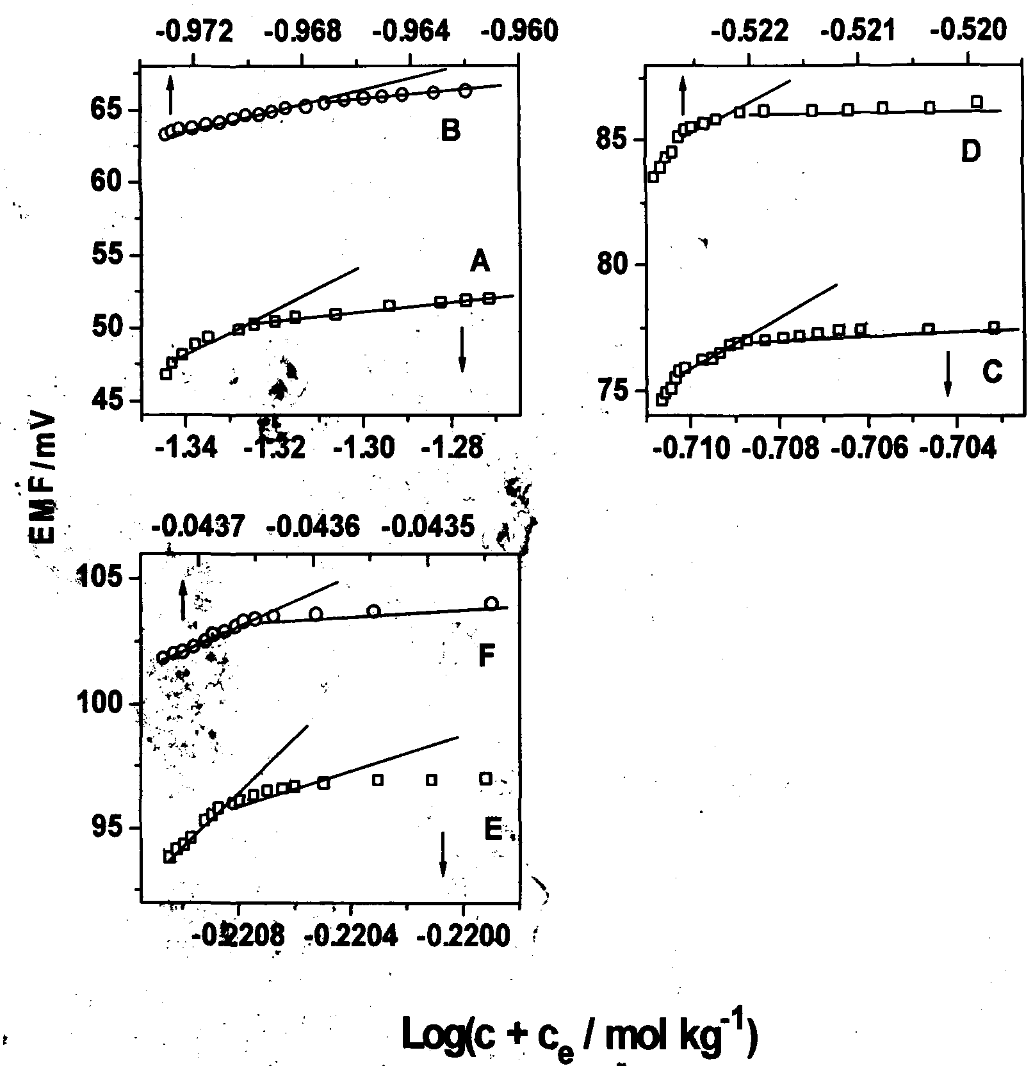

Figure 6.10 - Variation of EMF of aqueous solution of SDS in the presence of NaCit with Log [Na^+] at 25 °C. The concentrations of NaCit in mol kg^{-1} are 0.0151 (A), 0.0355 (B), 0.0649 (C), 0.1000 (D), 0.2004 (E) and 0.3014 (F).

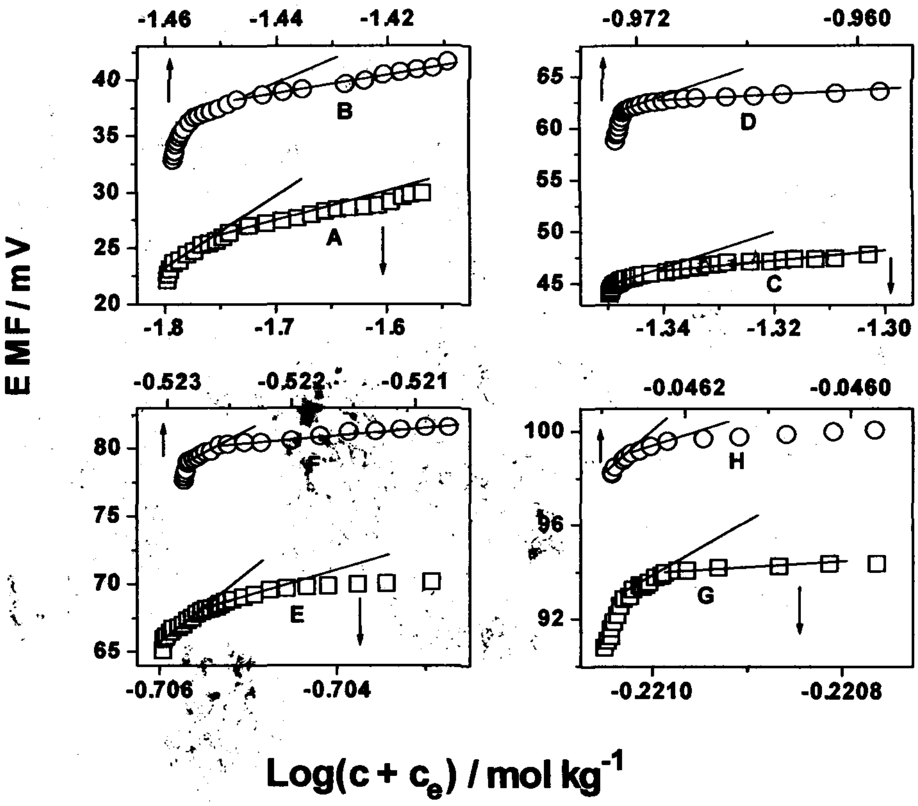

Figure 6.11 - Variation of EMF of aqueous solution of AOT in the presence of NaCit with log[Na^+] at 25 °C. The concentrations of NaCit in mol kg^{-1} are 0.0053 (A), 0.0116 (B), 0.0149 (C), 0.0355 (D), 0.0656 (E), 0.1000 (F), 0.2003 (G) and 0.2996 (H).

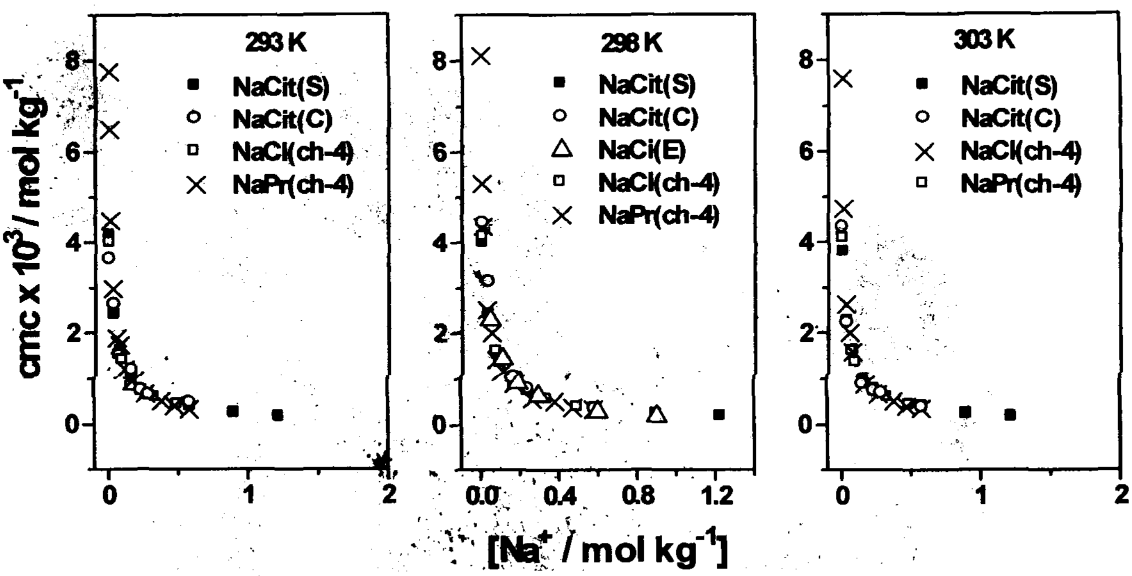

Figure 6.12 - Variation of cmc of SDS with the added Na^+ concentration. S, C and E letters given in the parentheses indicate that cmc is from surface tension, conductance and emf data, respectively. Cmc values of SDS in NaCl and NaPr solutions are taken from chapter 4.

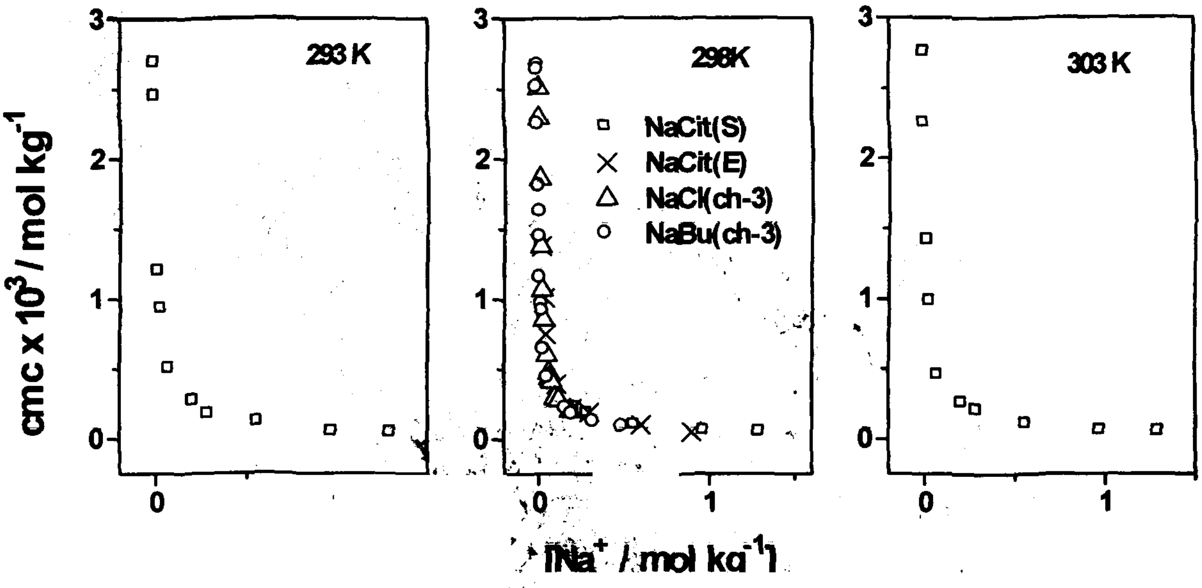

Figure 6.13 – Variation of cmc of AOT with the added Na^+ concentration. S and E letters given in the parentheses indicate that cmc is from surface tension and EMF, respectively. Cmc values of AOT in NaCl and NaBu solutions are taken from chapter 3.

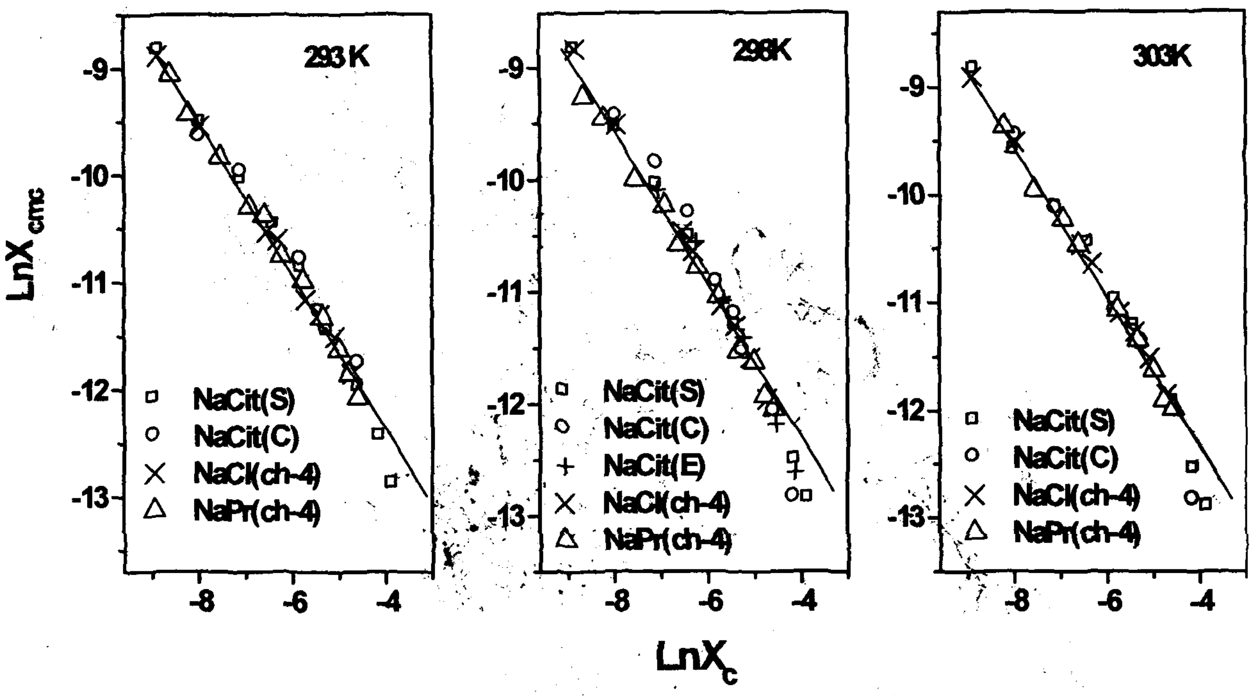

Figure 6.14 – Variation of ln X_{cmc} with ln X_c of SDS in NaCit solution. S, C and E letters given in the parentheses indicate that cmc is from surface tension, conductance and emf data, respectively. Data for SDS in NaCl and NaPr solutions were taken from chapter

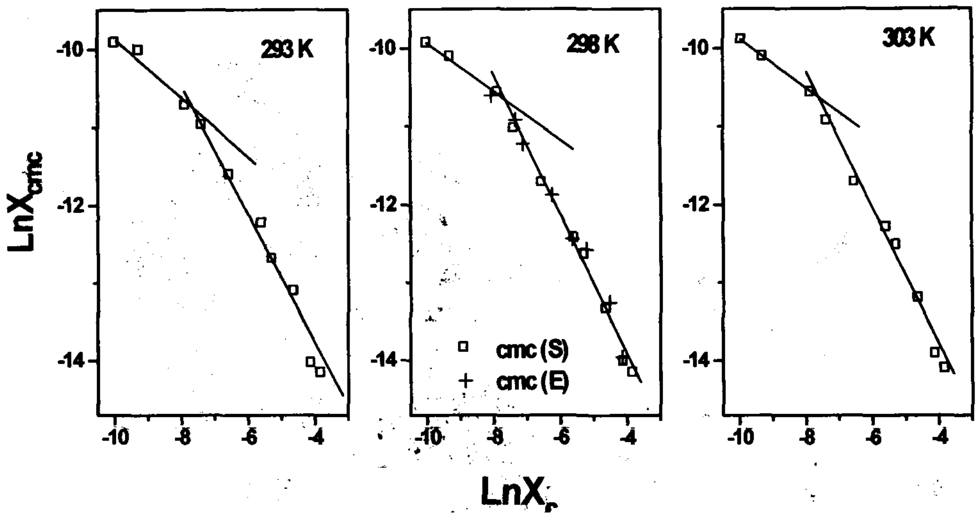

Figure 6.15 – Variation of ln X_{cmc} with ln X_c of AOT in NaCit solution. S and E letters given in the parentheses indicate that cmc is from surface tension and emf data, respectively. Data for SDS in NaCl and NaPr solutions were taken from chapter 4.

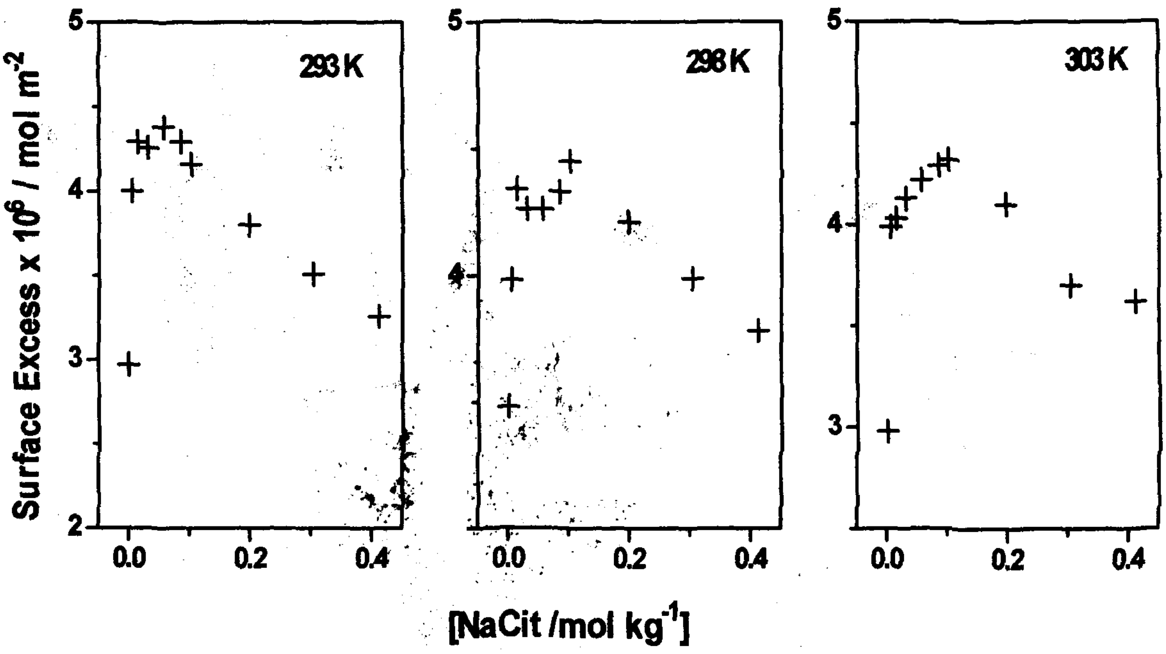

Figure 6.16 – Variation of surface excess of SDS at cmc with NaCit concentration.

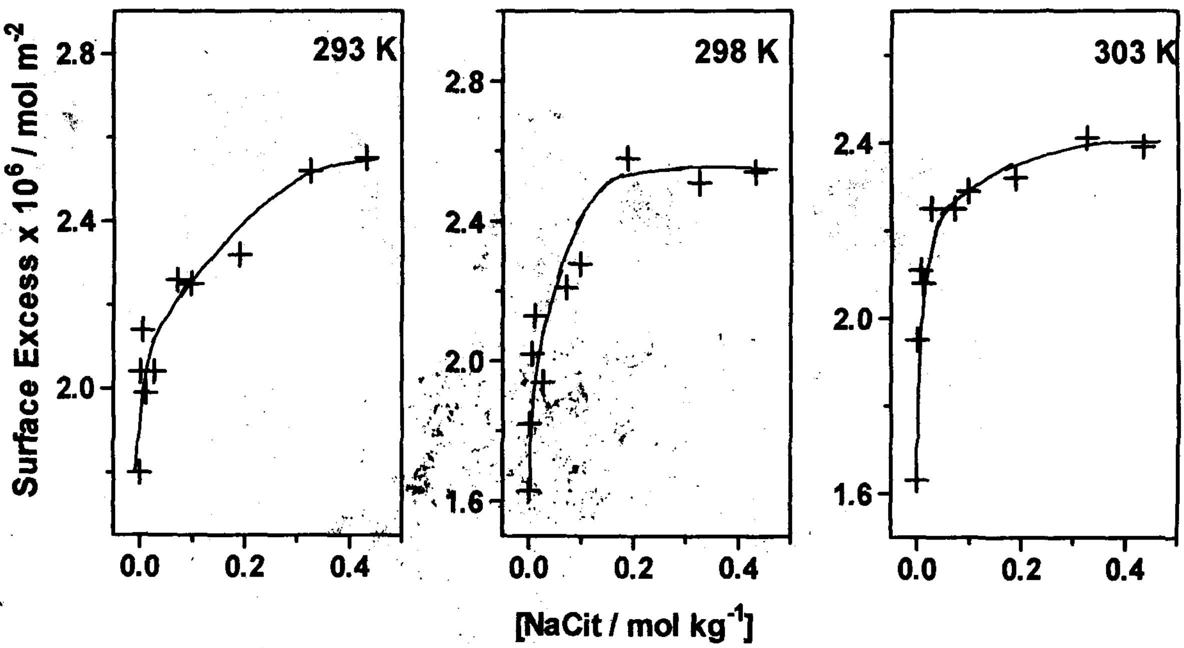

Figure 6.17 – Variation of surface excess of AOT at cmc with NaCit concentration.

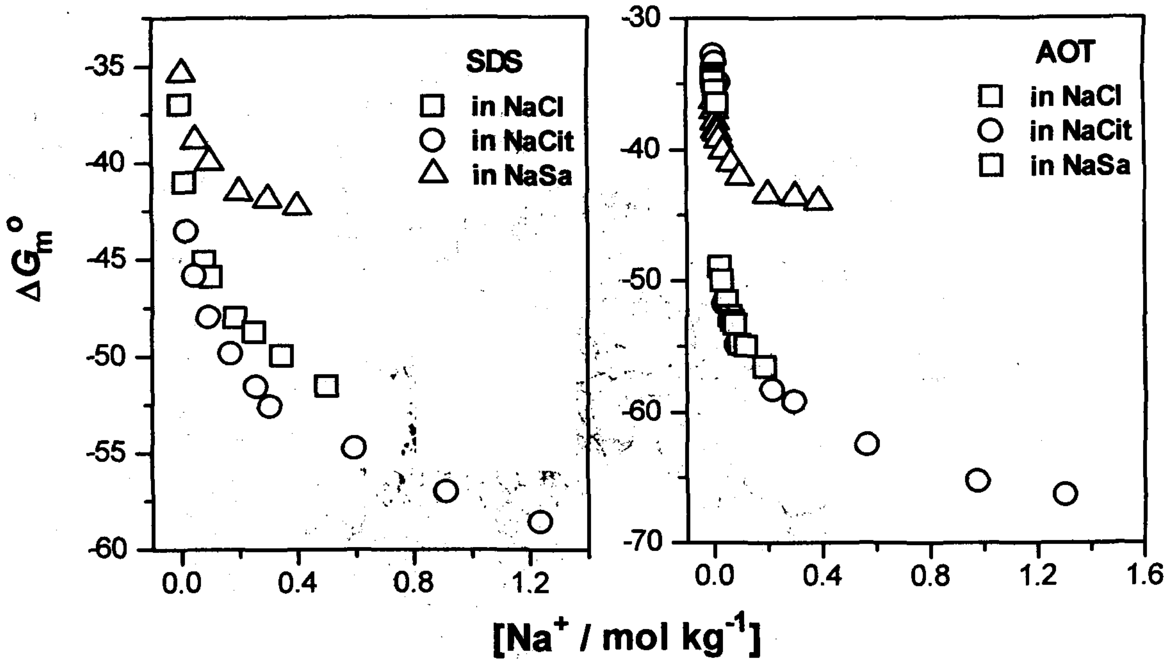

Figure 6.18 – Variation of standard free energy of micellization of SDS and AOT at 25 °C with the concentration of added sodium ion. Values of ΔG_c^0 in NaCl and NaSa are taken from chapters 3 –5.

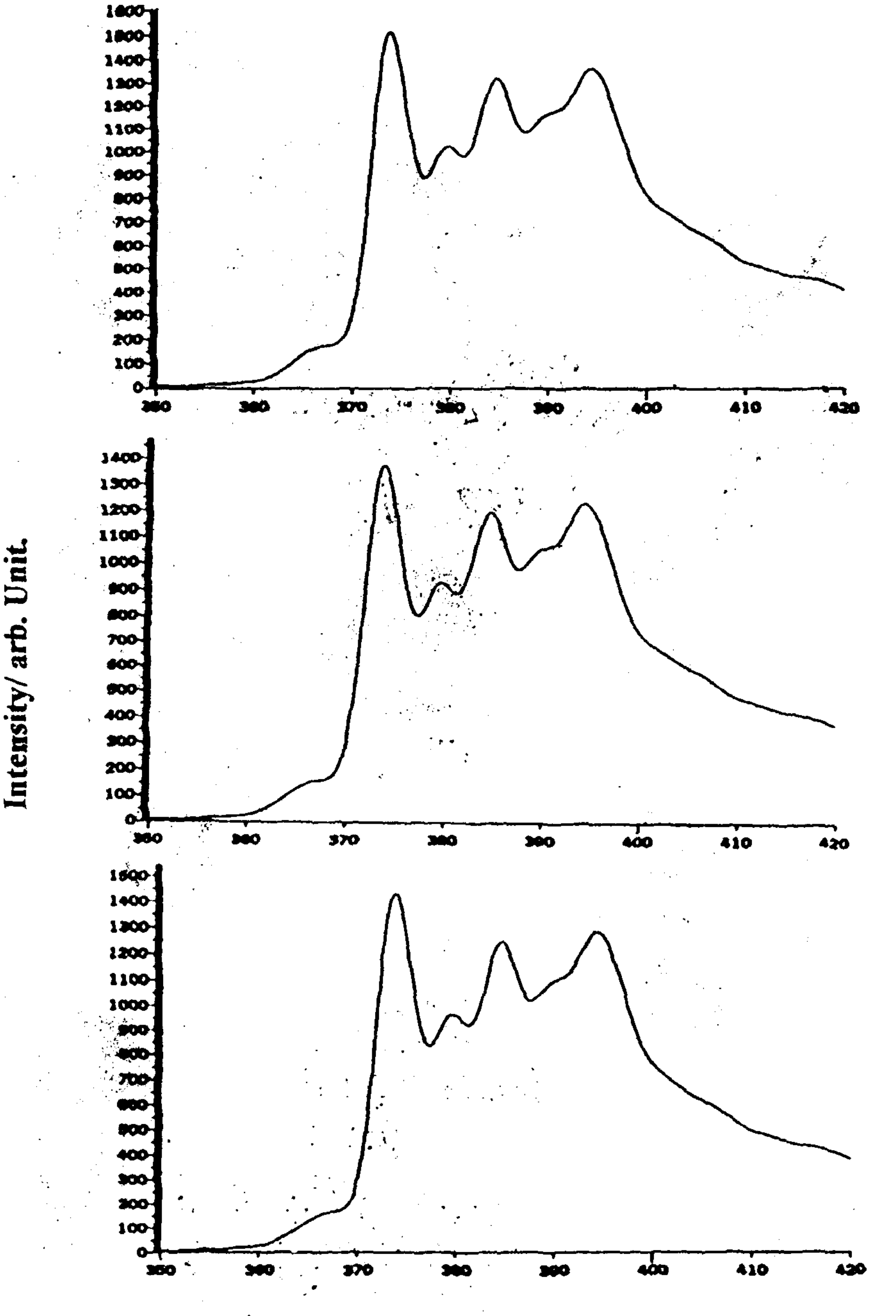

Figure 6.19 (a) – Few characteristic fluorescence emission spectra of pyrene in aqueous SDS (Conc. = 0.0010 mol kg^{-1}) in NaCit medium (Conc. = 0.0349 mol kg^{-1}). Top row contains no quencher, middle row, quencher conc.= 3.4 x10^{-6} and bottom row quencher conc = 8.95 x 10^{-6} mol kg^{-1}.

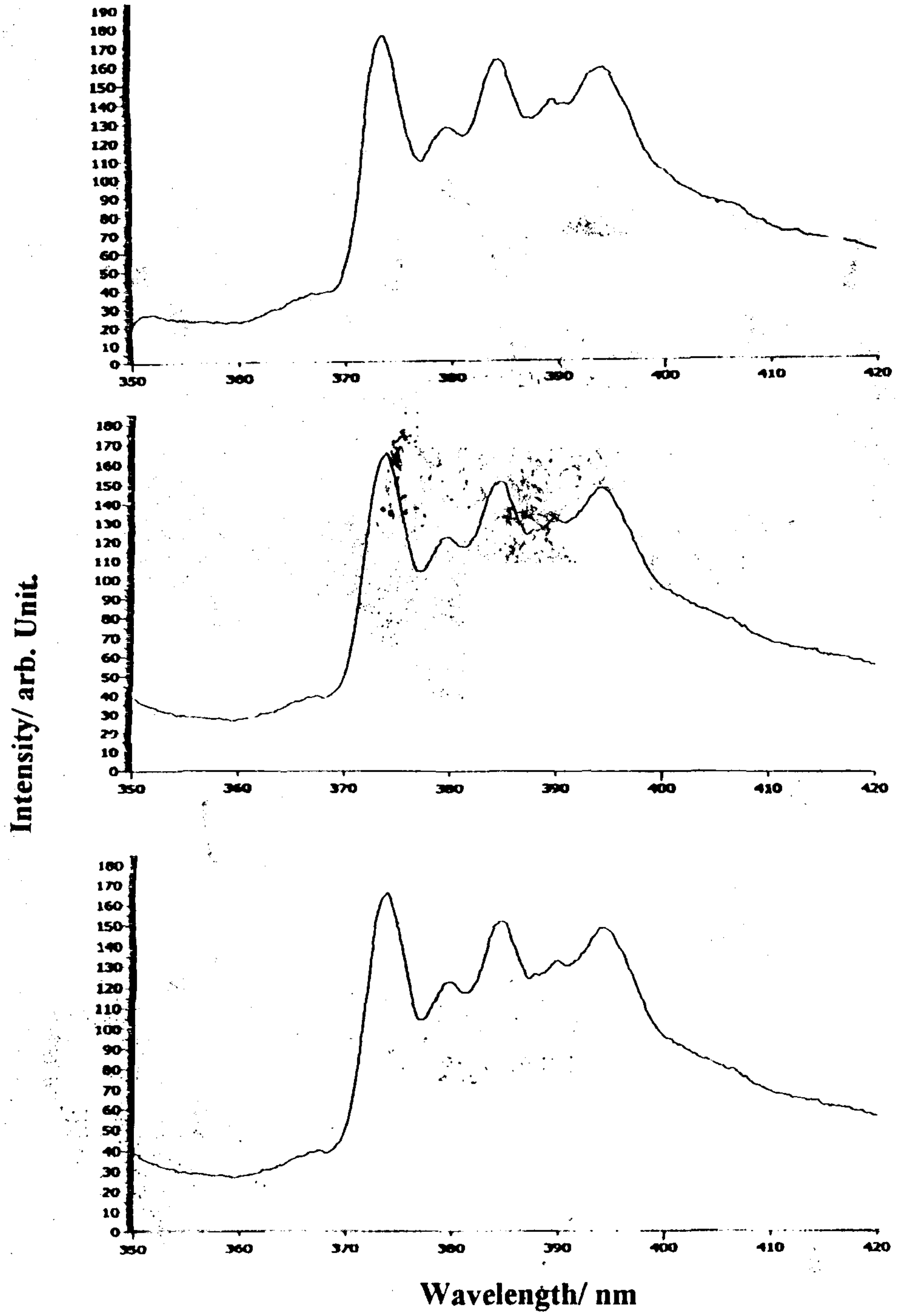

Figure 6.19 (b) – Few characteristic fluorescence emission spectra of pyrene in aqueous AOT (Conc. = 0.0030 mol kg^{-1}) in NaCit medium (Conc. = 0.009 mol kg^{-1}). Top row contains no quencher, middle row, quencher conc.= 1 $\times 10^{-6}$ and bottom row quencher conc=1.5 x 10^{-6}.

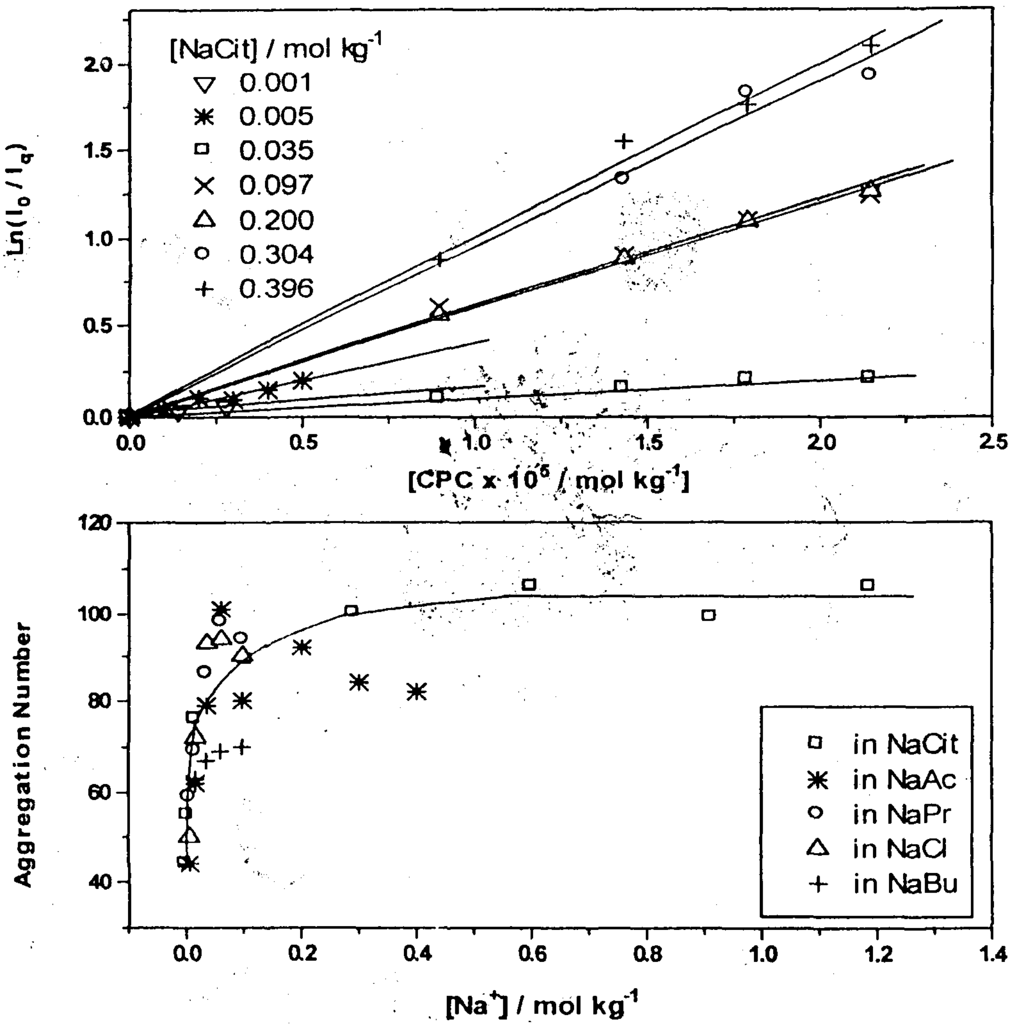

Figure 6.20 - Variation of ln(I_o/I_q) of pyrene with quencher concentration in aqueous SDS + NaCit solutions and plot of aggregation number of SDS versus added sodium ion concentration at 25 °C (Aggregation numbers of SDS in NaAc, NaPr, NaCl and NaBu solutions are taken from chapter 4).

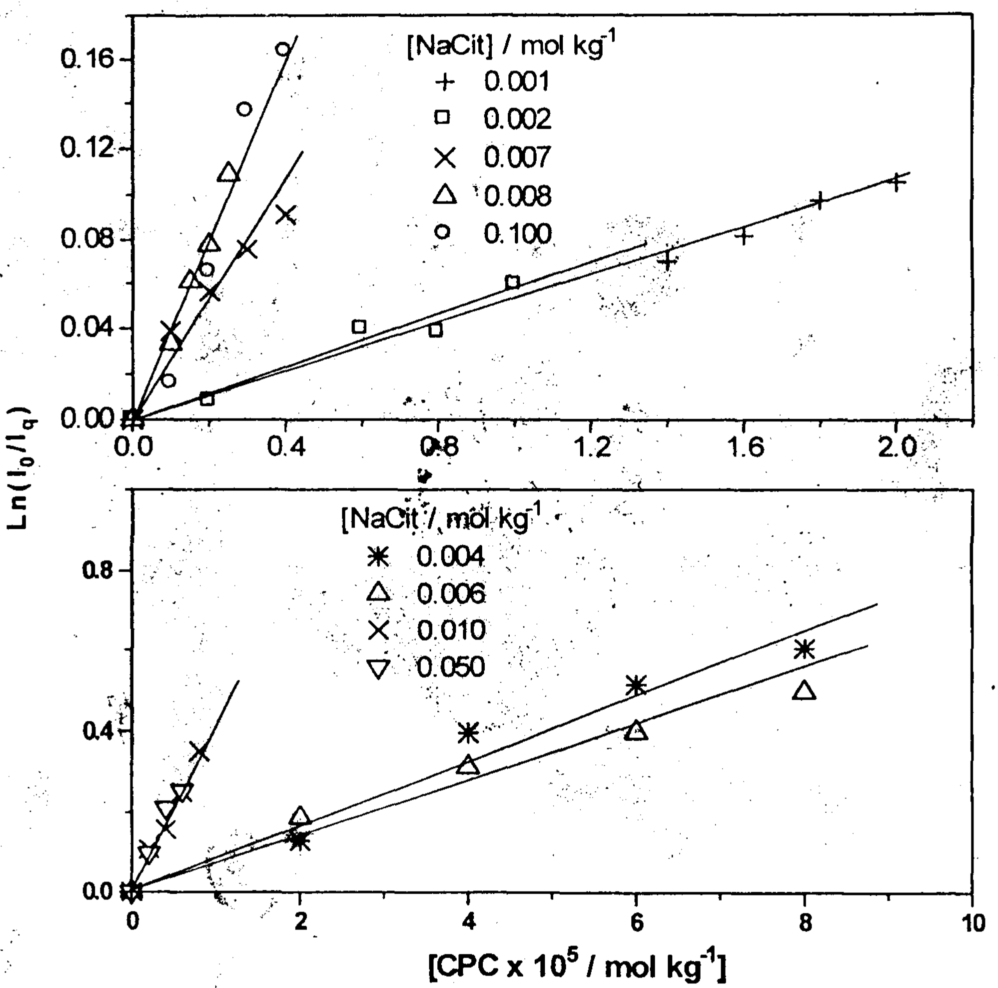

Figure 6.21 - Variation of $\ln(I_o/I_q)$ of pyrene with quencher concentration in aqueous AOT + NaCit solutions at 25 °C.

Research Publication

1) Effect of Surfactants on the Kinetics of base catalyzed hydrolysis of Methyl, Ethyl, Isopropyl and n-Butyl Acetates

   T. R. Choudhary, I. M.Umlong and S. N. Bhat.

   J. Indian Chem. Soc., **79**, 538 (2002)

2) Electrical Conductance Behavior of Oil-in-Water Microemulsions stabilized by Sodium Dodecyl Sulfate and 1- Butanol.

   K. Gunaseelan, I. M. Umlong, T. Mukhim and K. Ismail.

   Langmiur, **19**, 7276 (2003)

3) Micellization of AOT in aqueous sodium chloride, sodium acetate, sodium propionate and sodium butyrate media: A case of two different concentration regions of counter ion binding.

   I. M. Umlong and K. Ismail

   J. Colloid Interface Sci. **291**, 529 (2005).

4) Micellization Behaviour of Sodium Dodecyl Sulfate in different Electrolyte Media.

   I. M. Umlong and K. Ismail

   [Communicated to *Colloids surf. A*]

5) Micellization Behaviour of Sodium Dodecyl Sulfate in the presence of Sodium Salicylate.

   I. M. Umlong and K. Ismail

   [Communicated to *J. Surf. Sci. Technol.*]

Seminar/Conference Attended

1) Tenth National Conference on Surfactants, Emulsion and Bio colloids organized jointly by Dept. of Chemistry, N.E.H.U., Shillong and Indian Society for Surface Science and Technology, Kolkata during October 3-5th 2001

2) Conference on Energy and Societal Development in India organized by the Dept. of Atomic Energy, Govt. of India during September17-18th,2002.

3) 72nd Session of the National Academy of Sciences, India during October 25-27th, 2002

4) International Conference on Soft Matter organized jointly by the Indian Society for Surface Science and Technology and Centre for Surface Science, Jadavpur University, Kolkata during November 18-20th,2004.

Place: Shillong

Date: [illegible]/2006

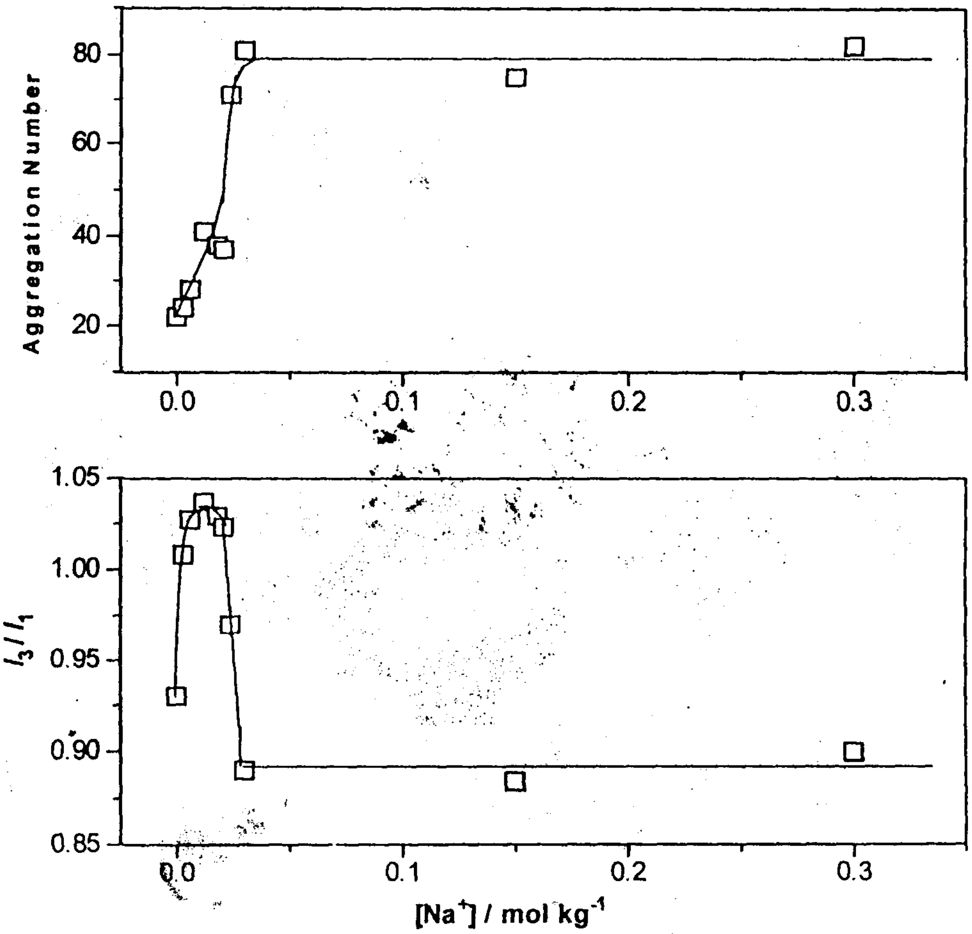

Figure 6.22 –Plots (i) of N_0 of AOT in presence of NaCit (top) and (ii) of I_3/I_1 ratio of pyrene in AOT+NaCit solution (bottom) against added sodium ion concentration at 25 °C

CURRICULUM VITAE

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Mother Tongue: Khasi

Nationality: Indian

Educational Qualifications:

M. Sc (Physical Chemistry – Specialization, 2000)	I Class with 64.2 %
B. Sc (Chemistry – Major 1998)	I Class with 60[illegible]
P.U. Sc (1995)	II class with 56.1 %
H. S. L. C. (1993)	II Class with 57.9 %

Instruments Handled

I have a sound knowledge in operating different instruments such as K11 Krüss Tensiometer, Jenway 3345 Ion Meter, Wayne Kerr B905 Automatic Precision Bridge, Hitachi F4500 FL spectrophotometer, and Anton Paar DMA 5000 Density Meter.