PHYSICOCHEMICAL STUDIES OF MICELLAR AND MICROEMULSION SYSTEMS

ABSTRACT

SUJIT DAS

DEPARTMENT OF CHEMISTRY

NORTH-EASTERN HILL UNIVERSITY

SHILLONG-793022,

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Chemistry

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In chapter 3, the values of the critical micelle concentration (cmc) of sodium deoxycholate (SDC) in water and in aqueous sodium oxalate, sodium salicylate (NaSa) and sodium chloride media were determined at 25, 30, 35 and 40 °C by the conductance, surface tension, EMF and fluorescence methods. Based on the present and reported data it has become clear that in unbuffered water medium surface tension data and fluorescence emission intensity data of pyrene probe provide similar value for the first cmc of SDC, which at 25 °C is equal to 2.5 ± 0.5 mM. Besides counter ion, salicylate, oxalate and chloride co-anions also influence the cmc values of SDC. In the range from 25 to 40 °C, cmc increases almost linearly with temperature. Counter ion binding constant (β) of SDC micelles has almost same value (about 0.15 ± 0.05) in the presence of sodium chloride and sodium salicylate. On the other hand, in sodium oxalate solution $\beta = 0.05 \pm 0.02$ when oxalate concentration is less than or equal to c* and $\beta = 0.48 \pm 0.04$ above c*, where $c^* \approx 0.038$ mol kg^{-1}. EMF measurement also supported this type of counter ion binding to SDC micelles in sodium oxalate solution. Thus, binding behaviour of sodium ion to SDC micelles is similar in the presence of sodium chloride and sodium salicylate, but different in

the presence of oxalate. Contrary to the suggestion made by Partay et al. (L. B. Partay, M. Sega, P. Jedlovszky, *Langmuir* **24** (2008) 10729), the present study reveals that in the presence of sodium oxalate a particular experimental method itself provides both the lower and higher values of β for SDC micelles. Salicylate, oxalate and chloride co-anions have similar effect on the adsorption of SDC. Since SDC has similar micellization and adsorption behaviours in aqueous NaCl and NaSa media, the present study shows that the choleretic effect of salicylate ion is not due to its influence on the micellization of SDC. The special effect of oxalate co-anion on the counter ion binding constant of SDC may have relevance to bile salts affecting the colonic absorption of oxalate.

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In chapter 6, Oil-in-water microemulsions containing water/SDC/benzene were prepared and the phase diagram of this system at 25 °C has been constructed. Density, viscosity and conductivity measurements of these microemulsions were made. This study revealed that (i) SDC, like AOT, has the ability to form microemulsions without cosurfactant and (ii) forming microemulsion without cosurfactant is dependent not only on the characteristic of the surfactant, but also on the structure of the oil used. By analyzing the viscosity and conductivity data, it has been shown that the droplets of the water/SDC/benzene o/w microemulsions have ellipsoidal shape.

PHYSICOCHEMICAL STUDIES OF MICELLAR AND MICROEMULSION SYSTEMS

By

SUJIT DAS, M.Sc.

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SCHOOL OF PHYSICAL SCIENCES

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Chemistry

DEDICATED TO MY PARENTS

The North Eastern Hill University

Declaration

Month: **Year: 2010**

I, SUJIT DAS, 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.

Sujit Das

Prof. B. Myrboh
Head
Department of Chemistry

विभागाध्यक्ष
Head
रसायन विज्ञान विभाग
Chemistry Department
पूर्वोत्तर पर्वतीय विश्वविद्यालय
North Eastern Hill University
शिलांग

Prof. K. Ismail
(Supervisor)

Professor
Department of Chemistry
North-Eastern Hill University
Shillong- 793022

SUJIT DAS
(Candidate)

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Shillong

Dated SUJIT DAS

CONTENTS

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CHAPTER 1

General Introduction

1.1 Surfactants and their classification

Surfactants are molecules having surface-activity and self-associating ability. The necessary criterion for a molecule to behave as a surfactant is that it should have dual characteristics of solvophobicity and solvophilicity. Due to the dual nature of surfactants, they are also called amphiphiles. In order to exhibit amphiphilicity, a surfactant molecule must have a solvophobic part of sufficient size and a solvophilic end. In conventional surfactants, the solvophobic part consists of hydrocarbon chain with eight or more carbon atoms, which is simply called 'tail' and the solvophilic part is called 'head'. In certain surfactants, hydrocarbon surface of sufficient area act as solvophobic part and the surface attached with solvophilic groups behave as solvophilic part

Surfactants occurring naturally are called biosurfactants as they are found in biological systems. Examples are phospholipids, fatty acids and bile salts. The other type of surfactants is synthetic, which are synthesized for specific domestic or industrial uses. Soaps and detergents are formulations containing mainly synthetic surfactants as active components. Surfactants, both natural and synthetic, are further classified as anionic, cationic, nonionic and zwitterionic.

Anionic surfactants are represented by the general formula RA^-M^+, where R is the hydrophobic chain with A^- head group and M^+ is the counter ion. When dissolved in polar solvents, they dissociate to give negatively charged monomeric species and the corresponding counter ions. They aggregate to give anionic micelles. Sodium dodecyl sulfate (SDS; $CH_3(CH_2)_{11}SO_4^-Na^+$) and sodium alkyl benzene sulfonate ($RC_6H_4SO_3^-Na^+$) are some of the widely used anionic surfactants. Cationic surfactants have the general formula RX^+Y^-, which dissociate in polar solvents to give positively charged surfactant moiety and negatively charged counter ions. They form cationic micelles. Examples of cationic surfactants are hexadecyl trimethylammonium bromide (CTAB; $CH_3(CH_2)_{15}N^+(CH_3)_3Br^+$) and cetyl pyridinium chloride (CPC; $C_{16}H_{33}C_5H_4N^+Cl^-$). Nonionic surfactants do not carry any electrical charge nor their aggregates have any surface charge. Polyoxyethylene (23) dodecanol (brij 35), polyoxyethylene (9-10) octyl phenol (Triton X–100) and polyoxyethylene (20) sorbitan monooleate (Tween 80) are some well known nonionic surfactants. Zwitterionic surfactants possess both anionic and cationic groups on the hydrophobic moiety and can behave as anionic, cationic or neutral species depending on the pH of the medium. N-alkyl and C-alkyl betaines, phosphatidyl amino alcohols and acids are examples of such surfactants.

Conventional surfactants have one head group attached to one hydrocarbon chain (single-chained) or two hydrocarbon chains (double-chained) or even three hydrocarbon chains (triple-chained).[1] The hydrocarbon chains may be branched also. A new class of synthetic surfactants having remarkable surface-active properties is called gemini surfactants.[2] These are surfactant molecules containing two head groups and two hydrocarbon chains. The two hydrocarbon chains are connected through another hydrocarbon chain known as spacer. The surfactant is called gemini or dimeric when the spacer is between the two head groups and bolaform if the spacer is between the hydrocarbon chains. The length of the spacer can be varied by varying the number of carbon atoms and nature of the spacer governs the properties of these surfactants. Research is going on to synthesize newer surfactants with special properties, for e.g., photo-sensitive surfactants.[3-5]

1.1.2 Two important properties: Adsorption and aggregation

Surfactants possess two important properties due to their amphiphilic nature, viz., solvophobicity and solvophilicity. These are (i) surface activity or adsorption at an interface and (ii) self-organization or aggregation in a given medium. Due to adsorbing ability of surfactants, they can lower the surface tension of a solution and form monolayers, films and multilayers. Due to self-organizing ability of surfactants, they form aggregates like micelles, vesicles and membranes. Adsorption and micellization abilities of surfactant molecules are solely responsible for their importance and applications in various fields.

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_s at constant temperature and pressure is given as

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

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

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

where dγ is the change in the surface or interfacial tension of the solvent and dμ$_i$ is the change in chemical potential of the ith component. Γ_i is the surface excess of the ith component and is defined as

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

$n_{i\sigma}$ and Γ_i can be positive or negative. 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

$$d\gamma = -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 \tag{1.4}$$

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

$$d\gamma = -\Gamma_2 d\mu_2 = -RT\Gamma_2 d\ln a_2 \tag{1.5}$$

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

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

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.

Eq. (1.6) is, however, found to be valid in the case of nonionic surfactants only. For ionic surfactants, Gibbs adsorption isotherm has a form different from Eq. (1.6), which was discussed in detail by Prosser and Franses[6] as shown in the following section.

1.3 Gibbs adsorption isotherm for ionic surfactants

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

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

$$XM \longrightarrow n_{-e} X^{z-} + n_{+e} M^{z+} \tag{1.8}$$

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

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

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

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

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

$$\Gamma = \frac{\Gamma_R}{n_-},\ \Gamma_e = \frac{\Gamma_{\backslash}}{n_{-e}} \tag{1.11}$$

Electro-neutrality condition gives the following relations:

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

$$c_{\backslash /} = n_+ c + n_{+e} c_e \tag{1.13}$$

$$z_+ c_{\backslash /} = s_- c_{\backslash} + z_- c_R = s_- n_{-e} c_e + z_- n_- c = n_{+e} z_+ c_e + n_+ z_+ c \tag{1.14}$$

$$z_+ \Gamma_{\backslash /} = z_- \Gamma_R + s_- \Gamma_{\backslash} \tag{1.15}$$

Substituting Eqs. (1.10) - (1.15) into Eq. (1.9) and by considering the surface excess of co-ion, $\Gamma_{\backslash}$, 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, Eq. (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 Eq. (1.17) an expression of the type

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

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

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

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

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

1.4 Thermodynamics of micelle formation

The second important property of a surfactant is its ability to undergo aggregation. Aggregation of a surfactant in solution is commonly known as micellization and the aggregates are called micelles. The surfactant concentration in a given medium at which surfactant molecules start aggregating to form micelles is known as the critical micelle concentration (cmc). Two approaches are used to understand the thermodynamics of the micellization, which are phase - separation and mass - action models. These two models are briefly discussed below.

1.4.1 Phase – separation model

In this model the micelle is treated as a separate phase. 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.[7]

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

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

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

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

In the case of ionic surfactants, ΔG_m^0 must also include the free energy change for the transfer of β moles of counter ion from its standard state in the solution phase to the micellar phase. β is the number of moles of counter ion per mole of the associated monomer in the micellar phase and is known as the counter ion binding constant. If one mole of micelle consist of *n* mole of surfactant and *m* moles of counter ion, $\beta = m/n$. *n* is generally know 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

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

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

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

1.4.2 Mass – action model

In this model applicable to 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

$$n R^- + m M^+ \rightleftharpoons A^{(n-m)-} \tag{129}$$

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

$$K = \frac{a_A}{a_R^n a_M^m} \tag{1.30}$$

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

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

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

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

Eq. (1.32) can be rearranged to the form

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

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

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

Just above the cmc, we can approximate

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

c_0 denotes cmc. Eq. (1.34) now becomes

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

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

$$\ln x_{cmc} = A - \beta \ln x_M \tag{1.37}$$

where $\Delta G_m^0 / RT$ 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.[8]

1.5 Micellization parameters

Micellization behaviour of surfactants is characterized and quantified in terms of different parameters, which are known as micellization parameters. A brief account of the most commonly used micellization parameters are given below.

1.5.1 Critical micelle concentration

In solution surfactants begin to micellize or self-organize only when their concentrations attain critical values. The critical value of a surfactant concentration at which micellization starts is known as its critical micelle concentration (cmc) as mentioned above in section 1.4. When micelle forms, sudden change in several physical properties of surfactant solutions takes place enabling us to determine experimentally values of cmc. Normally, changes in physical properties like surface tension, conductivity, viscosity, solubilization, osmotic pressure, etc, take place over a narrow concentration range. Therefore, a precise determination of the cmc is difficult and moreover values of cmc estimated from different experimental methods may also differ to a certain extent. Thus, numerous methods are available for determining the value of cmc. Tensiometry, conductometry, fluorimetry and calorimetry are some of the commonly used methods.

Critical micelle concentration is an important property of a surfactant, which reflects on its micellization ability. Smaller the cmc better the surfactant. Cmc of a surfactant is affected by several factors.[9,10] It is dependent on the number of carbon atoms in the hydrocarbon chain of the surfactant. As the number of carbon atoms increases cmc decreases. The dependence of cmc on the number of carbon atoms beyond 16 is not very significant. Branching of the hydrocarbon chain also affects the cmc. Nature of hydrophilic group is another factor on which cmc shows strong dependence. There is a pronounced difference between the cmc's of ionic and nonionic surfactants with identical hydrophobic moieties indicating the influence of hydrophilic head group on cmc. The lower cmc's of the nonionic surfactants are a consequence of the lack of electrical work necessary in forming the micelles. Nature of counter ion, its radius and valence, also largely affect the value of cmc of ionic surfactants.[11-17] Cmc has interesting temperature dependence.[18-27] Most of the ionic surfactants exhibit at some temperature a minimum in the cmc.[18,19,25,28] This property of ionic surfactants is used in the differential scanning calorimetry technique for studying the micellization behaviour of ionic surfactants.[29] With increase in pressure cmc of ionic surfactants in water show a maximum.[30-37] Added electrolytes have significant effect on the cmc of both ionic and nonionic surfactants.[11-17,25,38-45] Non-electrolytes like urea, amides, alcohols, etc on addition produce both increase and decrease of cmc of surfactants.[46-53]

1.5.2 Aggregation number

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. It is determined using experimental techniques like dynamic light scattering (DLS), small-angle neutron scattering (SANS), steady-state fluorescence quenching and time-resolved fluorescence quenching.[39,55-61] Some of the factors affecting aggregation number are structure of a surfactant, concentration of surfactant,[56,60-62] concentration of added electrolyte,[41-43,52,61-63] counter-ion binding constant, nature of solvent, etc. Significant changes in aggregation number lead to micellar shape transition. In a micellar solution, all micelles may not have same aggregation number and poly-dispersity exists.[64] However, for the sake of simplicity such polydispersity is generally ignored for calculation purpose and only monodispersed micelles with single aggregation number are taken into account.

1.5.3 Counter ion binding constant

In the case of ionic surfactants counter ion binding constant is an important parameter. As mentioned above in section 1.4.1, counter ion binding constant (β) is equal to the number of moles of counter ion bound to the ionic micelle divided by the aggregation number. β is always found to be less than one thereby signifying presence of residual electric charge on the surface of an ionic micelle. Counter ion binding ability is one of the important characteristics of ionic micelles. Counter ions control not only the critical micelle concentration (cmc) and aggregation number (N_{agg}) of ionic surfactants, but also the reactions[65] 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.

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.

1.6 Mixed Micelles

Mixed micelles contain more than one type of surfactant. They are important because most of the commercial formulations of surfactants used for various purposes consist mixtures of surfactants, because mixtures of surfactants have better properties and hence perform better than single surfactants. Therefore, mixed surfactant systems are studied extensively and continues to be an active area of research.

1.6.1 Clint Model

Mixed micelles can be either ideal or non-ideal. The Clint's equation[66] for an ideal mixed micelle is of the form,

$$\frac{1}{c_{0m}} = \sum_i \frac{\alpha_i}{c_{0i}} \tag{1.38}$$

For non-ideal mixed micelle the equation is,

$$\frac{1}{c_{0m}} = \sum_i \frac{\alpha_i}{f_i c_{0i}} \tag{1.39}$$

where, α_i and f_i denote the bulk mole fraction of the component 'i' and its activity coefficient in mixed micelle, respectively. c_{0i} and c_{0m} are the critical micelle concentrations of the component 'i' and the mixture, respectively. The above equations can be derived by writing thermodynamic expressions for the chemical potentials of different species in the bulk and micellar phases and equating them for equilibrium condition.

1.6.2 Rubingh Model

In this model,[67,68] Rubingh employed the regular solution approximation to describe the non-ideality of the mixed micelle. According to this approximation, the relation between the interaction parameter (β_m) responsible for non-ideality and the activity coefficient is given by

$$\beta_m = \ln\frac{f_1}{(1-x_1)^2} = \ln\frac{f_2}{x_1^2} \tag{1.40}$$

$$f_i = \frac{\alpha_i c_{0m}}{x_i c_{0i}} \tag{1.41}$$

At c_{0m}, after substituting for the activity coefficients in Eq. (1.40), we get the expression,

$$x_1^2 \ln\frac{\alpha_1 c_{0m}}{x_1 c_{01}} = (1-x_1)^2 \ln\frac{(1-\alpha_1)c_{0m}}{(1-x_1)c_{02}} \tag{1.42}$$

Values of x_1 can be computed from Eq. (1.42) by using an iterative method and the interaction parameter β_m can be determined using Eq. (1.40). Negative value of β_m indicates attractive interaction, positive value indicates repulsion and zero value indicates ideal micellization between the surfactants.

1.6.3 RVV Model

Rodenas, Valiente and Villafruela (RVV)[69] developed an approach to determine x_1 by using the Gibbs-Duhem relation and without resorting to the regular solution approximation. According to this model the equation for x_1 is of the form

$$x_1 = \alpha_1 - \alpha_1(1 - \alpha_1)d\ \ln c_{0m}/d\alpha_1 \qquad (1.43)$$

The values of x_1 can be computed from Eq. (1.43) using the value of the slope, $d\ \ln c_{0m}/d\alpha_1$, determined by least-squares fitting the $\ln c_{0m}$ versus α_1 data.

Different other models are available in the literature[70-72] for determining micellar composition and energetics of micellization of mixed surfactants.

1.7 Microemulsion

Microemulsions are homogenous and transparent systems formed from a mixture of surfactant, oil, water and cosurfactant. They represent an intermediate state between micellar solutions and true emulsions. Microemulsions consist of dispersed and dispersing medium. The dispersed media exists in the form of droplets having diameters in the range 10-100 nm. Micelles have diameters less than 10 nm whereas emulsion droplets have diameters in the range of 100-1000 nm. Microemulsions are classified as water-in-oil (w/o) and oil-in-water (o/w) depending upon the type of dispersed and dispersing media. The changeover from one type to another is known as phase inversion zone or a bicontinous phase.

Formation of a microemulsion requires the free energy of formation to be negative, but generation of a huge interfacial area makes a large positive contribution to the free energy of formation if the interfacial tension has a finite value. To overcome this thermodynamic restriction, Schulman et al.[73] postulated that in microemulsions the interfacial tension is zero and cosurfactants help in bringing down the interfacial tension to such a low value. Short chain alcohols are commonly used as cosurfactants.

1.7.1 Electrical conductance of microemulsions

Microemulsions can exhibit different types of conductance behaviour[74-77] depending upon its type and the composition path chosen. Water-in-oil microemulsions are known to show low conductance and percolation feature. Percolative conductance in a microemulsion is explained by an expression similar to the one used for conductor-insulator composite materials.[78] The theories of percolation conduction in microemulsions have been examined by Moulik et al.[79,80] to evaluate several structural features of w/o microemulsions. The conductance behaviour of w/o microemulsions below the percolation threshold has been interpreted by charge fluctuation model.[81-85] The conductance behaviour of o/w microemulsion is explained by the Bruggman equation.[86] Clausse et al[74] showed that the different regions such as o/w, bicontinous and w/o in phase diagram can be located using conductance data.

1.7.2 Viscosity of microemulsions

Viscosity measurements of microemulsions are considered to be of significant importance as they provide useful information about the structure, shape and size of the droplets. In a microemulsion several composition paths can be chosen and the viscosity of a microemulsion may decrease or increase or even exhibit maximum or minimum depending upon the composition path chosen.[75,76,87,88] By analyzing the viscosity data of microemulsions using theoretical and semi-empirical equations, shape and dimensions of the droplets can be inferred.

1.8 Scope of the work

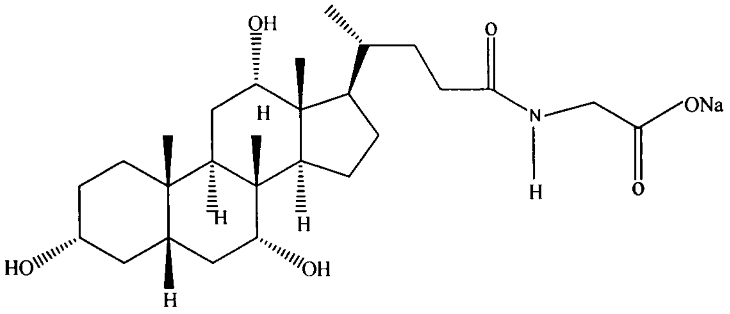
Bile salts are anionic type surfactants and the physiological functions of bile salts are related to their ability to aggregate.[89-91] Bile salts are the salts of four different kinds of free bile acids, viz., cholic (three hydroxyl groups at positions 3, 7 and 12), deoxycholic (two hydroxyl groups at positions 3 and 12), chenodeoxycholic (two hydroxyl groups at positions 3 and 7), and lithocholic (one hydroxyl group at position 3) acids. Each of these acids may in turn combine with glycine or taurine to form more complex acids and salts.[89] Structures of some bile salts are shown in Fig. 1.1. As can be seen from Fig. 1.1, the molecular structure of bile salts, which have a rigid framework due to the steroid nucleus, is quite different from the conventional head-and-tail type surfactants. The convex side (β-face) of the steroid ring system acts as a hydrophobic surface, while the other side of the steroid ring system possessing hydroxyl groups is concave (α-face) and acts as hydrophilic surface. Because of their structural difference, micellization characteristics of bile salts can be different from that of the conventional surfactants. Due to the biological importance of bile salts, the physical chemistry of bile salt micellization continues to be an active area of research. In this thesis we have chosen sodium deoxycholate for investigation.

From the studies made on conventional surfactants, added electrolytes are known to have significant influence on the micellization behaviour of surfactants. In spite of extensive research on the micellization of bile salts, the studies made on the effect of electrolyte on bile salt micellization have been restricted to only NaCl. Although the effect of electrolyte on micellization of ionic surfactants is attributed to mainly to counter ion effect, co-ions of the electrolyte have also known to influence micellization. Therefore, in Chapter 3 we have studied the influence of two physiological important ions, salicylate and oxalate anions, on the micellization of sodium deoxycholate.

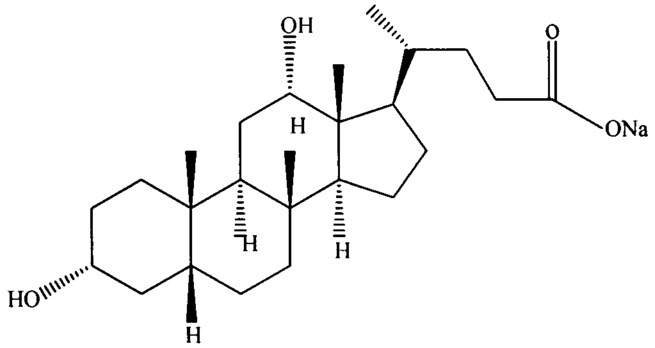
Hydrophobic or solvophobic interaction is responsible for micellization and it is one type of solute – solvent interaction induced by the solvent. Solvent thus determines solvophobicity and solvophilicity of surfactants and, in turn, plays a decisive role in controlling the adsorption and micellization behaviours of surfactants. Not much is known about the micellization characteristics of bile salts in solvents other than water. Therefore, in Chapter 4 we have studied the aggregation and adsorption behaviours of sodium deoxycholate in water + ethylene glycol mixed solvent medium.

Mixed surfactants perform better than single surfactants. Moreover, digestive function of bile salts is due to its mixed micelle formation ability with fats, cholesterol, etc. Sodium dioctylsulfosuccinate (AOT) is a double-chained anionic surfactant having special counter ion binding behaviour. Therefore, in Chapter 5 we have studied the micellization behaviour of mixtures of sodium deoxycholate with AOT with more emphasis on the counter ion binding behaviour of this mixed system.

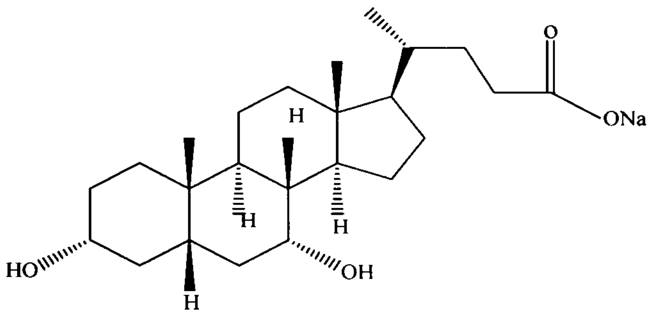
Microemulsions are important media having wide range of applications. Microemulsion forming ability of bile salts has not been explored much, although microemulsions stabilized by bile salts can provide biocompatible media. Therefore, in Chapter 6 we have studied phase, viscosity and conductance behaviours of benzene/sodium deoxycholate/water microemulsion.



Sodium Cholate



Sodium deoxycholate



Sodium chenodeoxycholate

Fig. 1.1 Structures of some bile salts

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CHAPTER 2

Experimental Techniques

2.1 Surface Tension Measurement

Surface tension of the experimental surfactant solutions was measured using a K11 Krüss Tensiometer. The surface tension of the test solution is determined with the help of an optimally wettable probe suspended from a precision balance. The probe is either a ring or a plate. We used here a plate known as Wilhelmy plate method. Using a height-adjustable sample carrier, the liquid or solution in the sample vessel is brought 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 andθ 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 equation (2.1) since the length of the plate, L = 0.0402 m.

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

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

2.2 EMF Measurement

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

2.3 Electrical Conductance Measurement

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

2.4 Fluorescence Quenching Method for Aggregation Number Measurement

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

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

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

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

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

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

$$N_0 = \frac{C - C_0}{[micelle]} \qquad (2.4)$$

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

2.5 Density Measurement

Density of solutions whenever required to convert molal to molar concentration was measured using Anton Paar DMA 5000 Density Meter. Mettler Toledo AG245 Electronic Balance was used for weighing.

2.6 Viscosity

Viscosity was measured by using a Cannon-Ubbelohde type viscometer having viscometer constant 4.15 x 10^{-4} St s^{-1}.

CHAPTER 3

Micellization and adsorption behaviours of sodium deoxycholate in aqueous sodium salicylate, sodium oxalate and sodium chloride media

3.1. Introduction

Bile salts, which belong to the category of biosurfactants of anionic type, perform important physiological functions during the digestion of food. The physiological functions of bile salts are related to their ability to aggregate.

The molecular structure of bile salts, which have a rigid framework due to the steroid nucleus, is quite different from the conventional head-and-tail type surfactants. The convex side of the steroid ring system acts as a hydrophobic surface, while the other side of the steroid ring system is concave and possesses hydrophilicity due to hydroxyl groups. Owing to such a molecular structure, aggregation properties of bile salts are different from those of conventional surfactants. Bile salts form primary aggregates with a small number of monomers, wherein the hydrophobic surfaces face each other and the hydrophilic groups (hydroxyl and carboxylate) point outward towards the solvent. Bile salts are therefore called as facial amphiphiles[1] and their aggregates may be called as facial micelles. On increasing the bile salt concentration primary aggregates form secondary aggregates of bigger size. Accordingly, two critical micelle concentrations (cmc) are reported for bile salts; first cmc and second cmc.

Electrolytes are known to affect adsorption and aggregation behaviours of ionic surfactants. This effect of electrolytes is mainly due to the influence of its counter ions on the adsorption and aggregation of hydrophobic moieties. Nevertheless, some co-ions may also influence the adsorption and aggregation. In the case of bile salts, only the effect of NaCl on their micellization has been studied up till now. To the best of our knowledge, the effect of added electrolyte on the micellization of bile salts by varying the co-ions has not been investigated.

The secretion of bile by the liver into the gallbladder is called choleresis and salicylate ion is known to have choleretic effect in rats, dogs and humans[2,3]. Choleretic effect refers to increasing the rate of bile flow and the mechanism by which salicylate exhibits this effect is not clearly known. It is reported[2] that the influence of salicylate anion on the bile salt micelles might be one of the reasons for its choleretic effect. Further, there are reports of bile salts affecting the colonic absorption of oxalate and inhibition of calcium oxalate precipitation by bile salts[4,5].

The above reports reveal the physiological importance of salicylate and oxalate ions and how these two organic anions influence the micellization of bile salts is, however, not known. This prompted us to investigate the aggregation and adsorption behaviours of sodium deoxycholate (SDC) in the presence of salicylate and oxalate ions. Therefore, micellization and adsorption characteristics of SDC in aqueous sodium oxalate (Na_2Ox), sodium salicylate (NaSa) and sodium chloride media were studied and the results are presented in this chapter.

3.2. Experimental Section

SDC (Fluka, 98%), NaSa (Fluka, 99.5%), Na_2Ox (Himedia, A.R. grade, 99.9%) and NaCl (Merck, GR grade, 99.5%) were used as received. Solutions were prepared using Milli-Q grade water. Surface tension measurements were made by the Wilhelmy plate method using a K11 Krüss tensiometer. EMF measurements were made using a Jenway 3345 ion meter and a Jenway 924-329 sodium ion selective combined electrode. Electrical conductance measurements were made using B905 Wayne Kerr Automatic Precision Bridge and a dip-type conductivity cell. Fluorescence emission intensities (excitation wavelength = 335 nm) of pyrene (Fluka) were recorded at 373 (I_1) and 384 (I_3) nm using Hitachi F4500 FL spectrophotometer.

3.3. Results and Discussion

3.3.1. Critical micelle concentration.

Experimental values of surface tension (γ) of aqueous solutions of SDC in the presence of Na_2Ox, NaSa and NaCl are given in Table 3.1(a-l). Representative surface tension (γ) isotherms of these solutions are shown in Fig. 3.1. The values of cmc determined from the surface tension isotherms are given in Table 3.2 and shown in Fig. 3.2.

We also employed conductance method to determine the cmc of SDC in water. The measured conductance data are given in Table 3.3. The plot of specific conductance versus surfactant concentration did not show a change in slope over a wide range of concentration rendering the conductance method not suitable for bile salts. The non-suitability of specific conductance versus concentration plots for determining cmc of bile salts has been discussed by Matsuoka and Moroi[6], which is attributed partially to the low counter ion binding constant of bile salts. However, the plot of molar conductance versus square root of SDC concentration (Fig. 3.3) exhibits a minimum and a maximum, which is similar to the reported trend[7,8]. Such type of concentration dependence of molar conductance was attributed to aggregation of bile salts[7,8] and the concentration corresponding to minimum is taken to be the first cmc. These cmc values (Table 3.2) are found to be higher than those from surface tension data but within the acceptable range. It may be pointed out that such conductance behavior is not specific to only bile salts. Sodium dioctylsulfosuccinate (AOT), a double-chain anionic surfactant, is another example whose molar conductance in water exhibits a similar trend[9] and for AOT also cmc cannot be determined from its specific conductance versus concentration plot[10].

The cmc of SDC in water was also determined by the fluorescence method. The values of the ratio I_3/I_1 of the emission intensities of pyrene are given in Table 3.4 and plotted versus SDC concentration in Fig. 3.4. From Fig. 3.4 cmc was chosen as the concentration at which the value of I_3/I_1 starts increasing sharply. The values of cmc obtained thus are (Table 3.2) found to be comparable with those determined from surface tension data.

Cmc of SDC in both buffered and unbuffered aqueous media has been reported[11-28] by different groups by using variety of techniques and some of these values reported in the absence of added electrolyte are shown in Fig. 3.5. The present values of cmc of SDC in water are also shown in Fig. 3.5. It has generally been considered that the value of the first cmc of SDC falls in the range of 2 to 10 mM (M = mol dm^{-3}). However, from fluorescence study Matsuoka and Moroi[6] reported (using pyrene probe) first cmc at around 2 mM and second cmc at 6 mM (at 25 °C), whereas Bhattacharyya and coworkers[25] reported (using 2,6-p-toluidinonaphthalenesulfonate probe) first cmc at 7 mM and second cmc at 60 mM. So much variation in the values of cmc of bile salts in contrast to the case with conventional surfactants is considered to be due to small size of their aggregates. In view of such broad range for the cmc values of bile salts, the variation of cmc of SDC with temperature is considered to be almost linear as shown in Fig. 3.6.

3.3.2. Dependence of cmc on salt concentration and counter ion binding constant.

From Fig. 3.2, it is clear that the decreasing trend in cmc of SDC with counter ion (from the added salt) concentration is different in the presence of different salts thereby indicating the influence of co-ion on the cmc of SDC. The dependence of cmc on counter ion concentration can be explained in terms of the Corrin-Harkins (CH) equation

$$\ln c_0 = A - \beta \ln(c_0 + c_{eNa}) \qquad (3.1)$$

In Eq. (3.1) A is a constant related to the standard free energy of micellization, β is the counter ion binding constant, c_0 is the cmc of SDC in the presence of a particular concentration of electrolyte (c_e) and c_{eNa} is the sodium ion concentration contributed by c_e concentration of electrolyte. The CH plots are shown in Fig. 3.7 and values of β determined from these plots are listed in Table 3.5. The value of β is found to be about 0.15 ± 0.05 in the presence of NaCl and NaSa. Therefore, binding behaviour of sodium ion to deoxycholate micelles is same in the presence of chloride and salicylate anions. On the other hand, the binding behaviour of sodium ion to deoxycholate micelles is different in the presence of oxalate. β is equal to about 0.05 ± 0.02 up to about 0.038 mol kg^{-1} oxalate concentration (c*) and it is equal to about 0.48 ± 0.04 above c*. A similar counter ion binding behaviour has been reported[29] for AOT in different aqueous electrolyte solutions.

In order to confirm such a counter ion binding behaviour in the presence of oxalate co-anion, we measured the emf (E) of SDC solution in the presence of Na_2Ox by using sodium ion-selective electrode. The emf data are given in Table 3.6(a-c) and the plots of emf versus log([Na$^+$]) are shown in Fig. 3.8. Up to 0.03 mol kg^{-1} Na_2Ox, the plots are linear in the entire range of SDC concentration indicating thereby that the binding of sodium counter ion is negligible and this observation is in agreement with the very low value of β obtained from CH plots. Above 0.03 mol kg^{-1} Na_2Ox, the emf data below and above cmc fall on two straight lines, which indicate binding of sodium counter ion to the micelle. To estimate the value of β from the emf data we adopted the method reported earlier[29]. First, we least-squares fitted the emf data lying below cmc to the equation of the form

$$E = E_0 + B\log(c + c_{eNa}) \qquad \text{at } c \leq c_0 \qquad (3.2)$$

The emf data above the cmc were then least-squares fitted to another equation of the form

$$E = E_0 + B\log\{\beta c_0 + (1-\beta)c + c_{eNa}\} \qquad \text{at } c \geq c_0 \qquad (3.3)$$

In Eqs. 3.2 and 3.3, E_0 and B refer to empirical constants and c is the concentration of SDC. While least-squares fitting the emf data above cmc to Eq.

3.3, we substituted for E_0 and B the values obtained from Eq. 3.2 and the best-fit value of β was evaluated by an iteration process. The values of E_0, B and β are given in Table 3.5. These values of β are comparable with the β values obtained above from CH plots. Thus, oxalate co-anion depending upon its concentration has a suppressing as well as enhancing effect on the binding of sodium ion to deoxycholate micelles. Oxalate anion appears to bind to the deoxycholate micelles by undergoing hydrogen bonding with the hydroxyl groups.

As in the case of cmc, a wide range of values have been reported for β of bile salt micelles also. The reported values vary from 0 to 0.7[6,13-17,30]. Recently, Partay et al.[31] from molecular dynamics simulations reported two types of counter ion binding for SDC. At 30 mM SDC concentration, they reported for β a lower value of 0.02 and a higher value of 0.15. Both these values increased with increase in surfactant concentration. The lower value refers to contact counter ion binding, while the higher value refers to binding of both contact and solvent-separated counter ions. Partay et al.[31] further suggested that certain techniques (e.g., freezing point depression) provide value of contact counter ion binding only, while techniques (e.g., emf, nmr) providing higher value of β include contribution from the binding of solvent-separated counter ions also. Contrary to the suggestion made by Partay et al.[31], the present study in the presence of oxalate reveals that a particular technique itself, in this case tensiometry or potentiometry, can provide for SDC both lower and higher values.

3.3.3. Free energy.

The standard free energy of micellization per mole of SDC was calculated using the relation

$$\Delta G_m^0 = RT(1 + \beta)\ln c_0 \tag{3.4}$$

In Eq. 3.4, R and T represent gas constant and absolute temperature, respectively. The values of ΔG_m^0 evaluated from Eq. 3.4 are listed in Table 3.7. From the values of ΔG_m^0, it is apparent that in the temperature range from 30 to 40 °C salicylate co-anion has no special effect on the micellization of SDC. In the temperature range from 25 to 40 °C, oxalate co-anion, however, has a hindering influence on the micellization of SDC in comparison to both chloride and salicylate.

3.3.4. Adsorption.

Surface excess of SDC at the cmc, Γ_{cmc}, in the presence of added salts was evaluated using the relation[32]

$$\Gamma_{cmc} = -\frac{1}{RT}\left[\frac{1}{1+\frac{c_0}{c_0+c_{eNa}}}\right]\left(\frac{d\gamma}{d\ln c}\right)_{cmc} \tag{3.5}$$

The computed values of Γ_{cmc} for SDC in water and in the different electrolyte solutions are given in Table 3.8 and shown in Fig. 3.9. It is clear from Fig. 3.9 that on adding electrolyte Γ_{cmc} initially increases, reaches a maximum value and then starts decreasing. The maximum in Γ_{cmc} occurs at about 0.03, 0.07 and 0.05 mol kg^{-1} of oxalate, salicylate and chloride ion concentration, respectively. Since the sodium ion concentration at the maximum correspond to 0.06 ± 0.01 mol kg^{-1} in the case of all the three salts, the counter ion seems to control the position of maximum in the plot of Γ_{cmc} versus salt concentration. Such a dependence of Γ_{cmc} on electrolyte concentration was reported[33] for sodium dodecylsulfate (SDS) in aqueous sodium butyrate. Adsorption of an ionic surfactant is influenced by salts because of salting-out effect, which, in turn, is controlled by the hydration of the ions of the added salts. In aqueous SDC solution, it appears from Fig. 3.9 that the hydration of salicylate, oxalate and chloride co-anions has similar effect on the surface excess of SDC.

3.4. Conclusions

Based on the present and reported data, it has become clear that in unbuffered water medium surface tension data and fluorescence emission intensity data of pyrene probe provide similar value for the first cmc of SDC, which at 25 °C is equal to 2.5 ± 0.5 mM. Besides counter ion effect, salicylate, oxalate and chloride co-anions also influence the cmc values of SDC. In the range from 25 to 40 °C, cmc increases almost linearly with temperature. Counter ion binding constant β of SDC micelles has almost same value (about 0.15 ± 0.05) in the presence of sodium chloride and sodium salicylate. On the other hand, in sodium oxalate solution $\beta = 0.05 \pm 0.02$ when oxalate concentration is less than or equal to c* and $\beta = 0.48 \pm 0.04$ above c*, where c* ≈ 0.038 mol kg^{-1}. EMF measurement also supported this type of counter ion binding to SDC micelles in sodium oxalate solution. Thus, binding behaviour of sodium ion to SDC micelles is similar in the presence of sodium chloride and sodium salicylate, but different in the presence of oxalate. Contrary to the suggestion made by Partay et al.[31] the present study reveals that in the presence of sodium oxalate a particular experimental method itself provides both the lower and higher values of β for SDC micelles. Salicylate, oxalate and chloride co-anions have similar effect on the adsorption of SDC. Since SDC has similar micellization and adsorption behaviours in aqueous NaCl and NaSa media, the present study shows that the choleretic effect of salicylate ion is not due to its influence on the micellization of SDC. The special effect of oxalate co-anion on the counter ion binding constant of SDC may have relevance to bile salts affecting the colonic absorption of oxalate.

3.5 References

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Table 3.1(a). Surface tension (γ) values of SDC in aqueous Sodium Oxalate solution at 298 K

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
		[Na_2Ox] = 0.00mol kg^{-1}			
0.0021	69.6	0.1236	54.7	1.5057	46.4
0.0041	66.5	0.1643	54.5	1.8394	46.1
0.0083	64.5	0.2453	53.1	2.1582	45.4
0.0124	63.0	0.3254	52.2	2.4631	45.5
0.0166	61.9	0.4047	51.9	2.7551	45.9
0.0207	61.4	0.4832	50.9	3.0349	45.9
0.0414	58.9	0.6379	50.0	3.3033	45.9
0.0620	57.8	0.7896	49.1	3.5610	45.9
0.0826	56.9	1.1562	47.9	3.8086	45.9
		[Na_2Ox] =5.0 x 10^{-3} mol kg^{-1}			
0.0013	71.4	0.5983	50.6	2.1754	45.3
0.0026	70.8	0.6914	49.7	2.2410	45.0
0.0132	65.5	0.7827	49.2	2.3056	45.1
0.0264	63.2	0.8723	49.0	2.3691	45.2
0.0395	61.3	0.9603	48.9	2.4318	45.3
0.0526	60.5	1.0466	48.4	2.5840	45.3
0.0787	58.5	1.1314	48.3	2.7306	45.3
0.1047	57.7	1.2147	47.6	2.8718	45.3
0.1563	55.8	1.2965	47.5	3.0079	45.3
0.2074	54.7	1.3769	47.2	3.1391	45.3
0.2579	53.2	1.6845	46.6	3.2658	45.3
0.3080	52.8	1.9719	45.9	3.3881	45.3
0.4066	51.7	2.0408	45.7		
0.5034	51.0	2.1086	45.5		
		[Na_2Ox] =1.0 x 10^{-2} mol kg^{-1}			
0.0024	65.6	0.2790	53.4	2.1722	44.8
0.0141	64.3	0.3701	52.1	2.3188	44.9
0.0705	62.4	0.4604	51.2	2.4629	45.0

Table 3.1(a)- continued

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
		[Na_2Ox] =1.0 x 10^{-2} mol kg^{-1}			
0.1405	59.6	0.5498	50.4	2.8124	45.0
0.0024	58.2	0.7261	48.9	3.1472	45.0
0.0141	57.8	0.8990	48.5	3.4686	45.0
0.0705	55.8	1.3172	46.9		
0.1405	54.7	1.7164	45.6		
		[Na_2Ox] =2.0 x 10^{-2} mol kg^{-1}			
0.0018	67.2	0.2183	53.3	2.4482	43.1
0.0037	65.9	0.2896	52.5	2.6962	43.1
0.0074	64.2	0.3602	51.7	2.9341	43.1
0.0111	63.7	0.4301	50.7	3.1624	43.1
0.0148	62.9	0.5677	49.6	3.3815	43.1
0.0185	62.5	0.7026	48.4	3.5923	43.1
0.0369	60.1	1.0286	46.7	3.7949	43.1
0.0552	58.8	1.3392	45.7	3.9901	43.1
0.0735	58.0	1.6355	44.3	4.1780	43.1
0.1100	56.4	1.9186	43.7	4.3592	43.1
0.1463	55.2	2.1892	43.0		
		[Na_2Ox] = 3.0 x 10^{-2} mol kg^{-1}			
0.0025	69.4	0.1499	55.6	1.4021	46.0
0.0050	67.4	0.1994	53.8	1.8256	45.1
0.0101	65.2	0.2976	52.8	2.2297	44.5
0.0151	63.8	0.3948	51.6	2.6157	44.5
0.0201	63.2	0.4910	50.4	2.9846	44.5
0.0252	62.4	0.5862	49.9	3.3378	44.5
0.0502	59.9	0.7739	48.5	3.6761	44.5
0.0753	58.4	0.9578	47.8	4.0006	44.5
0.1002	57.2	1.1381	47.2		

Table 3.1(a)- continued

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[Na_2Ox] =5.0 x 10^{-2} mol kg^{-1}					
0.0016	69.5	0.1297	55.8	1.7252	45.3
0.0033	67.9	0.1936	54.3	1.9729	44.4
0.0065	65.5	0.2570	53.2	2.0931	44.4
0.0098	64.4	0.3198	52.7	2.2110	44.4
0.0131	64.0	0.3820	51.5	2.4401	44.4
0.0163	63.3	0.5049	50.7	2.6605	44.4
0.0326	60.7	0.6256	49.6	2.8729	44.4
0.0489	58.9	0.9182	48.1	3.0777	44.4
0.0651	58.1	1.1985	46.7	3.2751	44.4
0.0975	57.1	1.4673	46.0		
[Na_2Ox] = 1.0 x 10^{-1} mol kg^{-1}					
8.8x10^{-4}	65.3	0.1038	53.3	1.6812	43.4
0.0018	64.3	0.1379	52.4	1.8980	43.4
0.0035	63.0	0.1717	51.7	2.1012	43.4
0.0053	62.1	0.2052	51.0	2.2920	43.4
0.0070	61.6	0.2713	49.9	2.4716	43.4
0.0088	61.0	0.3364	49.1	2.6409	43.4
0.0175	58.9	0.4947	47.8	2.8007	43.4
0.0262	57.4	0.6469	46.5	2.9520	43.4
0.0349	56.6	0.9343	45.1	3.0951	43.4
0.0522	55.7	1.2011	44.1	3.2310	43.4
0.0695	54.9	1.4495	43.5		
[Na_2Ox] = 2.0 x 10^{-1} mol kg^{-1}					
0.0015	63.3	0.0883	52.4	1.0793	44.2
0.0030	62.6	0.1175	51.0	1.5489	44.2
0.0059	61.2	0.1754	50.1	1.9794	44.2

Table 3.1(a)- continued

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
		[Na_2Ox] =2.0 x 10^{-1} mol kg^{-1}			
0.0089	60.0	0.2327	49.2	2.3756	44.2
0.0119	59.0	0.2895	48.5	2.7414	44.2
0.0148	58.4	0.3457	47.7	3.0803	44.2
0.0296	55.8	0.4565	46.6	3.3950	44.2
0.0443	54.4	0.5652	46.0	3.6880	44.2
0.0590	53.3	0.8282	44.7	3.9616	44.2

Table 3.1(b)- Surface tension (γ) values of SDC in aqueous Sodium Oxalate solution at 303K

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
		[Na_2Ox] = 0.00mol kg^{-1}			
0.0013	70.1	0.1795	55.5	1.5778	47.3
0.0026	68.9	0.2047	55.0	1.7693	46.8
0.0039	68.0	0.2547	54.3	2.1314	46.3
0.0052	67.4	0.3043	53.3	2.4681	45.9
0.0078	65.8	0.3535	52.9	2.7821	45.5
0.0104	64.8	0.4023	52.5	3.0756	45.2
0.0208	62.8	0.4507	52.0	3.3504	45.0
0.0260	62.1	0.4986	51.6	3.6084	44.8
0.0389	60.6	0.6167	50.7	3.7316	44.8
0.0518	59.7	0.7324	50.3	3.8511	44.9
0.0647	58.9	0.8457	49.7	3.9670	45.0
0.0776	58.1	0.9567	49.1	4.1890	45.0
0.1032	57.2	1.0654	48.8	4.3988	45.0
0.1288	56.6	1.1720	48.3	4.5971	45.0
0.1542	55.8	1.3789	47.8	4.7851	45.0
		[Na_2Ox] =5.0 x 10^{-3}mol kg^{-1}			
0.0014	70.6	0.3173	53.5	3.4586	44.9
0.0027	69.6	0.4188	52.3	3.5780	45.1
0.0055	67.6	0.5183	51.5	3.6934	45.1
0.0082	66.6	0.7585	50.2	3.8050	45.1
0.0109	65.7	0.9874	49.3	3.9128	45.1
0.0136	64.9	1.2056	48.5	4.0172	45.1
0.0272	62.5	1.4139	48.0	4.1183	45.1
0.0408	61.0	1.6131	47.5	4.2163	45.1
0.0543	59.7	1.8035	47.1	4.3112	45.1
0.0812	58.0	1.9859	46.8	4.4032	45.1
0.1080	57.6	2.3284	46.3	4.4926	45.1
0.1611	55.0	2.4894	46.1	4.5793	45.1
0.2137	54.5	2.9361	45.6	3.4586	44.9
0.2658	54.0	3.3350	45.1	3.5780	45.1

Table 3.1(b)- continued

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
		$[Na_2Ox]$ =1.0 x 10^{-2} mol kg^{-1}			
0.0013	65.7	0.2040	53.0	2.4021	43.5
0.0026	64.8	0.2538	52.1	2.6988	43.3
0.0039	63.9	0.3031	51.3	2.9743	43.1
0.0052	63.3	0.4002	50.4	3.2308	43.0
0.0078	62.8	0.4956	49.6	3.4702	43.3
0.0104	61.7	0.7261	47.8	3.6943	43.3
0.0130	61.0	0.9461	46.9	3.9043	43.3
0.0260	60.2	1.3575	45.7	4.1016	43.3
0.0518	57.5	1.7347	44.4	4.2873	43.3
0.1030	55.0	1.9118	44.1		
0.1538	53.6	2.0818	43.7		
		$[Na_2Ox]$ =2.0 x 10^{-2} mol kg^{-1}			
0.0020	65.5	0.3080	51.6	3.3195	43.9
0.0039	64.5	0.3829	51.0	3.5461	43.9
0.0079	63.1	0.4570	50.3	3.7635	43.9
0.0118	62.1	0.6029	49.3	3.9723	43.9
0.0157	61.2	0.7458	48.6	4.1728	43.9
0.0196	60.6	1.0901	46.9	4.3658	43.9
0.0392	58.4	1.4173	46.2	4.5515	43.9
0.0588	57.2	1.7287	45.3	4.7302	43.9
0.0783	56.2	2.0252	44.8	4.9025	43.9
0.1171	54.9	2.3080	44.4	5.0687	43.9
0.1557	53.9	2.5780	44.1		
0.2322	52.6	3.0830	43.7		
		$[Na_2Ox]$ =3.0 x 10^{-2} mol kg^{-1}			
0.0013	65.7	0.2040	53.0	2.4021	43.5
0.0026	64.8	0.2538	52.1	2.6988	43.3

Table 3.1(b)- continued

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[Na_2Ox] =3.0 x 10^{-2} mol kg^{-1}					
0.0039	63.9	0.3031	51.3	2.9743	43.1
0.0052	63.3	0.4002	50.4	3.2308	43.0
0.0078	62.8	0.4956	49.6	3.4702	43.3
0.0104	61.7	0.7261	47.8	3.6943	43.3
0.0130	61.0	0.9461	46.9	3.9043	43.3
0.0260	60.2	1.3575	45.7	4.1016	43.3
0.0518	57.5	1.7347	44.4	4.2873	43.3
0.1030	55.0	1.9118	44.1		
0.1538	53.6	2.0818	43.7		
[Na_2Ox] = 5.0 x 10^{-2} mol kg^{-1}					
0.0018	68.7	0.1457	55.0	1.9051	44.8
0.0037	67.2	0.2174	53.6	2.4290	44.4
0.0074	65.4	0.2883	52.6	2.6741	44.3
0.0110	64.1	0.3585	51.5	2.9090	44.3
0.0147	63.2	0.4280	50.9	3.1342	44.3
0.0184	62.6	0.5649	49.7	3.3503	44.3
0.0367	60.3	0.6990	48.9	3.5580	44.3
0.0550	58.7	1.0228	47.2	3.7575	44.3
0.0732	57.9	1.3310	46.4		
0.1095	56.5	1.6248	45.5		
[Na_2Ox] = 1.0 x 10^{-1} mol kg^{-1}					
0.0010	65.0	0.1208	53.4	1.8963	43.2
0.0020	64.0	0.1603	52.5	2.1319	43.2
0.0041	62.4	0.1994	51.7	2.3510	43.2
0.0061	61.4	0.2381	51.1	2.5553	43.2
0.0082	60.8	0.3145	50.2	2.7462	43.2
0.0102	60.1	0.3895	49.5	2.9251	43.2
0.0204	58.6	0.5709	47.8	3.0929	43.2

Table 3.1(b)- continued

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[Na_2Ox] =1.0 x 10^{-1} mol kg^{-1}					
0.0305	57.2	0.7443	46.8	3.2506	43.2
0.0406	56.6	1.0690	45.5	3.3993	43.2
0.0608	55.5	1.3673	44.4	3.5396	43.2
0.0809	54.6	1.6421	43.6		
[Na_2Ox] =2.0 x 10^{-1} mol kg^{-1}					
0.0012	62.0	0.1947	50.7	1.0851	44.7
0.0049	59.8	0.2425	50.0	1.1672	44.4
0.0074	59.2	0.2899	49.3	1.3280	43.8
0.0099	58.8	0.3836	48.2	1.4067	43.7
0.0123	58.6	0.4759	47.4	1.4843	43.7
0.0247	56.6	0.5668	46.6	1.5609	43.7
0.0370	55.4	0.6564	46.3	1.6364	43.7
0.0493	55.0	0.7447	45.4	1.7109	43.7
0.0737	53.8	0.8316	45.4	1.7844	43.7
0.0981	52.9	0.9174	45.1	1.8569	43.7
0.1466	51.5	1.0018	44.7	1.9285	43.7

Table 3.1(c)- Surface tension (γ) values of SDC in aqueous Sodium Oxalate solution at 308K

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[Na_2Ox] = 0.00mol kg^{-1}					
0.0013	68.8	0.1252	56.7	2.7545	45.8
0.0025	67.2	0.1499	56.0	3.0512	45.5
0.0038	66.7	0.1991	55.2	3.3302	45.1
0.0051	66.0	0.2479	54.5	3.5930	44.7
0.0063	65.5	0.2963	53.8	3.7188	44.4
0.0076	64.9	0.3443	53.4	3.8411	44.4
0.0101	63.7	0.3919	53.0	3.9599	44.5
0.0126	63.2	0.4860	52.0	4.0754	44.6
0.0252	61.7	0.7151	51.0	4.1879	44.6
0.0378	60.5	0.9354	50.0	4.2973	44.6
0.0504	59.6	1.3522	48.7	4.4039	44.6
0.0629	59.0	1.7396	47.9	4.5078	44.6
0.0754	58.3	2.1009	47.0	4.6089	44.6
0.1004	57.4	2.4384	46.4		
[Na_2Ox] =5.0 x 10^{-3} mol kg^{-1}					
0.0019	70.1	0.3006	55.4	3.1153	44.6
0.0038	69.9	0.3741	54.5	3.3643	44.3
0.0077	68.2	0.4470	53.2	3.6044	44.2
0.0115	67.1	0.5907	52.0	3.8359	44.4
0.0153	66.7	0.7319	51.4	4.0595	44.4
0.0191	65.8	1.0744	49.6	4.2755	44.4
0.0382	63.6	1.4026	48.4	4.4843	44.4
0.0572	62.1	1.7173	47.4	4.6861	44.4
0.0762	61.3	2.0194	46.6	4.8815	44.4
0.1140	59.8	2.3096	45.9	5.0706	44.4
0.1517	58.6	2.5885	45.4	5.2538	44.4
0.2265	56.7	2.8569	44.9		

Table 3.1(c)- continued

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[Na_2Ox] =1.0 x 10^{-2} mol kg^{-1}					
0.0024	70.9	0.3825	52.4	3.5645	44.8
0.0049	68.7	0.4757	51.5	3.7236	44.8
0.0098	66.4	0.5680	51.1	3.8794	44.8
0.0146	64.5	0.7498	49.6	4.1816	44.8
0.0195	64.0	0.9281	48.7	4.4718	44.8
0.0244	63.1	1.3588	47.3	4.7509	44.8
0.0487	60.9	1.7694	46.1	5.0194	44.8
0.0729	58.8	2.1612	45.2	5.2779	44.8
0.0971	58.1	2.5356	44.9	5.5270	44.8
0.1453	56.3	2.8935	44.6	5.7671	44.8
0.1932	55.1	3.2362	44.4		
0.2883	53.4	3.4020	44.7		
[Na_2Ox] =2.0 x 10^{-2} mol kg^{-1}					
0.0016	63.9	0.1942	52.3	2.6672	44.3
0.0033	62.7	0.2578	51.5	3.0851	44.0
0.0066	61.6	0.3208	50.7	3.2829	43.7
0.0098	60.6	0.3832	50.2	3.4738	43.8
0.0131	60.0	0.5064	49.5	3.6583	43.8
0.0164	59.4	0.6275	48.8	3.8365	43.8
0.0327	57.4	0.9209	47.7	4.0088	43.8
0.0491	56.5	1.2020	46.5	4.1754	43.8
0.0653	55.6	1.4714	45.7	4.3367	43.8
0.0978	54.3	1.7300	45.4	4.4929	43.8
0.1301	53.5	2.2168	44.7		
[Na_2Ox] =3.0 x 10^{-2} mol kg^{-1}					
0.0013	69.6	0.1491	55.7	2.3287	42.4
0.0025	69.1	0.1978	54.6	3.0100	41.3

Table 3.1(c)- continued

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[Na_2Ox] =3.0 x 10^{-2} mol kg^{-1}					
0.0050	67.4	0.2460	53.7	3.2503	40.0
0.0076	66.3	0.2938	53.0	3.4748	40.0
0.0101	65.3	0.3880	51.7	3.5816	40.0
0.0126	64.7	0.4804	50.8	3.9766	40.0
0.0252	62.0	0.7038	49.1	4.1566	40.0
0.0377	61.0	0.9171	47.0	4.3264	40.0
0.0502	60.0	1.3160	45.2	4.4868	40.0
0.0751	58.4	1.6817	43.9		
0.0999	57.4	2.0181	43.0		
[Na_2Ox] = 5.0 x 10^{-2} mol kg^{-1}					
0.0019	67.8	0.1502	55.0	1.9633	44.3
0.0038	66.5	0.2241	53.3	2.2391	43.9
0.0076	64.4	0.2973	52.3	2.5028	43.6
0.0114	63.5	0.3697	51.6	2.7551	43.4
0.0152	62.6	0.4413	50.9	2.9968	43.4
0.0190	62.0	0.5824	49.8	3.2286	43.4
0.0379	59.9	0.7207	48.9	3.4510	43.4
0.0567	58.8	1.0543	47.1	3.6646	43.4
0.0755	57.5	1.3719	46.0	3.8699	43.4
0.1130	56.0	1.6746	44.8		
[Na_2Ox] = 1.0 x 10^{-1} mol kg^{-1}					
0.0017	69.0	0.0998	56.3	1.2234	46.1
0.0033	67.8	0.1327	55.2	1.4967	45.3
0.0067	65.9	0.1981	53.5	1.7587	44.8
0.0100	64.4	0.2630	52.4	2.0100	44.4
0.0134	63.7	0.3272	51.8	2.2512	44.4

Table 3.1(c)- continued

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[Na_2Ox] =1.0 x 10^{-1} mol kg^{-1}					
0.0167	63.1	0.3908	50.9	2.4830	44.4
0.0334	60.4	0.5163	49.5	2.7058	44.4
0.0501	59.2	0.6395	48.9	2.9202	44.4
0.0667	57.8	0.9379	47.1	3.1268	44.4
[Na_2Ox] =2.0 x 10^{-1} mol kg^{-1}					
0.0013	62.7	0.2003	49.6	1.1978	43.6
0.0025	61.2	0.2494	49.0	1.2806	43.4
0.0051	59.3	0.2981	48.3	1.3622	43.2
0.0076	58.5	0.3943	47.3	1.4427	43.1
0.0102	58.0	0.4891	46.5	1.5221	43.1
0.0127	58.0	0.5824	46.0	1.6003	43.1
0.0254	55.6	0.6743	45.4	1.6774	43.1
0.0380	54.6	0.7649	45.0	1.7535	43.1
0.0507	54.0	0.8540	44.6	1.8285	43.1
0.0759	52.6	0.9419	44.2	1.9025	43.1
0.1009	51.8	1.0284	44.0	1.9756	43.1
0.1508	50.5	1.1137	43.7	1.1978	43.6

Table 3.1(d)- Surface tension (γ) values of SDC in aqueous Sodium Oxalate solution at 313K

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[Na_2Ox] = 0.00mol kg^{-1}					
0.0013	68.0	0.2001	55.2	3.6264	44.9
0.0025	67.0	0.2490	54.3	3.7417	44.8
0.0038	66.4	0.2975	53.5	3.8536	44.7
0.0051	65.6	0.3455	53.0	3.9623	44.6
0.0064	65.0	0.3931	52.6	4.0678	44.5
0.0076	64.6	0.4404	52.4	4.1703	44.3
0.0102	63.7	0.4872	51.9	4.2699	44.4
0.0127	63.1	0.7153	50.3	4.3669	44.5
0.0153	62.6	0.9340	49.4	4.4611	44.6
0.0254	61.3	1.3453	48.2	4.5528	44.6
0.0381	59.8	1.7250	47.4	4.6421	44.6
0.0507	59.1	2.0769	46.7	4.7289	44.6
0.0633	58.5	2.4036	46.2	4.8136	44.6
0.0759	58.0	2.7080	45.7	4.8961	44.6
0.1009	57.1	2.9921	45.5	4.9766	44.6
0.1259	56.5	3.2581	45.2	5.0550	44.6
0.1507	56.0	3.5074	45.0		
[Na_2Ox] =5.0 x 10^{-3} mol kg^{-1}					
0.0022	68.9	0.5084	52.5	4.2422	44.3
0.0044	68.3	0.6711	51.3	4.4812	44.3
0.0131	66.1	0.8306	50.0	4.7113	44.3
0.0175	65.2	1.2157	48.2	4.9329	44.3
0.0218	64.6	1.5827	46.8	5.1465	44.3
0.0436	62.3	1.9327	46.1	5.3525	44.3
0.0653	60.9	2.2670	45.7	5.5514	44.3
0.0869	60.1	2.5865	45.3	5.7434	44.3
0.1301	58.2	2.8922	44.6	5.9290	44.3
0.1730	57.3	3.1850	44.5	6.1084	44.3
0.2581	56.0	3.4657	44.4	6.2819	44.3

Table 3.1(d)- continued

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[Na_2Ox] =5.0 x 10^{-3} mol kg^{-1}					
0.3424	54.7	3.7350	44.0	6.4499	44.3
0.4258	53.4	3.9936	44.1	5.9290	44.3
[Na_2Ox] =1.0 x 10^{-2} mol kg^{-1}					
0.0013	69.0	0.2092	54.8	2.1495	44.4
0.0027	68.9	0.2603	53.8	2.3195	44.1
0.0053	67.4	0.3109	52.8	2.7931	43.5
0.0080	66.4	0.4107	51.3	3.3503	42.9
0.0107	65.5	0.5087	50.5	3.4782	43.0
0.0133	64.9	0.7459	48.6	4.0589	43.3
0.0266	62.3	0.9728	47.8	4.2672	43.3
0.0531	59.8	1.3979	46.2	4.5574	43.3
0.1056	57.3	1.7888	45.0		
[Na_2Ox] =2.0 x 10^{-2} mol kg^{-1}					
0.0017	68.9	0.2050	54.3	2.2724	45.0
0.0035	68.1	0.2718	53.5	2.4995	44.5
0.0069	66.3	0.3379	52.6	2.7167	44.2
0.0104	64.9	0.4034	51.4	3.1239	44.1
0.0139	64.0	0.5321	50.6	3.3150	43.7
0.0173	63.2	0.6581	49.3	3.4984	43.3
0.0346	60.6	0.9617	47.9	3.5874	43.1
0.0519	59.1	1.2501	47.1	3.8441	43.4
0.0691	58.3	1.5244	46.3	4.0071	43.5
0.1033	56.7	1.7857	45.8	4.1641	43.5
0.1374	55.3	2.0347	45.3	4.3154	43.5
[Na_2Ox] =3.0 x 10^{-2} mol kg^{-1}					
0.0022	63.6	0.2578	51.5	2.6352	43.8
0.0044	62.9	0.3423	50.7	2.9544	43.6

Table 3.1(d)- continued

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[Na$_2$Ox] =3.0 x 10^{-2} mol kg^{-1}					
0.0087	61.6	0.4259	49.9	3.2617	43.4
0.0131	60.4	0.5089	49.4	3.4702	43.2
0.0174	59.6	0.6727	48.4	3.5579	43.2
0.0218	59.2	0.8336	47.8	3.8433	43.2
0.0651	55.6	1.2242	46.5	4.1187	43.2
0.0867	54.9	1.5987	45.6	4.3845	43.2
0.1298	53.6	1.9581	44.6	4.6412	43.2
0.1726	52.7	2.3034	44.4		
[Na$_2$Ox] = 5.0 x 10^{-2} mol kg^{-1}					
0.0018	68.9	0.2165	54.1	3.3974	43.0
0.0037	68.3	0.2872	52.9	3.8195	43.0
0.0073	66.7	0.3573	51.7	4.2119	43.0
0.0110	65.5	0.4267	50.7	4.5777	43.0
0.0146	64.6	0.5637	49.3	4.9195	43.0
0.0183	63.7	0.6980	48.4	5.2396	43.0
0.0365	61.5	1.0232	46.5	5.5400	43.0
0.0547	59.7	1.3339	45.5	5.8224	43.0
0.0729	58.3	1.9157	43.9	6.0885	43.0
0.1090	56.7	2.4500	43.3		
0.1450	55.2	2.9423	43.0		
[Na$_2$Ox] = 1.0 x 10^{-1} mol kg^{-1}					
9.5x10^{-4}	65.9	0.1119	53.5	1.7497	43.0
0.0019	64.7	0.1484	52.8	1.9662	42.6
0.0038	63.1	0.1846	52.0	2.1672	42.3
0.0057	61.8	0.2205	51.3	2.3545	42.3
0.0076	61.2	0.2912	50.1	2.5294	42.3
0.0094	60.7	0.3606	49.5	2.6930	42.3

Table 3.1(d)- continued

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[Na_2Ox] =1.0 x 10^{-1} mol kg^{-1}					
0.0189	58.8	0.5283	47.9	2.8464	42.3
0.0283	57.7	0.6886	46.5	2.9906	42.3
0.0377	56.8	0.9882	45.1	3.1264	42.3
0.0563	55.6	1.2631	44.2	3.2544	42.3
0.0749	54.9	1.5161	43.4		
[Na_2Ox] =2.0 x 10^{-1} mol kg^{-1}					
0.0014	62.0	0.1139	52.2	0.9526	44.6
0.0029	61.1	0.1701	50.2	1.0491	44.3
0.0057	59.7	0.2257	49.4	1.2372	43.9
0.0086	59.1	0.2808	48.3	1.3288	43.7
0.0115	58.5	0.3354	47.9	1.4188	43.5
0.0144	58.1	0.4430	47.2	1.5073	43.4
0.0287	56.4	0.5487	46.4	1.5944	43.4
0.0430	54.9	0.6525	45.9	1.6800	43.4
0.0572	54.1	0.7543	45.4	0.9526	44.6
0.0857	52.7	0.8543	44.9		

Table 3.1(e)- Surface tension (γ) values of SDC in aqueous Sodium Salicylate solution at 298K

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[NaSa] =5.0 x 10^{-3}mol kg^{-1}					
0.0031	65.9	0.1867	52.0	2.2427	45.0
0.0063	63.5	0.2482	51.2	2.7304	45.4
0.0125	60.7	0.3700	50.2	3.1932	45.4
0.0188	59.6	0.4905	49.3	3.6333	45.4
0.0251	58.6	0.6096	48.7	4.0520	45.4
0.0313	57.7	0.7273	47.8	4.4510	45.4
0.0626	55.8	0.9586	47.2	4.8316	45.4
0.0938	54.6	1.1847	46.6	5.1951	45.4
0.1248	53.6	1.7282	45.5		
[NaSa] =1.0 x 10^{-2}mol kg^{-1}					
0.0037	63.1	0.5740	48.6	3.3452	45.5
0.0073	61.8	0.7138	47.9	3.5689	45.5
0.0147	59.7	0.8521	47.7	3.7886	45.5
0.0220	58.5	1.1244	46.6	4.0042	45.5
0.0293	57.5	1.3913	45.9	4.2159	45.5
0.0366	57.0	1.6527	45.2	4.4238	45.5
0.0731	54.9	1.9089	45.0	4.6280	45.5
0.1095	54.0	2.1601	45.0	4.8286	45.5
0.1458	53.0	2.4064	45.5	5.0257	45.5
0.2181	51.7	2.6479	45.5	5.2194	45.5
0.2900	51.1	2.8848	45.5	5.4098	45.5
0.4328	50.0	3.1172	45.5		
[NaSa] =2.0 x 10^{-2}mol kg^{-1}					
0.0031	66.4	0.1869	51.2	2.2825	43.5
0.0063	63.9	0.2485	50.4	2.7898	43.5
0.0125	61.4	0.3710	49.2	3.2752	43.5
0.0188	59.8	0.4922	48.1	3.7399	43.5
0.0251	59.2	0.6123	47.3	4.1853	43.5

Table 3.1(e)- continued

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaSa] =2.0 x 10^{-2} mol kg^{-1}			
0.0313	57.9	0.7312	46.9	4.6126	43.5
0.0626	55.8	0.9656	45.6	5.0228	43.5
0.0938	53.8	1.1955	44.7		
0.1249	52.8	1.7516	43.3		
		[NaSa] =3.0 x 10^{-2} mol kg^{-1}			
0.0015	70.4	0.1809	52.8	2.1006	44.8
0.0031	68.3	0.2403	52.0	2.5371	44.8
0.0061	65.6	0.2992	50.9	2.7445	44.9
0.0092	64.1	0.3576	50.5	2.9452	44.8
0.0122	63.0	0.4730	49.5	3.1394	44.8
0.0152	61.9	0.5866	49.0	3.3274	44.8
0.0305	59.5	0.8631	47.7	3.5095	44.8
0.0456	57.7	1.1292	46.8	3.6861	44.8
0.0608	56.9	1.3855	46.1	3.8574	44.8
0.0910	55.3	1.6325	45.7		
0.1211	54.0	1.8707	44.8		
		[NaSa] =5.0 x 10^{-2} mol kg^{-1}			
0.0019	66.9	0.1103	52.8	1.3352	44.3
0.0037	64.8	0.1466	51.9	1.6286	43.9
0.0074	62.5	0.2187	50.3	1.9082	43.8
0.0111	61.2	0.2901	49.5	2.1749	43.8
0.0148	60.0	0.3606	48.4	2.4295	43.8
0.0185	59.2	0.4304	47.9	2.6728	43.8
0.0370	57.0	0.5679	47.0	2.9057	43.8
0.0554	55.5	0.7024	46.2		
0.0737	54.7	1.0269	45.2		

Table 3.1(e)- continued

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[NaSa] =1.0 x 10^{-1} mol kg^{-1}					
0.0025	67.5	0.1467	53.0	1.7731	44.3
0.0049	65.0	0.1951	52.0	2.1618	44.3
0.0099	62.7	0.2910	50.1	2.5317	44.3
0.0148	61.3	0.3858	49.6	2.8843	44.3
0.0197	60.2	0.4796	48.9	3.2207	44.3
0.0246	59.2	0.5724	48.2	3.5420	44.3
0.0492	56.9	0.7550	47.2	3.8492	44.3
0.0737	55.7	0.9337	46.4		
0.0981	54.6	1.3643	45.1		
[NaSa] =2.0 x 10^{-1} mol kg^{-1}					
0.0033	66.0	0.1953	53.0	1.2470	46.7
0.0066	64.1	0.2597	51.9	1.3650	46.4
0.0131	62.5	0.3876	50.5	1.4817	46.1
0.0197	60.9	0.5141	50.0	1.5973	46.1
0.0262	60.0	0.6394	49.4	1.7119	46.1
0.0328	59.3	0.7634	48.2	1.8252	46.1
0.0654	57.2	0.8861	48.0	2.1040	46.1
0.0980	55.7	1.0076	47.6	2.3762	46.1
0.1305	54.9	1.1279	47.1		
[NaSa] =4.0 x 10^{-1} mol kg^{-1}					
0.0030	53.9	0.1799	47.2	1.1528	43.1
0.0060	53.2	0.2393	46.5	1.2623	42.8
0.0121	52.0	0.3572	45.6	1.3709	42.6
0.0181	51.5	0.4740	44.9	1.4784	42.5
0.0241	51.2	0.5898	44.4	1.5851	42.5
0.0302	51.0	0.7045	44.2	1.6907	42.5
0.0602	49.6	0.8181	43.8	1.9508	42.5

Table 3.1(e)- continued

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaSa] =4.0 x 10^{-1} mol kg^{-1}			
0.0903	48.8	0.9307	43.5	2.2053	42.5
0.1202	48.0	1.0422	43.3	2.4543	42.5

Table 3.1(f)- Surface tension (γ) values of SDC in aqueous Sodium Salicylate solution at 303K

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaSa] =5.0 x 10^{-3}mol kg^{-1}			
0.0028	67.1	0.2197	52.3	2.8745	44.4
0.0056	64.7	0.3279	51.1	3.2786	44.1
0.0111	61.5	0.4349	50.5	3.6651	44.2
0.0166	59.3	0.5409	49.5	4.0352	44.3
0.0222	59.4	0.6457	49.2	4.3897	44.3
0.0277	58.2	0.8522	48.1	4.7296	44.3
0.0554	56.3	1.0545	47.5	5.0559	44.3
0.0829	55.6	1.5430	46.2	5.3693	44.3
0.1105	54.5	2.0081	45.3		
0.1652	53.2	2.4514	44.8		
		[NaSa] =1.0 x 10^{-2}mol kg^{-1}			
0.0031	63.7	0.4934	50.1	2.9180	44.1
0.0063	62.5	0.6140	49.3	3.1170	44.4
0.0126	61.3	0.7336	48.7	3.3126	44.4
0.0188	60.1	0.9694	47.8	3.5052	44.4
0.0251	59.3	1.2011	47.2	3.6947	44.4
0.0314	58.7	1.4288	46.5	3.8811	44.4
0.0627	57.0	1.6526	46.0	4.0648	44.4
0.0939	55.5	1.8725	45.4	4.2455	44.4
0.1251	54.6	2.0887	45.2	4.4235	44.4
0.1872	53.3	2.3013	44.9	4.5988	44.4
0.2490	52.8	2.5103	44.5	4.7713	44.4
0.3718	50.9	2.7158	44.3		
		[NaSa] =2.0 x 10^{-2}mol kg^{-1}			
0.0034	66.6	0.2020	51.4	2.4505	42.8
0.0068	64.5	0.2686	50.9	2.9903	43.6
0.0136	61.6	0.4007	49.6	3.5051	43.6
0.0203	60.2	0.5315	48.4	3.9965	43.7

Table 3.1(f)- continued

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[NaSa] =2.0 x 10^{-2} mol kg^{-1}					
0.0271	59.2	0.6609	47.9	4.4661	43.8
0.0339	58.5	0.7889	47.1	4.9153	43.8
0.0677	56.2	1.0410	46.0	5.3454	43.8
0.1014	54.3	1.2880	45.3		
0.1350	53.2	1.8837	43.7		
[NaSa] =3.0 x 10^{-2} mol kg^{-1}					
0.0020	65.8	0.1545	51.4	1.4145	41.2
0.0039	63.6	0.2306	49.7	1.7274	40.4
0.0078	61.5	0.3059	48.6	2.0264	39.8
0.0117	60.6	0.3805	47.1	2.3122	39.0
0.0156	59.5	0.4543	46.3	2.5857	39.0
0.0195	59.2	0.5996	44.9	2.8476	39.0
0.0389	56.4	0.7421	44.0	3.0988	39.0
0.0583	55.5	0.9164	43.2	3.3399	39.0
0.0777	54.8	1.0864	42.4		
0.1162	52.7	1.2524	41.7		
[NaSa] =5.0 x 10^{-2} mol kg^{-1}					
0.0018	68.2	0.1414	52.7	1.8492	43.9
0.0036	65.9	0.2110	51.4	2.1092	43.6
0.0071	63.5	0.2799	50.0	2.3577	43.4
0.0107	62.1	0.3480	48.7	2.5956	43.4
0.0143	61.3	0.4155	48.9	2.8234	43.4
0.0178	60.6	0.5484	47.4	3.0420	43.4
0.0356	57.7	0.6785	46.7	3.2518	43.4
0.0534	56.3	0.9928	45.5	3.4533	43.4
0.0711	55.3	1.2920	44.8	3.6470	43.4
0.1063	53.6	1.5771	44.2	3.8333	43.4

Table 3.1(f)- continued

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[NaSa] =1.0 x 10^{-1} mol kg^{-1}					
0.0024	67.5	0.1878	52.5	2.4494	44.5
0.0047	65.5	0.2801	51.0	2.7927	44.5
0.0095	63.2	0.3715	49.8	3.1207	44.5
0.0142	61.5	0.4620	49.2	3.4344	44.5
0.0190	60.7	0.5515	48.6	3.7347	44.5
0.0237	59.8	0.7277	47.9	4.0226	44.5
0.0473	57.7	0.9003	47.3	4.2987	44.5
0.0709	56.3	1.3166	46.3	4.5637	44.5
0.0944	54.8	1.7127	45.2		
0.1412	53.3	2.0898	44.5		
[NaSa] =2.0 x 10^{-1} mol kg^{-1}					
0.0033	66.4	0.2918	51.8	1.5107	46.3
0.0066	64.5	0.4193	50.5	1.6261	46.0
0.0131	63.0	0.5455	49.5	1.7403	45.8
0.0197	61.9	0.6705	49.1	1.8534	45.8
0.0262	61.1	0.7942	48.4	1.9655	45.8
0.0328	60.2	0.9166	48.0	2.1040	45.8
0.0654	57.6	1.0378	47.5	2.3762	45.8
0.0980	55.6	1.1578	47.1	2.6420	45.8
0.1630	53.7	1.2766	46.8		
0.2275	52.9	1.3942	46.5		
[NaSa] =4.0 x 10^{-1} mol kg^{-1}					
0.0032	61.1	0.1913	51.0	1.2231	45.0
0.0064	60.0	0.2544	50.3	1.3390	44.8
0.0128	59.0	0.3798	48.9	1.4537	44.6
0.0193	58.3	0.5038	47.8	1.5674	44.4
0.0257	57.3	0.6267	47.0	1.6800	44.4

Table 3.1(f)- continued

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaSa] =4.0 x 10^{-1} mol kg^{-1}			
0.0321	56.5	0.7483	46.6	1.7915	44.4
0.0641	54.4	0.8688	46.2	2.0657	44.4
0.0960	53.2	0.9880	45.8	2.3337	44.4
0.1279	52.4	1.1061	45.4		

Table 3.1(g)- Surface tension (γ) values of SDC in aqueous Sodium Salicylate solution at 308K

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[NaSa] =5.0 x 10^{-3}mol kg^{-1}					
0.0030	66.7	0.1782	53.0	2.1507	45.4
0.0060	64.5	0.2369	51.9	2.6212	44.8
0.0120	62.3	0.3534	50.7	3.0687	44.2
0.0180	60.7	0.4686	49.3	3.4949	44.2
0.0239	59.9	0.5825	49.4	3.9013	44.3
0.0299	58.9	0.6951	48.5	4.2892	44.5
0.0597	56.7	0.9167	47.9	4.6598	44.5
0.0895	55.2	1.1335	47.3	5.0144	44.5
0.1191	54.5	1.6555	46.3		
[NaSa] =1.0 x 10^{-2}mol kg^{-1}					
0.0030	68.9	0.4737	51.9	2.8116	44.6
0.0060	67.2	0.5895	51.1	3.0042	44.2
0.0120	65.2	0.7044	50.1	3.1938	44.3
0.0181	63.9	0.9313	49.0	3.3804	44.3
0.0241	62.9	1.1543	47.8	3.5643	44.3
0.0301	62.3	1.3735	47.0	3.7452	44.3
0.0601	59.8	1.5892	46.4	3.9236	44.3
0.0901	57.8	1.8013	45.8	4.0992	44.3
0.1200	57.2	2.0100	45.3	4.2722	44.3
0.1796	55.5	2.2152	45.2	4.4426	44.3
0.2389	54.8	2.4172	44.8		
0.3568	53.0	2.6160	44.7		
[NaSa] =2.0 x 10^{-2}mol kg^{-1}					
0.0038	65.0	0.2259	51.2	2.7116	43.4
0.0076	62.4	0.3003	50.5	3.3006	43.9
0.0152	60.3	0.4477	49.0	3.8594	43.9
0.0228	58.4	0.5935	47.8	4.3905	43.9

Table 3.1(g)- continued

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[NaSa] =2.0 x 10^{-2} mol kg^{-1}					
0.0304	57.7	0.7375	47.3	4.8955	43.9
0.0379	57.3	0.8798	46.6	5.3768	43.9
0.0757	54.7	1.1596	45.8	5.8357	43.9
0.1135	53.5	1.4330	45.2		
0.1510	52.2	2.0900	43.9		
[NaSa] =3.0 x 10^{-2} mol kg^{-1}					
0.0019	69.1	0.1530	53.1	2.0152	45.0
0.0039	67.2	0.2283	51.9	2.3010	44.7
0.0077	64.9	0.3029	51.0	2.5750	44.6
0.0116	63.6	0.3768	49.9	2.8378	44.4
0.0154	62.6	0.4500	49.4	3.0901	44.4
0.0193	61.7	0.5942	48.5	3.3324	44.4
0.0385	59.1	0.7356	47.9	3.5655	44.4
0.0577	57.1	1.0778	46.6	3.7897	44.4
0.0769	56.0	1.4045	45.7	4.0058	44.4
0.1150	54.7	1.7166	45.3		
[NaSa] =5.0 x 10^{-2} mol kg^{-1}					
0.0015	68.2	0.1809	52.1	2.0695	43.9
0.0031	66.5	0.2402	51.0	2.2843	43.8
0.0061	64.5	0.2989	50.2	2.4912	43.5
0.0092	63.2	0.3571	49.9	2.6905	43.5
0.0122	62.1	0.4720	48.7	2.8827	43.5
0.0153	61.2	0.5848	48.0	3.0682	43.5
0.0305	58.9	0.8586	46.5	3.2473	43.5
0.0457	57.1	1.1209	45.7	3.4203	43.5
0.0609	56.2	1.3726	44.5	3.5876	43.5
0.0911	55.1	1.6142	44.6	3.7493	43.5

Table 3.1(g)- continued

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[NaSa] =5.0 x 10^{-2} mol kg^{-1}					
0.1212	53.8	1.8463	44.0		
[NaSa] =1.0 x 10^{-1} mol kg^{-1}					
0.0025	66.6	0.0987	54.2	0.9395	45.7
0.0050	63.5	0.1476	52.4	1.3725	44.2
0.0099	61.7	0.1963	51.7	1.7835	43.5
0.0149	60.7	0.2928	49.7	2.1742	42.9
0.0198	59.9	0.3883	48.5	2.5458	42.9
0.0248	59.0	0.4827	47.9	2.9000	42.9
0.0495	56.6	0.5760	47.2	3.2379	42.9
0.0741	55.0	0.7597	46.1		
[NaSa] =2.0 x 10^{-1} mol kg^{-1}					
0.0033	64.4	0.2644	52.2	1.5069	46.2
0.0067	63.0	0.3945	51.0	1.6244	46.0
0.0134	61.2	0.5232	49.8	1.7407	45.7
0.0200	60.4	0.6506	49.1	1.8558	45.5
0.0267	59.6	0.7767	48.5	2.1388	45.5
0.0334	59.3	0.9016	47.9	2.4150	45.5
0.0666	56.9	1.0251	47.5	2.6847	45.5
0.0998	55.6	1.1474	47.1	2.9479	45.5
0.1329	54.7	1.2684	46.7		
0.1988	53.2	1.3883	46.5		
[NaSa] =4.0 x 10^{-1} mol kg^{-1}					
0.0032	60.5	0.1907	49.3	1.2193	43.9
0.0064	58.9	0.2536	48.5	1.3348	43.6
0.0128	57.5	0.3785	47.4	1.4492	43.4
0.0192	56.4	0.5022	46.6	1.5625	43.3

Table 3.1(g)- continued

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaSa] =4.0 x 10^{-1} mol kg^{-1}			
0.0256	55.6	0.6246	45.8	1.6748	43.0
0.0320	55.0	0.7459	45.3	1.7860	43.0
0.0639	52.7	0.8660	45.0	2.0594	43.0
0.0957	51.5	0.9849	44.5	2.3266	43.0
0.1274	50.7	1.1026	44.2		

Table 3.1(h)– Surface tension (γ) values of SDC in aqueous Sodium Salicylate solution at 313K

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[NaSa] =5.0 x 10^{-3}mol kg^{-1}					
0.0032	66.9	0.2551	52.3	3.2693	43.7
0.0065	64.4	0.3803	51.2	3.7176	43.3
0.0129	62.7	0.5040	49.9	4.1437	43.7
0.0193	60.7	0.6262	49.1	4.5493	44.2
0.0258	60.4	0.7470	48.5	4.9357	44.2
0.0322	59.5	0.9844	47.4	5.3044	44.2
0.0644	57.1	1.2162	46.8	5.6567	44.2
0.0964	55.7	1.7728	45.6	5.9932	44.2
0.1283	55.1	2.2990	44.8		
0.1919	53.2	2.7970	44.3		
[NaSa] =1.0 x 10^{-2}mol kg^{-1}					
0.0026	67.9	0.5141	51.4	2.7586	44.7
0.0053	66.3	0.6140	50.3	2.9179	44.5
0.0105	65.1	0.8110	49.2	3.0745	44.5
0.0158	63.7	1.0044	48.3	3.2285	44.3
0.0210	62.7	1.1943	47.8	3.3799	44.7
0.0263	62.1	1.3807	47.0	3.5290	44.7
0.0525	60.1	1.5638	46.4	3.6756	44.7
0.0787	58.9	1.7436	45.9	3.8200	44.7
0.1048	57.9	1.9202	45.7	3.9620	44.7
0.1568	55.8	2.0938	45.4	4.1018	44.7
0.2086	54.8	2.2643	44.9	4.2394	44.7
0.3114	53.4	2.4319	44.9		
0.4132	52.0	2.5967	45.1		
[NaSa] =2.0 x 10^{-2}mol kg^{-1}					
0.0032	66.9	0.1934	51.3	2.3554	44.2
0.0065	64.5	0.2572	50.7	2.8769	43.7
0.0130	62.1	0.3839	49.9	3.3752	43.7
0.0195	60.7	0.5092	48.9	3.8516	43.9

Table 3.1(h)- continued

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaSa] =2.0 x 10^{-2} mol kg^{-1}			
0.0260	59.8	0.6333	48.4	4.3076	43.9
0.0324	59.2	0.7562	47.2	4.7445	43.9
0.0648	56.5	0.9982	47.0	5.1636	43.9
0.0971	55.2	1.2355	46.1		
0.1293	52.9	1.8089	44.8		
		[NaSa] =3.0 x 10^{-2} mol kg^{-1}			
0.0018	68.2	0.2080	51.5	2.3783	44.1
0.0035	66.4	0.2761	50.9	2.6251	43.8
0.0070	64.0	0.3435	50.3	2.8628	43.6
0.0105	62.3	0.4104	49.4	3.0918	43.6
0.0140	61.5	0.5424	48.9	3.3126	43.6
0.0175	60.3	0.6721	47.9	3.5257	43.6
0.0351	58.4	0.9868	46.6	3.7315	43.6
0.0525	56.8	1.2882	45.6	3.9302	43.6
0.0700	55.8	1.5775	45.3	4.1224	43.6
0.1047	54.5	1.8551	44.5		
0.1393	53.1	2.1218	44.3		
		[NaSa] =5.0 x 10^{-2} mol kg^{-1}			
0.0019	67.4	0.1143	54.1	1.3932	44.9
0.0038	65.6	0.1520	52.7	1.7021	44.1
0.0077	63.1	0.2269	51.4	1.9972	43.8
0.0115	62.3	0.3010	50.2	2.2796	43.3
0.0153	61.4	0.3743	49.5	2.5500	42.9
0.0192	60.4	0.4470	48.6	2.8092	42.9
0.0383	58.1	0.5901	47.8	3.0578	42.9
0.0574	56.7	0.7305	46.6	3.2965	42.9
0.0764	55.9	1.0697	45.8		

Table 3.1(h)- continued

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaSa] = 1.0 x 10^{-1} mol kg^{-1}			
0.0023	66.1	0.1390	52.8	1.6887	43.3
0.0047	64.2	0.1849	51.6	2.0612	43.0
0.0093	62.6	0.2759	50.3	2.4167	42.3
0.0140	61.1	0.3659	49.2	2.7562	42.3
0.0187	60.4	0.4550	49.3	3.0808	42.3
0.0233	59.5	0.5432	47.6	3.3915	42.3
0.0466	57.0	0.7169	46.2	3.6891	42.3
0.0698	55.4	0.8870	45.3	3.9744	42.3
0.0929	54.3	1.2977	44.4	4.2482	42.3
		[NaSa] =2.0 x 10^{-1} mol kg^{-1}			
0.0032	64.2	0.2542	52.0	1.4520	45.8
0.0064	62.6	0.3795	50.7	1.5655	45.6
0.0128	61.5	0.5034	49.7	1.6779	45.3
0.0192	60.4	0.6261	48.7	1.7892	45.1
0.0257	59.8	0.7476	48.1	2.0630	44.6
0.0321	59.2	0.8679	47.6	2.3303	44.6
0.0640	57.3	0.9870	47.0	2.5916	44.6
0.0959	55.8	1.1050	47.0	2.8470	44.6
0.1278	55.0	1.2218	46.5	3.0966	44.6
0.1912	53.4	1.3375	46.1		
		[NaSa] =4.0 x 10^{-1} mol kg^{-1}			
0.0030	61.0	0.2366	49.1	1.3561	43.3
0.0060	59.4	0.3532	47.6	1.4626	43.1
0.0119	58.2	0.4687	46.7	1.5681	42.8
0.0179	57.1	0.5832	46.1	1.6727	42.6
0.0239	56.2	0.6967	45.5	1.7765	42.4
0.0298	55.6	0.8091	44.9	1.8793	42.3
0.0596	53.3	0.9205	44.5	1.9812	42.3

Table 3.1(h)- continued

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaSa] =4.0 x 10^{-1} mol kg^{-1}			
0.0892	52.0	1.0309	44.1	2.1824	42.3
0.1188	50.9	1.1402	43.8	2.4290	42.3
0.1778	49.9	1.2486	43.5	2.6705	42.3

Table 3.1(i)- Surface tension (γ) values of SDC in aqueous Sodium Chloride solution at 298K

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaCl] =5.0 x 10^{-3}mol kg^{-1}			
0.0030	65.7	0.4732	49.9	1.7760	45.6
0.0060	63.4	0.5882	49.2	1.8774	45.3
0.0121	61.7	0.7021	48.8	1.9777	45.1
0.0181	60.1	0.8147	48.3	2.0770	45.2
0.0242	59.1	0.9261	47.9	2.1753	45.2
0.0302	58.6	1.0363	47.3	2.2726	45.2
0.0603	56.4	1.1453	47.1	2.3690	45.2
0.0903	55.1	1.2532	46.7	2.4643	45.2
0.1203	54.1	1.3599	46.4	2.5588	45.2
0.1799	52.9	1.4656	46.2	2.6523	45.2
0.2392	51.9	1.5701	46.0		
0.3568	50.6	1.6736	45.8		
		[NaCl] =1.0 x 10^{-2}mol kg^{-1}			
0.0030	66.8	0.2377	52.5	1.3614	46.5
0.0060	63.8	0.3549	50.8	1.4682	46.4
0.0120	61.5	0.4710	49.8	1.5740	46.1
0.0180	60.2	0.5860	49.1	1.6788	45.9
0.0240	59.3	0.6999	48.7	1.7827	46.1
0.0300	58.6	0.8127	48.3	1.8857	46.1
0.0599	56.5	0.9245	47.8	1.9878	46.1
0.0897	55.4	1.0352	47.3	2.0890	46.1
0.1194	54.6	1.1450	47.2	2.1892	46.1
0.1787	53.3	1.2537	47.0	2.2886	46.1
		[NaCl] =2.0 x 10^{-2}mol kg^{-1}			
0.0027	66.7	0.2175	51.7	1.2441	45.4
0.0055	64.2	0.3247	50.2	1.3415	45.2
0.0110	61.5	0.4308	49.0	1.4380	44.8
0.0165	60.3	0.5359	48.4	1.5336	44.5

Table 3.1(i)- continued

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[NaCl] =2.0 x 10^{-2} mol kg^{-1}					
0.0219	59.3	0.6400	47.8	1.6283	44.3
0.0274	58.5	0.7431	47.3	1.7221	44.5
0.0548	55.9	0.8452	46.6	1.8152	44.5
0.0821	54.7	0.9463	46.4	1.9073	44.5
0.1093	53.7	1.0465	46.0	1.9987	44.5
0.1635	52.4	1.1458	45.6	2.0892	44.5
[NaCl] =3.0 x 10^{-2} mol kg^{-1}					
0.0034	62.1	0.2010	50.6	1.2851	44.3
0.0068	60.6	0.2674	49.6	1.4068	43.9
0.0135	58.8	0.3991	48.3	1.5273	43.6
0.0202	58.2	0.5294	47.4	1.6467	43.8
0.0270	57.0	0.6585	46.6	1.7649	43.8
0.0337	56.6	0.7863	46.0	1.8821	43.8
0.0674	54.0	0.9129	45.6	1.9981	43.8
0.1009	52.8	1.0381	45.0	2.1131	43.8
0.1344	51.9	1.1622	44.6	2.2269	43.8
[NaCl] =5.0 x 10^{-2} mol kg^{-1}					
0.0029	66.7	0.2318	51.0	1.3273	44.5
0.0058	64.3	0.3460	49.3	1.4314	44.3
0.0088	62.8	0.4592	48.4	1.5345	44.3
0.0117	61.9	0.5713	47.6	1.6368	44.3
0.0175	60.3	0.6823	47.1	1.7381	44.3
0.0234	59.3	0.7923	46.5	1.8385	44.3
0.0292	58.4	0.9013	46.0	1.9380	44.3
0.0584	55.9	1.0093	45.5	2.0366	44.3
0.1164	53.5	1.1163	45.0		
0.1743	52.0	1.2223	44.7		

Table 3.1(i)- continued

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaCl] =1.0 x 10^{-1} mol kg^{-1}			
0.0035	62.1	0.1380	51.9	1.0637	45.0
0.0069	60.6	0.2064	50.6	1.1905	44.6
0.0139	58.8	0.2745	49.6	1.3160	44.6
0.0208	58.2	0.4096	48.3	1.4401	44.6
0.0277	57.0	0.5432	47.4	1.5630	44.6
0.0346	56.6	0.6754	46.6	1.6847	44.6
0.0692	54.0	0.8062	46.0	1.8051	44.6
0.1036	52.8	0.9356	45.6	1.9243	44.6

Table 3.1(j)- Surface tension (γ) values of SDC in aqueous Sodium Chloride solution at 303K

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[NaCl] =5.0 x 10^{-3}mol kg^{-1}					
0.0029	68.7	0.5743	50.2	1.9339	45.4
0.0059	67.3	0.6855	49.3	2.0312	45.2
0.0118	65.1	0.7956	49.0	2.1276	44.9
0.0177	63.4	0.9045	48.5	2.3644	44.5
0.0236	62.3	1.0123	47.4	2.5956	44.2
0.0295	61.4	1.1189	47.8	2.8212	44.0
0.0588	58.4	1.2244	47.2	3.0416	43.7
0.0881	57.0	1.3289	46.7	3.1283	43.5
0.1174	55.9	1.4323	46.4	3.2569	43.7
0.1756	54.8	1.5347	46.2	3.4672	43.7
0.2335	53.5	1.6360	45.9	3.6727	43.7
0.3483	52.0	1.7363	45.8	3.8736	43.7
0.4619	50.9	1.8356	45.6		
[NaCl] =1.0 x 10^{-2}mol kg^{-1}					
0.0033	65.8	0.5197	48.5	1.9561	44.0
0.0066	64.1	0.6462	47.7	2.0682	43.7
0.0133	62.2	0.7714	47.3	2.1792	43.6
0.0199	60.7	0.8954	46.8	2.2891	43.4
0.0265	59.8	1.0181	46.3	2.3980	43.1
0.0331	58.8	1.1395	46.0	2.6656	42.7
0.0662	56.3	1.2597	45.5	2.9270	42.4
0.0991	54.9	1.3787	45.2	3.1823	42.6
0.1320	53.8	1.4965	45.0	3.4317	42.6
0.1975	52.3	1.6131	44.7	3.6754	42.6
0.2626	51.3	1.7286	44.3	3.9136	42.6
0.3918	49.8	1.8429	44.2		
[NaCl] =2.0 x 10^{-2}mol kg^{-1}					
0.0031	65.6	0.4924	48.3	1.8465	43.6

Table 3.1(j)- continued

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[NaCl] =2.0 x 10^{-2} mol kg^{-1}					
0.0063	64.2	0.6121	47.4	1.9517	43.4
0.0126	61.6	0.7304	46.7	2.0559	43.2
0.0189	60.1	0.8475	46.3	2.1590	43.0
0.0251	59.0	0.9634	45.9	2.2610	42.8
0.0314	58.3	1.0779	45.6	2.5117	42.5
0.0628	55.8	1.1913	45.2	2.7560	42.7
0.0940	54.3	1.3034	44.8	2.9944	42.7
0.1252	53.5	1.4143	44.5	3.2270	42.7
0.1872	51.8	1.5241	44.3	3.4540	42.7
0.2490	50.8	1.6327	44.0	3.6756	42.7
0.3713	49.3	1.7401	43.8		
[NaCl] =3.0 x 10^{-2} mol kg^{-1}					
0.0035	66.6	0.4122	49.0	1.8200	43.1
0.0070	64.6	0.5468	47.9	1.9405	42.9
0.0139	62.8	0.6800	47.1	2.0598	42.6
0.0209	61.3	0.8118	46.3	2.1780	42.4
0.0279	60.2	0.9423	45.7	2.2950	42.2
0.0348	59.3	1.0715	45.1	2.4109	41.9
0.0696	56.4	1.1994	44.7	2.5257	42.2
0.1043	54.8	1.3260	44.2	2.8080	42.2
0.1388	53.6	1.4513	44.1	3.0838	42.2
0.2077	51.8	1.5754	43.7	3.3531	42.2
0.2762	50.6	1.6983	43.4	3.6164	42.2
[NaCl] =5.0 x 10^{-2} mol kg^{-1}					
0.0032	64.7	0.3771	49.3	1.6648	43.5
0.0064	63.2	0.5002	48.5	1.7750	43.3
0.0128	61.7	0.6220	47.4	1.8842	43.0

Table 3.1(j)- continued

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[NaCl] =5.0 x 10^{-2} mol kg^{-1}					
0.0191	60.4	0.7426	46.8	1.9923	42.9
0.0255	59.6	0.8620	46.0	2.0993	42.6
0.0319	58.6	0.9801	45.4	2.2054	42.6
0.0637	56.0	1.0971	45.2	2.3104	42.6
0.0954	54.6	1.2129	44.8	2.5686	42.6
0.1270	53.5	1.3276	44.4	2.8209	42.6
0.1900	51.7	1.4411	44.0	3.0673	42.6
0.2527	50.8	1.5535	43.7		
[NaCl] =1.0 x 10^{-1} mol kg^{-1}					
0.0035	68.7	0.2752	53.5	1.5666	46.7
0.0070	67.3	0.4105	52.0	1.6885	46.4
0.0139	65.1	0.5445	50.9	1.8091	46.2
0.0208	63.4	0.6770	50.2	1.9286	45.9
0.0278	62.3	0.8081	49.3	2.0469	45.6
0.0347	61.4	0.9378	49.0	2.1640	45.6
0.0694	58.4	1.0662	48.5	2.2799	45.6
0.1039	57.0	1.1932	47.4	2.3946	45.6
0.1383	55.9	1.3190	47.8	2.5083	45.6
0.2069	54.8	1.4434	47.2	2.7876	45.6

Table 3.1(k)- Surface tension (γ) values of SDC in aqueous Sodium Chloride solution at 308K

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[NaCl] =5.0 x 10^{-3}mol kg^{-1}					
0.0029	68.0	0.5624	50.6	1.8964	46.2
0.0058	65.5	0.6714	49.8	1.9920	46.0
0.0115	63.8	0.7793	49.2	2.0867	45.8
0.0173	62.4	0.8861	48.9	2.3196	45.5
0.0231	61.6	0.9917	48.3	2.5469	45.0
0.0288	61.1	1.0963	47.7	2.7690	44.8
0.0576	58.5	1.1999	47.8	2.9859	44.6
0.0863	57.1	1.3024	47.1	3.1979	44.3
0.1149	56.1	1.4038	47.3	3.4052	44.3
0.1719	54.6	1.5043	46.9	3.6078	44.6
0.2285	53.6	1.6038	46.7	3.8059	44.6
0.3410	52.2	1.7023	46.5	3.9997	44.6
0.4523	51.1	1.7998	46.3	4.1894	44.6
[NaCl] =1.0 x 10^{-2}mol kg^{-1}					
0.0033	67.3	0.8931	47.5	2.5000	43.7
0.0066	65.4	1.0155	47.2	2.6066	43.6
0.0132	63.8	1.1367	46.6	2.7121	43.4
0.0198	62.6	1.2566	46.1	2.8167	43.2
0.0264	61.5	1.3753	45.9	2.9203	43.1
0.0330	60.5	1.4928	45.8	3.0229	43.0
0.0989	56.3	1.6092	45.2	3.1246	43.2
0.1643	54.4	1.7244	45.0	3.2253	43.2
0.2295	53.2	1.8385	45.2	3.4240	43.2
0.2619	52.6	1.9514	44.6	3.6672	43.2
0.3908	51.0	2.0633	44.6	3.9051	43.2
0.5183	49.9	2.1741	44.3	4.1377	43.2
0.6446	49.0	2.2838	44.1		
0.7695	48.0	2.3924	43.8		

Table 3.1(k)- *continued*

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaCl] =2.0 x 10^{-2} mol kg^{-1}			
0.0032	65.6	0.4934	48.5	1.8501	44.0
0.0063	64.3	0.6134	48.0	1.9556	43.6
0.0126	62.0	0.7320	47.2	2.0599	43.5
0.0189	60.8	0.8493	46.5	2.1632	43.3
0.0252	59.5	0.9653	46.2	2.2654	43.0
0.0315	58.3	1.0801	45.8	2.5164	42.6
0.0629	56.1	1.1937	45.3	2.7612	42.2
0.0942	54.8	1.3060	45.1	2.9999	42.4
0.1254	53.8	1.4172	44.9	3.2329	42.4
0.1876	52.1	1.5271	44.6	3.4603	42.4
0.2495	51.1	1.6359	44.3	3.6822	42.4
0.3721	49.7	1.7436	44.2		
		[NaCl] =3.0 x 10^{-2} mol kg^{-1}			
0.0041	62.0	0.3207	48.7	1.9546	43.3
0.0081	59.9	0.4782	47.6	2.0931	43.1
0.0162	57.8	0.6337	46.8	2.2300	43.0
0.0243	56.6	0.7875	46.1	2.3654	42.8
0.0324	55.7	0.9394	45.5	2.4994	42.6
0.0405	55.0	1.2379	44.8	2.6318	42.3
0.0809	53.0	1.3846	44.4	2.7627	42.5
0.1212	51.8	1.5295	44.0	2.8923	42.5
0.1613	50.9	1.6729	43.7	3.2101	42.5
0.2413	49.6	1.8145	43.5	3.5195	42.5
		[NaCl] =5.0 x 10^{-2} mol kg^{-1}			
0.0031	66.5	0.4788	48.6	1.8082	43.5
0.0061	65.0	0.5956	48.0	1.9123	43.3
0.0122	62.6	0.7112	47.2	2.0155	43.1

Table 3.1(k)- continued

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[NaCl] =5.0 x 10^{-2} mol kg^{-1}					
0.0183	61.2	0.8257	46.3	2.1177	42.9
0.0244	60.0	0.9391	45.9	2.2190	42.7
0.0305	59.3	1.0514	45.4	2.3193	42.6
0.0609	56.6	1.1626	45.1	2.4187	42.5
0.0912	54.9	1.2728	44.7	2.5173	42.5
0.1215	53.8	1.3819	44.5	2.6149	42.5
0.1818	52.3	1.4900	44.3	2.7117	42.5
0.2418	51.2	1.5971	44.0	2.9499	42.5
0.3609	49.7	1.7031	43.7		
[NaCl] =1.0 x 10^{-1} mol kg^{-1}					
0.0035	66.5	0.2749	51.2	1.5649	44.5
0.0069	65.0	0.4101	49.7	1.6867	44.3
0.0139	62.6	0.5439	48.6	1.8072	44.0
0.0208	61.2	0.6762	48.0	1.9265	43.7
0.0278	60.0	0.8072	47.2	2.0447	43.5
0.0347	59.3	0.9368	46.3	2.1617	43.5
0.0693	56.6	1.0650	45.9	2.2775	43.5
0.1038	54.9	1.1919	45.4	2.3922	43.5
0.1382	53.8	1.3175	45.1	2.5056	43.5
0.2067	52.3	1.4418	44.7	2.7847	43.5

Table 3.1(l)- Surface tension (γ) values of SDC in aqueous Sodium Chloride solution at 313K

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
		NaCl] =5.0 x 10^{-3}mol kg^{-1}			
0.0029	68.9	0.6856	50.3	2.1278	45.3
0.0059	66.8	0.7957	49.3	2.3647	44.8
0.0118	65.4	0.9046	48.7	2.5959	44.4
0.0177	64.0	1.0123	48.4	2.8215	44.0
0.0236	63.2	1.1190	47.9	3.0419	43.7
0.0295	62.5	1.2246	47.4	3.2572	43.5
0.0588	59.6	1.3290	47.4	3.4675	43.2
0.0881	58.2	1.4325	47.0	3.6731	43.1
0.1174	57.1	1.5348	46.5	3.8740	43.0
0.1756	55.1	1.6361	46.5	4.0705	43.2
0.2335	54.3	1.7364	46.2	4.2628	43.2
0.3483	52.5	1.8357	45.8	4.4507	43.2
0.4620	51.6	1.9341	45.6	4.6348	43.2
0.5744	50.7	2.0314	45.5		
		[NaCl] =1.0 x 10^{-2}mol kg^{-1}			
0.0034	65.5	0.6637	48.5	2.2342	44.0
0.0068	64.3	0.7922	47.9	2.3467	43.9
0.0136	62.6	0.9193	47.4	2.4580	43.7
0.0204	61.4	1.0451	46.9	2.5682	43.6
0.0272	60.4	1.1696	46.5	2.9984	42.9
0.0340	59.6	1.2928	46.3	3.2590	42.4
0.0680	57.0	1.4148	46.0	3.5134	42.4
0.1019	55.6	1.5354	45.5	3.7619	42.6
0.1356	54.4	1.6549	45.2	4.0048	42.6
0.2029	53.0	1.7731	45.0	4.2421	42.6
0.2698	51.7	1.8902	44.8	4.4740	42.6
0.4025	50.3	2.0060	44.5		
0.5338	49.0	2.1207	44.3		

Table 3.1(I)- continued

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[NaCl] =2.0 x 10^{-2}mol kg^{-1}					
0.0030	65.0	0.5930	48.3	1.9960	44.1
0.0061	63.3	0.7078	47.6	2.0965	43.9
0.0122	62.1	0.8214	47.2	2.1959	43.7
0.0183	60.8	0.9338	46.7	2.2943	43.5
0.0243	59.7	1.0451	46.3	2.6785	43.0
0.0304	59.0	1.1552	46.0	2.9112	42.7
0.0608	56.5	1.2641	45.7	3.1383	42.4
0.0910	54.9	1.3719	45.4	3.3602	42.6
0.1212	54.0	1.4786	45.0	3.5770	42.6
0.1813	52.7	1.5842	44.7	3.7889	42.6
0.2411	51.6	1.6887	44.5	3.9959	42.6
0.3597	50.2	1.7922	44.4	4.1984	42.6
0.4770	49.1	1.8947	44.2		
[NaCl] =3.0 x 10^{-2}mol kg^{-1}					
0.0033	66.0	0.3944	49.7	1.7454	43.3
0.0067	64.2	0.5233	48.5	1.8613	42.9
0.0133	62.6	0.6509	47.6	1.9762	42.8
0.0200	61.1	0.7772	46.7	2.4250	41.8
0.0267	60.1	0.9024	45.8	2.6973	41.4
0.0333	59.3	1.0263	45.4	2.9635	41.2
0.0666	56.5	1.1490	45.0	3.2239	41.4
0.0997	54.9	1.2706	44.4	3.4786	41.4
0.1328	53.7	1.3910	44.0	3.7277	41.4
0.1987	51.9	1.5102	43.7	3.9715	41.4
0.2642	50.8	1.6284	43.6	4.2102	41.4
[NaCl] =5.0 x 10^{-2}mol kg^{-1}					
0.0031	66.8	0.6107	47.3	2.0636	42.4

Table 3.1(l)- continued

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[NaCl] =5.0 x 10^{-2}mol kg^{-1}					
0.0063	65.3	0.7292	47.0	2.1680	42.2
0.0125	63.2	0.8465	46.1	2.2714	42.1
0.0188	62.0	0.9626	45.5	2.3738	42.0
0.0250	60.8	1.0776	45.3	2.4754	41.7
0.0313	59.8	1.1914	44.9	2.5759	41.6
0.0625	56.9	1.3042	44.4	2.7743	41.4
0.0936	55.3	1.4158	44.0	3.0172	41.4
0.1247	54.0	1.5264	43.8	3.2548	41.4
0.1865	52.4	1.6359	43.5	3.4871	41.4
0.2480	51.2	1.7443	43.3	3.7142	41.4
0.3702	49.7	1.8518	43.0		
0.4910	48.4	1.9582	42.7		
[NaCl] =1.0 x 10^{-1} mol kg^{-1}					
0.0035	65.5	0.4086	50.3	1.8010	45.0
0.0069	64.3	0.5419	49.0	1.9200	44.8
0.0138	62.6	0.6738	48.5	2.0377	44.5
0.0207	61.4	0.8043	47.9	2.1543	44.3
0.0277	60.4	0.9334	47.4	2.2698	44.0
0.0346	59.6	1.0612	46.9	2.3841	43.9
0.0690	57.0	1.1877	46.5	2.4973	43.9
0.1034	55.6	1.3129	46.3	2.7756	43.9
0.1377	54.4	1.4368	46.0	3.0471	43.9
0.2059	53.0	1.5594	45.5	3.3122	43.9
0.2738	51.7	1.6808	45.2		

Table 3.2. Critical micelle concentrations of SDC

[Salt] / mol kg^{-1}	Temperature			
	298 K	303 K	308 K	313 K
	cmc / mmol kg^{-1}			
		Salt = Na_2Ox		
0	2.34[a] (4.37)[b] {2.04}[c]	3.55 (4.57) {2.33}	3.78 (4.90)	4.13 {4.03}
0.005	2.25	3.28	3.59	3.80
0.01	2.17	3.16	3.43	3.57
0.02	2.16	3.05	3.30	3.54
0.03	2.14	2.92	-	3.44
0.05	1.92	2.43	2.70 [2.47][d]	3.00
0.1	1.44	1.82 [1.88]	2.00	2.16
0.2	1.03	1.30	1.35 [1.47]	1.47
		Salt = NaSa		
0.005	2.11	3.16	3.31	3.72
0.01	1.95	2.88	3.09	3.30
0.02	1.82	2.57	2.81	3.09
0.03	1.78	-	2.63	2.82
0.05	1.70	2.24	2.46	2.60
0.1	1.60	1.95	2.14	2.29
0.2	1.46	1.70	1.89	2.00
		Salt = NaCl		
0.005	1.93	2.98	3.20	3.78
0.01	1.73	2.60	3.00	3.47
0.02	1.57	2.34	2.69	3.11
0.03	1.51	2.26	2.58	2.95
0.05	1.37	2.03	2.33	2.75
0.1	1.18	1.96	2.03	2.37

[a] from surface tension, [b] from conductance, [c] from fluorescence, [d] from emf

Table 3.3. Molal Conductance (Λ) Values of SDC Systems in Water at different temperatures

[SDC] x 10^3 / mol kg^{-1}	Λ / S cm^2 mol^{-1}	[SDC] x 10^3 / mol kg^{-1}	Λ / S cm^2 mol^{-1}	[SDC] x 10^3 / mol kg^{-1}	Λ / S cm^2 mol^{-1}
		Temperature = 298 K			
0.0010	61.534	0.0029	56.020	0.0107	57.678
0.0012	59.871	0.0031	55.683	0.0123	58.400
0.0014	58.965	0.0035	55.565	0.0138	58.400
0.0016	58.788	0.0037	55.280	0.0152	58.213
0.0018	58.064	0.0038	55.200	0.0167	58.110
0.0020	57.604	0.0048	55.380	0.0193	57.712
0.0022	57.360	0.0057	55.425	0.0242	57.112
0.0023	56.751	0.0065	55.711	0.0286	56.711
0.0025	56.401	0.0074	56.199	0.0324	55.969
0.0027	56.181	0.0091	56.914		
		Temperature = 303 K			
0.0010	67.560	0.0033	60.056	0.0167	63.731
0.0012	64.695	0.0035	59.717	0.0193	63.839
0.0014	64.151	0.0038	59.600	0.0242	63.237
0.0016	63.220	0.0048	59.563	0.0286	62.792
0.0018	63.188	0.0057	59.667	0.0324	62.050
0.0020	62.559	0.0065	60.390	0.0359	61.625
0.0022	62.158	0.0074	61.388	0.0390	61.180
0.0023	61.370	0.0091	62.092	0.0418	60.653
0.0025	61.180	0.0107	62.688	0.0444	60.281
0.0027	60.685	0.0123	62.937	0.0468	59.887
0.0029	60.421	0.0138	63.044		
0.0031	60.126	0.0152	63.619		
		Temperature = 313 K			
0.0010	74.017	0.0031	67.671	0.0123	68.300
0.0012	73.440	0.0033	67.255	0.0138	68.495
0.0014	72.964	0.0035	66.847	0.0152	68.723
0.0016	72.142	0.0037	66.600	0.0167	68.693
0.0018	71.382	0.0038	66.554	0.0193	68.577
0.0020	70.402	0.0048	66.018	0.0242	68.110
0.0022	69.970	0.0057	65.837	0.0286	67.479
0.0023	69.416	0.0065	66.390	0.0324	66.866
0.0025	68.946	0.0074	66.776	0.0359	66.471
0.0027	68.729	0.0091	67.400	0.0324	66.866
0.0029	68.189	0.0107	68.055		

Table 3.4. Ratio of the intensities of Fluarescence Emission of Pyrene at 373 nm and at 384 nm in SDC + Water Solution at different temperatures

[SDC] x 10^3 / mol kg^{-1}	I_3/I_1	[SDC] x 10^3 / mol kg^{-1}	I_3/I_1	[SDC] x 10^3 / mol kg^{-1}	I_3/I_1
Temperature = 298 K					
0.0011	0.6728	0.0030	0.8297	0.0041	0.8994
0.0016	0.6941	0.0032	0.8495	0.0043	0.8863
0.0019	0.6969	0.0035	0.8592		
0.0022	0.7118	0.0038	0.8985		
Temperature = 303 K					
0.0013	0.7000	0.0025	0.7432	0.0044	0.9600
0.0016	0.6992	0.0028	0.7666	0.0051	0.9319
0.0022	0.7004	0.0032	0.8074	0.0054	0.9585
Temperature = 313 K					
0.0029	0.7539	0.0051	0.8962	0.0070	1.1200
0.0035	0.7679	0.0054	0.9298	0.0073	1.1356
0.0038	0.7613	0.0057	0.9547	0.0076	1.1492
0.0045	0.8619	0.0060	1.0013	0.0079	1.1874
0.0048	0.8920	0.0064	1.0159		

Table 3.5. Values of counter ion binding constant, E_0 and B

				Na$_2$Ox					
T / K	c*/ mol kg^{-1}	β from CH plot		β from EMF			β in NaSa	β in NaCl	Reported β
		c < c*	c > c*	[Na$_2$Ox] in mol kg^{-1}					
				0.05	0.1	0.2			
298	0.038	0.03	0.45	-	-	-	0.10	0.18	0.2,[a] 0.08,[b] 0.32,[c] 0.3,[d] 0.38,[e]
303	0.030	0.07	0.44	-	0.45 E_0 = 455.5 B = 562.7	-	0.18	0.18	0.7[f]
308	0.034	0.06	0.47	0.36 E_0 = 159.8 B = 110.6	-	0.5 E_0 = 298.7 B = 616.2	0.17	0.18	0[g]
313	0.039	0.07	0.52	-	0.48 E_0 = 264.7 B = 291.0	-	0.19	0.17	

[a] ref. 6, [b] ref. 15, [c] ref. 16 (temperature not indicated), [d] ref. 17 (temperature = 301 K), [e] ref. 30, [f] ref. 13 and [g] ref. 14. E_0 and B are in mV.

Table 3.6(a)- EMF Values of SDC Systems in aqueous sodium oxalate Solution at 303 K

[SDC] / mol kg^{-1}	EMF / mV	[SDC] / mol kg^{-1}	EMF / mV	[SDC] / mol kg^{-1}	EMF / mV
		[Na_2Ox] =2.0 x 10^{-2} mol kg^{-1}			
0.0002	30.0	0.0014	30.4	0.0036	31.0
0.0003	30.1	0.0018	30.5	0.0038	31.1
0.0004	30.1	0.0024	30.7	0.0041	31.2
0.0007	30.2	0.0030	30.9	0.0044	31.3
0.0011	30.3	0.0033	30.9	0.0046	31.4
		[Na_2Ox] = 1.0 x 10^{-1} mol kg^{-1}			
0.0004	62.5	0.0014	64.0	0.0027	65.2
0.0006	62.9	0.0018	64.4	0.0030	65.4
0.0007	63.2	0.0021	64.7	0.0033	65.6
0.0011	63.6	0.0024	64.9		

Table 3.6(b)- EMF Values of SDC Systems in aqueous sodium oxalate Solution at 308 K

[SDC] / mol kg^{-1}	EMF / mV	[SDC] / mol kg^{-1}	EMF / mV	[SDC] / mol kg^{-1}	EMF / mV
$[Na_2Ox] = 5.0 \times 10^{-3}$ mol kg^{-1}					
0.0002	-0.8	0.0027	2.8	0.0054	5.4
0.0004	*-0.1*	*0.0030*	*3.1*	*0.0059*	*5.8*
0.0008	0.4	0.0034	3.5	0.0062	6.1
0.0012	1.0	0.0037	3.8	0.0064	6.3
0.0016	1.5	0.0040	4.1	0.0069	6.6
0.0020	2.0	0.0043	4.4		
0.0023	2.4	0.0049	4.9		
$[Na_2Ox] = 1.0 \times 10^{-2}$ mol kg^{-1}					
0.0003	12.6	0.0022	14.5	0.0039	15.9
0.0005	13.0	0.0024	14.7	0.0041	16.0
0.0007	13.1	0.0027	15.0	0.0043	16.2
0.0010	13.4	0.0030	15.2	0.0046	16.4
0.0013	13.7	0.0032	15.4	0.0048	16.5
0.0016	14.0	0.0034	15.5	0.0050	16.7
0.0019	14.2	0.0037	15.7	0.0052	16.8
$[Na_2Ox] = 3.0 \times 10^{-2}$ mol kg^{-1}					
0.0002	23.6	0.0018	24.4	0.0043	25.5
0.0004	23.6	0.0022	24.6	0.0046	25.6
0.0005	23.8	0.0026	24.7	0.0049	25.7
0.0007	23.9	0.0029	24.9	0.0053	25.8
0.0009	24.0	0.0033	25.1	0.0055	26.0
0.0013	24.2	0.0036	25.2		
$[Na_2Ox] = 5.0 \times 10^{-2}$ mol kg^{-1}					
0.0001	49.1	0.0012	49.8	0.0030	50.5
0.0002	49.3	0.0014	49.9	0.0033	50.6
0.0004	49.4	0.0016	50.0	0.0036	50.7
0.0006	49.7	0.0020	50.1	0.0039	50.8
0.0008	49.8	0.0023	50.1	0.0042	50.9
0.0010	49.7	0.0027	50.4	0.0045	51.0

Table 3.6(b)- Continued

[SDC] / mol kg^{-1}	EMF / mV	[SDC] / mol kg^{-1}	EMF / mV	[SDC] / mol kg^{-1}	EMF / mV
[Na$_2$Ox] = 2.0 x 10^{-1} mol kg^{-1}					
0.0005	53.8	0.0023	54.7	0.0042	55.4
0.0007	53.9	0.0027	54.9	0.0046	55.4
0.0010	54.3	0.0031	55.1	0.0049	55.5
0.0014	54.4	0.0035	55.1	0.0052	55.6
0.0019	54.6	0.0038	55.3		

Table 3.6(c)- EMF Values of SDC Systems in aqueous sodium oxalate Solution at 313 K

[SDC] / mol kg^{-1}	EMF / mV	[SDC] / mol kg^{-1}	EMF / mV	[SDC] / mol kg^{-1}	EMF / mV
		[Na$_2$Ox] = 1.0 x 10^{-1} mol kg^{-1}			
0.0018	62.4	0.0031	63.1	0.0042	63.5
0.0021	62.6	0.0034	63.2	0.0045	63.6
0.0025	62.8	0.0037	63.3	0.0047	63.7
0.0028	63.0	0.0039	63.4		

Table 3.7. Values of Standard free energy of micellization of SDC

[Salt] / mol kg^{-1}	ΔG^0_m / kJ mol^{-1}			
	T = 298 K	T = 303 K	T = 308 K	T = 313 K
		Salt = Na_2Ox		
0	-15.5	-15.2	-15.2	-15.3
0.005	-15.6	-15.4	-15.3	-15.5
0.01	-15.7	-15.5	-15.4	-15.7
0.02	-15.7	-15.6	-15.5	-15.7
0.03	-15.7	-15.7	-	-15.8
0.05	-22.5	-21.8	-22.3	-23.0
0.1	-23.5	-22.9	-23.4	-24.3
0.2	-24.7	-24.1	-24.9	-25.8
		Salt = NaSa		
0.005	-16.8	-17.3	-17.1	-17.2
0.01	-17.0	-17.5	-17.3	-17.5
0.02	-17.2	-17.9	-17.6	-17.7
0.03	-17.3	-	-17.8	-18.0
0.05	-17.4	-18.3	-18.0	-18.3
0.1	-17.5	-18.7	-18.4	-18.7
0.2	-17.8	-19.1	-18.8	-19.1
0.4	-17.9	-19.5	-19.1	-19.4
		Salt = NaCl		
0.005	-18.3	-17.3	-17.4	-17.0
0.01	-18.6	-17.7	-17.6	-17.2
0.02	-18.9	-18.0	-17.9	-17.6
0.03	-19.0	-18.1	-18.0	-17.7
0.05	-19.3	-18.4	-18.3	-17.9
0.1	-19.7	-18.5	-18.7	-18.4

Table 3.8. Values of Surface excess of SDC in aqueous salt solutions

[Salt] / mol kg^{-1}	10^6 x Γ_{cmc} /mol m^{-2}			
	T = 298	T = 303	T = 308	T = 313
		Salt = Na_2Ox		
0	0.69	0.69	0.68	0.67
0.005	1.22	1.21	1.26	1.18
0.01	1.40	1.18	1.25	1.30
0.02	1.66	1.27	1.07	1.29
0.03	1.55	1.35	1.81	1.14
0.05	1.62	1.46	1.54	1.58
0.1	1.48	1.47	1.55	1.49
0.2	1.33	1.34	1.31	1.18
		Salt = NaSa		
0.005	0.90	0.91	0.83	0.85
0.01	1.12	1.11	1.00	0.82
0.02	1.32	1.27	1.08	1.03
0.03	1.24	1.45	1.00	1.04
0.05	1.39	1.42	1.15	1.18
0.1	1.38	1.42	1.29	1.43
0.2	1.39	1.36	1.31	1.45
0.4	1.37	1.31	1.28	1.36
		Salt = NaCl		
0.005	1.09	1.07	0.99	0.95
0.01	1.11	1.31	1.16	1.31
0.02	1.37	1.30	1.52	1.25
0.03	1.37	1.54	1.05	1.46
0.05	1.52	1.37	1.33	1.27
0.1	1.37	1.70	1.47	1.45

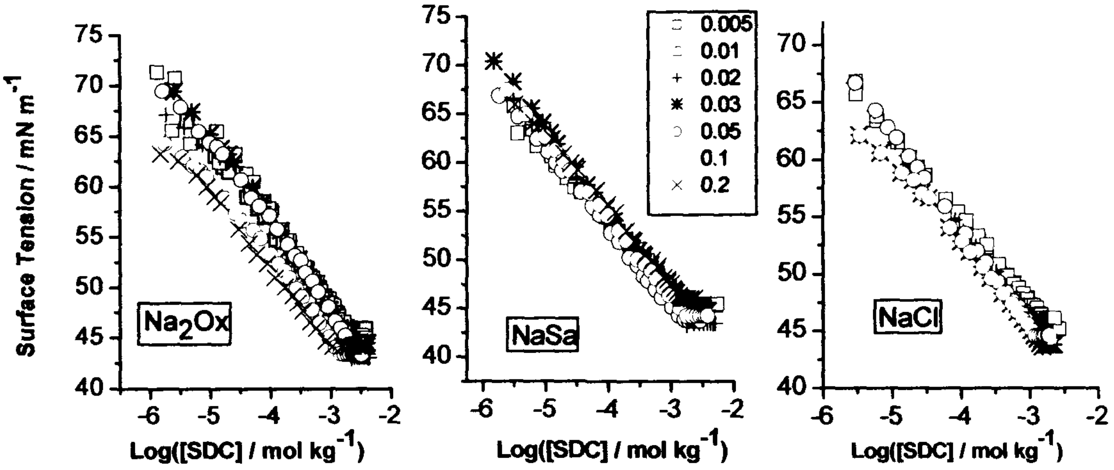

Fig. 3.1. Surface tension isotherms of aqueous SDC solution in the presence of Na_2Ox, NaSa and NaCl at 25 °C.

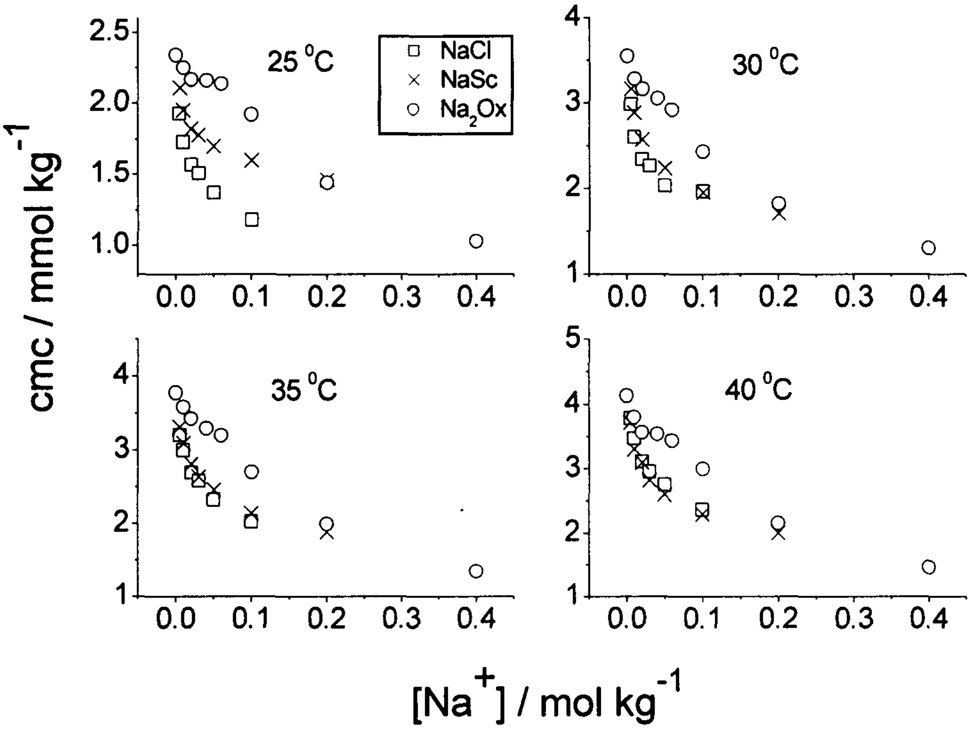

Fig. 3.2. Variation of cmc of SDC with sodium ion concentration (sodium ion concentration increased by adding salt)

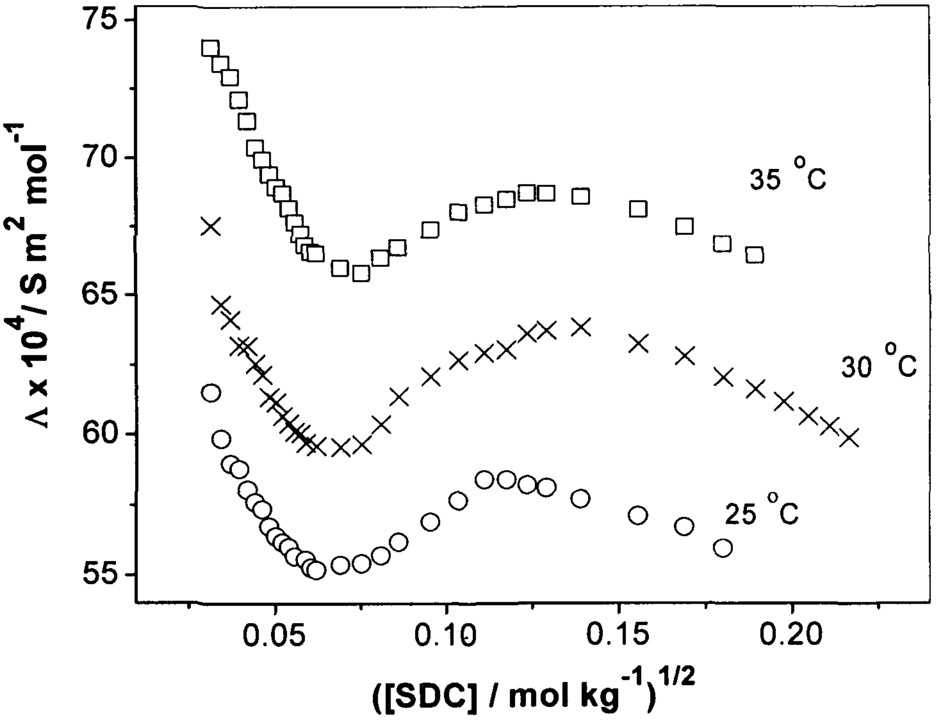

Fig. 3.3. Molar conductance of SDC in water at different temperatures as a function of square root of its concentration.

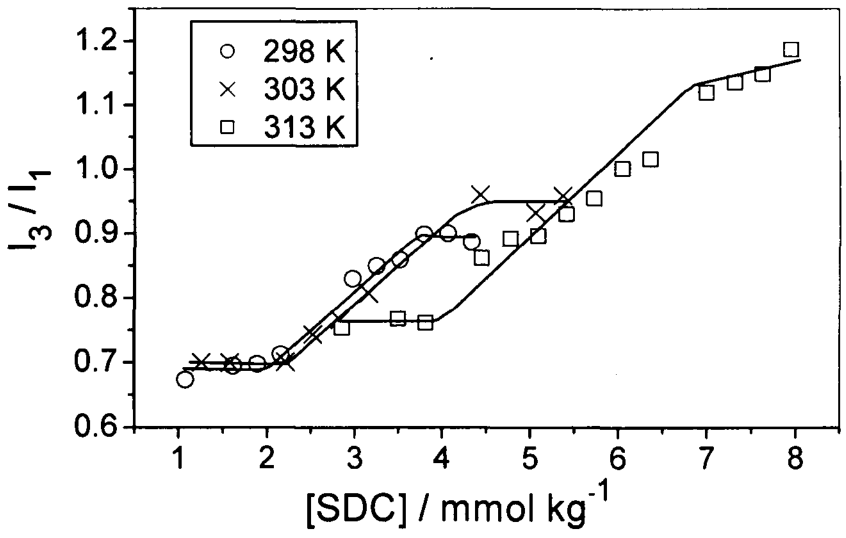

Fig. 3.4. Ratio of fluorescence emission intensities, I_3/I_1, of pyrene in aqueous SDC solution

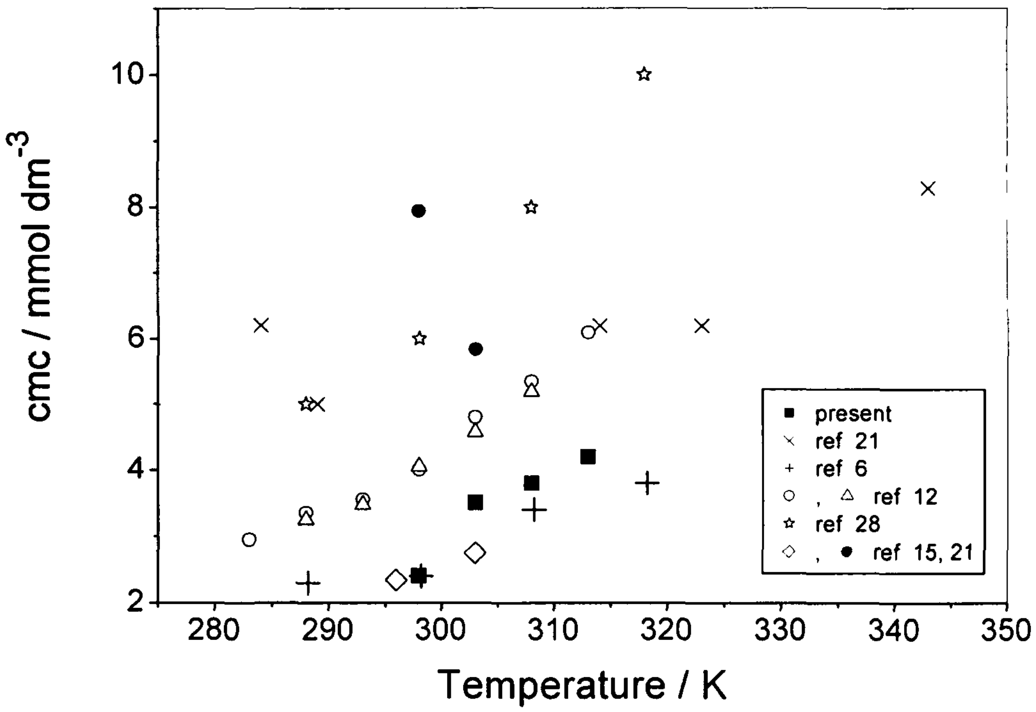

Fig. 3.5. Reported and present values of cmc of SDC in aqueous medium in the absence of added electrolyte.

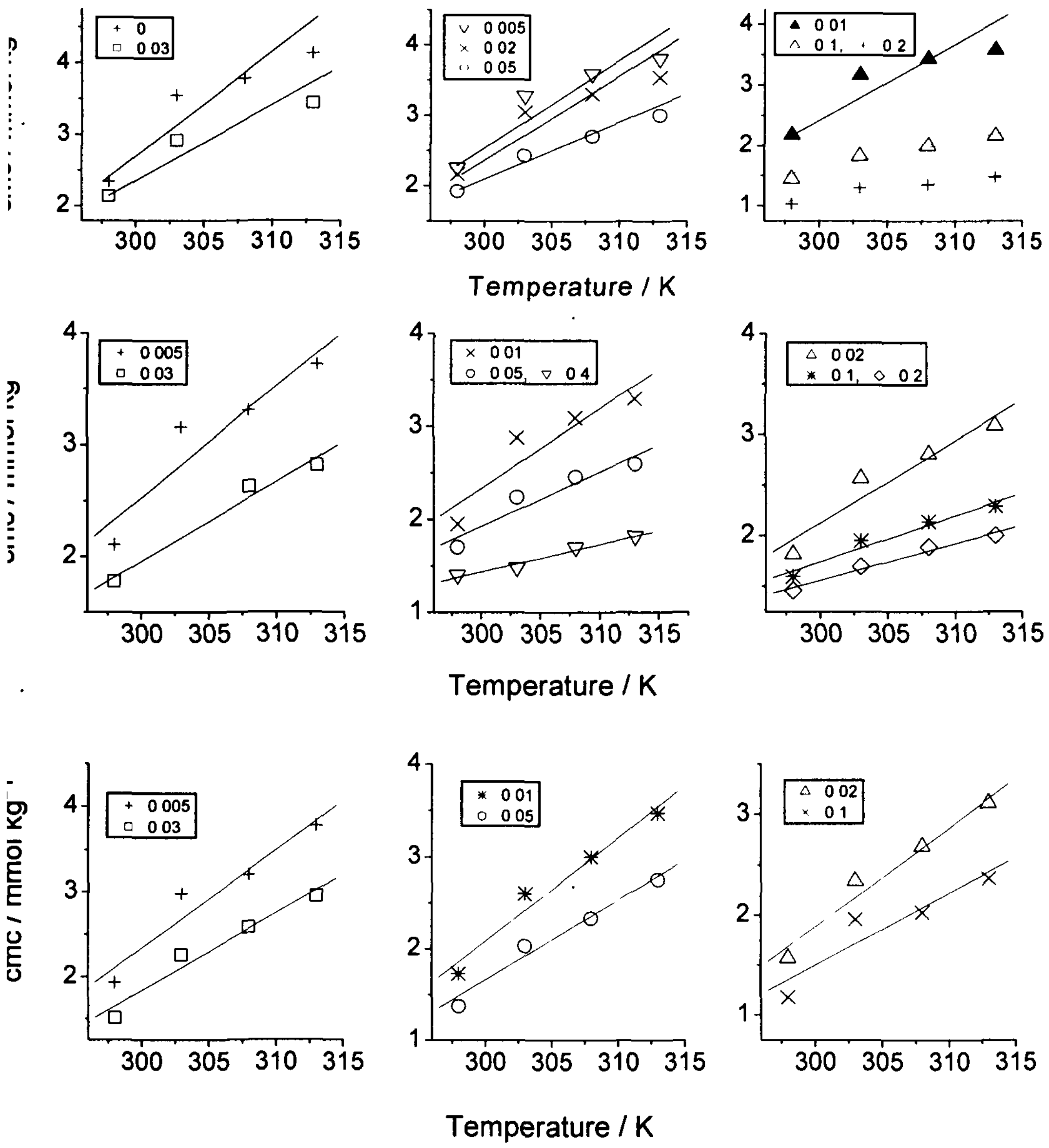

Fig. 3.6. Variation of cmc of SDC in aqueous Na_2Ox (upper layers), NaSa (middle layers) and NaCl (bottom layers) media with temperature. Concentrations of salts are shown in the insets.

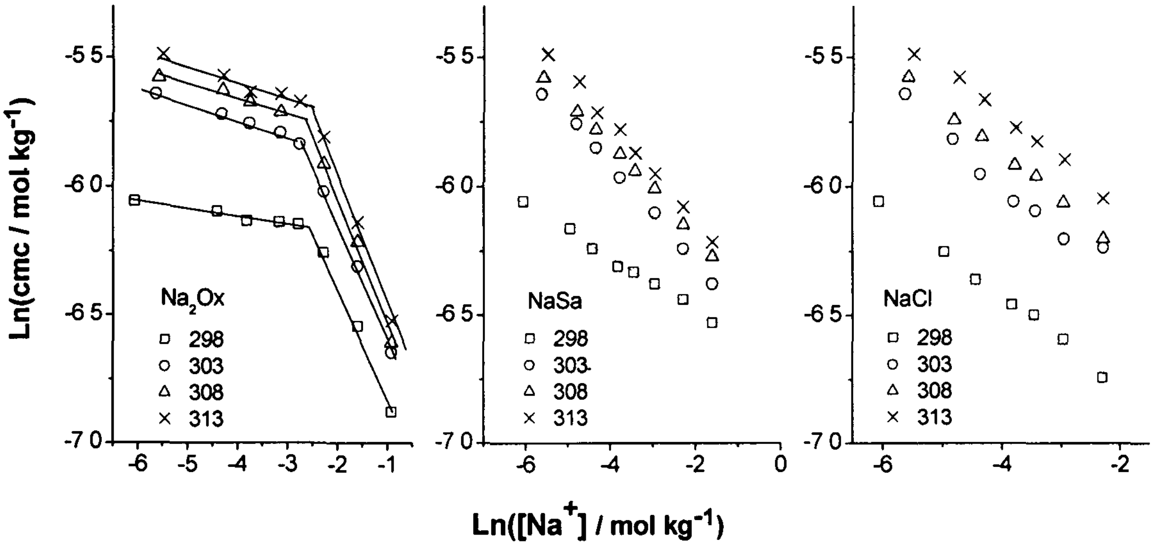

Fig. 3.7. Corrin – Harkins plots for SDC at different temperatures in the presence of different salts (indicated in the insets).

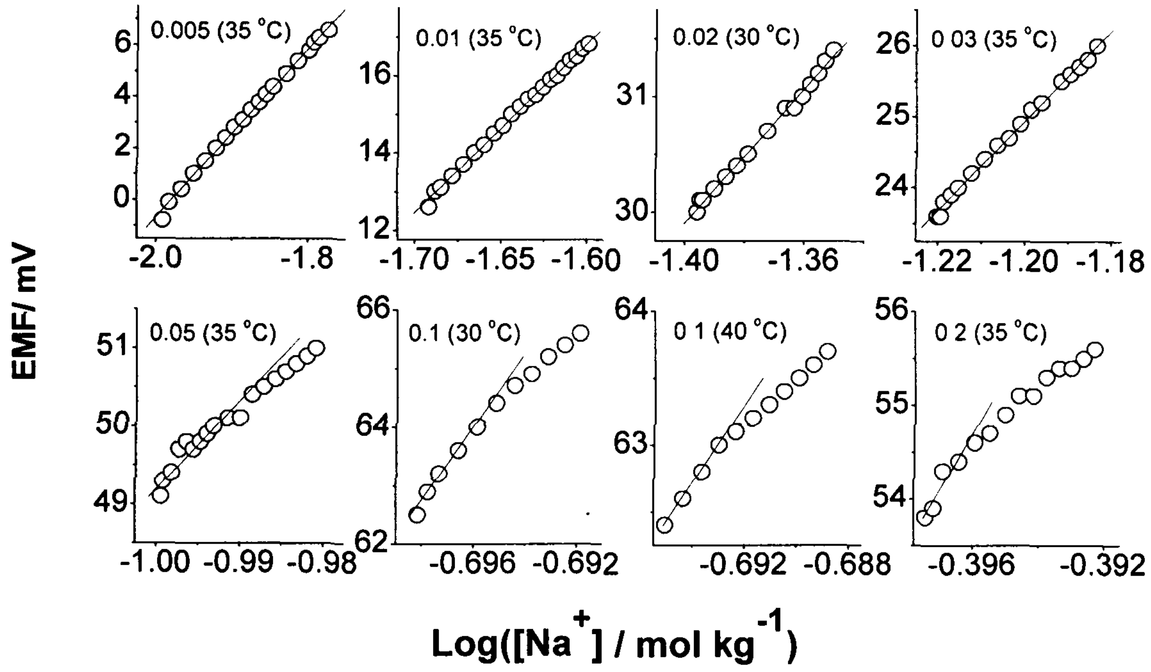

Fig. 3.8. Variation of EMF with sodium ion concentration at different concentrations of Na_2Ox. Sodium ion concentration increased by adding SDC. Temperature and Na_2Ox concentration (in mol kg^{-1}) are indicated in the insets.

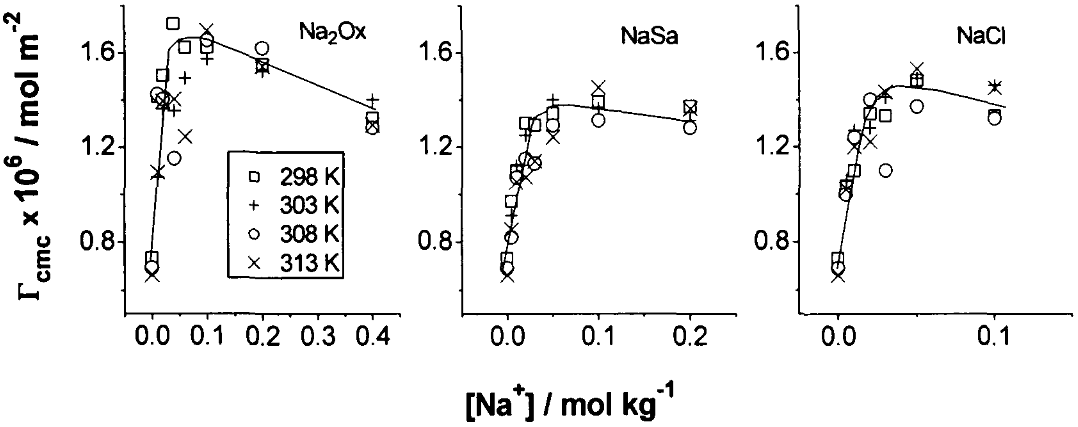

Fig. 3.9. Surface excess at cmc of SDC as a function of added sodium ion concentration

CHAPTER 4

Aggregation and Adsorption Behaviours of Sodium Deoxycholate in Water – Ethylene Glycol Medium

4.1. Introduction

As described in chapter 3, bile salts form primary aggregates due to hydrophobic interactions in which the hydrophobic surfaces face each other and the hydrophilic groups point outward towards the aqueous phase. As the bile salt concentration increases, secondary aggregates are formed due to hydrogen bonding between the hydroxyl groups.[1] This is a generally accepted model[1] for bile salt aggregates and these aggregates are also called facial micelles.[2] In the second model, a helical structure of bile salt micelles in polar solvents has been proposed,[3] in which the hydrophobic surfaces of the bile salts are oriented outward towards the aqueous phase.

Aggregation of bile salts is responsible for their important physiological functions. Therefore, different aspects of aggregation process of bile salts are being investigated by using various experimental[4-24] and computational techniques.[25-27] All these investigations on bile salts are carried out in aqueous medium for the obvious reason that water is the most important biological liquid.

Solvent plays key role in determining the adsorption and aggregation behaviours of amphiphiles, since aggregation is a solvent – induced phenomenon. For instance, Seguin et al.[28] showed that aggregation of nonionic surfactants in a mixture of ethylene and propylene glycols can be switched on or off by adjusting the composition of the mixed glycol media. It is also known that depending upon the polarity of solvent a surfactant may form regular or reverse micelles.

The influence of varying solvent type on adsorption and micellization properties of conventional surfactants has been studied extensively. Hardly any study has been made on the micellization behaviour of bile salts in mixed or non-aqueous solvents. To the best of our knowledge, only two such studies have been reported. Park and Chung[11] studied the effect of adding a maximum of about 5 % mole fraction of *N*-methylacetamide, dimethylformamide, acetamide and formamide to water on the critical micelle concentration (*cmc*) of sodium deoxycholate (SDC). Recently, Skorka and Asztemborska[29] applied formamide solutions of sodium cholate and SDC as stationary phases in gas chromatography and for this purpose determined the *cmc* of these two bile salts in formamide.

Our aim was to obtain basic knowledge about the influence of varying solvent type or solvophobicity on the adsorption and micellization characteristics of bile salts, since they behave differently from conventional surfactants due to formation of facial micelles. With this aim in mind, we studied in this chapter the aggregation as well as adsorption behaviours of SDC in water + ethylene glycol (EG) media. EG was chosen because (i) it is widely used in the studies of conventional surfactants (hence comparison can be made) and in protein conformation studies, and (ii) it is considered to be a water-like solvent in terms of hydrogen-bonding ability.

4.2. Experimental Section

SDC (Fluka, 98%), EG (Rankem, AR grade), NaCl (Merck, GR grade, 99.5%) and pyrene (Fluka; as fluorescence probe) were used as received.

Solutions were prepared using Milli-Q grade water. Surface tension measurements were made by the Wilhelmy plate method using a K11 Krüss tensiometer. Fluorescence emission intensities (excitation wavelength = 335 nm) of pyrene were recorded at 373 (I_1) and 384 (I_3) nm using a Hitachi F4500 FL spectrophotometer. In water + EG medium, amount of EG is expressed in mass fraction x 10^2. Density of the water + EG mixtures was measured by using an Anton Paar DMA 5000 density meter. Conductance measurements were made using a Wayne Kerr B905 automatic precision bridge and a dip-type cell. Studies on bile salts were generally carried out either in unbuffered or buffered media. In the present study we used unbuffered media and the pH of the SDC solutions was found to vary between 7.2 and 8.5 (measured using Jenway 3345 ion meter and combined glass electrode), which indicates that SDC undergoes hydrolysis. All measurements were carried out at 25 °C.

4.3. Results and Discussion

4.3.1. Surface tension and cmc.

Experimental values of surface tension (γ) of SDC in water + EG media in the absence and presence of NaCl are given in Table 4.1(a-f). Representative plots of surface tension isotherms of SDC in water + EG medium in the absence of NaCl are shown in Fig. 4.1. Surface tension isotherms in the presence of NaCl are found to be similar to those in Fig. 4.1. The values of *cmc* of SDC determined from the surface tension isotherms in media containing 0 to 60 % EG and different amounts of NaCl are given in Table 4.2.

4.3.2. Fluorescence and cmc.

In the absence of NaCl, we also determined the *cmc* values of SDC from the I_1/I_3 values of pyrene (Table 4.3 and Fig. 4.2). As described by Matsuoka and Moroi,[16] *cmc* value is chosen as the SDC concentration at which the I_1/I_3 value of pyrene starts decreasing sharply. As the micelle is formed, most of the pyrene molecules get solubilized in the micelle and hence I_1/I_3 value of pyrene suddenly decreases. The value of I_1/I_3 above *cmc* is found to be 1.0 ± 0.1 in 0 to 40 % EG media, and hence in these media pyrene molecules, which are solubilized inside the micelle, seem to experience similar environment. With increase in the percent amount of EG the medium becomes less solvophobic and hence more and more pyrene molecules can remain in the bulk. Such a change in the distribution of pyrene in the micellar and bulk phases affects the sigmoidal shape of the plot of I_1/I_3 versus surfactant concentration. In 50 % EG the value of I_1/I_3 above *cmc* increased to about 1.4 indicating that in this medium pyrene resides at the micellar – solution interface and not inside the micelle as in 0 to 40 % EG media. Eventually, in 60 % EG the plot of I_1/I_3 versus SDC concentration did not show sigmoidal shape. Hence *cmc* of SDC in 60 % EG could not be determined correctly from the I_1/I_3 data of pyrene. When the EG amount in the mixed solvent exceeded 60 %, correct *cmc* values could not be determined even from surface tension data. Good agreement is found between the *cmc* values obtained from surface tension and fluorescence methods (Table 4.2). One noteworthy observation in water medium is that in the region below *cmc* I_1/I_3 of pyrene decreases sharply with increase in SDC concentration. A similar trend is observed in the I_1/I_3 data reported by Matsuoka and Moroi[16] (Figs. 1 and 2 of reference 16). We are unable to explain this observation, but the hydrolysis of SDC causing change in the pH of the aqueous medium may be a probable reason.

4.3.3. Counter ion binding.

With increasing NaCl concentration *cmc* of SDC decreases (Fig. 4.3), a normal trend for ionic surfactants. Addition of NaCl increases the concentration of counter ions in the surfactant solution, which causes decrease in the repulsive interaction between the head groups favouring thereby micellization and hence *cmc* decreases. In Fig. 4.3, we have shown the reported[30] *cmc* values of sodium dodecyl sulfate (SDS) in water as a function of NaCl concentration for the sake of comparison. It is clear from Fig. 4.3 that in water the dependence of *cmc* of SDC on ionic strength of the solution is much less than that of SDS. The dependence of *cmc* on the concentration of added electrolyte (c_e) having the same counter ion as that of the surfactant is described by the Corrin – Harkins (CH) equation of the form

$$\ln(cmc) = A - \beta \ln(cmc + c_e) \tag{4.1}$$

where A is a constant related to the standard free energy of micellization and β is the binding constant of sodium counter ion. The linear plots of $\ln(cmc)$ versus $\ln(cmc + c_e)$ for SDC in water + EG media are shown in Fig. 4.4.

SDC undergoes hydrolysis in aqueous medium to produce deoxycholic acid (HDC), which is a weak acid. The influence of hydrolysis species on the micellization behaviour of SDC has generally been ignored. Sugihara and coworkers[4,5] developed a treatment to describe the behaviour of aqueous SDC solutions by considering that HDC and undissociated SDC also undergo aggregation along with DC^-. Eq. 4.1 was modified by Sugihara and coworkers[4,5] to the form

$$\log(cmc) = A_1 + \alpha\text{pH} + \beta\text{pNa} \qquad (4.2)$$

where A_1 is a constant and α is the binding constant of hydrogen counter ion. The binding of proton to the micelle can be visualized in two ways: (i) aggregation of HDC along with DC^- (equivalent to binding of one mole of proton to the micelle) and (ii) hydrolysis of the micelle. In water + EG media, undissociated SDC would exist in solution which can also aggregate with DC^- and HDC. Thus, in water + EG media sodium ion binding can take place by aggregation of undissociated SDC along with DC^- and by binding of sodium ion to the micelle. The linearity of the plots in Fig. 4.4, however, envisages that Eq. 4.1 is applicable in SDC + NaCl + water + EG systems. Therefore in water + EG medium having a particular mass fraction of EG, the αpH term of Eq. 4.2 appears to remain approximately constant as the NaCl concentration is varied so that it can be absorbed in the A_1 term, and consequently Eqs. 4.1 and 4.2 become equivalent. The least-squares fitted values of A and β are given in Table 4.4. In water β for SDC is much less than the value 0.74 reported[30] for SDS. A vast difference in the β values of SDC and SDS in water envisages that structure of SDC micelles is different from that of conventional surfactant micelles. By adding 10 % EG the value of β suddenly decreased from 0.177 to 0.094 and thereafter further addition of EG up to 60 % caused only small decrease in β. In the case of conventional ionic surfactants also β decreases by the addition of polar organic solvent to water.

4.3.4. Conductance, cmc and counter ion binding.

In order to confirm the values of β through another method, we measured specific conductance of SDC in water and water + EG media as a function of SDC concentration. The values of specific conductance are presented in Table 4.5(a-b) and Fig. 4.5. We could not determine *cmc* or β of SDC in water from the conductance plot (Fig. 4.5) since no perceivable change in the slope was observed near *cmc*. This has been explained by Matsuoka and Moroi[16] as they also made similar observation about the conductance of SDC in water. In water + EG media, change in the slopes of plots of specific conductance versus SDC concentration was observed near the *cmc*, the change was however not so prominent. From the ratio of the slopes above (S_2) and below (S_1) *cmc*, the value of β was determined by using the relation $\beta = 1 - S_2/S_1$. The values of *cmc* and β derived from the conductance data are listed in Tables 4.2 and 4.4, respectively. The values of β obtained from the CH plots and the slope-ratio method are found to be comparable in 10 to 30 % EG, the agreement is however poor in 40 to 60 % EG (Table 4.4). Determination of β from the slope-ratio method is based on the assumptions that (i) ionic surfactant is completely dissociated and (ii) ionic conductance of micelle is equal to $n(1-\beta)\lambda_1$, where n is the aggregation number and λ_1 is the molar ionic conductance of the monomer (in the present case deoxycholate ion). As mentioned above, in water + EG media undissociated SDC would exist and the degree of dissociation of SDC is expected to decrease with increasing amount of EG in the medium. Consequently, the two assumptions of slope-ratio method may become less applicable as the amount of EG increases. This may be the reason for the increase in difference between the values of β obtained from the slope-ratio and CH methods with increasing EG content of the medium.

Two types of counter ion binding have been reported by Partay et al.[27] for SDC based on molecular dynamics simulations. At 30 mM SDC concentration, the reported[27] values of β are 0.02 and 0.15. According to Partay et al.[27] the lower value refers to contact counter ion binding, while the higher value refers to binding of both contact and solvent-separated counter ions. β determined from the above two methods therefore refers to binding of contact as well as solvent-separated counter ions.

As the EG amount in the medium increases, the dielectric constant of the medium decreases and this should cause increase in counter ion binding if electrostatic interaction is only responsible for the binding. The decrease of β of ionic surfactants by adding an organic polar solvent to water clearly indicates that interaction other than electrostatic controls the counter ion binding. Therefore, it is considered that solvophobic interaction controls, besides aggregation, counter ion binding also. This implies that during aggregation of monomers counter ions also simultaneously get bound to form an ionic micelle, rather than first aggregation of monomers and then condensation of counter ions on to the micellar surface. Due to these simultaneous processes of aggregation and counter ion binding, β appears to be controlled by solvophobicity as is the case with aggregation. β has also been reported to have a dependence on the shape of ionic micelle.[31-33] Low value of β for facial type of SDC micelle and much higher value of β for spherical type SDS micelle also reveal dependence of β on shape of ionic micelle.

4.3.5. Surface excess.

Surface excess of SDC at the *cmc*, Γ_{cmc}, was evaluated by using the expression[34]

$$\Gamma_{\mathrm{cmc}} = -\frac{1}{RT}\left[\frac{1}{1+\frac{cmc}{cmc+c_{\mathrm{e}}}}\right]\left(\frac{\mathrm{d}\gamma}{\mathrm{d}\ln(c/\mathrm{mol\,kg^{-1}})}\right)_{\mathrm{cmc}} \tag{4.3}$$

where R and T are the gas constant and absolute temperature, respectively, and c is the surfactant concentration. In deriving Eq. 4.3, the ionic surfactant is considered to be completely dissociated and this condition may not be satisfied by the solutions of SDC in water + EG media. Since both dissociated and undissociated SDC will be adsorbed at the air – solution interface, Eq. 4.3 can still be assumed to be applicable to the solutions of SDC in water + EG media. The values of Γ_{cmc} are given in Table 4.6 and shown in Fig. 4.6 and adsorption of deoxycholate ion at the air – water interface decreases as the EG content in the bulk increases. With the addition of EG, the solvophobicity of the medium decreases and hence more and more deoxycholate can reside in the bulk resulting in decrease of Γ_{cmc}. In water, in the absence of NaCl, Eq. 4.3 becomes $\Gamma_{\mathrm{cmc}} = -\,[1/(2RT)](\mathrm{d}\gamma/\mathrm{d}\ln c)_{\mathrm{cmc}}$ and the value of Γ_{cmc} is found to be equal to 0.73 μmol m^{-2}, which matches with the value 0.75 μmol m^{-2} calculated by Jana and Moulik[13] using the same equation. Using the relation $\Gamma = -\,[1/(RT)](\mathrm{d}\gamma/\mathrm{d}\ln c)$, the maximum values of Γ for SDC in water are reported to be 1.66 and 2 μmol m^{-2} by Tis et al.[35] and by Thomas and Christian,[36] respectively. These reported values of surface excess in water, after correcting for the factor 2 in the denominator of the expression for Γ, show good agreement with the value of Γ_{cmc} obtained in this study. By adding NaCl, Γ_{cmc} increases in water as well as water + EG media and attains almost constant value when the NaCl concentration becomes more than about 0.03 mol kg^{-1}. The increase in surface excess on adding NaCl may be explained as due to the following reasons: (i) When NaCl is added, due to salting-out effect more deoxycholate ions go to the interface and get adsorbed. (ii) Added NaCl increases counter ion concentration in the Stern layer at the air–solution interface, which decreases repulsive interaction between the carboxyl head groups of the adsorbed deoxycholate ions causing area per adsorbed ion (A_0) to decrease or surface excess (proportional to $1/A_0$) to increase. (iii) In Eq. 4.3 the value of the terms in the square bracket increases due to increase in NaCl concentration, which also causes increase in surface excess.

4.3.6. Free energy.

Standard free energy of micellization per mole of monomer (ΔG_{m}^{0}) has been calculated using the expression

$$\Delta G_{\text{m}}^{0} = RT(1+\beta)\ln(cmc) \qquad (4.4)$$

The values of ΔG_{m}^{0} in water + EG media are given in Table 4.4. Since *cmc* increases with increase in EG amount, ΔG_{m}^{0} also increases with mass fraction of EG. The variation of ΔG_{m}^{0} with NaCl concentration is shown in Fig. 4.7. For the increase in ΔG_{m}^{0} with increasing amount of EG, the decreasing solvophobicity of the medium is responsible, while for the decrease in ΔG_{m}^{0} with increasing concentration of NaCl in a particular medium the reduction in the repulsive interaction between the carboxyl head groups is responsible. The solvophobicity of the medium has been expressed in terms of Gordon parameter (*GP*)[37,38] and the ratio of surface tension of the medium (γ_0) to the surface tension at the *cmc* (γ_{cmc}).[39,40] *GP* is defined as $\gamma_0/V^{1/3}$, where V is the molar volume of the medium. The values of *GP* and $\gamma_0/\gamma_{\text{cmc}}$ are given in Table 4.7. The values of these parameters decrease with increase in the amount of EG and thus their values directly reflect the solvophobicity of the medium. ΔG_{m}^{0} varies with *GP* and $\gamma_0/\gamma_{\text{cmc}}$ in a similar fashion as apparent from Fig. 4.8. The value of *GP* depends entirely on the property of the medium irrespective of the surfactant, while the value of $\gamma_0/\gamma_{\text{cmc}}$ depends both on the properties of medium and the surfactant. Thus, $\gamma_0/\gamma_{\text{cmc}}$ represents solvophobicity of a particular surfactant in a particular medium, and hence is a better parameter to express solvophobicity.

4.4. Conclusions

Critical micelle concentrations (*cmc*) of sodium deoxycholate (SDC) were determined at 25 °C in water + ethylene glycol (EG) medium (mass fraction of EG, w_{EG} = 0, 10, 20, 30, 40, 50 and 60 %) by measuring surface tension, fluorescence emission intensities of pyrene probe and conductance. The *cmc* of SDC increases similar to that of conventional surfactants by the addition of EG. By adding 50 % EG, *cmc* of SDC increased by a factor of about 4.4, while reported[39] *cmc* values of sodium dodecyl sulfate, cetyltrimethylammonium bromide and tetradecyltrimethylammonium bromide increased by factors of about 2.8, 4.6 and 3.6, respectively. *Cmc* was also determined in the presence of NaCl from the surface tension isotherms, and counter ion binding constants (β) of SDC were evaluated by applying the Corrin – Harkins equation and slope – ratio method. The value of β in water is about 0.18 and becomes almost half of this value in water + EG. Surface excess at the *cmc* decreases as the EG amount increases, but increases on adding NaCl. Gordon parameter and ratio of surface tension of the medium to that of the surfactant solution at the *cmc* are used to represent solvophobicity.

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Table 4.1(a)- Surface tension (γ) values of SDC in 10 % Ethylene Glycol – water mixture at 298K

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaCl] = 0.00mol kg^{-1}			
0.0067	66.2	0.5331	52.7	5.8897	47.3
0.0135	63.5	0.7951	51.3	6.8933	47.3
0.0269	61.2	1.0542	50.6	7.8489	47.3
0.0673	58.9	1.3103	50.0	8.7597	47.3
0.1344	56.9	1.9382	48.9	9.6285	47.3
0.2014	55.8	2.5490	48.0	10.4585	47.3
0.2681	54.5	3.7218	47.1		
0.4010	53.4	4.8338	47.3		
		[NaCl] =5.0 x 10^{-3}mol kg^{-1}			
0.0058	67.3	0.9027	52.1	6.8560	47.4
0.0115	66.3	1.1228	51.4	7.6722	47.5
0.0230	64.4	1.6639	50.2	8.4551	47.5
0.0575	61.2	2.1921	49.4	9.2066	47.5
0.1148	59.3	3.2117	47.5	9.9286	47.5
0.2290	56.5	4.1849	47.5		
0.4558	54.3	5.1149	47.5		
0.6803	53.1	6.0044	47.5		
		[NaCl] =7.0 x 10^{-3}mol kg^{-1}			
0.0178	62.7	1.4099	51.0	9.8896	47.7
0.0356	61.1	2.1037	49.4	12.8656	47.7
0.0712	59.4	2.7902	48.4	15.7004	47.7
0.1779	57.3	3.4694	47.7	18.4035	47.7
0.3553	55.1	5.1368	47.7	20.9846	47.7
0.7087	53.0	6.7615	47.7	23.4509	47.7
		[NaCl] =7.0 x 10^{-3}mol kg^{-1}			
0.0065	63.6	0.5104	53.0	3.5639	47.1
0.0129	62.2	0.7613	52.1	4.6290	47.1

Table 4.1(a)- continued

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaCl] =7.0 x 10^{-3} mol kg^{-1}			
0.0258	60.6	1.0093	50.9	5.6404	47.1
0.0644	58.0	1.2546	50.1	6.6019	47.1
0.1287	56.7	1.8559	48.8	7.5174	47.1
0.2567	54.8	2.4408	48.1		
		[NaCl] =1.1 x 10^{-2} mol kg^{-1}			
0.0065	63.6	0.5104	53.0	3.5639	47.1
0.0129	62.2	0.7613	52.1	4.6290	47.1
0.0258	60.6	1.0093	50.9	5.6404	47.1
0.0644	58.0	1.2546	50.1	6.6019	47.1
0.1287	56.7	1.8559	48.8	7.5174	47.1
0.2567	54.8	2.4408	48.1		
		[NaCl] =1.8 x 10^{-2} mol kg^{-1}			
0.0070	64.6	0.8204	51.2	6.0770	47.2
0.0139	63.4	1.0877	50.3	7.1128	47.2
0.0278	61.1	1.3519	49.6	8.0988	47.2
0.0694	58.5	1.9998	48.4	9.0386	47.2
0.1387	56.9	2.6300	47.6	9.9353	47.2
0.2766	54.5	3.8401	47.2	10.7917	47.2
0.5500	52.5	4.9875	47.2		
		[NaCl] =2.2 x 10^{-2} mol kg^{-1}			
0.0066	66.2	0.5232	52.7	5.7798	47.3
0.0132	63.5	0.7803	51.3	6.7647	47.3
0.0264	61.2	1.0345	50.6	7.7025	47.3
0.0661	58.9	1.2859	50.0	8.5961	47.3
0.1319	56.9	1.9021	48.7	9.4487	47.3
0.1976	55.8	2.5015	47.8	10.2629	47.3

Table 4.1(a)- continued

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaCl] =2.2 x 10^{-2} mol kg^{-1}			
0.2631	54.5	3.6524	47.3		
0.3935	53.4	4.7436	47.3		
		[NaCl] =1.0 x 10^{-1} mol kg^{-1}			
0.0060	64.5	0.7083	49.0	5.3183	44.6
0.0120	62.7	0.9397	48.1	6.2415	44.6
0.0240	60.4	1.1688	47.2	7.1249	44.6
0.0598	57.4	1.7318	46.2	7.9713	44.6
0.1195	54.8	2.2812	45.4	8.7825	44.6
0.2385	52.0	3.3413	44.6	9.5611	44.6
0.4746	50.4	4.3525	44.6	10.3088	44.6

Table 4.1(b)- Surface tension (γ) values of SDC in 20 % Ethylene Glycol – water mixture at 298K

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaCl] = 0.00mol kg^{-1}			
0.0064	65.2	1.2203	53.2	5.8645	47.8
0.0128	65.5	1.7860	52.1	6.2293	47.8
0.0321	64.3	2.3250	51.1	6.5801	47.8
0.0640	62.6	2.8390	50.4	6.9177	47.8
0.1277	60.9	3.3298	49.6	7.2429	47.8
0.2541	59.1	3.7990	49.1	7.5563	47.8
0.3793	57.6	4.2479	48.5	7.8585	47.8
0.5031	56.7	4.6777	48.6	8.1502	47.8
0.6257	55.9	5.0897	48.1	8.4320	47.8
0.9267	54.1	5.4850	47.9		
		[NaCl] =5.0 x 10^{-3}mol kg^{-1}			
0.0069	64.2	0.8081	52.0	5.9836	45.4
0.0137	64.1	1.0714	51.0	7.0028	45.4
0.0274	62.8	1.3317	50.0	7.9730	45.4
0.0684	60.5	1.9697	48.4	8.8973	45.4
0.1366	57.8	2.5903	47.7	9.7791	45.5
0.2725	55.3	3.7818	46.5	10.6214	45.4
0.5418	52.9	4.9112	45.6	11.4267	45.4
		[NaCl] =7.0 x 10^{-3}mol kg^{-1}			
0.0038	65.2	0.7493	54.4	5.5594	48.0
0.0077	64.9	1.1092	53.1	6.0445	48.0
0.0154	64.8	1.4598	52.2	6.5091	48.0
0.0384	63.5	2.1343	51.0	6.9546	48.0
0.0768	61.8	2.7755	50.1	7.3821	48.0
0.1531	59.7	3.3859	49.4	7.7927	48.0
0.3046	57.5	3.9676	48.9	8.1875	48.0
0.4544	56.3	4.5226	48.4		
0.6027	55.2	5.0527	48.0		

Table 4.1(b)- continued

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[NaCl] = 1.1×10^{-2} mol kg^{-1}					
0.0063	59.9	0.9804	51.4	7.3358	46.2
0.0125	59.9	1.2188	50.8	8.1924	46.2
0.0250	58.3	1.8038	49.6	9.0105	46.2
0.0626	57.3	2.3732	48.7	9.7931	46.2
0.1249	55.9	3.4681	47.5	10.5422	46.2
0.2492	54.5	4.5079	46.6	11.2600	46.2
0.4956	52.9	5.4967	46.2		
0.7393	51.7	6.4383	46.2		
[NaCl] = 1.8×10^{-2} mol kg^{-1}					
0.0079	64.3	0.9281	52.6	6.8713	47.3
0.0157	63.5	1.2304	51.8	8.0416	47.6
0.0315	62.3	1.5294	51.4	9.1555	47.3
0.0786	59.9	2.2621	50.1	10.2169	47.3
0.1569	57.8	2.9747	49.3	11.2295	47.3
0.3129	55.8	4.3430	48.0		
0.6223	53.9	5.6400	47.3		
[NaCl] = 2.2×10^{-2} mol kg^{-1}					
0.0063	64.1	0.7407	52.6	5.4905	47.4
0.0126	63.1	0.9821	52.0	6.4272	47.4
0.0251	61.9	1.2207	51.1	7.3191	47.4
0.0627	59.7	1.8059	50.0	8.1694	47.4
0.1252	57.9	2.3751	49.2	8.9809	47.4
0.2497	55.5	3.4685	48.2	9.7560	47.4
0.4966	53.9	4.5056	47.5	10.4974	47.4
[NaCl] = 1.0×10^{-1} mol kg^{-1}					
0.0068	64.7	1.0721	51.0	8.2166	47.0

Table 4.1(b)- continued

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaCl] =1.0 x 10^{-1} mol kg^{-1}			
0.0136	63.2	1.3341	50.4	9.2060	47.0
0.0273	61.6	1.9786	49.2	10.1573	47.0
0.0682	58.7	2.6087	48.4	11.0729	47.0
0.1362	56.6	3.8280	47.1	11.9545	47.0
0.2718	54.5	4.9952	47.0	12.8038	47.0
0.5410	52.8	6.1138	47.0		
0.8078	51.8	7.1867	47.0		

Table 4.1 (c)- Surface tension (γ) values of SDC in 30 % Ethylene Glycol – water mixture at 298K

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[NaCl] = 0.00mol kg^{-1}					
0.0036	63.0	1.3529	54.3	6.8308	48.4
0.0071	62.9	1.9777	53.1	7.2099	48.4
0.0143	62.8	2.5715	52.0	7.5743	48.4
0.0356	62.6	3.1365	51.2	7.9246	48.4
0.0712	62.4	3.6747	50.8	8.2619	48.4
0.1420	61.4	4.1881	49.7	8.5868	48.4
0.2824	59.9	4.6783	49.8	8.8998	48.4
0.4213	59.0	5.1468	49.6	9.2017	48.4
0.5587	57.7	5.5951	49.1	9.4931	48.4
0.6946	57.3	6.0245	48.7	9.7746	48.4
1.0281	55.7	6.4361	48.4		
[NaCl] =5.0 x 10^{-3}mol kg^{-1}					
0.0088	62.9	1.3836	53.3	10.3262	48.3
0.0177	62.3	1.7200	52.6	11.5279	48.3
0.0354	61.7	2.5448	51.1	12.6754	48.3
0.0883	60.7	3.3474	50.2	13.7718	48.3
0.1764	59.3	4.8894	49.0	14.8207	48.3
0.3518	57.5	6.3529	48.3	15.8252	48.3
0.6996	55.5	7.7432	48.3		
1.0435	54.3	9.0661	48.3		
[NaCl] =7.0 x 10^{-3}mol kg^{-1}					
0.0052	62.6	1.0166	53.4	7.5690	47.7
0.0104	62.5	1.5052	52.0	8.2323	47.8
0.0209	62.4	1.9814	51.4	8.8681	47.9
0.0521	61.5	2.8984	50.3	9.4781	47.9
0.1041	60.0	3.7710	49.2	10.0640	47.9
0.2076	58.3	4.6024	48.4	10.6270	47.9
0.4131	56.5	5.3954	47.9	11.1684	47.9

Table 4.1(c)- continued

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[NaCl] =7.0 x 10^{-3}mol kg^{-1}					
0.6164	55.2	6.1526	47.9		
0.8175	54.3	6.8764	47.9		
[NaCl] =1.1 x 10^{-2} mol kg^{-1}					
0.0086	61.0	1.0120	54.7	7.4824	48.9
0.0172	61.0	1.3416	53.9	8.7545	48.9
0.0343	60.9	1.6674	53.1	9.9646	48.4
0.0857	59.8	2.4659	51.8	11.1171	48.7
0.1711	58.8	3.2422	51.1	12.2160	48.5
0.3413	57.4	4.7319	50.0	13.2651	48.8
0.6786	55.9	6.1433	48.9	14.2676	48.6
[NaCl] =1.8 x 10^{-2} mol kg^{-1}					
0.0082	62.7	1.2902	53.2	8.4959	48.7
0.0329	62.0	1.6042	52.7	9.6846	48.8
0.0823	60.6	2.3747	51.6	10.8201	48.7
0.1644	58.8	3.1253	50.7	11.9058	48.7
0.3278	57.1	4.5696	49.4	12.9449	48.7
0.6521	55.2	5.9428	48.7	13.9402	48.7
0.9728	54.0	7.2500	48.7		
[NaCl] =2.2 x 10^{-2} mol kg^{-1}					
0.0079	62.7	1.2357	52.9	10.2709	48.4
0.0158	62.5	1.5360	52.3	11.2902	48.4
0.0316	61.7	2.2722	51.2	12.2637	48.4
0.0789	60.0	2.9882	50.3	13.1944	48.4
0.1576	58.7	4.3632	49.1	14.0854	48.4
0.2360	58.1	5.6671	48.4	14.9389	48.4
0.3143	56.9	6.9051	48.4	15.7572	48.4

Table 4.1(c)- continued

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[NaCl] =2.2 x 10^{-2} mol kg^{-1}					
0.6249	54.9	8.0824	48.4		
0.9321	53.6	9.2030	48.4		
[NaCl] =1.0 x 10^{-1} mol kg^{-1}					
0.0062	62.9	0.9809	52.1	7.4876	47.6
0.0125	62.5	1.2203	51.5	8.3847	47.6
0.0250	61.6	1.8093	50.5	9.2463	47.6
0.0624	59.9	2.3847	49.6	10.0747	47.6
0.1247	58.0	3.4968	48.6	10.8715	47.6
0.2487	56.0	4.5602	48.0	11.6386	47.6
0.4951	54.1	5.5779	47.6		
0.7391	53.0	6.5528	47.6		

Table 4.1(d)- Surface tension (γ) values of SDC in 40 % Ethylene Glycol – water mixture at 298K

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaCl] = 0.00mol kg^{-1}			
0.0043	60.2	1.2451	54.6	7.2299	49.5
0.0087	59.9	1.6375	53.7	7.7179	49.4
0.0173	60.1	2.3909	52.7	8.1856	49.2
0.0432	59.6	3.1054	51.6	8.6340	49.2
0.0864	58.5	3.7838	51.3	9.0644	49.2
0.1722	58.7	4.4288	51.0	9.4776	49.2
0.3425	57.6	5.0429	50.5	9.8751	49.2
0.5108	57.1	5.6281	50.1	10.2572	49.2
0.6772	56.5	6.1866	49.9	10.6253	49.2
0.8417	55.8	6.7199	49.7	10.9797	49.2
		[NaCl] =5.0 x 10^{-3}mol kg^{-1}			
0.0101	60.1	1.5862	53.5	11.8337	48.7
0.0203	60.1	1.9718	53.1	13.2102	48.7
0.0405	59.9	2.9173	51.6	14.5241	48.7
0.1013	59.6	3.8372	50.7	15.7797	48.7
0.2022	58.4	5.6045	49.8	16.9809	48.7
0.4033	57.2	7.2815	49.0	18.1309	48.7
0.8021	55.6	8.8746	48.7		
1.1964	54.6	10.3903	48.7		
		[NaCl] =7.0 x 10^{-3}mol kg^{-1}			
0.0066	60.3	1.0372	54.7	7.7222	48.8
0.0133	60.3	1.2892	54.0	8.6181	48.8
0.0265	60.2	1.9070	52.9	9.4728	48.8
0.0662	59.7	2.5078	52.1	10.2894	48.8
0.1323	59.3	3.6617	51.0	11.0701	48.8
0.2638	57.9	4.7558	50.2	11.8171	48.8
0.5245	56.5	5.7946	49.6		
0.7823	55.5	6.7820	49.2		

Table 4.1(d)- continued

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaCl] =1.1 x 10^{-2} mol kg^{-1}			
0.0099	59.9	1.5539	52.9	11.5388	48.5
0.0199	59.6	1.9312	52.2	12.8730	48.5
0.0397	59.1	2.8559	51.1	14.1452	48.5
0.0993	58.6	3.7550	50.4	15.3596	48.5
0.1982	57.4	5.4802	49.4	16.5196	48.5
0.3953	56.3	7.1146	48.6	17.6295	48.5
0.7860	54.8	8.6650	48.5		
1.1721	53.6	10.1379	48.5		
		[NaCl] =1.8 x 10^{-2} mol kg^{-1}			
0.0115	60.5	1.3569	54.0	10.0411	49.1
0.0230	60.5	1.7990	53.2	11.7501	49.1
0.0460	60.1	2.2359	52.6	13.3764	49.0
0.1149	59.5	3.3070	51.6	14.9255	49.1
0.2294	58.3	4.3486	50.8	16.4033	49.1
0.4576	57.0	6.3479	49.8	17.8144	49.1
0.9099	55.2	8.2427	49.1		
		[NaCl] =2.2 x 10^{-2} mol kg^{-1}			
0.0095	60.4	1.4904	53.2	11.2530	49.1
0.0190	60.7	1.8535	52.7	12.5823	49.1
0.0380	60.3	2.7452	51.7	13.8554	49.1
0.0950	59.9	3.6148	51.0	15.0758	49.1
0.1897	58.3	5.2907	50.0	16.2461	49.1
0.3784	56.6	6.8872	49.3	17.3704	49.1
0.7529	54.9	8.4099	49.1	18.4506	49.1
1.1235	53.9	9.8635	49.1	19.4895	49.1

Table 4.1(d)- continued

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[NaCl] = 1.0×10^{-1} mol kg^{-1}					
0.0074	60.5	0.8705	53.3	6.5500	48.3
0.0147	60.5	1.1550	52.6	7.6904	48.1
0.0294	60.2	1.4368	52.0	8.7825	48.1
0.0735	59.0	2.1294	51.0	9.8295	48.1
0.1469	57.9	2.8057	50.3	10.8340	48.1
0.2930	55.8	4.1114	49.3	11.7986	48.1
0.5832	54.3	5.3582	48.7	16.0987	48.1

Table 4.1(e)- Surface tension (γ) values of SDC in 50 % Ethylene Glycol – water mixture at 298K

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[NaCl] = 0.00mol kg^{-1}					
0.0045	57.7	3.2680	54.0	10.6096	50.7
0.0090	57.9	3.9901	53.4	11.0334	50.5
0.0180	58.0	4.6795	53.0	11.4422	50.5
0.0451	57.6	5.3383	52.6	11.8370	50.5
0.0900	57.8	5.9684	52.3	12.2186	50.5
0.1796	57.7	6.5717	52.1	12.5872	50.5
0.3574	57.3	7.1501	51.8	12.9437	50.5
0.5333	57.4	7.7046	51.6	13.2889	50.5
0.7074	57.1	8.2372	51.5	13.6232	50.5
0.8797	56.7	8.7488	51.3	13.9470	50.5
1.3029	56.2	9.2408	51.1	14.2607	50.5
1.7156	55.7	9.7143	51.0		
2.5107	55.1	10.1702	50.9		
[NaCl] =5.0 x 10^{-3}mol kg^{-1}					
0.1415	57.4	4.0680	52.1	18.2953	49.8
0.2825	57.3	5.3476	51.5	20.0979	49.8
0.5634	56.4	7.8014	50.5	21.8172	49.8
1.1200	55.5	10.1242	49.8	23.4590	49.8
1.6702	54.3	12.3265	49.8	25.0288	49.9
2.2140	53.6	14.4168	49.8	26.5314	49.8
2.7514	53.0	16.4040	49.8		
[NaCl] =7.0 x 10^{-3}mol kg^{-1}					
0.0053	58.0	1.5386	53.3	9.0228	49.4
0.0107	58.0	2.0248	52.8	9.6398	49.3
0.0213	58.3	2.9601	51.9	10.2318	49.3
0.0533	57.8	3.8492	51.4	10.8002	49.3
0.1065	57.4	4.6954	51.0	11.3467	49.3
0.2124	57.0	5.5016	50.6	11.8722	49.3

Table 4.1(e)- continued

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[NaCl] =7.0 x 10^{-3} mol kg^{-1}					
0.4226	56.0	6.2708	50.3	12.3780	49.3
0.6304	55.2	7.0052	50.1	12.8653	49.3
0.8360	54.6	7.7073	49.8	13.3352	49.3
1.0394	54.2	8.3792	49.6	13.7883	49.3
[NaCl] =1.1 x 10^{-2} mol kg^{-1}					
0.0153	57.9	1.8049	54.5	13.3423	50.3
0.0306	57.9	2.3927	53.8	15.6103	50.3
0.0612	57.9	2.9737	53.3	17.7672	50.4
0.1528	57.6	4.3977	52.4	19.8217	50.3
0.3052	57.0	5.7822	51.6	21.7806	50.3
0.6087	56.0	8.4386	50.7	23.6499	50.3
1.2103	55.0	10.9549	50.4	25.4367	50.4
[NaCl] =1.8 x 10^{-2} mol kg^{-1}					
0.0136	58.1	1.6072	53.8	11.8705	49.9
0.0273	58.1	2.1306	53.0	13.8858	49.9
0.0545	58.0	2.6479	52.6	15.8016	49.9
0.1361	57.9	3.9153	51.8	17.6258	49.9
0.2718	57.4	5.1473	51.2	19.3647	49.9
0.5421	56.1	7.5105	50.4	21.0237	49.9
1.0778	54.5	9.7483	49.9	22.6084	49.9
[NaCl] =2.2 x 10^{-2} mol kg^{-1}					
0.0111	58.0	1.7336	54.0	12.8212	50.2
0.0222	58.0	2.1542	53.4	14.2962	50.2
0.0444	58.1	3.1846	52.6	15.7007	50.2
0.1108	57.7	4.1855	52.0	17.0400	50.2
0.2213	57.3	6.1042	51.2	18.3189	50.2

Table 4.1(e)- continued

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
		[NaCl] =2.2 x 10^{-2} mol kg^{-1}			
0.4412	56.0	7.9194	50.7	19.5407	50.2
0.8771	55.4	9.6392	50.2	20.7095	50.2
1.3079	54.5	11.2709	50.2	21.8288	50.2
		NaCl] =1.0 x 10^{-1} mol kg^{-1}			
0.0085	58.0	1.3306	53.8	8.8219	49.9
0.0170	58.3	1.6549	53.3	10.0677	49.9
0.0339	58.0	1.9760	53.0	11.2600	49.9
0.0848	57.8	2.4517	52.5	12.4028	49.9
0.1693	57.0	3.2288	52.0	13.4983	49.9
0.3378	56.6	4.7274	51.2	18.3667	49.9
0.6721	55.1	6.1560	50.7		
1.0030	54.3	7.5193	50.3		

Table 4.1(f)- Surface tension (γ) values of SDC in 60 % Ethylene Glycol – water mixture at 298K

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[NaCl] = 0.00mol kg^{-1}					
0.0066	56.4	3.6124	53.5	13.6248	50.4
0.0131	56.2	4.6893	53.0	14.2416	50.3
0.0262	56.3	5.7107	52.3	14.8341	50.3
0.0654	56.4	6.6810	52.1	15.4035	50.3
0.1307	56.4	7.6036	51.8	15.9518	50.3
0.2606	56.1	8.4822	51.3	16.4793	50.3
0.5182	55.8	9.3197	51.1	16.9879	50.3
0.7728	55.6	10.1191	51.0	17.4783	50.3
1.0245	55.2	10.8828	50.8	17.9511	50.3
1.2733	55.1	11.6131	50.6	18.4077	50.3
1.8829	54.7	12.3123	50.5	18.8491	50.3
2.4755	54.1	12.9823	50.4	19.2752	50.3
[NaCl] =5.0 x 10^{-3}mol kg^{-1}					
0.0180	56.0	3.4970	54.2	25.6094	50.9
0.0360	55.9	5.1714	53.2	27.8074	50.9
0.0720	55.8	6.7994	52.6	29.9075	50.9
0.1797	55.6	9.9229	51.7	31.9161	50.8
0.3589	55.5	12.8819	51.1	33.8392	50.9
0.7158	55.3	15.6888	50.9	35.6821	50.9
1.4232	54.9	18.3552	50.9	37.4498	50.9
2.1225	54.5	20.8915	50.9		
2.8137	54.2	23.3067	50.9		
[NaCl] =7.0 x 10^{-3}mol kg^{-1}					
0.0063	55.6	2.3908	54.1	11.9812	51.1
0.0126	55.8	3.4920	53.6	12.6398	51.0
0.0253	55.7	4.5366	53.3	13.2718	50.9
0.0631	55.7	5.5292	53.1	13.8794	50.9
0.1260	55.5	6.4732	52.8	14.4634	50.9

Table 4.1(f)- continued

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[NaCl] =7.0 x 10^{-3} mol kg^{-1}					
0.2513	55.5	7.3724	52.3	15.0255	50.9
0.4998	55.4	8.2298	52.1	15.5665	50.9
0.7454	55.1	9.0484	51.8	16.0879	50.9
0.9884	55.0	9.8304	51.6	16.5909	50.9
1.2286	54.7	10.5786	51.4	17.0762	50.9
1.8176	54.4	11.2948	51.3		
[NaCl] =1.1 x 10^{-2} mol kg^{-1}					
0.0136	55.9	2.6501	53.8	19.6223	49.9
0.0272	55.9	3.9223	52.8	21.3300	49.9
0.0544	55.9	5.1612	52.1	22.9652	49.9
0.1360	55.9	7.5438	51.3	24.5318	49.9
0.2716	55.7	9.8078	50.7	26.0351	49.9
0.5417	55.4	11.9616	50.2	27.4789	49.9
0.8103	55.1	14.0133	49.9	28.8656	49.9
1.6074	54.6	15.9695	49.9		
2.1316	54.2	17.8373	49.9		
[NaCl] =1.8 x 10^{-2} mol kg^{-1}					
0.0163	56.1	2.5504	54.0	18.8995	50.5
0.0326	56.1	3.1696	53.5	21.0790	50.5
0.0652	56.1	4.6864	52.7	23.1558	50.5
0.1630	56.0	6.1606	52.1	25.1368	50.5
0.3254	55.9	8.9875	51.3	27.0290	50.5
0.6490	55.7	11.6638	50.7	28.8383	50.5
1.2903	55.2	14.2010	50.5	30.5696	50.5
1.9240	54.6	16.6096	50.5	32.2278	50.5

Table 4.1(f)- continued

[SDC] x 10^3 / mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3/ mol kg^{-1}	γ / mN m^{-1}	[SDC] x 10^3/ mol kg^{-1}	γ / mN m^{-1}
[NaCl] =2.2 x 10^{-2} mol kg^{-1}					
0.0157	55.5	3.0570	51.4	22.5393	48.3
0.0314	55.4	4.5231	50.6	24.4901	48.3
0.0628	55.3	5.9499	50.1	26.3566	48.3
0.1570	54.8	8.6916	49.2	28.1443	48.3
0.3135	54.6	11.2935	48.7	29.8580	48.3
0.6252	54.0	13.7661	48.3	31.5021	48.3
1.2434	53.3	16.1191	48.3	33.0803	48.3
1.8546	52.5	18.3603	48.3		
2.4592	51.8	20.4984	48.3		
[NaCl] =1.0 x 10^{-1} mol kg^{-1}					
0.0097	56.5	1.8856	53.6	13.9239	49.9
0.0194	56.3	2.7903	52.8	15.1314	49.9
0.0388	56.4	3.6709	52.2	16.2870	49.9
0.0968	56.3	5.3635	51.5	17.3940	49.9
0.1933	56.3	6.9706	51.0	18.4557	49.9
0.3856	56.1	8.4985	50.5	19.4742	49.9
0.7668	55.5	9.9527	50.2	20.4522	49.9
1.1439	54.6	11.3386	50.0	23.1681	49.9
1.5168	54.0	12.6611	49.9		

Table 4.2. The *Cmc* Values of SDC in Water + EG Media at Different NaCl Concentrations Determined from Surface Tension, Fluorescence and Conductance Measurements

[NaCl] / mol kg^{-1}	w_{EG} x 10^2						
	0	10	20	30	40	50	60
	cmc / mmol kg^{-1}						
0	2.34	3.63	5.50	6.31	8.13	10.2	14.1
	(2.04)[a]	(3.6)	(5.2)	(6.5)	(8.3)	(10.9)	-
	-	[3.7][b]	[5.2]	[6.8]	[9.0]	[10.9]	[13.7]
0.005	1.93	3.35	5.20	6.00	7.83	9.90	13.8
0.007	-	3.27	5.13	5.94	7.74	9.79	13.7
0.010	1.73	3.19	5.00	5.80	7.60	9.63	13.5
0.018	-	3.07	4.80	5.65	7.42	9.44	13.3
0.020	1.57	-	-	-	-	-	-
0.022	-	3.00	4.77	5.60	7.36	9.38	13.2
0.1	1.18	2.65	4.20	5.00	6.67	8.60	12.2

[a] from fluorescence; [b] from conductance

Table 4.3. Ratio of the intensities of Fluorescence Emission of Pyrene at 373 nm and at 384 nm of SDC + EG + Water Solution at 298 K

[SDC] x 10^3 / mol kg^{-1}	I_1/I_3	[SDC] x 10^3 / mol kg^{-1}	I_1/I_3	[SDC] x 10^3 / mol kg^{-1}	I_1/I_3
Wt. % EG = 0					
0.0000	1.7200	0.0019	1.4349	0.0035	1.1639
8.1E-4	1.5400	0.0022	1.4050	0.0038	1.1130
0.0011	1.4863	0.0030	1.2053	0.0041	1.1118
0.0016	1.4408	0.0032	1.1772	0.0043	1.1282
Wt. % EG = 10					
6.45E-4	1.9342	0.0039	1.7301	0.0068	1.0695
0.0013	1.9268	0.0045	1.5291	0.0079	0.9671
0.0019	1.9011	0.0052	1.1990		
0.0026	1.8484	0.0058	1.1416		
Wt. % EG = 20					
0.0018	1.8342	0.0073	1.4438	0.0134	0.9542
0.0028	1.8252	0.0083	1.3019	0.0154	0.9183
0.0037	1.8188	0.0092	1.1806	0.0184	0.8741
0.0055	1.7304	0.0110	1.0477		
Wt. % EG = 30					
0.0031	1.7953	0.0082	1.6807	0.0124	1.3812
0.0041	1.8083	0.0093	1.6129	0.0144	1.2642
0.0052	1.7889	0.0103	1.5291	0.0160	1.0811
0.0062	1.7637	0.0113	1.4556	0.0185	1.0225
Wt. % EG = 40					
0.0035	1.8215	0.0138	1.6026	0.0383	1.1351
0.0052	1.8083	0.0156	1.5385	0.0431	1.1148
0.0069	1.7794	0.0173	1.4859	0.0479	1.0858
0.0086	1.7606	0.0190	1.4306		
0.0104	1.7007	0.0208	1.3870		
Wt. % EG = 50					
0.0049	1.7483	0.0195	1.6207	0.0366	1.4045
0.0073	1.7391	0.0293	1.4771	0.0391	1.4265
0.0098	1.7182	0.0318	1.4472		
0.0147	1.6750	0.0342	1.4265		

Table 4.4. Least-Squares Fitted Values of the Parameters of Eq. 1 and of ΔG_m^0 for SDC in Water + EG Media. Values of β from Conductance Data are Given in Parentheses

w_{EG} x 10^2	A	β	ΔG_m^0 / kJ mol^{-1}
0	-7.131	0.177	-15.46
10	-6.151	0.094 (0.09)	-15.23
20	-5.680	0.092 (0.09)	-14.08
30	-5.482	0.082 (0.10)	-13.58
40	-5.182	0.076 (0.11)	-12.83
50	-4.919	0.072 (0.12)	-12.17
60	-4.559	0.069 (0.15)	-11.29

Table 4.5(a)- Specific Conductance (κ) Values of SDC in Ethylene Glycol - Water Mixture at 298 K

[SDC]/ mol kg^{-1}	κ x 10^{4}/ S m^{-1}	[SDC]/ mol kg^{-1}	κ x 10^{4}/ S m^{-1}	[SDC]/ mol kg^{-11}	κ x 10^{4}/ S m^{-1}
		Wt. % EG = 0			
9.8973E-4	0.6090	0.0027	1.5300	0.0074	4.1600
0.0012	0.7090	0.0029	1.6300	0.0091	5.1700
0.0014	0.8140	0.0031.	1.7300	0.0107	6.1700
0.0016	0.9230	0.0035	1.9300	0.0123	7.1800
0.0018	1.0300	0.0037	2.0200	0.0138	8.0600
0.0020	1.1300	0.0038	2.1200	0.0153	8.8800
0.0022	1.2300	0.0048	2.6400	0.0167	9.6800
0.0023	1.3300	0.0056	3.1300	0.0193	11.000
0.0025	1.4300	0.0065	3.6400		
		Wt. % EG = 10			
9.2308E-4	0.5030	0.0066	3.2100	0.0148	7.0900
0.0014	0.7260	0.0080	3.8800	0.0158	7.4000
0.0018	0.9420	0.0093	4.5200	0.0167	7.9600
0.0022	1.1500	0.0105	5.0800	0.0175	8.4100
0.0027	1.3600	0.0117	5.5500	0.0184	8.7200
0.0035	1.8600	0.0128	6.1200		
0.0051	2.5800	0.0138.	6.6200		
		Wt. % EG = 20			
0.0001	0.0494	0.0015	0.6850	0.0129	5.3600
0.0002	0.1040	0.002	0.8740	0.0141	5.8100
0.0003	0.1510	0.0025	1.0700	0.0152	6.2100
0.0004	0.1970	0.003	1.2500	0.0163	6.6300
0.0005	0.2450	0.0039	1.6800	0.0173	7.0100
0.0006	0.2930	0.0057	2.4300	0.0183	7.3400
0.0007	0.3380	0.0073	3.1000	0.0192	7.6700
0.0008	0.3890	0.0088	3.7200	0.02	8.0200
0.0009	0.4390	0.0103	4.3400		
0.0010	0.4830	0.0116	4.8600		

Table 4.5(a)- Continued

[SDC]/ molkg^{-1}	κ x 10^{4}/ S m^{-1}	[SDC]/mol kg^{-1}	κ x 10^{4}/ S m^{-1}	[SDC]/ mol kg^{-11}	κ x 10^{4}/ S m^{-1}
Wt. % EG = 30					
9.1562E-4	0.3520	0.0033	1.1300	0.0128	4.2400
0.0010	0.3980	0.0043	1.5200	0.0142	4.6600
0.0011	0.4400	0.0063	2.1600	0.0155	5.0600
0.0017	0.6230	0.0080	2.7400	0.0167	5.4400
0.0022	0.7870	0.0097	3.2800	0.0179	5.7700
0.0028	0.9600	0.0113	3.7800	0.0190	6.0900
Wt. % EG = 40					
9.4792E-4	0.2940	0.0033	0.9090	0.0133	3.5300
0.0011	0.3350	0.0039	1.0700	0.0151	3.9700
0.0012	0.3730	0.0051	1.4300	0.0167	4.3600
0.0014	0.4150	0.0074	2.0400	0.0183	4.7300
0.0020	0.5840	0.0095	2.5900	0.0197	5.0500
0.0026	0.7450	0.0115	3.0900		
Wt. % EG = 50					
8.2454E-4	0.2030	0.0024	0.5670	0.0115	2.5200
9.8753E-4	0.2420	0.0032	0.7320	0.0139	3.0000
0.0012	0.2800	0.0040	0.8880	0.0162	3.4400
0.0013	0.3240	0.0047	1.0400	0.0183	3.8500
0.0015	0.3670	0.0062	1.4000	0.0203	4.2300
0.0016	0.4000	0.0089	1.9900	0.0222	4.5800
Wt. % EG = 60					
9.3147E-4	0.1760	0.0023	0.4280	0.0126	2.0900
0.0012	0.2220	0.0034	0.6120	0.0162	2.6300
0.0014	0.2600	0.0045	0.7740	0.0196	3.1300
0.0016	0.2970	0.0056	0.9310	0.0227	3.5700
0.0019	0.3440	0.0066	1.1000	0.0257	3.9600
0.0021	0.3870	0.0087	1.4700	0.0285	4.3300

Table 4.6. Values of Surface excess of SDC in water + EG at 298 K

[NaCl] / mol kg^{-1}	w_{EG} x 10^2						
	0	10	20	30	40	50	60
	10^6 x Γ_{cmc} /mol m^{-2}						
0	0.73	0.60	0.75	0.75	0.56	0.55	0.45
0.005	1.03	0.97	0.90	0.87	0.73	0.60	0.55
0.007	-	0.99	0.96	0.90	0.77	0.61	0.59
0.01	1.10	1.01	0.98	0.95	0.77	0.64	0.60
0.018	-	1.07	1.00	0.98	0.85	0.64	0.61
0.02	1.34	-	-	-	-	-	-
0.022		1.08	1.01	0.98	0.85	0.66	0.61
0.03	1.33	-	-	-	-	-	-
0.05	1.48	-	-	-	-	-	-
0.1	1.33	1.24	1.18	1.07	0.95	0.75	0.73

Table 4.7. Density, Molar Volume, Gordon Parameter and Surface Tension of Water + EG Media, and Surface Tension of SDC in Water + EG at the Cmc

w_{EG} x 10^2	Density x10^{-3} /kg m^{-3}	V x 10^6/ m^3 mol^{-1}	$\gamma/V^{1/3}$ /J m^{-3}	γ_0 / mN m^{-1}	γ_{cmc} / mN m^{-1}	γ_0 / γ_{cmc}
0	0.99704	18.00	2.75	72.0	46.0	1.56
10	1.01234	19.14	2.51	67.2	47.3	1.42
20	1.02055	20.56	2.37	65.4	47.8	1.37
30	1.04109	21.97	2.24	63.0	48.4	1.30
40	1.05482	23.83	2.06	60.0	49.2	1.22
50	1.06774	26.14	1.95	57.8	50.5	1.14
60	1.07951	29.05	1.81	56.3	50.3	1.12

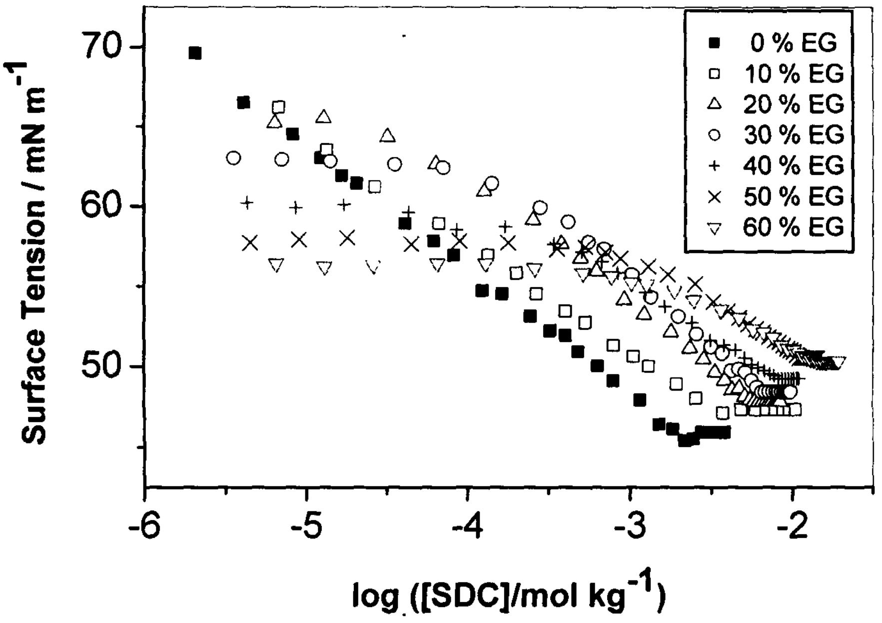

Figure 4.1. Variation of surface tension of SDC + water + EG with SDC concentration when the medium contains no NaCl and different mass fraction x 10^2 (given in inset) of EG.

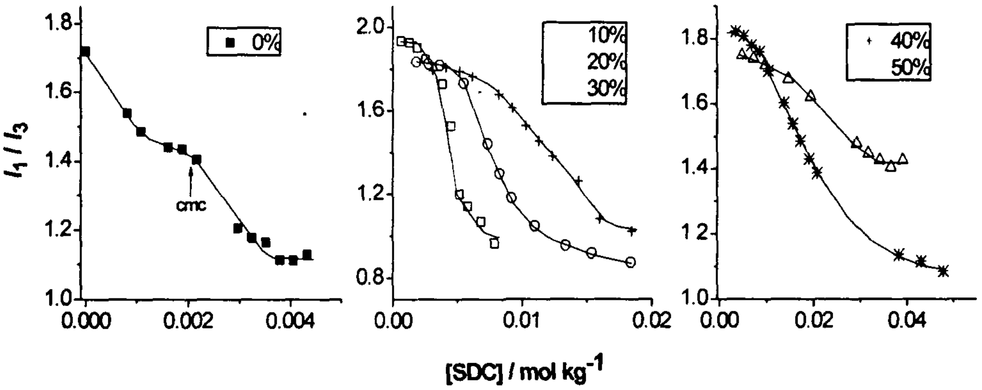

Figure 4.2. Variation of I_1/I_3 values of pyrene with SDC concentration in water + EG media. The mass fraction x 10^2 values of EG are indicated in the insets.

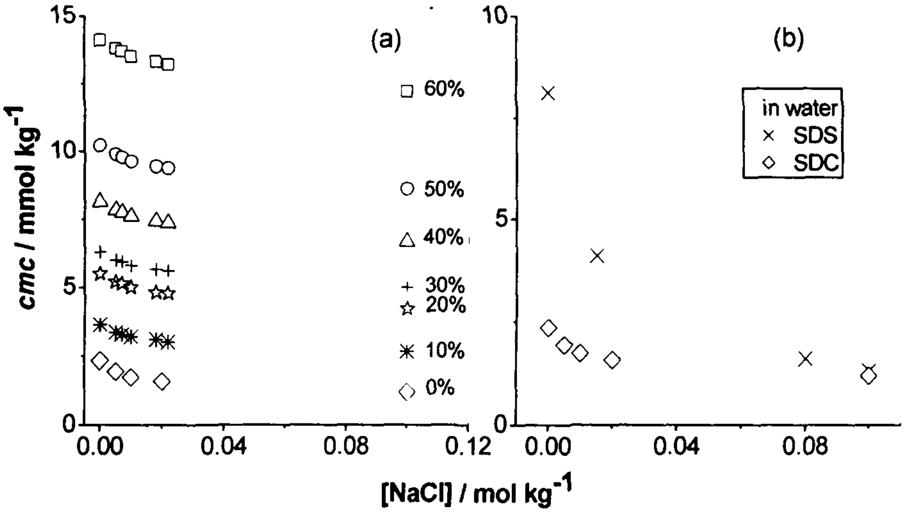

Figure 4.3. Variation of *cmc* of SDC with NaCl concentration in water + EG media. The *cmc* values of SDS in water are from reference 30.

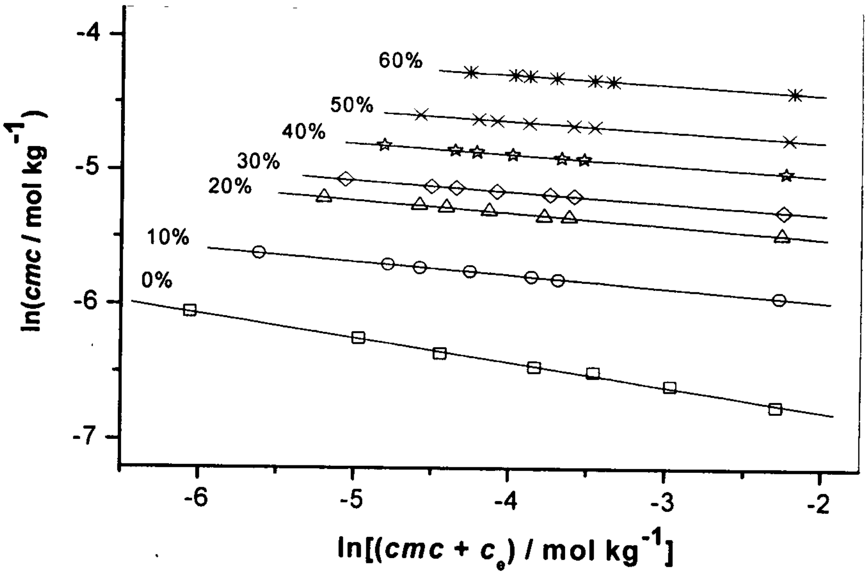

Figure 4.4. Corrin – Harkins plots for SDC in water + EG media.

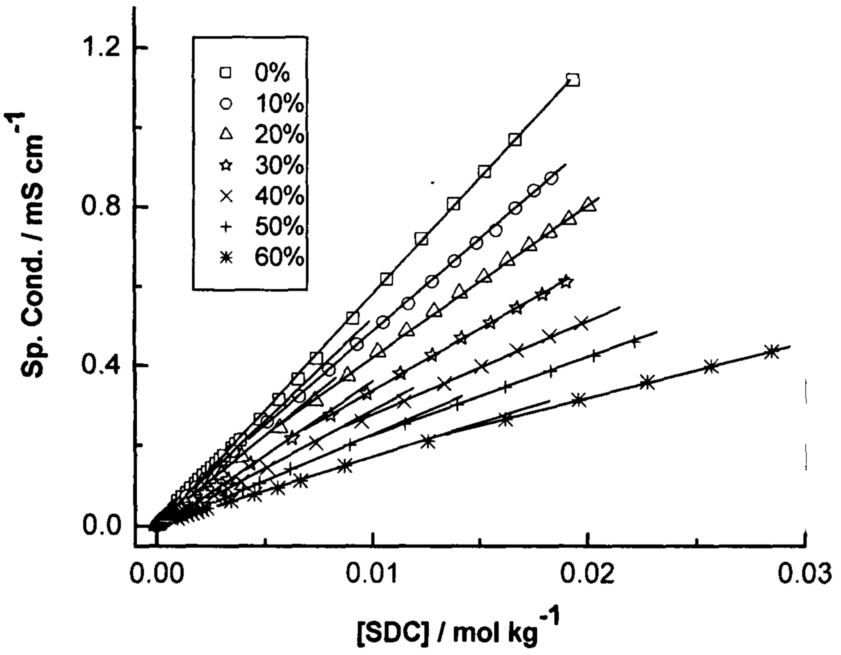

Figure 4.5. Variation of specific conductance with SDC concentration in water + EG media. The mass fraction x 10^2 values of EG are indicated in the inset.

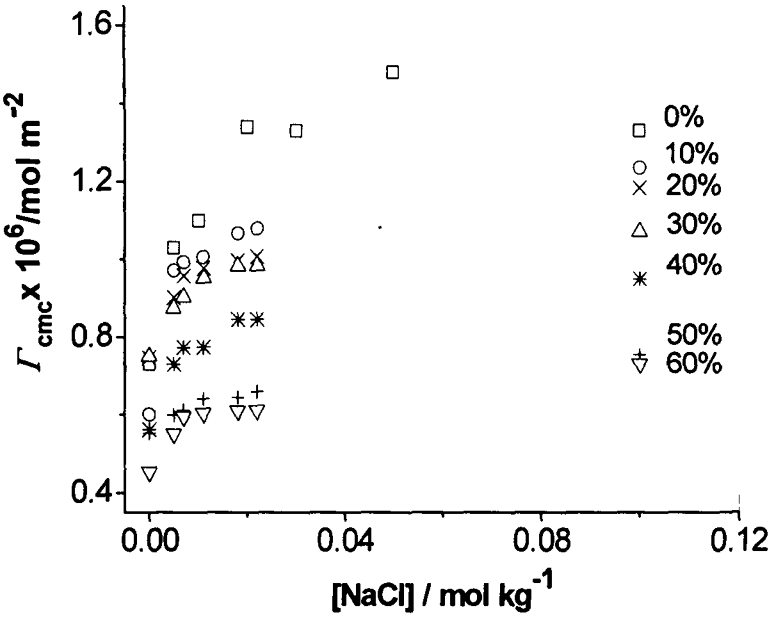

Figure 4.6. Surface excess of SDC at *cmc* in water + EG media as a function of NaCl concentration.

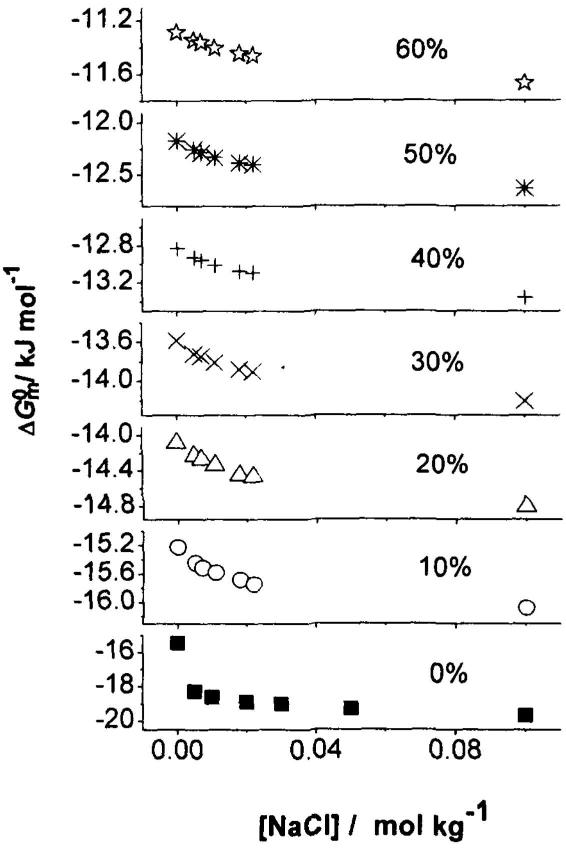

Figure 4.7. Variation of ΔG^0_m of SDC with NaCl concentration.

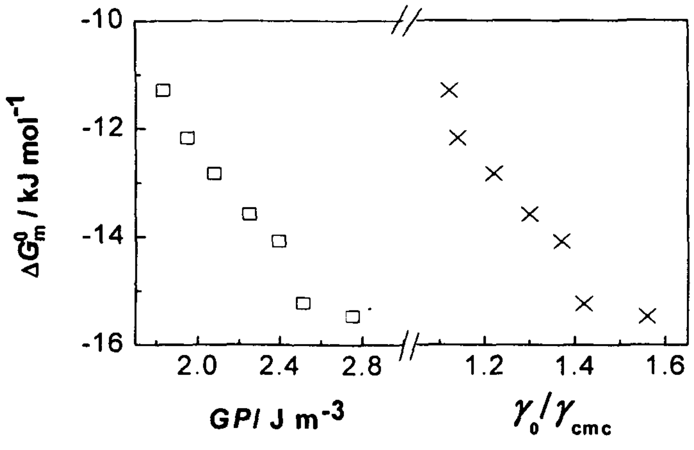

Figure 4.8. Variation of ΔG_m^0 of SDC with Gordon parameter and the ratio γ_0/γ_{cmc}.

CHAPTER 5

Micellization and Counter Ion Binding Behaviours of Sodium Deoxycholate and Sodium Dioctylsulfosuccinate Mixtures in Water

5.1 Introduction

In the preceding chapters we assessed the aggregation, adsorption and counter ion binding behaviours of pure sodium deoxycholate (SDC) in aqueous and aqueous ethylene glycol media. Micellization ability of a surfactant improves when it is mixed with another surfactant and owing to this synergistic effect mixed surfactants are used for various applications. The physicochemical properties of SDC in its mixed state with cationic, anionic and nonionic surfactants have been studied extensively. However, the micellization and counter ion binding characteristics of mixtures of SDC with sodium dioctylsulfosuccinate (AOT) has not been investigated. SDC and AOT micelles have much different counter ion binding behaviours. In the presence of added NaCl, the ability of SDC micelle to bind sodium counter ion is low as stated in chapter 3, whereas AOT micelle has, on the other hand, relatively high ability to bind sodium counter ion.[1-5] Moreover, AOT micelle has a special counter ion binding property,[1-5] viz., the value of counter ion binding constant switches from about 0.4 to 0.8 when the added NaCl concentration becomes approximately equal to or more than 0.015 mol kg^{-1}. What will be the effect of the special counter ion binding property of AOT micelle on the poor counter ion binding ability of SDC micelle when these two surfactants are mixed? To address this question, we have studied the micellization behaviour of mixtures of SDC and AOT in the presence of NaCl in aqueous medium and the results are presented in this chapter.

5.2 Experimental Section

SDC (Fluka, 98%), AOT (Sigma, 99%) and Sodium Chloride (Merck, GR grade 99.5%) were used as received. All solutions were prepared in Millipore water and measurements were made at 25 °C. An aqueous solution containing a mixture of SDC (surfactant 1) and AOT (surfactant 2) of a particular composition was prepared by mixing required amounts of the solutions of pure surfactants. Surface tension measurements were made by the Wilhelmy plate method using a Krüss K11 tensiometer.

5.3 Results and Discussion

The measured values of surface tension (γ) of α_{SDC}SDC + (1-α_{SDC})AOT mixtures at 25 °C in water as well as aqueous NaCl media are listed in Tables 5.1(a-j) . The plots of γ as a function of concentration (c) of SDC + AOT mixture corresponding to different values of α_{SDC} are shown in Fig. 5.1.

5.3.1 Critical micelle concentration.

The values of critical micelle concentration (cmc) of SDC + AOT mixtures in water and aqueous NaCl media determined from the surface tension isotherms are given in Table 5.2. The cmc values of SDC (c_{0SDC}) and AOT (c_{0AOT}) as a function of NaCl concentration are taken from chapter 3 and literature,[1] respectively. The variation of cmc of the mixture (c_{0m}) with α_{SDC} in the absence and presence of NaCl is shown in Fig. 5.2. The relation between c_{0m}, c_{0SDC} and c_{0AOT} is given by[6,7]

$$\frac{1}{c_{0m}} = \frac{\alpha_{SDC}}{f_{SDC}c_{0SDC}} + \frac{\alpha_{AOT}}{f_{AOT}c_{0AOT}} \tag{5.1}$$

The term f refers to activity coefficient in the mixed micellar phase and is given by

$$f_i = \frac{\alpha_i c_{0m}}{x_i c_{0i}}, \quad \text{i = SDC or AOT} \tag{5.2}$$

In Eq. (5.2), x_i is the mole fraction of SDC or AOT in the mixed micelle. When the mixed micelle is considered to behave ideally (f_i = 1), Eq. (5.1) gives the Clint's equation[8] (Eq. 5.3).

$$\frac{1}{c_{0m}} = \frac{\alpha_{SDC}}{c_{0SDC}} + \frac{\alpha_{AOT}}{c_{0AOT}} \tag{5.3}$$

The ideal values of c_{0_m} calculated using Clint's equation are shown in Fig. 5.2. We also checked the additivity of cmc using the relation

$$c_{0m} = \alpha_{SDC} c_{0SDC} + \alpha_{AOT} c_{0AOT} \tag{5.4}$$

It may be seen from Fig. 5.2 that for the SDC + AOT mixtures cmc calculated from Eqs. (5.3) and (5.4) are almost same in water and aqueous NaCl solutions when [NaCl] $\leq$ 0.01 mol kg^{-1}. It can be shown that the values of c_{0_m} obtained from Clint's equation and additivity rule become equal when the condition given in Eq. (5.5) holds good.

$$\alpha_{SDC}\alpha_{AOT}(c_{0AOT} - c_{0SDC})^2 \approx 0 \tag{5.5}$$

Therefore for mixtures in which the difference between $c_{0_{AOT}}$ and $c_{0_{SDC}}$ is not significant Clint's equation and additivity rule give almost same c_{0_m} values. Experimental values of c_{0_m} are less than the ideal values in water (Fig. 5.2) thereby indicating synergism. However, addition of NaCl removes synergism and causes antagonism. Thus, presence of NaCl can hamper the performance of the SDC + AOT mixture.

The variation of cmc of the SDC + AOT mixture with NaCl concentration is shown in Fig. 5.3. For mixtures of $0 \le \alpha_{SDC} \le 0.5$, the plots of cmc versus NaCl concentration cross each other and the points of crossing lie in the region where $0.005 \le [\text{NaCl}] < 0.015$ mol kg^{-1}. As a result, as α_{SDC} decreases from 0.5 to 0, cmc of mixtures increases in water, but decreases in aqueous NaCl medium if [NaCl] > 0.015 mol kg^{-1}. This kind of dependence of cmc on NaCl concentration can be attributed to the variation in the counter ion binding of sodium ion to mixed micelles with change in the AOT amount. The values of counter ion binding constant (β) are determined in the following section.

5.3.2 Counter ion binding constant

The dependence of cmc of single surfactant solutions on the concentration of added NaCl (c_e) can be described by the Corrin – Harkins (CH) equation of the form

$$\ln c_{0i} = A_1 - \beta \ln(c_{0i} + c_e), \qquad \text{i = SDC or AOT} \tag{5.6}$$

where A_1 is a constant related to the standard free energy of micellization and β is the binding constant of sodium counter ion. The plots of $\ln c_{0i}$ versus $\ln(c_{0i} + c_e)$ for SDC and AOT are shown in Fig. 5.4. Data for drawing the CH plots for SDC and AOT are taken from chapter 3 and literature,[1] respectively. For a mixed surfactant system the form of CH equation is different from Eq. (5.6). To show this, we consider the equilibrium for the micellization of a mixture of two anionic surfactants (RS$_1$ and RS$_2$) containing the same counter ion (R$^+$) as

$$n_1 S_{1_1}^- + n_2 S_2^- + mR^+ \rightleftharpoons M^{z-} \tag{5.7}$$

In the above equilibrium, $n_1$and n_2 are the aggregation numbers of surfactants RS$_1$ and RS$_2$ in the mixed micelle, respectively, m is the number of counter ions that binds to the mixed micelle, M refers to the mixed micelle and the charge on the micelle $z = n_1 + n_2 - m$. In the mixture, let α_1 and α_2 be the mole fractions of RS$_1$ and RS$_2$ in the bulk, respectively. Writing the expression for the equilibrium constant of the equilibrium (5.7) and then relating it to standard free energy of micellization (ΔG^0), we get the relation just above the cmc as

$$x_1 \ln[S_1^-] + x_2 \ln[S_2^-] \approx (\Delta G^0 / nRT) - \beta \ln[R^+] \tag{5.8}$$

In Eq. (5.8), $n = n_1 + n_2$, which gives the total aggregation number of the mixed micelle and $x_i = n_i/n$ (i =1 or 2) is the mole fraction of surfactant in the mixed micelle. In writing Eq. (5.8), near the cmc the value of ln[M]/n has been neglected in comparison to $\Delta G^0/n$, which is an approximation made while deriving CH equation for single surfactants also. Applying Eq. (5.8) to the present mixed surfactant system of a particular composition, we get in the presence of an added electrolyte having same counter ion an expression of the form

$$\ln(\alpha_{AOT} c_{0m}) + x_{SDC} \ln(\alpha_{SDC} / \alpha_{AOT}) = A - \beta \ln(c_{0m} + c_e) \tag{5.9}$$

In Eq. (5.9), the term A is given by the expression

$$A = \Delta G^0 / nRT = \Delta G_m^0 / RT = (1+\beta) \ln c_{0m} + x_{SDC} \ln \alpha_{SDC} + x_{AOT} \ln \alpha_{AOT} \tag{5.10}$$

Eq. (5.9) is a modified form of CH equation for a mixture of two ionic surfactants containing a common counter ion. In Eq. (5.10), c_{0_m} refers to cmc in the absence of electrolyte (at $c_e = 0$) and ΔG_m^0 is the standard free energy of micellization per mole of monomer. β of mixed surfactants corresponding to different values of α_{SDC} was determined by plotting the terms in the left hand side of Eq. (5.9) against ln (c_{0m} + c_e). These plots are shown in Fig. 5.4 and the values of β obtained from the slopes of these plots are shown in Table 5.3 and Fig. 5.5. AOT has been reported[1-5] to exhibit a special type of counter ion binding behaviour, viz., $\beta \approx 0.4$ when [NaCl] ≤ 0.015 mol kg^{-1} and $\beta \approx 0.8$ when [NaCl] > 0.015 mol kg^{-1}. SDC, on the other hand, has only one value of β in aqueous NaCl solution. It is interesting to note that SDC + AOT mixture also exhibits counter ion binding behaviour similar to that of AOT. However, the lower and higher values of β and the NaCl concentration at which sudden change in the value of β occurs are found to be dependent on the amount of SDC in the mixture. In mixtures having composition in the range of $0.206 \leq \alpha_{SDC} \leq 0.917$, the switch over from lower to higher value of β occurs at [NaCl] ≈ 0.005 mol kg^{-1}, whereas in the mixture of $\alpha_{SDC} = 0.107$ the change in β occurs at [NaCl] ≈ 0.007 mol kg^{-1}. Therefore, presence of SDC lowers the value of β and the concentration limit of NaCl at which β shifts to higher value. The counter ion binding behaviour of SDC + AOT mixtures thus has interesting features, which depend on the value of α_{SDC} and the concentration of NaCl. In the case of neat AOT, the shift in the β value is reported[5] to be due to change of shape of AOT micelle from prolate ellipsoidal to rod-type. Therefore, in SDC + AOT mixtures also the shape of the mixed micelle is expected to change from prolate to rod-type near the NaCl concentration where β value suddenly changes. A schematic diagram depicting shape change of mixed micelle is shown in Fig. 5.6, which was drawn in the light of the reported[9] schematic representation of the mixed micelles of SDC and dimyristoylphosphatidylcholine.

5.3.3. Composition of mixed micelle

Ideal compostion. The mole fraction of SDC in the mixed micellar phase, x_{SDC}, is defined as

$$x_{SDC} = \frac{n_{SDC}}{n_{SDC} + n_{AOT}} \tag{5.11}$$

x_{AOT} is also similarly defined. n_i (i = SDC or AOT) represents aggregation number of SDC or AOT in the mixed micellar phase. The value of x_{SDC} under ideal condition represented by $x_{SDC}{}^{id}$ was calculated using the expression

$$x_{SDC}{}^{id} = \frac{\alpha_{SDC} c_{0AOT}}{\alpha_{SDC} c_{0AOT} + \alpha_{AOT} c_{0SDC}} \tag{5.12}$$

Eq. (5.12) was obtained from Eq. (5.2) after substituting the value one for activity coefficients. The values of $x_{SDC}{}^{id}$ are given in Table 5.4 and also plotted versus α_{SDC} in Fig. 5.7. It is found that in water and aqueous NaCl medium containing NaCl $\leq$ 0.007 mol kg^{-1}, $x_{SDC}{}^{id} > \alpha_{SDC}$. Therefore, under ideal condition the mixed micelle would have more SDC and less AOT compared to the corresponding amounts of SDC and AOT in the bulk, which is due to lower cmc of SDC than that of AOT in these media. In aqueous NaCl medium containing

NaCl ≥ 0.01 mol kg^{-1}, the cmc of SDC is, on the other hand, higher than that of AOT and accordingly $x_{SDC}{}^{id} < \alpha_{SDC}$.

Composition from Rubingh's model. According to this model,[6,7] the interaction parameter (β_{int}) responsible for non-ideality of the mixed micelle is related to the activity coefficient through the expression

$$\beta_{\text{int}} = \ln f_{SDC} / (1 - x_{SDC})^2 = \ln f_{AOT} / (x_{SDC})^2 \tag{5.13}$$

Substituting for f_i from Eq. (5.2) in Eq. (5.13), we get

$$\frac{(x_{SDC})^2 \ln[\alpha_{SDC} c_{0m} / (x_{SDC} c_{0SDC})]}{(1 - x_{SDC})^2 \ln[(1 - \alpha_{SDC}) c_{0m} / \{(1 - x_{SDC}) c_{0AOT}\}]} = 1 \tag{5.14}$$

Using iteration method Eq. (5.14) was solved to determine the values of x_{SDC} corresponding to different values of α_{SDC} and these values of x_{SDC} were identified as $x_{SDC}{}^{Rb}$, which are given in Table 5.4. The variation of $x_{SDC}{}^{Rb}$ with α_{SDC} is shown in Fig. 5.7. Substituting the values of $x_{SDC}{}^{Rb}$ in Eq. (5.2), activity coefficients in mixed micellar phase were evaluated and then using Eq. (5.13) values of β_{int} were, in turn, determined. The values of f_i and β_{int} are given in Table 5.4. Only in water medium we observed synergism (Fig. 5.2) and as expected β_{int} has negative values implying attractive interaction.

Composition from Motomura-Yamanaka-Aratono model. By applying Gibbs-Duhem relation rigorously, Motomura et al.[10] proposed a general approach for determining composition of mixed micelles formed by mixing different types of surfactants. This model when applied to the present system, which is a mixture of two ionic surfactants with common counter ion, we get the relation

$$x_{SDC} = \alpha_{SDC} - 2\alpha_{SDC}\alpha_{AOT}(\partial \ln c_{0m} / \partial \alpha_{SDC}) \tag{5.15}$$

x_{SDC} calculated from Eq. (5.15) are denoted by $x_{SDC}{}^{\mathrm{Mo}}$. The slope $\partial \ln c_{0m} / \partial \alpha_{SDC}$ was determined by least-squares fitting the $\ln c_{0m}$ versus α_{SDC} data to a polynomial. The values of $x_{SDC}{}^{\mathrm{Mo}}$ are shown in Table 5.4 and Fig. 5.7.

Composition from Rodenas-Valiente-Villafruela model. Rodenas et al.[11] also proposed an expression for determining the mole fraction of surfactant components in the mixed micelle by applying Gibbs-Duhem equation and it is of the form

$$x_{SDC} = \alpha_{SDC} - \alpha_{SDC}\alpha_{AOT}(\partial \ln c_{0m} / \partial \alpha_{SDC}) \tag{5.16}$$

It has been shown that Eq. (5.16) is a special case of the Motomura's general equation applicable for mixtures of two nonionic surfactants. x_{SDC} evaluated from Eq. (5.16) is denoted by $x_{SDC}{}^{\mathrm{Rd}}$ and its values are also shown in Table 5.4 and Fig. 5.7.

In aqueous electrolyte media when NaCl concentration is ≥ 0.02 mol kg^{-1}, all the above models appear to fail beyond some values of α_{SDC} (Table 5.4). For e.g., from Rubingh's model, we could not get x_{SDC} corresponding to (i) $\alpha_{SDC} =$ 0.107 in 0.02 mol kg^{-1} NaCl medium and (ii) $\alpha_{SDC} =$ 0.206 and 0.107 in 0.03 mol kg^{-1} NaCl medium because Eq. (5.14) could not be solved. This type of problem in solving Eq. (5.14) was faced by Jana and Moulik[12] in sodium dodecyl sulfate + sodium taurochenodeoxycholate mixed system. Similarly, we could not get x_{SDC} from Motomura's model corresponding to (i) $\alpha_{SDC} =$ 0.206 and 0.107 in 0.02 mol kg^{-1} NaCl medium and (ii) $\alpha_{SDC} =$ 0.311, 0.206 and 0.107 in 0.03 mol kg^{-1} NaCl medium because x_{SDC} value becomes negative. Added NaCl appears to push more of AOT to mixed micellar phase in the region where $\alpha_{SDC} \leq 0.640$ and [NaCl] ≥ 0.01 mol kg^{-1} (Fig. 5.8), which may be due to special counter ion binding property of AOT.

5.3.4. Free energy of micellization

The values of standard free energy of micellization per mole of monomer for single component micelles and mixed micelles are evaluated from Eqs. (5.17) and (5.18), respectively,[13]

$$\Delta G_m^0 = RT(1+\beta)\ln c_{0m} \tag{5.17}$$

$$\Delta G_m^0 = RT[(1+\beta)\ln c_{0m} + x_{SDC}\ln\alpha_{SDC} + x_{AOT}\ln\alpha_{AOT}] \tag{5.18}$$

Eq. (5.18) is obtained by rearranging Eq. (5.10). The values of ΔG_m^0 calculated from the above equations are shown in Table 5.5 and Fig. 5.9. From Fig. 5.9 it can be seen that there is an overall decrease in free energy of micellization as α_{SDC} decreases from 1 to 0 indicating that AOT favours micellization. For SDC + AOT mixture of α_{SDC}=0.107 in aqueous media containing 0.007 and 0.01 mol kg^{-1} NaCl the values of ΔG_m^0 are found to be out of the regular trend and this was due to shift in the value of β. For SDC + AOT mixture of a particular composition (at a fixed α_{SDC}) ΔG_m^0 decreases with increasing concentration of NaCl, which is the general trend.

5.3.5. Adsorption parameters

For SDC + AOT mixture, it can be shown[13] by using the Gibbs adsorption isotherm that

$$d\gamma = -2RT\Gamma(d\ln c + x_{aSDC} d\ln\alpha_{SDC} + x_{aAOT} d\ln\alpha_{AOT}) \tag{5.19}$$

where Γ is the surface excess of the mixed surfactant system, $x_{ai} = \Gamma_i / \Gamma$ is the mole fraction of the surfactant i (i= SDC or AOT) in the adsorbed layer. c is the concentration of the mixed surfactant of a particular composition (fixed α_{SDC}) in the bulk. For SDC + AOT system at constant α_{SDC}, Eq. (5.19) reduces to the form

$$d\gamma = -2RT\Gamma d\ln c \tag{5.20}$$

which is the same equation used for calculating the surface excess of a single ionic surfactant. Accordingly, surface excess at the cmc (Γ_{cmc}) of SDC + AOT mixture in water medium was calculated (Table 5.6) from Eq. (5.20) after evaluating the slope $d\gamma / d\ln c$ near the cmc (c_{0m}) by least-squares fitting. In the light of Prosser and Franses treatment,[14] for SDC + AOT mixture in the presence of c_e mol kg^{-1} of NaCl Eq. (5.19) takes the form

$$d\gamma = -RT\Gamma[d\ln c + d\ln(c + c_e) + x_{aSDC} d\ln\alpha_{SDC} + x_{aAOT} d\ln\alpha_{AOT}] \tag{5.21}$$

For SDC + AOT + NaCl system at constant α_{SDC} and c_e, Eq. (5.21) becomes

$$d\gamma = -RT\Gamma\left[1 + \frac{c}{c + c_e}\right] d\ln c \tag{5.22}$$

Γ_{cmc} of SDC + AOT mixture in aqueous NaCl medium was calculated (Table 5.6) from Eq. (5.22) after evaluating the slope $d\gamma / d\ln c$ near the cmc (c_{0m}) by least-squares fitting. Γ_{cmc} of SDC + AOT mixture (i) has very weak dependence on α_{SDC} in the region from α_{SDC} = 0.1 to α_{SDC} = 0.8 (Fig. 5.10) and (ii) increases with increase in NaCl concentration up to [NaCl] = 0.01 mol kg^{-1} and thereafter the change in the region from [NaCl] = 0.01 to [NaCl] = 0.03 mol kg^{-1} is found to be not much (Fig. 5.11).

5.4 Conclusions

In water medium cmc of SDC + AOT mixed system exhibits synergism. Addition of NaCl removes synergism and causes antagonism. Therefore, presence of NaCl can hamper the performance of SDC + AOT mixture. As α_{SDC} decreases from 0.5 to 0, cmc of mixtures increases in water, but decreases in aqueous NaCl medium if [NaCl] > 0.015 mol kg^{-1}. SDC + AOT mixture exhibits counter ion binding behaviour similar to that of AOT. The values (lower and higher) of β and the NaCl concentration at which sudden change in the value of β occurs are dependent on the amount of SDC in the mixture. Added NaCl affects significantly the micellar composition and surface excess of the mixed system.

5.5 References

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Table 5.1(a)- Surface tension (γ) values of SDC in aqueous sodium chloride at 298K

c x 10^3 / mol kg^{-1}	γ / mN m^{-1}	c x 10^3 / mol kg^{-1}	γ / mN m^{-1}	c x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[NaCl] = 0.00mol kg^{-1}					
0.0021	69.6	0.1236	54.7	1.5057	46.4
0.0041	66.5	0.1643	54.5	1.8394	46.1
0.0083	64.5	0.2453	53.1	2.1582	45.4
0.0124	63.0	0.3254	52.2	2.4631	45.5
0.0166	61.9	0.4047	51.9	2.7551	45.9
0.0207	61.4	0.4832	50.9	3.0349	45.9
0.0414	58.9	0.6379	50.0	3.3033	45.9
0.0620	57.8	0.7896	49.1	3.5610	45.9
[NaCl] =5.0 x 10^{-3}mol kg^{-1}					
0.0030	65.7	0.4732	49.9	1.7760	45.6
0.0060	63.4	0.5882	49.2	1.8774	45.3
0.0121	61.7	0.7021	48.8	1.9777	45.1
0.0181	60.1	0.8147	48.3	2.0770	45.2
0.0242	59.1	0.9261	47.9	2.1753	45.2
0.0302	58.6	1.0363	47.3	2.2726	45.2
0.0603	56.4	1.1453	47.1	2.3690	45.2
0.0903	55.1	1.2532	46.7	2.4644	45.2
0.1203	54.1	1.3600	46.4	2.5588	45.2
0.1799	52.9	1.4656	46.2	2.6523	45.2
0.2392	51.9	1.5701	46.0		
0.3568	50.6	1.6736	45.8		
[NaCl] =1.0 x 10^{-2} mol kg^{-1}					
0.0040	66.3	0.6283	48.4	4.1367	44.7
0.0080	64.0	0.7813	47.5	4.7153	44.7
0.0401	58.2	1.1565	46.3	5.2680	44.7
0.0800	55.9	1.5220	45.4	5.7963	44.7
0.1597	53.3	2.2252	44.7	6.3020	44.7
0.3176	50.9	2.8938	44.7		
0.4738	49.5	3.5302	44.7		

Table 5.1(a)- continued

c x 10^3 / mol kg^{-1}	γ / mN m^{-1}	c x 10^3 / mol kg^{-1}	γ / mN m^{-1}	c x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[NaCl] =2.0 x 10^{-2} mol kg^{-1}					
0.0027	66.7	0.2175	51.7	1.2441	45.4
0.0055	64.2	0.3247	50.2	1.3415	45.2
0.0110	61.5	0.4308	49.0	1.4380	44.8
0.0165	60.3	0.5359	48.4	1.5336	44.5
0.0219	59.3	0.6400	47.8	1.6283	44.3
0.0274	58.5	0.7431	47.3	1.7221	44.5
0.0548	55.9	0.8452	46.6	1.8152	44.5
0.0821	54.7	0.9463	46.4	1.9073	44.5
0.1093	53.7	1.0465	46.0	1.9987	44.5
0.1635	52.4	1.1458	45.6	2.0892	44.5
[NaCl] =3.0 x 10^{-2} mol kg^{-1}					
0.0034	62.1	0.2010	50.6	1.2851	44.3
0.0068	60.6	0.2674	49.6	1.4068	43.9
0.0135	58.8	0.3991	48.3	1.5273	43.6
0.0202	58.2	0.5294	47.4	1.6467	43.8
0.0270	57.0	0.6585	46.6	1.7650	43.8
0.0337	56.6	0.7863	46.0	1.8821	43.8
0.0674	54.0	0.9128	45.6	1.9981	43.8
0.1009	52.8	1.0381	45.0	2.1130	43.8
0.1344	51.9	1.1622	44.6	2.2269	43.8

Table 5.1(b) - Surface tension (γ) values of SDC (α_{SDC} = 0.917) + AOT at 298K

c x 10^3 / mol kg^{-1}	γ / mN m^{-1}	c x 10^3 / mol kg^{-1}	γ / mN m^{-1}	c x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[NaCl] = 0.00mol kg^{-1}					
0.0031	66.0	0.2463	50.8	1.9932	40.2
0.0062	63.6	0.3675	49.4	2.2506	39.5
0.0124	61.2	0.4874	47.7	2.5021	39.5
0.0187	59.9	0.6061	47.2	2.7476	39.5
0.0249	59.2	0.8976	44.8	2.9874	39.5
0.0311	58.4	1.1818	43.2	3.2219	39.5
0.0621	56.1	1.4590	42.0	3.4510	39.5
0.1238	53.2	1.7293	40.9	3.6750	39.5
[NaCl] =5.0 x 10^{-3}mol kg^{-1}					
0.0022	66.1	0.2581	46.3	1.9380	37.5
0.0044	63.2	0.3424	45.9	2.2745	37.5
0.0087	59.9	0.4259	43.9	2.5965	37.5
0.0218	57.3	0.6311	42.5	2.9050	37.5
0.0436	54.1	0.8313	42.1	3.2007	37.4
0.0869	50.9	1.2176	40.0	3.4845	37.5
0.1729	49.0	1.5861	38.5	3.7570	37.5
[NaCl] =7.0 x 10^{-3}mol kg^{-1}					
0.0021	66.4	0.3333	46.0	2.1977	37.6
0.0043	63.1	0.4144	45.1	2.5058	37.6
0.0085	60.9	0.6135	43.2	2.8002	37.6
0.0212	56.9	0.8076	42.0	3.0819	37.5
0.0424	54.5	0.9967	40.8	3.3516	37.6
0.0847	51.8	1.1811	40.2	3.6101	37.4
0.1684	48.8	1.5365	38.8	3.8580	37.6
0.2513	47.2	1.8749	37.6		
[NaCl] =1.0 x 10^{-2}mol kg^{-1}					
0.0016	70.3	0.0318	57.4	0.2500	47.4
0.0032	68.1	0.0635	53.7	0.3109	46.2
0.0064	65.0	0.1263	50.2	0.4606	43.7
0.0159	60.9	0.1884	48.5	0.6066	42.5

Table 5.1(b)- continued

$c \times 10^3$ / mol kg^{-1}	γ / mN m^{-1}	$c \times 10^3$ / mol kg^{-1}	γ / mN m^{-1}	$c \times 10^3$ / mol kg^{-1}	γ / mN m^{-1}
		[NaCl] =1.0 x 10^{-2}mol kg^{-1}			
0.8881	40.7	1.8915	37.1	2.7338	37.1
1.1565	39.2	2.1155	37.1	2.9236	37.2
1.4127	38.4	2.3302	37.1	3.1062	37.3
1.6574	37.4	2.5361	37.1	3.2818	37.1
		[NaCl] =2.0 x 10^{-2} mol kg^{-1}			
0.0022	68.5	0.3386	43.0	2.5303	33.1
0.0043	65.7	0.4210	42.4	2.8252	33.0
0.0087	61.8	0.6229	40.3	3.1069	32.8
0.0216	57.7	0.8194	38.5	3.3761	32.7
0.0432	54.3	1.1972	36.9	3.6338	32.9
0.0861	49.7	1.5558	35.7	3.8806	32.8
0.1712	46.5	1.8967	34.7		
0.2554	43.7	2.2211	34.0		
		[NaCl] =3.0 x 10^{-2} mol kg^{-1}			
0.0033	64.6	0.2628	41.3	1.4987	31.1
0.0066	61.3	0.3922	38.8	1.6156	31.1
0.0133	57.8	0.5202	37.0	1.7313	31.1
0.0199	55.9	0.6469	35.7	1.8459	31.1
0.0265	54.2	0.7724	35.0	1.9594	31.1
0.0332	53.1	0.8965	33.6	2.0717	31.1
0.0662	49.7	1.0194	32.9	2.1830	31.1
0.0992	47.5	1.1410	32.0	2.2933	31.1
0.1321	45.6	1.2615	31.6	2.4024	31.1
0.1976	43.2	1.3807	31.2		

Table 5.1(c)- Surface tension (γ) values of SDC (α_{SDC} = 0.79) + AOT at 298K

c x 10^3 / mol kg^{-1}	γ / mN m^{-1}	c x 10^3 / mol kg^{-1}	γ / mN m^{-1}	c x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[NaCl] = 0.00mol kg^{-1}					
0.0025	67.0	0.4781	45.8	2.3560	35.2
0.0049	66.1	0.7080	43.8	2.5408	35.2
0.0098	62.7	0.9321	41.3	2.7214	35.2
0.0245	60.1	1.1507	39.8	2.8980	35.1
0.0489	56.7	1.3639	39.0	3.0707	35.1
0.0976	53.6	1.5720	38.3	3.2396	35.2
0.1942	50.7	1.7750	37.5	3.4049	35.1
0.2898	47.0	1.9732	36.5	3.5666	35.2
0.3845	47.1	2.1669	35.9		
[NaCl] =5.0 x 10^{-3}mol kg^{-1}					
0.0313	54.1	0.9026	39.1	4.0810	34.3
0.0626	51.2	1.1870	37.4	4.4861	34.2
0.1248	48.3	1.7333	35.0	4.8731	34.3
0.2482	45.3	2.2514	34.2	5.2431	34.2
0.3702	43.6	2.7433	34.2	5.5973	34.2
0.4909	42.3	3.2111	34.2	5.9367	34.2
0.6101	40.9	3.6565	34.2		
[NaCl] =7.0 x 10^{-3}mol kg^{-1}					
0.0020	67.3	0.3195	43.2	2.4079	33.9
0.0041	64.2	0.3973	42.5	2.6916	33.9
0.0082	61.1	0.5883	40.7	2.9633	33.9
0.0204	56.4	0.7746	39.4	3.2235	33.9
0.0407	52.9	1.1333	37.3	3.4731	33.9
0.0811	49.6	1.4749	35.7	3.7126	33.9
0.1614	46.6	1.8004	34.3		
0.2409	44.7	2.1111	33.9		
[NaCl] =1.0 x 10^{-2} mol kg^{-1}					
0.0015	67.7	0.0299	54.2	0.2349	44.0
0.0030	64.7	0.0597	50.6	0.2921	42.8
0.0060	63.1	0.1187	47.3	0.4325	40.8

Table 5.1(c)- continued

c x 10^3 / mol kg^{-1}	γ / mN m^{-1}	c x 10^3 / mol kg^{-1}	γ / mN m^{-1}	c x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[NaCl] =1.0 x 10^{-2} mol kg^{-1}					
0.0150	57.8	0.1771	44.9	0.5695	38.7
0.8332	36.9	1.7702	33.2	2.5532	33.0
1.0843	35.5	1.9788	33.2	2.7292	33.2
1.3236	34.6	2.1784	33.2	2.8983	33.3
1.5520	33.6	2.3697	33.2	3.0609	33.2
[NaCl] =2.0 x 10^{-2} mol kg^{-1}					
0.0020	66.5	0.2319	41.6	1.7280	31.2
0.0039	62.4	0.3076	40.4	2.0249	30.8
0.0079	58.9	0.3824	38.8	2.3081	30.1
0.0196	54.9	0.5661	36.9	2.5786	30.2
0.0392	51.2	0.7450	35.7	2.8372	30.1
0.0782	47.1	1.0893	34.1	3.0847	30.2
0.1555	43.3	1.4165	32.7	3.3217	29.8
[NaCl] =3.0 x 10^{-2} mol kg^{-1}					
0.003474	60.7	0.274855	39.2	1.562954	30.6
0.006946	57.7	0.410022	37.1	1.684398	30.6
0.013888	54.2	0.543714	35.7	1.804586	30.6
0.020827	51.9	0.675957	34.9	1.923538	30.6
0.027761	50.6	0.806772	34.1	2.041271	30.6
0.034692	49.6	0.936184	33.5	2.157806	30.6
0.069287	46.0	1.064214	32.9	2.273159	30.6
0.103786	44.1	1.190885	32.2	2.38735	30.6
0.138189	42.6	1.316218	31.6	2.500395	30.6
0.206711	40.9	1.440234	31.1		

Table 5.1(d)- Surface tension (γ) values of SDC (α_{SDC} = 0.64) + AOT at 298K

c x 10^3 / mol kg^{-1}	γ / mN m^{-1}	c x 10^3 / mol kg^{-1}	γ / mN m^{-1}	c x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[NaCl] = 0.00mol kg^{-1}					
0.0025	66.7	0.5928	44.1	1.8534	35.8
0.0051	64.9	0.6884	42.5	1.9375	35.6
0.0102	62.6	0.7830	42.3	2.0208	35.3
0.0152	60.8	0.8768	41.9	2.1034	35.1
0.0203	59.5	0.9697	40.9	2.1853	34.7
0.0254	58.4	1.0617	40.3	2.2665	34.6
0.0507	56.2	1.1529	39.8	2.3470	34.4
0.0760	55.1	1.2433	38.8	2.4268	34.4
0.1012	53.3	1.3328	38.4	2.5059	34.4
0.1514	51.4	1.4216	38.1	2.5843	34.4
0.2014	50.3	1.5095	37.5	2.6621	34.4
0.3007	47.7	1.5966	36.7	2.8536	34.4
0.3990	45.9	1.6830	36.9	3.0412	34.4
0.4964	45.5	1.7686	36.1	3.2249	32.6
[NaCl] =5.0 x 10^{-3}mol kg^{-1}					
0.0023	64.8	0.2759	42.5	1.6854	32.8
0.0047	60.9	0.3659	41.1	2.0561	31.6
0.0093	58.1	0.4550	39.7	2.4093	31.6
0.0233	54.0	0.6735	38.0	2.7464	31.6
0.0466	50.9	0.8864	36.5	3.0684	31.6
0.0930	47.4	1.0938	35.0	3.3762	31.6
0.1849	44.5	1.2960	34.2	3.6708	31.6
[NaCl] =7.0 x 10^{-3}mol kg^{-1}					
0.0021	66.0	0.2470	42.8	1.8349	31.0
0.0042	63.1	0.3275	41.2	2.1490	31.0
0.0084	59.1	0.4071	40.1	2.4483	31.0
0.0209	54.7	0.6024	38.2	2.7339	31.0
0.0417	51.5	0.7925	36.7	3.0066	30.9
0.0832	48.1	1.1580	34.1	3.2674	31.0
0.1655	44.6	1.5050	32.3	3.5171	31.0

Table 5.1(d)- continued

$c \times 10^3$ / mol kg^{-1}	γ / mN m^{-1}	$c \times 10^3$ / mol kg^{-1}	γ / mN m^{-1}	$c \times 10^3$ / mol kg^{-1}	γ / mN m^{-1}
		[NaCl] =1.0 x 10^{-2} mol kg^{-1}			
0.0015	67.7	0.2394	41.2	1.8044	29.7
0.0031	64.8	0.2977	40.0	2.0172	29.7
0.0061	60.6	0.4408	37.8	2.2208	29.7
0.0153	55.5	0.5804	36.1	2.4159	29.7
0.0305	52.4	0.8492	34.0	2.6030	29.7
0.0608	48.6	1.1052	32.6	2.7826	29.7
0.1209	45.2	1.3491	31.1	2.9551	29.7
0.1805	43.0	1.5820	30.2	3.1210	29.7
		[NaCl] =2.0 x 10^{-2} mol kg^{-1}			
0.0017	66.9	0.2701	38.6	2.0413	28.6
0.0034	62.5	0.3360	37.2	2.2827	28.3
0.0069	58.8	0.4976	35.3	2.5139	28.1
0.0172	54.0	0.6553	33.6	2.7356	28.2
0.0344	49.9	0.9592	31.9	2.9483	28.4
0.0686	45.2	1.2489	30.6	3.1526	28.1
0.1365	42.1	1.5252	29.4		
0.2036	39.5	1.7890	28.8		
		[NaCl] =3.0 x 10^{-2} mol kg^{-1}			
0.0039	59.0	0.4577	33.3	2.0087	26.5
0.0078	55.1	0.6068	31.8	2.1406	26.5
0.0155	51.7	0.7542	30.6	2.2710	26.5
0.0233	49.2	0.8999	29.6	2.4001	26.5
0.0310	47.7	1.0439	28.9	2.5278	26.5
0.0388	46.7	1.1864	28.2	2.6542	26.5
0.0774	43.0	1.3272	27.7	2.7792	26.5
0.1159	40.6	1.4666	27.1	3.0862	26.5
0.1543	39.3	1.6043	26.7	3.3852	26.5
0.2308	37.2	1.7406	26.5		
0.3069	35.4	1.8754	26.5		

Table 5.1 (e)- Surface tension (γ) values of SDC (α_{SDC} = 0.05) + AOT at 298K

c x 10^3 / mol kg^{-1}	γ / mN m^{-1}	c x 10^3 / mol kg^{-1}	γ / mN m^{-1}	c x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[NaCl] = 0.00mol kg^{-1}					
0.0027	69.2	0.2109	48.4	1.9239	34.5
0.0053	65.7	0.3147	46.4	2.1383	33.5
0.0107	62.2	0.4173	45.0	2.3476	32.9
0.0160	60.8	0.5189	43.3	2.5521	32.8
0.0213	59.1	0.7683	40.9	2.7517	32.8
0.0266	58.0	1.0113	39.3	2.9468	32.8
0.0531	54.7	1.2481	37.6	3.1374	32.8
0.0796	53.5	1.4790	36.4	3.3238	32.8
0.1060	51.8	1.7042	36.0	3.5060	32.8
[NaCl] =5.0 x 10^{-3}mol kg^{-1}					
0.0024	62.1	0.2859	41.0	2.1217	29.9
0.0048	59.1	0.3791	39.5	2.4841	29.7
0.0097	56.5	0.4713	38.5	2.8294	29.2
0.0242	52.1	0.6973	36.5	3.1586	29.0
0.0483	49.2	0.9172	34.9	3.4729	28.9
0.0964	46.3	1.3398	32.7	3.7733	28.9
0.1917	43.2	1.7407	31.3	4.0607	28.6
[NaCl] =7.0 x 10^{-3}mol kg^{-1}					
0.0018	66.6	0.2780	40.4	2.1183	28.5
0.0035	64.2	0.3459	38.9	2.3715	28.4
0.0071	61.2	0.5127	36.8	2.6145	28.3
0.0177	55.5	0.6757	35.5	2.8480	28.1
0.0353	51.6	0.9905	32.7	3.0726	28.2
0.0705	47.5	1.2912	30.9	3.2886	28.2
0.1404	44.0	1.5789	29.5		
0.2095	42.2	1.8544	28.6		
[NaCl] =1.0 x 10^{-2} mol kg^{-1}					
0.0016	67.8	0.0328	51.0	0.2574	39.5
0.0033	65.0	0.0654	46.6	0.3200	38.3
0.0066	60.9	0.1301	43.4	0.4735	36.2

Table 5.1(e)- continued

$c \times 10^3$ / mol kg^{-1}	γ / mN m^{-1}	$c \times 10^3$ / mol kg^{-1}	γ / mN m^{-1}	$c \times 10^3$ / mol kg^{-1}	γ / mN m^{-1}
[NaCl] =1.0 x 10^{-2} mol kg^{-1}					
0.0164	54.7	0.1941	41.5	0.6230	34.7
0.9104	32.5	1.9259	28.4	2.7679	28.4
1.1834	31.1	2.1509	28.4	2.9564	28.4
1.4431	30.0	2.3657	28.4	3.1372	28.4
1.6903	29.0	2.5712	28.4	3.3107	28.4
[NaCl] =2.0 x 10^{-2} mol kg^{-1}					
0.0016	*66.0*	*0.1933*	*38.9*	*1.4454*	*28.2*
0.0033	61.6	0.2564	37.3	1.6949	27.7
0.0065	57.8	0.3188	36.0	1.9334	27.4
0.0163	52.6	0.4721	34.1	2.1615	27.4
0.0326	48.9	0.6216	32.5	2.3798	27.3
0.0651	44.5	0.9096	30.7	2.5891	27.2
0.1295	41.4	1.1839	29.2	2.7897	27.0
[NaCl] =3.0 x 10^{-2} mol kg^{-1}					
0.0031	59.3	0.1832	37.2	1.1735	27.1
0.0062	55.3	0.2437	35.6	1.2849	26.6
0.0123	51.5	0.3638	33.4	1.3953	26.5
0.0184	49.4	0.4828	31.7	1.5047	26.5
0.0246	47.7	0.6006	30.6	1.6131	26.5
0.0307	46.7	0.7174	29.8	1.7205	26.5
0.0614	42.8	0.8330	28.9	1.9849	26.5
0.0919	41.0	0.9476	28.0	2.2434	26.5
0.1224	39.4	1.0611	27.6	2.4963	26.5

Table 5.1 (f)- Surface tension (γ) values of SDC (α_{SDC} = 0.4) + AOT at 298K

c x 10^3 / mol kg^{-1}	γ / mN m^{-1}	c x 10^3 / mol kg^{-1}	γ / mN m^{-1}	c x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[NaCl] = 0.00mol kg^{-1}					
0.0024	69.0	0.3771	45.0	1.9293	33.3
0.0048	66.6	0.4689	43.8	2.1178	32.6
0.0096	63.9	0.6940	40.9	2.3018	32.0
0.0241	59.1	0.9133	39.0	2.4814	31.4
0.0480	56.3	1.1270	37.6	2.6569	31.4
0.0958	52.6	1.3352	36.1	2.8283	31.4
0.1906	49.2	1.5382	34.9	2.9957	31.6
0.2844	46.8	1.7362	34.1	3.1594	31.4
[NaCl] =5.0 x 10^{-3}mol kg^{-1}					
0.0267	53.5	0.7693	35.9	3.4909	28.8
0.0533	49.5	1.0121	34.5	3.8391	28.8
0.1063	46.0	1.4788	32.1	4.1721	28.8
0.2114	42.8	1.9219	30.5	4.4907	28.8
0.3154	40.8	2.3432	29.9	4.7959	28.4
0.4182	39.5	2.7441	29.5	5.0886	28.3
0.5199	38.6	3.1263	29.3	5.3695	28.5
[NaCl] =7.0 x 10^{-3}mol kg^{-1}					
0.0019	66.9	0.2977	39.6	2.2419	28.7
0.0038	63.0	0.3701	38.3	2.5059	28.8
0.0076	59.2	0.5481	36.3	2.7585	28.8
0.0190	54.4	0.7216	34.9	3.0006	28.6
0.0379	50.8	1.0556	32.6	3.2326	28.8
0.0756	46.4	1.3736	30.8	3.4553	28.8
0.1504	43.2	1.6767	29.7		
0.2244	41.4	1.9658	28.8		
[NaCl] =1.0 x 10^{-2}mol kg^{-1}					
0.0015	68.2	0.0595	46.7	0.4325	36.7
0.0030	65.3	0.1185	42.9	0.5698	35.0
0.0060	60.3	0.1769	41.0	0.8348	33.0
0.0149	54.9	0.2346	39.6	1.0876	31.2
0.0298	50.9	0.2919	38.3	1.3293	30.2

Table 5.1(f)- continued

$c \times 10^3$ / mol kg^{-1}	γ / mN m^{-1}	$c \times 10^3$ / mol kg^{-1}	γ / mN m^{-1}	$c \times 10^3$ / mol kg^{-1}	γ / mN m^{-1}
		[NaCl] =1.0 x 10^{-2} mol kg^{-1}			
1.5603	29.1	2.1968	28.0	2.7597	28.2
1.7816	28.2	2.3920	28.2		
1.9935	28.2	2.5795	28.0		
		[NaCl] =2.0 x 10^{-2} mol kg^{-1}			
0.0017	65.0	0.2594	36.9	1.9423	27.1
0.0033	62.0	0.3224	35.4	2.1694	27.1
0.0066	57.8	0.4772	33.4	2.3864	27.3
0.0165	52.1	0.6279	31.9	2.5939	27.0
0.0330	48.4	0.9178	29.8	2.7926	26.7
0.0659	44.5	1.1931	28.5	2.9831	26.9
0.1311	40.7	1.4550	27.9	3.1658	26.9
0.1956	38.6	1.7045	27.3		
		[NaCl] =3.0 x 10^{-2} mol kg^{-1}			
0.0031	59.6	0.1875	37.1	1.1975	27.3
0.0063	55.7	0.2494	35.7	1.3107	26.8
0.0126	53.4	0.3721	33.6	1.4229	26.8
0.0189	50.0	0.4936	32.0	1.5339	26.8
0.0252	48.6	0.6139	30.6	1.6439	26.8
0.0315	47.1	0.7330	30.1	1.7529	26.8
0.0628	43.5	0.8509	29.0	2.0206	26.8
0.0941	41.1	0.9675	28.2	2.2821	26.8
0.1253	39.4	1.0831	27.8		

Table 5.1 (g)- Surface tension (γ) values of SDC (α_{SDC} = 0.31) + AOT at 298K

c x 10^3 / mol kg^{-1}	γ / mN m^{-1}	c x 10^3 / mol kg^{-1}	γ / mN m^{-1}	c x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[NaCl] = 0.00mol kg^{-1}					
0.0023	69.5	0.3558	44.9	1.8274	33.6
0.0045	66.8	0.4424	44.4	2.0069	32.7
0.0091	63.5	0.6553	41.5	2.1823	32.5
0.0227	60.6	0.8628	39.8	2.3536	32.0
0.0453	56.8	1.0652	38.0	2.5212	31.2
0.0903	54.3	1.2627	36.7	2.6850	31.2
0.1797	50.3	1.4555	35.6	2.8453	31.2
0.2682	47.5	1.6437	34.2	3.0021	31.2
[NaCl] =5.0 x 10^{-3}mol kg^{-1}					
0.0244	52.8	0.4755	37.4	2.5017	28.9
0.0488	49.5	0.7033	35.8	2.8485	28.8
0.0973	46.1	0.9250	34.1	3.1790	28.8
0.1934	42.6	1.3506	31.9	3.7956	28.5
0.2885	40.7	1.7542	30.1	4.0837	28.6
0.3825	39.2	2.1373	28.9		
[NaCl] =7.0 x 10^{-3}mol kg^{-1}					
0.0017	63.5	0.2610	39.9	1.9651	28.7
0.0033	61.6	0.3245	39.0	2.1964	28.7
0.0067	58.8	0.4806	36.9	2.4178	28.7
0.0166	52.1	0.6326	35.5	2.6298	28.7
0.0332	50.6	0.9255	33.1	2.8331	28.7
0.0663	46.6	1.2042	31.4	3.0281	28.7
0.1319	43.4	1.4698	30.6	3.2154	28.7
0.1968	41.6	1.7231	29.7		
[NaCl] =1.0 x 10^{-2} mol kg^{-1}					
0.0016	66.1	0.0642	45.7	0.4654	35.4
0.0032	60.8	0.1277	42.1	0.6127	33.9
0.0065	58.5	0.1906	40.0	0.8964	31.8
0.0161	53.4	0.2528	38.3	1.1664	29.9
0.0322	49.7	0.3143	37.4	1.4237	28.7

Table 5.1(g)- continued

c x 10^{3} / mol kg^{-1}	γ / mN m^{-1}	c x 10^{3} / mol kg^{-1}	γ / mN m^{-1}	c x 10^{3} / mol kg^{-1}	γ / mN m^{-1}
[NaCl] =1.0 x 10^{-2} mol kg^{-1}					
1.6692	27.9	2.3424	27.9	2.9341	27.9
1.9037	27.9	2.5480	27.9		
2.1279	27.9	2.7450	27.9		
[NaCl] =2.0 x 10^{-2} mol kg^{-1}					
0.0017	66.3	0.2584	36.2	1.9245	26.4
0.0033	62.6	0.3212	35.1	2.1478	26.4
0.0066	57.7	0.4751	33.0	2.3609	26.7
0.0165	51.7	0.6249	31.1	2.5645	26.4
0.0330	47.8	0.9124	28.9	2.7591	26.4
0.0657	43.9	1.1851	27.8	2.9454	26.4
0.1307	40.3	1.4440	26.9	3.1239	26.4
0.1949	37.9	1.6901	26.6	3.2950	26.6
[NaCl] =3.0 x 10^{-2} mol kg^{-1}					
0.0026	62.1	0.1549	38.2	0.9914	27.1
0.0052	58.4	0.2060	36.7	1.0854	26.8
0.0104	54.0	0.3076	34.2	1.1785	26.6
0.0156	51.3	0.4081	32.6	1.2708	26.1
0.0208	50.0	0.5076	31.2	1.3622	26.1
0.0260	48.6	0.6062	30.0	1.4528	26.1
0.0519	44.6	0.7039	29.0	1.6757	26.1
0.0777	42.2	0.8006	28.3	1.8935	26.1
0.1035	40.2	0.8965	27.8	2.1065	26.1

Table 5.1 (h)- Surface tension (γ) values of SDC (α_{SDC} = 0.206) + AOT at 298K

c x 10^3 / mol kg^{-1}	γ / mN m^{-1}	c x 10^3 / mol kg^{-1}	γ / mN m^{-1}	c x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[NaCl] = 0.00mol kg^{-1}					
0.0023	67.0	0.6512	41.3	2.5035	30.9
0.0045	64.9	0.8574	39.3	2.6659	30.9
0.0090	61.0	1.0584	37.5	2.8248	30.9
0.0225	58.4	1.2546	35.9	2.9802	30.9
0.0450	55.6	1.4459	34.9	3.1323	30.9
0.0898	52.8	1.6328	34.2	3.2811	30.9
0.1787	48.9	1.8151	33.2	3.4267	30.9
0.2666	47.1	1.9932	32.6	3.5694	30.9
0.3536	44.8	2.1672	31.6		
0.4398	43.5	2.3372	31.3		
[NaCl] =5.0 x 10^{-3}mol kg^{-1}					
0.0242	53.2	0.6958	34.9	3.1486	27.9
0.0482	49.9	0.9152	33.1	3.4615	27.8
0.0962	46.1	1.3365	30.9	3.7605	27.9
0.1913	42.9	1.7362	29.2	4.0464	27.9
0.2854	40.0	2.1159	27.9	4.3201	27.8
0.3784	38.6	2.4770	27.9	4.5824	27.9
0.4703	37.1	2.8208	27.9		
[NaCl] =7.0 x 10^{-3}mol kg^{-1}					
0.0016	66.7	0.2459	39.9	1.8716	28.5
0.0031	63.9	0.3059	38.7	2.0950	28.1
0.0063	60.2	0.4534	36.6	2.3094	28.1
0.0157	54.9	0.5975	34.8	2.5154	28.1
0.0313	51.2	0.8757	32.8	2.7133	28.1
0.0624	47.2	1.1414	31.1	2.9037	28.1
0.1242	43.5	1.3955	30.0	3.0871	28.1
0.1853	41.3	1.6387	29.0	3.2637	28.1
[NaCl] =1.0 x 10^{-2} mol kg^{-1}					
0.0017	66.2	0.0173	52.8	0.1372	40.7
0.0035	62.8	0.0346	45.3	0.2046	38.3

Table 5.1(h)- continued

c x 10^3 / mol kg^{-1}	γ / mN m^{-1}	c x 10^3 / mol kg^{-1}	γ / mN m^{-1}	c x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[NaCl] =1.0 x 10^{-2} mol kg^{-1}					
0.0069	58.2	0.0690	43.9	0.2713	36.7
0.3373	35.7	1.2466	28.2	2.2637	26.1
0.4991	33.5	1.5197	26.9	2.4894	26.1
0.6566	32.1	1.7797	26.1	2.7052	26.1
0.9593	29.4	2.0274	26.1	2.9117	26.1
[NaCl] =2.0 x 10^{-2} mol kg^{-1}					
0.0028	63.0	0.1659	38.3	1.0624	27.3
0.0056	58.7	0.2207	36.5	1.1632	26.9
0.0111	54.4	0.3294	34.3	1.2631	26.5
0.0167	52.0	0.4372	32.4	1.3621	26.3
0.0223	50.0	0.5438	31.1	1.4602	26.3
0.0278	49.1	0.6495	30.2	1.5574	26.3
0.0556	45.2	0.7542	29.1	1.7965	26.3
0.0833	42.6	0.8579	28.6	2.0304	26.3
0.1109	40.8	0.9606	28.0	2.2591	26.3
[NaCl] =3.0 x 10^{-2} mol kg^{-1}					
0.0030	59.0	0.1772	36.6	1.1309	27.3
0.0060	56.1	0.2356	35.5	1.2378	26.9
0.0119	52.1	0.3516	33.1	1.3437	26.0
0.0178	49.0	0.4664	31.8	1.4485	26.0
0.0238	46.8	0.5800	31.1	1.5523	26.0
0.0297	46.2	0.6924	29.6	1.6550	26.0
0.0594	42.8	0.8037	29.1	1.9076	26.0
0.0889	40.6	0.9139	28.6	2.1541	26.0
0.1184	39.2	1.0230	28.0	2.3949	26.0

Table 5.1(i)- Surface tension (γ) values of SDC (α_{SDC} = 0.106) + AOT at 298K

c x 10^3 / mol kg^{-1}	γ / mN m^{-1}	c x 10^3 / mol kg^{-1}	γ / mN m^{-1}	c x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[NaCl] = 0.00mol kg^{-1}					
0.0024	69.1	0.3738	45.0	2.0921	31.8
0.0048	67.1	0.4646	44.4	2.4497	30.8
0.0096	66.1	0.6874	40.6	2.7902	30.5
0.0239	60.7	0.9043	39.0	3.1151	30.4
0.0476	58.4	1.1154	37.0	3.4252	30.3
0.0950	54.8	1.3210	35.7	3.7217	30.2
0.1890	50.6	1.5212	34.7	4.0053	30.0
0.2819	47.8	1.7164	33.7		
[NaCl] =5.0 x 10^{-3}mol kg^{-1}					
0.0242	53.1	0.6980	34.5	3.1557	27.7
0.0484	49.5	0.9180	33.0	3.4688	27.9
0.0965	45.4	1.3405	30.7	3.7680	27.7
0.1920	41.7	1.7411	29.1	4.0540	27.7
0.2863	39.6	2.1215	27.7	4.3278	27.7
0.3796	38.0	2.4831	27.9	4.5900	27.6
0.4719	36.4	2.8275	27.7		
[NaCl] =7.0 x 10^{-3}mol kg^{-1}					
0.0017	66.8	0.2625	39.3	1.9861	27.1
0.0033	62.8	0.3265	37.7	2.2214	27.1
0.0067	59.1	0.4837	35.6	2.4468	27.1
0.0167	53.7	0.6370	33.9	2.6629	27.1
0.0334	50.3	0.9327	31.7	2.8704	27.1
0.0666	46.6	1.2145	30.0	3.0697	27.1
0.1326	42.8	1.4834	28.8	3.2613	27.1
0.1979	40.8	1.7404	27.9	3.4457	27.1
[NaCl] =1.0 x 10^{-2}mol kg^{-1}					
0.0017	63.3	0.0168	51.9	0.1332	41.0
0.0034	60.6	0.0336	48.1	0.1988	38.8
0.0067	56.8	0.0670	44.7	0.2636	37.5

Table 5.1(i)- continued

c x 10^3 / mol kg^{-1}	γ / mN m^{-1}	c x 10^3/ mol kg^{-1}	γ / mN m^{-1}	c x 10^3/ mol kg^{-1}	γ / mN m^{-1}
[NaCl] =1.0 x 10^{-2} mol kg^{-1}					
0.3278	36.5	1.4853	27.7	2.6587	26.5
0.4855	34.3	1.7415	26.8	2.8644	26.5
0.6391	32.1	1.9863	26.5	3.0618	26.5
0.9351	30.2	2.2202	26.5		
1.2168	28.6	2.4442	26.5		
[NaCl] =2.0 x 10^{-2} mol kg^{-1}					
0.0026	61.0	0.1532	38.0	0.9823	27.6
0.0051	55.3	0.2038	36.0	1.0756	27.3
0.0103	51.3	0.3043	34.0	1.1682	26.9
0.0154	48.6	0.4039	32.4	1.2599	26.6
0.0206	47.6	0.5025	31.2	1.3508	26.6
0.0257	47.4	0.6002	30.3	1.4408	26.6
0.0513	42.6	0.6970	29.6	1.6626	26.6
0.0769	41.6	0.7930	28.7	1.8796	26.6
0.1024	40.1	0.8881	28.0	2.0919	26.6
[NaCl] =3.0 x 10^{-2} mol kg^{-1}					
0.0031	57.0	0.1829	35.0	1.1680	25.5
0.0061	53.4	0.2432	33.5	1.2785	25.5
0.0123	49.8	0.3630	31.2	1.3879	25.5
0.0184	47.5	0.4815	29.8	1.4963	25.5
0.0246	45.8	0.5988	28.8	1.6035	25.5
0.0307	44.7	0.7150	27.7	1.7098	25.5
0.0613	41.0	0.8300	27.0	1.9710	25.5
0.0918	38.7	0.9438	26.4	2.2260	25.5
0.1222	37.3	1.0565	25.5	2.4750	25.5

Table (j)- Surface tension (γ) values of AOT in aqueous sodium chloride at 298K

$c \times 10^3$ / mol kg^{-1}	γ / mN m^{-1}	$c \times 10^3$ / mol kg^{-1}	γ / mN m^{-1}	$c \times 10^3$ / mol kg^{-1}	γ / mN m^{-1}
[NaCl] = 0.00mol kg^{-1}					
0.0123	65.0	0.9779	39.2	3.1996	30.4
0.0368	60.1	1.1700	38.8	3.3806	29.8
0.0612	57.3	1.3900	36.3	3.5703	30.1
0.0856	55.7	1.6099	34.9	3.7402	30.1
0.1100	54.1	1.8197	33.9	3.9201	29.6
0.1340	52.1	2.0300	32.9	4.0898	29.8
0.1820	50.4	2.2300	31.7	4.2599	29.3
0.2780	46.4	2.4300	31.4	4.4259	29.5
0.4210	45.3	2.6303	30.9	4.5899	29.5
0.6100	43.1	2.8197	30.6	4.7501	29.0
0.7951	41.1	3.0102	30.6	4.9797	29.4
[NaCl] =5.0 x 10^{-3}mol kg^{-1}					
0.0024	68.3	0.4623	37.9	3.1028	28.0
0.0048	64.7	0.6841	35.6	3.4121	27.5
0.0237	55.2	0.9000	34.0	3.7078	27.8
0.0474	51.3	1.3148	31.9	3.9908	27.7
0.0945	47.0	1.7087	30.5	4.2618	27.5
0.1880	43.2	2.0831	29.5	4.5217	27.5
0.2805	40.6	2.4394	28.4	4.7711	27.7
0.3719	38.9	2.7789	27.8		
[NaCl] =7.0 x 10^{-3}mol kg^{-1}					
0.0022	67.7	0.6458	35.9	3.5149	27.1
0.0045	63.4	0.8498	34.5	3.7847	27.1
0.0224	54.8	1.2422	32.4	4.0433	26.7
0.0447	51.1	1.6152	31.2	4.2914	26.8
0.0892	46.9	1.9702	28.8	4.5296	27.1
0.1774	43.5	2.3083	28.1	4.7586	26.6
0.2646	41.1	2.6309	27.5	4.9788	26.7
0.3509	38.9	2.9388	27.4	5.1907	26.4
0.4363	38.2	3.2332	27.1	5.3948	26.7

Table 5.1(j)- continued

c x 10^3 / mol kg^{-1}	γ / mN m^{-1}	c x 10^3 / mol kg^{-1}	γ / mN m^{-1}	c x 10^3 / mol kg^{-1}	γ / mN m^{-1}
[NaCl] =1.0 x 10^{-2} mol kg^{-1}					
0.0023	62.3	0.6719	32.2	3.6577	27.1
0.0047	58.1	0.8841	30.4	3.9385	27.0
0.0233	50.2	1.2925	28.6	4.2076	26.3
0.0465	46.7	1.6806	27.6	4.4659	27.0
0.0928	42.9	2.0500	27.2	4.7139	26.8
0.1845	39.2	2.4019	26.9	4.9523	26.4
0.2753	37.2	2.7376	26.9	5.1815	26.7
0.3651	35.3	3.0581	26.9		
0.4539	34.2	3.3645	26.7		
[NaCl] =2.0 x 10^{-2} mol kg^{-1}					
0.0691	41.1	0.6385	28.7	1.2985	26.2
0.1549	36.6	0.8359	27.4	1.3891	26.1
0.2441	34.7	0.9269	26.8	1.4785	26.2
0.3412	32.3	1.0213	26.7	1.5676	26.1
0.4413	31.1	1.1144	26.3		
0.5404	30.0	1.2068	26.3		
[NaCl] =3.0 x 10^{-2} mol kg^{-1}					
0.0530	41.1	0.5352	28.6	1.0283	25.6
0.1234	36.8	0.6710	27.3	1.0920	25.8
0.1933	34.3	0.7373	26.7	1.1554	25.6
0.2626	32.5	0.7690	26.4	1.2182	25.4
0.3303	31.6	0.8345	25.9		
0.4694	29.4	0.9641	25.7		

Table 5.2.Values of cmc of SDC+AOT mixtures in aqueous NaCl solutions at 25 °C

[NaCl] / mol g^{-1}	α_{SDC} = 1 (SDC)	α_{SDC} = 0.917	α_{SDC} = 0.793	α_{SDC} = 0.640	α_{SDC} = 0.500	α_{SDC} = 0.406	α_{SDC} = 0.311	α_{SDC} = 0.206	α_{SDC} = 0.107	α_{SDC} = 0 (AOT)
	cmc / mmol kg^{-1}									
0	2.34	2.28	2.32	2.31	2.35	2.40	2.45	2.50	2.58	2.66
0.005	1.93	1.95	1.97	2.00	2.04	2.08	2.08	2.10	2.10	2.06
0.007	1.84a)	1.86	1.87	1.88	1.90	1.95	1.95	1.97	1.97	1.87
0.01	1.73	1.76	1.75	1.77	1.75	1.78	1.72	1.78	1.77	1.65
0.02	1.57	1.58	1.63	1.67	1.54	1.51	1.44	1.33	1.24	1.07
0.03	1.51	1.49	1.55	1.59	1.33	1.30	1.22	1.18	1.00	0.85

Table 5.3.Values of counterion binding constant for SDC+AOT mixtures in aqueous sodium chloride solutions at 25 °C

α SDC	Counterion binding constant	
1.0 (pure SDC)	0.18	
	0< [C] ≤ 0.005 (mol kg^{-1})	[C] > 0.005 (mol kg^{-1})
0.917	0.15	0.28
0.793	0.16	0.26
0.640	0.14	0.20
0.500	0.13	0.27
0.406	0.13	0.27
0.311	0.14	0.29
0.206	0.15	0.33
	0< [C] ≤ 0.007 (mol kg^{-1})	[C] > 0.007 (mol kg^{-1})
0.107	0.20	0.50
	0< [C] ≤ 0.015 (mol kg^{-1})	[C] > 0.015 (mol kg^{-1})
0.0 (pure AOT)	0.39	0.82

Table 5.4- Values of X_{SDC}^{Rb} , X_{SDC}^{Rd} and β^{Rb} for SDC+AOT system in aqueous Sodium Chloride solution at 298 K

α_{SDC}	x_{SDC}^{Rb}	f_{SDC}	f_{AOT}	β_{int}	x_{SDC}^{Rd}	x_{SDC}^{Mo}	x_{SDC}^{id}
[NaCl] = 0.0 mol kg^{-1}							
1.0	1.0	1.0	-	-	1	1	1
0.917	0.898	1.00	0.70	-0.45	0.918	0.918	0.926
0.793	0.793	0.99	0.87	-0.21	0.805	0.816	0.813
0.640	0.652	0.97	0.90	-0.25	0.670	0.700	0.669
0.500	0.529	0.95	0.94	-0.23	0.543	0.587	0.532
0.406	0.443	0.94	0.96	-0.20	0.454	0.502	0.437
0.311	0.351	0.93	0.98	-0.18	0.359	0.408	0.339
0.206	0.245	0.90	0.99	-0.19	0.248	0.290	0.228
0.107	0.132	0.90	1.0	-0.15	0.134	0.162	0.119
0	0	-	1.0	-	0	0	0
[NaCl] = 0.005 mol kg^{-1}							
1.000	1.000	1	-	-	1	1	1
0.917	0.926	1.00	1.06	0.07	0.924	0.931	0.922
0.793	0.808	1.00	1.03	0.05	0.809	0.826	0.803
0.640	0.659	1.00	1.02	0.06	0.669	0.697	0.655
0.500	0.517	1.02	1.02	0.09	0.534	0.567	0.516
0.406	0.416	1.05	1.02	0.15	0.436	0.466	0.422
0.311	0.314	1.07	1.01	0.14	0.331	0.351	0.325
0.206	0.197	1.14	1.01	0.20	0.210	0.214	0.217
0.107	0.092	1.27	1.00	0.29	0.099	0.091	0.113
0	0	-	1.0	-	0	0	0

Table 5.4- continued

α_{SDC}	x_{SDC}^{Rb}	f_{SDC}	f_{AOT}	β_{int}	x_{SDC}^{Rd}	x_{SDC}^{Mo}	x_{SDC}^{id}
NaCl] = 7.0 x10^{-3}mol kg^{-1}							
1.000	1	1	-	-	1	1	1
0.917	0.922	1.00	1.06	0.07	0.921	0.925	0.918
0.793	0.802	1.00	1.05	0.07	0.795	0.797	0.795
0.640	0.654	1.00	1.05	0.11	0.661	0.682	0.644
0.500	0.519	0.99	1.06	0.20	0.531	0.562	0.504
0.406	0.425	1.01	1.08	0.42	0.436	0.467	0.410
0.311	0.328	1.00	1.07	0.62	0.336	0.360	0.314
0.206	0.218	1.01	1.07	1.42	0.214	0.222	0.209
0.107	0.115	0.99	1.06	4.65	0.090	0.073	0.108
0	0	-	1	-	0	0	0
[NaCl] = 1.0 x10^{-2}mol kg^{-1}							
1.000	1	1	-	-	1	1	1
0.917	0.932	1.00	1.29	0.30	0.918	0.919	0.913
0.793	0.801	1.00	1.11	0.16	0.793	0.793	0.785
0.640	0.652	1.02	1.16	0.35	0.651	0.663	0.629
0.500	0.510	0.99	1.08	0.30	0.487	0.474	0.488
0.406	0.415	1.01	1.09	0.53	0.388	0.371	0.395
0.311	0.331	0.93	1.07	0.65	0.314	0.317	0.301
0.206	0.214	0.99	1.09	1.88	0.229	0.252	0.198
0.107	0.120	0.91	1.09	5.92	0.098	0.088	0.102
0	0	-	1	-	0	0	0

Table 5.4 continued

α_{SDC}	x_{SDC}^{Rb}	f_{SDC}	f_{AOT}	β_{int}	x_{SDC}^{Rd}	x_{SDC}^{Mo}	x_{SDC}^{id}
			[NaCl] = 2.0 x10^{-2}mol kg^{-1}				
1.000	1	1	-	-	1	1	1
0.917	0.920	1.00	1.53	0.50	0.939	0.961	0.883
0.793	0.800	1.03	1.58	0.71	0.809	0.824	0.723
0.640	0.584	1.17	1.37	0.91	0.607	0.575	0.548
0.500	0.347	1.41	1.10	0.81	0.410	0.321	0.405
0.406	0.195	2.00	1.04	1.07	0.285	0.163	0.318
0.311	0.082	3.49	1.01	1.48	0.172	0.032	0.235
0.206	0.014	12.8	1.00	2.62	0.073	-	0.150
0.107	-	-	-	-	0.015	-	0.075
0	0	-	1	-	0	0	0
			[NaCl] = 3.0 x10^{-2}mol kg^{-1}				
1.000	1.000				1	1	1
0.917	0.901	1.00	1.46	0.47	0.930	0.943	0.861
0.793	0.780	1.04	1.71	0.89	0.786	0.778	0.683
0.640	0.500	1.38	1.38	1.29	0.569	0.498	0.500
0.500	0.268	1.64	1.07	0.93	0.363	0.226	0.360
0.406	0.107	3.27	1.02	1.49	0.235	0.064	0.278
0.311	0.011	22.1	1.00	3.17	0.124	-	0.203
0.206	-	-	-	-	0.034	-	0.127
0.107	-	-	-	-	-	-	0.063
0	0	-	-	-	0	0	0

Table 5.5. Values of standard free energy of micellization for SDC+AOT mixtures in aqueous sodium chloride solutions at 25 °C

[NaCl] / mol kg^{-1}	Standard free energy of micellization / kJ mol^{-1}									
	α_{SDC} = 1.0	α_{SDC} = 0.917	α_{SDC} = 0.793	α_{SDC} = 0.640	α_{SDC} = 0.500	α_{SDC} = 0.406	α_{SDC} = 0.311	α_{SDC} = 0.206	α_{SDC} = 0.107	α_{SDC} = 0
0	-17.7	-18.2	-18.7	-18.7	-18.7	-18.6	-18.6	-18.5	-18.7	-20.4
0.005	-18.3	-18.4	-19.1	-19.1	-19.1	-19.0	-19.0	-18.8	-19.1	-21.3
0.007	-18.4	-20.6	-20.8	-20.3	-21.4	-21.3	-21.5	-21.8	-19.4	-21.6
0.01	-18.6	-20.7	-21.1	-20.4	-21.7	-21.6	-21.9	-22.1	-24.5	-22.1
0.02	-18.9	-21.1	-21.3	-20.7	-22.1	-21.9	-22.0	-22.4	-25.5	-30.8
0.03	-19.0	-21.4	-21.5	-21.0	-22.6	-22.3	-22.4	-23.2	-26.3	-31.9

Table 5.6. Values of surface excess for SDC+AOT mixtures in aqueous NaCl solutions at 25 °C

[NaCl] / mol kg^{-1}	Γcmc × 10^{6} / mol m^{-2}									
	α_{SDC} = 1	α_{SDC} = 0.917	α_{SDC} = 0.793	α_{SDC} = 0.640	α_{SDC} = 0.500	α_{SDC} = 0.406	α_{SDC} = 0.311	α_{SDC} = 0.206	α_{SDC} = 0.107	α_{SDC} = 0
0	0.73	0.64	1.56	1.28	1.46	1.52	1.75	1.53	1.65	1.63
0.005	1.03	1.43	1.74	1.78	1.83	1.91	1.94	1.91	1.90	1.82
0.007	-	1.57	1.90	2.05	1.91	2.03	1.99	1.99	1.99	1.84
0.01	1.10	1.86	1.93	2.03	1.97	2.18	2.15	2.07	2.02	1.93
0.02	1.34	1.94	2.00	1.90	2.00	2.01	2.15	2.09	2.01	2.15
0.03	1.33	2.02	1.84	1.87	1.98	1.91	1.87	1.92	2.07	2.38

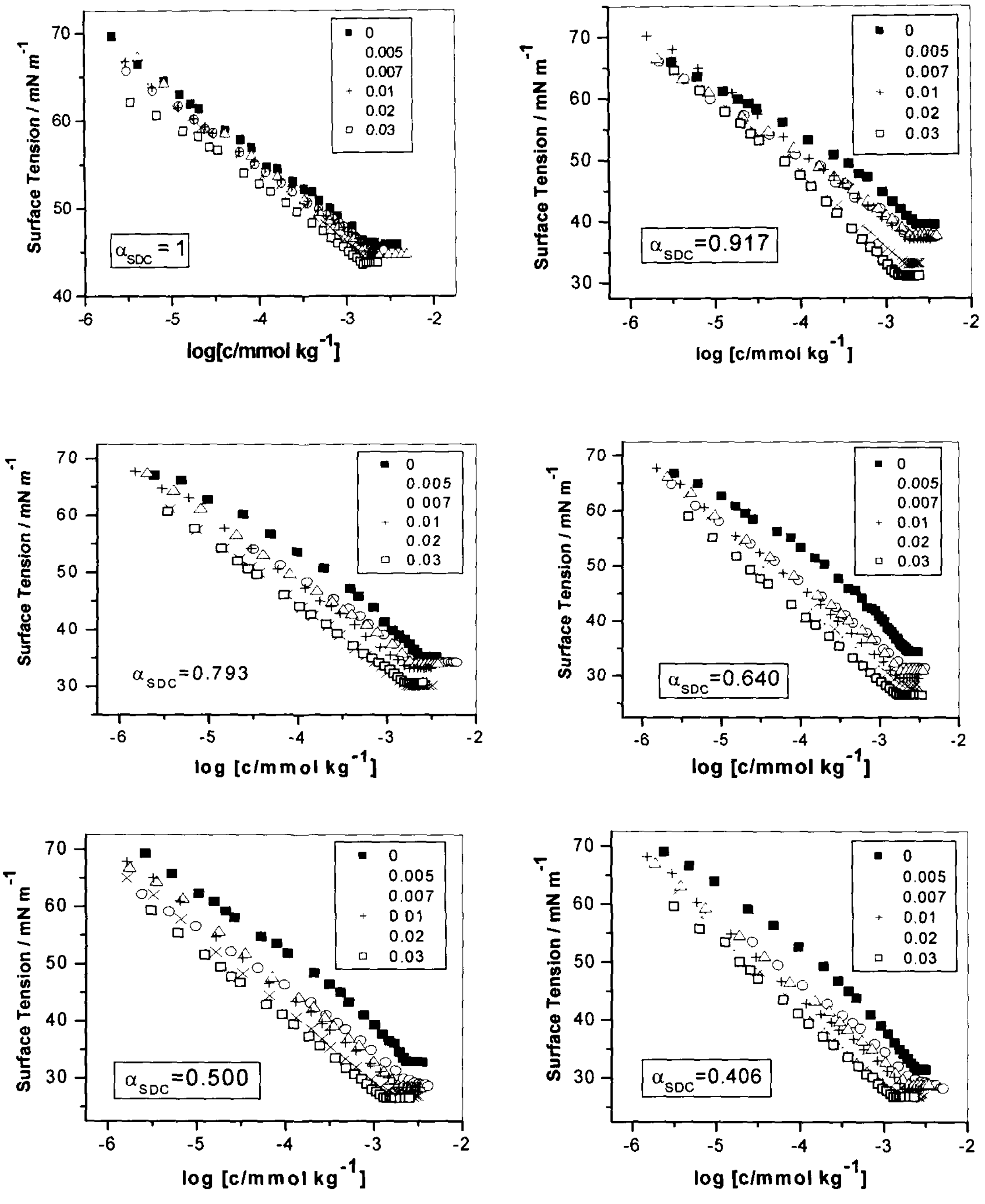

Fig. 5.1 Surface tension plots of SDC + AOT mixed systems

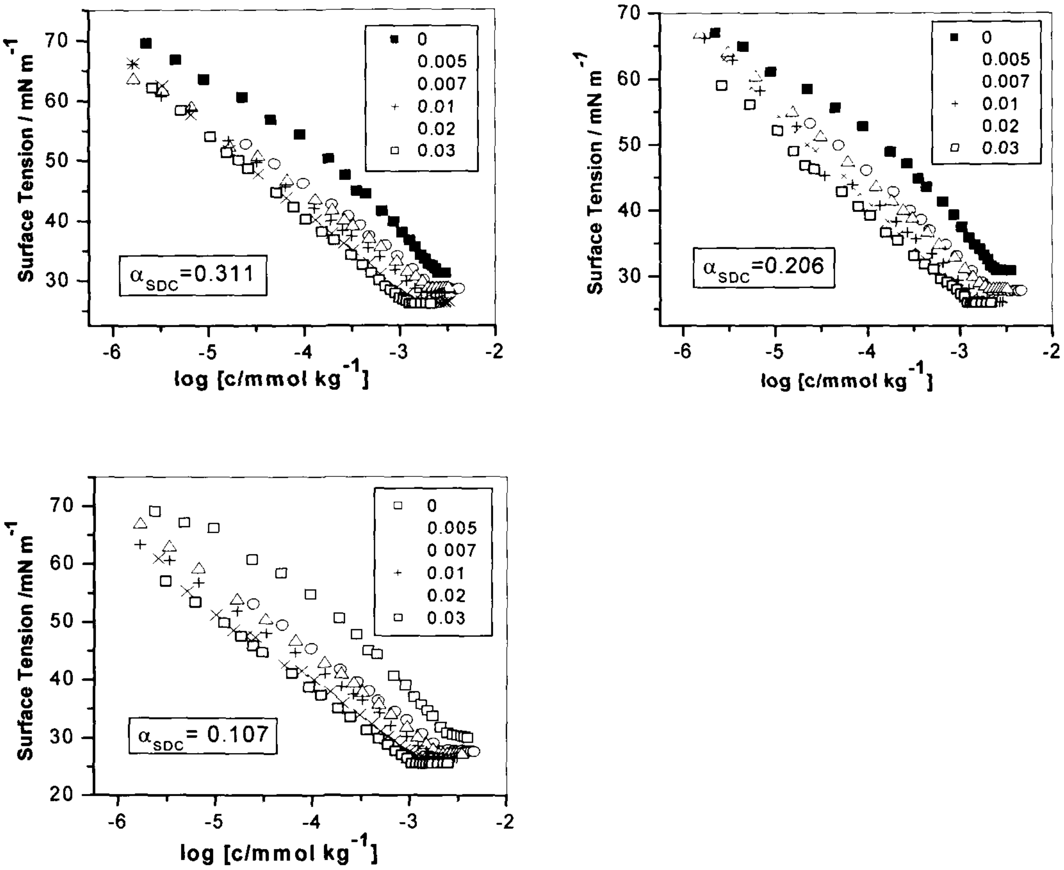

Fig. 5.1 continued

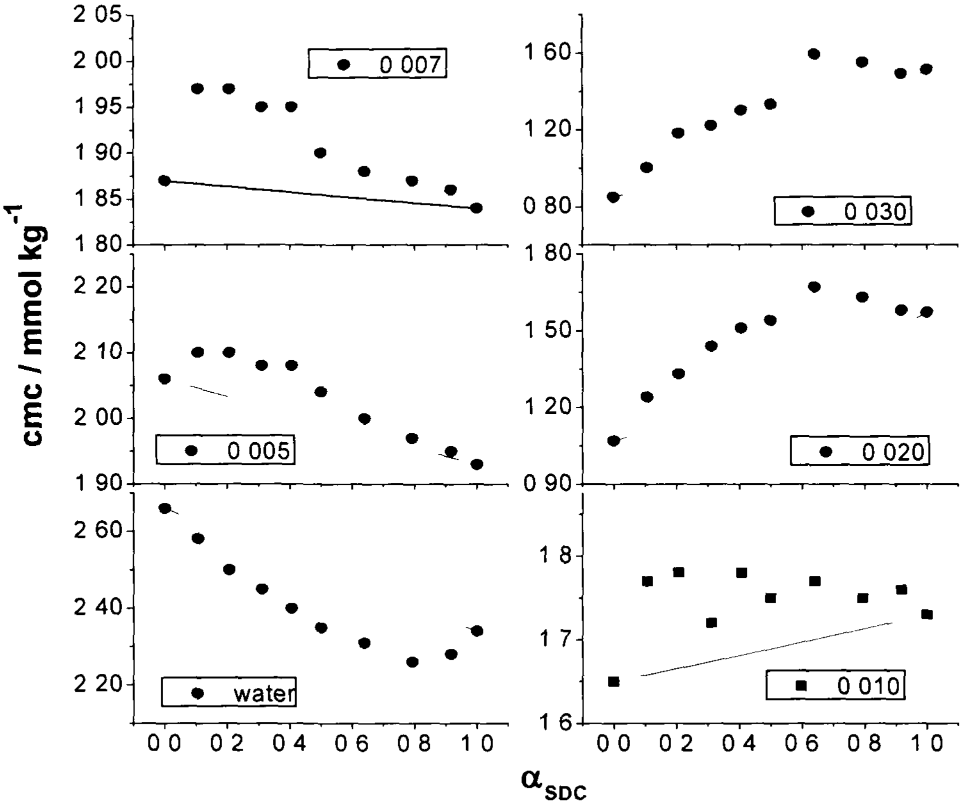

Fig. 5.2 Variation of cmc of SDC + AOT mixtures as a function of mole fraction of SDC in the bulk. *Symbols represent experimental values.* Solid black lines represent cmc values calculated from the Clint's equation and solid red lines represent cmc values calculated from the additivity principle using Eq. 5.4.

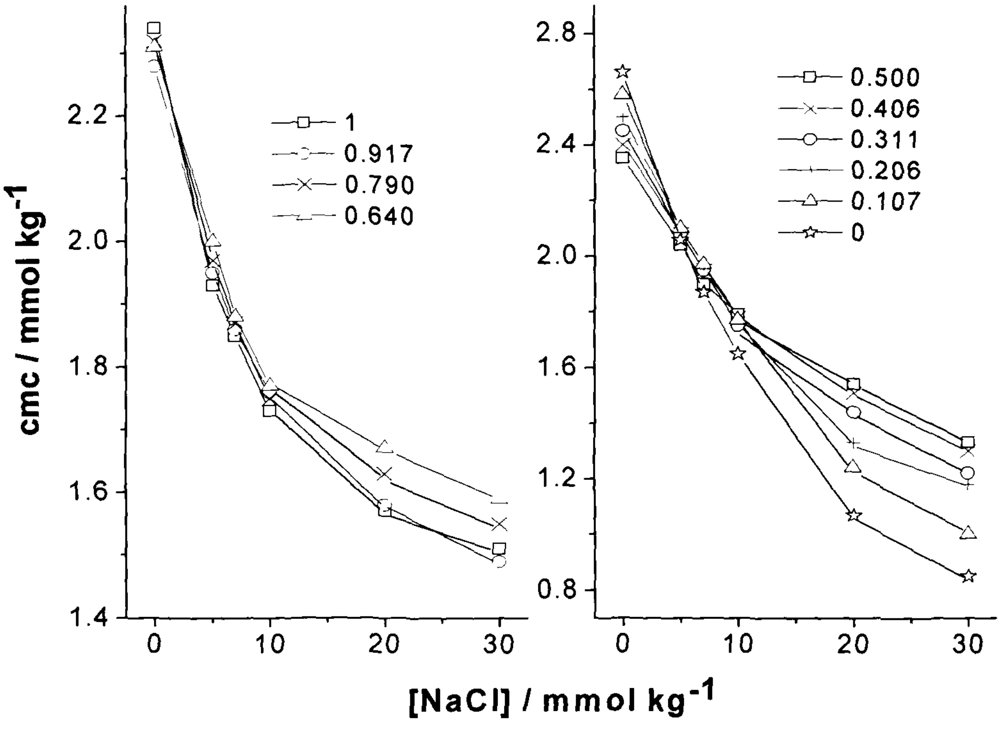

Fig. 5.3 Cmc values of SDC + AOT mixtures as a function of concentration of added NaCl.

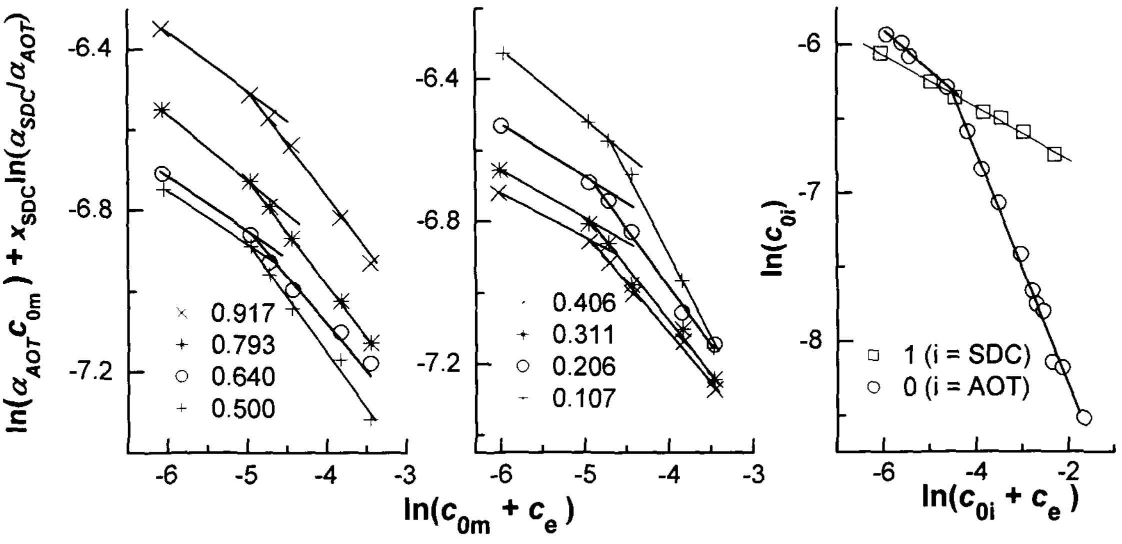

Fig. 5.4 Corrin – Harkins plots for SDC, AOT and mixtures of SDC and AOT

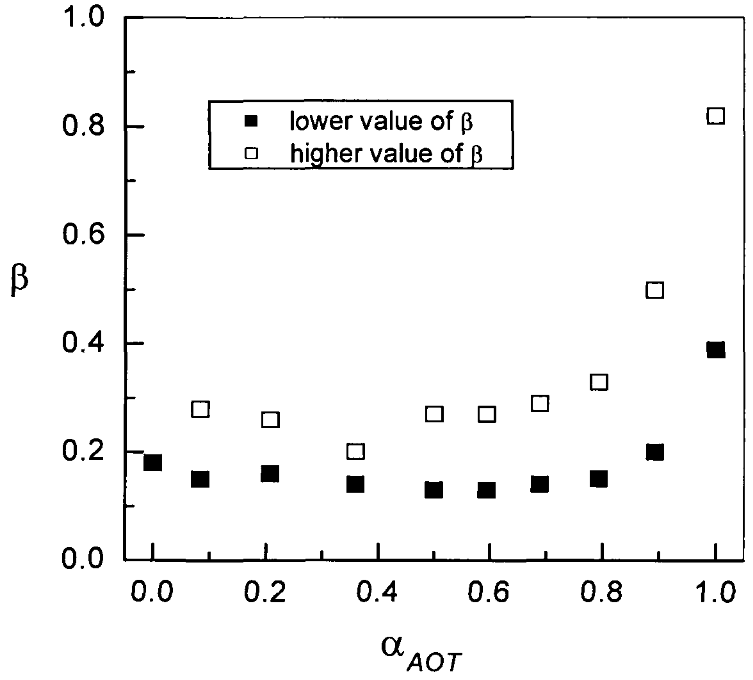

Fig. 5.5 Variation of counter ion binding constant of SDC + AOT mixtures with mole fraction of AOT in the bulk

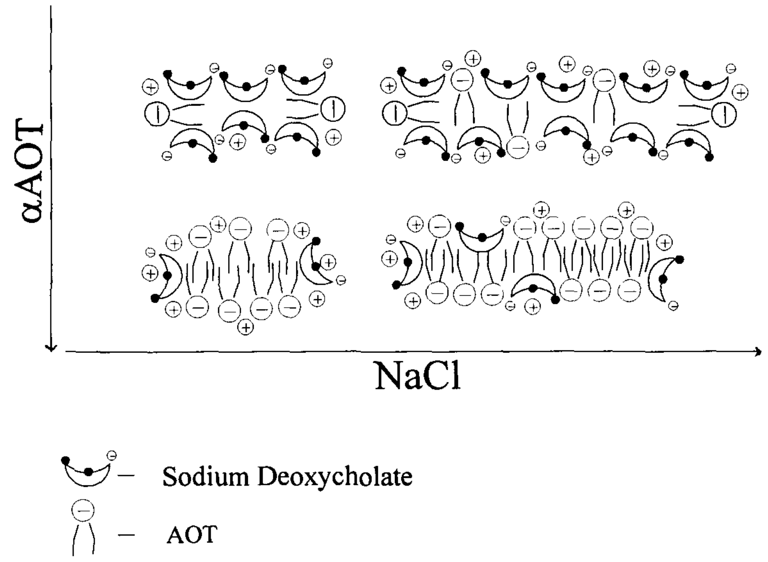

Fig. 5.6 Schematic representation of SDC + AOT mixed micelles

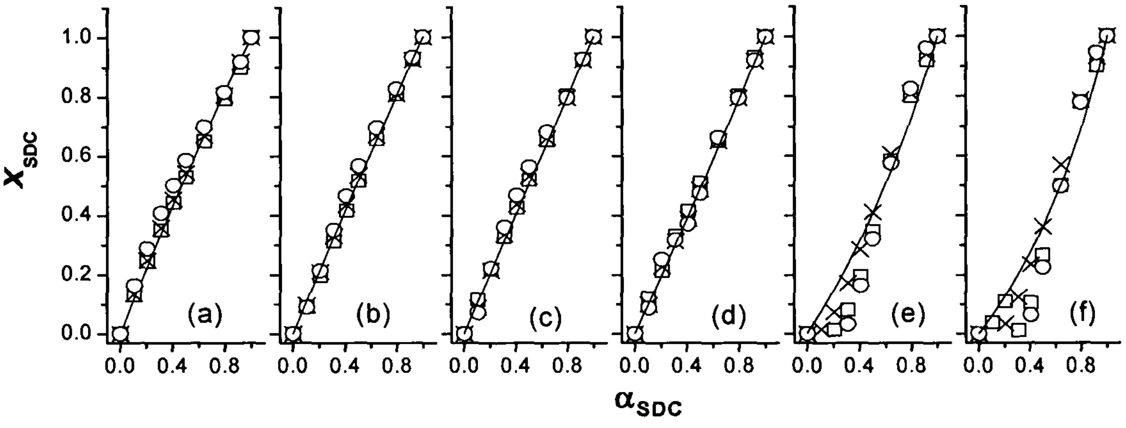

Fig. 5.7. Composition of SDC + AOT mixed micelle as a function of the bulk composition of SDC calculated from Rubingh's model (open squares), Rodenas model (crosses), Motomura model (open circles), and ideal model (Eq. (5.12); solid line). (a) in water and (b) – (f) in 0.005, 0.007, 0.01, 0.02 and 0.03 mol kg^{-1} aqueous NaCl.

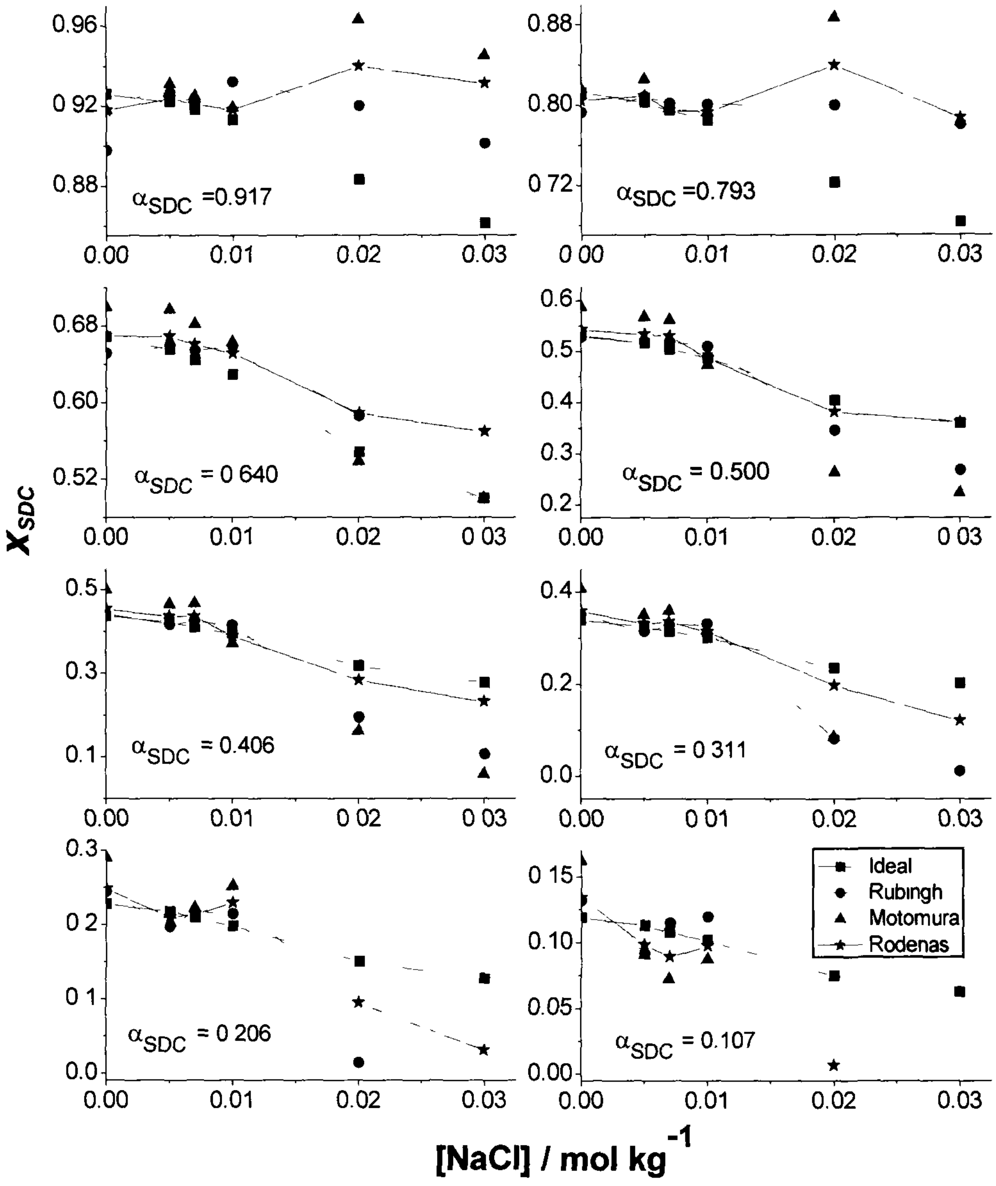

Fig. 5.8 Composition of SDC + AOT mixed micelle as a function of NaCl concentration calculated from Rubingh's model (circles), Rodenas model (stars), Motomura model (triangles), and ideal model (squares).

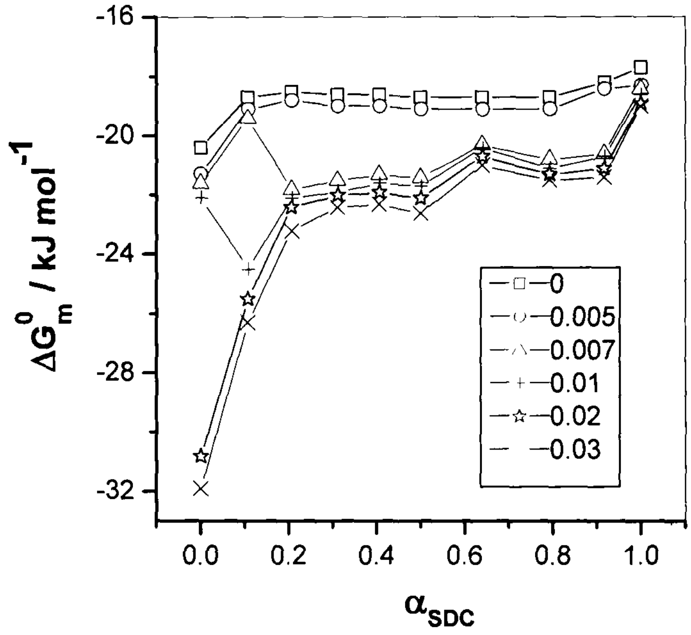

Fig. 5.9 Standard free energy of micellization of SDC + AOT mixtures as a function of composition of SDC in the bulk

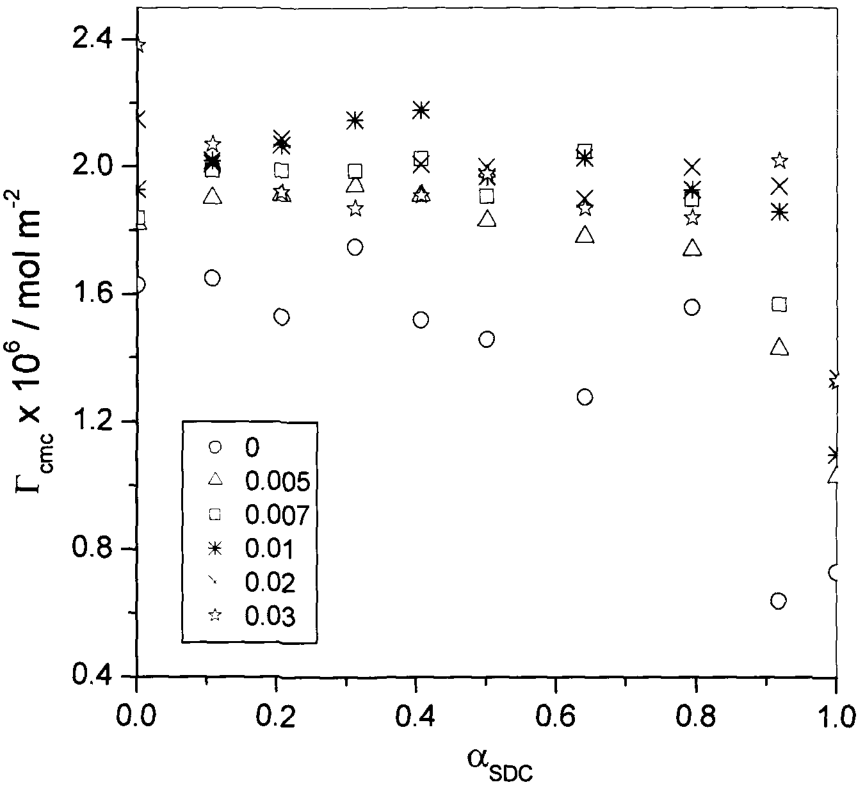

Fig. 5.10 Surface excess of SDC + AOT mixtures in the presence of NaCl as a function of composition of SDC in the bulk. Concentrations of NaCl are given in the inset.

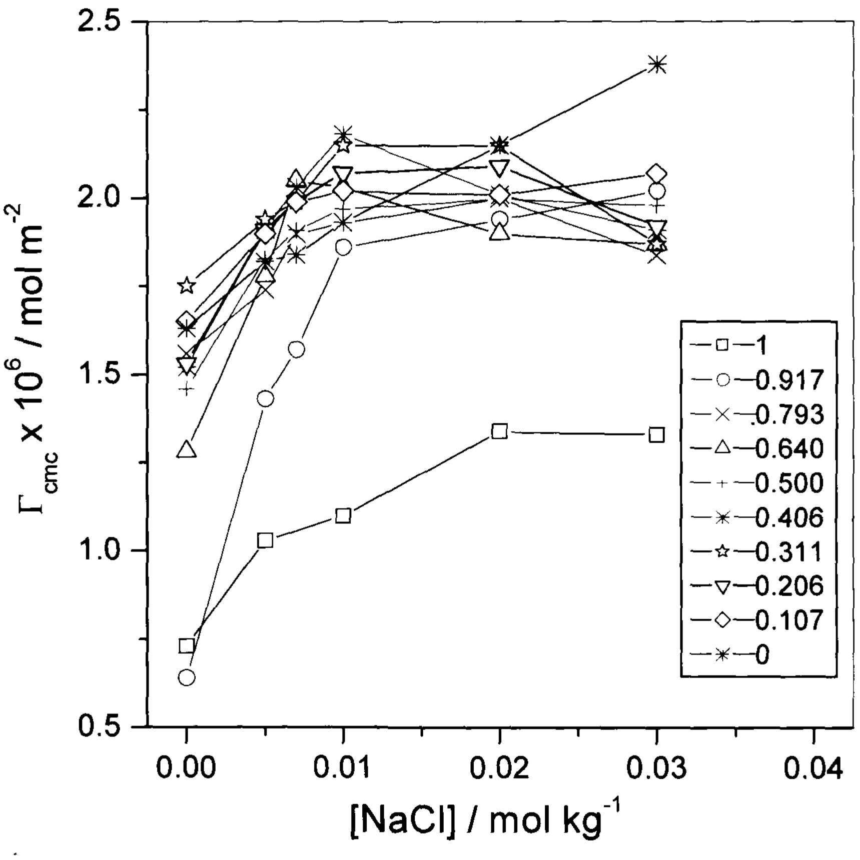

Fig. 5.11 Surface excess of SDC + AOT mixtures as a function of NaCl concentration. Compositions of SDC in the bulk are given in the inset.

CHAPTER 6

Phase, Conductance and Viscosity Behaviours of Benzene/Sodium Deoxycholate/Water Microemulsion. A Cosurfactant Free Microemulsion

6.1 Introduction

As explained in chapter 1, microemulsions are thermodynamically stable, isotropic and transparent phases. Although in principle microemulsions are three-component systems, in practice a fourth component known as cosurfactant is needed to stabilize the system. Cosurfactants are actually not surfactants, but small chain alcohol molecules. Amines (e.g. hexylamine) are also known to behave as cosurfactants. Among the ionic surfactants only AOT (sodium dioctylsulfosuccinate) is known to form microemulsion without a cosurfactant.

Innumerable microemulsions are prepared and studied extensively due to the obvious reason that they have got wide ranging applications.[1] They are used in the fields of chemical reactions, nanoparticles synthesis, drug delivery systems and human care products. Various surfactants including mixed surfactants are being used for the formulation of microemulsions. Microemulsions using polar organic liquids including ionic liquids in lieu of water are also being prepared and studied. During literature survey we, however, noticed that bile salts have not been employed much for the preparation of microemulsions. We could find only a few reports on microemulsions stabilized by bile salts.[2-5] Since bile salts are biocompatible, it is worthwhile to explore the ability of bile salts to form microemulsions with various water/oil combinations. In this chapter we have chosen water/sodium deoxycholate (SDC)/benzene system for investigation.

6.2 Experimental Section

SDC (Fluka, 98%) and benzene (SRL, Spectroscopy grade) were used as received. For the study of phase behaviour, a fixed weight of the total solution mixture was taken in a glass sample tube by mixing appropriate amounts of SDC, water (Milli-Q grade) and benzene and then the glass tube was sealed. All the samples were kept in a thermostatic water bath (HAAKE G) maintained at 25 ± 0.1 °C, stirred occasionally and then allowed to attain equilibrium. Formation of single transparent phase was checked visually. Mixtures of the three components were prepared by keeping weight % of SDC constant as well as R (molar ratio of water to surfactant) value constant.

Electrical conductivity of the microemulsions was measured at 25 ± 0.1°C using B905 Wayne Kerr Automatic Precision Bridge and a dip-type conductivity cell. Viscosity of the microemulsions was also measured at 25 ± 0.1°C using Cannon-Ubbelohde type viscometer having viscometer constant 4.15×10^{-4} St s^{-1}. Density of the microemulsions was measured using Anton Paar DMA 5000 densitometer.

6.3 Results and Discussion

6.3.1 Phase behaviour

Phase diagram of the water/SDC/benzene system is shown in Fig. 6.1. From the water – SDC coordinate of Fig. 6.1 it may be seen that the solubility of SDC in water is about 50 weight % and this value is in good agreement with the reported[6] value of 49.5 %. A more precise phase diagram study of the water + SDC system by Marques et al.[7] by using different experimental techniques has shown the presence of liquid-crystals in the isotropic phase in the region from 20 to 45 weight % of SDC and liquid-crystal single-phase in the region from 45 to 50 weight % SDC. The kinetics of liquid-crystal formation is, however, reported[7] to be considerably slow requiring time span of a few weeks. We observed that microemulsion phase was formed within a period of two days when the mixtures contained SDC < 30 weight %, and within a duration of 5 hours when the mixtures contained SDC $\geq$ 30 weight %. The microemulsions after formation remained stable for about ten days. Interestingly, no cosurfactant was needed for the formation of microemulsion with benzene. However, attempts to make microemulsions with toluene and xylene as oils without using cosurfactant failed. In fact, Das et al.[5] used butanol cosurfactant to prepare xylene/SDC/water microemulsion. Fontell[2] reported that xylene could be solubilized to an extent of 0.008 volume fraction in an aqueous solution containing about 7 weight % SDC at 40 °C. The present study therefore reveals that forming microemulsion without cosurfactant is dependent not only on the characteristic of the surfactant, but also on the structure of the oil used. In the 2-phase region of Fig. 6.1 it was noticed that the lower layer is gel-type when the mixtures contained SDC $\geq$ 30 weight %.

6.3.2 Density.

Measured density (d) values of the microemulsions of different R (water to SDC mole ratio) values as a function of volume fraction of benzene (ϕ_o) are given in Table 6.1. By plotting density versus ϕ_o (Fig. 6.2) it is found that density of these microemulsions decreases linearly with increase in ϕ_o. Moreover, density decreases with decrease in R at a fixed value of ϕ_o. The least-squares fitted values of the parameters d_0 (intercept) and b (slope) of the empirical Eq. (6.1) are given in Table 6.2.

$$d = d_0 - b\phi_o \tag{6.1}$$

At a fixed value of R, added benzene gets solubilized within the SDC micellar core and the micelle (or droplet) swells causing increase in volume of the microemulsion, which would decrease the density. At a fixed value of ϕ_o, as R increases the SDC amount in the microemulsion increases causing increase in the size of micelle (or droplet), which also results in volume increase or decrease in density.

6.3.3 Viscosity

Viscosity (η) was measured as a function of ϕ_o along two composition paths; (i) fixed weight fraction of SDC and (ii) fixed R. The experimental values of η are listed in Table 6.3. The variation of η with ϕ_o at constant weight fractions of SDC is shown in Fig. 6.3. The micellar solution (microemulsion without oil) with 0.1 weight fraction of SDC has about 3 times more viscosity than water and the viscosity increases with increase in the weight fraction of SDC. From Fig. 6.3 it can be observed that irrespective of the amount of SDC, as oil is added viscosity of the microemulsions increases and attains asymptotically a constant value of about 4.7 mPa.s at $\phi_o > 0.25$.

The variation of η with ϕ_o at constant R values is shown in Fig. 6.4. In Fig. 6.4 we have also shown the reported[8] viscosity behaviour of benzene/sodium dodecylsulfate (SDS) + butanol/water microemulsions (ME_{rep}) for the sake of comparison. The present microemulsion has viscosity values in the same range as that for ME_{rep}. The variation of η with ϕ_o for the microemulsion of R = 197 is linear which is similar to the variation in ME_{rep} of

R = 120. The viscosity data of R = 197 microemulsion were fitted to Einstein-type equation of the form

$$\eta/\eta_{mic} = 1 + k_e\phi_o \qquad (6.2)$$

where η_{mic} is the viscosity of the SDC + water system (R = 197) without benzene (Table 6.3). The term k_e is known as intrinsic viscosity or shape factor and its value has been reported[8,9] to be 2.5 for spherical droplets. In the case of ME_{rep} *the value of* k_e *was reported*[8] *to be equal to* 2.31. *Hence,* ME_{rep} *of* R = 120 was treated as oil-in-water (o/w) microemulsion with spherical droplets. The plot of η/η_{mic} versus ϕ_o is shown in Fig. 6.5 and the least-squares fitted value of k_e for the present microemulsion of R = 197 is given in Table 6.4. Since k_e = 3.589, the shape of the droplets of the o/w microemulsion (benzene/SDC/water) of R = 197 is ellipsoidal. In the case of microemulsions of R = 155 and R = 126, the variation of η with ϕ_o is not linear (Fig. 6.4). However, in both these microemulsions up to certain values of ϕ_o ($\phi_o < 0.09$ in R = 155 and $\phi_o < 0.06$ in R = 126) linear variation of η versus ϕ_o has been observed (Fig. 6.5). Therefore, viscosity data within the range of $\phi_o < 0.09$ for R = 155 and $\phi_o < 0.06$ for R = 126 were least-squares fitted to Eq. (6.2). From the fitted values of k_e (Table 6.4) it is obvious that in R = 155 and R = 126 o/w microemulsions also the droplets are ellipsoidal. The intercepts of Eq. (6.2) for R = 197, 155 and 126 microemulsions are not exactly equal to 1. This implies that the viscosity of the dispersing medium when $\phi_o > 0$ is different from η_{mic} (experimental value of η when $\phi_o = 0$). It therefore appears that the shape of the micelle (droplet when ϕ_o = 0) slightly changes when the added oil is solubilized within the droplet. This particular observation is more conspicuous in the case of microemulsions of R = 88 and 51. In these two microemulsions, although plots of η versus ϕ_o within the range $0 < \phi_o < 0.032$ for R = 88 and $0 < \phi_o < 0.027$ for R = 51 are linear, the data corresponding to $\phi_o = 0$ ($\eta/\eta_{mic} = 1$) deviate significantly from the linear plots (Fig. 6.5). The shape of the SDC micelle in R = 88 and 51 appears to undergo considerable change on solubilization of oil. On comparison with ME_{rep}, it is also noticed that η versus ϕ_o plots of R = 88 and 51 microemulsions look similar to that of ME_{rep} of R = 100. Benzene and water thus form o/w microemulsions in the presence of SDC when $R \geq 51$.

6.3.4 Conductivity

The measured specific conductivity (κ) values of the microemulsions of different R values as a function of ϕ_o are given in Table 6.3. The trend in the variation of κ with ϕ_o is shown in Fig. 6.6. In Fig. 6.6, we have also shown the reported[9] trend in the variation of κ with ϕ_o of ME_{rep}. κ shows similar dependence on ϕ_o in the two types of o/w microemulsions, one stabilized by SDC and the other by SDS and butanol. However, the magnitude of conductivity of the microemulsions stabilized by SDC is less by about 3 orders than that of ME_{rep}. The variation of κ with ϕ_o at constant weight fractions of SDC (Fig. 6.7) is almost similar to that at constant R values.

The decrease in κ with increase in ϕ_o is a common trend observed in o/w microemulsions. In the plots of κ versus ϕ_o (Fig. 6.6) three regions can be identified. (i) In the first region at very low values of ϕ_o, a slight decrease in κ occurs with increase in ϕ_o. (ii) In the middle region, κ decreases sharply with increase in ϕ_o. (iii) In the third region where $\phi_o > 0.05$, κ again decreases with increase in ϕ_o, but the rate of decrease is less than that in the middle region. The decrease in κ with increase in ϕ_o may be attributed to obstruction and dilution effects. The obstruction effect may be considered as due to viscosity of the microemulsion, which increases by the addition of oil. In Fig. 6.8, we plotted the product $\kappa\eta$ versus ϕ_o and from this plot it can be seen that in the first region $\kappa\eta$ increases with increase in ϕ_o. Therefore, in the first region κ is controlled by viscosity or obstruction effect. In this region the increase in η caused by the addition of oil is actually responsible for the decrease in κ. In the middle region, the decrease in κ appears to be controlled by the dilution effect. In the third region also the decrease in κ may be due to dilution effect, but due to larger size of the swollen droplets the effect of dilution on κ appears to be less than in the middle region.

The conductance behaviour of o/w microemulsions is generally explained by the Bruggeman equation[11]

$$(\kappa/\kappa_0)^q = 1 - \phi_o \qquad (6.3)$$

κ_0 refers to κ of the dispersing medium. The value of the exponent q is dependent on the shape of the droplets, and is taken to be 2/3 ($\approx$ 0.667) for spherical droplets. The slope of Eq. (6.3) is hardly found to be equal to 1 in microemulsions.[10-12] Hence, modified Bruggeman Eq. (6.3) is used for data analysis of o/w microemulsions.[10,11]

$$(\kappa/\kappa_0)^q = 1 - f\phi_o \qquad (6.4)$$

In Eq. (6.4), the slope f is found to be greater than 1 and it is due to hydration of the droplets. Only in the case of un-hydrated droplets f is equal to 1. First, we fitted the κ data of the present microemulsions to the equation

$$(\kappa/\kappa_{mic})^{0.667} = 1 - f\phi_o \qquad (6.5)$$

The fitted values of the intercept and f are given in Table 6.5 and the plots are shown in Fig. 6.9. Although the conductivity data fit into Eq. (6.5), the values of the slope are found to be unreasonably high. Even for polyethylene glycols (PEG), which have significantly high capacity for hydration, the reported[11] values of f are in the range of 1.4 (for PEG 200) to 2.15 (for PEG 1000). The values of the intercept are also deviated from the expected value of 1. Therefore, Eq. (6.5) cannot be considered to be applicable to the present microemulsions. Moreover, from the viscosity data we observed that the droplets containing SDC micelles and solubilized benzene are not spherical. We therefore fitted the κ data to an empirical equation of the form

$$(\kappa/\kappa_{mic})^{0.067} = 1 - f\phi_o \qquad (6.6)$$

The value of the exponent $q = 0.067$ was chosen arbitrarily during iteration. The plots of Eq. (6.6) are shown in Fig. 6.9 and the fitted values of the intercept and f of Eq. (6.6) are given in Table 6.5. The values of the intercept and f of Eq. (6.6) are in the acceptable range. Moreover, the value of the exponent, which is different from 0.667, imply non-spherical shape of SDC-stabilized droplets.

6.4 Conclusions

Oil-in-water microemulsions containing water/SDC/benzene were prepared and the phase diagram of this system at 25 °C has been constructed. Density, viscosity and conductivity measurements of these microemulsions were made. This study revealed that (i) SDC, like AOT, has the ability to form microemulsions without cosurfactant and (ii) forming microemulsion without cosurfactant is dependent not only on the characteristic of the surfactant, but also on the structure of the oil used. By analyzing the viscosity and conductivity data, it has been shown that the droplets of the water/SDC/benzene o/w microemulsions have ellipsoidal shape.

6.5 References

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Table 6.1 Density values of water/SDC/benzene microemulsions at 25 °C

ϕ_o	Density / g. cm^{-3}	ϕ_o	Density / g. cm^{-3}	ϕ_o	Density / g. cm^{-3}
R = 197					
0.0051	1.0212	0.0240	1.0186	0.0750	1.0119
0.0086	1.0208	0.0284	1.0181	0.1397	1.0032
0.0134	1.0204	0.0317	1.0176	0.1963	0.9953
0.0163	1.0200	0.0359	1.0171	0.2457	0.9886
0.0202	1.0193	0.0435	1.0165		
R = 155					
0.0054	1.0110	0.0289	1.0079	0.0899	0.9998
0.0116	1.0098	0.0343	1.0071	0.1650	0.9900
0.0160	1.0095	0.0380	1.0068	0.2283	0.9811
0.0192	1.0092	0.0436	1.0058	0.2833	0.9741
0.0242	1.0084	0.0481	1.0052		
R = 126					
0.0066	1.0089	0.0353	1.0050	0.1063	0.9949
0.0139	1.0079	0.0410	1.0041	0.1914	0.9830
0.0194	1.0070	0.0466	1.0032	0.2616	0.9733
0.0231	1.0065	0.0517	1.0023	0.3200	0.9652
0.0288	1.0056	0.0579	1.0017		
R = 88					
0.0045	1.0058	0.0239	1.0030	0.0735	0.9949
0.0094	1.0049	0.0278	1.0027	0.1367	0.9861
0.0131	1.0046	0.0317	1.0018	0.1926	0.9783
0.0156	1.0044	0.0353	1.0013	0.2397	0.9717
0.0195	1.0034	0.0396	1.0017		
R = 51					
0.0051	1.0039	0.0268	1.0008	0.0820	0.9921
0.0106	1.0034	0.0312	1.0001	0.1502	0.9814
0.0147	1.0030	0.0354	0.9994	0.2094	0.9733
0.0176	1.0023	0.0394	0.9987	0.2607	0.9652
0.0219	1.0015	0.0442	0.9982		

Table 6.2 Values of the parameters of Eq. (6.1)

R	d_0 / g cm^{-3}	b / g cm^{-3}
197	1.0221	0.1359
155	1.0117	0.1326
126	1.0097	0.1393
88	1.0065	0.1461
51	1.0049	0.1525

Table 6.3 Viscosity and conductance data of water/SDC/benzene microemulsions at 25 °C

ϕ_o	Viscosity / mPa.s	Conductiviy / mS m^{-1}	ϕ_o	Viscosity / mPa.s	Conductiviy / mS m^{-1}
R = 197					
0	0.0024	11.9641	0.0317	0.0028	9.1028
0.0051	0.0026	11.8313	0.0359	0.0028	8.4536
0.0086	0.0026	11.8069	0.0435	0.0029	7.6848
0.0134	0.0026	11.6264	0.0750	0.0032	5.9973
0.0163	0.0027	11.5544	0.1397	0.0037	4.7829
0.0202	0.0027	11.2996	0.1963	0.0042	3.6974
0.0240	0.0027	9.9924	0.2457	0.0046	2.7215
0.0284	0.0028	9.6722			
R = 155					
0	0.0025	11.2095	0.0380	0.0029	7.7110
0.0054	0.0026	11.0082	0.0436	0.0030	6.5790
0.0116	0.0027	10.6052	0.0481	0.0030	6.0450
0.0160	0.0027	10.0113	0.0899	0.0034	4.4335
0.0192	0.0028	9.6812	0.1650	0.0040	3.5837
0.0242	0.0028	9.2553	0.2283	0.0043	2.6222
0.0289	0.0029	8.2490	0.2833	0.0045	1.6130
0.0343	0.0029	7.7150			
R = 126					
0	0.0026	10.2327	0.0466	0.0031	5.6460
0.0066	0.0027	10.1360	0.0517	0.0032	5.1750
0.0139	0.0028	9.4120	0.0580	0.0032	4.6310
0.0194	0.0029	8.7940	0.1063	0.0036	3.7260
0.0231	0.0029	8.1450	0.1914	0.0040	2.7860
0.0288	0.0029	7.4920	0.2616	0.0043	1.6650
0.0353	0.0030	6.8390	0.3200	0.0044	1.0110
0.0410	0.0031	6.0440			
R = 88					
0	0.0027	10.0887	0.0317	0.0031	5.4016
0.0045	0.0029	9.8561	0.0353	0.0031	4.6716
0.0094	0.0029	9.0120	0.0396	0.0032	4.3127
0.0131	0.0029	8.6242	0.0735	0.0034	3.3259
0.0156	0.0030	7.8709	0.1368	0.0037	2.6701
0.0195	0.0030	7.2417	0.1926	0.0039	1.4833
0.0239	0.0031	6.5128	0.2397	0.0040	0.9815
0.0278	0.0031	5.6886			

Table 6.3- Continued

ϕ_o	Viscosity / mPa.s	Conductiviy / mS m^{-1}	ϕ_o	Viscosity / mPa.s	Conductiviy / mS m^{-1}
		R = 51			
0	0.0028	9.4288	0.0354	0.0032	4.9375
0.0051	0.0030	9.2146	0.0394	0.0032	4.3548
0.0106	0.0030	8.7106	0.0442	0.0033	4.1797
0.0147	0.0031	8.3107	0.0820	0.0034	3.2603
0.0176	0.0031	7.5452	0.1502	0.0035	2.4970
0.0219	0.0031	6.9791	0.2094	0.0036	1.2817
0.0268	0.0032	6.0182	0.2607	0.0039	0.7888
0.0312	0.0032	5.3300			
		Weight fraction of SDC (w) = 0.1			
0	0.0027	11.7408	0.2226	0.0044	2.6194
0.0541	0.0029	6.5139	0.2772	0.0046	2.0350
0.0750	0.0032	-	0.3277	0.0046	1.5908
0.1154	0.0035	3.4962	0.3687	0.0046	1.1162
0.1671	0.0040	3.3289	0.3919	0.0047	0.9724
		Weight fraction of SDC (w) = 0.2			
0	0.0029	9.9671	0.2205	0.0044	2.0683
0.0468	0.0033	5.5468	0.2652	0.0045	1.6351
0.0924	0.0036	3.1982	0.3122	0.0047	1.0668
0.1365	0.0039	2.6613	0.3478	0.0047	0.7891
0.1787	0.0042	2.2197			
		Weight fraction of SDC (w) = 0.3			
0	0.0029	9.3865	0.1593	0.0041	2.1436
0.0408	0.0033	4.3276	0.1940	0.0044	1.8279
0.0442	0.0033	-	0.2344	0.0046	1.5310
0.0801	0.0036	3.2603	0.2679	0.0046	1.3238
0.1222	0.0039	2.4493	0.3105	0.0047	0.7755

Table 6.3- Continued

ϕ_o	Viscosity / mPa.s	Conductiviy / mS m^{-1}	ϕ_o	Viscosity / mPa.s	Conductiviy / mS m^{-1}
		Weight fraction of SDC (w) = 0.4			
0	0.0032	9.0005	0.1650	0.0044	1.7802
0.0347	0.0033	3.9648	0.1986	0.0045	1.5619
0.0668	0.0037	3.0387	0.2306	0.0046	1.3150
0.1009	0.0039	2.4283	0.2632	0.0047	0.7721
0.1332	0.0041	2.0760			
		Weight fraction of SDC (w) = 0.5			
0	0.0033	8.7112	0.1376	0.0043	1.7536
0.0280	0.0033	3.3322	0.1642	0.0044	1.4169
0.0559	0.0037	2.7518	0.1910	0.0046	1.1074
0.0833	0.0039	2.3264	0.2179	0.0047	0.8829
0.1116	0.0042	2.0251			

Table 6.4 Least-squares fitted values of the parameters of Eq. (6.2)

R	Intercept	k_e	Range of ϕ_o
197	1.035	3.589	$0 \le \phi_o < 0.25$
155	1.026	3.982	$0 \le \phi_o < 0.09$
126	1.016	4.122	$0 \le \phi_o < 0.06$

Table 6.5 Fitted values of the intercept and slope of Eqs. (6.5) and (6.6)

R	Eq. (6.5)			Eq. (6.6)		
	Intercept	f	Corr. coeff.	Intercept	f	Corr. coeff.
197	1.120	8.88	-0.981	1.015	1.03	-0.987
155	1.062	8.13	-0.993	1.009	0.98	-0.989
126	1.053	8.15	-0.998	1.010	1.05	-0.999
88	1.047	12.45	-0.996	1.010	1.47	-0.997
51	1.088	12.57	-0.997	1.014	1.60	-0.997

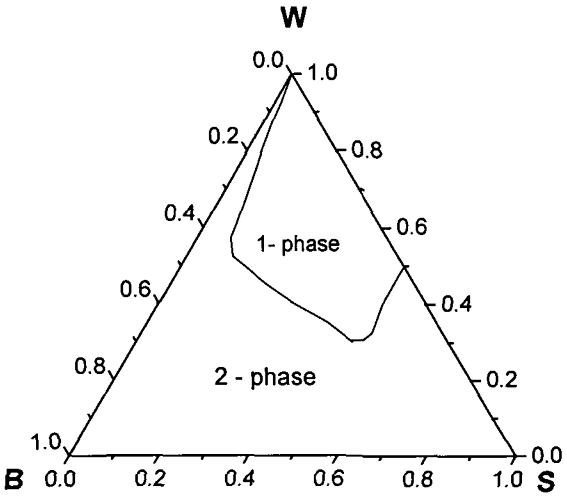

Fig. 6.1 Phase diagram of water (W)/benzene (B)/SDC (S) microemulsion at 25 °C. The amounts of the three components are expressed in weight fraction.

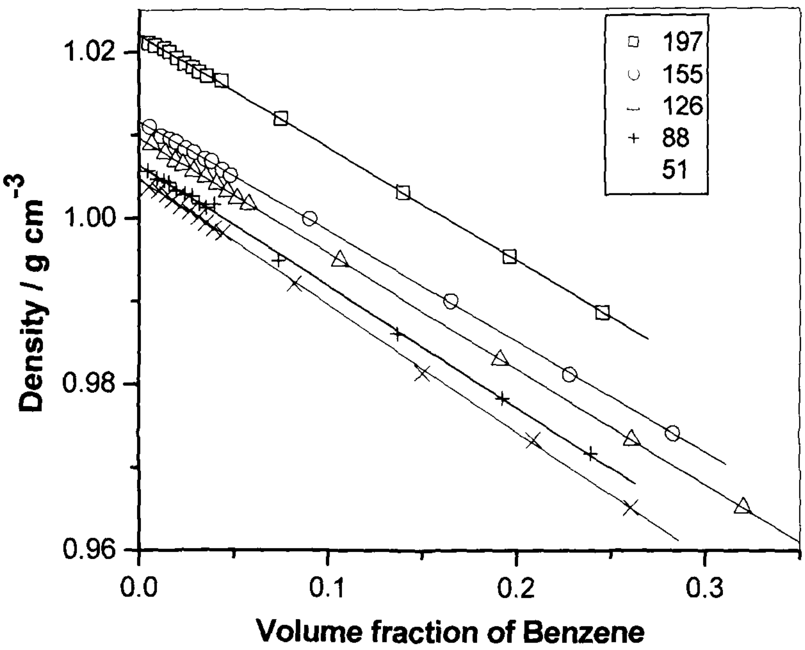

Fig. 6.2 Variation of density of water/SDC/benzene microemulsion with volume fraction of benzene

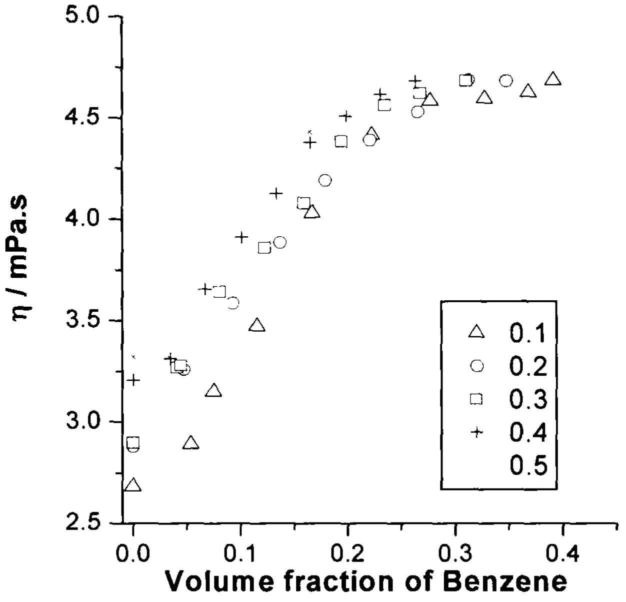

Fig. 6.3 Variation of viscosity of water/SDC/benzene microemulsion with volume fraction of benzene at constant weight fractions of SDC (values given in the inset).

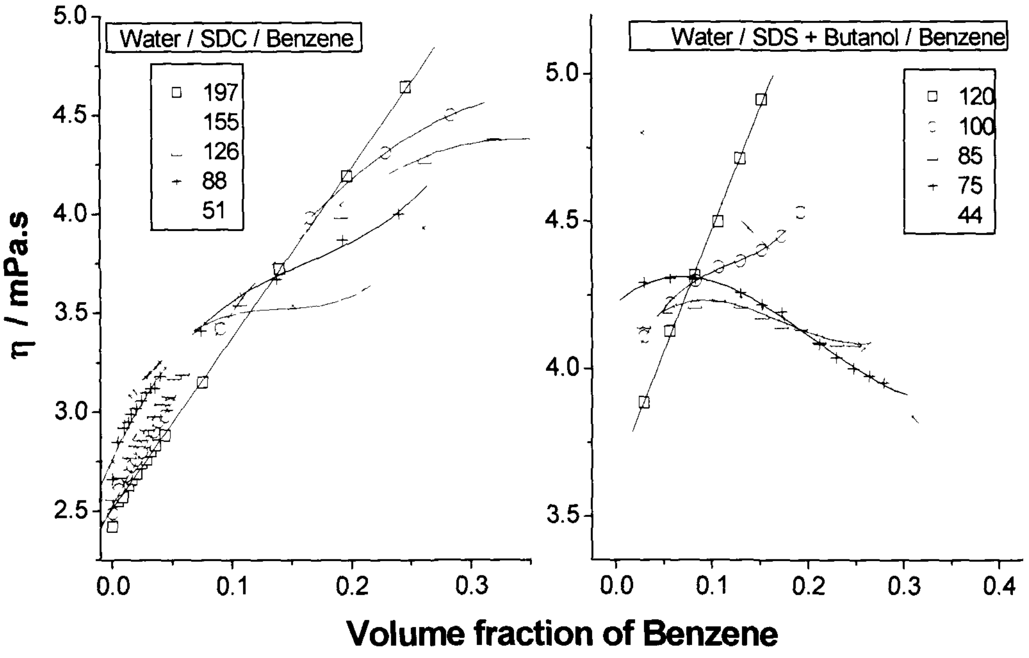

Fig. 6.4 Variation of viscosity of water/SDC/benzene and water/SDS + butanol/benzene (data from ref. 7) microemulsions with volume fraction of benzene at constant R values (given in the inset).

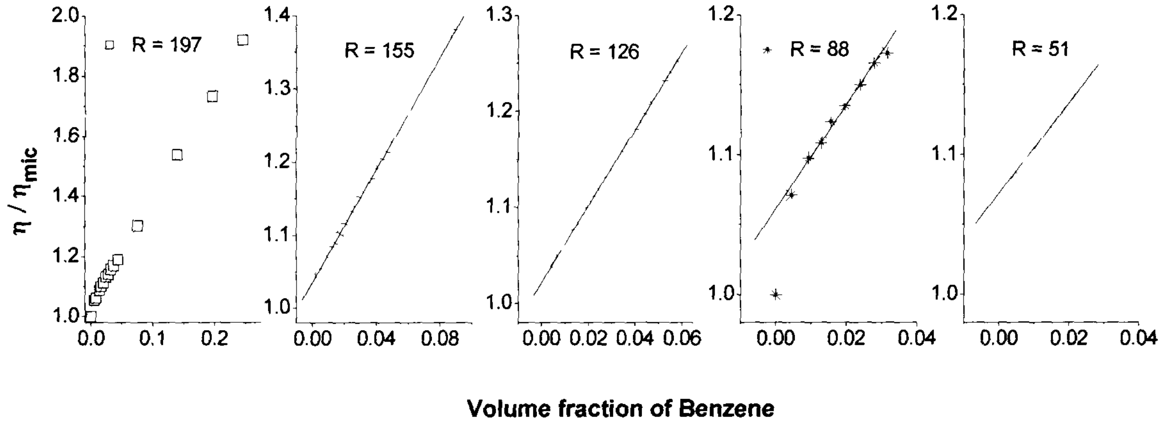

Fig. 6.5 Variation of η/η_{mic} of water/SDC/benzene microemulsions with ϕ_o.

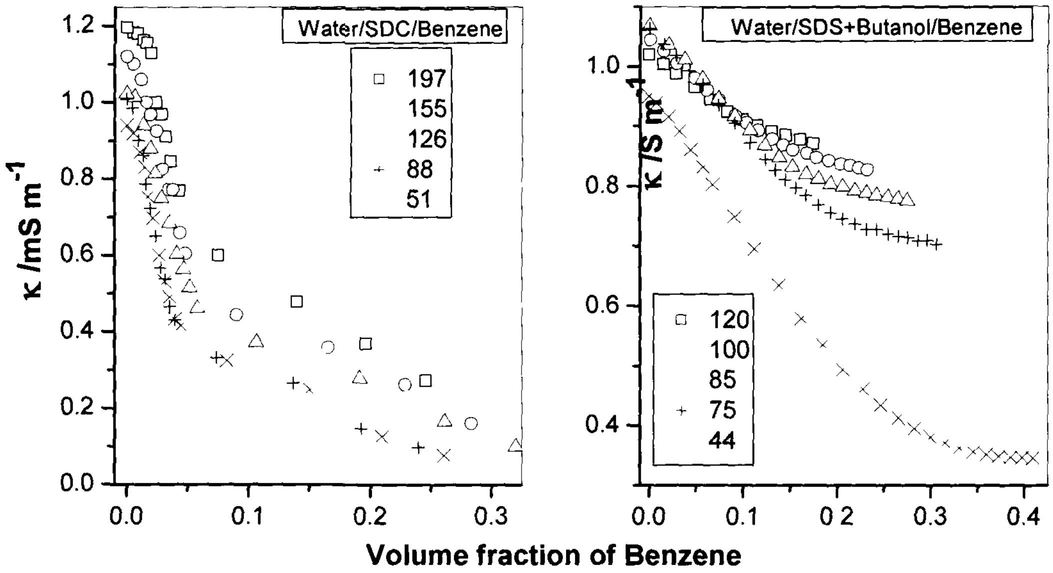

Fig. 6.6 Variation of specific conductivity of water/SDC/benzene and water/SDS + butanol/benzene (data from ref. 9) microemulsions with volume fraction of benzene at constant R values (given in the inset).

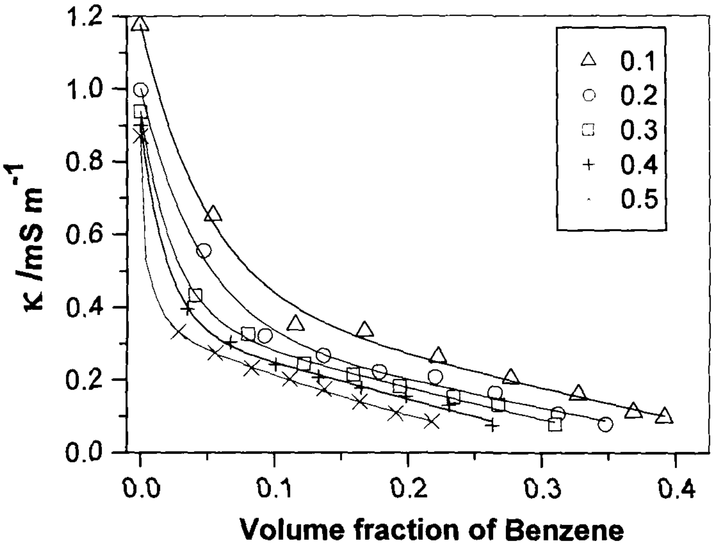

Fig. 6.7 Variation of specific conductivity of water/SDC/benzene microemulsion with volume fraction of benzene at constant weight fractions of SDC (values given in the inset).

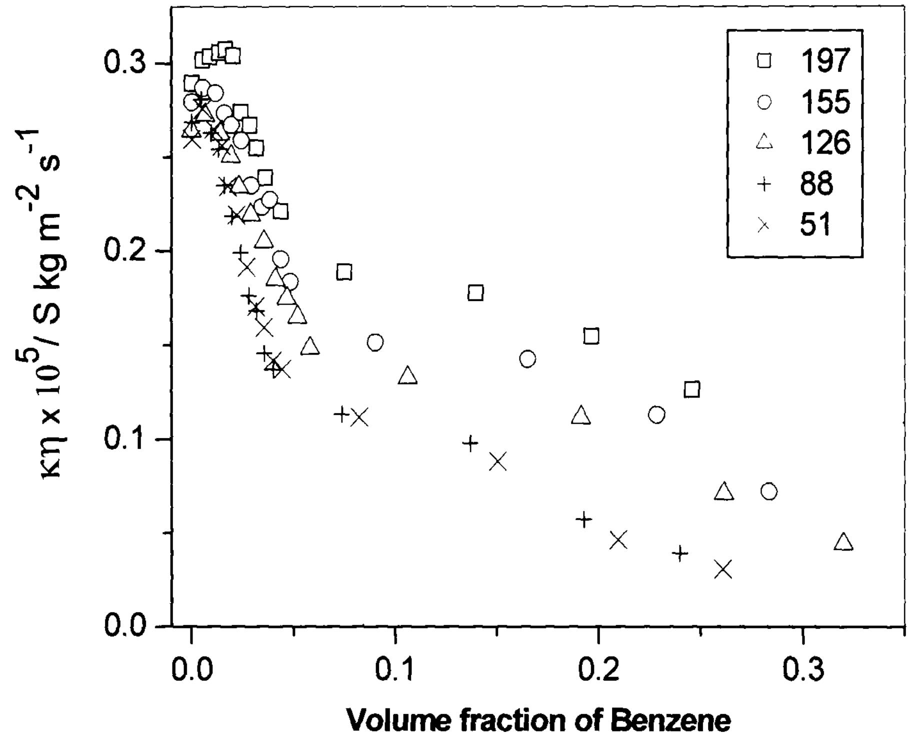

Fig. 6.8 Variation of $\kappa\eta$ of water/SDC/benzene microemulsions with ϕ_o at constant R values (given in the inset).

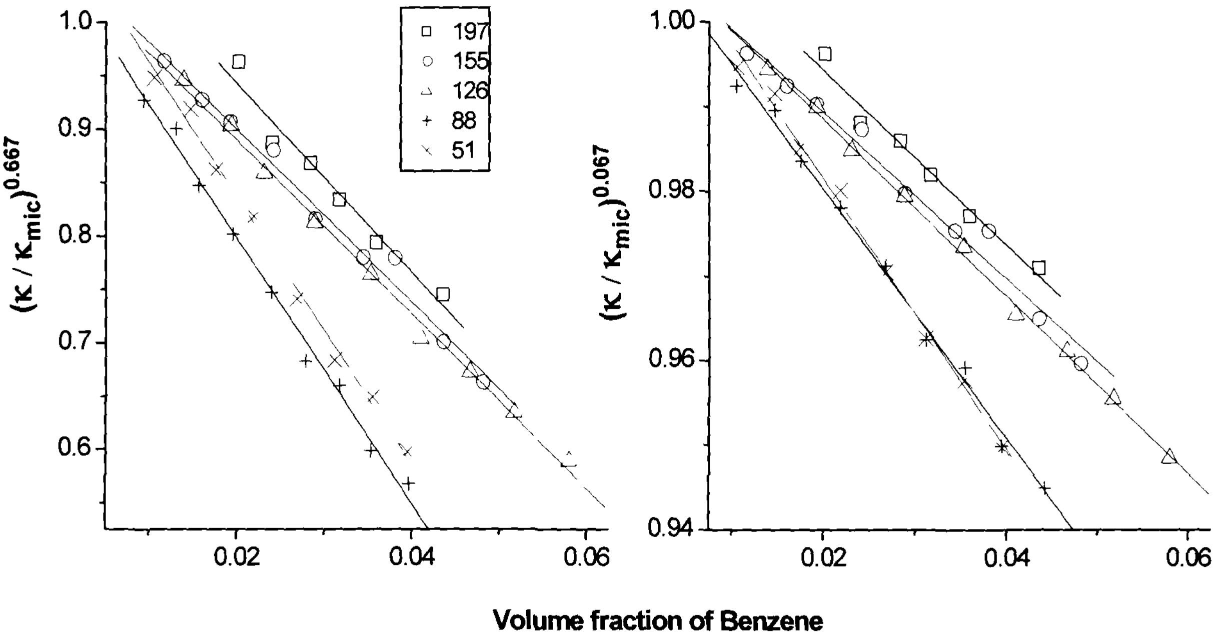

Fig. 6.9 Plots of $(\kappa/\kappa_{mic})^{0.667}$ and $(\kappa/\kappa_{mic})^{0.067}$ versus volume fraction of benzene for water/SDC/benzene microemulsions of different R values.

SUJIT DAS

Phone No. 0364-2722611

Research Scholar

E- mail: suj_it1980@yahoo.co.in

Personal Profile

Date of Birth:	15.07.1981
Address for correspondence:	Sujit Das C/o. Prof. K. Ismail Department of Chemistry NEHU, Shillong-22
Mother Tongue:	Bengali
Nationality:	Indian

Educational Qualifications

Class XII (1998)	I Class with 64.0%
B. Sc. (Chemistry Honours 2001)	I Class with 64.0%
M. Sc. (Specialization – Physical Chemistry 2003)	I Class with 64.0%

Rajiv Gandhi National Fellowship, April 2005

Research 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. **Sujit Das**, Uttam Thapa, and Kochi Ismail. "Aggregation and Adsorption Behaviours of Sodium Deoxycholate in Water – Ethylene Glycol Medium". ***Bulletin of the Chemical Society of Japan*** (accepted).

3. 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.*

Seminars/ Symposia / Conferences attended;

1. A one day workshop on Science and Technology for the Better Quality of Life (25th February 2006)

2. National Symposium on Advances in Chemistry and Environmental Impact (2-3 November 2006) organized by Department of Chemistry, North-Eastern Hill University, Shillong-793022, Meghalaya, India.

3. National Conference on Disperse Systems (23-25 November 2006) organized by Assam University in collaboration with Indian Society for Surface Science and Technology, Jadavpur University, Kolkata.

4. Active participation in the 96th Indian Science Congress 2009 (3-7 January 2009) held at North-Eastern Hill University, Shillong-793022, Meghalaya, India.

5. National Conference on Surfactants, Emulsions and Biocolloids (NATCOSEB -XIV, 28-30 July 2009) organized by Department of Chemistry, University of Kashmir in collaboration with Indian Society for Surface Science and Technology (ISSST).

6. National Seminar on Membranes, Microemulsions and Self-assembled Systems (MMSAS, 28-30 September 2010) organized by Department of Chemistry, Sikkim Manipal Institute of Technology in collaboration with North-Eastern Chapter of Indian Society for Surface Science and Technology (ISSST).

Place: Shillong

Sujit Das

Date:

SUJIT DAS