STUDIES ON THE MICELLIZATION BEHAVIOUR OF SURFACTANTS IN SELECTED SOLVENT MEDIA

ABSTRACT

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In Chapter 1, a general introduction to the subject is given and the scope of the work is described.

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also occurs. Therefore, it is concluded that counterion binding constant of ionic micelle is a micellar shape dependent parameter. From the present study it is proposed that β of prolate ellipsoidal shaped micelle is less than that of rod-like shaped micelle. This is consistent with the proposition made by Fujio et al. that the value of β follow the order, spherical < oblate ellipsoidal < rod-like micelle. Generally, the counterion binding is thought to be one of the factors determining size and shape of ionic micelles. It emerges from this study that counterion binding controls the size of micelles, but shape change occurs due to geometrical requirement. Since a shift in the value of β takes place as the micellar shape changes, surface charge density (ratio of micellar charge to its surface area) rather than surface charge appears to control β. This concept can be applied to explain why sodium deoxycholate (bile salt) micelle has very low value of β.

Chapter 4 deals with the study on the aggregation and adsorption characteristics of AOT in aqueous ammonium chloride solutions. Critical micelle concentration of AOT in aqueous medium at 25 °C as a function of NH_4Cl concentration has been determined by measuring surface tension and fluorescence emission of pyrene probe. This study revealed that the SCB of AOT exists in the presence of mixed counterions also. The concentration c* of NH_4Cl (0.009 mol kg^{-1}) at which the counterion binding constant of AOT changes suddenly is lower than that of NaCl (0.015 mol kg^{-1}). In the presence of added NH_4Cl, as in the case of added NaCl, the sudden change of counterion binding constant of AOT is attributed to the change in the micellar

shape. Due to binding of NH_4^+ the surface area of the AOT micelle increases causing increase in the surface area-to-volume ratio of the micelle, which may be responsible for a transition from prolate to cylindrical shape of AOT micelle at a lower concentration of NH_4Cl. In the region of prolate shape (below c*) the amounts of bound sodium and ammonium counterions are almost equal, whereas in the region of cylindrical shape (above c*) bound counterions are predominantly ammonium. It is concluded from this study that (i) cmc depends mostly on the total counterion concentration in the solution and very less on the specific type of the cationic counterions present in the solution and (ii) synergism in the cmc retarding ability of counterions takes place when they are mixed and added to ionic surfactant solutions. In the AOT + NH_4Cl system, the plots of Corrin-Harkins (CH) equation and modified CH equation look similar unlike in the case of CPC + NaSa / NaBz system, which implied that when the mixed counterions are inorganic cations CH equation can still be used as an empirical equation. It has been shown that the expression for the surface excess of AOT in the presence of Na^+ and NH_4^+ counterions becomes similar to the expression for surface excess of AOT in the presence of Na^+ counterion alone, provided we consider the mixed counterions to obey Henry's adsorption isotherm. This approach provides a method to compute the surface excess of ionic surfactants in the presence of mixed counterions.

In Chapter 5 we studied the counterion binding behaviour of AOT and SDS (sodium dodecylsulfate) in aqueous ethylene glycol medium. It has been

confirmed that cmc of AOT in ethylene glycol is more (about 68 times) than that in water and the variation of cmc of AOT in water + EG media as a function of EG content follow the general trend. The special counterion binding behaviour of AOT has a dependence on the solvent and disappears in water + EG media containing $\geq$ 30 weight % EG. In water + EG medium, the CH equation is not applicable to ionic surfactants for determining the counterion binding constant when the EG content becomes $\geq$ 40 weight %.

In Chapter 6 we have studied the competitive counterion binding controlled conductivity behaviour of sodium dodecylsulfate in aqueous nitric acid medium. This study has revealed that SDS in aqueous HNO_3 medium can exhibit both the unusual and the normal conductance behaviours. The normal conductance behaviour of SDS in acid medium is observed only if $c_0/c_a > 3.4$ (c_0 and c_a refer to critical micelle concentration and acid concentration, respectively), which was not reported from the earlier studies in aqueous HCl medium. On the basis of the present results, it is predicted that solutions of ionic surfactant + electrolyte with foreign counterion would exhibit unusual conductance behaviour (i) if the two counterions have large difference in their limiting ionic conductivity and undergo competitive binding to the ionic micelle, and (ii) if $c_0/c_a < 3.4$. The mixed-electrolyte model together with the Debye-Huckel-Onsager and the pseudophase-ion exchange models is applied successfully to analyze the conductivity data of ionic surfactant + electrolyte solutions no matter such solutions consist of mixed counterions and show unusual conductance behaviour. The relative values of the binding constants

of the two counterions are controlled by c_a, c_s (surfactant concentration) and c_0. The exchange of sodium and hydrogen counterions at the micellar surface has no significant effect on the cmc of SDS implying that these two counterions are not markedly discriminated by the dodecylsulfate micelle. A very useful conclusion of this study is that SDS + aqueous HNO_3 medium with $[HNO_3] \geq 0.02M$ can be used as an alternative soft and green medium for nitration of organic molecules.

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By

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DEPARTMENT OF CHEMISTRY
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SUBMITTED

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NORTH EASTERN HILL UNIVERSITY
SHILLONG – 793022
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2011

DEDICATED TO

ALL MY TEACHERS

The North Eastern Hill University

Declaration

Month: August **Year: 2011**

I, Jahar Dey, 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.

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CONTENTS

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CHAPTER 1

General Introduction

1.1 Surfactants

Surfactants are molecules having the unique property to aggregate in the systems in which they contain. They have the ability to modify the physico-chemical properties of the surfaces or interfaces. For this reason they are referred to as surface-active-agents. The chemical structure of a surfactant comprises of two parts: a non-polar hydrophobic portion and a polar hydrophilic portion due to which they possess amphiphilic behaviour, viz., hydrophobicity and hydrophilicity towards water medium. The polar hydrophilic part of a surfactant molecule is known as head group and the hydrophobic part consisting of hydrocarbon chain with eight or more carbon atoms is called the tail. Surfactants are known to exhibit amphiphilic character in solvents other than water also. Hence, in general, solvophobicity and solvophilicity terms are used to represent the dual characters of surfactants.

1.1.1 Classification

Surfactants can be broadly classified into two broad categories, i.e., biosurfactants and synthetic surfactants. The surfactants which occur naturally are called biosurfactants and are mostly found in the biological systems. Examples are phospholipids, fatty acids, bile salts, etc. The surfactants used for domestic and commercial purposes are the synthetic ones. Soaps and detergents are formulations containing mainly synthetic surfactants as active components. Both natural and synthetic surfactants are further classified as anionic, cationic, nonionic and zwitterionic.[1]

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

Cationic surfactants contain positively charged head groups. 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 these surfactants can behave as anionic or cationic or neutral species. The more commonly used zwitterionic surfactants include N-alkyl and C-alkyl betaines, phosphatidyl amino alcohols and acids.

Surfactant molecules containing two hydrophobic tails attached to one head group are also known. Sodium dioctylsulfosuccinate (anionic; commonly known as Aerosol-OT or simply AOT) and dioctadecyldimethylammonium chloride (cationic) are examples of such surfactants. 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 gemini (or dimeric) surfactants if the spacer is between the two head groups or bolaforms if the spacer is between the hydrocarbon chain.[3] The length of the spacer can be varied by varying the number of carbon atoms. Efforts are being made to synthesize newer surfactants with special properties, for e.g., photo-sensitive surfactants.[4-6]

1.1.2 Adsorption and aggregation

The amphiphilic character of surfactants provides them with the unique dual property of aggregation and adsorption. Due to adsorption, surfactants have the property to lower the surface tension of a solution forming monolayers, films and multilayers. The aggregation property of the surfactants is responsible for the formation of structures such as micelle, vesicles, membranes, etc. The various applications of surfactants are due to these two important properties.

1.2 Thermodynamics of adsorption: Gibbs adsorption isotherm

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

$$dG_\sigma = \gamma d\sigma + \sum_i \mu_i dn_{i\sigma} \qquad (1.1)$$

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 i^{th} component and $dn_{i\sigma}$ is the change in the amount of the i^{th} 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

$$d\gamma = -\sum_i \Gamma_i \, d\mu_i \qquad (1.2)$$

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 i^{th} component. Γ_i is the surface excess of the i^{th} component and is defined as

$$\Gamma_i = n_{i\sigma} / \sigma \qquad (1.3)$$

$n_{i\sigma}$ and Γ_i can be positive or negative. Eq. (1.2) is known as the *Gibbs adsorption isotherm*. For a two-component system at constant temperature and pressure Eq. (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. Eq. (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 a_2 can be replaced by the concentration term c_2. For a surfactant solution, we can now write the Gibbs adsorption isotherm as

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

where c and Γ are the concentration and surface excess of the surfactant, respectively. Since Γ is positive for surfactants, $d\gamma/d\ln c$ 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.[7] 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

$$RM \rightarrow n_- R^{z-} + n_+ M^{z+} \qquad (1.7)$$

$$XM \rightarrow n_{-e} X^{s-} + n_{+e} M^{s+} \qquad (1.8)$$

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

$$d\gamma = -RT\,[\Gamma_M d\ln c_M + \Gamma_R d\ln c_R + \Gamma_X d\ln c_X] \qquad (1.9)$$

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

$$c = \frac{c_R}{n_-}, \qquad c_e = \frac{c_X}{n_{-e}} \qquad (1.10)$$

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

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

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

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

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

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

1.4 Micelle formation

The second important property of surfactant molecules is their property to aggregate in a particular solvent media to form associated species known as micelles.[8] The forces responsible for micelle formation is the hydrophobic interaction. Water molecules become more ordered around the hydrocarbon tail of a surfactant. Transfer of hydrophobic tails of a surfactant

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

The process of micellization of surfactants takes place beyond a particular concentration of the surfactants referred to as the critical micelle concentration (cmc). The onset of micellization is accompanied by a sudden change in the physical properties of the solution, thus enabling us to measure the cmc experimentally. Normally, changes in physical properties like surface tension, conductivity, viscosity, solubilization, osmotic pressure, etc, take place over a narrow concentration range. Since the changes take place over a narrow concentration range, precise determination of cmc is difficult and the cmc values obtained by different methods may also differ. Thus, numerous methods are available for determining the value of cmc.[9] Tensiometry, conductometry, fluorimetry and calorimetry are some of the commonly used methods. The determination of the critical micelle concentration is the first step in understanding the micellization behavior of surfactants. Various factors affect the cmc of which the most widely studied are the affect of added electrolytes and the structure of the surfactant monomers. Cmc is also 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. As mentioned, added electrolytes affect cmc drastically. In fact the nature of counter ion, its radius and valence, also largely affects the value of cmc of ionic surfactants.[10-16] Added electrolytes have significant effect on the cmc of both ionic and nonionic surfactants.[10-18] The addition of electrolytes also affects other properties of surfactants like cloud point,[19-21] free energy of micellization,[17] aggregation number,[22-29] etc. Non-electrolytes like urea, amides, alcohols, etc on addition produce both increase and decrease of cmc of surfactants.[30-34] The temperature dependence[35-41] of cmc is quite interesting. Most of the ionic surfactants exhibit at some temperature a minimum in the cmc.[35,36,38] This property of ionic surfactants is used in the differential scanning calorimetry technique for studying the micellization behavior of ionic surfactants.[42] With increase in pressure cmc of ionic surfactants in water show a maximum.[43-50] Our recent study also revealed that aromatic counter ions drastically lower the cmc of ionic surfactants as these counter ions can bind both electrostatically as well as hydrophobically to the ionic micelle.[51]

Aggregation number is another important fundamental parameter concerning a micelle and it is equal to the number of monomers present in a

micelle. It gives an idea about the size of a micelle. Aggregation number also shows dependence on the structure of a surfactant and on the amount of added electrolyte.[22-29] 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.[52-55] In a particular surfactant solution micelles of different aggregation number can exist.[56] Such polydispersity is generally ignored for calculation purpose and only monodispersed micelles with single (average) 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.[22-24, 28, 29, 53, 57, 58]

Counter ion binding constant (β) is an important characteristic of ionic micelles. Counter ions control, besides cmc and aggregation number of ionic surfactants, also the reactions[59] that take place in the presence of ionic surfactants. The shape of an ionic micelle appears to have an influence on the value of β. In non-aqueous polar solvent media, β generally has lower value than in water.

Thermodynamic functions such as Gibbs function, enthalpy and entropy of micellization and surface potential of ionic surfactants are other related micellization parameters. Due to the presence of effective electric charge on the ionic micelle, an electric potential is developed at the surface of the ionic micelle, which is known as surface potential of the ionic micelle.

The surface potential value controls different processes that take place near the micelle – solution interface. Some other parameters/properties of surfactants that are related to their micellization are Kraft temperature, cloud point and solubilization.

1.6 Structure and shape of ionic micelles

Micelles have regular structures and shapes. A general structure of a regular ionic micelle formed in polar solvents[60] 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[61,62] to penetrate into the liquid-like hydrocarbon core.

Since micelles are in dynamic equilibrium with the surfactant monomers, considering them to have rigid structures with precise shapes may be unrealistic. Small-angle neutron scattering experiments on micellar solutions,[23,53,57,63,64] dynamic light scattering experiments and phase diagram

studies support the concept of micelles having regular shapes.[22-24,52,65,66] It is assumed that micelles at concentrations near to the cmc 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. The other proposed structures of micelles include the rod-like,[67] the lamellar model[68] and the disk or cylindrical model.[69] 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.[22,23,66,70-72] 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.[26]

1.7 Thermodynamics of micelle formation

Two approaches are used to understand the thermodynamics of the micellization process, which are Phase – Separation and Mass – Action models. In the Phase – Separation model the micelles are considered to form a separate phase at the cmc in equilibuium with the solution phase, while in the Mass – Action model 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[73] has also

been applied to the aggregation of solutes. The phase – separation and the mass – action models are briefly discussed below.

1.7.1 Phase – Separation model

In this approach the micelle is treated as a separate phase. Appropriate standard states are to be defined first in order to calculate the thermodynamic parameters of micellization. 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.[74,75]

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

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

For a non-ionized surfactant

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

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 Eq. (1.22) is therefore written as

$$\mu_s = \mu_s^0 + RT \ln X_s \qquad (1.23)$$

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

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

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

$$\Delta G_{mic}^0 = \mu_m^0 - \mu_s^0 = \mu_m - \mu_s + RT \ln X_s = RT \ln X_s \qquad (1.25)$$

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

$$\Delta G_{mic}^0 = RT \ln X_{cmc} \qquad (1.26)$$

In the case of ionic surfactants, ΔG_{mic}^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 consists of n moles of surfactant monomer and m moles of counter ion, β = 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 Eq. (1.26) therefore modifies to

$$\Delta G_{mic}^0 = RT \ln X_{cmc} + \beta RT \ln X_c \qquad (1.27)$$

where X_c 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 Eq. (1.27) becomes

$$\Delta G^0_{mic} = (1 + \beta)RT \ln X_{cmc} \qquad (1.28)$$

1.7.2 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

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

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

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

Substituting the value of K from Eq. (1.30), we get

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

Eq. (1.32) can be rearranged to the form

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

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 Eq. (1.33) becomes

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

Just above the cmc, we can approximate

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

c_0 denotes cmc. Eq. (1.34) now becomes

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

In mole fraction units Eq. (1.36) can be written as

$$\ln X_{cmc} = A - \beta \ln X_M \qquad (1.37)$$

where $\Delta G^0_{mic}/RT$ is represented by A. Eq. (1.37) is similar to Eq. (1.28). Eqs. (1.27), (1.28), (1.36) and (1.37) are the different forms of the Corrin – Harkins equation.[76]

1.8 Scope of the work

Solvophobic interaction is a type of solvent – solute interaction where the solute has either full or partial solvophobicity. Similarly, solvophilicity is

also due to solvent – solute interaction. When the solutes are amphiphilic in nature, solvophobic interaction leads to two significant phenomena, viz. adsorption and aggregation. Thus, adsorption and self-organization of surfactants take place only in the presence of a solvent. Solvents therefore play a decisive role in controlling the adsorption and micellization characteristics of surfactants. For instance, solvophobicity of the tail part of a surfactant towards one solvent can change over to solvophilicity in another solvent. Consequently, a particular surfactant may form normal micelles, no micelles or reverse micelles by changing the polarity of solvent. Recent works of Eastoe and coworkers[77] illustrate the profound effects of solvent properties on aggregation and adsorption of surfactants. Despite extensive studies made on the micellization behaviour of surfactants in different types of media, it is still not exactly clear which property of a solvent controls the micellization process, although hydrogen bonding between the solvent molecules is considered to be a prerequisite for aggregation of surfactants. Moreover, quantifying solvophobicity and solvophilicity is still an unsettled problem. Studying the adsorption and aggregation behaviours of surfactants in different solvents of varying property therefore provides useful information of fundamental and practical importance. The different solvent media used for such study are (i) water in the absence and presence of various types of additives that alter the water structure, (ii) non-aqueous polar solvents including ionic liquids, (iii) mixed solvents containing water and organic polar solvent, and (iv) non-polar organic solvents. Continued studies on the

adsorption and micellization behaviours of surfactants in organic polar solvents and their aqueous mixtures indicate the importance and relevance of such studies.[77,78-127]

The importance of solvent quality on the ability of a surfactant to aggregate/micellize/self-organize is stated above. Added to this, in a chosen solvent medium there are several aspects which affect the micellization characteristics of a surfactant. As mentioned in section 1.5, addition of electrolytes and even non-electrolytes has pronounced effect on the micellization of both ionic as well as nonionic surfactants. Electrolytes affect cmc, aggregation number, surface activity, micellar shape, polarity at the micellar interface and many other related micellization parameters. The effect of electrolytes on the micellization parameters of ionic surfactants has been attributed mainly to the binding of counterions to ionic micelles.

In our previous work,[128-130] we had reported a special type of counterion binding behaviour for sodium dioctylsulfosuccinate. Sodium dioctylsulfosuccinate is an anionic double-chained surfactant commonly known as Aerosol-OT or simply AOT. It was shown that AOT has two values of counterion binding constant (β), a lower value below 0.015 mol kg^{-1} (c*) of added NaCl and a two-fold higher value above c*. This type of special counterion binding behaviour (SCB) of AOT was not observed in the presence of sodium salicylate (NaSa). Since counterions have profound influence on the micellization characteristics and performance of ionic surfactants, it is of fundamental importance to ascertain the cause of the sudden shift in the β

value of AOT micelle. Moreover, the SCB of AOT has been studied till now only in aqueous[128-130] and water + propylene carbonate (PC)[131] media only. Other mixed solvents have not been explored to address the effect of solvent on the SCB of AOT. The SCB of AOT has been observed only with respect to sodium counterion and it is worthwhile to investigate whether this SCB exists in the case of other counterions also.

In view of the above points, we have carried out the following studies in this thesis:

(i) In chapter3, small-angle neutron scattering (SANS) study of AOT is made in aqueous NaCl and NaSa solutions in order to ascertain the reason for the SCB of AOT.

(ii) In chapter 4, the counterion binding behaviour of AOT has been investigated in the presence of sodium and ammonium mixed counterions in order to know whether SCB of AOT exists in the presence of other counterions also.

(iii) In chapter 5, we studied the counterion binding behaviour of AOT in water + ethylene glycol (EG) medium in order to have more knowledge about the effect of solvent on the SCB of AOT. For comparison purpose, counterion binding behaviour of sodium dodecylsulfate (SDS) has also been investigated in water + EG medium.

(iv) In chapter 6, the aggregation behaviour of SDS has been studied in aqueous nitric acid medium since nitric acid is a commonly used medium for nitration of organic molecules.

1.9 References

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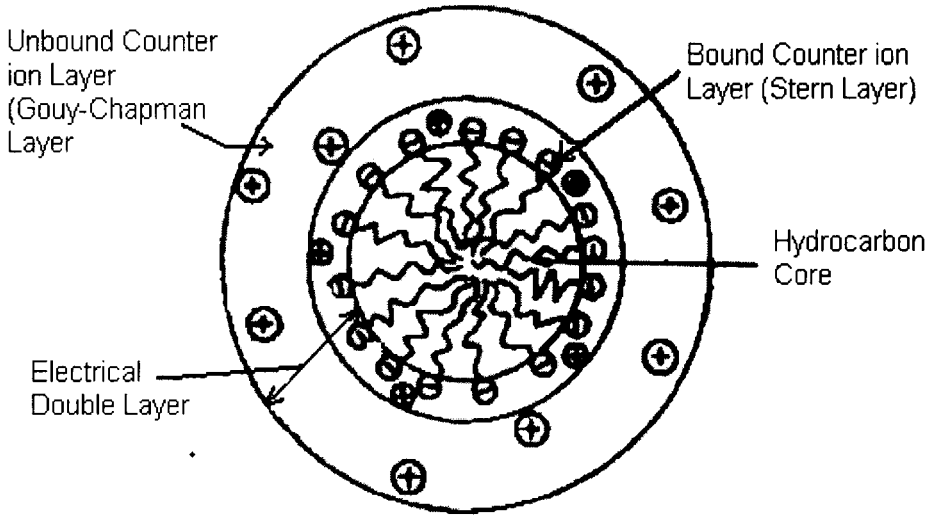

Figure 1.1 - A schematic representation of a spherical ionic micelle showing bound counter ions and the electrical double layer.

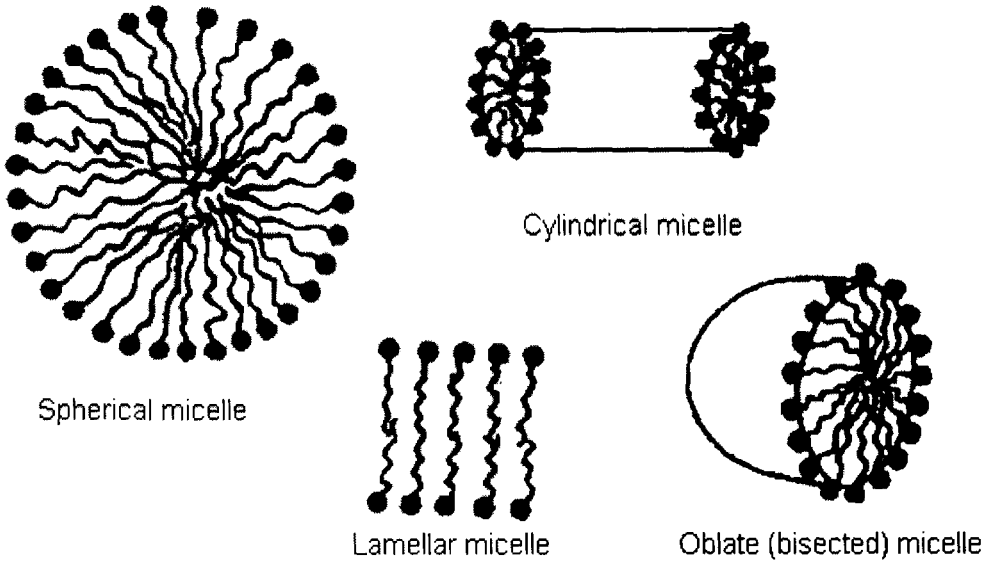

Figure 1.2 - Schematic representation of different shapes of micelles

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. Here we used 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

$$\gamma = \frac{F}{L \cos \theta} \qquad (2.1)$$

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^{o} such that $\cos\theta$ has a value of approximately 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 Eq. (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 Millipore 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 0.01 mN m^{-1}. The reproducibility of the measured surface tension values of the solutions was found to be within ±1 mN m^{-1}. A schematic diagram of the Wilhelmy Plate method is shown in Fig. 2.1.

2.2 Electrical Conductance Measurement

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 elecrtrodes was used. The cell constant was determined using standard KCl solution. The desired temperature for the solution under test is maintained with the help of Haake D8 circulation bath.

2. 3 Density Measurement and Weighing

The density of solutions whenever required was measured using Anton Paar DMA 5000 Density Meter.

Weighing was done with the help of a Mettler Toledo AG245 Electronic Balance.

2.4. Fluorescence measurements

Fluorescence emission intensities of probe molecule were recorded using a Hitachi F4500 FL spectrophotometer. In our studies we have used pyrene as the probe and cetylpyridinium chloride as the quencher.

2.5. Zeta potential measurements

Zeta potential measurements were carried out on a Malvern Zetasizer 3000HS instrument.

2.6. ^{1}NMR studies

^{1}H NMR spectra were recorded at 25 °C on a Bruker Avance II-400 spectrometer operating at 400 MHz with TMS as the internal reference.

2.7. Small angle neutron scattering measurements

SANS experiments were carried out at the Dhruva Reactor, Bhabha Atomic Research Center, Trombay, India. The SANS diffractometer makes use of a beryllium oxide filtered neutron beam of mean wavelength (λ) 5.2 Å and the data were collected within the Q (scattering vector $Q = 4\pi\sin\theta/\lambda$, where 2θ is the scattering angle) range of 0.02–0.20 Å^{-1}. The samples were taken in quartz sample holder of 0.5 cm path length having tight fitting Teflon stopper. The details of SANS data analysis are described in detail in Chapter 3. A schematic diagram of the SANS spectrometer at Dhruva reactor at BARC, Mumbai is shown in Fig.2.2.

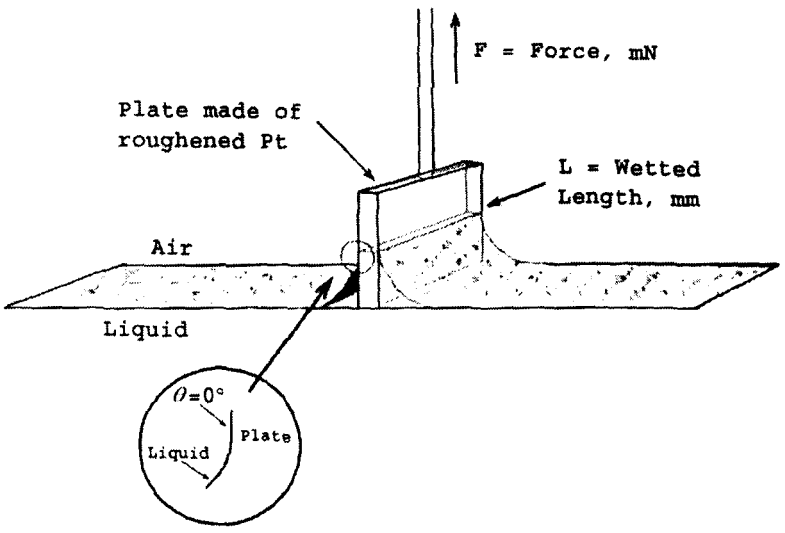

Figure 2.1 - Schematic diagram of Wilhelmy Plate.

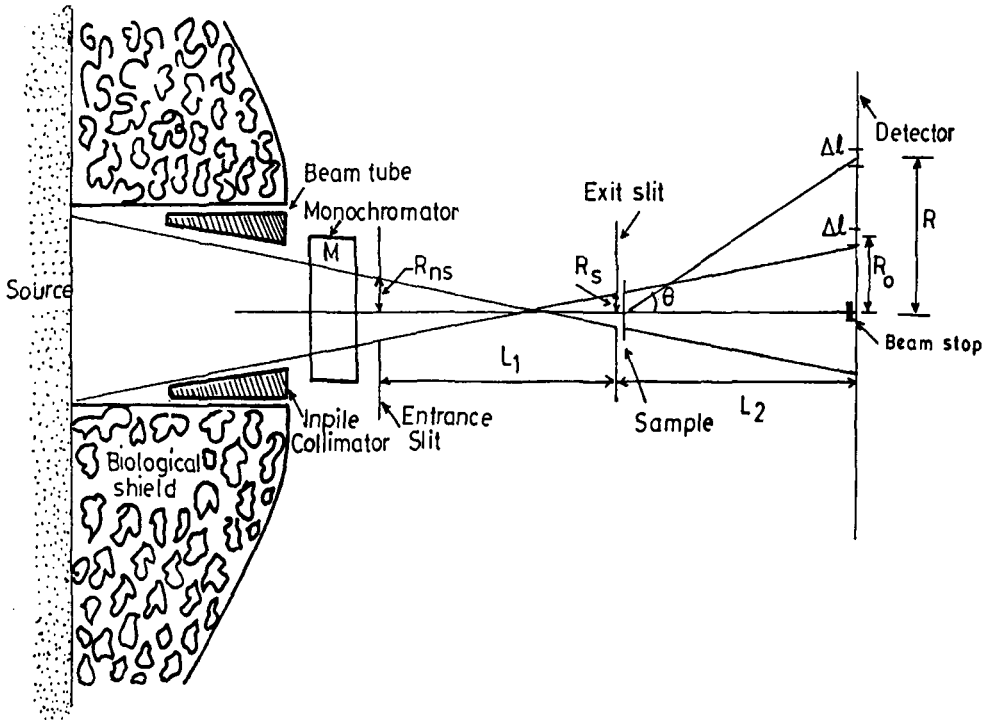

Figure 2.2 - Schematic representation of a SANS instrument.

CHAPTER 3

Aggregation and Counterion Binding Characteristics of Sodium Dioctylsulfosuccinate in Aqueous Sodium Chloride Medium

3.1 Introduction

Sodium dioctylsulfosuccinate (AOT), a double-chained anionic surfactant, has an unique type of counterion binding behaviour in the presence of electrolytes.[1,2] In aqueous NaCl solution, counter ion binding constant (β) for AOT is about 0.4 when NaCl concentration is less than 0.015 mol kg^{-1} and a sudden two-fold increase in the value of β occurs when NaCl concentration becomes about 0.015 mol kg^{-1} (c*). Occurrence of such a sudden shift in the value of β of AOT micelles at c* has been confirmed in the presence of different sodium salts,[1,2] but surprisingly not in aqueous sodium salicylate (NaSa) medium.[3]

A change in the value of β in the presence of added electrolyte has been reported in the case of a few more ionic surfactants,[4-10] but in all these cases the change occurred at fairly high electrolyte concentration (≥ 0.1M, M = mol dm^{-3}) and it was attributed to the salting-out effect. AOT is the only example known presently where change in β occurs at a very low electrolyte concentration. In the light of the reported[11-14] phase behaviour studies of AOT – water system in the absence and presence of NaCl, it is clear that the sudden change in β cannot be due to a phase change.

Counter ion binding ability is one of the important characteristics of ionic micelles since counter ions are known to influence cmc values of ionic surfactants, size and shape of ionic micelles, and also reactions in solutions of

ionic surfactants. Therefore, it is of fundamental importance to ascertain the cause for the sudden shift in the β value of AOT micelle. It has been proposed that a change in micellar shape may be responsible for the shift in the counterion binding.[1,15] However, no experimental evidence is available to confirm this proposition in AOT + water + salt system. With this objective in mind, we carried out small angle neutron scattering (SANS) measurements of AOT + D_2O + NaCl/NaSa systems. The results are presented in this chapter.

3.2 Experimental Section

AOT (Sigma, 99 % assay), NaCl (Merck, 99.5 % assay), NaSa (Fluka, ≥ 99.5 % assay) were used without further purification. Stock solutions of AOT and the salts were prepared in Milli-Q water and the required concentrations were obtained by dilution. Solutions for SANS measurements were prepared in D_2O (99.4 atom % D), which was obtained from the Heavy Water Division, BARC, Trombay. During SANS measurements on AOT, low solubility of AOT in D_2O (as well as water) posed problem because of low SANS intensity. Hollamby et al.[16] had also pointed out about this particular problem with SANS study of AOT. The solubility of AOT in water and D_2O decreased further in the presence of NaCl. We therefore had to fix the AOT concentration at 15 mM (~ 0.7 weight %) and carry out SANS measurements at 40 °C. This necessitated verification of the abrupt change in β value of AOT at 40 °C, since all earlier measurements were at 25 °C. Therefore, in addition to SANS, we also carried out surface tension measurement of AOT in aqueous NaCl and NaSa solutions at 40 °C to determine cmc as a function of

electrolyte concentration. Surface tension measurements were made by the Wilhelmy plate method using a Krüss K11 tensiometer attached with a thermostat (Haake DC 10). Surface tension of aqueous solutions was measured as a function of AOT concentration at fixed amounts of electrolyte (NaCl or NaSa). This was done in three steps. (i) A stock solution of NaCl or NaSa of a chosen concentration was prepared by weighing (Mettler Toledo AG245 Electronic Balance was used) the salt and water. (ii) By using a portion of this electrolyte solution as solvent, stock solution of AOT of required concentration was prepared. (iii) From the remaining portion of the stock electrolyte solution, weighed amount is taken in the sample vessel of the tensiometer and surface tension measurement of the solution was made after addition of aliquots (in the range of 0.001 cm^3) of AOT stock solution using a Finn pipette. Thermal equilibrium was ensured before every measurement. Density of the solutions was measured using Anton Parr DMA 5000 density meter.

For fluorescence measurements, a stock solution of NaCl of a chosen concentration was prepared by weighing the salt and water. Using this NaCl solution of known concentration as solvent we prepared a stock solution of AOT of fixed concentration. From this stock solution of AOT in aqueous NaCl, we prepared by dilution (Stock solution of NaCl was used for dilution) AOT solutions of different concentrations. A stock solution of pyrene of known concentration (in the range of ~5 x 10^{-6} mol dm^{-3}) was prepared in water. To a known amount of aqueous AOT + NaCl solution, aliquot of

pyrene solution was added. The excitation wavelength was 335 nm and fluorescence emission intensities of pyrene were recorded at 373 (I_1) and 384 nm (I_3). Emission intensities were similarly recorded at different concentrations of AOT with concentrations of pyrene and NaCl fixed and also by varying NaCl amount. The fluorescence spectra were recorded using Hitachi F4500 FL spectrophotometer.

Zeta potential measurements were carried out on a Malvern Zetasizer 3000HS instrument. For these measurements 15 mM solution of AOT was prepared in aqueous NaCl or NaSa solutions of known concentrations. About 5 ml of the AOT solution prepared in aqueous solution of NaCl or NaSa of fixed concentration was injected into the capillary tube of the instrument using a syringe. Care was taken to ensure that the capillary is bubble free. The measurement of zeta potential was repeated 5 to 6 times till stable readings are obtained. Measurements were repeated by changing the concentration of the salt.

SANS experiments were carried out at the Dhruva Reactor, Bhabha Atomic Research Center, Trombay, India. The SANS diffractometer makes use of a beryllium oxide filtered neutron beam of mean wavelength (λ) 5.2 Å and the data were collected within the Q (scattering vector $Q = 4\pi\sin\theta/\lambda$, where 2θ is the scattering angle) range of 0.02–0.20 $Å^{-1}$. The samples were taken in quartz sample holder of 0.5 cm path length having tight fitting Teflon stopper. Concentration of AOT was fixed at 15 mM and the concentrations of NaCl and NaSa were varied from 5 to 15 mM. The measured SANS

distributions were corrected for the background, empty cell scattering and the sample transmission, and the corrected data were then normalized to absolute cross sectional unit using standard procedures.[17]

^{1}H NMR spectra of solutions of NaSa in D_2O (Aldrich, 99.9 atom % D) in the absence and presence of AOT were recorded at 25 °C on a Bruker Avance II-400 spectrometer operating at 400 MHz with TMS as the internal reference.

The analysis of the SANS data was done according to the procedure described elsewhere.[18,19] In this method of data analysis, the differential scattering cross section per unit volume ($d\Sigma/d\Omega$) is represented by the expression

$$d\Sigma/d\Omega = n(\rho_m - \rho_s)^2V^2[\langle F^2(Q)\rangle + \langle F(Q)\rangle^2(S(Q) - 1)] + B \qquad (3.1)$$

In Eq. (3.1), ρ_m and ρ_s denote the scattering length densities of the micelle and the solvent, respectively, n is the number density of the micelles, V is the volume of the micelle, F(Q) is the single particle form factor, S(Q) is the inter-particle structure factor and B is a constant term. F(Q) depends on the shape and size of the particles and S(Q) is decided by the spatial distribution of the particles. B accounts for the incoherent scattering background that occurs in the case of neutrons mainly due to the presence of hydrogen in the sample. The relations used for prolate ellipsoidal micelles are

$$\langle F^2(Q)\rangle = \int_0^1 F(Q,\mu)^2 d\mu \qquad (3.2)$$

$$\langle F(Q)\rangle^2 = \left[\int_0^1 F(Q,\mu)d\mu\right]^2 \tag{3.3}$$

$$F(Q,\mu) = 3(\sin x - x\cos x)/x^3 \tag{3.4}$$

$$x = Q[a^2\mu^2 + b^2(1-\mu^2)]^{1/2} \tag{3.5}$$

In Eq. (3.5), a and b are the semimajor and semiminor axes of the ellipsoidal micelle, respectively. The term μ in the above equations refer to the cosine of the angle between the directions of a and Q. In the analysis of SANS data the ellipsoidal shape ($a \neq b = c$) of the micelles is widely used because it can represent other different probable shapes like spherical ($a = b$) and rod-like ($a >> b$). The expression for S(Q) is given by the Fourier transform of the radial distribution function g(r). g(r) gives the probability of finding the centre of another micelle at a distance r from the centre of a reference micelle. S(Q) is calculated using the mean spherical approximation developed by Hayter and Penfold.[20] In this approximation, the micelle is treated as a rigid equivalent sphere of diameter $d = 2(ab^2)^{1/3}$ interacting with another micelle through a screened coulomb potential u(r) given by the relation

$$u(r) = u_0 d\exp[-\kappa(r-d)]/r, \qquad r>d \tag{3.6}$$

where u_0 is the potential at $r = d$ and the Debye-Hückel inverse screening length κ is evaluated by using the expression

$$\kappa = \left(\frac{8\pi N_A e^2 I}{10^3\,\varepsilon k_B T}\right)^{1/2} \tag{3.7}$$

In Eq. (3.7), N_A, e, ε, k_B and T denote Avogadro number, electronic charge, dielectric constant of the solvent, Boltzmann constant and absolute temperature, respectively. The ionic strength I of the micellar solution is calculated as

$$I = c_0 + 0.5\alpha c_s + c_e \tag{3.8}$$

where c_0, c_s and c_e are the critical micelle concentration (cmc), concentration of the surfactant and concentration of the electrolyte in the solution, respectively. α is the fractional charge, which is equal to the micellar charge (Z) divided by the aggregation number (N). The contact potential u_0 is calculated as

$$u_0 = \frac{Z^2 e^2}{\pi \varepsilon \varepsilon_0 d(2+\kappa d)^2} \tag{3.9}$$

where ε_0 is the permittivity of vacuum. To simplify calculations polydispersity of micelles was ignored and the micellar solution was considered to have monodisperse ellipsoids only.

3.3 Results and Discussion

Surface tension, γ, values of AOT at 40 °C in aqueous NaCl and NaSa solutions are presented in Tables 3.1 – 3.2 and Figs. 3.1 and 3.2 in the form of γ versus $\log c_s$ plots. The cmc values of AOT determined from these plots are given in Table 3.3. Cmc values of AOT at 40 °C in aqueous NaCl and NaSa solutions determined from the measured surface tension data are depicted in Fig. 3.3(a). The cmc values of AOT at 40°C has been found to be less than

those reported[1] at 25 °C, which is attributed to endothermic micellization of AOT in water.[21]

The values of β of AOT micelle in aqueous NaCl and NaSa media at 40 °C, were calculated using the Corrin - Harkins (CH) equation,[22]

$$\ln c_0 = A - \beta \ln(c_0 + c_e) \qquad (3.10)$$

where A is a constant related to the standard free energy of micellization. From the CH plot given in Fig. 3.3(b), it is clear that in aqueous NaCl solution the special counterion binding behaviour (SCB) of AOT reported[1] earlier at 25 °C prevails at 40 °C also. The values of β at 40 °C are found to be 0.45 below c* and 0.85 above c*. Similarly, in the presence of NaSa at 40 °C, as observed previously[3] at 25 °C, β has only one value equal to 0.45. Thus, the counterion binding behaviour of AOT is same at 25 and 40 °C.

To confirm that in the presence of 0.015 mol kg^{-1} of NaCl the fractional charge on AOT micelle decreases, we measured zeta potential (ψ) values of aqueous solutions of AOT (concentration = 0.015 mol kg^{-1}) as functions of concentration of NaCl and NaSa at 40 °C and the values of ψ are listed in Table.3.4. The plot showing the variation of ψ with the electrolyte concentration is shown in Fig. 3.4(a). An abrupt change in ψ near 0.015 mol kg^{-1} NaCl from about -100 to -50 mV, but not in NaSa solution was observed. The abrupt change in ψ confirms condensation of greater number of counterions into the Stern layer of AOT micelle near 0.015 mol kg^{-1} NaCl

thereby supporting the observation that at this concentration of NaCl a sudden increase in the value of β of AOT takes place.

The change in the counterion binding constant of AOT should also be accompanied by a change in the polarity at the micellar interface. To observe these change, we also carried out fluorescence emissions measurements of AOT in presence of NaCl at 40 °C, using pyrene as the probe. The values of the intensity ratio (I_3/I_1) of peak 3 (at 384nm) to peak 1 (at 373nm) of pyrene fluorescence emission in AOT solution at 40 °C are shown in Table 3.5 and in Fig. 3.4(b) as a function of $c_s - c_0$ at fixed NaCl concentrations. From the plots it can be seen that the plot of I_3/I_1 starts passing through a maximum when the concentration of NaCl becomes equal or greater than 0.02 M, which indicate that near c* a sudden change in the polarity of the AOT micellar interface occurs. This sudden change in the polarity at the micellar interface is, in turn, indicative of abrupt change in the surface charge of AOT micelle at about 0.02 M NaCl. Since NaSa also shows fluorescence emission in the wavelength range from 375 to 450 nm, we did not measure the intensity ratio of pyrene fluorescence emission in AOT solution in the presence of NaSa.

Thus, the SCB of AOT in aqueous medium has been found to be similar even at higher temperature. Now, to ascertain the reason behind this SCB of AOT, we carried out SANS measurements for AOT + NaCl / NaSa systems at 40 °C.

The values of $d\Sigma/d\Omega$ as a function of scattering vector Q obtained from SANS experiments at 40 °C are shown in Fig. 3.5. For AOT, the values

of the semiminor axis and the volume (v) of the monomer with head group were taken from the literature[23] as 12.6 Å and 611 $Å^3$, respectively. The values of the aggregation number ($N = 4\pi ab^2/(3v)$), fractional charge and the axial ratio a/b determined from the fitting are shown in Fig. 3.6 and Table 3.6. The SANS spectrum of AOT in D_2O with no salt shows the characteristic correlation peak at $Q \approx 0.059$ $Å^{-1}$, which is in good agreement with the literature[23] value, and this peak is indicative of repulsive interactions operating between the negatively charged AOT micelles. For AOT in D_2O, we obtained from the present data analysis, aggregation number = 30 and fractional charge = 0.24. These values are in good agreement with those reported by Sheu et al.[23] and Hollamby et al.[16] The characteristics of the SANS spectra of AOT micelles in NaCl up to 10 mM and in NaSa up to 15 mM are almost similar and the spectra show strong correlation peaks. Compared to the reported SANS profiles of ionic surfactant + salt systems,[24-28] we observed some peculiarities in the SANS spectra of AOT + NaCl/NaSa systems. For e.g., in the SANS spectra of systems like SDS (sodium dodecylsulfate) + NaCl/PTHC (p-toluidine hydrochloride),[24-27] CTAB (cetyltrimethylammonium bromide) + KBr/KCl,[25-27] CTAC (cetyltrimethylammonium chloride) + KBr/KCl,[25-27] and CPC (cetylpyridinium chloride) + NaCl/NaBr[28] the peak positions shifted to lower Q value by the addition of salts due to increase in micellar size and the peaks also broadened due to decrease in micellar charge. On the other hand, in AOT + NaCl/NaSa systems up to 10 mM NaCl and 15 mM NaSa the peak positions

remained almost at the same Q value (Figure 3.5) and consequently aggregation number and axial ratio of AOT micelles derived from the fitting were found to be constant (Table 3.6 and Fig. 3.6). Moreover, the peaks did not broaden by the addition of NaCl or NaSa. On the contrary, the width of the peaks slightly decreased by the addition of NaCl/NaSa, the decrease in width being relatively more in NaSa. This observation about the width of SANS peaks of AOT micelles is reflected in the fitted values as listed in Table3.6 for the fractional charge, which shows an increasing trend with increasing concentration of added salt as shown in Fig.3.6, unlike the case with the reported systems.[24-28] Interestingly, the correlation peak of AOT micelles disappears in 15 mM NaCl, but not in 15 mM NaSa (Figure 3.5). In 15 mM NaCl, since there is no correlation peak the surface charge was fixed as close to zero and the semimajor axis was used as the fitting parameter. The value of axial ratio so obtained clearly indicates that the shape of AOT micelles changes near 15 mM NaCl from prolate spheroid ($a/b \approx 2$; aggregation number ≈ 30) to rod-like ($a/b \approx 21$; aggregation number ≈ 280). The values of the factional charge obtained from the SANS data are not in agreement with those determined from CH plots. According to the results from the CH plots and emf data,[1] α should have been (i) about 0.6 in water and in the presence of NaSa, and (ii) about 0.6 below 15 mM NaCl and about 0.2 when NaCl concentration is $\geq$ 15 mM. However, such expected fractional charge is not obtained from the fitting of SANS data of AOT (Fig. 3.6). Low SANS intensity of AOT micelles hampered obtaining accurate values of

fractional charge, axial ratio and aggregation number from the fitting of SANS data. Nevertheless, from the SANS data of AOT in the absence and presence of NaCl/NaSa it is very clear that (i) the shape of AOT micelles changes when NaCl concentration becomes 0.015 mM, (ii) the shape change of AOT micelles does not occur in the presence of NaSa, and (iii) the fractional charge (equal to $1 - \beta$) on the AOT micelle suddenly decreases when its shape changes.

The dependence of β on the shape of a micelle may be explained as follows: As the concentration of added electrolyte is increased, more counterions bind to a micelle thereby reducing the repulsion between the head groups at the micellar surface and consequently increasing the aggregation number. Increase in aggregation number increases the size of the micelle, but the value of β remains almost unchanged since it is the ratio of the bound counterions to the aggregation number. However, as the size of the micelle increases, at some point its shape must also change due to geometric factors so as to accommodate the increased number of hydrocarbon tails in the micelle. When such a shape change of the ionic micelle takes place due to geometric constraints, surface area of micelle per head group changes and causes, in turn, a change in the value of β. Thus, the value of β does not change due to increase in the size of ionic micelle until the micellar shape changes. Change of β due to micellar shape change was proposed by Fujio et al.[15] also who reported that β of ionic micelles increase in the order of sphere < oblate ellipsoidal < rod-like.

The difference in the counterion binding behaviour of AOT in aqueous NaSa solution compared to that in NaCl solution may be explained due to the binding of salicylate coanion to AOT micelle. In spite of possessing negative charge, salicylate ion can still bind to the anionic AOT micelle due to (i) hydrophobic interactions between the phenyl ring of salicylate and water, (ii) short-range van der Waals interactions between hydrocarbon tails of AOT and phenyl ring of salicylate, and (iii) shielding of electrostatic repulsive interactions between the negatively charged head groups of salicylate and AOT due to hydration. The binding of salicylate ion to AOT micelle is similar to the binding of SDS to AOT during the formation of their mixed micelle.[29] A schematic diagram of salicylate binding to AOT micelle is shown in Fig. 3.7. Due to the salicylate binding the effective surface charge of AOT micelle becomes more and hence no change in micellar shape and increase in β occur in aqueous NaSa solution.

To ascertain the binding of salicylate co-anion to AOT micelle and its position in the micelle, we performed proton NMR measurements of neat NaSa and NaSa in the presence of AOT. The NMR spectra are shown in Fig. 3.8. In the presence of AOT micelle, the chemical shift values of protons in the 3, 4, 5 and 6 positions of salicylate are lowered by 0.074 ± 0.001 ppm (Fig. 8), suggesting non-polar environment of these protons. A similar lowering of chemical shift values of the protons of salicylate bound to CTAB cationic micelle was reported by Rao et al.[30] Thus, NMR spectra confirm the binding of salicylate co-anion to the AOT micelle as visualized in Fig. 3.7.

3.4. Conclusions

Critical micelle concentrations of AOT in presence of NaCl and NaSa have been determined from surface tension measurements at 40 °C. The aggregation process in AOT + aqueous NaCl / NaSa is endothermic. The special counterion binding has been found to be independent of the temperature. The greater condensation of counterions to AOT micelles has also been confirmed by zeta potential measurements at 40°C for AOT + NaCl, while for NaSa no such observation was made.

SANS profiles of AOT in the presence of NaCl clearly reveal a change in the shape of AOT micelle near the NaCl concentration where a two-fold increase in its β value occurs. From the SANS data analysis this shape change has been shown to be from prolate spheroid to rod-like shape. On the other hand, SANS profiles of AOT in the presence of NaSa do not indicate any shape change of AOT micelle and interestingly in NaSa solution no abrupt change in the value of β also occurs. Therefore, it can be concluded that counterion binding constant of ionic micelle is a micellar shape dependent parameter. From the present study it can be proposed that β of prolate ellipsoidal shaped micelle is less than that of rod-like shaped micelle. This is consistent with the proposition made by Fujio et al.[15] that the value of β follow the order, spherical < oblate ellipsoidal < rod-like micelle.

Generally, the counterion binding is thought to be one of the factors determining size and shape of ionic micelles. It emerges from this study that counterion binding controls the size of micelles, but shape change occurs due

to geometrical requirement. Since a shift in the value of β takes place as the micellar shape changes, surface charge density (ratio of micellar charge to its surface area) rather than surface charge appears to control β. This concept can be applied to explain why sodium deoxycholate (bile salt) micelle has very low value of β. Sodium deoxycholate due to formation of facial micelle[31] has low surface charge (low aggregation number) and large surface area resulting low surface charge density and hence low β value.

3.5. References

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Table.3.1. Surface Tension (γ) values of AOT in aqueous Sodium Chloride solution at 40 °C.

[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0 mol kg^{-1}			
0.0040	68.6	0.5523	44	3.9194	30.3
0.0158	65.1	0.8754	40.5	4.9141	29.8
0.0394	59.9	1.3178	36.8	6.3242	29.2
0.0786	57.5	1.8568	33.9	7.8865	28.6
0.1758	52.3	2.4677	31.8	9.3588	28.2
0.3287	47.7	3.1508	30.8		
		[NaCl] = 0.0010 mol kg^{-1}			
0.0041	61.1	0.5113	40.9	3.3907	29.5
0.0124	58.0	0.7949	37.6	4.2963	29.0
0.0330	54.2	1.1558	35.0	5.4137	28.8
0.0741	50.8	1.5982	32.3	6.7055	28.5
0.1556	47.6	2.1047	30.5	8.2966	28.3
0.2960	43.9	2.6858	30.1	9.2510	28.1
		[NaCl] = 0.0033 mol kg^{-1}			
0.0036	61.9	0.1796	42.0	2.2921	27.7
0.0071	58.3	0.3066	38.7	3.351	27.7
0.0143	55.0	0.4742	36.3	4.6474	27.4
0.0285	51.5	0.7010	33.3	6.0146	27.3
0.0534	48.4	1.0104	30.9	7.4586	27.3
0.0993	45.0	1.5277	28.5		
		[NaCl] = 0.0060 mol kg^{-1}			
0.0036	60.3	0.2636	38.6	4.3379	27.0
0.0073	56.9	0.4528	35.6	5.7359	26.7
0.0145	54.1	0.7185	32.8	7.5381	26.6
0.0326	50.1	0.8153	29.9		
0.0687	45.9	1.2780	28.0		
0.1402	41.8	1.9247	27.7		
0.0036	60.3	3.0084	27.1		

Table.3.1 Continued.

[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0140 mol kg^{-1}			
0.0030	59.3	0.0030	59.3	1.7533	26.2
0.0090	53.7	0.2025	36.4	0.2025	36.4
0.0179	50.3	0.3445	33.6	2.4349	26.1
0.0328	47.3	0.5641	30.6	3.2491	25.9
0.0624	43.3	0.8516	28.2	4.2692	25.6
0.1154	40.0	1.2422	26.6		
		[NaCl] = 0.0210 mol kg^{-1}			
0.0009	64.4	0.1033	38.5	0.9183	26.4
0.0027	58.7	0.1564	35.8	1.1384	26.1
0.0062	53.7	0.2232	33.9	1.3903	25.8
0.0115	50.0	0.3052	32.7	1.6278	25.4
0.0221	46.9	0.4099	30.6		
0.0395	43.5	0.5562	29.1		
0.0654	40.9	0.7249	27.3		
		[NaCl] = 0.0400 mol kg^{-1}			
0.0010	63.4	0.1317	34.9	0.9328	25.3
0.0051	53.2	0.2052	32.2	1.1838	24.7
0.0151	47.3	0.2929	29.8	1.4997	25.5
0.0251	43.7	0.4003	28.0	1.9125	25.4
0.0450	40.5	0.5306	26.3		
0.0792	37.4	0.7040	25.4		

Table.3.1 Continued.

[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0560 mol kg^{-1}			
0.0007	62.0	0.0559	37.4	0.4203	25.6
0.0028	56.0	0.0859	35.1	0.5654	24.8
0.0063	50.1	0.1280	32.8	0.7553	24.7
0.0120	46.7	0.1808	30.5	0.9917	24.6
0.0203	43.4	0.2400	28.6	1.2631	25.2
0.0341	40.4	0.3179	27.1	1.5300	25.4
		[NaCl] = 0.0700 mol kg^{-1}			
0.0007	58.6	0.0681	34.7	0.8464	24.8
0.0028	53.3	0.1103	32.1	1.1943	24.8
0.0070	48.3	0.1663	29.5		
0.0139	44.3	0.2540	27.1		
0.0208	41.6	0.3858	25.1		
0.0379	38.6	0.5665	24.7		
		[NaCl] = 0.1000 mol kg^{-1}			
0.0003	67.1	0.0351	38.9	0.2911	26.3
0.0016	59.9	0.0564	36.1	0.3746	25.4
0.0049	51.5	0.0826	33.7	0.4792	25
0.0082	47.5	0.1183	31.5	0.6152	25
0.0130	44.5	0.1640	29.6		
0.0210	41.7	0.2212	27.8		

Table.3.2 Surface Tension (γ) values of AOT in aqueous Sodium Salicylate solution at 40 °C.

[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaSa] = 9.78x 10^{-4} mol kg^{-1}			
0.0044	59.6	0.871	37.1	5.4239	29
0.0219	55.9	1.3632	33.4	6.5129	28.4
0.0656	51.7	1.9594	31.1	7.5718	28.9
0.1522	47.6	2.6609	30.1	8.5939	28.6
0.3015	44.3	3.4562	29.7		
0.5304	40.5	4.3916	29.5		
		[NaSa] = 0.0040 mol kg^{-1}			
0.0024	63.6	0.5524	36.8	3.8585	28.6
0.0120	56.7	0.8567	33.9	4.7437	28.5
0.0360	50.9	1.2809	31.2	5.4148	28.2
0.0835	47.0	1.8139	29.2		
0.1770	43.1	2.4387	28.6		
0.3358	39.4	3.0985	28.7		
		[NaSa] = 0.0070 mol kg^{-1}			
0.0024	62.1	0.5279	35.1	3.0068	27.9
0.0122	54.7	0.839	32.1	3.4862	27.6
0.0365	49.3	1.2187	29.4	4.0360	27.9
0.0847	45.2	1.6448	28.1	4.8960	27.7
0.1677	41.4	2.0961	27.9		
0.3065	38.4	2.5548	27.2		
		[NaSa] = 0.0094 mol kg^{-1}			
0.0023	59.6	0.6775	31.9	5.1771	27.4
0.0113	52.1	1.0067	29.6		
0.0339	47.8	1.4345	27.7		
0.0788	43.5	2.0017	27.1		
0.1560	40.3	2.7951	27.2		
0.2745	37.1	3.6312	27.5		
0.4408	34.5	4.7118	26.9		

Table.3.2 Continued

[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaSa] = 0.0210 mol kg^{-1}			
0.0014	57.4	0.3075	33.4	2.5327	25.8
0.0071	51.2	0.4886	31	3.1867	25.7
0.0213	46.3	0.7306	28.6		
0.0493	42.6	1.0399	26.4		
0.0977	39.1	1.4069	26.2		
0.1785	35.9	1.8607	25.7		
		[NaSa] = 0.0290 mol kg^{-1}			
0.0010	67.0	0.2064	38.4	1.1715	26.9
0.0048	60.3	0.3279	36.0	1.3574	26.3
0.0143	53.2	0.4761	33.1	1.5702	25.3
0.0331	48.3	0.8178	31.1	1.8062	25.8
0.0656	44.8	0.8178	29.7	2.1307	25.7
0.1199	41.4	0.9961	28.0		
		[NaSa] = 0.0400 mol kg^{-1}			
0.0009	58.9	0.1790	33.8	1.3113	25.6
0.0046	53.4	0.2669	31.2	1.7817	25.5
0.0138	47.3	0.3788	29.2		
0.0321	43.4	0.5344	27.2		
0.0635	39.7	0.7294	25.9		
0.1116	36.8	0.9752	25.0		
		[NaSa] = 0.0580 mol kg^{-1}			
0.0006	60.2	0.114	34.5	0.9022	25.3
0.0028	54.7	0.1764	32.5	1.1363	25.7
0.0084	48.9	0.2517	29.8		
0.0195	44.1	0.3512	28.7		
0.0387	40.4	0.4874	26.5		
0.0680	37.5	0.6754	25.4		

Table 3.3 Critical Micelle Concentrations of AOT in Aqueous Electrolytes determined from Surface Tension measurements at 40 °C.

Sodium Chloride		Sodium Salicylate	
[Electrolyte] / mol kg^{-1}	cmc / mmol kg^{-1}	[Electrolyte] / mol kg^{-1}	cmc / mmol kg^{-1}
0	2.46	9.78×10^{-4}	2.20
0.0010	2.30	0.0040	1.75
0.0033	1.80	0.0070	1.50
0.0060	1.50	0.0094	1.30
0.0140	1.11	0.0210	0.90
0.0210	0.79	0.0290	0.79
0.0400	0.55	0.0400	0.70
0.0560	0.40	0.0580	0.60
0.0700	0.31		
0.1000	0.22		

Table 3.4 Values of zeta potential (ψ) for aqueous AOT + NaCl / NaSa at 40 °C.

[NaCl]/ mol kg^{-1}	ψ/mV	[NaSa]/ mol kg^{-1}	ψ/mV
0	-100.00	0	-100.00
0.0050	-98.00	0.0050	-82.30
0.0120	-110.00	0.0098	-102.95
0.0160	-50.00	0.0146	-95.11
0.0200	-48.00	0.0200	-95.39
0.0250	-45.00	0.0310	-104.11
0.0300	-45.00		

Table 3.5 Values of the intensity ratio (I_3/I_1) of peak 3 (384nm) to peak 1 (373nm) of pyrene fluorescence emission in AOT solution at 40 °C.

[NaCl] = 0.0010 mol kg^{-1}		[NaCl] = 0.0033 mol kg^{-1}		[NaCl] = 0.0200 mol kg^{-1}		[NaCl] = 0.0560 mol kg^{-1}		[NaCl] = 0.1000 mol kg^{-1}	
$c_s - c_o$ / mmol kg^{-1}	I_3/I_1	$c_s - c_o$ / mmol kg^{-1}	I_3/I_1	$c_s - c_o$ / mmol kg^{-1}	I_3/I_1	$c_s - c_o$ / mmol kg^{-1}	I_3/I_1	$c_s - c_o$ / mmol kg^{-1}	I_3/I_1
0	0.5587	0	0.5749	0.3400	0.8357	0.3200	0.8259	0.3200	0.8134
0.0100	0.637	0.1800	0.6786	0.5600	0.8682	0.8000	0.8624	0.6800	0.8667
0.1000	0.6771	0.3600	0.8028	1.0100	0.9567	1.4000	0.8912	1.2800	0.8879
0.2500	0.7032	0.9000	0.8784	1.6100	0.9083	2.3000	0.8666	2.1800	0.8573
0.7000	0.8034	1.2000	0.8979	1.8100	0.8964	3.8000	0.8543	3.3800	0.8432
2.2000	0.9286	2.4000	0.9582	4.6100	0.8964	5.6000	0.8431	4.5800	0.8421
3.7000	0.9658	3.6000	1.0079	6.7100	0.8863	6.9200	0.8432	6.2000	0.8398
7.5000	0.9807	5.7000	1.0235	7.5800	0.8768				
8.9700	1.0075	7.1000	1.0334						

Table 3.6. Micellar Parameters of AOT Micelles in the Presence of Salts at 40 °C Obtained by Fitting SANS Data. The concentration of AOT is fixed at 15 mM.

Electrolyte	Semimajor axis, a (Å)	Semiminor axis, b = c (Å)	Agg. No.	Fractional charge, α	Axial Ratio, a/b
0	29.7 ± 3.0	12.6 ± 1.4	30 ± 5	0.24 ± 0.04	2.36 ± 0.35
5 mM NaCl	28.4 ± 3.0	12.6 ± 1.4	31 ± 5	0.27 ± 0.04	2.25 ± 0.35
10 mM NaCl	27.9 ± 2.8	12.6 ± 1.4	30 ± 5	0.35 ± 0.06	2.21 ± 0.35
15 mM NaCl	261.2 ± 14.0	12.6 ± 1.4	284 ± 35	0.0	20.73 ± 2.5
5 mM NaSa	28.2 ± 3.0	12.6 ± 1.4	31 ± 5	0.28 ± 0.04	2.24 ± 0.35
10 mM NaSa	26.0 ± 2.8	12.6 ± 1.4	28 ± 5	0.43 ± 0.06	2.06 ± 0.30
15 mM NaSa	25.8 ± 2.8	12.6 ± 1.4	28 ± 5	0.52 ± 0.06	2.02 ± 0.30

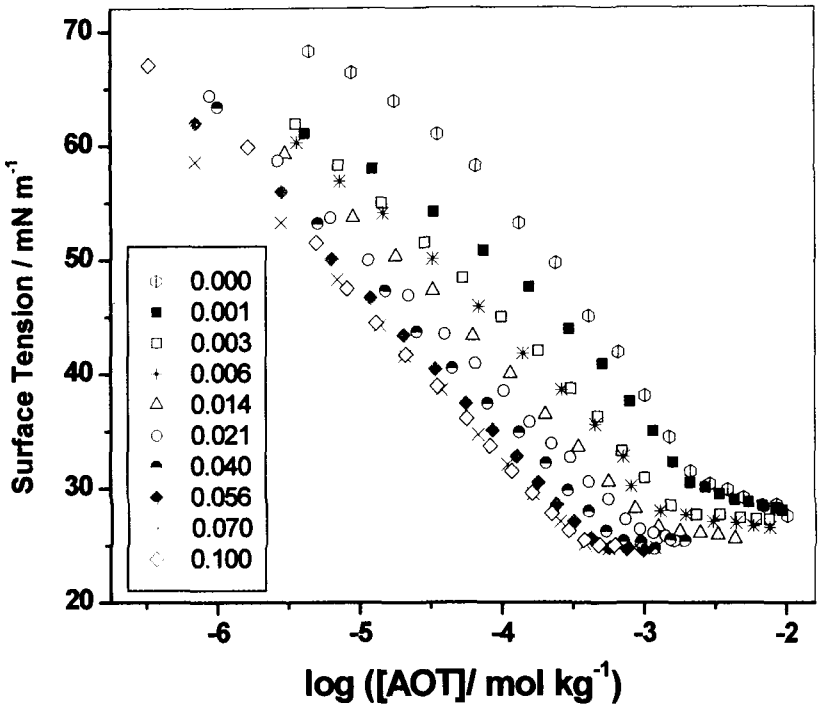

Fig. 3.1. Plots of variation of surface tension of AOT in presence of varying amounts of NaCl at 40 °C. The concentrations of NaCl are shown on the insets in mol kg^{-1}.

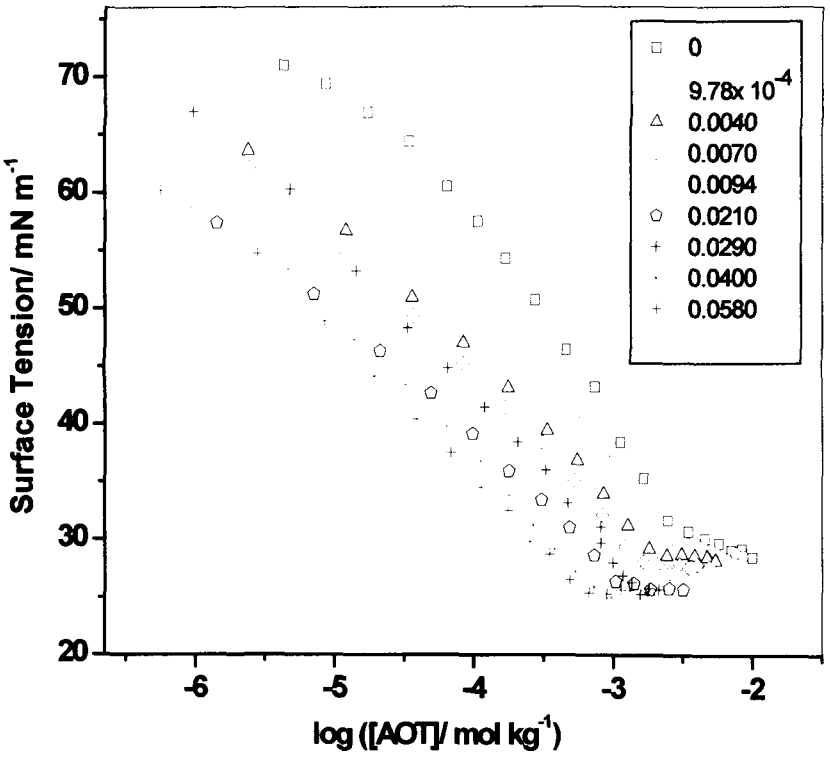

Fig. 3.2. Plots of variation of surface tension of AOT in presence of varying amounts of NaSa at 40 °C. The concentrations of NaSa are shown on the insets in mol kg^{-1}.

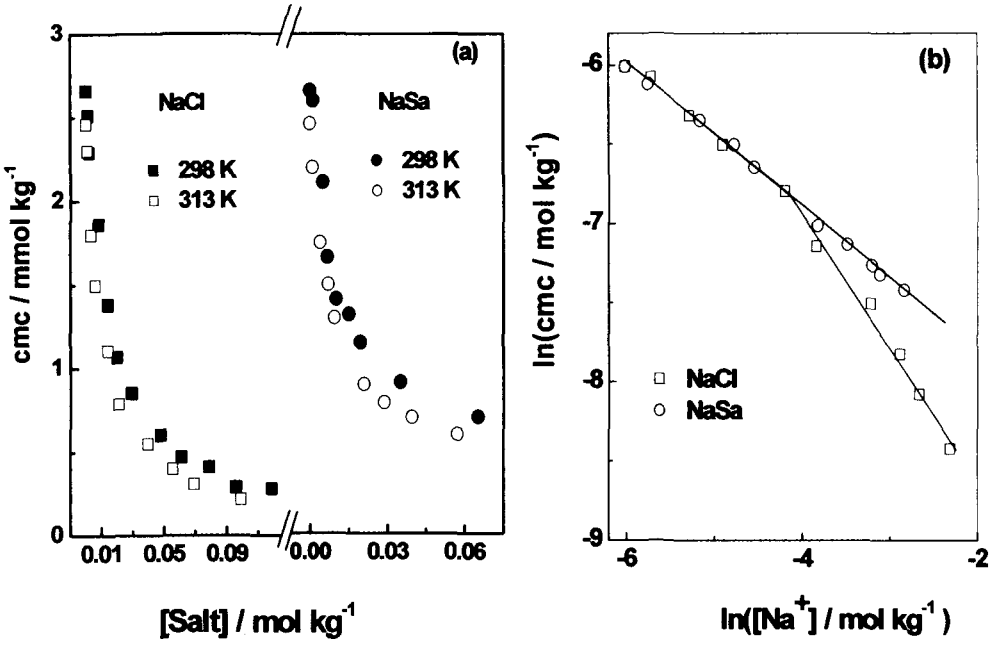

Fig. 3.3. (a) Variation of cmc (data at 298 K are from ref. 1) and (b) Corrin-Harkins plots of AOT in aqueous NaCl and NaSa solutions with salt concentration at 40 °C.

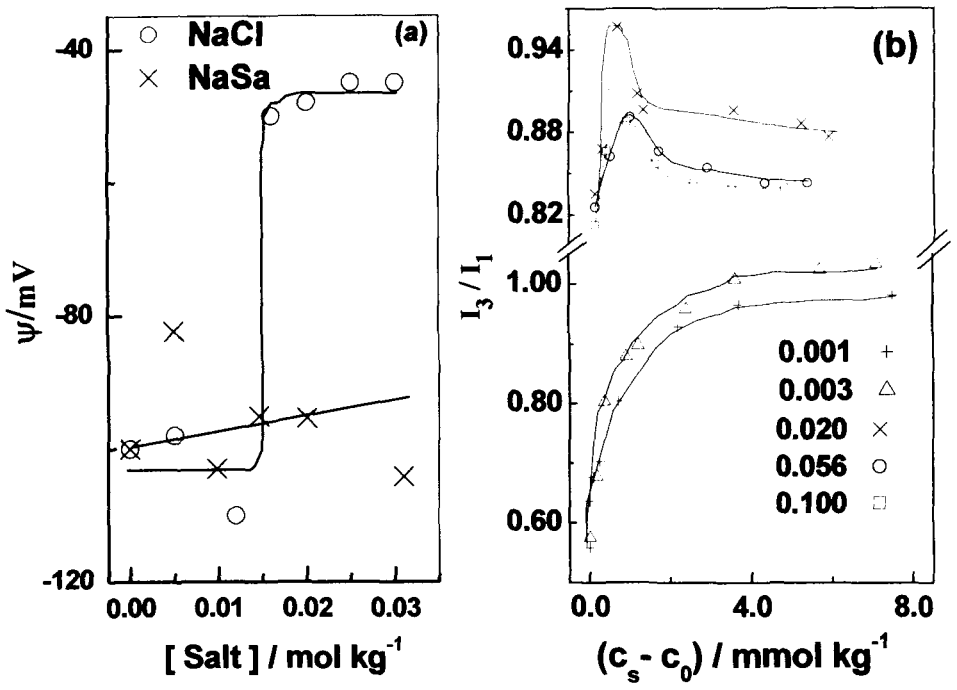

Fig. 3.4. Variation of (a) zeta potential of AOT micelles in aqueous NaCl and NaSa solutions with salt concentration, and (b) I_3/I_1 of pyrene with the amount of AOT that has undergone aggregation in the presence of NaCl (concentrations of NaCl are indicated in the inset) at 40 °C.

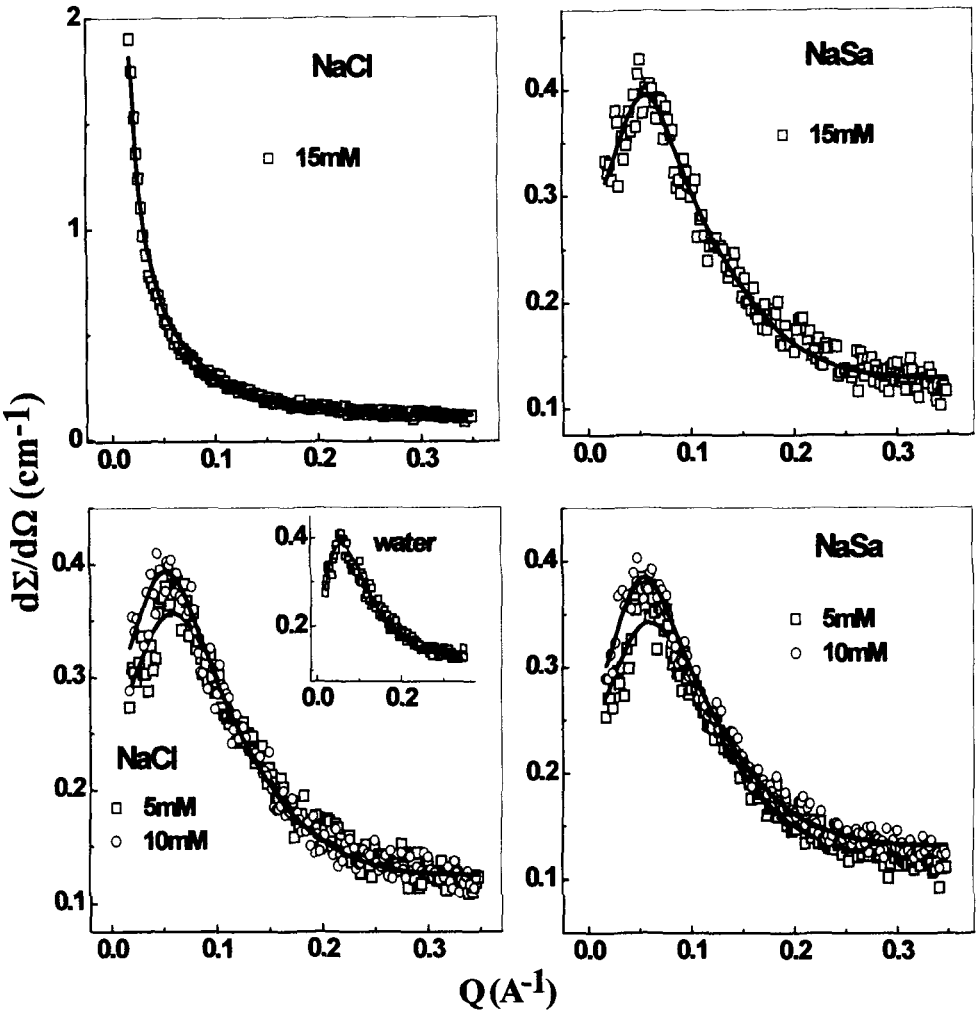

Fig. 3.5. Plots of SANS data (differential scattering cross section per unit volume versus scattering vector) for AOT (15mM) in water (inset) and aqueous solutions of NaCl and NaSa at 40 °C. Concentrations of NaCl and NaSa are shown in the insets. The lines shown are theoretical fits.

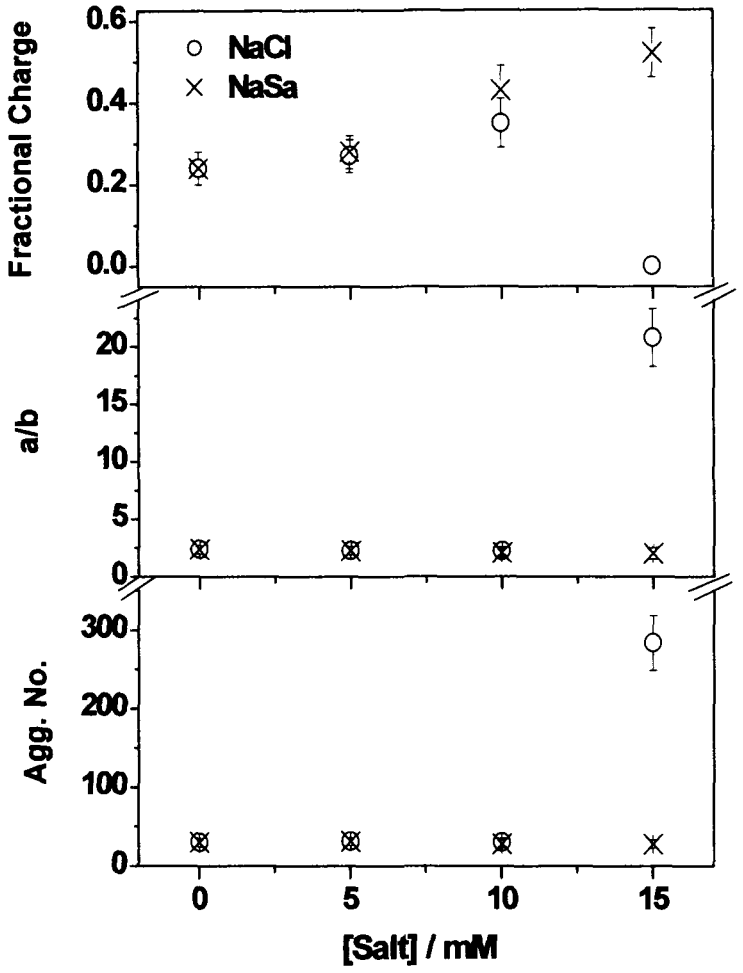

Fig. 3.6. Plots of aggregation number, ratio (a/b) of semi major to semi minor axes, and fractional charge (from the SANS data fitting) of AOT micelle versus salt concentration at 40 °C. Error bars are shown in red.

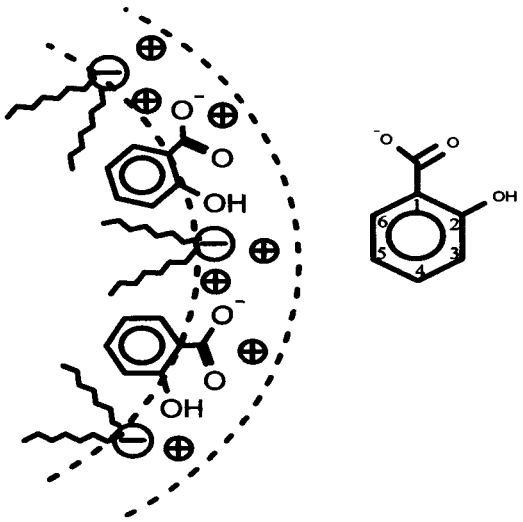

Fig. 3.7. (a) Schematic representation of the binding of salicylate coanion at the AOT micelle – water interface and (b) structure of salicylate ion

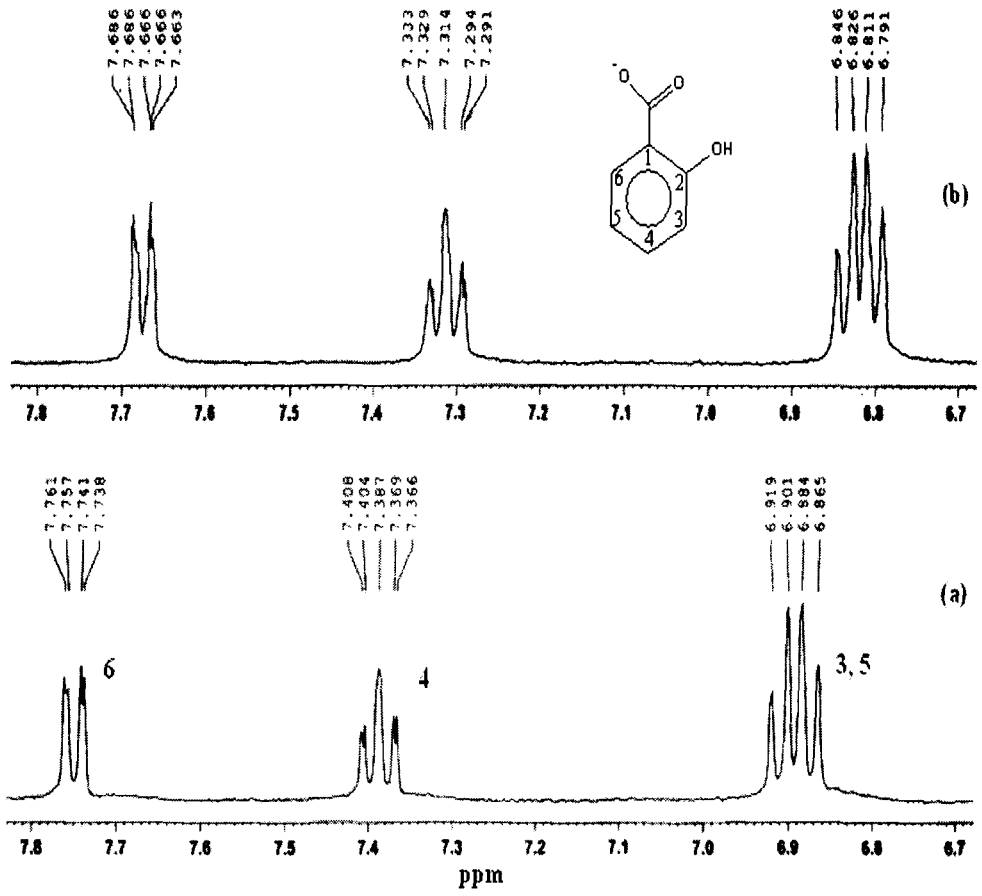

Fig. 3.8. ^{1}H NMR spectra of (a) 16 mM NaSa in D_2O and (b) 16 mM NaSa + 10 mM AOT in D_2O at 25 °C.

CHAPTER 4

Aggregation and Adsorption Characteristics of Sodium Dioctylsulfosuccinate in Aqueous Ammonium Chloride Solutions. Role of Mixed Counter ions.

4.1 Introduction

The special counterion binding behaviour (SCB) of sodium dioctylsulfosuccinate (AOT) has been established[1-4] and from SANS measurements we could further ascertain that the change in the micellar shape is responsible for the sudden two-fold increase in the value of counterion binding constant of AOT (cf. chapter 3) in aqueous NaCl solution. AOT, which is considered to be a special surfactant,[5-8] is perhaps the only anionic surfactant whose micelle undergoes a shape change in aqueous medium at a very low concentration (around 0.015 mol kg^{-1}) of added sodium ion, since micellar shape change in other anionic surfactants occurs at low concentration of electrolyte only when the added counterion is multivalent.[9-13] The SCB of AOT is yet to be tested for counterions other than sodium. Although Saha and coworkers[14,15] studied the micellization of AOT after replacing Na^+ by various other counterions such as NH_4^+, $N^+(CH_3)_4$, $N^+(C_2H_5)_4$, $N^+(C_3H_7)_4$ and $N^+(C_4H_9)_4$ through ion exchange method, the SCB of AOT with these new counterions was not investigated. Further, the SCB of AOT has also not been tested in the presence of mixed counterions. In this chapter, the objective of the study is mainly to investigate the counterion binding behaviour of AOT in the presence of mixed counterions and we have chosen here Na^+ and NH_4^+ as the two counterions.

4.2 Experimental Section

AOT (Sigma, 99 % assay) and NH_4Cl (AR Grade, 99.8 % assay, sd fine chemicals) were used without further purification. Stock solutions of AOT and the salts were prepared in Milli-Q water and the required

concentrations were obtained by dilution. Surface tension and fluorescence measurements were made at 25 °C as described in chapter 3.

4.3 Results and Discussion

4.3.1 Surface tension, fluorescence emission and critical micelle concentration

The measured surface tension (γ) values of aqueous AOT + NH_4Cl solutions at 25 °C are given in Tables 4.1 and the plots of variation of γ versus log[AOT] are shown in Fig. 4.1. Due to low solubility of AOT in NH_4Cl, the present study has been restricted up to 0.05 mol kg^{-1} of NH_4Cl. In order to see the effect of mixed counterions on the surface tension, we have compared in Fig.4.2 the surface tension isotherms of AOT + NH_4Cl with those of AOT + NaCl at one particular electrolyte concentration (0.0012 mol kg^{-1}). From Fig. 4.2 it can clearly be seen that a mixture of NH_4^+ and Na^+ has the same effect on the surface tension of AOT as that of Na^+ alone, which can be attributed to the hydrophilic nature of the two counterions and similar effect of these two counterions on the adsorption of AOT. The critical micelle concentration (cmc) values determined from the surface tension isotherms are listed in Table 4.2 and shown in Fig. 4.3.

The cmc has also been determined by the fluorescence technique by using pyrene as the probe. The I_1/I_3 ratio of pyrene (Table 4.3) was plotted as a function of AOT concentration and the plots are shown in Fig. 4.4. The values of cmc were estimated by a treatment reported by Aguiar et.al.[16] The

nature of the variation of I_1/I_3 with AOT concentration is considered to be sigmoid type and the data were fitted to the equation

$$\frac{I_1}{I_3} = A_2 + \frac{A_1 - A_2}{1 + \exp\left(\frac{c_s - x_0}{b_0}\right)} \qquad (4.1)$$

In Eq. 4.1, c_s represents AOT concentration, x_0 is the value of c_s corresponding to the centre of the sigmoid, A_1 and A_2 are the upper and lower limits of the sigmoid, respectively, and b_0 is a term that reflects the range of c_s where sudden change in I_1/I_3 occurs. The values of the parameters of Eq. 4.1 obtained from the fitting are listed in Table 4.4. Aguiar et.al.[16] concluded on an empirical basis that cmc = $x_0 + 2b_0$ and $x_0/b_0 > 10$ for ionic surfactants, whereas cmc = x_0 and $x_0/b_0 < 10$ for non ionic surfactants. In the present case, it is found from Table.4.4 and Fig. 4.3 that cmc of AOT is close to x_0 and $x_0/b_0 < 10$, which according to Aguiar et.al.[16] are characteristics of non ionic surfactants. Thus, it can be concluded that the parameters of Eq.4.1 are strongly dependent on the nature of the surfactant and medium. This conclusion is similar to the one made in SDS + acetamide medium.[17]

In Fig. 4.3, we have compared the cmc values of AOT in NH_4Cl solutions with those in NaCl solutions[1] and it is apparent from Fig. 4.3 that the cmc of AOT is higher in aqueous NaCl solutions. Therefore, the mixture of NH_4^+ and Na^+ reduces the cmc of AOT slightly more than Na^+ alone. Saha and coworkers[14,15] reported that the cmc of AOT-NH_4 (ammonium dioctylsulfosuccinate) is equal to 2.70 mmol kg^{-1}, which is slightly higher than

that of AOT thereby indicating that the cmc lowering effect of NH_4^+ is almost same as that of Na counterion. Consequently, the cmc values of AOT in NH_4Cl solutions are expected to be either equal or slightly higher than in NaCl solutions contrary to what we observed in this study. It is, therefore, interesting to note that with respect to AOT the cmc lowering effect of NH_4^+ in the presence of Na^+ is more than that of Na^+ alone. This reveals synergism in the cmc retarding ability of counterions when they are mixed and added to ionic surfactant solutions.

4.3.2 Counterion binding constant

The counter ion binding constant (β) of an ionic surfactant is commonly determined by using the well known Corrin – Harkins (CH) equation, which is of the form (Eq. 3.10 of chapter 3),

$$\ln c_0 = A - \beta \ln(c_0 + c_e) \qquad (4.2)$$

where A is a constant related to the standard free energy of micellization, c_0 is the cmc and c_e is the concentration of the added electrolyte. Eq. (4.2) was derived for solutions of ionic surfactant + electrolyte, wherein the added electrolyte contains the same counterion as that of the surfactant. The system studied here contains mixed counterions, viz. NH_4^+ and Na^+, and hence theoretically Eq. (4.2) is not applicable to such a system. In fact, in one of our recent studies[18] on aqueous systems containing cetylpyridinium chloride (CPC) + sodium salicylate (NaSa) / sodium benzoate (NaBz), we have shown that in the low concentration region of electrolyte the plot of CH equation deviated sharply from Eq. (4.2) to the extent that the slope of the plot became

positive instead of negative. Such a deviation was however not observed in the CH plot (Fig. 4.5) of the present system and instead the nature of the plot is similar to that of AOT + aqueous NaCl system (cf. chapter 3).[1] This demonstrates that cmc of AOT in aqueous medium in the presence of 1:1 inorganic salts depends mostly on the total counterion concentration (C) and very less on the specific type of the cationic counterions present in the solution. We can therefore write Eq. (4.2) in an empirical form as

$$\ln c_0 = A_e - \beta_e \ln C \qquad (4.3)$$

The terms A_e and β_e are considered as empirical constants. It may be noted that when the added electrolyte is of 1:1 type and contains same counterion as that of the surfactant, then Eqs. (4.2) and (4.3) become identical with $A_e = A$ and $\beta_e = \beta$. Alargova et al.[9-11] studied the micellization of the anionic surfactant sodium dodecyl dioxyethylene sulfate (SDDS) in aqueous medium in the presence of $NaCl/AlCl_3$ and expressed the variation of cmc with $NaCl/AlCl_3$ concentration using an expression similar to Eq. (4.3) wherein they used ionic strength (I) term in place of C. The terms I and C are, however, equal to each other when the added electrolyte is of 1:1 type. By comparing the plot of Eq. (4.3) for AOT + NH_4Cl (Fig. 4.5a) with that reported for AOT + NaCl solution,[1] by analogy we can conclude that shape change of AOT micelle takes place in aqueous NH_4Cl solution also as in the case of NaCl, but at a lower electrolyte concentration equal to 0.009 mol kg^{-1}. Thus, plots based on Eq. (4.2) or (4.3) exhibit different linear regions depending upon the shape of the ionic micelle. Alargova et al.[9-11] reported

micellar shape transition from sphere to cylinder in SDDS + NaCl + $AlCl_3$ system and their observation that the plot of $\ln c_0$ versus lnI was linear in a chosen range of ionic strength which corresponded to the region of cylindrical micellar shape also supports the view that graphical representation of Eq. (4.2) or (4.3) falls on different linear regions if micellar shape changes within the chosen range of electrolyte concentration. The β_e values obtained from Fig. 4.5a for the AOT + NH_4Cl system are 0.37 and 0.84, which are in close agreement with the β values reported[1] for AOT + NaCl system. The ionic size[19,20] of NH_4^+ is higher than that of Na^+ and both these ions have approximately same hydration numbers[21,22] (4 or 5). Therefore, due to binding of NH_4^+ the surface area of the AOT micelle increases causing increase in the surface area-to-volume ratio of the micelle, which may be responsible for a transition from prolate to cylindrical shape of AOT micelle (cf. chapter 3) at a lower concentration of NH_4Cl.

As mentioned above, theoretically Eq. (4.2) is not applicable to ionic surfactant solutions containing mixed counterions and we recently[18] proposed a modified form of the CH equation that was successfully applied to CPC + NaSa / NaBz systems. The modified CH equation was derived by considering the micellization equilibrium in the presence of two counterions as

$$N(S^-) + m_1(C_1^+) + m_2(C_2^-) \leftrightharpoons M^{z_n^-} \qquad (4.4)$$

S and M represent surfactant monomer with one negative charge and micelle with z_n negative charges, respectively. C_1 is the counterion (Na^+) from the surfactant molecule and C_2 is the counterion (in this case NH_4^+) from the

added electrolyte. The negative charge on the micelle, z_n, is equal to N - m_1- m_2. The number of monomers N, which aggregate to form the micelle M, is known as the aggregation number. Using the mass-action model and the thermodynamic relation between the equilibrium constant and the free energy change, we get

$$\ln[S] = \left[\frac{\ln[M]}{N} + \frac{\Delta G^0_{mic}}{NRT}\right] - \frac{m_1}{N}\ln[C_1] - \frac{m_2}{N}\ln[C_2] \qquad (4.5)$$

ΔG^0_{mic} refers to the standard free energy of micellization. R and T represent gas constant and absolute temperature, respectively. Considering the equilibrium (4.4) at a surfactant concentration, c_s, which is slightly above cmc, we can write Eq.(4.5) as

$$\ln c_0 \approx \frac{\Delta G^0_m}{RT} - \beta_1 \ln[c_0 + (c_s - c_0)(1 - \beta_1)] - \beta_2 \ln[c_e - (c_s - c_0)(\beta_2)] \qquad (4.6)$$

The commonly used approximation that ln[M]/N is negligible in comparison to ΔG^0_m / (RT) when c_s is slightly above c_0 has been applied in Eq.(4.6). ΔG^0_m ($=\Delta G^0_{mic}/N$) is the standard free energy of micellization per mole of surfactant monomer. β_1 ($= m_1/N$) and β_2 ($= m_2/N$) represent counterion binding constants of the counterions C_1 and C_2, respectively. The total counterion binding constant (β) of the surfactant is given by $\beta = \beta_1 + \beta_2$. Since the equilibrium (4.4) was considered at a surfactant concentration slightly above cmc, Eq. (4.6) can be reduced by approximating $(c_s - c_0) \approx 0+$ to the form

$$\ln c_0 \approx \frac{\Delta G^0_m}{RT} - \beta_1 \ln c_0 - \beta_2 \ln c_e \qquad (4.7)$$

Eq. (4.7) can also be rearranged to give

$$\ln c_0 = A' - B\ln c_e \qquad (4.8)$$

where $A' = \Delta G_m^0/[(1+\beta_1)RT]$ and $B = \beta_2/(1+\beta_1)$. Thus, we get a modified theoretical form of the CH equation (Eq. (4.8)) for surfactant systems containing mixed counter ions. Eq. (4.8) is applicable only when $c_e > 0$ and the added electrolyte contains counterion different from that in the surfactant molecule. In the high concentration region of electrolyte where $c_e >> c_0$, $c_0 + c_e \approx c_e$, it is interesting to note that the CH equation becomes similar to the modified CH equation. However, the modified form of the CH equation, unlike the CH equation, does not give the value of β directly from the slope. An attempt has been made to apply Eq. (4.8) to the present system under investigation by plotting $\ln c_0$ versus $\ln c_e$ in Fig. 4.5b. From Fig. 4.5b it can be seen that the modified CH plot also falls on two linear regions, which is similar to the nature of the CH plot of AOT in aqueous NaCl solution (cf. chapter 3) as well as to the nature of the plot (Fig. 4.5a) corresponding to Eq. (4.3). The change over in the value of the slope takes place at $[NH_4Cl] \approx 0.009$ mol kg^{-1} (c*), which coincides with that observed from Fig. 4.5a also. The values of the slope are: B = 0.19 below c* and B = 0.77 above c*. The values of the intercept A' obtained from the fitting in the two concentration regions are A'= -7.34 below c* and A' = -10.05 above c*. Since B is related to the two counterion binding constants, a sudden change in the value of B at c* implies sudden changes in the values of β_1 and β_2. The two values of B indicate that β

must be more than 0.19 below c* and it must be more than 0.77 above c* (otherwise $\beta_2 > \beta$, which is not allowed). Therefore, at c* the values of β, β_1 and β_2 suddenly change and this may be attributed to shape change of AOT micelle that may be anticipated to occur at c* in the light of the SANS measurements made on AOT + NaCl systems (cf. chapter 3). Presuming β_e as almost equal to β, we get $\beta_1 = 0.15$ and $\beta_2 = 0.22$ below c* and $\beta_1 = 0.04$ and $\beta_2 = 0.80$ above c*. Thus, above c* majority of the counterions bound to the micelle are NH_4^+ which is most probably the cause of shape change due to the increase in surface area-to-volume ratio of the micelle. The present study establishes that the SCB of AOT exists in the presence of mixed counterions also.

4.3.3. Free energy

The standard free energy of micellization per mole of ionic surfactant, ΔG^0_m, has two components, one for the transfer of ionic monomer and the other for the transfer of counter ions from the bulk to the micellar phase. These two components can be evaluated by using the relations $\Delta G^0_{hc} = RT\ln X_{cmc}$ and $\Delta G^0_{el} = \beta RT\ln X_{cmc}$. ΔG^0_{hc} is the standard free energy change due to transfer of one mole of hydrocarbon chain of the surfactant from the bulk to the micellar phase which also includes a free energy term due to repulsive interaction between the head groups. ΔG^0_{el} is the standard free energy change due to the transfer of counter ions from the bulk to the micellar interface and it includes free energy term due to electrostatic interactions between the head groups and counter ions. Considering $\beta_e \approx \beta$ as stated above,

we calculated the values of ΔG^0_m, ΔG^0_{hc} and ΔG^0_{el} (Table 4.5). A plot showing the variation of ΔG^0_m with the concentration of electrolyte is shown in Fig.4.6. For comparison, the values of ΔG^0_m for AOT + NaCl[1] are also shown in Fig. 4.6. It is clear from the plot that mixed counterions have a favouring effect on the micellization of AOT. The sudden decrease in ΔG^0_m at c*, which is not there in ΔG^0_{hc}, is due to the sudden shift in the value of β.

4.3.4. Adsorption

For systems containing only surfactants without added electrolytes and treating the adsorbed layer at the air-solution interface to be electroneutral, the expression for surface excess (Γ) is of the form,[23]

$$\Gamma = -\left(\frac{1}{2RT}\right)\left(\frac{d\gamma}{d\ln c_s}\right) \qquad (4.9)$$

In the presence of an added electrolyte XC_1, which contributes same counterion as that of the surfactant molecule, and again presuming electroneutrality of the adsorbed layer, Prosser and Frances[23] derived the relation for the surface excess at the cmc (Γ_{cmc}) as

$$\Gamma_{cmc} = -\frac{1}{RT}\left[\frac{1}{1+\frac{c_e}{c_o+c_e}}\right]\left(\frac{d\gamma}{d\ln c_s}\right)_{c_e} \qquad (4.10)$$

Eq. (4.10) reduces to equation (4.9) in the absence of electrolyte, i.e., when $c_e = 0$. Instead of electroneutrality ($\beta_{1ad} = 1$) of adsorbed layer, if we consider

partial counterion binding at the adsorbed layer ($0 < \beta_{1ad} < 1$), it can be shown that

$$\Gamma_{cmc} = -\frac{1}{RT}\left[\frac{1}{1+\frac{\beta_{1ad}c_o}{c_o+c_e}}\right]\left(\frac{d\gamma}{d\ln c_s}\right)_{c_e} \qquad (4.11)$$

β_{1ad} is defined as $\beta_{1ad} = \Gamma_{c1}/\Gamma$, where Γ_{c1} is surface excess of the counterion C_1.

For systems containing ionic surfactant with mixed counterions, expression for Γ has been modified.[18] In order to obtain the modified expression for Γ, we consider a surfactant SC_1 in the presence of an electrolyte XC_2 of concentration c_e. Both the ionic surfactant and added electrolyte are treated as 1:1 systems, and we will call C_1 and C_2 as native and foreign counterions, respectively. The Gibbs adsorption isotherm for this system can be written as

$$d\gamma = -RT(\Gamma_s d\ln a + \Gamma_{c1} d\ln a + \Gamma_{c2} d\ln a_e) \qquad (4.12)$$

In this system containing mixed counterions, Γ_{c1} is the surface excess of the native counterion and Γ_{c2} is the surface excess of the foreign counterion. The adsorption of the coion X^- has been neglected. The term 'a' refers to the activity of surfactant monomer S and also that of native counterion and 'a_e' refers to the activity of the foreign counterion. Presuming again electroneutrality of the adsorption layer, we can write

$$\Gamma = \Gamma_s = \Gamma_{c1} + \Gamma_{c2} \qquad (4.13)$$

In writing Eq. (4.13) we have considered that $\Gamma_{c1} = \beta_{1ad}\Gamma_s$, $\Gamma_{c2} = \beta_{2ad}\Gamma_s$ and $\beta_{1ad} + \beta_{2ad} = \beta_{ad} = 1$, where β_{1ad} and β_{2ad} are the binding constants of native

and foreign counterions at the adsorption layer, respectively. The activity is calculated from the relation $a = cf_{\pm}$ and the mean activity coefficient $f_{\pm}$ at 25 °C was evaluated from the Debye – Hückel theory as $\ln f_{\pm} = -1.172I^{1/2}$, where I is the ionic strength equal to $c_s + c_e$. While calculating $f_{\pm}$ from the Debye–Hückel theory, the effect of ionic size has been ignored. Eq. (4.12) becomes

$$d\gamma = -RT\Gamma[(1+\beta_{1ad})d\ln c_s + \beta_{2ad}d\ln c_e + 2d\ln f_{\pm}] \quad (4.14)$$

At constant c_e, Eq. (4.14) reduces to the form

$$d\gamma = -RT\Gamma[(1+\beta_{1ad})d\ln c_s + 2d\ln f_{\pm}] \quad (4.15)$$

Substituting the expression for $\ln f_{\pm}$, we get

$$d\gamma = -RT\Gamma[(1+\beta_{1ad})d\ln c_s - 1.172dc_s/(c_s + c_e)^{1/2}] \quad (4.16)$$

At the cmc, Eq. (4.16) can be rearranged as

$$\Gamma_{cmc} = -\left(\frac{1}{RT}\right)\left(\frac{1}{1+\beta_{1ad} - \frac{1.172c_0}{(c_0+c_e)^{1/2}}}\right)\left(\frac{d\gamma}{d\ln c_s}\right)_{c_e} \quad (4.17)$$

If the activity coefficient terms are neglected, then we get from Eq. (4.14)

$$\Gamma_{cmc} = -\frac{1}{RT(1+\beta_{1ad})}\left(\frac{d\gamma}{d\ln c_s}\right)_{c_e} \quad (4.18)$$

It may be noted that in the above Eqs. (4.17) and (4.18) $\beta_{1ad} = \beta_{ad} - \beta_{2ad}$. The surface excess at the cmc, Γ_{cmc}, was evaluated from Eqs. (4.17) or (4.18) by substituting the value of the slope $d\gamma/d\ln c_s$ determined near the cmc and by taking arbitrary values of β_{ad} and β_{2ad}. The maximum difference in the values of Γ_{cmc} calculated from Eqs. (4.17) and (4.18) is found to be about 0.08×10^{-6} mol m^{-2}, and hence we chose Eq. (4.18) for estimating Γ_{cmc}. Although Eq. (4.18) is an exact theoretical expression for the surface excess of ionic

surfactants in the presence of mixed counterions, its application is hampered due to non-availability of actual values of β_{1ad} or β_{2ad}.

To overcome the above problem in using Eq. (4.18) we adopted the following treatment: For a chosen value of β_{ad}, the value of β_{2ad} will vary depending upon the concentration of NH_4Cl. We consider electroneutral adsorption layer, i.e. $\beta_{ad} = \beta_{1ad} + \beta_{2ad} = 1$. We presume that the counterions obey Henry's adsorption isotherm (limiting Langmuir's adsorption isotherm) near the cmc. Theoretical modeling of adsorption in aqueous SDS + NaCl system done by Kralchevsky and coworkers[24,25] indicates for counterions near the cmc, in fact, adsorption similar to Henry's type isotherm. We can therefore write,

$$\beta_{1ad} \approx K_{1ad}c_s \quad \text{and} \quad \beta_{2ad} \approx K_{2ad}c_e \tag{4.19}$$

Further, the adsorption coefficients K_{1ad} (for Na^+) and K_{2ad} (for NH_4^+) are treated to have approximately same value, which is justified by the observation that AOT + NH_4Cl and AOT + NaCl solutions corresponding to a particular concentration of electrolyte have almost same surface tension near the cmc. We then obtain at the cmc

$$\beta_{1ad}/\beta_{2ad} \approx c_0/c_e \tag{4.20}$$

From Eq. (4.20) we can easily get the relation that

$$\beta_{1ad} = c_0/(c_0 + c_e) \tag{4.21}$$

It is interesting to note that by substituting the value of β_{1ad} given by Eq. (4.21) in Eq. (4.18) we get the same relation for Γ_{cmc} as that given by Eq. (4.10). This finding enables us to evaluate from Eq. (4.10) the surface excess

of AOT in the presence of Na^+ and NH_4^+ counterions without knowing the values of β_{1ad} or β_{2ad}. It may be noted that Eq. (4.10) is applicable to compute the surface excess in the electroneutral adsorbed layer of ionic surfactants under the influence of single as well as mixed counterions, but the significance of the term $c_0/(c_0 + c_e)$ in Eq. (4.10) is different in the two cases. *(i) In the presence of mixed counterions, $c_0/(c_0 + c_e)$ term accounts for the* number of native counterions bound per adsorbed monomer of the surfactant (β_{1ad}) under the assumption that counterions obey Henry's adsorption isotherm. (ii) On the other hand, in the presence single counterion $c_0/(c_0 + c_e)$ term appears in Eq. (4.10) due to the contribution of added electrolyte to the concentration of the native counterion in the solution and more specifically this term emerges while transforming $d\ln(c_s + c_e)$ into $d\ln c_s$ at the cmc and at constant c_e. The values of Γ_{cmc} of AOT in the presence of mixed counterions evaluated from Eq. (4.10) are presented in Fig.4.7.

4.4. Conclusions

Critical micelle concentration of AOT in aqueous medium at 25 °C as a function of NH_4Cl concentration has been determined by measuring surface tension and fluorescence emission of pyrene probe. The present study revealed that the SCB of AOT exists in the presence of mixed counterions also. The concentration c* of NH_4Cl (0.009 mol kg^{-1}) at which the counterion binding constant of AOT changes suddenly is lower than that of NaCl (0.015 mol kg^{-1}). In the presence of added NH_4Cl, as in the case of added NaCl, the sudden change of counterion binding constant of AOT is attributed to the

change in the micellar shape. Due to binding of NH_4^+ the surface area of the AOT micelle increases causing increase in the surface area-to-volume ratio of the micelle, which may be responsible for a transition from prolate to cylindrical shape of AOT micelle at a lower concentration of NH_4Cl. In the region of prolate shape (below c*) the amounts of bound sodium and ammonium counterions are almost equal, whereas in the region of cylindrical shape (above c*) bound counterions are predominantly ammonium. It is concluded from this study that (i) cmc depends mostly on the total counterion concentration in the solution and very less on the specific type of the cationic counterions present in the solution and (ii) synergism in the cmc retarding ability of counterions takes place when they are mixed and added to ionic surfactant solutions. In the AOT + NH_4Cl system, the plots of CH equation and modified CH equation look similar unlike in the case of CPC + NaSa / NaBz system,[18] which implied that when the mixed counterions are inorganic cations CH equation can still be used as an empirical equation by treating the term $c_0 + c_e$ as the total counterion concentration. It has been shown that the expression for the surface excess of AOT in the presence of Na^+ and NH_4^+ counterions becomes similar to the expression for surface excess of AOT in the presence of Na^+ counterion alone, provided we consider the mixed counterions to obey Henry's adsorption isotherm. This approach provides a method to compute the surface excess of ionic surfactants in the presence of mixed counterions.

4.5. References

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Table 4.1 - Surface Tension (γ) values of AOT in aqueous ammonium chloride solution at 25 °C.

[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}
		[NH_4Cl] = 0.0 mol kg^{-1}			
0.0043	71.0	0.2748	50.7	4.5662	30.1
0.0086	69.4	0.4597	46.4	5.7574	29.7
0.0172	66.9	0.7388	43.2	7.0105	29.1
0.0343	64.4	1.1208	38.4	8.4104	29.2
0.0643	60.5	1.6595	35.3	9.9844	28.5
0.1068	57.5	2.4764	31.7		
0.1702	54.3	3.4767	30.7		
		[NH_4Cl] =0 .0012 mol kg^{-1}			
0.0041	64.5	0.1206	48.8	2.3133	30.7
0.0081	61.4	0.1841	46.2	2.9963	30.1
0.0121	59.3	0.2823	44.1	3.7238	29.8
0.0162	58.2	0.4176	41.7	4.4673	29.5
0.0202	57.3	0.6065	39.6	5.2041	29.2
0.0283	55.0	0.8628	37.1	5.9901	29.4
0.0445	53.3	1.2134	34.9	6.8975	29.1
0.0766	51.1	1.7076	32.6		
		[NH_4Cl] = 0.0022 mol kg^{-1}			
0.0026	64.5	0.1221	46.8	1.4827	31.8
0.0051	61.7	0.1869	43.8	2.0014	29.9
0.0077	60.1	0.2752	42.1	2.5987	29.8
0.0129	57.6	0.3952	39.8	3.2261	29.5
0.0257	53.9	0.5581	38.1	3.938	29.1
0.0461	51.5	0.7812	36.1	4.7193	29.0
0.0766	48.7	1.096	33.9	5.7797	28.6
		[NH_4Cl] = 0.0054 mol kg^{-1}			
0.0031	63.5	0.2265	40.4	2.0410	28.3
0.0062	59.8	0.3452	37.9	2.6255	28.0
0.0125	55.5	0.5070	35.8	3.2970	28.4
0.0249	52.1	0.7026	33.6	4.1262	28.0
0.0498	48.7	0.9437	32.0	5.0854	27.8
0.0868	45.2	1.2484	30.6	6.4945	27.6
0.1419	42.7	1.6044	29.2		

Table 4.1 - Continued

[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}
		[NH_4Cl] = 0.0070 mol kg^{-1}			
0.0026	63.1	0.1305	42.1	1.7755	28.0
0.0053	59.5	0.1944	40.2	2.2741	27.5
0.0079	57.2	0.2826	38.1	2.8498	27.3
0.0106	55.8	0.4057	36.1	3.4561	27.1
0.0185	52.7	0.5728	34.2	4.1463	27.6
0.0316	50.2	0.8014	32.0	4.9064	27.4
0.0526	47.3	1.0822	30.4	5.7270	27.2
0.0839	44.7	1.4046	28.8		
		[NH_4Cl] = 0.0098 mol kg^{-1}			
0.0017	63.9	0.1092	42	1.3396	27.7
0.0034	61.0	0.1583	39.7	1.7259	27.0
0.0051	58.5	0.2226	38.1	2.1299	26.9
0.0102	54.3	0.3087	36.0	2.5276	26.7
0.0188	51.2	0.4148	34.3	2.9031	27.1
0.0323	48.7	0.5599	32.9	3.3228	27.1
0.0509	46.2	0.7512	31.2	3.8582	26.9
0.0760	43.7	1.0029	29.2		
		[NH_4Cl] = 0.0123 mol kg^{-1}			
0.0011	66.3	0.1299	40.3	1.2452	28.0
0.0022	63.8	0.1857	38.1	1.4808	27.5
0.0044	59.6	0.2592	36.7	1.7145	27.3
0.0099	54.4	0.3528	35.0	1.9650	27.3
0.0208	50.2	0.4847	33.0	2.2506	26.9
0.0371	46.9	0.6463	31.6	2.5794	26.8
0.0586	44.4	0.8282	30.1		
0.0882	42.2	1.0217	28.7		

Table 4.1 - Continued

[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}
		[NH_4Cl] = 0.0200 mol kg^{-1}			
0.0010	61.3	0.1470	35.8	0.8008	26.1
0.0020	58.8	0.1781	35.0	0.9121	25.9
0.0039	54.8	0.2129	33.5	1.0390	25.9
0.0059	53.1	0.2512	32.7	1.1757	25.8
0.0097	50.5	0.2936	32.2	1.3285	25.9
0.0156	47.9	0.3404	31.2	1.5013	25.7
0.0243	46.0	0.3914	30.5	1.6886	25.9
0.0367	43.5	0.4459	29.6	1.8758	25.8
0.0529	41.6	0.5042	29.0	2.0778	25.5
0.0718	39.8	0.5673	28.4	2.3399	25.5
0.0941	38.1	0.6343	27.6		
0.1189	37.1	0.7107	27.3		
		[NH_4Cl] = 0.0290 mol kg^{-1}			
0.0008	62.9	0.0560	39.5	0.4519	28.2
0.0025	56.9	0.0721	38.0	0.5280	27.1
0.0042	53.7	0.0920	36.9	0.6207	26.2
0.0067	51.1	0.1170	35.6	0.7449	25.8
0.0100	49.2	0.1476	34.2	0.9184	25.3
0.0142	47.1	0.1850	33.0	1.0837	25.4
0.0192	45.6	0.2286	31.4	1.2936	25.8
0.0258	43.8	0.2778	30.5	1.5233	25.8
0.0340	42.6	0.3319	29.5	1.7696	25.8
0.0439	40.6	0.3901	29.0	1.9911	25.7
		[NH_4Cl] = 0 .03890 mol kg^{-1}			
0.0004	68.2	0.0691	38.4	0.5402	26.9
0.0012	64.3	0.0997	36.4	0.6199	26.6
0.0027	58.3	0.1415	34.2	0.6961	26.5
0.0057	51.3	0.1923	32.4	0.7748	26.7
0.0111	48.5	0.2470	31.0	0.8620	26.3
0.0186	45.7	0.3089	29.9	0.9281	26.6
0.0297	42.9	0.3845	28.5		
0.0461	40.6	0.4605	27.7		

Table 4.1 - Continued

[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}
		$[NH_4Cl]$ = 0.0500 mol kg^{-1}			
0.0003	70.3	0.0152	47.4	0.1952	32.2
0.0030	67.5	0.0225	44.9	0.2971	29.5
0.0020	63.4	0.0319	43.1	0.4223	28.0
0.0033	59.9	0.0456	41.0	0.5548	26.9
0.0049	56.0	0.0664	38.6	0.7210	26.5
0.0072	52.6	0.0948	36.4	0.7838	26.4
0.0104	50.0	0.1348	34.4		

Table 4.2 - Values of cmc of AOT in aqueous NH_4Cl solutions at 25 °C obtained from surface tension data

$[NH_4Cl]$/ mol kg^{-1}	cmc/ mmol kg^{-1}	$[NH_4Cl]$/ mol kg^{-1}	cmc/ mmol kg^{-1}
0.0	2.60	0.0123	1.30
0.0012	2.42	0.0200	0.90
0.0022	2.04	0.0290	0.69
0.0054	1.78	0.0389	0.51
0.0070	1.70	0.0500	0.43
0.0098	1.48		

Table 4.3 – Ratio of Intensities (I_1/ I_3) of Fluorescence Emission of Pyrene in aqueous NH_4Cl at 25° C.

[AOT]/ mmol kg^{-1}	I_1/ I_3	[AOT]/ mmol kg^{-1}	I_1/ I_3	[AOT]/ mmol kg^{-1}	I_1/ I_3
		[NH_4Cl] = 0.0012 mol kg^{-1}			
0.0280	1.7743	1.9600	1.5460	4.8000	1.0739
0.1400	1.7665	2.2400	1.4644	5.6000	1.0475
0.2800	1.7532	2.5200	1.3306	7.0000	1.0241
0.5600	1.7414	2.8000	1.2475	8.0000	1.0192
0.8400	1.7061	3.0800	1.1993		
1.2000	1.6600	3.3600	1.1902		
1.4000	1.6330	3.6400	1.1252		
1.6800	1.5699	3.9200	1.1067		
		[NH_4Cl] = 0.0054 mol kg^{-1}			
0.0280	1.7987	1.4000	1.5708	3.3600	1.0400
0.1400	1.7774	1.6800	1.4237	3.9200	1.0243
0.2800	1.7618	1.9600	1.2551	4.7600	1.0010
0.5600	1.7343	2.2400	1.1657	5.6000	0.9410
0.8400	1.6959	2.5200	1.1052	6.7200	0.9854
1.1200	1.6591	2.8000	1.0745	7.5600	0.9803
		[NH_4Cl] = 0.0098 mol kg^{-1}			
0.0140	1.7583	0.4200	1.7328	2.3800	1.0427
0.0280	1.7874	0.7000	1.6781	2.8000	1.0169
0.0840	1.7488	0.9800	1.6143	4.2000	0.9875
0.1400	1.7625	1.2600	1.4924	5.6000	0.9729
0.2240	1.7482	1.5400	1.2428		
0.3080	1.7250	1.9600	1.0993		
0.0140	1.7583	0.4200	1.7328		
		[NH_4Cl] = 0.0123 mol kg^{-1}			
0.0140	1.7393	0.8400	1.6537	3.6400	0.9918
0.0280	1.7438	1.1200	1.5178	4.4800	0.9783
0.1400	1.7530	1.4000	1.2515	5.6000	0.9864
0.2800	1.7298	1.9600	1.0589	6.4400	0.9863
0.5600	1.6911	2.8000	0.9994		
		[NH_4Cl] = 0 .0220 mol kg^{-1}			
0.0100	1.7518	0.2800	1.7153	1.9600	1.1501
0.0300	1.7656	0.5600	1.6528	2.8000	1.1498
0.0800	1.7696	0.8400	1.4985		
0.1400	1.7419	1.1200	1.2121		

Table 4.3 – Continued

[AOT]/ mmol kg^{-1}	I_1/ I_3	[AOT]/ mmol kg^{-1}	I_1/ I_3	[AOT]/ mmol kg^{-1}	I_1/ I_3
		[NH_4Cl] = 0.0380 mol kg^{-1}			
0.0140	1.7959	0.2800	1.7771	0.8960	1.2026
0.0280	1.7848	0.3920	1.7028	1.1200	1.1726
0.0840	1.7877	0.5040	1.6590	1.6800	1.1675
0.1680	1.7608	0.7000	1.3054		

Table 4.4 - Values of the fitted parameters of Eq. 4.1 for AOT in different concentrations of aqueous NH_4Cl solutions at 25° C.

[NH_4Cl] / mol kg^{-1}	A_1	A_2	$10^3 x_o$	$10^4 b_0$	$10^3(x_0 + 2b_0)$	x_0 / b_0
0.0012	1.7896	1.0361	2.31	6.6	3.63	3.5
0.0054	1.7900	1.0051	1.72	4.0	2.52	4.3
0.0098	1.7549	0.9981	1.39	2.8	1.95	5.0
0.0123	1.7433	0.9923	1.28	2.3	1.74	5.6
0.0220	1.7510	1.1432	0.87	1.5	1.17	5.8
0.0380	1.7794	1.1733	0.60	0.8	0.76	7.5

Table 4.5. Calculated values of the different standard free energy terms and surface excess at the cmc for AOT in different concentrations of aqueous NH_4Cl at 25° C.

[NH_4Cl] / mol kg^{-1}	ΔG_m^0 / kJ mol^{-1}	ΔG_{hc}^0 / kJ mol^{-1}	ΔG_{hc}^0 / kJ mol^{-1}	$\Gamma_{cmc} \times 10^6$ / mol m^{-2}
0.0	-33.8	-24.7	-9.1	1.79
0.0012	-34.1	-24.9	-9.2	1.61
0.0022	-34.7	-25.3	-9.4	1.73
0.0054	-35.1	-25.6	-9.5	1.82
0.0070	-35.3	-25.8	-9.5	1.95
0.0098	-48.0	-26.1	-21.9	2.05
0.0123	-48.6	-26.4	-22.2	1.98
0.0200	-50.3	-27.3	-23.0	2.23
0.0290	-51.5	-28.0	-23.5	2.17
0.0389	-52.9	-28.7	-24.2	2.19
0.0500	-53.7	-29.2	-24.5	2.09

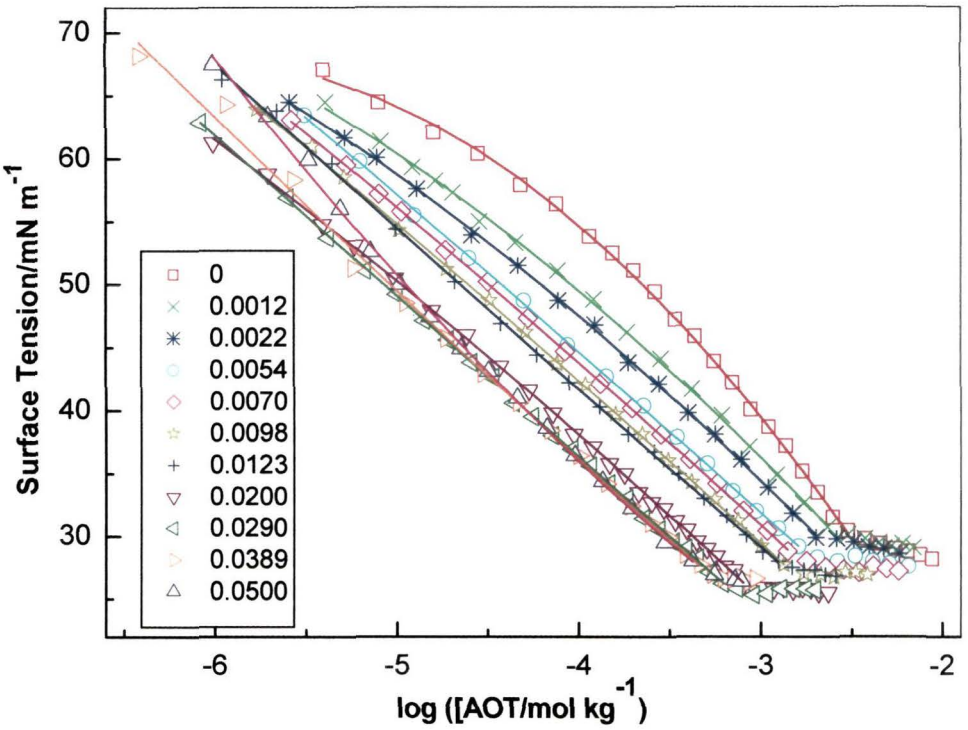

Fig.4.1. Variation of surface tension of aqueous AOT + NH_4Cl solution with AOT concentration. The molal concentrations of NH_4Cl are indicated in the inset. The lines represent the surface tension values calculated by the polynomial fitting of the experimental data below cmc.

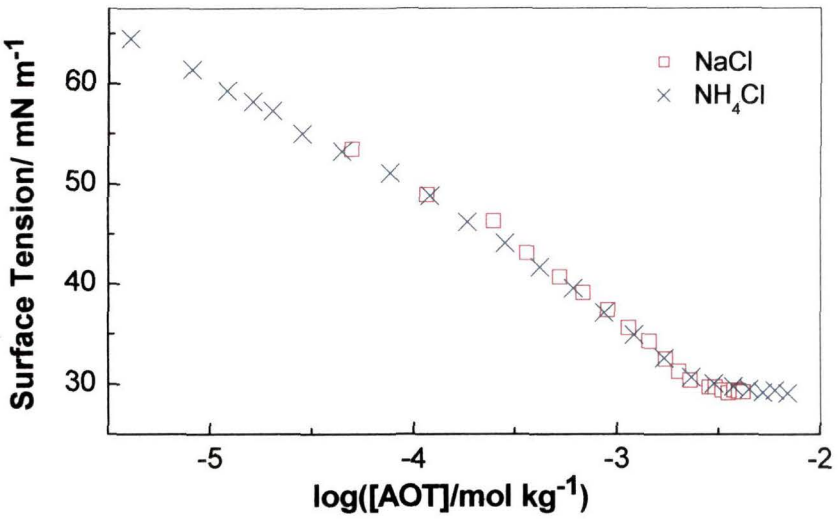

Fig. 4.2. Variation of surface tension of AOT + NH_4Cl and AOT + NaCl (ref.1) with AOT concentration at 25° C for 0.0012 mol kg^{-1} of the electrolyte.

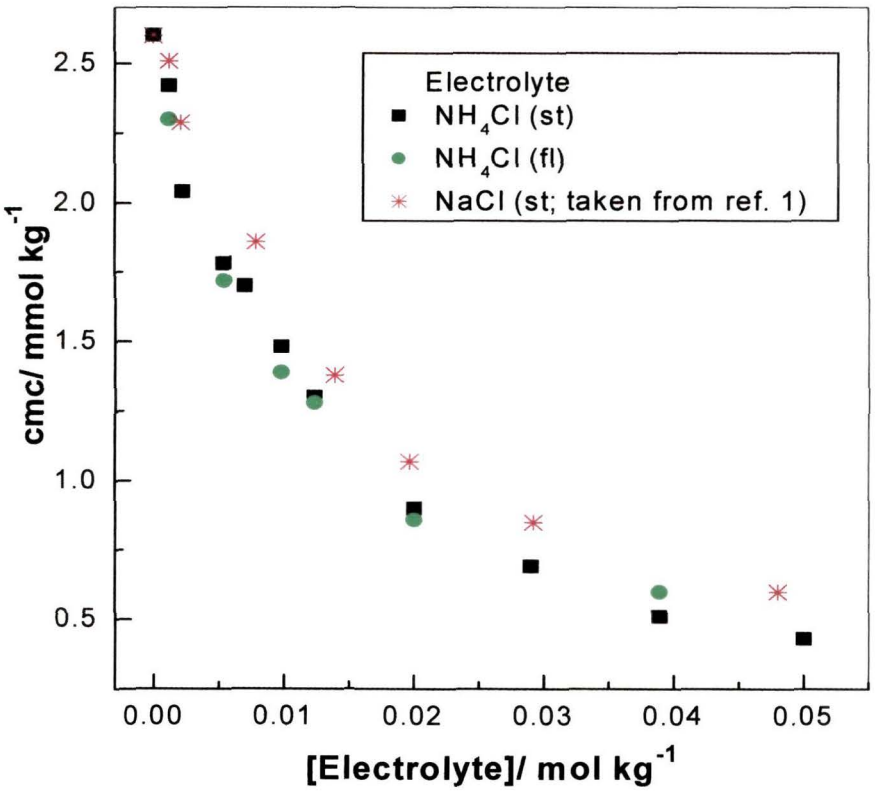

Fig. 4.3. Variation of cmc of AOT with added electrolyte concentration at 25°C. 'st' and 'fl' indicate that cmc values are from surface tension and fluorescence (x_0 of Eq. 4.1) data, respectively.

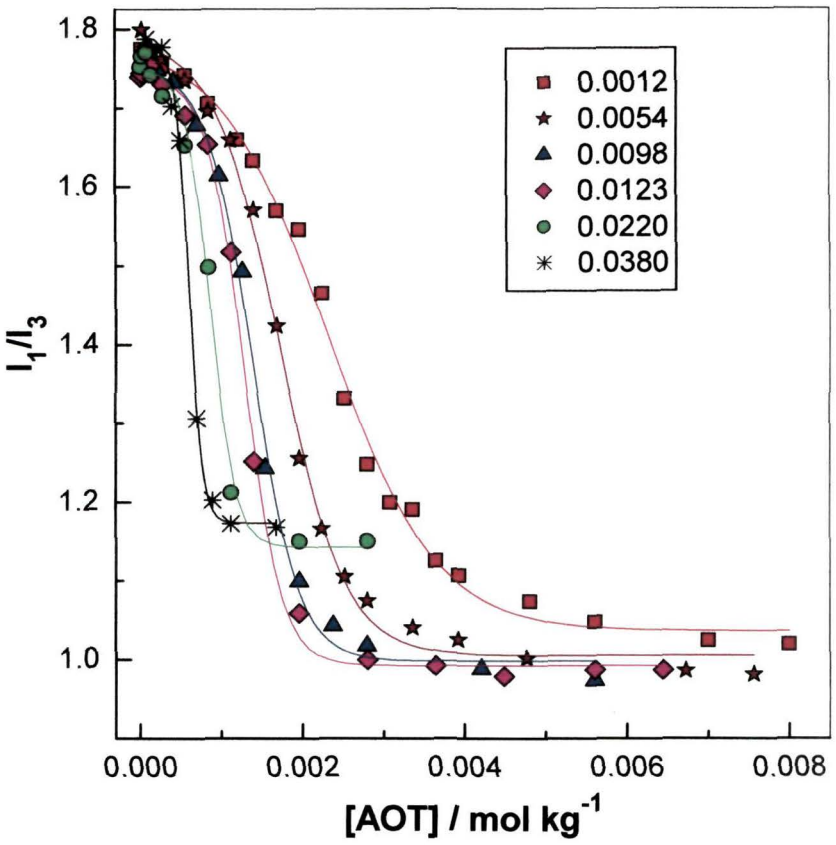

Fig. 4.4. Variation of I_1/I_3 of pyrene with AOT concentration at 25°C in aqueous NH_4Cl solutions. The concentrations of NH_4Cl are indicated in the inset.

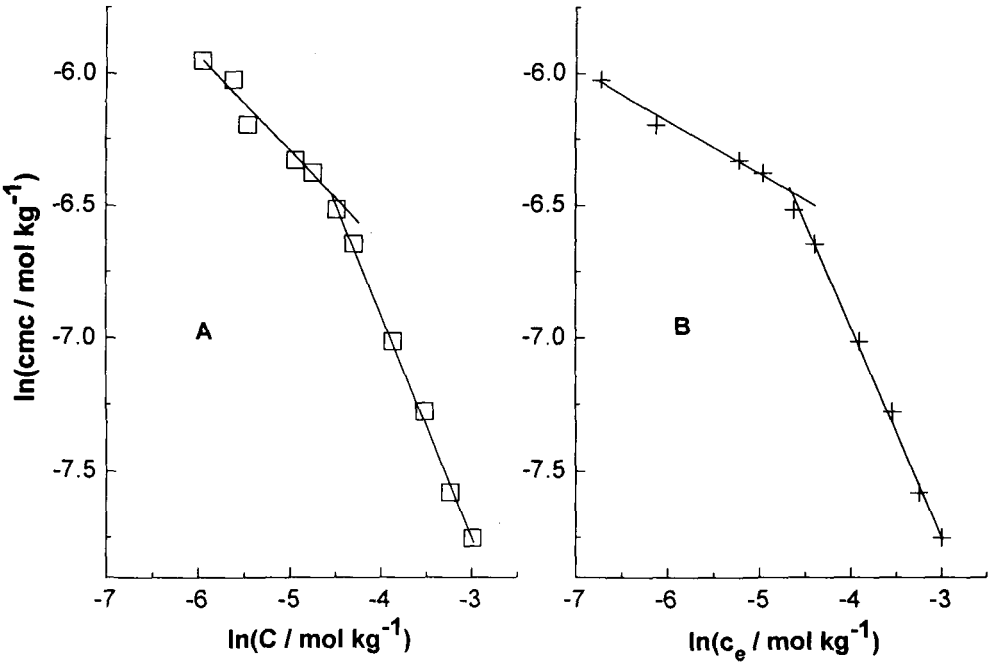

Fig. 4.5. Plots of (A) Eq. (4.3) and (B) modified CH Eq. (4.8) for aqueous solutions of AOT + NH_4Cl at 25° C.

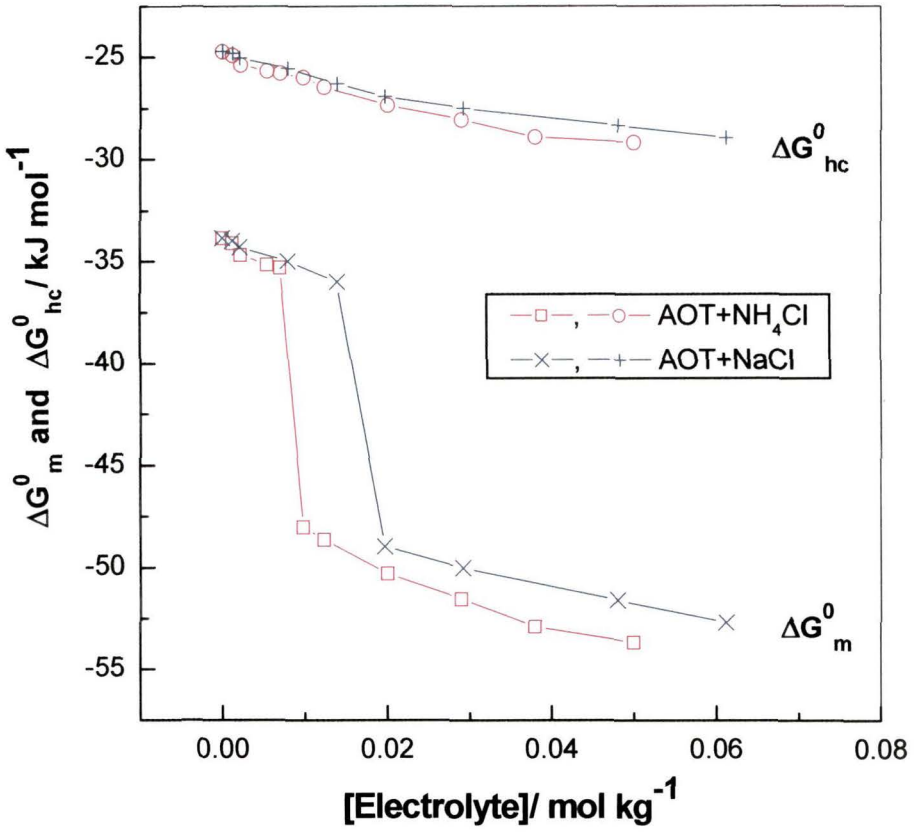

Fig. 4.6. Variation of ΔG^0_m and ΔG^0_{hc} of AOT with concentration of NH_4Cl and NaCl (data from ref.1)

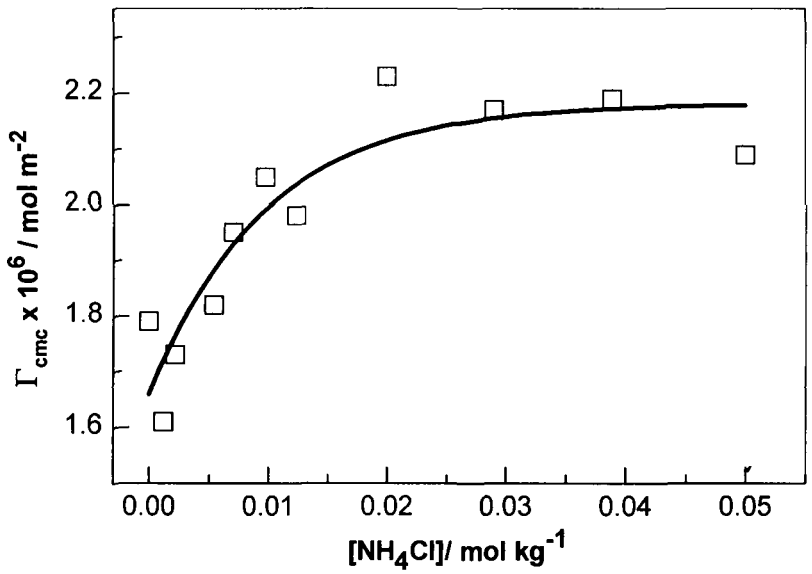

Fig.4.7. Surface excess of AOT at 25 °C in aqueous medium in the presence of NH_4Cl calculated from Eq. (5).

CHAPTER 5

Counterion Binding Behaviour of Sodium Dioctylsulfosuccinate and Sodium Dodecylsulfate in Aqueous Ethylene Glycol Medium. Breakdown of Corrin-Harkins Equation

5.1. Introduction

The role of solvent on the aggregation phenomenon of surfactants has been highlighted in section 1.8 of chapter 1. In this chapter, we have chosen water + ethylene glycol (EG) mixed solvent media for investigating the aggregation behaviour of AOT. The main objective of this study is to examine how variation in the solvent property caused by the addition of EG affects the special counterion binding behaviour (SCB) of AOT. Our earlier work[1] showed that the cmc of AOT increases with increase in EG content of the medium and also revealed occurrence of a new break in the surfactant isotherm of AOT far below the cmc when the media contain 60 weight % or more of EG. Mukherjee et al.,[2,3] on the contrary, had reported decrease in cmc of AOT with increase in EG content particularly in the region where the EG amount is more than 63 weight % and the cmc of AOT reported by them in EG was surprisingly lower than in water. The new break in the surface tension isotherm was due to hydrogen bonding between AOT and EG which was supported by the UV spectra.[1] But this surface tension break appears similar to that at the cmc thereby misleading one to consider that AOT has lower cmc values in water + EG media when EG amount is $\geq$ 60 weight %. Therefore, in this study we also intend to ascertain the correct cmc values of AOT in water + EG media. To achieve our above mentioned objectives, we have measured the surface tension of AOT in water + EG media as a function of NaCl concentration. Adding NaCl serves two purposes. (i) Firstly, the actual cmc

value would decrease with increase in NaCl concentration, whereas the surface tension break due to hydrogen bonding is expected to vanish by adding NaCl thereby enabling us to distinguish the actual cmc from any virtual or pseudo cmc. (ii) Secondly, counterion binding constants can be determined by using the Corrin – Harkins (CH) method, which would enable us to examine the SCB of AOT. For the purpose of comparison, we have also made surface tension and conductance measurements of sodium dodecylsulfate (SDS) in water + EG media.

5.2. Experimental Section

AOT (Sigma, > 99 %), NaCl (Merck, 99.5 %) and EG (SRL, > 99 %) were used without further purification. Milli-Q grade water was used for making samples. Surface tension measurements were made as described in the preceding chapters. Conductance measurements were made by using B905 Wayne Kerr Automatic Precision Bridge and a dip-type conductivity cell. Temperature is maintained at 25 °C.

5.3. Results and Discussion

The experimental values of surface tension (γ) of AOT in water + EG media as a function of NaCl concentration are given in Tables 5.1a - 5.1j and the surface tension isotherms are shown in Figs. 5.1 – 5.10. The surface tension break corresponding to the cmc monotonically shifts to lower surfactant concentration when the amount of NaCl in the medium increases resulting in the lowering of cmc with increase in NaCl concentration. On the other hand, the surface tension break due to the hydrogen bonding between

water, EG and AOT occurring in the region where EG weight % is ≥ 60, tends to vanish gradually or becomes less and less pronounced with increasing amount of NaCl in the medium, which may be attributed to the weakening of the hydrogen bonding between water, EG and AOT by the presence of electrolyte in accordance with the report[4-6] that in water added NaCl or KCl reduces hydrogen bonding between water molecules. Hydrogen bonding between AOT and EG has been reported[7,8] in the AOT reverse micellar medium also.

The cmc values are given in Table 5.2 and the cmc of AOT in water + EG medium increases with increase in the amount of EG (Fig. 5.11) similar to the general trend observed for the variation of cmc in aqueous polar organic solvents. The dependence of these cmc values on NaCl concentration (Table 5.2) confirms that these are the true cmc values of AOT.

The Corrin – Harkins (CH) plots according to the CH equation

$$\ln c_0 = A - \beta \ln(c_0 + c_e) \qquad (5.1)$$

are shown in Fig. 5.12. The terms c_0 and c_e represent cmc and electrolyte concentration, respectively. As evident from Fig. 5.12, the SCB of AOT exists in 10 and 20 % EG. However, in 10 and 20 % EG, the two values of the counterion binding constant (β) and the concentration c* at which the value of β suddenly changes are different from those in water (Table 5.3). In 30 % EG, the SCB of AOT disappears and β has one value equal to 0.44. Thus, the SCB of AOT is greatly influenced by the nature of the solvent medium as reported[9] in water + propylene carbonate medium also.

At 40 % and above 40 % EG, a new type of deviation from the CH equation is observed (Figs. 5.12 and 5.13). This deviation is different from that observed in 0 to 20 weight % EG. Such type of deviation from the CH equation in aqueous organic solvent medium has not been reported till now to the best of our knowledge. This particular deviation occurs because the rate of decrease of cmc with the initial addition of electrolyte is more up to a certain electrolyte concentration (c#). As a result, the value of the term cmc + c_e, which accounts for the total counterion concentration in the solution, decreases with increase in c_e initially and starts increasing only above c#. This is shown in Fig. 5.14 by drawing representative plots in 70 and 80 % EG media. Therefore, in these water + EG media, there is limitation on using the CH equation for determination of β. We, however, made an attempt to determine β in water + EG media with weight % of EG ≥ 40 by considering in Fig. 5.12 only the data points lying above c#. The values of β obtained thus are listed in Table 5.3. Generally, the value of β decreases with increase in the amount of polar organic solvent. Surprisingly, such a general trend is not observed in the present case of AOT in water + EG media. No regular trend in the variation of β with EG amount has also been observed.

The other common method used for determining β is the slope-ratio method from the conductivity data. For AOT in water, conductance method is not a suitable method as no break in the plot of specific conductivity (κ) versus concentration occurs near the cmc. We however observed that conductivity data of AOT in water + EG media exhibits break near cmc when

the amount of EG is equal to or more than 40 %. The experimental values of κ are given in Table 5.4 and also shown in Fig. 5.15. Values of the cmc of AOT in water + EG media determined from κ data are given in Table 5.2 and are comparable to the values obtained from the surface tension. The values of β determined from the slope-ratio method are given in Table 5.3. It is surprising to observe that the values of β estimated from the CH plots are considerably higher than those obtained from the slope-ratio method. It therefore appears that there is limitation in applying the CH equation in water + EG media when EG amount is ≥ 40 weight %.

In order to ascertain the above observation about the limitation in applying the CH equation for AOT in water + EG medium, we also measured surface tension and conductance of SDS in water + EG media. Surface tension of SDS was also measured in water + EG media at varying amounts of NaCl. The experimental data of surface tension and κ are given in Tables 5.5a – 5.5g and 5.6, respectively. The surface tension and κ data of SDS are also shown in Figs. 5.16 – 5.22 and Fig. 5.23, respectively. The values of cmc of SDS in water + EG media as a function of NaCl concentration determined from the surface tension data are given in Table 5.7. The cmc values of SDS in water + EG media determined from the κ data are also listed in Table 5.7 and are comparable with those obtained from the surface tension data. The variation of cmc of SDS with EG content is similar to that of AOT (Fig. 5.11). The present cmc values of SDS are in close agreement with the reported[10-12] values as shown in Fig. 5.24. Using the cmc data of SDS, CH plots were drawn in

Fig. 5.25. In the case of SDS also, deviation from the CH plot similar to that observed in AOT has been found to take place when the EG amount exceeds 40 %. An expanded view of this deviation in 70 % EG medium is shown in Fig. 5.26. It is therefore clear that the deviation from the CH plot occurring in water + EG media is not specific to AOT, but rather is of a general type. We again compared the values of β of SDS determined from the CH plots with those calculated from the slope-ratio method (Table 5.3). As observed in the case of AOT, the values of β of SDS estimated from the CH plot are considerably higher than those obtained from the slope-ratio method (in the region of weight % of EG wherein deviation from the CH equation occurs).

5.4. Conclusions

It has been confirmed that cmc of AOT in ethylene glycol is more (about 68 times) than that in water and the variation of cmc of AOT in water + EG media as a function of EG content follow the general trend. The SCB of AOT has a dependence on the solvent and disappears in water + EG media containing ≥ 30 weight % EG. In water + EG medium, the Corrin-Harkins equation is not applicable to ionic surfactants for determining the counterion binding constant when the EG content becomes ≥ 40 weight %. For a better understanding of this deviation from the CH plot in aqueous organic solvent, further studies are to be undertaken.

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Table 5.1a. Experimental values of surface tension of AOT in water + 10 % EG media containing varying amounts of NaCl at 25 °C

[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0 mol kg^{-1}			
0.0060	62.4	0.4403	44.4	3.3297	30.4
0.0240	57.8	0.6395	42.1	4.3307	29.8
0.0538	55.2	0.9175	39.1	5.5555	29.6
0.1133	51.3	1.2941	36.7	7.0225	28.7
0.1901	49.5	1.8083	34.0	8.8662	27.7
0.2956	46.6	2.4846	31.6	10.729	28.1
		[NaCl] = 0.0020 mol kg^{-1}			
0.0039	61.2	0.3536	41.8	3.3130	29.4
0.0158	56.4	0.5202	40.0	4.0588	29.0
0.0354	53.3	0.7536	37.6	4.8765	29.0
0.0667	50.7	1.0973	35.2	5.7771	28.7
0.1096	48.0	1.5494	33.0	6.8358	28.1
0.1637	45.7	2.0860	31.0	8.0983	28.9
0.2403	43.8	2.6818	30.4	9.2171	28.1
		[NaCl] = 0.0053 mol kg^{-1}			
0.0031	60.4	0.3860	38.4	2.4643	28.7
0.0123	54.5	0.5552	36.4	2.9886	28.3
0.0307	50.5	0.7727	34.5	3.7337	28.3
0.0612	47.2	1.0322	33.2	4.8766	28.0
0.1066	44.6	1.3507	31.4	6.0508	27.6
0.1666	42.6	1.6940	30.0	7.0648	27.5
0.2555	40.7	2.0753	29.0		
		[NaCl] = 0.0076 mol kg^{-1}			
0.0030	60.9	0.6779	34.3	3.3095	27.8
0.0118	54.5	1.0027	31.6	3.8167	27.5
0.0295	50.3	1.3513	30.2	4.4533	27.7
0.0589	46.7	1.7161	28.8	5.2762	27.5
0.1316	43.0	2.0902	28.0	6.3812	27.1
0.2598	39.5	2.4676	28.1		
0.4395	36.9	2.8741	27.9		

Table 5.1a. Continued

[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0110 mol kg^{-1}			
0.0021	60.3	0.3444	35.9	2.4674	27.7
0.0103	54.0	0.5269	34.1	2.9493	27.2
0.0309	48.2	0.7666	31.9	3.4576	27.1
0.0513	44.5	1.0806	29.7	3.9446	27.0
0.1119	41.2	1.4982	28.1	4.4765	27.0
0.2009	38.6	1.9738	27.6		
		[NaCl] = 0.0210 mol kg^{-1}			
0.0015	61.4	0.2238	36.2	1.1151	27.3
0.0075	54.0	0.358	33.7	1.3739	26.7
0.0225	47.9	0.4851	31.7	1.6708	26.3
0.0375	45.2	0.6055	30.6	2.0370	26.1
0.0671	42.3	0.7530	29.3	2.5000	26.1
0.1252	39.0	0.9218	28.2		
		[NaCl] = 0.0310 mol kg^{-1}			
0.0019	62.7	0.1349	37.9	0.9741	27.0
0.0058	56.2	0.1902	35.8	1.1372	26.3
0.0116	51.9	0.2625	34.1	1.3279	26.4
0.0193	48.1	0.3505	32.4	1.5620	26.4
0.0290	46.4	0.4529	31.0	1.8758	26.3
0.0443	44.0	0.5681	29.8	2.3183	26.1
0.0634	42.1	0.6945	28.4		
0.0918	40.0	0.8304	27.6		
		[NaCl] = 0.0410 mol kg^{-1}			
0.0004	65.9	0.0828	39.3	0.5510	29.1
0.0018	61.2	0.1135	37.5	0.6507	28.3
0.0054	54.2	0.1512	36.8	0.7261	27.4
0.0125	49.6	0.1969	35.1	0.7851	27.0
0.0231	45.0	0.2577	33.6	0.8529	26.8
0.0368	43.7	0.3419	32.2		
0.0569	41.5	0.4448	30.7		

Table 5.1a. Continued

[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0630 mol kg^{-1}			
0.0004	65.4	0.0409	40.7	0.3960	28.7
0.0009	63.7	0.0656	38.0	0.4844	27.3
0.0018	60.2	0.1011	35.9	0.5935	27.0
0.0035	56.1	0.1458	33.4	0.7313	26.8
0.0066	51.8	0.1978	32.0		
0.0131	47.2	0.2613	30.0		
0.0239	43.6	0.3189	30.4		

Table 5.1b. Experimental values of surface tension of AOT in water + 20 % EG media containing varying amounts of NaCl at 25 °C.

[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0 mol kg^{-1}			
0.0072	58.2	0.4438	43.3	4.8875	30.4
0.0215	55.2	0.6497	41.3	6.3868	29.7
0.0430	52.7	0.9520	39.3	8.1761	29.3
0.0787	50.7	1.3756	36.9	10.415	28.8
0.1355	48.7	1.9684	34.3	12.491	28.6
0.2063	47.3	2.7328	32.0	15.253	27.9
0.3047	45.1	3.6585	31.1	16.632	28.0
		[NaCl] = 0.0023 mol kg^{-1}			
0.0063	56.0	0.5450	40.1	3.6994	30.2
0.0188	53.2	0.8165	38.0	4.7361	29.7
0.0501	50.2	1.1608	35.7	6.0099	28.9
0.1124	47.5	1.6032	33.9	7.6812	28.9
0.2052	44.9	2.1312	32.2	9.5874	28.5
0.3460	42.2	2.8272	30.7	11.379	28.4
		[NaCl] = 0.0037 mol kg^{-1}			
0.0067	54.9	0.4336	39.0	3.0540	29.3
0.0201	51.4	0.6444	37.0	4.0170	29.3
0.0468	48.0	0.9318	35.3	5.3013	28.9
0.0933	46.8	1.2959	33.5	7.1001	28.7
0.1727	43.7	1.7634	31.5	9.3340	28.2
0.2843	41.2	2.3206	30.4	11.892	28.1
		[NaCl] = 0.0061 mol kg^{-1}			
0.0015	58.2	0.1331	42.9	1.1773	32.3
0.0045	55.3	0.2026	41.6	1.6459	30.7
0.0119	52.5	0.3033	39.2	2.1224	29
0.0266	49.8	0.4314	37.9	2.5628	28.6
0.0485	47.2	0.6114	36.0	2.9478	28.3
0.0833	45.4	0.8622	34.1	3.3862	28.4
		[NaCl] = 0.0079 mol kg^{-1}			
0.0027	56.8	0.2082	40.9	1.9616	28.9
0.0109	52.4	0.3115	38.5	2.6683	28.6
0.0272	49.6	0.4623	36.7	3.4862	28.1
0.0543	46.7	0.6677	34.9	4.3458	27.4
0.0892	44.6	0.9867	32.7	5.3451	27.0
0.1371	42.7	1.4050	30.8		

Table 5.1b. Continued

[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0100 mol kg^{-1}			
0.0015	56.7	0.1686	40.9	1.6646	29.1
0.0058	53.8	0.2290	39.3	2.1162	28.6
0.0131	50.8	0.3136	37.7	2.5349	27.6
0.0275	48.2	0.4381	36.1	2.9021	27.4
0.0490	46.0	0.6130	34.0	3.2330	28.1
0.0773	44.2	0.8568	32.5	3.4020	28.1
0.1165	42.2	1.2223	30.6		
		[NaCl] = 0.0150 mol kg^{-1}			
0.0015	57.3	0.1377	40.5	1.1679	29.4
0.0044	54.2	0.1997	38.9	1.5234	28.2
0.0118	51.0	0.2800	37.1	1.9349	27.8
0.0220	48.7	0.3830	35.6	2.3676	27.5
0.0366	46.7	0.5056	34.2	2.7860	27.3
0.0583	44.7	0.6778	32.4	3.1545	26.8
0.0912	42.8	0.8880	31.2		
		[NaCl] = 0.0230 mol kg^{-1}			
0.0009	58.9	0.0878	40.9	0.7403	29.6
0.0028	55.5	0.1251	39.3	0.9516	28.3
0.0066	52.4	0.1728	37.7	1.1720	27.6
0.0142	49.1	0.2314	36.2	1.3882	26.6
0.0254	46.6	0.3115	34.6	1.6173	26.5
0.0403	44.5	0.4170	33.1	1.8377	26.1
0.0606	42.7	0.5555	31.6		
		[NaCl] = 0.0298 mol kg^{-1}			
0.0009	57.5	0.1277	38.1	1.4885	26.4
0.0037	53.4	0.1830	36.2	1.7759	26.2
0.0084	50.2	0.2563	34.5	2.0429	26.2
0.0158	47.8	0.3639	32.3	2.2209	26.1
0.0260	45.4	0.5051	30.7	3.2059	25.6
0.0397	43.2	0.6933	29.2	3.9518	25.9
0.0597	41.5	0.9326	27.7	4.7376	26.0
0.0883	39.7	1.1911	26.5		

Table 5.1b. Continued

[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0390 mol kg^{-1}			
0.0011	56.6	0.1485	37.0	0.9515	26.8
0.0044	51.7	0.1985	35.2	1.1274	26.2
0.0120	47.6	0.2662	33.6	1.4006	26.0
0.0229	44.6	0.3497	32.1	1.6962	25.7
0.0380	42.3	0.4638	30.2	1.9958	25.6
0.0593	40.1	0.6023	28.8		
0.0867	38.4	0.7515	27.8		
		[NaCl] = 0.0510 mol kg^{-1}			
0.0005	57.7	0.0702	38.9	0.5358	28.3
0.0022	54.5	0.1021	36.9	0.6392	27.2
0.0048	51.4	0.1446	35.0	0.7523	26.9
0.0102	48.1	0.2026	33.6	0.8602	26.3
0.0182	45.3	0.2689	32.0	0.9698	26.1
0.0303	43.2	0.3449	30.8	1.1043	25.9
0.0474	40.8	0.4370	29.5	1.2266	26.0
		[NaCl] = 0.0690 mol kg^{-1}			
0.0004	51.7	0.0611	38.0	0.5133	27.6
0.0019	50.5	0.0893	36.0	0.6425	26.4
0.0048	49.0	0.1267	34.4	0.7791	25.9
0.0095	46.8	0.1777	32.8	0.9119	25.6
0.0165	44.3	0.2394	31.2	1.0293	25.6
0.0272	41.8	0.3151	29.7	1.1372	25.7
0.0409	40.0	0.4022	29.2		

Table 5.1c. Experimental values of surface tension of AOT in water + 30 % EG media containing varying amounts of NaCl at 25 °C

[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0 mol kg^{-1}			
0.0046	59.2	0.4681	45.1	4.3592	31.7
0.0184	56.8	0.7649	42.9	5.6320	30.9
0.0458	54.3	1.1694	40.1	6.9407	30.3
0.0914	52.3	1.7000	37.8	8.0564	30.0
0.1592	50.0	2.3939	35.4	9.2417	29.7
0.2710	48.0	3.3142	32.7	10.482	28.8
		[NaCl] = 0.0015 mol kg^{-1}			
0.0030	58.5	0.4588	42.2	3.5988	30.9
0.0120	55.5	0.7252	40.2	4.4740	30.1
0.0299	52.9	1.0746	38.2	5.2889	29.9
0.0597	50.6	1.5314	35.8	6.1541	28.9
0.1333	47.6	2.0420	34.0	6.6909	28.7
0.2632	45.3	2.7450	31.9		
		[NaCl] = 0.0025 mol kg^{-1}			
0.0038	57.6	0.7335	39.5	4.5356	30.2
0.0189	53.6	1.1258	37.2	5.6547	29.7
0.0566	50.2	1.6115	35.3	6.8717	29.5
0.1314	47.0	2.2180	33.2	8.1999	29.7
0.2601	44.4	2.9027	31.3		
0.4573	41.8	3.6455	30.8		
		[NaCl] = 0.0050 mol kg^{-1}			
0.0031	53.1	0.2733	42.2	2.2367	31.9
0.0125	52.3	0.5047	39.6	3.0261	30.6
0.0311	50.7	0.7796	37.5	3.9342	29.9
0.0620	47.8	1.1403	35.6	4.8822	30.0
0.1384	44.8	1.6117	33.8	6.0344	28.8
		[NaCl] = 0.0071 mol kg^{-1}			
0.0035	54.4	0.6257	37.2	4.4589	29.0
0.0173	50.9	0.9297	35.4	5.5343	28.4
0.0519	47.7	1.3294	33.6	6.7839	28.2
0.1203	44.5	1.8533	31.6	7.9880	28.5
0.2383	41.6	2.5504	30.3		
0.4028	39.3	3.4352	29.4		

Table 5.1c. Continued

[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0100 mol kg^{-1}			
0.0027	55.4	0.2144	40.8	2.4197	29.6
0.0110	51.3	0.3943	38.3	3.3539	28.8
0.0273	48.6	0.6871	35.3	4.3332	28.6
0.0545	45.9	1.0931	33.5	5.3363	28.3
0.1084	43.3	1.6560	31.1	6.2002	28.2
		[NaCl] = 0.0154 mol kg^{-1}			
0.0026	55.7	0.4031	37.0	3.0961	27.9
0.0102	52.0	0.6302	34.7	3.8534	27.5
0.0255	48.7	0.9284	32.8	4.5611	27.9
0.0635	45.1	1.3189	30.6	5.5116	27.5
0.1261	41.9	1.8379	29.3		
0.2367	39.6	2.4286	28.0		
		[NaCl] = 0.0220 mol kg^{-1}			
0.0027	54.8	0.3236	36.6	2.0457	27.8
0.0134	49.9	0.5193	34.4	2.7844	27.5
0.0400	45.8	0.7975	32.0	3.7006	27.2
0.0929	42.2	1.1217	30.5	4.8762	26.8
0.1840	39.0	1.5178	29.0		
		[NaCl] = 0.0320 mol kg^{-1}			
0.0025	55.5	0.3419	35.8	2.045	26.9
0.0123	50.5	0.5616	32.7	2.5562	27.0
0.0367	46.2	0.8496	30.6	3.1826	26.7
0.0852	42.0	1.1896	28.7	3.9682	26.8
0.1804	38.7	1.5971	27.7	4.9824	26.6
		[NaCl] = 0.0450 mol kg^{-1}			
0.0017	57.6	0.3267	34.7	1.3956	26.9
0.0085	51.6	0.5004	32.2	1.5755	26.9
0.0253	47.3	0.6889	30.9	1.7948	26.7
0.0587	43.1	0.8875	29.1	2.0448	26.7
0.1161	40.4	1.1030	28.1	2.3483	26.3
0.2039	37.1	1.2392	27.3	2.7362	26.2

Table 5.1d. Experimental values of surface tension of AOT in water + 40 % EG media containing varying amounts of NaCl at 25 °C

[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0 mol kg^{-1}			
0.0245	57.7	0.8973	43.8	9.8367	30.5
0.0490	56.6	1.2084	42.4	12.113	29.7
0.0734	55.2	1.6121	40.5	14.785	29.5
0.0979	53.9	2.1291	38.9	18.080	29.2
0.1467	52.7	2.7786	36.6	22.525	28.9
0.2199	50.4	3.6451	34.9	28.266	28.3
0.3173	49.2	4.7598	33.2	35.516	28.1
0.4630	47.3	6.1672	31.5	44.061	27.7
0.6566	45.7	7.8380	30.9		
		[NaCl] = 0.0008 mol kg^{-1}			
0.0318	55.5	1.2566	40.1	17.472	29.1
0.0635	53.1	1.8744	37.9	21.784	28.9
0.0952	51.7	2.6975	35.1	27.560	28.4
0.1270	50.0	3.7462	33.5	34.195	27.5
0.1586	49.6	5.0653	31.7	41.148	27.1
0.2220	47.9	6.6343	30.7	48.001	26.9
0.3168	46.7	8.5655	30.1	55.302	27.1
0.4746	45.1	10.947	29.5		
0.7887	42.7	13.955	29.3		
		[NaCl] = 0.0010 mol kg^{-1}			
0.0290	55.3	1.3199	40.1	13.177	29.7
0.0580	53.5	1.8559	37.9	15.596	29.3
0.0870	51.6	2.5533	36.1	18.506	28.9
0.1450	49.5	3.3784	34.3	22.367	28.6
0.2029	48.5	4.4592	32.4	27.590	28.2
0.2896	47.1	5.7801	31.6	33.665	28.0
0.4339	45.2	7.3224	30.8	40.116	27.6
0.6352	43.8	9.0656	30.3	47.526	26.9
0.9215	42.1	10.987	30.1	55.769	27.3

Table 5.1d. Continued

[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0053 mol kg^{-1}			
0.0293	0.0293	0.0293	0.0293	0.0293	0.0293
0.0585	0.0585	0.0585	0.0585	0.0585	0.0585
0.0878	0.0878	0.0878	0.0878	0.0878	0.0878
0.1170	0.1170	0.1170	0.1170	0.1170	0.1170
0.1754	0.1754	0.1754	0.1754	0.1754	0.1754
0.2337	0.2337	0.2337	0.2337	0.2337	0.2337
0.2920	0.2920	0.2920	0.2920	0.2920	0.2920
0.3792	0.3792	0.3792	0.3792	0.3792	0.3792
0.4954	0.4954	0.4954	0.4954	0.4954	0.4954
0.6401	0.6401	0.6401	0.6401	0.6401	0.6401
		[NaCl] = 0.0100 mol kg^{-1}			
0.0300	51.6	0.6871	38.6	7.1740	28.9
0.0601	49.1	0.9832	37.4	9.2392	28.6
0.0901	47.6	1.3951	35.1	11.709	28.5
0.1201	46.5	1.9202	33.7	14.974	27.9
0.1800	44.7	2.5553	32.2	19.080	27.6
0.2399	43.6	3.3531	30.7	23.982	27.4
0.3296	42.3	4.3342	29.8	30.835	27.2
0.4788	40.4	5.5698	29.2	39.325	26.9
		[NaCl] = 0.0155 mol kg^{-1}			
0.0210	51.1	0.7295	36.1	5.3520	28.6
0.0420	48.1	0.9151	34.9	6.3243	28.0
0.0630	46.8	1.1409	34.0	7.4862	28.0
0.0840	45.7	1.4267	32.4	8.8722	27.8
0.1259	44.2	1.7106	32.0	10.539	27.6
0.1678	43.0	2.0328	31.2	12.760	27.6
0.2306	41.7	2.3925	30.7	15.724	27.4
0.2932	40.4	2.8083	29.7	19.760	27.4
0.3766	39.2	3.2982	29.2	25.581	26.8
0.4807	38.0	3.8788	28.6		
0.5845	37.1	4.5462	28.6		

Table 5.1.d. Continued

[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0240 mol kg^{-1}			
0.0075	53.6	0.3627	39.5	3.0156	28.7
0.0150	51.8	0.5081	36.9	3.4301	28.2
0.0225	50.5	0.7236	35.2	3.8879	28.0
0.0374	48.6	0.9708	33.8	4.3838	27.9
0.0598	46.7	1.2481	32.3	4.9124	27.8
0.0897	44.7	1.5536	31.3	5.6638	27.7
0.1269	43.5	1.8853	30.1	6.5958	27.7
0.1788	42.1	2.2409	29.6		
0.2526	40.7	2.6184	28.8		
		[NaCl] = 0.0480 mol kg^{-1}			
0.0060	53.1	0.1548	40.1	1.3463	29.5
0.0120	51.2	0.2078	38.7	1.7280	28.2
0.0180	49.4	0.2781	37.4	2.2125	27.1
0.0300	47.4	0.3651	36.0	2.8479	27.0
0.0419	46.0	0.4800	34.5	3.6783	26.5
0.0598	44.7	0.6217	33.1	4.9473	26.6
0.0837	43.1	0.8055	31.9	6.4420	26.5
0.1134	41.8	1.0396	30.5		
		[NaCl] = 0.0870 mol kg^{-1}			
0.0036	53.2	0.1236	38.9	2.0799	26.6
0.0071	51.5	0.1758	37.4	2.5601	26.1
0.0107	49.9	0.2620	35.2	3.2059	25.6
0.0142	48.0	0.3974	33.1	3.9518	25.9
0.0214	46.7	0.5790	31.3	4.7376	26.0
0.0320	44.6	0.8026	29.7		
0.0426	43.8	1.0635	28.2		
0.0603	41.8	1.3565	27.4		
0.0885	40.2	1.6895	26.5		

Table 5.1e. Experimental values of surface tension of AOT in water + 50 % EG media containing varying amounts of NaCl at 25 °C

[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0 mol kg^{-1}			
0.1365	52.6	13.908	42.2	132.76	30.5
0.5457	51.3	22.723	39.5	172.35	29.6
1.3617	49.3	34.730	37.3	213.67	29.5
2.7154	47.4	50.476	35.0	253.32	29.1
4.7311	45.9	71.054	33.0	288.01	28.9
8.0515	44.1	98.326	31.6	312.77	29.0
		[NaCl] = 0.0010 mol kg^{-1}			
0.0130	52.3	1.2141	41.7	9.0488	31.6
0.0390	50.6	1.7610	39.8	11.012	31.0
0.0908	48.7	2.5274	38.3	13.426	30.2
0.1941	47.3	3.4895	36.4	16.336	29.9
0.3482	45.7	4.5672	34.9	19.614	29.7
0.5647	44.4	5.7889	33.4	22.872	29.3
0.8418	42.9	7.3077	32.0	25.632	29.1
		[NaCl] = 0.0074 mol kg^{-1}			
0.0066	54.6	0.5954	42.4	7.5309	30.5
0.0199	52.7	0.8755	40.8	8.8890	30.1
0.0398	51.1	1.2677	39.2	10.230	30.1
0.0729	49.3	1.7883	37.6	10.622	30.0
0.1190	47.7	2.6021	35.9	12.263	29.4
0.1846	46.3	3.5940	34.1	14.035	29.3
0.2757	45.2	4.9117	32.1		
0.4047	43.9	6.2375	31.5		
		[NaCl] = 0.0100 mol kg^{-1}			
0.0051	53.8	0.6381	39.4	5.0783	30
0.0204	51.0	0.8941	37.8	6.2312	29.5
0.0559	47.9	1.2308	36.5	7.4407	28.9
0.1114	46.1	1.6588	35.1	8.7368	28.9
0.1915	44.1	2.2598	33.4	10.012	28.7
0.3005	42.3	2.9929	32.3	11.467	28.6
0.4468	40.8	3.9678	30.8		

Table 5.1.e. Continued

[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0190 mol kg^{-1}			
0.0051	53.8	0.6381	39.4	5.0783	30
0.0204	51.0	0.8941	37.8	6.2312	29.5
0.0559	47.9	1.2308	36.5	7.4407	28.9
0.1114	46.1	1.6588	35.1	8.7368	28.9
0.1915	44.1	2.2598	33.4	10.012	28.7
0.3005	42.3	2.9929	32.3	11.467	28.6
0.4468	40.8	3.9678	30.8		
		[NaCl] = 0.0250 mol kg^{-1}			
0.0049	53.5	0.6113	39.1	5.8481	28.8
0.0195	50.6	0.9222	37.1	7.0317	28.5
0.0487	48.6	1.3459	35.2	8.2969	28.4
0.0971	46.4	1.9402	33.5	9.7956	28.3
0.1691	44.4	2.664	31.9	11.115	28.3
0.2643	42.3	3.6248	30.5		
0.4049	40.8	4.7170	29.4		
		[NaCl] = 0.0350 mol kg^{-1}			
0.0041	52.4	0.5227	38.9	3.5283	29.8
0.0166	50.4	0.7679	36.8	4.2848	29.1
0.0454	48.1	1.0931	35.4	5.1950	28.7
0.0865	46.0	1.4363	34.1	6.2180	28.5
0.1476	44.3	1.8564	32.8	7.3288	28.2
0.2283	42.3	2.3653	31.5	8.5099	28.2
0.3475	40.5	2.9123	30.4		
		[NaCl] = 0.0520 mol kg^{-1}			
0.0030	54.0	0.3648	39.1	3.0278	28.8
0.0119	50.7	0.5066	37.4	3.7485	28.5
0.0267	48.4	0.6860	36.3	4.4773	28.2
0.0504	46.6	0.9009	35.0	5.1998	27.6
0.0828	44.8	1.1416	33.6	5.9160	27.4
0.1265	43.3	1.4581	32.5	6.5977	27.6
0.1843	41.9	1.8732	31.2		
0.2612	40.5	2.3915	30.0		

Table 5.1e. Continued

[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0680 mol kg^{-1}			
0.0067	52.1	0.4347	37.2	4.1827	27.5
0.0268	48.0	0.6267	35.8	5.4235	27.1
0.0536	45.4	0.9086	33.8	6.8365	27.2
0.0870	44.0	1.3030	31.7	8.5631	26.7
0.1402	42.0	1.8258	30.3	10.345	26.8
0.2129	40.7	2.4838	28.8	12.015	26.8
0.3048	39.0	3.2493	28.1		
		[NaCl] = 0.1000 mol kg^{-1}			
0.0020	52.7	0.1727	39.4	1.6536	28.9
0.0059	50.6	0.2558	37.7	2.0639	27.5
0.0138	48.6	0.3721	36.3	2.4914	27.3
0.0275	46.3	0.5347	34.6	2.9724	26.7
0.0489	44.4	0.7441	32.8	3.4498	26.6
0.0779	42.9	0.9974	31.4	3.8893	26.5
0.1161	41.3	1.2948	30.2	4.2764	26.5

Table 5.1f. Experimental values of surface tension of AOT in water + 60 % EG media containing varying amounts of NaCl at 25 °C.

[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0 mol kg^{-1}			
0.0296	53.7	6.7626	36.5	41.568	29.5
0.1477	51.5	10.237	34.1	48.789	29.5
0.4418	48.7	14.778	32.0	56.270	28.8
1.0248	46.1	20.798	31.6	65.526	29.2
2.1709	43.3	27.631	30.4		
4.1146	39.8	34.696	30.1		
		[NaCl] = 0.0010 mol kg^{-1}			
0.0301	52.9	7.6773	35.1	38.060	29.0
0.1504	50.5	11.648	32.8	45.631	29.2
0.4500	48.5	16.175	31.4	53.879	29.2
1.0439	45.4	21.250	30.6	64.972	28.8
2.2118	42.3	26.622	29.8		
4.4703	38.5	32.076	29.7		
		[NaCl] = 0.0060 mol kg^{-1}			
0.0270	52.5	6.3009	34.7	34.709	29.5
0.1350	48.3	9.6870	32.6	43.676	29.3
0.4038	45.6	13.810	31.5	52.916	29.4
0.9368	43.2	18.423	30.4	60.916	28.7
1.9845	40.5	23.294	30.1		
3.8860	37.6	28.876	29.7		
		[NaCl] = 0.0120 mol kg^{-1}			
0.0287	51.6	4.2573	35.4	21.071	29.8
0.1434	47.9	6.3130	33.9	24.453	29.8
0.4288	44.7	8.7591	31.9	28.284	29.2
0.8539	42.3	11.527	30.9	33.021	29.3
1.5543	40.1	14.547	30.2	38.770	29.1
2.6540	37.7	17.750	30.1	46.113	29.0

Table 5.1f. Continued

[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0250 mol kg^{-1}			
0.0254	50.0	2.5977	35.3	11.786	35.3
0.1271	46.6	3.4318	34.2	14.961	34.2
0.3802	42.9	4.4820	32.9	19.207	32.9
0.7572	40.6	5.7328	32.2	25.794	32.2
1.2553	38.6	7.2747	30.9	35.012	30.9
1.8704	36.7	9.1793	30.1	45.607	30.1
		[NaCl] = 0.0480 mol kg^{-1}			
0.0179	52.5	4.0832	31.6	20.144	28.2
0.0892	47.3	6.0351	30.2	24.439	28.3
0.2668	43.4	8.2608	29.1	29.887	28.0
0.6189	40.1	10.801	28.8	37.023	28.1
1.3109	36.9	13.651	28.7		
2.4845	34.1	16.671	28.5		
		[NaCl] = 0.0700 mol kg^{-1}			
0.0161	52.8	2.5987	32.4	14.048	28.0
0.0802	47.8	3.5270	30.3	17.987	27.7
0.2399	42.6	4.6241	29.7	23.903	27.6
0.4777	39.8	5.9297	28.6	29.827	27.6
0.7914	37.5	7.4074	28.5	34.823	27.7
1.2551	35.8	9.1305	28.3		
1.8609	33.8	11.237	28.4		
		[NaCl] = 0.1000 mol kg^{-1}			
0.0144	52.0	0.2576	41.1	3.7519	29.2
0.0288	49.7	0.3145	40.3	4.6566	28.4
0.0431	48.2	0.3996	39.3	5.6966	27.9
0.0575	47.0	0.5126	38.5	6.9046	27.6
0.0718	45.9	0.6531	37.4	8.2499	27.3
0.0862	45.4	0.8485	36.1	9.7944	27.3
0.1077	44.6	1.0974	35.0	11.571	27.3
0.1291	44.0	1.4254	33.6	13.959	27.0
0.1577	43.1	1.8293	32.3	17.341	27.1
0.1863	42.3	2.3575	31.5	21.603	27.0
0.2149	42.0	3.0016	30.5	26.879	26.9

Table 5.1g. Experimental values of surface tension of AOT in water + 70 % EG media containing varying amounts of NaCl at 25 °C

[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0 mol kg^{-1}			
0.0980	49.8	6.7390	37.9	76.870	29.3
0.1960	47.0	9.5524	36.3	88.670	29.1
0.2939	45.8	13.236	34.4	102.14	28.8
0.3918	45.7	17.736	33.0	116.71	28.8
0.5874	44.9	22.988	31.6	133.81	28.5
0.7828	44.3	28.921	31.0	152.18	28.4
1.1730	43.7	35.457	30.7	173.57	28.4
1.7567	42.6	42.517	30.3	197.71	27.9
2.5321	41.7	50.018	30.0	219.83	27.9
3.4968	41.0	57.882	29.7		
4.8388	39.5	66.690	29.5		
		[NaCl] = 0.0016 mol kg^{-1}			
0.1203	47.0	7.1089	37.7	56.588	30.1
0.2405	45.0	10.007	35.9	63.896	29.6
0.3606	44.9	13.438	34.3	71.813	29.5
0.4807	44.4	17.376	32.8	80.254	29.1
0.6008	44.1	21.794	32.0	90.704	29.2
0.8406	43.6	26.663	31.3	103.55	29.0
1.2000	43.1	31.949	30.9	120.93	28.9
1.7977	42.0	37.619	30.7	145.53	28.5
2.9885	40.9	43.639	30.2	185.59	28.1
4.7634	39.2	49.974	30.1	236.04	28.0
		[NaCl] = 0.0024 mol kg^{-1}			
0.1212	47.3	4.3254	39.5	55.205	29.7
0.2423	44.6	5.3951	38.7	64.594	29.6
0.3633	44.5	6.8142	37.6	75.352	29.4
0.4843	44.2	8.5767	36.6	88.074	29.2
0.7261	43.9	10.907	35.3	103.89	28.9
0.9677	43.2	14.361	34.0	125.47	28.8
1.2091	43.0	18.892	32.7	150.84	28.2
1.6910	42.0	24.438	31.7	183.04	28.3
2.1721	41.4	30.927	30.9	225.28	27.9
2.7721	40.8	38.277	30.3		
3.4902	40.0	46.401	29.9		

Table 5.1g. Continued

[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0037 mol kg^{-1}			
0.0781	48.5	6.3431	37.7	42.277	29.8
0.1562	45.5	8.1999	36.0	46.763	29.8
0.2342	44.9	10.396	35.2	51.515	29.7
0.3901	44.2	12.916	33.9	56.695	29.5
0.6236	43.5	15.741	33.1	62.624	29.6
0.9345	43.0	18.851	32.3	69.626	29.2
1.3995	42.3	22.226	31.8	78.322	29.2
2.0171	41.3	25.843	31.1	90.158	29.2
2.7855	40.6	29.680	30.8	104.03	29.0
3.7023	39.4	33.714	30.5	121.60	28.8
4.8400	38.8	37.920	30.3	144.54	28.4
		[NaCl] = 0.0150 mol kg^{-1}			
0.0781	49.0	3.6266	37.8	46.186	29.3
0.1562	45.6	5.1427	36.4	53.184	29.5
0.2342	44.5	7.3873	34.5	60.779	29.4
0.3122	43.5	10.326	33.4	70.186	28.8
0.3901	43.4	13.915	31.9	82.948	28.9
0.5459	42.3	18.103	31.1	97.845	28.6
0.7792	41.7	22.834	30.9	116.61	28.3
1.1673	40.8	28.044	30.3	136.63	28.2
1.7088	39.9	33.669	29.9		
2.4790	39.0	39.645	29.6		
		[NaCl] = 0.0240 mol kg^{-1}			
0.0663	49.4	3.3983	37.0	31.437	29.6
0.1325	45.9	4.6794	35.3	35.251	29.4
0.1988	44.0	6.2611	34.2	39.386	29.3
0.2649	43.1	8.1308	33.2	43.883	29.3
0.3972	42.5	10.274	32.2	49.430	29.2
0.5293	42.0	12.674	31.7	56.218	28.9
0.7930	40.8	15.314	31.0	64.302	28.9
1.0562	39.9	18.176	30.6	74.222	28.6
1.3187	39.2	21.239	30.3	85.927	28.5
1.7768	38.8	24.484	30.0	98.233	28.5
2.4281	38.1	27.890	29.6	114.21	28.2

Table 5.1g. Continued

[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0530 mol kg^{-1}			
0.0495	46.9	3.1132	34.9	26.017	28.9
0.0990	44.6	4.2989	33.5	29.157	28.5
0.1485	43.7	5.6998	32.7	32.491	28.5
0.1979	42.9	7.3048	31.8	36.290	28.7
0.2967	42.3	9.1016	30.7	40.760	28.4
0.4447	41.4	11.076	30.1	46.277	28.5
0.6416	40.4	13.215	29.6	53.733	28.3
0.9362	39.4	15.503	29.4	64.367	28.2
1.4248	38.2	17.924	29.1	77.893	28.0
2.1525	36.7	23.107	29.2		
		[NaCl] = 0.0680 mol kg^{-1}			
0.0480	47.6	1.7557	36.3	18.867	28.9
0.0960	44.5	2.456	35.0	22.446	28.8
0.1439	43.1	3.3795	34.0	27.466	28.7
0.1918	42.7	4.5179	32.7	33.581	28.4
0.2875	41.5	5.8610	31.7	41.698	28.4
0.3831	40.9	7.3973	30.8	50.926	28.5
0.5263	40.3	9.1137	30.7	60.484	28.2
0.7167	39.2	11.078	29.8	72.491	28.3
0.9541	38.6	13.310	29.7		
1.2852	37.6	15.858	29.1		
		[NaCl] = 0.1000 mol kg^{-1}			
0.0351	48.6	1.6950	36.0	14.596	28.7
0.0702	45.9	2.2377	35.0	17.205	28.5
0.1052	44.4	2.9089	33.8	20.282	28.4
0.1403	43.6	3.7038	32.8	23.729	28.2
0.1753	42.2	4.6172	32.0	27.954	28.2
0.2802	41.7	5.7064	31.5	33.608	28.2
0.4198	40.7	6.9606	30.3	41.563	27.9
0.6285	39.5	8.4887	29.7	50.962	27.9
0.9056	38.4	10.266	29.5	64.032	28.1
1.2502	37.1	12.267	29.2		

Table 5.1h. Experimental values of surface tension of AOT in water + 80 % EG media containing varying amounts of NaCl at 25 °C

[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0 mol kg^{-1}			
0.0821	51.2	4.8492	43.1	87.004	31.2
0.1642	48.9	7.6077	41.5	105.85	30.5
0.2462	47.3	11.841	39.0	126.36	30.5
0.4101	46.4	17.790	37.3	147.59	30.2
0.6556	45.9	26.960	35.4	170.25	30.2
1.0639	45.2	38.735	33.5	196.40	30.1
1.7961	45.0	52.973	32.5		
3.0086	44.1	69.263	31.6		
		[NaCl] = 0.0005 mol kg^{-1}			
0.0952	47.4	5.8971	40.0	55.505	31.4
0.1903	44.5	8.6359	38.5	63.374	31.2
0.2854	44.0	12.220	36.8	69.617	30.6
0.4754	43.6	16.596	35.6	78.486	30.6
0.7600	43.2	21.700	34.5	88.416	30.3
1.1388	42.9	27.460	33.4	101.05	30.0
1.7054	42.3	33.800	32.7	118.92	30.0
2.6457	41.6	40.640	32.1	144.69	29.5
4.0467	40.9	47.902	31.4	184.27	29.2
		[NaCl] = 0.0011 mol kg^{-1}			
0.1403	46.2	6.3742	40.8	88.153	30.8
0.2805	45.4	9.7713	39.1	114.99	30.4
0.4207	45.0	15.111	37.4	149.33	30.2
0.7007	44.7	23.548	35.1	189.47	29.9
1.2599	43.8	34.151	33.5	236.14	29.4
2.2355	43.4	48.349	32.1	290.16	29.2
3.8992	42.0	66.000	31.5		

Table 5.1h. Continued

[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0140 mol kg^{-1}			
0.0619	50.4	1.7212	42.9	22.404	34.6
0.1857	46.8	2.6322	42.3	34.127	32.9
0.3094	46.2	4.1335	41.0	50.217	31.8
0.4946	44.8	6.4925	39.5	69.686	30.8
0.741	44.6	9.9352	38.0	91.675	30.3
1.1096	44.1	14.624	36.5	119.31	30.3
		[NaCl] = 0.0290 mol kg^{-1}			
0.0699	50.3	4.3927	39.4	56.457	30.8
0.2095	45.9	6.7280	38.0	74.930	30.5
0.4187	43.9	9.9854	36.8	97.87	30.1
0.6970	43.4	14.705	35.3	124.14	30.0
1.1134	42.6	20.707	33.7	133.27	30.0
1.8040	41.8	29.138	32.6		
2.8326	40.6	40.883	31.4		
		[NaCl] = 0.0425 mol kg^{-1}			
0.0901	48.9	4.4367	38.7	45.383	31.1
0.1801	45.9	6.1743	37.8	57.667	30.6
0.2700	45.7	8.3175	36.8	76.496	30.3
0.3599	45.2	11.015	35.9	98.759	30.1
0.5395	43.1	14.316	34.9	126.30	29.8
0.8085	42.9	18.337	33.5	161.58	29.5
1.2558	41.9	23.243	32.8	180.66	29.4
1.9686	41.2	28.862	31.9		
3.0315	40.0	36.003	31.3		
		[NaCl] = 0.0650 mol kg^{-1}			
0.1054	47.2	2.9281	39.5	45.859	30.5
0.2108	44.8	4.4768	37.6	63.878	30.0
0.3161	44.3	6.7235	36.5	89.619	29.7
0.5265	43.1	9.7408	35.3	122.88	29.7
0.8416	42.5	14.169	34.1	160.28	29.4
1.2609	41.3	20.834	32.3	198.00	29.3
1.8879	40.9	31.669	31.4		

Table 5.1h. Continued

[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.1050 mol kg^{-1}			
0.0840	44.2	2.4169	37.1	22.312	29.8
0.1679	43.5	3.2412	36.2	28.639	29.5
0.2518	42.6	4.3060	35.1	37.282	29.2
0.3357	42.1	5.6061	34.3	48.376	29.0
0.4614	41.7	7.2152	33.5	62.309	28.7
0.6288	40.9	9.2018	32.6	81.641	28.7
0.8796	40.2	11.550	31.7	108.81	28.5
1.2550	39.2	14.394	30.9	142.37	28.3
1.7541	38.1	17.928	30.6	167.50	27.9
		[NaCl] = 0.2000 mol kg^{-1}			
0.0369	48.4	1.3160	37.7	28.336	28.4
0.0738	46.8	1.6772	37.5	33.870	28.3
0.1106	44.1	2.2153	36.8	39.816	28.4
0.1475	44.2	3.1028	35.2	46.764	28
0.1843	44	4.3260	34.1	54.179	28.1
0.2211	43.4	5.8665	32.9	61.628	28.2
0.2946	42.2	7.7017	31.8	69.720	27.8
0.3681	41.5	9.806	31.5	77.708	27.9
0.4781	41	12.304	30.2		
0.6246	40.6	15.294	29.6		
0.8072	39.9	18.976	28.9		
1.0258	39.2	23.466	28.5		

Table 5.1i. Experimental values of surface tension of AOT in water + 90 % EG media containing varying amounts of NaCl at 25 °C

[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0 mol kg^{-1}			
0.1806	47.1	15.907	37.8	145.93	30.9
0.3611	43.3	22.759	36.4	178.87	30.4
0.5415	42.9	31.143	35.3	221.93	30.0
0.9021	42.8	41.270	34.1	274.88	29.8
1.6222	42.0	53.140	33.6	331.12	29.7
2.6997	41.4	66.860	32.7	395.77	29.4
4.4886	41.0	82.900	31.9	461.64	29.5
7.1556	39.8	100.89	31.3		
10.681	39.1	121.73	30.9		
		[NaCl] = 0.0013 mol kg^{-1}			
0.1718	43.2	8.3220	39.7	141.47	30.8
0.3435	42.6	12.495	38.5	168.99	30.8
0.5151	42.7	19.071	37.1	197.67	30.6
0.8581	42.1	28.710	35.7	231.57	30.3
1.3720	41.9	41.157	34.3	268.25	30.1
2.0561	41.3	56.102	33.5	311.26	30.0
2.9094	41.4	73.192	32.8	364.51	29.6
4.1006	40.6	93.359	32.1		
5.7954	40.0	115.96	31.5		
		[NaCl] = 0.0036 mol kg^{-1}			
0.3237	43.1	10.288	39.1	127.61	31.3
0.6472	42.2	15.063	37.7	156.77	30.7
0.9706	42.0	21.381	36.8	192.12	30.8
1.2939	41.5	29.203	35.8	239.50	30.5
1.9400	41.5	38.481	35.0	294.08	30.5
2.9081	41.0	49.762	33.9	372.18	29.7
4.1970	40.5	63.843	33.0	486.89	29.4
5.8050	40.0	81.425	32.2	637.09	29.3
7.0889	39.6	102.80	31.4	756.28	29.0

Table 5.1i. Continued

[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0175 mol kg^{-1}			
0.2681	42.9	14.292	37.2	132.51	30.6
0.5361	42.3	19.491	36.2	151.81	30.5
0.8039	41.7	25.921	35.5	173.22	30.5
1.0716	41.5	33.535	34.1	199.10	30.3
1.6066	40.9	42.284	33.7	233.66	29.8
2.1411	40.6	52.107	32.9	288.14	29.6
2.9419	40.4	62.943	32.3	367.12	29.3
4.0077	39.4	74.721	31.9	469.29	29.2
5.6026	38.8	87.372	31.3	553.07	28.9
7.7219	38.4	100.82	31.0		
10.359	38.1	115.67	30.9		
		[NaCl] = 0.0422 mol kg^{-1}			
0.2221	42.7	10.745	37.0	125.04	30.9
0.4441	41.6	15.051	36.3	149.76	30.4
0.6660	41.5	20.793	35.2	178.31	30.2
1.1094	41.4	28.531	34.2	216.90	29.9
1.7736	40.5	38.755	33.4	261.74	29.9
2.6576	40.1	51.661	32.5	309.31	29.7
3.7599	39.6	66.977	31.7	383.90	29.3
5.2982	39.0	84.398	31.1		
7.4858	38.1	103.598	30.8		
		[NaCl] = 0.0600 mol kg^{-1}			
0.1116	47.5	5.4049	37.8	60.679	31.3
0.2232	42.6	7.5731	37.0	74.286	31.0
0.3348	42.2	10.466	36.4	92.623	30.7
0.5577	41.5	14.368	35.3	118.49	30.0
0.8916	41.2	19.530	34.2	150.68	30.0
1.3360	40.7	25.563	33.5	192.15	29.7
1.8903	40.2	32.577	33.1	220.50	29.6
2.6640	39.4	40.560	32.1		
3.7645	39.0	49.560	31.8		

Table 5.1i. Continued

[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0850 mol kg^{-1}			
0.1504	46.0	5.8079	37.5	54.492	31.1
0.3008	42.3	7.2778	36.8	66.474	30.6
0.4511	41.8	9.0315	36.0	81.230	30.4
0.6013	41.6	11.208	35.1	100.27	30.3
0.9014	41.3	14.083	34.6	128.85	30.3
1.3510	40.5	17.636	34.0	169.38	29.7
1.9494	39.9	22.533	33.5	225.97	29.2
2.6956	39.3	28.701	32.7	291.07	29.3
3.5884	38.6	36.051	32.0		
4.6264	37.9	44.480	31.6		
		[NaCl] = 0.2000 mol kg^{-1}			
0.0636	46.8	1.7063	39.6	25.581	31.6
0.1273	43.8	2.3318	38.6	31.445	30.9
0.1908	42.5	3.2637	38	38.319	30.4
0.2544	42.5	4.4945	37.1	46.778	29.8
0.3814	42	6.3159	36.1	58.155	29.8
0.5716	41.5	8.6998	35.1	74.277	29.3
0.7615	40.4	11.894	33.6	92.363	29.5
0.951	40.5	15.830	33.1	111.96	29.3
1.2663	40.2	20.423	32.5	132.75	28.9

Table 5.1j. Experimental values of surface tension of AOT in 100 % EG media containing varying amounts of NaCl at 25 °C

[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0 mol kg^{-1}			
0.3043	47.2	15.978	39.0	383.81	31.3
0.9126	45.5	23.410	38.5	468.65	30.8
1.5205	43.1	35.166	37.2	556.91	30.8
2.1279	41.5	52.490	36.2	650.72	30.3
2.7349	41.5	76.418	35.0	753.95	30.2
3.6445	41.3	106.363	34.0	860.89	30.3
4.8559	40.7	142.899	32.9		
6.3676	40.6	187.461	32.2		
8.4794	40.1	243.02	32.0		
11.487	40.0	306.92	31.2		
		[NaCl] = 0.0150 mol kg^{-1}			
0.2818	47.3	4.2158	40.5	136.01	33.0
0.5635	46.2	5.8954	40.2	176.65	32.1
0.8451	45.4	8.6864	39.7	225.17	31.8
1.1265	43.7	12.853	39.2	283.32	31.5
1.4079	42.0	19.746	38.4	353.03	31.4
1.6892	41.7	30.642	37.4	429.61	31.1
1.9703	41.2	46.687	36.4	521.01	30.5
2.5323	40.8	70.105	35.2	627.27	30.5
3.0939	40.6	100.13	33.8	727.63	30.5
		[NaCl] = 0.0400 mol kg^{-1}			
0.2799	46.5	8.9042	39.2	123.85	32.7
0.5596	45.9	13.042	38.6	162.83	32.5
0.8393	43.4	18.523	38.6	220.43	31.9
1.1188	42.4	26.671	36.9	297.26	31.8
1.6776	41.2	37.398	36.3	396.76	30.7
2.5150	41.1	51.896	35.3	518.79	30.5
3.9086	40.5	69.942	34.5	713.02	30.2
6.1329	39.9	92.497	33.4		

Table 5.1j. Continued

[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}	[AOT] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0980 mol kg^{-1}			
1.0100	42.6	40.543	35.5	322.22	31.3
3.0232	39.8	63.851	34.1	450.69	31.2
7.0224	39.6	97.325	33.3	514.66	31.0
14.914	36.5	149.84	32.0		
25.539	36.9	225.41	31.6		
		[NaCl] = 0.2000 mol kg^{-1}			
0.1951	46.4	6.7745	38.4	110.16	31.5
0.3901	43.6	10.596	37.2	131.60	31.2
0.5850	42.8	16.264	36.1	155.71	31.2
0.7798	41.8	23.702	35.6	185.41	30.6
0.9745	41.5	34.609	34.6	219.09	30.5
1.3637	40.6	45.228	33.8	258.94	30.4
1.9468	40.2	58.114	33.3	309.94	30.1
2.9168	39.7	73.035	32.4	377.55	30.0
4.4642	38.8	90.514	31.8		
		[NaCl] = 0.3990 mol kg^{-1}			
1.4903	40.6	28.445	34.3	197.23	30.4
2.9732	39.6	45.513	33.0	254.08	30.4
5.9167	38.0	69.842	32.0	343.52	30.1
10.277	37.1	102.52	31.4	353.61	30.1
17.402	35.7	144.53	30.8		

Table 5.2. Cmc of AOT in water + EG media containing varying amounts of NaCl at 25 °C from surface tension measurements (cmc values given in parentheses are from conductance measurements)

10 % EG		20 % EG		30 % EG		40 % EG	
[NaCl]/ mol kg^{-1}	cmc / mmol kg^{-1}	[NaCl]/ mol kg^{-1}	cmc / mmol kg^{-1}	[NaCl]/ mol kg^{-1}	cmc / mmol kg^{-1}	[NaCl]/ mol kg^{-1}	cmc / mmol kg^{-1}
0	2.88	0	3.00	0	3.98	0	6.67 (6.50)
0.0020	2.51	0.0023	2.77	0.0015	3.55	8.3E-4	5.75
0.0053	2.20	0.0037	2.63	0.0025	3.31	0.0010	5.69
0.0076	2.00	0.0061	2.34	0.0050	2.95	0.0053	4.74
0.0110	1.75	0.0079	2.12	0.0071	2.69	0.0100	4.04
0.0210	1.15	0.0100	1.85	0.0100	2.45	0.0155	3.57
0.0310	0.95	0.0150	1.57	0.0154	2.14	0.0240	2.94
0.0410	0.74	0.0230	1.24	0.0220	1.82	0.0480	2.15
0.0630	0.52	0.0298	1.13	0.0320	1.58	0.0870	1.62
		0.0390	0.95	0.0450	1.32		
		0.0510	0.83				
		0.0690	0.69				

Table 5.2. continued

50 % EG		60 % EG		70 % EG	
[NaCl]/ mol kg^{-1}	cmc / mmol kg^{-1}	[NaCl]/ mol kg^{-1}	cmc / mmol kg^{-1}	[NaCl]/ mol kg^{-1}	cmc / mmol kg^{-1}
0	9.24 (10.0)	0	16.4 (15.9)	0	30.1 (30.7)
0.0010	8.18	0.0010	15.1	0.0016	27.4
0.0074	6.56	0.0060	13.4	0.0024	26.8
0.0100	6.17	0.0120	12.2	0.0037	26.3
0.0190	4.98	0.0250	9.60	0.0150	22.5
0.0250	4.55	0.0480	7.3	0.0240	20.6
0.0350	3.99	0.0700	6.0	0.0530	14.8
0.0520	3.27	0.1000	5.3	0.0680	13.1
0.0680	2.90			0.1000	11.0
0.1000	2.44				

Table 5.2. continued

80 % EG		90 % EG		100 % EG	
[NaCl]/ mol kg^{-1}	cmc / m mol kg^{-1}	[NaCl]/ mol kg^{-1}	cmc / m mol kg^{-1}	[NaCl]/ mol kg^{-1}	cmc / m mol kg^{-1}
0	50.0 (49.8)	0	117 (117.6)	0	183 (183.8)
0.0005	48.1	0.0013	114	0.0150	168
0.0011	46.8	0.0036	103.3	0.0400	154
0.0140	42.6	0.0175	91.0	0.0980	148
0.0290	38.9	0.0422	83.3	0.2000	134
0.0425	35.7	0.0600	79.7	0.3990	110
0.0650	32.5	0.0850	73.3		
0.1050	27.7	0.2000	56.1		
0.2000	21.0				

Table 5.3. Counterion binding constant of AOT and SDS in water + EG media at 25 °C (c* is in mol kg^{-1}).

Weight % EG	β of AOT		β of SDS	
	From CH Plot	From Slope Ratio	From CH Plot	From Slope Ratio
0	0.39 (0.82) (c* = 0.015)	-	0.74[a)]	0.64[a)]
10	0.29 (0.74) (c* = 0.010)	-	0.68	0.55
20	0.17 (0.57) (c* = 0.005)	-	0.68	0.54
30	0.44	-	0.78	0.48
40	0.48	0.17	-	-
50	0.50	0.24	0.57	0.34
60	0.57	0.44	0.57	0.36
70	0.69	0.31	0.66	0.28
80	0.52	0.28	0.93	0.28
90	0.56	0.34		-
100	0.41	0.31		-

a) From the reference: I. M. Umlong and K. Ismail, Colloid Surf. A, 299, 8 (2007).

Table 5.4. Experimental values of specific conductivity of AOT in water + EG media at 25 °C.

[AOT] / mmol kg^{-1}	10 κ/ S m^{-1}	[AOT] / mmol kg^{-1}	10 κ/ S m^{-1}	[AOT] / mmol kg^{-1}	10 κ/ S m^{-1}
		40 % EG + water			
0	0.0025	5.0970	0.1510	9.6283	0.2702
0.5381	0.0183	5.5739	0.1648	10.054	0.2804
1.0697	0.0342	6.0453	0.1779	10.474	0.2904
1.5947	0.0493	6.5113	0.1906	10.891	0.3005
2.1133	0.0643	6.9719	0.2029	11.303	0.3100
2.6256	0.0794	7.4273	0.2145	11.710	0.3200
3.1318	0.0943	7.8775	0.2266	12.113	0.3290
3.6319	0.1089	8.3226	0.2380	12.512	0.3378
4.1261	0.1231	8.7627	0.2491	12.906	0.3445
4.6144	0.1375	9.1979	0.2599		
		50 % EG + water			
0	0.0012	7.6619	0.1798	14.341	0.3072
0.6813	0.0187	8.2533	0.1928	14.859	0.3158
1.3543	0.0350	8.8380	0.2039	15.372	0.3252
2.0192	0.0513	9.4162	0.2161	15.879	0.3350
2.6762	0.0666	9.9878	0.2286	16.381	0.3427
3.3254	0.0827	10.553	0.2392	16.878	0.3505
3.9669	0.0987	11.112	0.2500	17.369	0.3582
4.6008	0.1130	11.665	0.2600	17.856	0.3672
5.2273	0.1273	12.212	0.2696	18.337	0.3749
5.8466	0.1410	12.753	0.2795	18.814	0.3825
6.4587	0.1542	13.288	0.2898	19.286	0.3891
7.0638	0.1675	13.817	0.2984	19.753	0.3962

Table 5.4. Continued

[AOT] / mmol kg^{-1}	10 κ/ S m^{-1}	[AOT] / mmol kg^{-1}	10 κ/ S m^{-1}	[AOT] / mmol kg^{-1}	10 κ/ S m^{-1}
		60 % EG + water			
0	0.0014	9.9170	0.2240	28.596	0.4998
0.6402	0.0157	10.442	0.2347	30.265	0.5196
1.2727	0.0304	10.962	0.2447	31.862	0.5381
1.8976	0.0453	11.475	0.2549	33.392	0.5567
2.5150	0.0599	12.487	0.2740	35.14	0.5776
3.1250	0.0738	13.476	0.2906	36.817	0.5959
3.7279	0.0877	14.445	0.3069	38.409	0.6143
4.3236	0.1012	15.393	0.3230	39.929	0.6308
4.9124	0.1153	16.322	0.3373	41.616	0.6496
5.4943	0.1278	17.679	0.3571	43.219	0.6671
6.0695	0.1408	18.996	0.3752	44.954	0.6857
6.6381	0.153	20.273	0.3933	46.594	0.7037
7.2002	0.1657	21.513	0.4100	48.335	0.7221
7.7559	0.1781	22.718	0.4259	49.976	0.7398
8.3054	0.1898	24.270	0.4459	51.691	0.7579
8.8486	0.2018	25.766	0.4646		
9.3858	0.2129	27.207	0.4824		

Table 5.4. Continued

[AOT] / mmol kg^{-1}	10 κ/ S m^{-1}	[AOT] / mmol kg^{-1}	10 κ/ S m^{-1}	[AOT] / mmol kg^{-1}	10 κ/ S m^{-1}
		70 % EG + water			
0	0.0012	3.1365	0.0484	39.771	0.4700
0.0688	0.0020	3.4587	0.0522	42.204	0.4898
0.1376	0.0031	3.7788	0.0576	44.452	0.5051
0.2062	0.0046	4.0969	0.0624	46.535	0.5220
0.2747	0.0057	4.4129	0.0666	48.469	0.5360
0.3432	0.0067	4.8518	0.0724	50.272	0.5471
0.4115	0.0077	5.2867	0.0793	51.955	0.5604
0.4798	0.0086	5.7178	0.0849	53.530	0.5717
0.5480	0.0096	6.2663	0.0928	55.007	0.5807
0.6161	0.0105	6.8684	0.1014	56.395	0.5913
0.6840	0.0115	7.4629	0.1103	57.702	0.6016
0.8197	0.0134	8.3408	0.1225	58.935	0.6098
0.9551	0.0155	9.4860	0.1389	60.100	0.6175
1.0900	0.0175	11.151	0.1595	61.202	0.6242
1.2246	0.0192	13.797	0.1944	62.246	0.6339
1.3589	0.0211	16.291	0.2262	63.237	0.6412
1.5596	0.0238	19.553	0.2650	64.179	0.6506
1.7594	0.0274	23.800	0.3149	65.075	0.6622
1.9585	0.0307	27.627	0.3548	65.928	0.6723
2.2227	0.0341	31.092	0.3913	67.520	0.6865
2.4855	0.0385	34.246	0.4189		
2.8121	0.0431	37.127	0.4485		

Table 5.4. Continued

[AOT] / mmol kg^{-1}	10 κ/ S m^{-1}	[AOT] / mmol kg^{-1}	10 κ/ S m^{-1}	[AOT] / mmol kg^{-1}	10 κ/ S m^{-1}
		80 % EG + water			
0	0.0011	44.742	0.2115	80.949	0.2845
5.961	0.0772	49.982	0.2236	84.697	0.2910
11.680	0.1081	54.990	0.2345	88.305	0.2972
17.159	0.1310	59.783	0.2445	91.780	0.3030
22.417	0.1497	64.374	0.2537	95.129	0.3084
27.466	0.1657	68.774	0.2622	98.360	0.3136
33.503	0.1830	72.997	0.2702		
39.255	0.1981	77.052	0.2776		
		90 % EG + water			
0	0.0010	105.0467	0.4927	182.8754	0.7378
11.5458	0.0635	113.0666	0.5235	188.9624	0.7528
21.7477	0.1252	120.8752	0.554	194.9094	0.7689
32.1266	0.1771	128.4807	0.5781	200.7210	0.7864
42.1952	0.2238	135.8909	0.5975	206.4019	0.7982
51.9673	0.2741	143.1134	0.6203	211.9565	0.8146
61.4558	0.3178	150.1550	0.6416	217.3888	0.8262
70.6728	0.3568	157.0226	0.6635	222.7029	0.8371
79.6299	0.3956	163.7225	0.6839	227.9026	0.8462
88.3378	0.4279	170.2608	0.7003		
96.8068	0.4605	176.6433	0.7181		
		100 % EG			
0	0.0011	187.95	0.4137	305.73	0.6014
21.592	0.0716	200.85	0.4394	314.29	0.6141
42.076	0.1229	213.22	0.4631	322.57	0.6240
61.533	0.1692	225.12	0.4874	330.58	0.6376
80.039	0.2125	236.55	0.5027	338.34	0.6488
97.662	0.2491	247.55	0.5214	345.86	0.6607
114.46	0.2900	258.15	0.5364	353.15	0.6725
130.50	0.3152	268.36	0.5479	360.21	0.6812
145.82	0.3447	278.20	0.5675	367.06	0.6878
160.47	0.3728	287.70	0.5790		
174.51	0.3952	296.87	0.5922		

Table 5.5a. Experimental values of surface tension of SDS in 10 % EG + water media containing varying amounts of NaCl at 25 °C

[SDS] / mmol kg^{-1}	γ/ mN m^{-1}	[SDS] / mmol kg^{-1}	γ/ mN m^{-1}	[SDS] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0 mol kg^{-1}			
0.0346	64.1	3.4034	44.0	11.232	39.2
0.0692	64.0	4.2178	40.5	12.652	39.1
0.1384	64.0	5.0214	37.8	14.446	39.0
0.2764	63.0	5.8145	35.6	16.578	38.7
0.4830	61.7	6.5973	34.5	19.132	38.8
0.8257	60.5	7.3700	36.8	22.747	38.7
1.1665	58.1	8.1329	38.7	27.204	38.5
1.7418	53.3	9.0354	39.3		
2.5782	48.4	10.071	39.2		
		[NaCl] = 0.0046 mol kg^{-1}			
0.0463	65.8	3.3487	40.2	21.360	38.0
0.1387	64.3	4.7510	36.1	27.830	37.9
0.2772	62.4	6.4667	36.5	36.403	37.8
0.5074	59.3	8.3903	38.4		
0.8743	55.4	10.663	38.2		
1.4212	51.1	13.405	38.8		
2.2342	45.9	16.775	38.4		
		[NaCl] = 0.0097 mol kg^{-1}			
0.0439	64.8	1.3491	48.5	8.4173	37.6
0.0877	63.0	1.6937	45.6	10.564	38.0
0.1315	61.8	2.0797	43.8	13.401	37.7
0.1753	61.4	2.5065	41.4	17.028	37.5
0.2628	59.2	3.0158	38.8	22.159	37.7
0.3939	56.7	3.6480	36.1	29.977	37.5
0.5684	55.1	4.4834	34.7	43.338	37.0
0.7860	53.1	5.5157	37.4		
1.0463	50.7	6.8183	37.8		

Table 5.5a. Continued

[SDS] / mmol kg^{-1}	γ/ mN m^{-1}	[SDS] / mmol kg^{-1}	γ/ mN m^{-1}	[SDS] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0150 mol kg^{-1}			
0.0386	64.5	1.5280	46.0	4.8523	37.2
0.1157	62.1	1.9050	42.8	5.2840	37.1
0.1928	60.3	2.2801	40.2	5.8200	37.0
0.3082	57.6	2.6533	38.3	6.5285	37.0
0.4618	54.9	3.0245	36.8	7.5778	37.4
0.6150	53.1	3.3938	35.2	9.1228	37.2
0.7680	51.4	3.7612	34.6	11.294	37.1
0.9587	49.5	4.1267	35.6	14.505	36.8
1.2249	47.4	4.4904	36.9		
		[NaCl] = 0.0320 mol kg^{-1}			
0.0216	64.5	0.5795	49.8	2.5605	34.6
0.0432	63.2	0.6860	47.8	3.0270	35.9
0.0648	62.1	0.7922	46.3	3.5882	36.0
0.0863	61.4	0.9194	45.1	4.2797	36.3
0.1294	59.3	1.0673	43.6	5.1527	36.3
0.1940	57.2	1.2357	42.2	6.6245	36.3
0.2585	55.6	1.4453	40.7	8.0820	36.2
0.3229	54.2	1.6540	39.2	9.8339	36.2
0.4086	52.3	1.9030	37.2	11.512	36.3
0.4941	50.9	2.1919	35.0	17.298	36.3

Table 5.5a. Continued

[SDS] / mmol kg^{-1}	γ/ mN m^{-1}	[SDS] / mmol kg^{-1}	γ/ mN m^{-1}	[SDS] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0500 mol kg^{-1}			
0.0217	63.9	0.6459	45.3	2.3153	34.8
0.0434	61.9	0.7738	43.9	2.7211	35.5
0.0651	60.4	0.9012	42.3	3.2816	35.7
0.1084	58.3	1.0493	40.6	4.0286	35.4
0.1733	55.6	1.1968	39.5	4.9881	35.5
0.2597	53.0	1.3647	38.4	6.2888	35.4
0.3459	50.6	1.5526	36.6	8.0656	35.5
0.4318	49.3	1.7603	35.7	9.7531	35.5
0.5390	47.4	2.0080	34.1	11.357	35.6
		[NaCl] = 0.0700 mol kg^{-1}			
0.0182	63.8	0.4339	46.8	1.9621	35.0
0.0364	61.8	0.5415	44.7	2.4734	35.4
0.0545	60.5	0.6667	42.4	3.2259	35.0
0.0908	57.8	0.8091	41.4	4.2833	35.1
0.1271	56.2	0.9687	38.8	5.6925	34.9
0.1815	53.8	1.1451	37.4	7.6230	35.0
0.2538	51.2	1.3556	35.2	10.109	34.7
0.3440	49.5	1.6169	33.9	13.834	34.7
		[NaCl] = 0.1210 mol kg^{-1}			
0.0434	61.5	0.7339	39.3	3.1482	34.3
0.0867	57.9	0.8628	37.5	3.9787	34.4
0.1300	55.2	1.0342	35.5	5.2089	34.1
0.2165	51.0	1.2481	33.7	7.0195	34.0
0.3030	48.3	1.5040	33.7	9.5644	34.0
0.3894	45.9	1.8015	34.2	13.324	34.0
0.4756	43.7	2.1403	34.2		
0.6049	41.3	2.5617	34.3		

Table 5.5b. Experimental values of surface tension of SDS in 20 % EG + water media containing varying amounts of NaCl at 25 °C

[SDS] / mmol kg^{-1}	γ/ mN m^{-1}	[SDS] / mmol kg^{-1}	γ/ mN m^{-1}	[SDS] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0 mol kg^{-1}			
0.0422	60.9	2.0546	47.9	10.855	39.4
0.1054	60.7	3.0406	44.6	12.368	39.4
0.2106	59.7	4.3775	40.9	15.193	39.0
0.4200	57.6	5.8465	37.3	18.988	39.0
0.8354	54.7	7.5997	35.7	22.335	38.8
1.4500	50.9	9.2672	38.3	27.115	39.1
		[NaCl] = 0.0049 mol kg^{-1}			
0.0418	61.1	1.8333	47.9	9.1110	38.7
0.1044	59.9	2.4235	45.6	12.131	38.8
0.2085	59.0	3.0037	43.4	14.870	38.7
0.3123	57.7	3.5741	41.5	18.530	38.4
0.4571	56.2	4.1350	39.8	21.741	38.2
0.6218	55.0	4.8685	37.7	26.298	38.8
0.8267	53.0	5.7630	35.8	33.273	37.4
1.0303	51.9	6.6336	37.0		
1.4341	49.1	7.8140	38.6		
		[NaCl] = 0.0096 mol kg^{-1}			
0.0368	60.9	1.2629	49.7	5.851	37.7
0.0918	59.8	1.6135	47.2	6.896	38.2
0.1834	58.4	2.1335	44.8	8.045	38.4
0.2747	57.4	2.6450	42.6	10.727	38.3
0.4020	56.1	3.1481	40.8	14.304	37.8
0.5470	54.5	3.6432	39.0	19.311	38.3
0.7272	52.2	4.2909	36.8	23.409	37.9
0.9065	51.7	5.0813	36.2	29.714	37.0

Table 5.5b. Continued

[SDS] / mmol kg^{-1}	γ/ mN m^{-1}	[SDS] / mmol kg^{-1}	γ/ mN m^{-1}	[SDS] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0200 mol kg^{-1}			
0.0271	60.9	0.9327	46.9	4.3408	36.9
0.0678	59.4	1.1928	46.1	5.1204	37.1
0.1354	57.6	1.5779	43.6	5.9796	37.5
0.2028	56.2	1.9570	41.4	7.9908	37.5
0.2701	55.1	2.3302	39.3	10.686	37.2
0.4040	53.1	2.6977	38.1	14.488	37.2
0.5372	51.2	3.1791	36.6	17.622	37.6
0.6697	49.2	3.7672	35.3	22.488	36.7
		[NaCl] = 0.0697 mol kg^{-1}			
0.0258	60.0	0.8865	42.1	4.6172	35.7
0.0646	57.6	1.1331	40.0	5.6207	35.4
0.1289	55.3	1.4976	37.0	7.4783	35.8
0.1931	52.6	1.8559	34.7	9.9427	35.4
0.2826	50.0	2.2080	35.1	13.369	35.7
0.3844	47.9	2.5542	35.7	16.153	35.0
0.5111	46.1	3.0067	35.6	20.400	34.8
0.6369	45.2	3.5583	35.7		

Table 5.5c. Experimental values of surface tension of SDS in 30 % EG + water media containing varying amounts of NaCl at 25 °C.

[SDS] / mmol kg^{-1}	γ/ mN m^{-1}	[SDS] / mmol kg^{-1}	γ/ mN m^{-1}	[SDS] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0 mol kg^{-1}			
0.0311	62.7	2.7942	52.9	18.472	41.0
0.0622	62.4	3.9689	48.9	21.706	41.1
0.1242	62.2	5.4046	45.4	25.711	40.4
0.2482	62.2	7.0814	41.8	31.143	40.8
0.4646	61.2	8.9767	39.7	38.213	40.0
0.7724	60.2	11.066	41.0	46.060	40.5
1.2310	58.5	13.325	41.4	57.125	40.0
1.8974	56.2	15.728	41.4		
		[NaCl] = 0.0050 mol kg^{-1}			
0.0253	62.3	0.9774	55.5	10.007	40.5
0.0506	61.9	1.5444	53.4	12.559	40.5
0.0759	61.7	2.2737	49.7	15.672	40.4
0.1264	61.0	3.2284	46.9	19.366	40.2
0.2022	60.8	4.5094	43.4	25.265	39.4
0.3532	59.8	6.0886	39.7	33.628	40.3
0.6039	57.7	7.9333	40.1	46.142	40.2
		[NaCl] = 0.0120 mol kg^{-1}			
0.0269	61.9	1.0665	53.2	8.0882	40.3
0.0539	61.6	1.7219	49.3	10.318	40.4
0.1077	60.7	2.3688	46.9	13.269	40.1
0.1883	59.8	3.1341	43.9	16.794	40.1
0.2687	59.0	4.0869	41.5	22.087	40.1
0.4026	57.5	4.7773	39.2	29.586	40.3
0.6692	55.5	6.2244	39.4		

Table 5.5c. Continued

[SDS] / mmol kg^{-1}	γ/ mN m^{-1}	[SDS] / mmol kg^{-1}	γ/ mN m^{-1}	[SDS] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0220 mol kg^{-1}			
0.0271	61.7	0.8854	51.2	10.782	38.9
0.0541	60.8	1.3615	48.4	14.271	38.8
0.0812	60.1	2.0151	45.2	18.919	38.5
0.1352	59.2	2.9152	41.4	25.358	38.7
0.2161	57.8	4.0975	38.7	35.503	39.3
0.3507	56.0	5.5642	38.4	44.75	39.0
0.5653	54.3	7.9086	39.2		
		[NaCl] = 0.0320 mol kg^{-1}			
0.0144	62.1	0.6947	51.4	5.2533	38.7
0.0287	61.4	0.9731	49.2	6.2794	38.5
0.0431	61.1	1.3305	46.7	7.5807	38.7
0.0717	60.1	1.7637	44.4	9.4018	38.8
0.1147	59.6	2.2820	42.0	12.131	39.1
0.1861	57.7	2.8799	39.9	16.677	39.0
0.3000	56.5	3.5640	38.2	23.279	38.8
0.4699	53.4	4.3630	38.5		
		[NaCl] = 0.0510 mol kg^{-1}			
0.0108	61.9	0.7234	48.1	3.9811	37.8
0.0217	61.4	0.9829	45.6	4.5689	37.7
0.0433	60.2	1.2897	43.4	5.2364	37.6
0.0757	59.2	1.6417	41.2	6.0363	37.8
0.1296	57.6	2.0361	39.4	7.0963	38.0
0.2155	55.6	2.4704	37.5	8.5009	37.8
0.3437	52.9	2.9413	36.9	10.396	37.7
0.5134	50.3	3.4460	37.6	13.096	37.7
		[NaCl] = 0.0790 mol kg^{-1}			
0.0074	62.6	0.3782	51.4	2.4882	37.1
0.0221	61.5	0.4996	49.1	2.9961	37.2
0.0442	60.2	0.6551	47.1	3.5679	37.3
0.0735	59.2	0.8435	45.0	4.2724	37.3
0.1102	57.3	1.0702	43.2	5.1334	37.3
0.154	56.1	1.3398	40.6	6.2895	37.2
0.2122	54.4	1.6693	39.1	7.9096	37.1
0.2846	53.3	2.0538	37.5	10.219	37.3

Table 5.5d. Experimental values of surface tension of SDS in 50 % EG + water media containing varying amounts of NaCl at 25 °C

[SDS] / mmol kg^{-1}	γ/ mN m^{-1}	[SDS] / mmol kg^{-1}	γ/ mN m^{-1}	[SDS] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0 mol kg^{-1}			
0.0770	58.4	8.9591	48.2	61.039	40.3
0.3845	58.1	14.634	43.4	86.859	39.7
1.1505	57.1	21.420	41.6	119.17	39.1
2.6706	55.5	31.002	41.1	160.79	39.0
5.2932	52.2	42.779	40.5	186.43	38.5
		[NaCl] = 0.0020 mol kg^{-1}			
0.0343	58.5	4.2970	51.8	26.276	40.9
0.1711	58.1	7.0970	47.9	32.176	40.5
0.5119	57.4	10.911	44.1	38.983	40.7
1.1878	56.2	15.529	41.2	49.876	40.1
2.3524	54.6	20.724	40.9		
		[NaCl] = 0.0036 mol kg^{-1}			
0.0297	57.9	2.1252	55.0	21.508	41.6
0.0890	58.0	3.8107	52.5	28.535	40.9
0.2370	57.7	6.5045	48.8	36.532	40.9
0.5319	57.4	10.295	45.3	47.613	40.0
1.1167	55.9	15.373	42.1		
		[NaCl] = 0.0076 mol kg^{-1}			
0.0506	57.9	4.6845	49.7	33.467	40.5
0.1516	57.8	7.5248	46.2	43.084	40.4
0.3533	57.1	11.177	43.1	55.458	40.0
0.7555	55.7	15.541	41.6	71.003	39.6
1.5049	54.7	20.502	41.0		
2.7408	52.5	26.315	40.8		

Table 5.5d. Continued

[SDS] / mmol kg^{-1}	γ/ mN m^{-1}	[SDS] / mmol kg^{-1}	γ/ mN m^{-1}	[SDS] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0120 mol kg^{-1}			
0.0541	58.4	6.7829	46.3	39.786	40.3
0.2701	57.1	11.201	42.3	50.761	39.7
0.8081	55.5	16.772	40.9	63.922	39.8
1.875	53.2	23.267	40.6		
3.7135	50.1	30.825	40.3		
		[NaCl] = 0.0170 mol kg^{-1}			
0.0456	58.0	3.5709	48.4	26.730	39.8
0.1823	57.0	6.5701	44.3	35.690	39.7
0.4550	55.7	10.6651	40.8	48.276	39.5
0.9076	54.1	14.552	40.5	67.249	39.1
1.8051	52.2	20.026	40.2		
		[NaCl] = 0.0260 mol kg^{-1}			
0.0361	58.2	3.8766	46.3	20.541	39.9
0.1083	57.4	5.5393	44.0	24.748	39.8
0.2164	56.6	7.4705	41.9	30.012	39.5
0.3961	55.8	9.6399	40.6	37.275	39.5
0.7539	53.9	12.016	40.0	47.409	39.6
1.4628	51.6	14.563	39.8	56.202	39.7
2.5099	49.0	17.252	40.1		
		[NaCl] = 0.0350 mol kg^{-1}			
0.0134	58.7	1.6869	51.0	10.884	39.7
0.0671	58.1	2.7886	47.9	14.233	39.7
0.2007	57.0	4.2927	45.2	18.936	39.7
0.4658	55.5	6.1187	42.6		
0.9229	53.3	8.2725	40.5		

Table 5.5d. Continued

[SDS] / mmol kg^{-1}	γ/ mN m^{-1}	[SDS] / mmol kg^{-1}	γ/ mN m^{-1}	[SDS] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0500 mol kg^{-1}			
0.0114	58.5	0.7796	52.8	6.3798	40.4
0.0341	58.2	1.3179	50.6	7.9021	39.5
0.0681	57.8	2.0467	48.3	9.6184	39.7
0.1133	57.4	3.0408	45.5	11.729	39.1
0.2259	56.2	3.9833	43.7	14.726	39.7
0.4493	54.4	5.0517	42.1	18.499	39.0
		[NaCl] = 0.0950 mol kg^{-1}			
0.0087	58.4	0.5112	52.9	4.7657	39.8
0.026	58.1	0.8427	51.6	6.2305	38.1
0.0519	57.9	1.3268	50.7	8.2621	38.1
0.0864	57.3	1.8722	47.7	11.116	38.2
0.1723	56.4	2.6175	45.2	14.876	38.1
0.3003	54.9	3.5991	42.2		

Table 5.5e. Experimental values of surface tension of SDS in 60 % EG + water media containing varying amounts of NaCl at 25 °C

[SDS] / mmol kg^{-1}	γ/ mN m^{-1}	[SDS] / mmol kg^{-1}	γ/ mN m^{-1}	[SDS] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0 mol kg^{-1}			
0.0825	56.4	7.9600	51.1	64.917	40.3
0.3296	56.1	12.594	47.8	79.676	40.1
0.7405	56.0	19.290	44.5	95.667	39.6
1.5593	55.4	28.460	41.6	113.12	39.5
2.7796	54.5	39.002	40.9		
4.7926	53.0	51.146	40.4		
		[NaCl] = 0.0004 mol kg^{-1}			
0.0608	56.1	7.848	50.5	45.849	40.8
0.2431	56.1	12.79	47.2	56.294	40.6
0.8483	55.6	19.534	43.5	68.315	40.3
2.0484	55.1	27.219	41.5	80.934	40.3
4.4077	53.0	35.996	40.6		
		[NaCl] = 0.0012 mol kg^{-1}			
0.0392	56.1	2.1229	54.4	20.009	43.3
0.1175	56.3	3.6271	53.5	28.090	41.2
0.2738	55.8	5.8233	51.2	37.323	40.7
0.5854	55.5	9.3319	48.8	48.653	40.4
1.1659	55.2	13.948	45.6	53.439	40.5
		[NaCl] = 0.0050 mol kg^{-1}			
0.0521	55.9	2.1645	53.9	24.986	41.5
0.1562	55.9	3.4302	52.5	32.553	41.0
0.3122	55.4	5.4211	51.2	41.114	40.8
0.5198	55.3	8.4741	48.8	50.266	40.2
0.8819	54.7	12.668	46.4	60.897	40.5
1.3970	54.4	18.404	43.7		

Table 5.5e. Continued

[SDS] / mmol kg^{-1}	γ/ mN m^{-1}	[SDS] / mmol kg^{-1}	γ/ mN m^{-1}	[SDS] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0064 mol kg^{-1}			
0.0426	56.1	2.1007	53.5	16.890	43.8
0.1702	55.6	3.5377	52.2	23.031	41.5
0.3824	55.2	5.5444	50.3	31.690	40.6
0.7207	54.6	8.2661	48.5	43.848	40.3
1.2673	54.5	11.986	45.8	60.607	40.0
		[NaCl] = 0.0100 mol kg^{-1}			
0.0392	56.2	3.6261	51.7	30.231	40.8
0.1176	55.9	5.8168	50.0	36.841	40.8
0.2741	56.0	8.9684	47.5	46.167	40.4
0.5859	55.3	13.256	45.2	50.950	40.3
1.1667	54.4	18.439	42.7		
2.1235	53.3	23.995	41.6		
		[NaCl] = 0.0220 mol kg^{-1}			
0.0270	56.2	2.2178	51.7	22.994	40.3
0.0810	55.8	3.9903	49.9	28.809	40.0
0.1618	55.8	6.4109	47.6	34.913	39.7
0.3231	55.2	9.5964	44.8	40.943	39.8
0.5908	54.5	13.378	42.9	47.380	39.8
1.1744	53.7	17.942	40.9		
		[NaCl] = 0.0310 mol kg^{-1}			
0.0155	56.5	1.0199	53.0	13.637	41.1
0.0465	56.1	1.6110	51.7	16.506	40.4
0.0929	55.9	2.4740	50.2	19.338	40.1
0.1546	55.3	3.8523	47.9	22.067	39.8
0.2624	55.0	5.7900	45.8	24.651	39.8
0.4156	54.6	8.1576	43.7	27.268	39.6
0.6438	53.9	10.816	41.9		

Table 5.5e. Continued

[SDS] / mmol kg^{-1}	γ/ mN m^{-1}	[SDS] / mmol kg^{-1}	γ/ mN m^{-1}	[SDS] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0410 mol kg^{-1}			
0.0260	56.0	1.6895	51.5	13.672	41.1
0.1041	55.4	2.5618	50.1	17.347	40.0
0.2857	54.7	3.7806	48.4	21.508	40.0
0.4667	53.9	5.4349	46.6	25.960	39.8
0.7240	53.1	7.6988	44.5	31.139	39.6
1.1075	52.7	10.479	42.5	37.629	39.7
		[NaCl] = 0.0570 mol kg^{-1}			
0.0286	56.8	2.2417	50.2	14.100	40.1
0.1430	55.4	3.5941	48.0	18.179	39.6
0.3710	54.7	5.4279	45.6	23.648	39.5
0.7111	53.7	7.9337	43.5	29.925	39.2
1.273	52.1	10.776	41.3	39.925	39.1

Table 5.5f. Experimental values of surface tension of SDS in 70 % EG + water media containing varying amounts of NaCl at 25 °C

[SDS] / mmol kg^{-1}	γ/ mN m^{-1}	[SDS] / mmol kg^{-1}	γ/ mN m^{-1}	[SDS] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0 mol kg^{-1}			
0.0724	54.4	9.5788	50.8	64.990	40.9
0.2172	54.7	13.569	49.2	74.623	40.6
0.4340	54.4	18.696	47.4	85.478	40.4
0.7947	54.5	24.832	45.5	98.231	40.3
1.5131	54.3	31.819	44.0	111.92	40.4
2.5837	53.9	39.489	42.2	127.85	40.1
4.2089	53.0	47.668	41.0		
6.5070	52.1	56.228	40.8		
		[NaCl] = 0.0007 mol kg^{-1}			
0.1172	54.1	11.392	48.9	90.654	39.5
0.2344	54.1	22.152	45.3	104.06	39.7
0.5855	54.0	27.311	43.7	122.12	39.5
1.1692	53.7	37.218	41.8	132.98	39.5
1.7512	53.5	46.611	40.6	147.77	39.3
3.4872	52.5	59.822	40.0	156.75	39.2
5.7784	51.7	75.971	39.9	169.08	39.1
		[NaCl] = 0.0011 mol kg^{-1}			
0.0732	54.2	9.1889	50.8	66.539	40.7
0.2195	54.2	14.204	48.9	78.105	40.4
0.4387	54.4	20.592	46.6	91.569	40.3
0.7303	54.3	28.424	44.2	105.88	40.2
1.4566	53.9	37.397	42.4	120.20	40.1
2.8971	53.1	46.708	41.1		
5.3805	52.5	56.194	40.4		

Table 5.5f. Continued

[SDS] / mmol kg^{-1}	γ/ mN m^{-1}	[SDS] / mmol kg^{-1}	γ/ mN m^{-1}	[SDS] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0031 mol kg^{-1}			
0.0969	54.0	6.2725	51.05	83.970	40.1
0.2905	53.7	9.9567	49.8	101.200	39.8
0.5805	53.6	15.764	47.7	118.078	39.4
0.9663	53.4	24.289	44.8	135.875	39.5
1.5433	53.3	36.224	42.4	153.533	39.1
2.5004	53.2	50.729	40.8	172.46	39.0
3.9254	52.7	66.917	40.4	190.90	38.7
		[NaCl] = 0.0100 mol kg^{-1}			
0.0633	54.6	5.480	51.7	45.633	40.8
0.1898	54.6	8.135	50.2	54.410	40.5
0.4424	54.4	11.563	48.8	63.678	40.6
0.8828	54.2	15.997	46.8	74.301	40.6
1.5086	53.7	22.387	45.0	85.399	39.8
2.4397	53.0	29.535	42.9		
3.6674	52.3				
		[NaCl] = 0.0200 mol kg^{-1}			
0.0762	54.0	5.2389	50.1	69.583	39.7
0.2286	53.7	8.8637	48.6	85.62	39.4
0.4568	53.3	14.470	46.4	102.58	39.2
0.7605	53.0	21.816	43.9	121.95	39.1
1.1392	52.9	31.208	41.5	143.36	38.8
1.8936	52.2	42.728	40.2		
3.0176	51.4	55.727	39.8		

Table 5.5f. Continued

[SDS] / mmol kg^{-1}	γ/ mN m^{-1}	[SDS] / mmol kg^{-1}	γ/ mN m^{-1}	[SDS] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0330 mol kg^{-1}			
0.0445	54.5	4.4966	50.4	33.281	40.4
0.1335	54.3	6.9729	48.5	39.254	40.2
0.3112	53.9	10.149	46.8	45.769	40.1
0.621	53.7	13.931	45.2	52.939	40.1
1.0616	53.2	18.215	43.6	61.670	39.8
1.7176	52.3	22.891	42.3		
2.7986	51.6	27.855	41.7		
		[NaCl] = 0.0500 mol kg^{-1}			
0.0337	54.3	2.7006	50.7	17.433	42.4
0.1010	54.7	3.9736	49.3	22.544	41.2
0.2355	54.3	5.6787	48.1	27.951	40.5
0.5702	53.4	7.7763	46.8	33.474	40.2
1.0688	52.5	10.360	45.4	39.863	39.9
1.7271	51.9	13.623	43.8	50.120	39.9
		[NaCl] = 0.0756 mol kg^{-1}			
0.0819	54.2	5.3081	47.6	52.758	39.0
0.2455	53.5	9.2027	45.3	65.762	38.8
0.4907	53.3	15.218	42.7	79.617	38.6
0.8983	52.8	22.388	40.4	95.651	38.4
1.7101	51.6	31.172	39.3		
2.9194	50.1	41.228	38.7		
		[NaCl] = 0.0960 mol kg^{-1}			
0.0246	54.1	3.1560	48.4	21.018	40.0
0.0982	54.1	5.3450	46.6	24.612	38.9
0.2206	53.6	8.3914	43.9	29.656	38.6
0.4641	53.0	12.065	42.4	37.247	38.7
0.9465	51.5	15.358	41.0		
1.7761	50.2	18.328	39.9		

Table 5.5g. Experimental values of surface tension of SDS in 80 % EG + water media containing varying amounts of NaCl at 25 °C

[SDS] / mmol kg^{-1}	γ/ mN m^{-1}	[SDS] / mmol kg^{-1}	γ/ mN m^{-1}	[SDS] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0 mol kg^{-1}			
0.0817	52.1	11.763	49.3	105.98	40.3
0.2451	52.0	19.086	47.3	123.69	39.9
0.5712	52.1	29.371	45.3	142.56	39.8
1.2212	52.0	41.921	43.4	163.95	39.4
2.4321	51.7	55.996	41.8	188.38	39.5
3.2337	51.2	70.898	40.6		
6.3956	50.2	88.028	40.5		
		[NaCl] = 0.0050 mol kg^{-1}			
0.0978	52.3	5.3007	50.6	65.906	40.2
0.2933	52.2	9.9818	49.3	89.531	40.1
0.6837	51.9	17.65	47.6	114.04	39.7
1.4618	51.6	29.562	45.6	139.76	39.6
2.9114	51.3	45.163	42.8	167.31	39.5
		[NaCl] = 0.0210 mol kg^{-1}			
0.0689	52.2	6.537	49.5	58.549	39.5
0.2067	52.0	10.953	48.1	73.748	39.3
0.5501	51.8	16.924	46.6	90.574	39.9
1.2336	51.1	24.679	44.8	106.56	39.5
2.2501	51.1	34.216	42.5		
3.9214	50.3	45.298	40.9		
		[NaCl] = 0.0320 mol kg^{-1}			
0.0617	52.2	5.9811	48.9	49.954	39.4
0.2468	52.2	9.3911	47.9	62.136	39.1
0.6157	51.7	14.273	46.5	74.652	39.2
1.2273	51.4	20.874	45.0	90.230	39.5
2.1374	51.1	29.231	42.3	95.028	39.1
3.6347	50.1	39.159	40.9		

Table 5.5g. Continued

[SDS] / mmol kg^{-1}	γ/ mN m^{-1}	[SDS] / mmol kg^{-1}	γ/ mN m^{-1}	[SDS] / mmol kg^{-1}	γ/ mN m^{-1}
		[NaCl] = 0.0470 mol kg^{-1}			
0.0537	52.1	4.6092	49.2	46.187	39.4
0.1611	52.4	8.1094	47.9	56.804	39.1
0.3755	52.1	12.872	46.3	68.163	39.3
0.8028	51.6	19.111	44.4	79.285	39.4
1.4928	51.1	26.865	42.4		
2.5439	50.5	35.990	41.0		
		[NaCl] = 0.0700 mol kg^{-1}			
0.0523	52.4	3.8895	48.7	32.109	40.7
0.1568	52.3	6.3587	47.3	38.873	39.9
0.3133	52.2	10.169	45.7	50.714	39.8
0.5215	51.9	14.706	44.2	65.196	39.5
0.8329	51.3	19.008	42.9	83.312	39.0
1.3497	50.9	23.094	41.7		
2.3743	49.8	26.979	41.3		

Table 5.6. Experimental values of specific conductivity of SDS in water + EG media at 25 °C

[SDS] / mmol kg^{-1}	10 κ/ S m^{-1}	[SDS] / mmol kg^{-1}	10 κ/ S m^{-1}	[SDS] / mmol kg^{-1}	10 κ/ S m^{-1}
		10 % EG + water			
0.6465	0.0440	5.8061	0.3950	10.011	0.6056
1.2769	0.0865	6.3152	0.4294	10.430	0.6178
1.8918	0.1288	6.8130	0.4624	10.841	0.6306
2.4918	0.1704	7.2999	0.4941	11.244	0.6413
3.0773	0.2097	7.7762	0.5230	11.640	0.6521
3.6490	0.2481	8.2423	0.5454	12.027	0.6635
4.2072	0.2869	8.6986	0.5632	12.407	0.6735
4.7525	0.3245	9.1452	0.5790		
5.2854	0.3601	9.5826	0.5931		
		20 % EG + water			
0.7550	0.0479	6.7166	0.3906	11.493	0.5677
1.4895	0.0948	7.2988	0.4234	11.965	0.5794
2.2042	0.1361	7.8670	0.4522	12.428	0.5910
2.9000	0.1760	8.4217	0.4762	12.880	0.6033
3.5777	0.2151	8.9635	0.4962	13.323	0.6140
4.2379	0.2529	9.4928	0.5125	13.757	0.6251
4.8812	0.2889	10.010	0.5280	14.182	0.6350
5.5084	0.3242	10.515	0.5413	14.598	0.6447
6.1200	0.3578	11.009	0.5550	15.006	0.6541

Table 5.6. Continued

[SDS] / mmol kg^{-1}	10 κ/ S m^{-1}	[SDS] / mmol kg^{-1}	10 κ/ S m^{-1}	[SDS] / mmol kg^{-1}	10 κ/ S m^{-1}
		30 % EG + water			
0.8209	0.0313	10.157	0.3488	18.635	0.5776
1.6348	0.0590	10.894	0.3718	19.306	0.5903
2.4420	0.0850	11.626	0.3945	19.973	0.6018
3.2424	0.1155	12.352	0.4158	20.634	0.6127
4.0362	0.1438	13.072	0.4367	21.291	0.6242
4.8235	0.1698	13.787	0.4563	21.942	0.6363
5.6042	0.1938	14.496	0.4918	22.588	0.6472
6.3786	0.2215	15.199	0.5091	23.230	0.6563
7.1466	0.2471	15.897	0.5239	23.867	0.6679
7.9084	0.2729	16.589	0.5381	24.499	0.6773
8.6641	0.2996	17.276	0.5519	25.127	0.6892
9.4136	0.3231	17.958	0.5650		
		50 % EG + water			
1.3896	0.0387	14.468	0.3597	26.219	0.6012
2.7635	0.077	15.699	0.3856	27.329	0.6190
4.1221	0.1144	16.917	0.4155	28.427	0.6352
5.4657	0.1500	18.123	0.4391	29.515	0.6523
6.7943	0.1831	19.316	0.4671	30.592	0.6683
8.1084	0.2169	20.496	0.4972	31.658	0.6835
9.4080	0.2507	21.664	0.5198	32.714	0.6991
10.693	0.2791	22.821	0.5420	33.759	0.7135
11.965	0.306	23.965	0.5632	34.795	0.7272
13.223	0.3342	25.098	0.5818	35.820	0.7392

Table 5.6. Continued

[AOT] / mmol kg^{-1}	10 κ/ S m^{-1}	[AOT] / mmol kg^{-1}	10 κ/ S m^{-1}	[AOT] / mmol kg^{-1}	10 κ/ S m^{-1}
		60 % EG + water			
0.2462	0.0050	18.559	0.3246	164.02	1.7124
0.7374	0.0136	20.720	0.3599	169.58	1.7140
1.2271	0.0230	22.860	0.3938	174.77	1.7645
1.7153	0.0314	26.014	0.4417	179.60	1.8101
2.2020	0.0420	30.110	0.5004	184.12	1.8522
2.6871	0.0512	36.043	0.5737	188.34	1.8952
3.1708	0.0612	43.583	0.6679	192.32	1.9364
3.6531	0.0710	52.460	0.7582	196.05	1.9728
4.1338	0.0814	62.382	0.8487	199.57	2.0031
4.8522	0.0937	73.060	0.9416	203.69	2.0421
5.5673	0.1085	84.221	1.0375	208.28	2.0862
6.2791	0.1224	96.819	1.1432	212.51	2.1283
7.2232	0.1379	108.129	1.2427	217.66	2.1711
8.3952	0.1564	119.305	1.3311	222.34	2.2169
9.5585	0.1739	128.479	1.4098	226.60	2.2451
10.713	0.1898	136.845	1.4787	232.33	2.2236
11.859	0.2117	144.502	1.5469		
14.125	0.2472	151.539	1.6096		
16.358	0.2849	158.027	1.6648		

Table 5.6. Continued

[AOT] / mmol kg^{-1}	10 κ/ S m^{-1}	[AOT] / mmol kg^{-1}	10 κ/ S m^{-1}	[AOT] / mmol kg^{-1}	10 κ/ S m^{-1}
		70 % EG + water			
6.3006	0.0989	38.655	0.5410	55.386	0.7247
11.906	0.1850	41.307	0.5763	56.926	0.7366
16.925	0.2587	43.763	0.6043	58.378	0.7528
21.447	0.3200	46.044	0.6302	59.750	0.7622
25.540	0.3778	48.169	0.6512	61.048	0.7798
29.263	0.4242	50.153	0.6718	62.278	0.7872
32.664	0.4688	52.010	0.6876	63.445	0.7941
35.784	0.5082	53.750	0.7057	64.554	0.8071
		80 % EG + water			
4.0739	0.0443	45.770	0.4484	84.648	0.7467
8.0110	0.0815	49.311	0.4771	87.469	0.7660
11.817	0.1262	53.560	0.5139	90.720	0.7884
15.501	0.1635	57.621	0.5456	93.834	0.8096
19.066	0.2013	61.508	0.5765	96.819	0.8301
22.519	0.2332	65.231	0.6055	100.150	0.8519
25.865	0.2664	68.801	0.6329	103.328	0.8706
30.168	0.3037	72.226	0.6589	106.363	0.8887
34.301	0.3461	75.516	0.6811	109.264	0.9045
38.273	0.3791	78.678	0.7054	111.652	0.9197
42.093	0.4172	81.720	0.7257	114.701	0.9389

Table: 5.7. Cmc of SDS in water + EG media containing varying amounts of NaCl at 25 °C from surface tension measurements (cmc values given in parentheses are from conductance measurements)

10 % EG		20 % EG		30 % EG	
[NaCl]/ mol kg^{-1}	cmc / mmol kg^{-1}	[NaCl]/ mol kg^{-1}	cmc / mmol kg^{-1}	[NaCl]/ mol kg^{-1}	cmc / mmol kg^{-1}
0	8.36 (8.10)	0	9.67 (8.55)	0	11.4 (10.26)
0.0046	7.34	0.0049	7.64	0.0050	9.35
0.0097	5.69	0.0096	6.12	0.0120	7.32
0.0150	4.54	0.0200	4.38	0.0220	5.92
0.0320	3.08	0.0697	2.43	0.0320	4.96
0.0500	2.52			0.0510	3.43
0.0700	1.95			0.0790	2.30
0.1210	1.40				

Table: 5.7. Continued

50 % EG		60 % EG		70 % EG		80 % EG	
[NaCl]/ mol kg^{-1}	cmc / mmol kg^{-1}	[NaCl]/ mol kg^{-1}	cmc / mmol kg^{-1}	[NaCl]/ mol kg^{-1}	cmc / mmol kg^{-1}	[NaCl]/ mol kg^{-1}	cmc / mmol kg^{-1}
0	19.0 (21.2)	0	28.2 (31.7)	0	46.7 (44.5)	0	70.2 (69.5)
0.0020	15.6	$4x10^{-4}$	26.3	$7x10^{-4}$	44.7	0.0050	63.5
0.0036	15.3	0.0012	26.1	0.0011	43.8	0.0210	57.0
0.0076	14.1	0.0050	25.1	0.0031	42.8	0.0320	52.5
0.0120	13.2	0.0064	24.5	0.0100	39.9	0.0470	47.9
0.0170	11.2	0.0100	23.7	0.0200	36.8	0.0770	38.9
0.0260	10.3	0.0220	20.4	0.0330	32.9		
0.0350	9.40	0.0310	19.0	0.0500	29.3		
0.0500	7.70	0.0410	17.7	0.0756	25.7		
0.095	5.90	0.0570	16.0	0.0960	22.8		
			14.1				

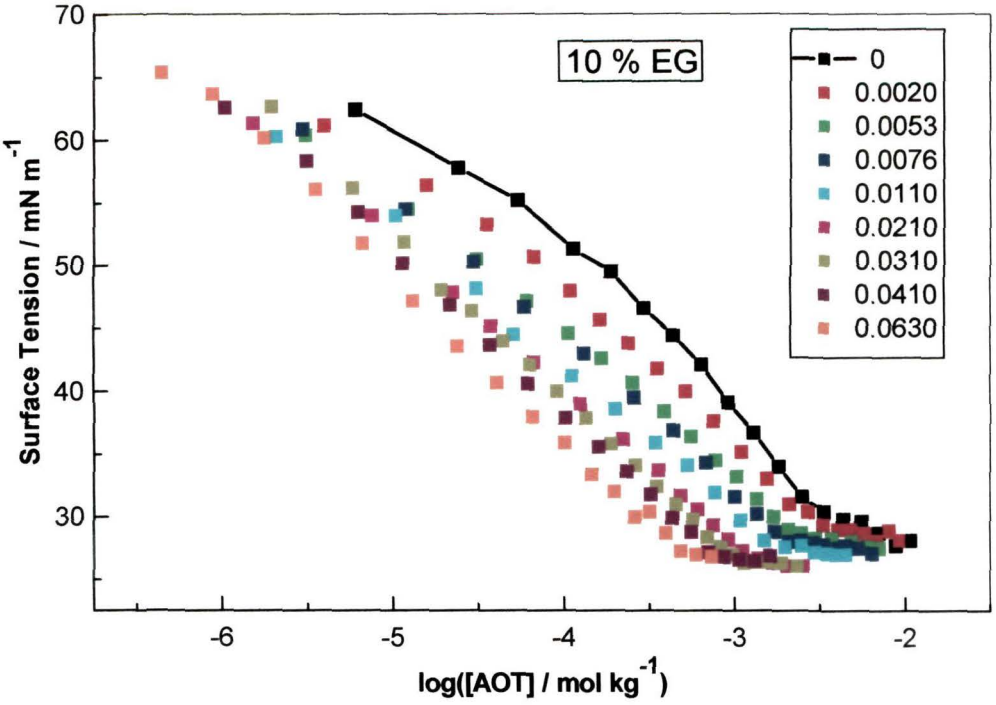

Fig. 5.1. Surface tension isotherms of AOT in 10% EG containing different amounts of NaCl. Concentrations of NaCl in mol kg^{-1} are shown in the inset.

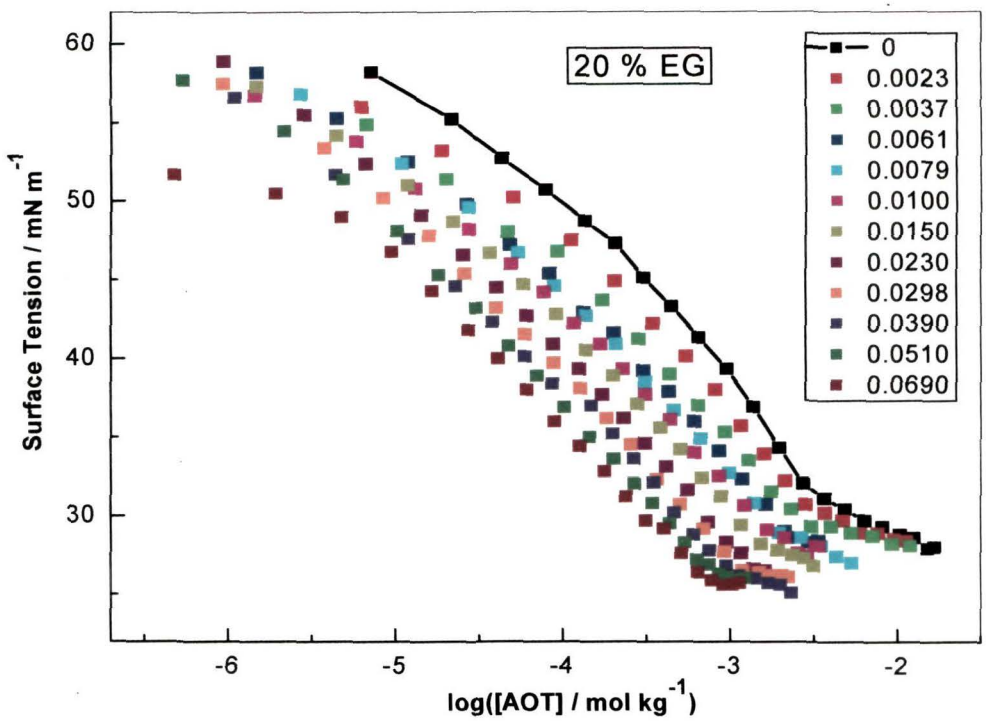

Fig. 5.2. Surface tension isotherms of AOT in 20% EG containing different amounts of NaCl. Concentrations of NaCl in mol kg^{-1} are shown in the inset.

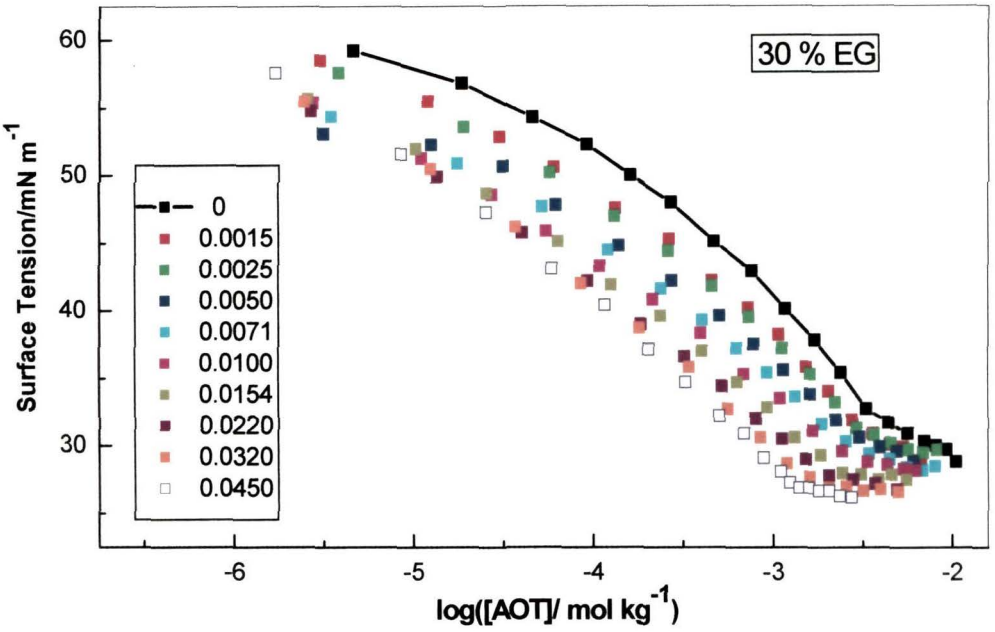

Fig. 5.3. Surface tension isotherms of AOT in 30% EG containing different amounts of NaCl. Concentrations of NaCl in mol kg^{-1} are shown in the inset.

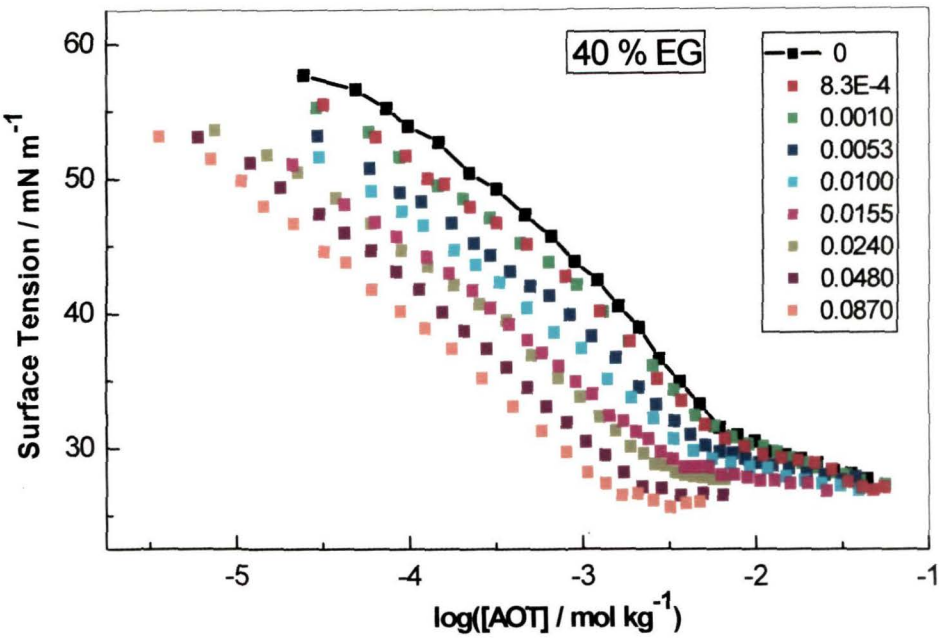

Fig. 5.4. Surface tension isotherms of AOT in 40% EG containing different amounts of NaCl. Concentrations of NaCl in mol kg^{-1} are shown in the inset.

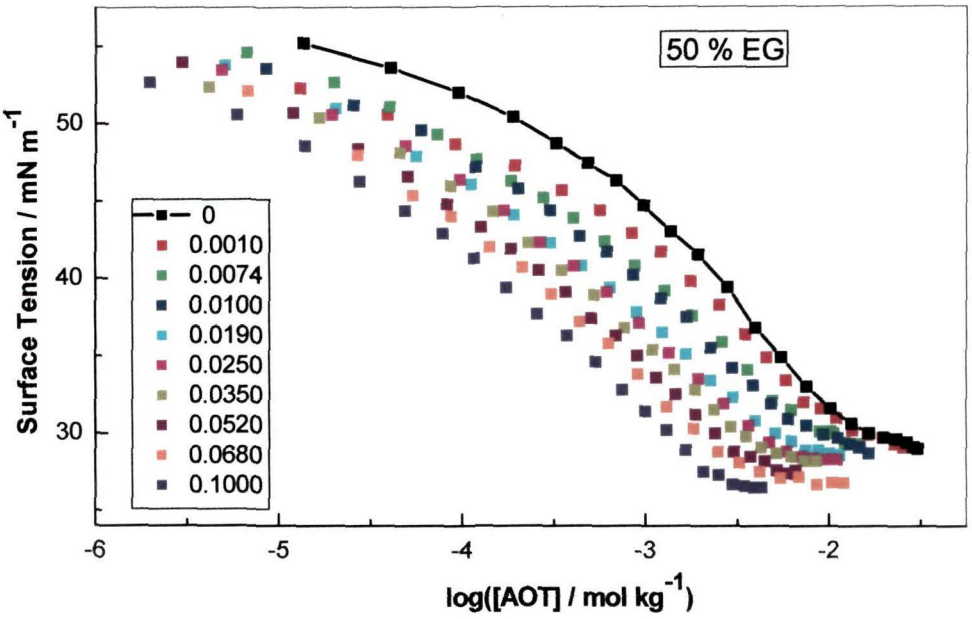

Fig. 5.5. Surface tension isotherms of AOT in 50% EG containing different amounts of NaCl. Concentrations of NaCl in mol kg^{-1} are shown in the inset.

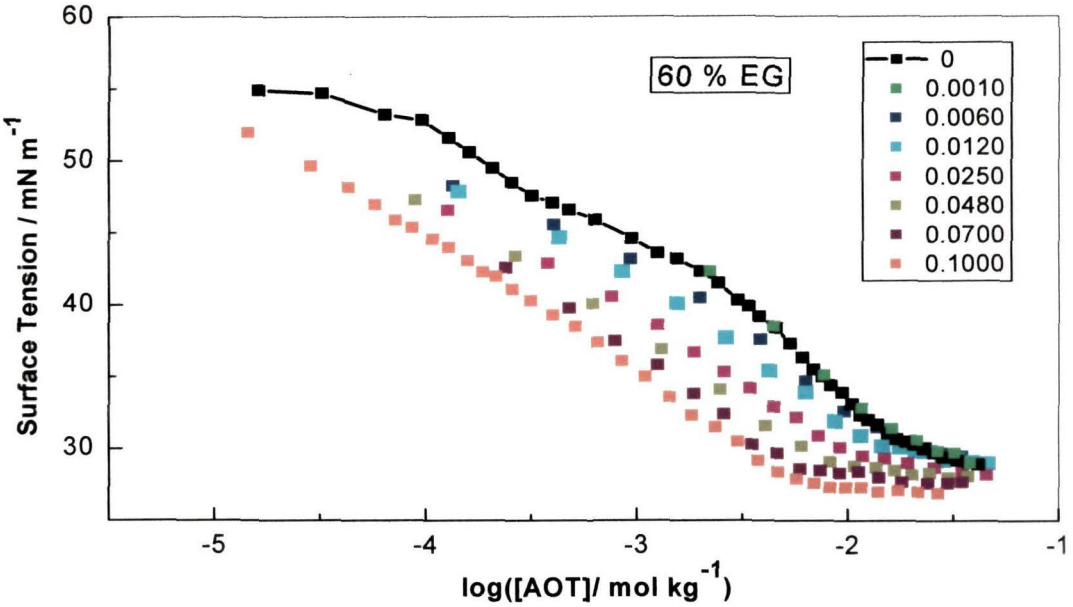

Fig. 5.6. Surface tension isotherms of AOT in 60% EG containing different amounts of NaCl. Concentrations of NaCl in mol kg^{-1} are shown in the inset.

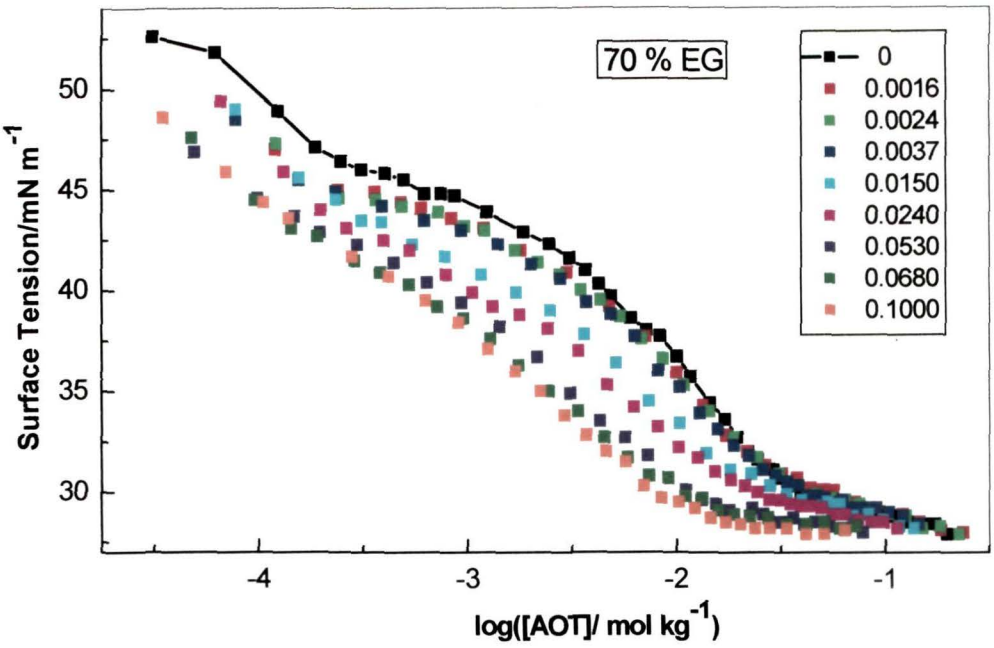

Fig. 5.7. Surface tension isotherms of AOT in 70% EG containing different amounts of NaCl. Concentrations of NaCl in mol kg^{-1} are shown in the inset.

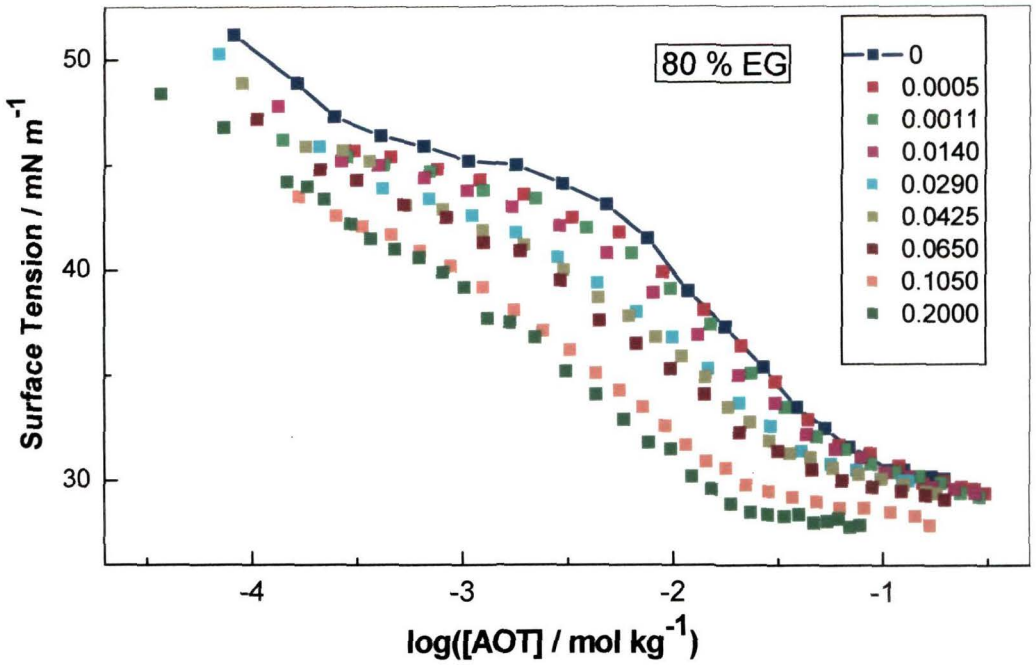

Fig. 5.8. Surface tension isotherms of AOT in 80% EG containing different amounts of NaCl. Concentrations of NaCl in mol kg^{-1} are shown in the inset.

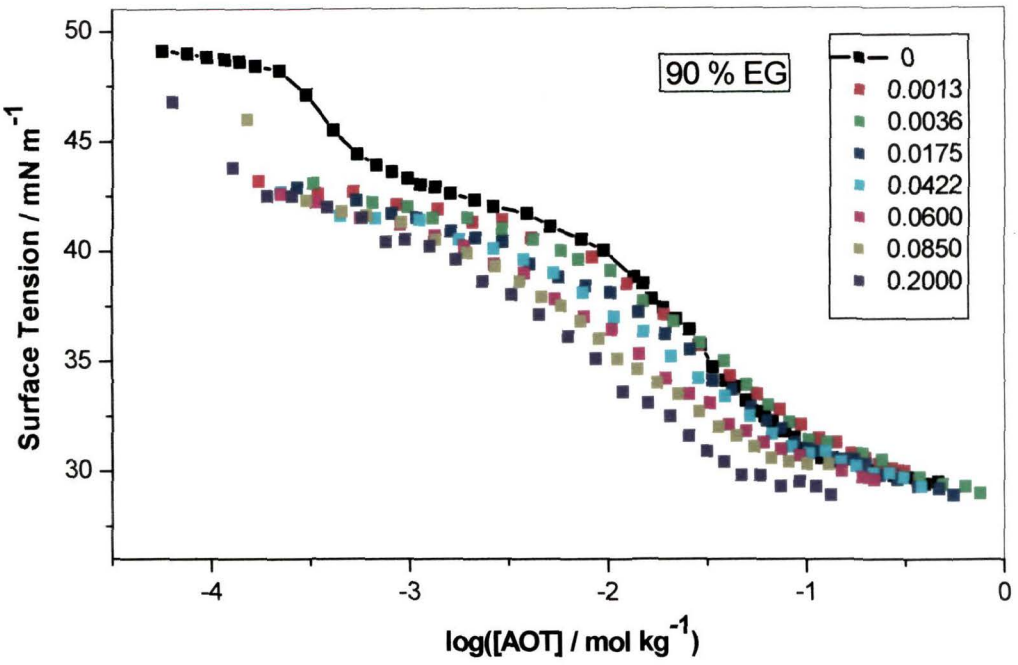

Fig. 5.9. Surface tension isotherms of AOT in 90% EG containing different amounts of NaCl. Concentrations of NaCl in mol kg^{-1} are shown in the inset.

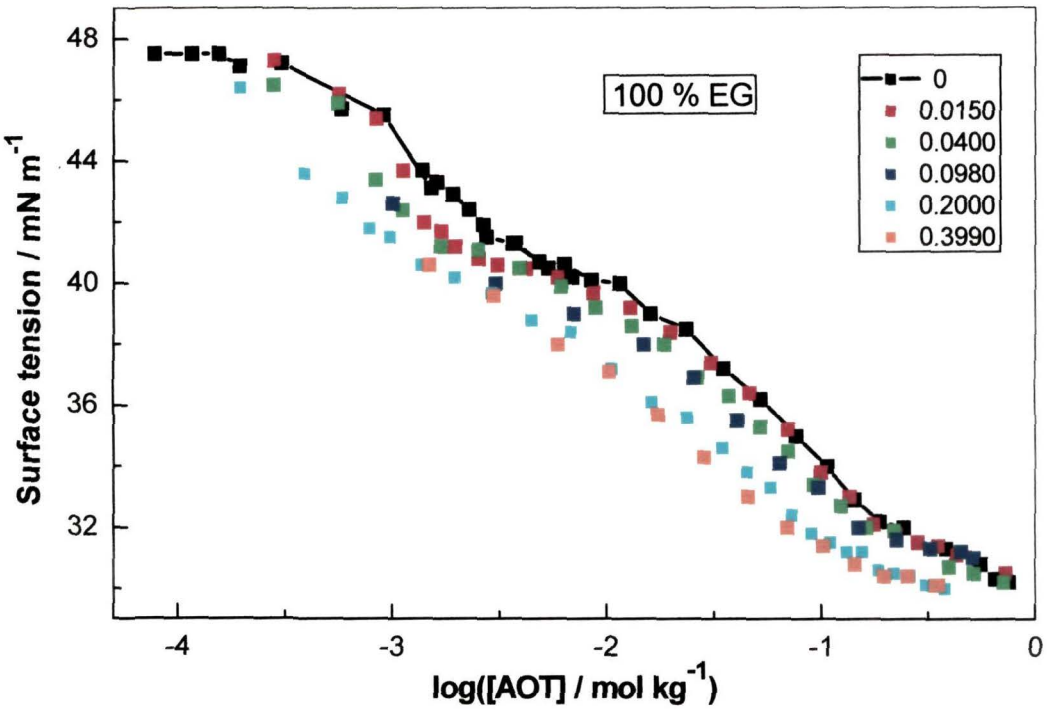

Fig. 5.10. Surface tension isotherms of AOT in 100% EG containing different amounts of NaCl. Concentrations of NaCl in mol kg^{-1} are shown in the inset.

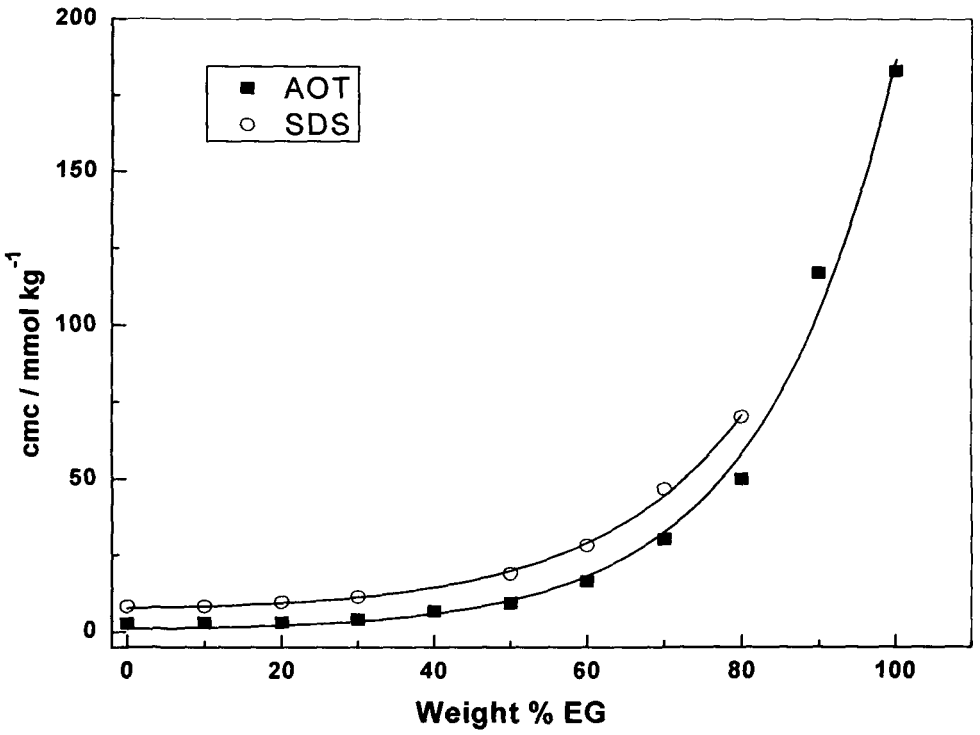

Fig. 5.11. Variation of cmc of AOT with EG content

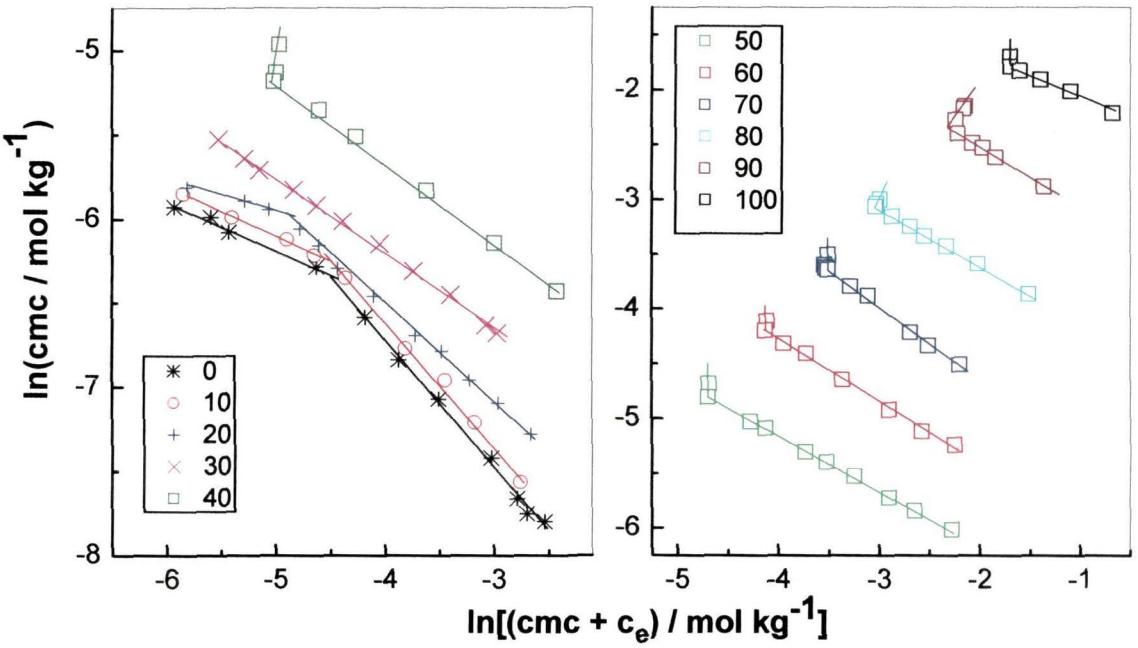

Fig. 5.12. CH plots of AOT in water + EG media. The values of weight % of EG are shown in the insets.

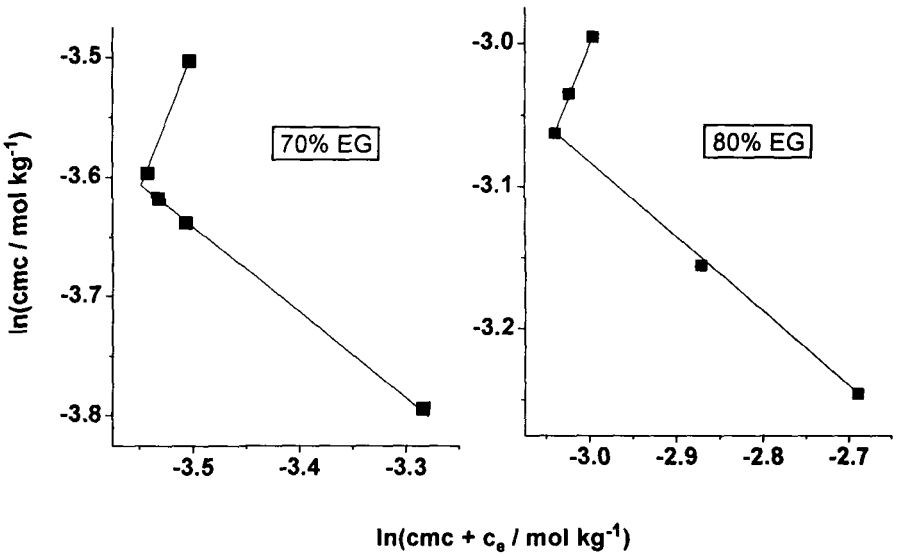

Fig. 5.13. CH plots of AOT in 70 and 80 % EG media on an expanded scale.

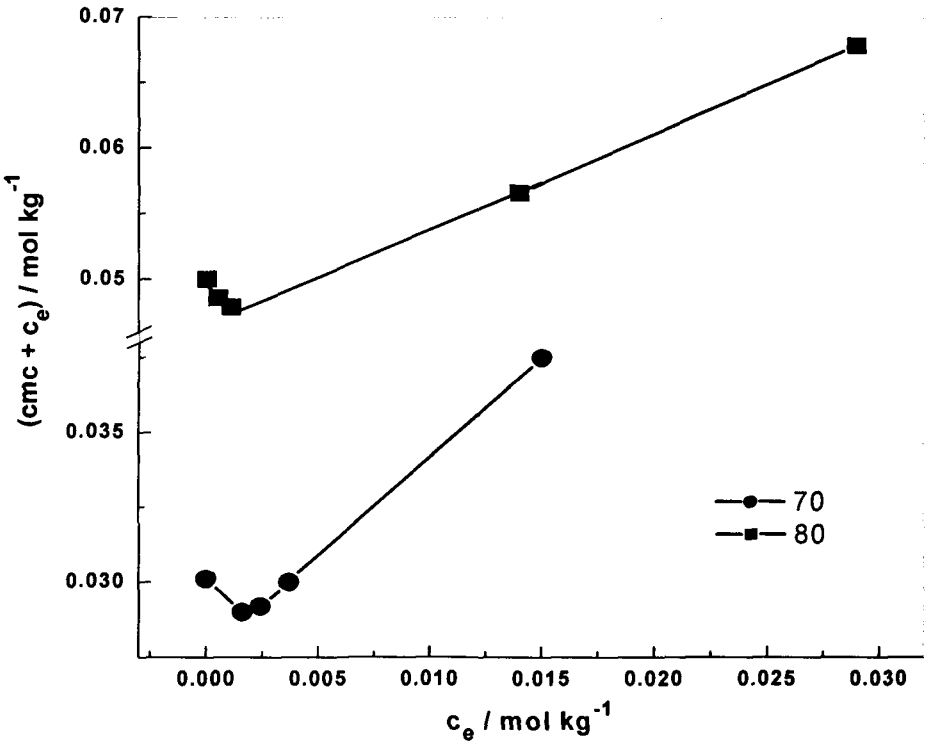

Fig. 5.14. Representative plots of variation of total counterion concentration (cmc + c_e) versus electrolyte concentration in water + EG media containing 70 and 80 weight % EG.

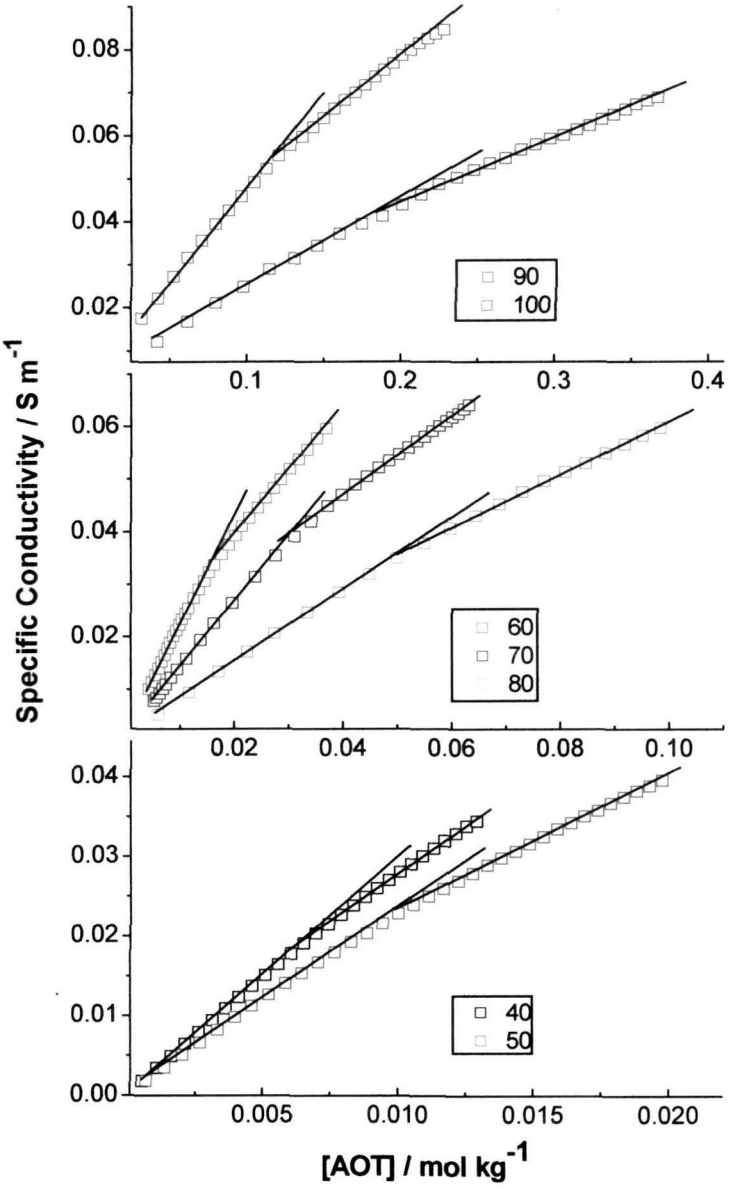

Fig. 5.15. Specific conductivity of AOT in water + EG media at 25 °C. Values of the weight % of EG are shown in the insets

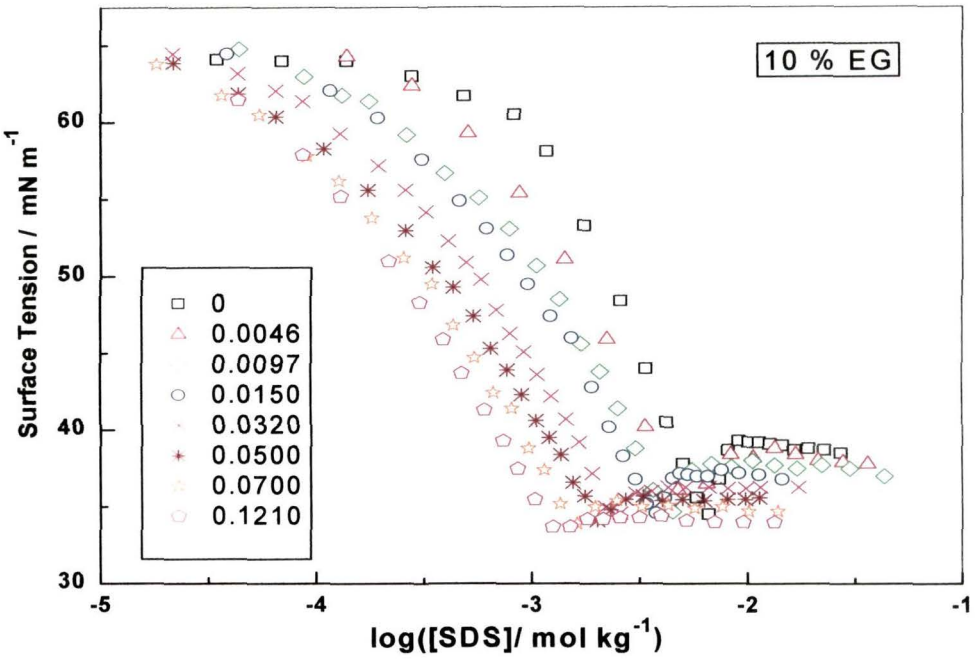

Fig. 5.16. Surface tension isotherms of SDS in 10% EG containing different amounts of NaCl. Concentrations of NaCl in mol kg^{-1} are shown in the inset.

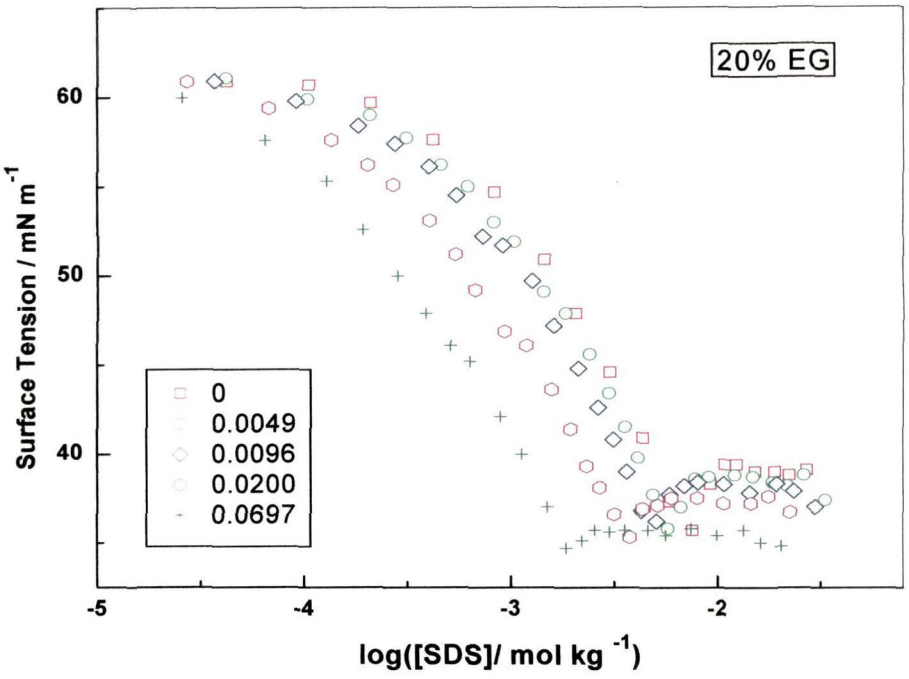

Fig. 5.17. Surface tension isotherms of SDS in 20% EG containing different amounts of NaCl. Concentrations of NaCl in mol kg^{-1} are shown in the inset.

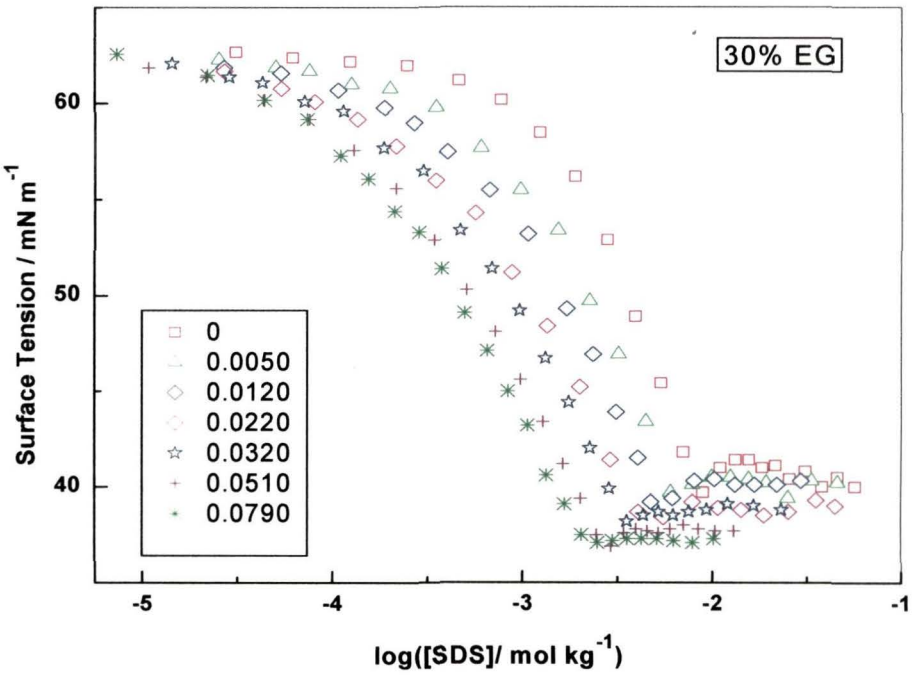

Fig. 5.18. Surface tension isotherms of SDS in 30% EG containing different amounts of NaCl. Concentrations of NaCl in mol kg^{-1} are shown in the inset.

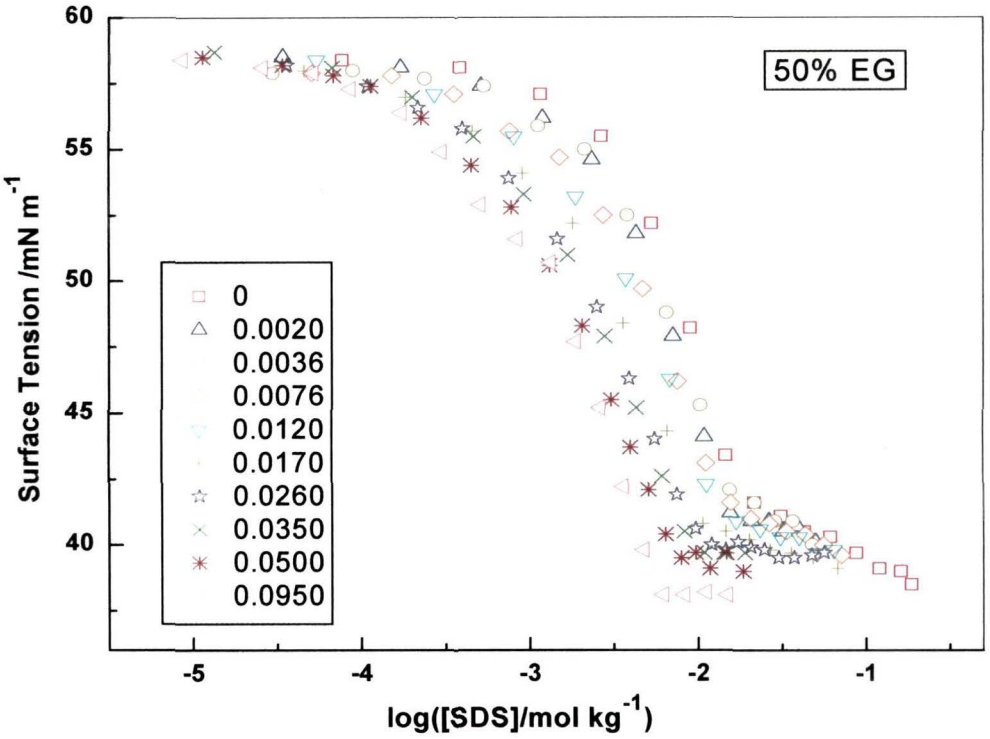

Fig. 5.19. Surface tension isotherms of SDS in 50% EG containing different amounts of NaCl. Concentrations of NaCl in mol kg^{-1} are shown in the inset.

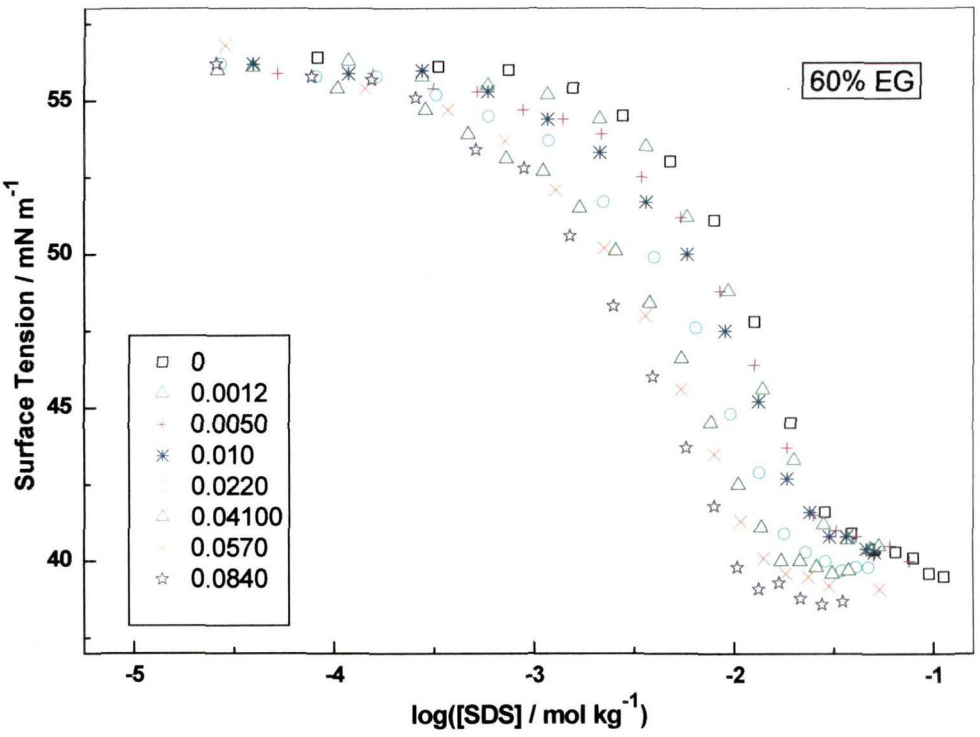

Fig. 5.20. Surface tension isotherms of SDS in 60% EG containing different amounts of NaCl. Concentrations of NaCl in mol kg^{-1} are shown in the inset.

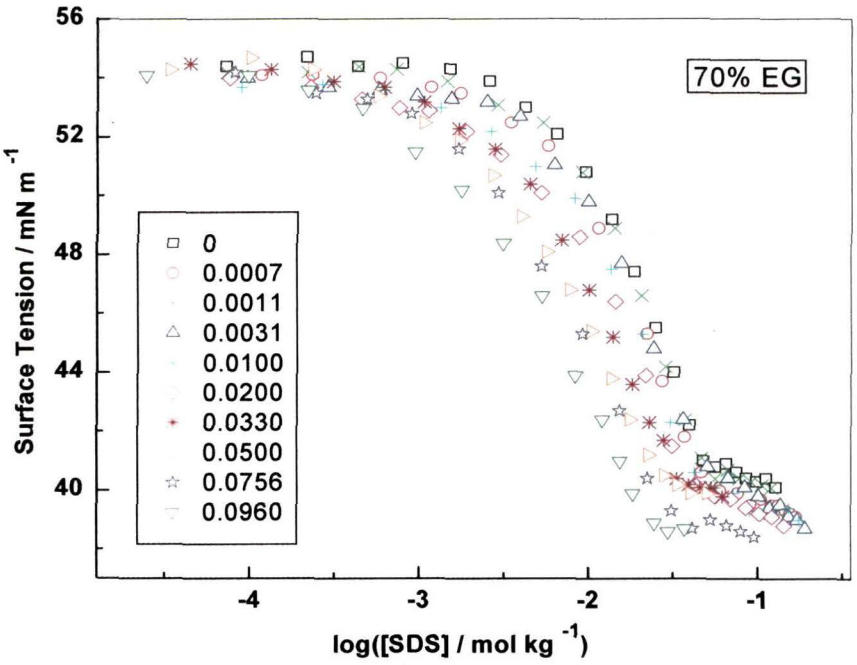

Fig. 5.21. Surface tension isotherms of SDS in 70% EG containing different amounts of NaCl. Concentrations of NaCl in mol kg^{-1} are shown in the inset.

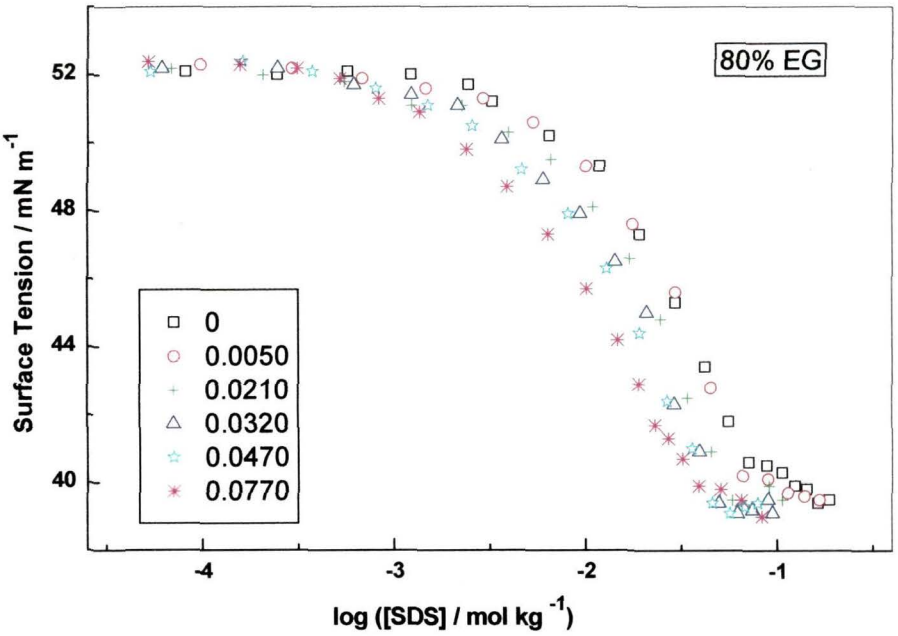

Fig. 5.22. Surface tension isotherms of SDS in 80% EG containing different amounts of NaCl. Concentrations of NaCl in mol kg^{-1} are shown in the inset.

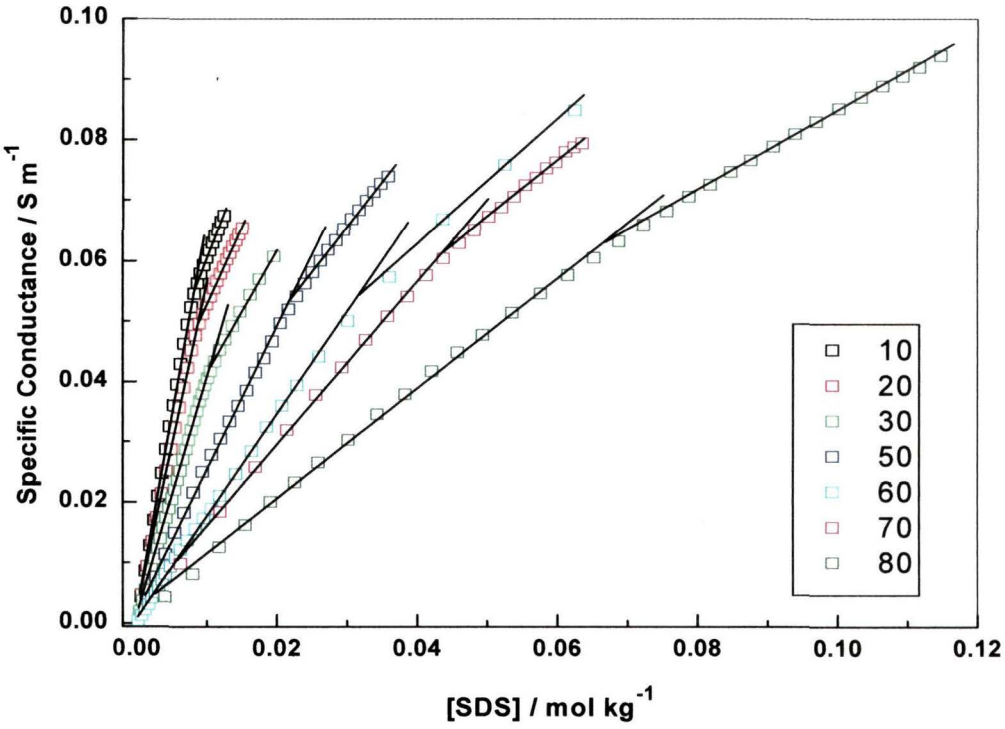

Fig. 5.23. Specific conductivity of SDS in water + EG media at 25 °C. Values of the weight % of EG are shown in the insets

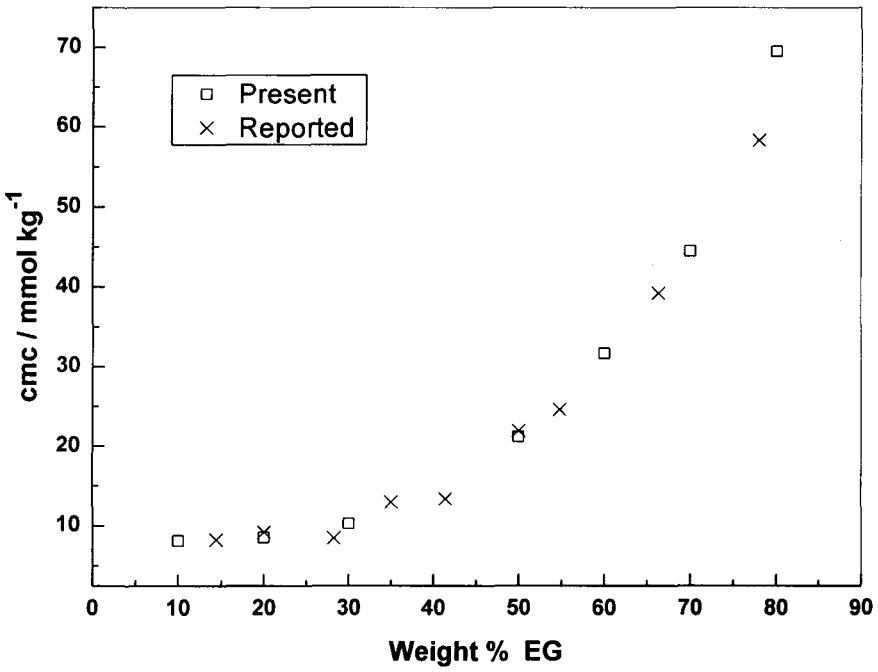

Fig. 5.24. Comparison of the cmc of SDS in water + EG media with the reported data (Both present and reported cmc values are from conductance method). Reported data are from references

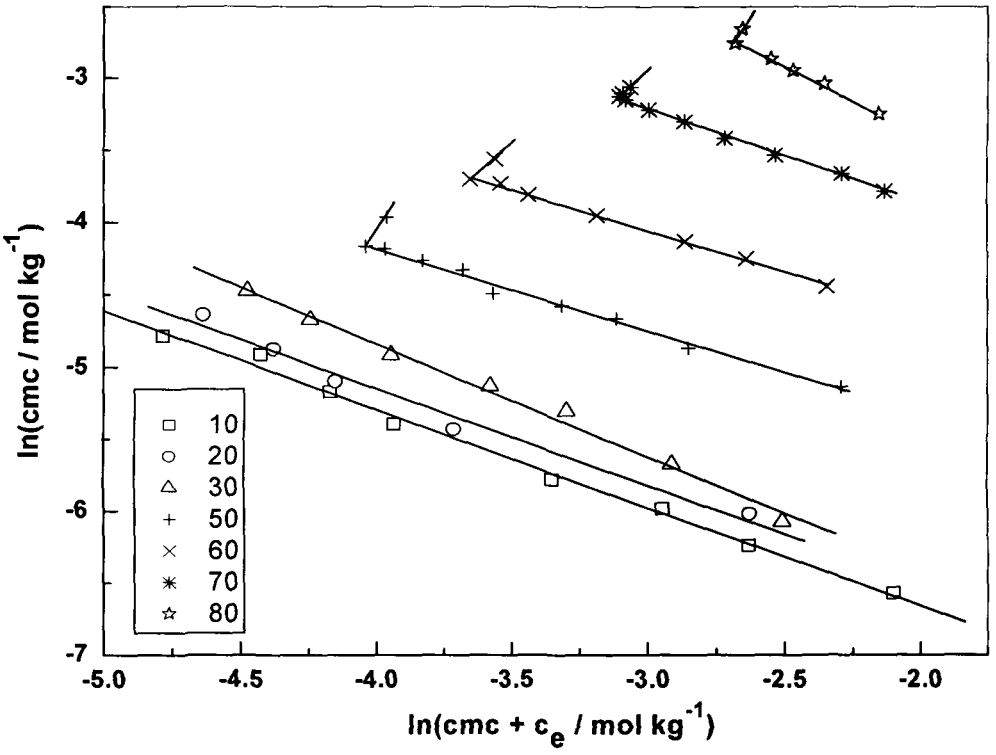

Fig. 5.25. CH plots of AOT in water + EG media. The values of weight % of EG are shown in the insets.

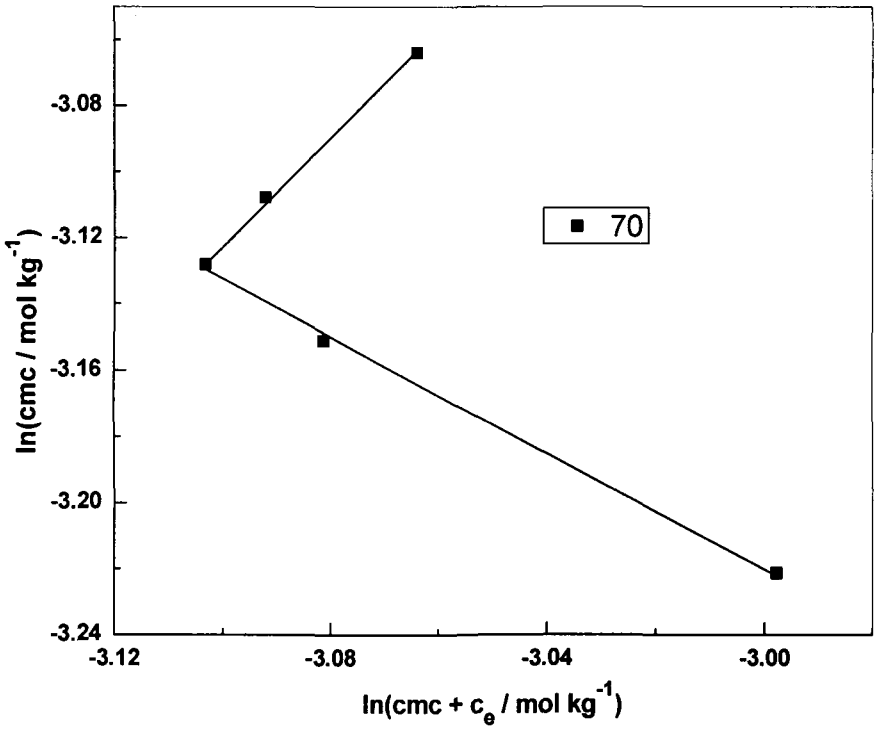

Fig. 5.26. CH plots of SDS in 70 % EG media on an expanded scale.

CHAPTER 6

Competitive Counterion Binding Controlled Conductivity Behaviour of Sodium Dodecylsulfate in Aqueous Nitric Acid Medium. A Potential Green Medium for Nitration

6.1. Introduction

The effect of added salts on the aggregation behaviour of ionic surfactants has been studied extensively. Majority of the ionic surfactant + salt systems studied, however, consist of one counterion only and in such systems the Corrin – Harkins (CH) equation[1] satisfactorily explains the influence of added salt on the critical micelle concentration (cmc). Systems containing ionic surfactant and salt with a different counterion, however, have more complicated counterion binding characteristics, which have been analyzed by using the pseudophase-ion-exchange (PIE) model[2-4] or the modified forms of CH equation.[5-9]

Among the different experimental techniques used for determining various micellization parameters like cmc and counterion binding constant of ionic surfactant containing systems, conductance method is the most convenient one. Generally, specific conductivity (κ) data when plotted versus ionic surfactant concentration fall on two straight lines having different positive slopes with the line in the premicellar concentration region having higher slope than that of the line in the micellar concentration region irrespective of the presence of single or mixed counterions in the solution (this we will refer as the normal conductance behaviour). Interestingly, sodium dodecylsulfate (SDS) in aqueous HCl solutions (an example of a surfactant system containing sodium and hydrogen mixed counter ions) exhibits unusual conductance behaviour. The first report about this system was made by Bunton et al.[10] who reported that addition of SDS to dilute HCl solutions

decreases the κ of the solution in contrast to the general trend of increase in κ. Domínguez et al.[11] reported the conductivity profile of SDS in 0.006M (M = mol dm^{-3}) which indicated a conductivity maximum at the cmc and a conductivity minimum at some SDS concentration above cmc. A detailed study of the conductance behaviour of SDS in aqueous HCl solutions was made by Bravo-Diaz and coworkers[12] by varying the HCl concentrations (≥ 0.01M) and they also reported conductivity profiles of SDS similar to that reported by Domínguez et al.[11] Applying the PIE model to the binding of sodium and hydrogen counter ions to the SDS micelle and by considering the contribution of different ionic species to κ of the solution, Bravo-Diaz and coworkers[12] could explain the unusual shape of the plots of κ versus SDS concentration. Bravo-Diaz and coworkers[12] while analyzing the conductivity data of SDS + HCl system did not, however, take into account ion – ion interactions and hydrolysis of SDS. In the previous studies[10-12] the question of whether SDS exhibits normal conductance behaviour in acidic medium had not been addressed.

In this chapter, we have made the conductance measurements of SDS in aqueous HNO_3 solutions by varying the acid concentration in the range from 0.001M to 0.05M. We have chosen nitric acid medium because it is invariably used for nitration of organic molecules and knowledge about the cmc and counterion binding behaviour of surfactants in nitric acid medium is useful to understand the kinetics of nitration reactions in surfactant medium. Therefore, the objectives of this study are (i) to determine cmc of SDS in

nitric acid medium, (ii) to analyze the conductance data by taking into account ion – ion interactions and hydrolysis of SDS, (iii) to examine whether SDS exhibits the normal conductance behaviour in acidic medium, and (iv) to examine the binding behaviour of sodium and hydrogen counterions to SDS micelle.

6.2. Experimental Section

SDS (Fluka, ≥ 99 % assay), HNO_3 (Merck), pyrene (Fluka) and cetylpyridinium chloride (CPC; Aldrich, > 99.0 %) were used as received. All solutions were prepared in Millipore water. A stock solution of the acid was prepared after standardization of HNO_3. From this stock solution other solutions of HNO_3 of required concentrations were made by dilution. Every solution of HNO_3 having a particular concentration is divided into two portions (portions A and B). Using portion A as solvent, a stock solution of SDS was prepared and this gives us SDS solution containing a particular amount of HNO_3 (solution C).

From portion B of the HNO_3 solution a known amount was taken in the sample tube and the conductance values were measured at 1 kHz after each addition of aliquots of solution C by using a dip-type conductivity cell with platinized platinum electrodes and Wayne Kerr B905 Automatic Precision Bridge.[13-17] For addition of solution C we used a Finn pipette. The cell constant of the conductivity cell was determined by using standard KCl solution. During conductance measurements, after each addition of solution C the sample tube was kept closed. The instrument (resolution = 0.01nS and

accuracy = 0.05%) has an averaging facility and each conductance reading corresponds to an average of 128 measurements taken in a time span of 36s.

For surface tension measurements, from portion B of the HNO_3 solution a known amount was taken in the sample vessel of the K11 Krüss Tensiometer and the surface tension values were measured by using the Wilhelmy plate method after each addition of aliquots of solution C.[18] The Wilhelmy plate, before use, was cleaned thoroughly and then heated red hot in Bunsen flame. During surface tension measurements, the sample vessel was however kept open for the convenience of dipping and lifting the plate from the solution. Therefore, in the surface tension measurement the error due to evaporation loss is not ruled out.

Aggregation numbers were determined by making steady-state fluorescence measurements for which we used Hitachi F4500 FL spectrophotometer, Hellma quartz 10mm fluorescence cell with Teflon lid, pyrene as the probe and CPC as the quencher.[18]

The temperature of the sample during conductance, surface tension and fluorescence measurements was maintained at 25 ^{0}C by using Haake DC 10 circulation bath.

6.3. Results and Discussion

The experimental values of κ of SDS in aqueous HNO_3 medium are given in Table 6.1 and were also shown in Fig. 6.1. From Fig. 6.1 it is clear that the trend in the variation of κ with SDS concentration (c_s) in HNO_3 medium is dependent on the acid concentration (c_a). The normal conductance

behaviour is observed in 0.001M HNO_3. In 0.002M HNO_3 the decreasing trend of κ above the cmc (c_0) just begins and the decrease of κ becomes very prominent as the acid concentration increases further. The present study therefore reveals that SDS exhibits the normal conductance behaviour even in the presence of an acid and this happens in aqueous HNO_3 medium when the acid concentration is below 0.002M. Thus, the unusual type of variation in the conductivity of SDS in aqueous HNO_3 medium occurs only in the region of acid concentration ≥ 0.002M (Fig. 6.1). For SDS in aqueous HNO_3 solutions it may therefore be predicted that if $c_0/c_a > 3.4$ then the κ versus SDS concentration would exhibit the normal conductance behaviour and if $c_0/c_a < 3.4$ then the conductance behaviour would be unusual with a conductivity maximum at the cmc as shown in Fig. 6.1.

6.3.1. Conductivity data analysis

Conductivity of ionic surfactant solutions is analyzed by using the mixed – electrolyte model (MEM) described elsewhere.[13-16,19] In this model a surfactant solution without any added electrolyte is considered to consist of a submicellar aqueous phase and a micellar phase. The surfactant monomers and an equivalent number of counterions are considered to be present in the submicellar phase, while the ionic micelles and the remaining counterions are treated to be present in the micellar phase. The MEM uses the Debye-Hückel-Onsager (DHO) approach to account for the ion – ion interactions. Dependence of aggregation number (n_a) on surfactant concentration and polydispersity of micelles have been ignored in the MEM. For fitting the

conductivity data to different equations (given in the following sections) and to obtain the best-fit values of micellzation parameters an iterative least-squares method of computation was used as described elsewhere.[13] In the system under study, since there are two counterions, it is difficult to substitute a correct ion-size parameter in the ion – ion interaction term of DHO approach. Therefore, in the first instance we did the data fitting by neglecting the ion-size effect. Thereafter, an attempt was made to fit the conductivity data by substituting approximate ion-size parameter in the conductivity equations.

6.3.1.1. Conductance equations in the absence of HNO_3

On the basis of the MEM, κ of SDS solution in the absence of any added electrolyte is expressed (i) at $c_s < c_0$ as

$$\kappa = [\Lambda_1^0 - (A_1\Lambda_1^0 + B_1)I^{1/2}/(1 + B_0a_1)]c_s \tag{6.1}$$

and (ii) at $c_s \geq c_0$ as

$$\begin{aligned}\kappa = {} & [\Lambda_1^0 - (A_1\Lambda_1^0 + B_1)I^{1/2}/(1 + B_0a_1)]c_0 + \\ & [\Lambda_n^0 - (A_n\Lambda_n^0 + B_n)I^{1/2}/(1 + B_0a_n)](c_s - c_0)(1-\beta)\end{aligned} \tag{6.2}$$

In the above expressions, I denotes the ionic strength. β refers to the counterion binding constant and is equal to m/n_a, where m is the number of counterions bound to a micelle. The ion-size parameters a_1 and a_n are evaluated from the relations $a_1 = r_{DS} + r_{Na}$ and $a_n = r_{mic} + r_{Na}$. r_{DS}, r_{Na} and r_{mic} are the radii of dodecylsulfate ion, sodium ion and ionic micelle, respectively. Expressions used to evaluate other terms in Eqs. (6.1) and (6.2) are

$$\Lambda_1^0 = \lambda_{DS}^0 + \lambda_{Na}^0 \tag{6.3}$$

$$\Lambda_n^0 = \lambda_{mic}^0 + \lambda_{Na}^0 \tag{6.4}$$

$$A_i = \frac{2.801\times10^6|z_+z_-|q}{(\varepsilon T)^{3/2}(1+q^{1/2})} \tag{6.5}$$

$$B_i = \frac{41.25(|z_+|+|z_-|)}{\eta(\varepsilon T)^{1/2}} \tag{6.6}$$

$$q = \frac{(\lambda_+^0+\lambda_-^0)|z_+z_-|}{(|z_+|+|z_-|)(|z_+|\lambda_-^0+|z_-|\lambda_+^0)} \tag{6.7}$$

$$B_0 = \left[\frac{8\pi e^2 N_A I}{10^3 \varepsilon k_B T}\right]^{1/2} \tag{6.8}$$

In Eqs. (6.3) and (6.4), λ_{DS}^0, λ_{Na}^0 and λ_{mic}^0 represent limiting ionic equivalent conductances of dodecylsulfate ion (monomer), sodium ion and ionic micelle, respectively. In Eqs. (6.5) – (6.7), ε is the dielectric constant of water, k_B is the Boltzmann constant, N_A is the Avogadro number, e is the electronic charge, η is the viscosity of water, T is the absolute temperature, λ_+^0 and λ_-^0 are the limiting ionic equivalent conductances of cationic and anionic species of effective charges z_+ and z_-, respectively. When $z_+ = z_- = 1$, $A_i = A_1$ in Eq. (6.5) and $B_i = B_1$ in Eq. (6.6). When $z_+ = 1$ and z_- (charge on the micelle) = $n_a(1-\beta)$, $A_i = A_n$ in Eq. (6.5) and $B_i = B_n$ in Eq. (6.6). The value of q = 0.5 in A_1, but the value of q in A_n was obtained by putting $z_+ = 1$, $z_- = n_a(1-\beta)$, $\lambda_+^0 = \lambda_{Na}^0$ and $\lambda_-^0 = \lambda_{mic}^0$ in Eq. (6.7). The value of λ_{mic}^0 was estimated from the expression[13,19]

$$\lambda_{mic}^0 = n_a^{2/3}(1-\beta)\lambda_{DS}^0 \tag{6.9}$$

The values of λ^0_{Na} and λ^0_{DS} at 25 °C were taken from the literature[12,13,19] as 50.1 and 22.9 $S.cm^2.mol^{-1}$, respectively (1equivalent = 1 mole for Na and DS ions).

Evaluating I of ionic surfactant solutions has been a problem. The problem arises due to unreasonably high increase in I that occurs when square of micellar charge is substituted in the expression for I. For example, if I calculated by including the contribution from ionic micelle is substituted in the DHO equation molar conductance becomes even negative at surfactant concentrations sufficiently higher than cmc. Based on conductivity and freezing point depression data, McBain and Searles[20] first reported that the ionic strength principle does not apply to ionic micelles and showed that I of ionic micelles resembles that for a uni-univalent electrolyte. Pashley and Ninham[21] as well as Richetti and Kékicheff[22] measured double-layer forces between two molecularly smooth mica surfaces coated with adsorbed bilayers of cetyltrimethylammonium bromide (CTAB) and separated by an aqueous solution of CTAB. They reported on the basis of the measured forces, which are related to the Debye length, that above the cmc micelles and their bound counterions do not contribute to I and hence to the Debye length. Similar observation regarding ionic micelles not contributing to I was also made by Marra and Hair[23] by using sodium dodecylsulfate and sodium polystyrene sulfonate instead of CTAB in the experiments for double-layer force measurement. Shielding factor is generally used to reduce the contribution of ionic micelles to I. Burchfield and Woolley[24] derived equations for activity

coefficients and osmotic coefficients of aqueous ionic surfactant solutions by treating these solutions as mixed electrolytes and reported that these equations become applicable to experimental data when shielding factor having values in the range 0.5 to 0.68 was used to shield the charge on the micelles. Jalšenjak[25] introduced a concentration-dependent shielding factor to assess the contribution of micelles to I of surfactant solution. Different values for shielding factor were also tested in the earlier studies[13,16,19] while analyzing the conductivity data of ionic surfactant solutions. In the light of the above reports,[13-16,19-25] we calculated I in the present study by using the expressions

$$I = c_s + c_a \qquad \text{at } c_s < c_0 \tag{6.10a}$$

$$I = c_0 + c_a \qquad \text{at } c_s \geq c_0 \tag{6.10b}$$

Using Eq. (6.10b) for I is equivalent to substituting zero for the shielding factor, which amounts to shielding completely the charge of ionic micelle and bound counterions.

6.3.1.2. Conductance equations in the presence of HNO_3

In the presence of acid, SDS is reported[26] to undergo hydrolysis. The hydrolysis reaction can be written as

$$C_{12}H_{25}SO_4^- + H_2O \xrightarrow{H^+} C_{12}H_{25}OH + HSO_4^- \tag{6.11}$$

Moreover, in the presence of HNO_3 the SDS micellar solution consists of sodium and hydrogen counterions and both these counterions tend to bind to the ionic micelle. Therefore, Eqs. (6.1) and (6.2) are to be modified for application in the presence of HNO_3. Denoting the degree of hydrolysis of

dodecylsulfate ion by α_h, κ of SDS in aqueous HNO_3 medium can be represented in the submicellar concentration region ($c_s < c_0$) as

$$\kappa = \kappa_{HNO3} + \lambda_1 c_s \tag{6.12}$$

$$\text{where} \quad \lambda_1 = \begin{Bmatrix} [\lambda^0_{DS} - (A_1\lambda^0_{DS} + 0.5B_1)I^{1/2}/(1+B_0a_1)](1-\alpha_h) + \\ [\lambda^0_{Na} - (A_1\lambda^0_{Na} + 0.5B_1)I^{1/2}/(1+B_0a_1)] - \\ [\lambda^0_{BS} - (A_1\lambda^0_{BS} + 0.5B_1)I^{1/2}/(1+B_0a_2)]\alpha_h \end{Bmatrix} \tag{6.13}$$

In the presence of HNO_3, the limiting equivalent conductance of the solution below c_0 (Λ^0_1) is given by the relation

$$\Lambda^0_1 = (1-\alpha_h)\lambda^0_{DS} + \alpha_h\lambda^0_{BS} + \lambda^0_{Na} \tag{6.14}$$

In Eq. (6.13), the ion-size parameter $a_2 = r_{BS} + r_{Na}$, where r_{BS} is the radius of the bisulfate ion. In the micellar region ($c_s \geq c_0$), κ of SDS solution in the presence of HNO_3 can be written as

$$\kappa = \kappa_{HNO3} + \lambda_1 c_0 + \lambda_2 (c_s - c_0) \tag{6.15}$$

$$\text{where } \lambda_2 = \begin{Bmatrix} [\lambda^0_{mic} - (A_n\lambda^0_{mic} + 0.5n_a(1-\beta)B_1)I^{1/2}/(1+B_0a_n)](1-\beta) + \\ [\lambda^0_{Na} - (A_n\lambda^0_{Na} + 0.5B_1)I^{1/2}/(1+B_0a_n)](1-\beta_{Na}) - \\ [\lambda^0_{H} - (A_n\lambda^0_{H} + 0.5B_1)I^{1/2}/(1+B_0a_n)]\beta_H \end{Bmatrix} \tag{6.16}$$

It may be noted that in Eq. (6.12) λ_1 (below cmc) is computed from Eq. (6.13) by using Eq. (6.10a) for I, whereas in Eq. (6.15) λ_1 (above cmc) is computed from Eq. (6.13) by using Eq. (6.10b) for I. In the presence of HNO_3, q required for calculating A_n was evaluated by substituting $z_+ = 1$, $z_- = n_a(1-\beta)$, $\lambda^0_+ = \lambda^0_{SH}$ and $\lambda^0_- = \lambda^0_{mic}$ in Eq. (6.7). λ^0_{SH} is defined as

$$\lambda^0_{SH} = (\beta_{Na}\lambda^0_{Na} + \beta_H\lambda^0_H)/\beta \tag{6.17}$$

The values λ^0_{BS} and λ^0_H at 25 °C were taken from the literature[12,27] as 51.2 and 349.7 $S.cm^2.mol^{-1}$, respectively. In Eqs. (6.16) and (6.17), β_{Na} and β_H are the counterion binding constants for sodium and hydrogen ions, respectively and the total counterion binding constant β is given by

$$\beta = \beta_{Na} + \beta_H \tag{6.18}$$

Due to the presence of mixed counterions, a competitive binding of sodium and hydrogen ions to the SDS micelle occurs in the micellar solution. Equilibria exist between the bound (Na_b) and unbound (Na_{ub}) sodium ions as well as between the bound (H_b) and unbound (H_{ub}) hydrogen ions. The PIE model[2-4] was developed by balancing the chemical potentials of the bound and unbound counterions as a thermodynamic requirement for equilibrium and this model is more often used for explaining the kinetics of micellar catalyzed reactions.[28-33] According to the PIE model we can write a counterion exchange equilibrium constant K_e as[2-4,12,34]

$$K_e = \frac{[H_b][Na_{ub}]}{[H_{ub}][Na_b]} \tag{6.19}$$

The different terms in Eq. (6.19) are defined as

$H_b = \beta_H(c_s - c_0)$, $Na_b = \beta_{Na}(c_s - c_0)$, $H_{ub} = (c_a - H_b)$ and $Na_{ub} = (c_s - Na_b)$. Equation (6.19) can be rearranged to give a quadratic equation of the form

$$(c_s - c_0)(K_e - 1)\beta_H^2 - [c_s + K_e c_a + \beta(c_s - c_0)(K_e - 1)]\beta_H + \beta c_a K_e = 0 \tag{6.20}$$

6.3.2. Conductivity Data Analysis by Neglecting Ion-Size Effect

Ion-size effect is neglected in Eqs. (6.1), (6.2), (6.12) and (6.15) by substituting $a_1 = a_2 = a_n = 0$. When the κ data of aqueous SDS solutions in the

absence of HNO_3 were least-squares fitted to Eqs. (6.1) and (6.2) by iterating the values of c_0, n_a and β (best-fit values are c_0 = 8 mM, $\beta = \beta_{Na}$ = 0.456, n_a = 35), it was found that the fitting in the submicellar concentration region is very poor with standard deviation (σ) in κ = 3.2 mS m^{-1} (Fig. 6.1, line A in 0.0M). Therefore, in the concentration region where $c_s < c_0$, simple DHO approach does not explain properly the concentration dependence of κ of SDS in water. This is in accordance with the observation made by Mukerjee et al.[35] and the inadequacy of the simple DHO approach was attributed to the formation of dodecylsulfate dimers in the submicellar concentration region. Incidentally, the fitting of the κ data to Eqs. (6.1) and (6.2) was found to be very good if the ion – ion interaction term is neglected (without the $(A_1\Lambda_1^0 + B_1)I^{1/2}$ term) in the $c_s < c_0$ region. The increase in conductivity due to dimer formation is thus coincidentally compensated by the decrease in conductivity due to ion – ion interactions. The best-fit values of c_0, n_a and β obtained in this fashion are given in Table 6.2 and the computed values of κ are shown in Fig. 6.1 (line C in 0.0M).

In the presence of HNO_3, experimental values of κ in the submicellar region were first least-squares fitted to Eq. (6.12). The value of α_h was iterated for obtaining the best fit. Using this value of α_h the experimental values of κ in the micellar region ($c_s \geq c_0$) were least-squares fitted to Eq. (6.14) by iterating the values of c_0, K_e, n_a and β and by substituting the value of β_H determined by solving the quadratic Eq. (6.20). In the present analysis of conductivity data, it has been presumed that hydrolysis causes change in the

conductivity of the aqueous submicellar phase, but not of the micellar phase. This is supported by the fact that the value of α_h obtained by fitting the κ data to Eq. (6.12) altered negligibly on iterating its value while fitting the κ data to Eq. (6.14). Nevertheless, the rate of acid-catalyzed hydrolysis of SDS has been reported[22] to increase in the micellar region. The best-fit values of α_h, c_0, K_e, n_a and β are listed in Table 6.2.

6.3.3. Aggregation Number

We determined n_a from the fluorescence quenching method. The expression used in this method is of the form[17,18]

$$\ln(I_0/I_Q) = \{n_a/(c_s - c_0)\}[Q] \qquad (6.21)$$

I_0 and I_Q are the intensities of fluorescence emission (at 373 nm) of pyrene in the absence and presence of the quencher, respectively. [Q] denotes the concentration of CPC, the quencher. Experimental values of I_0/I_Q as a function of [Q] are given in Table 6.3 and Fig. 6.2. The values of n_a determined from this method at a fixed $c_s - c_0$ are listed in Table 6.2. It is obvious from Table 6.2 that the values of n_a of SDS obtained from the least-squares fitting of κ data without considering the ion-size effect are low, particularly in 5.5, 10, 20 and 50 mM HNO_3 solutions. In the present analysis of κ data we made the following approximations: (i) No effect of ion size on ion – ion interaction. (ii) No effect of concentration of surfactant on n_a. (iii) No effect of ion – ion interaction on the κ of HNO_3 (κ_{HNO3}). The low values of n_a obtained by analyzing κ data may be attributed to the approximations involved in the fitting and to verify this an attempt has been made below to fit the κ data to

conductance equations by removing one of the above approximations, viz., by taking into account the ion-size effect.

6.3.4. Conductivity Data Analysis without Neglecting Ion-Size Effect.

The Stokes radii of sodium ion, dodecylsulfate ion and bisulfate ion were determined by using the Stokes – Einstein relation,[13]

$$r_i = \frac{z_i eF}{6\pi\eta\lambda_i^0} \tag{6.22}$$

where F is the Faraday constant. The values obtained from Eq. (6.22) are r_{Na} = 1.84 Å, r_{DS} = 4.02 Å and r_{BS} = 1.8 Å. The radius of the spherical micelle was determined from the relation[13,19]

$$r_{mic} = n_a^{1/3} r_{DS} \tag{6.23}$$

Using the above values of the radii, ion-size parameters a_1, a_2 and a_n were evaluated and substituted in Eqs. (6.1), (6.2), (6.12) and (6.15) while fitting the κ data to these equations. The best-fit values of α_h, c_0, K_e, n_a and β thus obtained are listed in Table 6.2. Conductance equations without and with ion-size parameter provide equally good fittings (Fig. 6.1); but it is interesting to note that improved values of n_a, which are comparable to the measured values, are obtained when only ion-size effect is taken into account. Moreover, the success of the data fitting reveal that the competitive binding of sodium and hydrogen ions to ionic micelle, which are counterions with large difference in their limiting ionic conductivity, is responsible for the unusual trend in the variation of κ with SDS concentration.

6.3.5. Critical Micelle Concentration

The best-fit values of cmc of SDS in aqueous HNO_3 solutions obtained from the κ data fitting are given in Table 6.2 and shown in Fig. 6.3. The cmc values of SDS in the presence of HNO_3 were also confirmed from surface tension (γ) measurements (Fig. 6.3). Experimental values of surface tension are given in Table 6.4 and Fig. 6.4. By comparing in Fig. 6.3 the present cmc values with those reported[13,17] in other aqueous electrolyte solutions, it is noted that the cmc values of SDS in aqueous HNO_3 media, in spite of the presence of mixed counter ions, are not very much different from those in aqueous NaCl[13] or NaAc[17] (sodium acetate) solutions. Therefore, the effect of hydrogen ion binding to dodecylsulfate micelle on the cmc of SDS seems to be similar to that due to sodium ion binding. This observation is in conformity with the inference made by Bunton et al.[10] that dodecylsulfate micelle does not discriminate markedly between hydrogen and sodium counterions.

6.3.6. Counterion Binding Constant

The values of β_H and β_{Na} as a function of SDS concentration computed from Eq. (6.20) during the fitting of κ data are shown in Fig. 6.5. From Fig. 6.5 it is clear that the value of β_H decreases with increase in SDS concentration, whereas β_{Na} has the opposite trend. Similar type of profiles for the variation of β_{Ca} (binding constant of calcium counterion) and β_{Na} with SDS concentration have been reported[9] very recently in aqueous solutions of SDS in the presence of $CaCl_2$. At higher concentrations of SDS sodium predominantly binds to the micelle irrespective of the HNO_3 concentration.

On the other hand, near the cmc the acid concentration largely controls the competitive counterion binding. Based on Eq. (6.20), at the cmc we can write an expression for β_H as

$$\beta_H = \beta K_e c_a / (K_e c_a + c_0) \quad (6.24)$$

The values of β_H and β_{Na} at the cmc determined from Eq. (6.24) are listed in Table 6.2. As evident from Table 6.2 and Fig. 6.5, the relative values of β_H and β_{Na} at the cmc differ depending upon the acid concentration. The different trends are as follows: (i) If $c_0 > c_a$ then $\beta_H < \beta_{Na}$ at $c_s \geq c_0$ and the plots of β_H and β_{Na} versus c_s are separated. (ii) If $c_0 \approx c_a$, then $\beta_H = \beta_{Na}$ at c_0 and $\beta_H < \beta_{Na}$ at $c_s > c_0$. (iii) If $c_0 < c_a$, then $\beta_H > \beta_{Na}$ at c_0 and the plots of β_H and β_{Na} versus c_s cross each other at a point where $c_s \approx K_e c_a$. Exchange between the two bound counterions starts at the cmc and it can be shown from Eq. (6.24) that $\beta_H/\beta_{Na} = K_e(c_a/c_0)$ at the cmc. Therefore, the ratio c_a/c_0 has a control over the relative values of β_H and β_{Na} as obvious from the above three trends.

6.3.7. Degree of Hydrolysis

From the analysis of κ data in the manner explained above we found that hydrolysis of SDS is negligible below 0.02M HNO_3. In the presence of 0.02M and 0.05M HNO_3 about 12% of SDS undergoes hydrolysis. Hydrolysis of SDS in the presence of HNO_3 may generate nitronium ion as shown below.

$$HSO_4^- \rightleftharpoons H^+ + SO_4^= \quad (6.25)$$

$$HNO_3 + H^+ \rightleftharpoons NO_2^+ + H_2O \quad (6.26)$$

This indicates that SDS solution in nitric acid with nitric acid concentration ≥ 0.02M may be used as a nitrating medium. This was confirmed by stirring at

room temperature the reaction mixture containing p-nitrophenol in SDS + HNO_3 (0.02M) solution for about 30 minutes. The reaction, which was monitored by thin layer chromatography, upon completion yielded about 75-80 % dinitrophenol. The product was extracted with ethyl acetate and was confirmed by IR and mass spectroscopy. Nitration of p-nitrophenol was negligible or did not take place when the HNO_3 concentration was less than 0.02M. Thus, this study reveals that aqueous SDS + HNO_3 solution can be used as a very convenient soft medium for nitration.

6.4. Conclusions

This study has revealed that SDS in aqueous HNO_3 medium can exhibit both the unusual and the normal conductance behaviours. The normal conductance behaviour of SDS in acid medium is observed only if $c_0/c_a > 3.4$, which was not reported from the earlier studies[10-12] in aqueous HCl medium. On the basis of the present results, it can be predicted that solutions of ionic surfactant + electrolyte with foreign counterion would exhibit unusual conductance behavior (i) if the two counterions have large difference in their limiting ionic conductivity and undergo competitive binding to the ionic micelle, and (ii) if $c_0/c_a < 3.4$. The mixed-electrolyte model together with the Debye-Huckel-Onsager and the pseudophase-ion exchange models can be applied successfully to analyze the conductivity data of ionic surfactant + electrolyte solutions no matter such solutions consist of mixed counterions and show unusual conductance behaviour. The relative values of the binding constants of the two counterions are controlled by c_a, c_s and c_0. The exchange

of sodium and hydrogen counterions at the micellar surface has no significant effect on the cmc of SDS implying that these two counterions are not markedly discriminated by the dodecylsulfate micelle. A very useful conclusion of this study is that SDS + aqueous HNO_3 medium with $[HNO_3] \geq$ 0.02M can be used as an alternative soft and green medium for nitration of organic molecules.

6.5. References

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Table 6.1. Experimental values of specific conductivity of SDS in aqueous HNO_3 solutions at 25 ^{0}C

[SDS] / mmol kg^{-1}	10 κ/ S m^{-1}	[SDS] / mmol kg^{-1}	10 κ/ S m^{-1}	[SDS] / mmol kg^{-1}	10 κ/ S m^{-1}
		[HNO_3] = 0.0010 mol kg^{-1}			
0.0218	0.3644	1.4600	0.4594	7.9800	0.8570
0.0435	0.3659	1.6900	0.4765	8.4300	0.8672
0.0869	0.3689	1.9500	0.4945	8.8800	0.8716
0.1301	0.3715	2.2500	0.5115	9.3200	0.8741
0.1732	0.3751	2.5700	0.5338	9.7500	0.8797
0.2161	0.3790	2.9200	0.5587	10.200	0.8833
0.2589	0.3817	3.2900	0.5844	10.670	0.8888
0.3016	0.3849	3.6800	0.6102	11.170	0.8936
0.3653	0.3889	4.0900	0.6344	11.700	0.8995
0.4287	0.3932	4.4900	0.6609	12.270	0.9055
0.5127	0.3985	4.9000	0.6890	12.850	0.9165
0.5962	0.4045	5.3200	0.7151	13.480	0.9249
0.6998	0.4112	5.7500	0.7431	14.190	0.93287
0.8025	0.4186	6.1900	0.7712	15.030	0.9502
0.9450	0.4279	6.6400	0.7947	16.070	0.96087
1.0900	0.4374	7.0800	0.8231		
1.2600	0.4489	7.5300	0.8436		
		[HNO_3] = 0.0020 mol kg^{-1}			
0.0206	0.7725	2.1163	0.9155	6.5529	1.1925
0.0411	0.7737	2.4020	0.9359	6.8774	1.2026
0.0821	0.7768	2.6963	0.955	7.1996	1.2072
0.1229	0.779	2.9981	0.9717	7.5189	1.2061
0.1839	0.7834	3.3064	0.9957	7.8350	1.2053
0.2646	0.7883	3.6203	1.018	8.1563	1.2038
0.3648	0.7954	3.9388	1.0375	8.4980	1.2009
0.5037	0.8049	4.2609	1.0548	8.8647	1.1987
0.6603	0.8142	4.5859	1.0784	9.2515	1.1942
0.8531	0.8266	4.913	1.099	9.6538	1.1928
1.0802	0.8436	5.2412	1.1182	10.101	1.1936
1.3211	0.8552	5.5700	1.1405	10.612	1.195
1.5748	0.8769	5.8986	1.1602	11.199	1.1952
1.8402	0.8967	6.2264	1.1762	11.985	1.1956

Table 6.1. Continued

[SDS] / mmol kg^{-1}	10 κ/ S m^{-1}	[SDS] / mmol kg^{-1}	10 κ/ S m^{-1}	[SDS] / mmol kg^{-1}	10 κ/ S m^{-1}
		$[HNO_3]$ = 0.0020 mol kg^{-1}			
12.888	1.1974	15.167	1.2072		
14.003	1.2033	16.458	1.2264		
		$[HNO_3]$ = 0.0055 mol kg^{-1}			
0.1132	1.8340	2.3335	1.9834	9.3942	2.0474
0.2263	1.8410	2.4423	1.9843	10.252	2.0216
0.3391	1.8489	2.6594	2.0024	11.283	1.9972
0.4517	1.8526	2.8757	2.0154	12.476	1.9761
0.5640	1.8571	3.0911	2.0288	13.909	1.9599
0.6762	1.8652	3.4128	2.0458	15.647	1.9519
0.7882	1.8712	3.7327	2.0625	17.740	1.9568
0.8999	1.8764	4.0508	2.0806	20.375	1.9665
1.0114	1.8829	4.3671	2.0976	23.391	1.9963
1.1228	1.8894	4.6818	2.1153	26.911	2.0373
1.2339	1.8956	4.9946	2.1280	30.806	2.1115
1.3448	1.9001	5.3058	2.1429	34.952	2.1814
1.4554	1.9088	5.6153	2.1518	39.236	2.2626
1.5659	1.9131	5.9231	2.1548	43.561	2.3416
1.6762	1.9230	6.2292	2.1533	47.846	2.4214
1.7863	1.9272	6.5337	2.1452	51.669	2.5055
1.8961	1.9343	6.9371	2.1302	55.100	2.5778
2.0058	1.9596	7.4373	2.1090		
2.1152	1.9682	7.9331	2.0922		
2.2245	1.9759	8.6198	2.0720		

Table 6.1. Continued

[SDS] / mmol kg^{-1}	10 κ/ S m^{-1}	[SDS] / mmol kg^{-1}	10 κ/ S m^{-1}	[SDS] / mmol kg^{-1}	10 κ/ S m^{-1}
		[HNO_3] = 0.0100 mol kg^{-1}			
0.0001	3.8258	0.0039	4.0201	0.0207	3.3989
0.0001	3.8282	0.0043	4.0352	0.0221	3.3892
0.0001	3.8294	0.0047	4.0394	0.0236	3.3822
0.0001	3.8318	0.0051	4.0222	0.0249	3.3776
0.0002	3.8355	0.0055	3.9981	0.0263	3.3756
0.0002	3.8397	0.0059	3.9660	0.0276	3.3768
0.0003	3.8442	0.0063	3.9291	0.0292	3.3819
0.00032	3.8459	0.0067	3.8904	0.0311	3.3899
0.00037	3.8497	0.0072	3.8498	0.0332	3.4181
0.00046	3.8568	0.0078	3.8085	0.0351	3.4337
0.00059	3.8668	0.0085	3.7614	0.0369	3.4481
0.00077	3.8791	0.0093	3.7195		
0.0013	3.8952	0.0103	3.6647		
0.0016	3.9069	0.0114	3.6140		
0.0019	3.9248	0.0126	3.5727		
0.0023	3.9431	0.0139	3.5306		
0.0027	3.9641	0.0155	3.4839		
0.0031	3.9842	0.0173	3.4444		
0.0035	4.0045	0.0191	3.4208		
		[HNO_3] = 0.0200 mol kg^{-1}			
0.1218	7.3434	3.4512	7.4849	7.7330	6.9517
0.2434	7.3660	3.6832	7.4654	8.0687	6.924
0.3648	7.3803	3.9144	7.4480	8.4937	6.8901
0.486	7.3844	4.1449	7.3844	8.9246	6.8573
0.6069	7.3957	4.3746	7.3424	9.3528	6.8378
0.8483	7.4008	4.6036	7.3260	9.7780	6.7978
1.0889	7.4162	4.8318	7.3044	10.201	6.7743
1.3286	7.4275	5.0593	7.2819	10.726	6.7425
1.5676	7.4459	5.2861	7.2614	11.247	6.7055
1.8058	7.4531	5.5121	7.2398	11.764	6.6768
2.0432	7.4757	5.7374	7.1957	12.379	6.6440
2.2798	7.4972	6.0740	7.1598	12.988	6.6112
2.5156	7.4952	6.4099	7.1106	13.592	6.5804
2.7506	7.5064	6.7424	7.0706	14.190	6.5435
2.9849	7.5105	7.0741	7.0091	14.881	6.5169
3.2184	7.4972	7.4043	6.9845	15.565	6.4799

Table 6.1. Continued

[SDS] / mmol kg^{-1}	10 κ/ S m^{-1}	[SDS] / mmol kg^{-1}	10 κ/ S m^{-1}	[SDS] / mmol kg^{-1}	10 κ/ S m^{-1}
		[HNO_3] = 0.0200 mol kg^{-1}			
16.338	6.4533	24.102	6.1887	49.574	6.0011
17.102	6.4143	25.610	6.1620	55.066	6.0277
17.951	6.3969	27.403	6.1210	60.797	6.0595
18.881	6.3384	29.609	6.0903	66.924	6.1323
19.797	6.3056	32.327	6.0503	73.440	6.1836
20.700	6.2779	35.620	6.0226	81.410	6.2769
21.679	6.2554	39.638	6.0042	91.383	6.3159
22.816	6.2123	44.264	5.9898		
		[HNO_3] = 0.0500 mol kg^{-1}			
0.0490	16.3501	2.6976	16.3234	20.138	14.8468
0.0979	16.3398	3.6920	16.2250	23.472	14.7114
0.1954	16.3511	5.0111	16.0814	27.354	14.4971
0.3410	16.3593	6.7124	15.9081	31.156	14.3453
0.5819	16.3727	8.8447	15.7081	34.544	14.2253
0.9627	16.3942	11.396	15.4764	37.413	14.1176
1.4309	16.3932	14.194	15.2672	40.057	14.0879
1.9816	16.3891	17.085	15.0570	41.284	14.0561

Table 6.2. Best-fit Values of Cmc, Degree of Hydrolysis, Ion Exchange Constant, Counterion Binding Constant and Aggregation Number of SDS in Aqueous HNO_3 Solutions at 25 ^{0}C Obtained from Data Fitting with and without Ion-Size Effect

parameters	nitric acid concentration / mM						
	0	1.00	2.00	5.50	10.0	20.0	50.0
cmc / mM	8.20	7.50	6.72	5.56	4.54	3.03	1.78
	[8.00]	*[7.57]*	*[6.75]*	*[5.75]*	*[4.53]*	*[2.94]*	*[1.8]*
	(8.40)	(8.26) [c]	(7.44)	(6.01)	(4.93)	(3.37)	(2.2)
K_e	-	0.74	0.75	0.87	0.87	0.73	1.51
		[0.57]	*[0.58]*	*[0.97]*	*[0.98]*	*[0.96]*	*[0.9]*
α_h	-	0	0	0	0	0.12	0.12
β	0.700	0.719	0.746	0.692	0.751	0.760	0.601
	[0.59]	*[0.72]*	*[0.76]*	*[0.66]*	*[0.69]*	*[0.69]*	*[0.5]*
β_H [a]		0.065	0.136	0.320	0.493	0.629	0.587
	-	*[0.05]*	*[0.11]*	*[0.32]*	*[0.47]*	*[0.59]*	*[0.5]*
β_{Na} [a]	0.700	0.654	0.610	0.372	0.258	0.131	0.014
	[0.59]	*[0.67]*	*[0.65]*	*[0.34]*	*[0.21]*	*[0.09]*	*[0.0]*
n_a	32	38	40	41	49	61	72
	[30]	*[29]*	*[36]*	*[18]*	*[15]*	*[18]*	*[17]*
	(31)	(40)	-	(44)	(51)	(68)	(69)
$10^2 \kappa_{HNO3}$ /S m^{-1}	0	3.6000	7.7000	18.180	38.000	73.482	163.32
σ [b] /mS m^{-1}	0.28	0.47	0.44	1.39	1.56	1.52	1.49
	[0.33]	*[0.29]*	*[0.30]*	*[1.08]*	*[1.43]*	*[1.65]*	*[1.5]*

[a] Values of β_H and β_{Na} given here are at the cmc; [b] σ denotes standard deviation in κ; Values in italics and square brackets are from the fitting without ion-size effect. Cmc values given in the parentheses are from surface tension; [c] This cmc value corresponds to $[HNO_3]$ = 0.90 mM; Aggregation numbers given in the parentheses are from fluorescence method

Table 6.3. Experimental values of I_0/I_Q of pyrene in aqueous solutions of SDS + HNO3 at $c_s - c_0 = 0.45$ mM and 25 ^{0}C

[CPC] / mM	$\ln(I_0/I_Q)$	[CPC] / mM	$\ln(I_0/I_Q)$	[CPC] / mM	$\ln(I_0/I_Q)$
		$[HNO_3]$ = 0 mM			
0.0025	0.1924	0.0075	0.5001	0.0125	0.8613
0.0050	0.3485	0.0100	0.6863		
		$[HNO_3]$ = 1.0 mM			
0.0025	0.2198	0.0075	0.6792	0.0125	1.0899
0.0050	0.4439	0.0100	0.9024		
		$[HNO_3]$ = 5.5 mM			
0.0025	0.2615	0.0075	0.7500	0.0125	1.2253
0.0050	0.4680	0.0100	0.9851		
		$[HNO_3]$ = 10.0 mM			
0.0025	0.2885	0.0075	0.8641	0.0125	1.4323
0.0050	0.5730	0.0100	1.1223		
		$[HNO_3]$ = 20.0 mM			
0.0025	0.4077	0.0075	1.1778	0.0125	1.8787
0.0050	0.7703	0.0100	1.5352		
		$[HNO_3]$ = 50.0 mM			
0.0025	0.4187	0.0075	1.2138	0.0125	1.8965
0.0050	0.8237	0.0100	1.5689		

Table 6.4. Experimental values of surface tension of SDS in aqueous HNO_3 solutions at 25 ^{0}C

[SDS] / mmol kg^{-1}	γ/ mN m^{-1}	[SDS] / mmol kg^{-1}	γ/ mN m^{-1}	[SDS] / mmol kg^{-1}	γ/ mN m^{-1}
		[HNO_3] = 0.0			
0.0083	72.4	1.2794	61.1	6.5540	34.1
0.0165	72.5	1.6590	57.1	7.2249	32.3
0.0303	72.4	2.0683	53.7	7.8743	35.8
0.0578	72.4	2.5023	50.9	8.4990	38.4
0.0961	72.0	2.9564	48.9	9.0970	38.7
0.1506	71.6	3.4640	45.5	9.6820	38.8
0.2319	70.9	4.0137	42.7	10.248	39.0
0.3923	70.1	4.6275	40.9	10.817	38.7
0.6283	67.4	5.2572	37.5	11.378	38.5
0.9343	64.2	5.8936	37.1	12.320	38.4
		[HNO_3] = 0.0009			
0.0032	72.3	0.4955	54.1	5.8041	30.8
0.0064	71.9	0.6422	52.4	6.3961	30.7
0.0128	71.3	0.8232	50.5	6.9873	32.6
0.0192	69.8	1.0428	48.5	7.5747	36
0.0256	69.1	1.3047	46.2	8.1556	37.8
0.0319	69.0	1.6173	43.8	8.7553	38.5
0.0447	66.6	2.0037	40.8	9.3662	38.7
0.0638	66.3	2.4563	39.2	10.005	38.8
0.0956	64.7	2.9670	37.6	10.704	39.3
0.1463	62.9	3.5032	34.8	11.440	39.5
0.2093	61.2	4.0598	33.7	12.211	39.4
0.2846	58.6	4.6318	32.2	13.026	38.5
0.3781	56.2	5.2147	31.5		
		[HNO_3] = 0.0020			
0.0039	72.4	0.5145	52.1	5.6262	31.9
0.0118	71.2	0.6659	50.2	6.7387	35.4
0.0197	70.1	0.8605	48.6	7.8910	38.5
0.0354	67.5	1.1186	46.0	9.1382	39.4
0.0589	63.3	1.4441	44.0	10.434	38.8
0.0902	62.2	1.8325	41.5	11.741	38.2
0.1370	61.1	2.3124	39.3	13.028	38.1
0.2071	59.0	2.8745	37.9	14.272	38.2
0.2922	56.2	3.5084	36.0	15.753	38.1
0.3922	54.0	4.5234	32.5		

Table 6.4.Continued

[SDS] / mmol kg^{-1}	γ/ mN m^{-1}	[SDS] / mmol kg^{-1}	γ/ mN m^{-1}	[SDS] / mmol kg^{-1}	γ/ mN m^{-1}
		[HNO_3] = 0.0055			
0.0050	68.3	0.5822	49.7	4.4286	33.1
0.0100	66.9	0.7227	48.4	4.8781	33.1
0.0150	66.1	0.8933	46.5	5.3309	34.3
0.0249	64.9	1.1013	45.0	5.7844	36.7
0.0399	63.3	1.3487	43.0	6.2362	38.2
0.0647	61.6	1.6409	41.2	6.7071	38.7
0.1043	59.2	1.9734	39.4	7.2542	38.8
0.1536	58.0	2.3418	37.9	7.9518	39.4
0.2125	55.8	2.7261	36.6	8.8311	38.6
0.2807	54.0	3.1306	35.2	9.8623	38.2
0.3630	52.9	3.5516	34.6		
0.4637	51.6	3.9854	33.5		
		[HNO_3] = 0.0100			
0.0027	69.5	0.4561	49.1	3.9889	33.5
0.0054	68.7	0.5691	47.7	4.5123	36.2
0.0108	67.2	0.7011	46.2	5.0378	38.6
0.0215	65.5	0.8613	44.3	5.5622	39.1
0.0403	63.1	1.0581	42.7	6.0829	39.2
0.0671	61.4	1.2991	41.0	6.6236	39.0
0.1045	59.0	1.6041	39.2	7.2253	39.0
0.1577	56.8	1.9895	37.4	7.9135	39.4
0.2160	54.4	2.4669	34.9	8.6972	39.2
0.2844	52.5	2.9622	33.7	9.6031	38.4
0.3628	50.7	3.4709	32.7		
		[HNO_3] = 0.0200			
0.0054	66.1	0.2928	48.9	2.5901	34.3
0.0109	63.2	0.3774	47.2	3.0076	36.3
0.0163	61.8	0.4822	45.4	3.4473	38.1
0.0218	60.7	0.6117	44.1	3.9048	38.7
0.0299	59.7	0.7754	42.8	4.4117	38.9
0.0462	58.6	0.9766	41.5	5.0243	28.9
0.0733	56.9	1.2228	39.5	5.8095	38.8
0.1111	55.1	1.5111	37.9	6.9292	39.2
0.1648	53.3	1.8376	36.4	8.3535	39.0
0.2237	50.6	2.1987	35.4		
		[HNO_3] = 0.0500			
0.0065	61.3	0.4943	37.3	2.1680	35.3
0.0130	59.3	0.6338	35.4	2.4286	35.9
0.0259	56.3	0.7851	33.6	2.7216	36.3
0.0389	54.2	0.9481	31.7	3.0686	36.7
0.0583	52.5	1.1224	30.2	3.5013	36.7
0.0970	49.8	1.3079	29.5	4.0592	37.0
0.1615	46.5	1.5043	29.7	4.7657	37.0
0.2515	43.4	1.7113	31.8	5.6590	37.3
0.3668	39.7	1.9286	34.0	6.6679	37.1

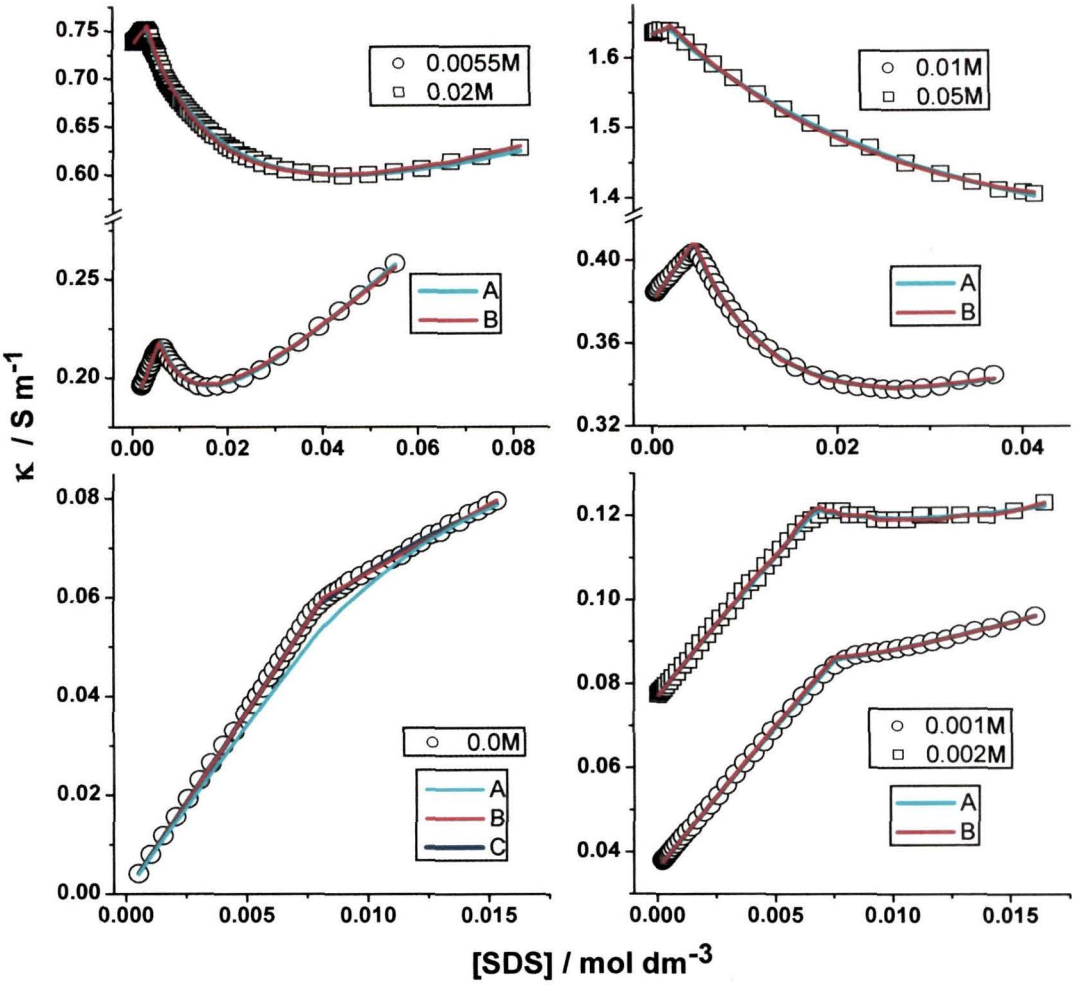

Fig. 6.1. Plots of κ versus SDS concentration in aqueous HNO_3 media at 25 ^{0}C. Numbers in the insets indicate concentration of HNO_3. The black symbols represent experimental data. Lines A and B (almost overlap in the presence of HNO_3) represent values of κ calculated without and with ion-size effect, respectively. In water, line C (overlaps with line B) represents values of κ calculated without ion-ion interaction term.

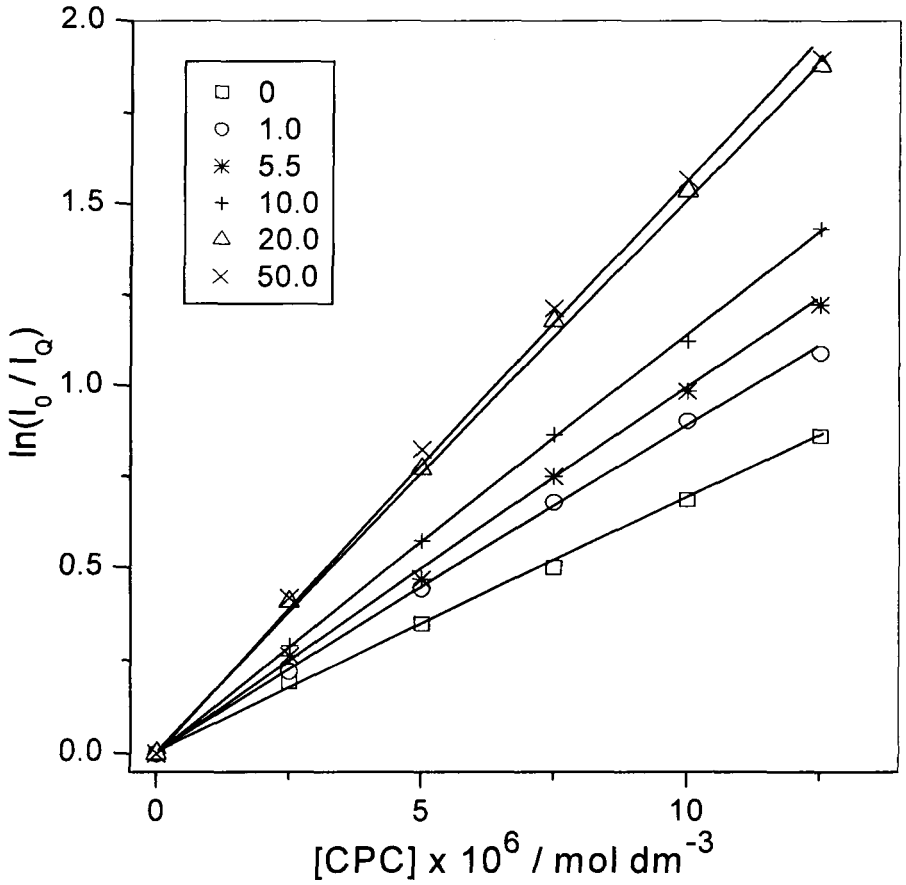

Fig. 6.2. Plots of $\ln(I_0/I_Q)$ of pyrene versus CPC concentration in aqueous solutions of SDS + HNO3 at 25 ^{0}C

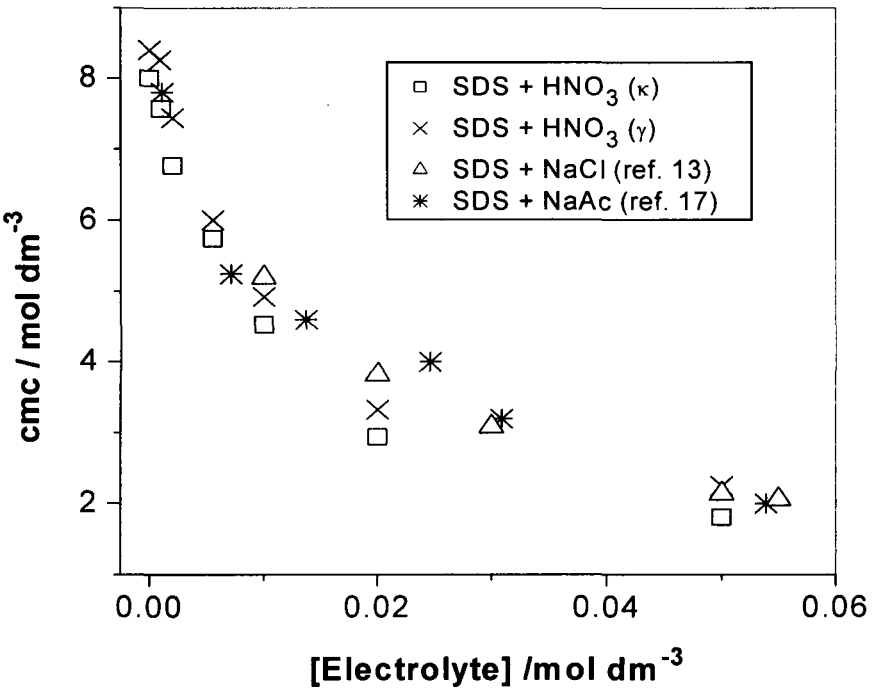

Fig. 6.3. Variation of cmc of SDS with the concentration of the added electrolyte. Electrolytes are indicated in the inset. In the case of HNO_3 (present data), κ and γ denote that cmc values are from specific conductivity and surface tension data, respectively.

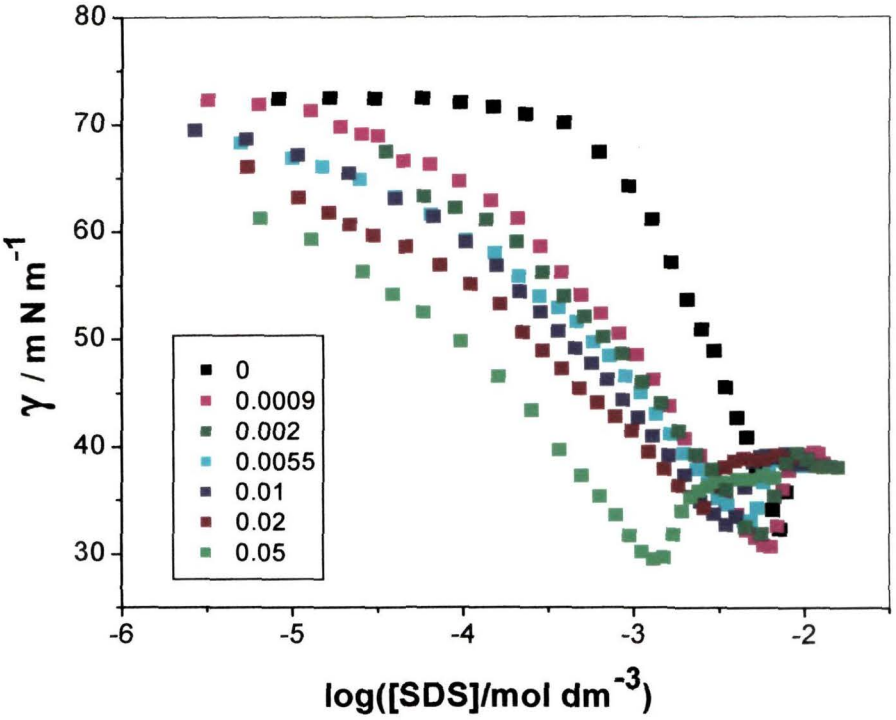

Fig. 6.4. Surface tension versus log([SDS]) isotherms of SDS in aqueous nitric acid solutions at 25 ^{0}C. The nitric acid concentrations in mol dm^{-3} are indicated in the inset.

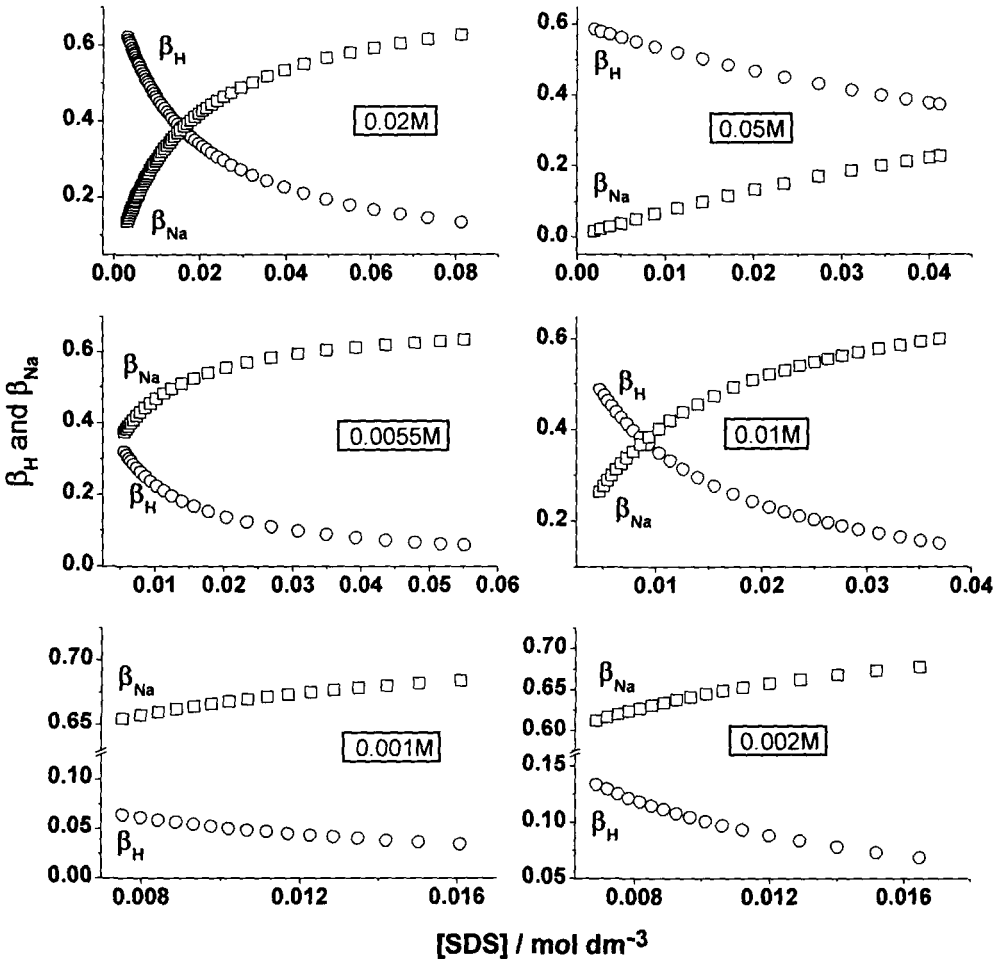

Fig. 6.5. Variation of β_H and β_{Na} with SDS concentration. The [HNO_3] in mol dm^{-3} are shown in the insets.

List of Publications

1. **J.Dey**, J. Bhattacharjee, P.A. Hassan, V.K. Aswal, S.Das and K.Ismail. "Micellar shape driven Counterion binding. Small-angle neutron scattering study of AOT micelle." ***Langmuir, 2010, 26(20),pp 15802-15806.***

2. **J.Dey** and K.Ismail. "Competitive Counterion Binding Controlled Conductivity Behaviour of Sodium Dodecylsulfate in Aqueous Nitric Acid Medium. A Potential Green Medium for Nitration ". ***(Revised manuscript submitted to Journal of Physical Chemistry B)***

3. **J.Dey,** U. Thappa and K.Ismail. "Aggregation, Counterion Binding and Adsorption Characteristics of Sodium Dioctylsulfosuccinate in Aqueous Ammonium Chloride Medium. A Case of Mixed Counterions". ***(Revised manuscript submitted to Journal of Colloid and Interface Science)***

4. T. Mukhim, **J.Dey**, S. Das, K. Ismail. "Aggregation and Adsorption behavior of cetylpyridinium chloride in aqueous sodium salicylate and sodium benzoate solutions." ***Journal of Colloid and Interface Science 350 (2010) 511–515.***

5. S.Das, **J. Dey**. , T. Mukhim and K.Ismail. "Micellization and Adsorption behaviors of sodium deoxycholate in aqueous sodium salicylate, sodium oxalate and sodium chloride media." ***Journal of Colloid and Interface Science 357 (2011) 434–439.***

6. I.M. Umlong, **J.Dey**, S.Chanda and K.Ismail." Micellization behaviour of AOT in the presence of Sodium citrate." ***Bull. Chem. Soc. Jan.,(2007), 80, 1522-1526.***

CURRICULUM VITAE

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Research Scholar E mail: **johar_dey2006@yahoo.com**

Personal Profile

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EDUCATION:

Ph.D. (2006 – Onward)	:	**Pursuing** in Chemistry, North Eastern Hill University, Shillong Meghalaya, India.
Supervisor	:	**Prof. K.Ismail**, Department of Chemistry, North Eastern Hill University, Shillong Meghalaya, India.
Title	:	**"Studies on the micellization of surfactants in selected solvent medium."**
M.Sc. (2004)	:	Chemistry, North Eastern Hill University, Shillong

		Meghalaya, India.
B.Sc. (2002)	:	Chemistry, North Eastern Hill University, Shillong Meghalaya, India.

WORK EXPERIENCE :

2006 – Onward	:	**Student Research Assistant** in North Eastern Hill University, Shillong Meghalaya, India.
Research field	:	**Surfactant Chemistry**
2007-2009	:	**Research Assistant** North Eastern Hill University, Shillong Meghalaya, India.
Research field	:	**Surfactant chemistry**
Project	:	**"Counterion binding-interfacial property correlation for AOT Micelles."**
12/2008 to 03/2009	:	Visiting **Student Research Assistant,** BARC, Mumbai, India
Research field	:	Surfactant Chemistry, DLS and SANS Measurements.
10/2009	:	Visiting **Student Research Assistant, NEIST, Jorhat**
Research field	:	Surfactant Chemistry, ZETA – Potential Measurements.

List of Publications

1. **J.Dey**, J. Bhattacharjee, P.A. Hassan, V.K. Aswal, S.Das and K.Ismail. "Micellar shape driven Counterion binding. Small-angle neutron scattering study of AOT micelle." ***Langmuir, 2010, 26(20),pp 15802-15806.***

2. **J.Dey** and K.Ismail. "Competitive Counterion Binding Controlled Conductivity Behaviour of Sodium Dodecylsulfate in Aqueous Nitric Acid Medium. A Potential Green Medium for Nitration ". ***(Revised manuscript submitted to Journal of Physical Chemistry B)***

3. **J.Dey,** U. Thappa and K.Ismail. "Aggregation, Counterion Binding and Adsorption Characteristics of Sodium Dioctylsulfosuccinate in Aqueous Ammonium Chloride Medium. A Case of Mixed Counterions". ***(Revised manuscript submitted to Journal of Colloid and Interface Science)***

4. T. Mukhim, **J.Dey**, S. Das, K. Ismail. "Aggregation and Adsorption behavior of cetylpyridinium chloride in aqueous sodium salicylate and sodium benzoate solutions." ***Journal of Colloid and Interface Science 350 (2010) 511–515.***

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6. I.M. Umlong, **J.Dey**, S.Chanda and K.Ismail." Micellization behaviour of AOT in the presence of Sodium citrate." ***Bull. Chem. Soc. Jan.,(2007), 80, 1522-1526.***

CONFERENCE PRESENTATIONS.

1. Attended the NATCOSEB – XII- BIMS, Manipur University, Imphal from Nov 9-11, 2005, Manipur University, Imphal.

2. Presented a paper entitled "Micellization behaviour of Sodiumdodecyl Sulphate (SDS) and Sodiumdioctylsulphosuccinate (AOT) in Nitric Acid", in the National Conference on Disperse Systems, Nov 23 – 25, 2006, Assam University, Silchar.

3. Presented a paper entitled "Micellization of Sodiumdioctylsulphosuccinate (AOT) in Nitric Acid medium", in NATCOSEB – XIII – BIMS, BITS Pillani, Feb 22 – 24, 2007.

4. Presented a paper entitled " Conductance Behaviour of Anionic Surfactants in presence of Nitric Acid" at the International Symposium on Recent Trends in Surface and Colloid Science" Nov 15- 16,2007.
5. Presented a poster entitled "Aggregation, adsorption and Counterion binding behavior of AOT in water + ethylene glycol mixtures." At the 14th national conference on surfactants, Emulsions and Bio-colloids at the university of Kashmir, Srinagar, Jammu and Kashmir, July 28-30, 2009.
6. Presented a poster entitled "Effect of solvent on the aggregation, adsorption and viscoelasticity of Cetylpyridinium chloride." At the national seminar on membranes, Microemulsions and self-assembled systems (MMSAS-2010) at the Sikkim Manipal university, Majitar, Sikkim, September 28-30, 2010.

AWARD:

1. Presented a poster entitled "Aggregation, adsorption and Counterion bindingbehavior of AOT in water + ethylene glycol mixtures." And was awarded the "**J.K. Mittal** " award for one of the best poster duing 14th national conference on surfactants, Emulsions and Bio-colloids at the university of Kashmir , Srinagar, Jammu and Kashmir, july 28-30, 2009.

FELLOWSHIP:

1. Junior research fellowship from Department Of Science and Technology, New Delhi.
2. Senior research fellowship from Department Of Science and Technology, New Delhi.
3. Visiting student fellowship for three months at chemistry Division, BARC, Mumbai. From Department Of Science and Technology, New Delhi through NER program.
4. Senior research fellow from UGC (from April, 2011 onwards)

Place: Shillong

Date:

JAHAR DEY