A STUDY ON THE EFFECT OF ELECTROLYTES ON THE MICELLIZATION OF CATIONIC SURFACTANTS

ABSTRACT

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Chapter 1 consists of general introduction and the scope of the work. In Chapter 2 the experimental techniques employed have been described.

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estimate the aggregation number of CPC in the presence of electrolytes. For more than 5.2×10^{-4} mol kg^{-1} electrolyte concentration, aggregation number of CPC is found to be higher in NaCl than in the presence of LiCl and KCl thereby envisaging a likely effect of the co-ion on aggregation number.

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In chapter 5, surface tension and conductance measurements of aqueous solutions of CPC at 30 °C in the presence of different pairs of coions and counter ions were made. The systems studied are CPC + sodium bromide and CPC + tetrabutylammonium bromide (TBAB). The bromide counter ion is found to decrease the cmc of CPC more than chloride counter ion. The modified Corrin-Harkins equation was used to describe the variation of cmc with added electrolyte concentration in the presence of mixed counter ions. From the slope of this equation the lower limit to the value of β was obtained. It is demonstrated that the mixed – electrolyte – model (MEM) can be applied to analyze the conductance data of surfactant solution containing chloride and bromide as mixed counter ions. The value of β obtained from the MEM was then used to determine the binding constants of the individual counter ions (β_1 and β_2). By this treatment we could show that (i) bromide preferentially binds to CPC micelle by replacing chloride counter ion, (ii) bromide binding is more than chloride and (iii) aggregation number of CPC is higher in the presence of bromide. Na^+ and tetrabutylammonium (TBA^+) coions do not have any effect on the cmc of CPC, but TBA^+ affects the adsorption of CPC. In TBAB solution, adsorption of CPC takes place on a surface that already contains adsorbed TBA^+ coions and above 0.02 mol kg^{-1} TBAB the adsorbed TBA^+ hinders the adsorption of CPC due to electrostatic and steric effects.

In chapter 6, the cmc of CPC in water + glycerol media as functions of glycerol and NaCl concentrations were determined at 25 °C from the experimental data of surface tension and specific conductance. Variation in cmc follows the normal trend, i.e., increases with increase in glycerol content and decreases on adding NaCl. Empirical analysis of the exponential increase in cmc of CPC with weight per cent of glycerol is indicative of cmc having two components; one component being dependent while the other independent of glycerol amount. Counter ion binding constant determined from both slope – ratio and Corrin-Harkins methods showed no dependence on glycerol amount, thus confirming the unusual trend in the behaviour of β. This anomalous behaviour of β is viewed as due to existence of a water-like environment around micellar surfaces in water + glycerol medium. In water + glycerol medium the ratio of solvent surface tension to limiting surface tension at cmc is also independent of glycerol amount, whereas Gordon Parameter decreases with increase in glycerol content as in other aqueous organic solvents and represents solovophobicity of the medium. The air – solution interface becomes saturated by the adsorption of CPC when the concentration of added NaCl is about 0.02 mol kg^{-1} irrespective of the glycerol amount.

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By

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DEPARTMENT OF CHEMISTRY
SCHOOL OF PHYSICAL SCIENCES

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2010

Thesis

DEDICATED TO

MY WIFE

AND

DAUGHTER

The North Eastern Hill University

Declaration

Month: April **Year: 2010**

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

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

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Shillong

Dated 22nd April 2010

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CONTENTS

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CHAPTER 1

General Introduction

1.1 Surfactants

Surfactants are surface-active molecules consisting of a non-polar hydrophobic portion and a polar hydrophilic portion due to which they possess amphiphilic behavior, viz., hydrophobicity and hydrophilicity towards water medium. The polar hydrophilic part of a surfactant molecule is known as head group and the hydrophobic part consisting of hydrocarbon chain with eight or more carbon atoms is called the tail. Surfactants are known to exhibit amphiphilic character in solvents other than water also. Hence, in general, solvophobicity and solvophilicity terms are used to represent the dual characters of surfactants.

1.1.1 Classification

Surfactants can be broadly classified as biosurfactants and synthetic surfactants. Naturally occurring surfactants are called biosurfactants which mostly occur in biological systems. Phospholipids, fatty acids and bile salts are some of the examples of naturally occurring surfactants. Surfactants used for domestic and industrial purposes are mostly synthetic surfactants. Soaps and detergents are formulations containing mainly synthetic surfactants as active components. Both natural and synthetic surfactants are further classified as anionic, cationic, nonionic and zwitterionic.[1]

Anionic surfactants have the general formula RA^-M^+, where R represents the solvoophobic chain with A^- head group and M^+ is the counter ion. These surfactants when dissolved in polar solvents dissociate to give negatively charged monomeric species and the corresponding counter ion and on micellization form anionic micelles. Examples of some of the widely used anionic surfactants are

$CH_3(CH_2)_{11}SO_4^-Na^+$ (sodium dodecyl sulfate) and $RC_6H_4SO_3^-Na^+$ (sodium alkyl benzene sulfonate).

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

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

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

Surfactant molecules containing two hydrophobic tails attached to one head group are also known. Sodium dioctylsulfosuccinate (anionic; commonly known as Aerosol-OT or simply AOT) and dioctadecyldimethylammonium chloride (cationic) are examples of such surfactants. Triple-chained ionic surfactants are also known.[2]

Surfactant molecules containing two head groups and two hydrocarbon chains have also been synthesized. Such surfactants are called gemini (or dimeric) surfactants if the spacer is between the two head groups or bolaforms if the spacer is between the hydrocarbon chain.[3] The length of the spacer can be varied by varying the number of carbon atoms. Efforts are being made to synthesize newer surfactants with special properties, for e.g., photo-sensitive surfactants.[4-6]

1.1.2 **Adsorption and aggregation**

Due to their amphiphilic character, surfactants exhibit two very important properties. These are (i) surface activity or adsorption at an interface and (ii) self-organization or aggregation. Due to surface activity, surfactants can lower the surface tension of a solution and form monolayers, films and multilayers. Self-organization or aggregation of surfactants is responsible for the formation of aggregates like micelles, vesicles and membranes. The importance and applications of surfactants in various fields are mainly because of their adsorption and micellization abilities.

1.2 Thermodynamics of adsorption: Gibbs adsorption isotherm

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

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

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

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

where $d\gamma$ is the change in the surface or interfacial tension of the solvent and $d\mu_i$ is the change in chemical potential of the i^th^ component. Γ_i is the surface excess of the i^th^ 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. Due to the ability of surfactants to lower interfacial tension, they are used as emulsifiers, foaming agents, etc.

1.3 Gibbs adsorption isotherm for ionic surfactants

Since we have studied in this thesis cationic surfactants in the presence of electrolytes, the Gibbs adsorption isotherm given by Eq. (1.2) has been looked into in more detail in the light of the treatment reported by Prosser and Franses.[7] We consider here an cationic 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

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

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

R^{z+} is the surfactant cation 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 is same, $z_- = s_-$. 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

$$c = \frac{c_R}{n_+}, \qquad c_e = \frac{c_X}{n_{+e}} \tag{1.10}$$

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

$$\Gamma = \frac{\Gamma_R}{n_+}, \qquad \Gamma_e = \frac{\Gamma_X}{n_{+e}} \tag{1.11}$$

Electro-neutrality condition gives the following relations:

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

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

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

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

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

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

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

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

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

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

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

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

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 Eq. (1.19) becomes

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

1.4 Micelle formation

The second important property of a surfactant is its ability to undergo aggregation. Aggregation of a surfactant in solution is commonly known as micellization and the aggregates are called micelles.[8] Hydrophobic interaction is considered to be responsible for micellization of a surfactant. Water molecules become more ordered around the hydrocarbon tail of a surfactant. Transfer of hydrophobic tails of a surfactant from bulk water into micellar phase results in positive entropy change due to disordering of the ordered water molecules around the hydrocarbon tail. The entropy generated thus in the solvent medium drives the micellization process. Micelles formed in polar solvents are called normal micelles, whereas those formed in non-polar solvents are called reverse micelles.

1.5 Micellization parameters

Micellization of surfactants in solution always begins at a particular critical concentration known as the critical micelle concentration (cmc). When micelle is formed, a sudden change in several physical properties of surfactant solutions takes place enabling us to determine experimentally values of cmc of surfactants. Normally, changes in physical properties like surface tension, conductivity, viscosity, solubilization, osmotic pressure, etc, take place over a narrow concentration range. Therefore, a precise determination of the cmc is difficult and moreover values of cmc estimated from different experimental methods may also differ to a certain extent. Thus, numerous methods are available for determining the value of cmc.[9] Tensiometry, conductometry, fluorimetry and calorimetry are some of the commonly used methods. Critical micelle concentration is one of the important properties of a surfactant by which its micellization behavior is characterized. Cmc depends on the structure of surfactant and on the concentration of added electrolytes. 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 of ionic and nonionic surfactants with identical hydrophobic moieties indicating the influence of hydrophilic group on cmc. The lower cmc of the nonionic surfactants are a consequence of the lack of electrical work necessary in forming the micelles. Nature of counter ion, its radius and valence, also largely affects the value of cmc of ionic surfactants.[10-16] Added electrolytes have significant effect on the cmc of both ionic and nonionic surfactants.[10-18] The addition of electrolytes also affects other properties of surfactants like cloud point,[19-21] free energy of micellization,[17] aggregation number,[22-29] etc. Non-electrolytes like urea, amides, alcohols, etc on addition produce both increase and decrease of cmc of surfactants.[30-34] The temperature dependence[35-41] of cmc is quite interesting. Most of the ionic surfactants exhibit at some temperature a minimum in the cmc.[35,36,38] This property of ionic surfactants is used in the differential scanning calorimetry technique for studying the micellization behavior of ionic surfactants.[42] With increase in pressure cmc of ionic surfactants in water show a maximum.[43-50]

Aggregation number is another important fundamental parameter concerning a micelle and it is equal to the number of monomers present in a micelle. It gives an idea about the size of a micelle. Aggregation number also shows dependence on the structure of a surfactant and on the amount of added electrolyte.[22-29] Marked changes in the aggregation number of surfactants indicate about changes in the micellar shape. Unlike cmc, aggregation number has dependence on the surfactant concentration.[51-54] In a particular surfactant solution micelles of different aggregation number can exist.[55] Such polydispersity is generally ignored for calculation purpose and only monodispersed micelles with single (average) aggregation number are taken into account. Aggregation number is determined using experimental techniques like quasi-elastic light scattering, small-angle neutron scattering, steady-state fluorescence quenching and time-resolved fluorescence quenching.[22-24, 28, 29, 52, 56, 57]

Counter ion binding constant (β) is another important characteristic of ionic micelles. Counter ions control, besides cmc and aggregation number of ionic surfactants, also the reactions[58] that take place in the presence of ionic surfactants. The shape of an ionic micelle appears to have an influence on the value of β. In non-aqueous polar solvent media, β generally has lower value than in water.

Thermodynamic functions such as Gibbs function, enthalpy and entropy of micellization and surface potential of ionic surfactants are other related micellization parameters. Due to the presence of effective electric charge on the ionic micelle, an electric potential is developed at the surface of the ionic micelle, which is known as surface potential of the ionic micelle. The surface potential value controls different processes that take place near the micelle – solution interface. Some other parameters/properties of surfactants that are related to their micellization are Kraft temperature, cloud point and solubilization.

1.6 Structure and shape of ionic micelles

Micelles have regular structures and shapes. A general structure of a regular ionic micelle formed in polar solvents[59] is shown in Fig. 1.1. An ionic micelle consists of a liquid core or interior, which is oil like, formed by the associated hydrocarbon chains. The charged head groups project out into the water phase. Similar structure of micelles exists in polar non-aqueous solvents also. In non-polar solvents the structure of micelle gets reversed. The region immediately surrounding the core is the Stern layer which contains the ionic head groups and a part of counter ions (bound counter ions). The Stern layer constitutes the inner part of the electrical double layer surrounding the micelle. The outer layer, which is a diffuse layer contains the remaining counter ions (free counter ions) and is known as Gouy-Chapman layer. The shear layer lies between the Stern and the diffuse layers. Appreciable amount of water has been reported[60, 61] to penetrate into the liquid-like hydrocarbon core.

Since micelles are in dynamic equilibrium with the surfactant monomers, considering them to have rigid structures with precise shapes may be unrealistic. Small-angle neutron scattering experiments on micellar solutions,[23,52,56,62,63] dynamic light scattering experiments and phase diagram studies support the concept of micelles having regular shapes.[22-24,52,64,65] It is assumed that micelles at concentrations near to the cmc are roughly spherical. The radius of a micelle cannot be greater than the stretched-out length of the surfactant molecule. Typically micelles may have average radii of 1.2 – 3 nm and can contain 20 – 100 monomers. The other proposed structures of micelles include the rod-like,[66] the lamellar model[67] and the disk or cylindrical model.[68] Added electrolyte has great influence on the shape of ionic micelles. As the counter ion concentration is increased, the shape of ionic micelles changes in the sequence spherical – cylindrical – hexagonal – lamellar.[22,23,65,69-71] Some of the shapes of micelles are shown in Fig. 1.2. Geometrical parameters like surface area of the head group, alkyl chain length, molecular volume of the hydrocarbon chain, etc. control the shapes adopted by micelles.[26]

1.7 Thermodynamics of micelle formation

Two approaches are used to understand the thermodynamics of the micellization process, which are Phase – Separation and Mass – Action models. In the Phase – Separation model the micelles are considered to form a separate phase at the cmc in equilibuium with the solution phase, while in the Mass – Action model micelles and unassociated monomers are considered to be in association-dissociation equilibrium. The two models merge asymptotically with increasing aggregation number. Besides these two approaches thermodynamics of small systems developed by Hill[72] has also been applied to the aggregation of solutes. The phase – separation and the mass – action models are briefly discussed below.

1.7.1 Phase – Separation model

In this approach the micelle is treated as a separate phase. Appropriate standard states are to be defined first in order to calculate the thermodynamic parameters of micellization. The hypothetical standard state for the surfactant in the aqueous phase is taken to be the solvated monomer at unit mole fraction with the properties of the infinitely dilute solution. For the surfactant in the micellar state, the micellar state itself is considered to be the standard state.[73, 74]

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

$$\mu_s = \mu_s^0 + RT \ln a_s \tag{1.22}$$

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

$$\mu_s = \mu_s^0 + RT \ln X_s \tag{1.23}$$

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

$$\mu_m = \mu_m^0 \tag{1.24}$$

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

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

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

$$\Delta G_{mic}^0 = RT \ln X_{cmc} \tag{1.26}$$

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

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

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

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

1.7.2 Mass – Action model

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

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

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

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

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

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

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

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

Eq. (1.32) can be rearranged to the form

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

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

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

Just above the cmc, we can approximate

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

c_0 denotes cmc. Eq. (1.34) now becomes

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

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

$$\ln X_{cmc} = A - \beta \ln X_M \tag{1.37}$$

where $\Delta G^0_{mic}/RT$ is represented by A. Eq. (1.37) is similar to Eq. (1.28). Eqs. (1.27), (1.28), (1.36) and (1.37) are the different forms of the Corrin – Harkins equation.[75]

1.8 Scope of the work

Electrolytes and non-electrolytes on addition alter the micellization characteristics of surfactants and hence affect their performance. In almost all formulations containing surfactants different additives are used so that these formulations acquire the required properties. Therefore, it is of practical/industrial importance to study the effect of additives on the micellization parameters of surfactants.

Generally, the effect of added electrolyte on micellization parameters is entirely attributed to the counterions. However, both counterion and coion of an added electrolyte may have influence on the adsorption and aggregation properties of an ionic surfactant.

Added counterions normally increase the surface excess, decrease the critical micelle concentration (cmc) and increase the aggregation number of ionic surfactants. Counterions also decrease the surface potential of ionic micelle[76-78] and induce shape change of micelles.[79-82] In some ionic surfactants, added counterions on exceeding a particular concentration alter even the value of counterion binding constant.[83-89]

Scattered works indicate that co-ions can also affect the behaviour and performance of ionic surfactants.[90-92] Muller and Birkhahn[90] were the first to report on the effect of coions on the cmc. They reported that the cmc values of $CF_3(CH_2)_8COONa$ and $CF_3(CH_2)_{10}COONa$ in aqueous NaOH and NaCl solutions were different. Ikeda et al.[91] reported that the aggregation number (or molecular weight) of sodium dodecylsulfate micelles in aqueous solutions of sodium salts changed in the order NaSCN < NaF < NaCl < NaBr < NaI. The study made by

Ranganathan et al.[92] on the dynamics of incorporation of N-alkylpyridinium ions into cetyltrimethylammonium chloride and acetate surfactants is indicative of coion – micelle interactions. The effect of acetate and propionate coions on the cmc of SDS observed by us from conductance study[77] has, however, not been detected by tensiometry.[93] Kabir-ud-Din et al.[94] had investigated the influence of LiCl, NaCl and KCl on the hexanol concentration required to produce the relative viscosity maximum in the 0.2 mol dm^{-3} CPC solution + hexanol system and reported that the co-ion effect is not significant.

In the light of the above reports, it is obvious that coions can produce perceivable changes in the values of micellization parameters and can also affect the solubilization process of surfactant systems. In order to obtain a clear understanding of the role of coions in the adsorption and micellization behaviours of ionic surfactants, it is necessary to study and document the adsorption and micellization characteristics of ionic surfactants in the presence of electrolytes containing different co-ions. Furthermore, the effect of mixed counter ions on the micellization characteristics of ionic surfactants has not been investigated in detail.

Therefore, the objective of the work is to investigate the effect of coions as well as counterions on the adsorption and aggregation behaviours of ionic surfactants. In this thesis, we have chosen cetylpyridinium chloride (CPC) as the surfactant (a cationic surfactant) for investigation. The adsorption and aggregation behaviours of CPC have been investigated in the presence of different types of electrolytes with varying coions and counterions. The effect of electrolyte has been investigated by changing the solvent also.

In chapter 3, surface tension and conductance studies of CPC in aqueous medium in the presence of LiCl, NaCl and KCl were carried out. In chapter 4, similar studies of CPC were made in aqueous medium in the presence of sodium salicylate and sodium benzoate. Sodium salicylate and sodium benzoate are electrolytes having hydrotropic property. In chapter 5, we carried out surface tension and conductance studies of CPC in aqueous sodium bromide and tetrabutylammonium bromide media.

Solvents play a decisive role in controlling the adsorption and micellization characteristics of surfactants. Mixing of solvents changes solvent property, particularly polarity, and we get important results of fundamental and practical importance by carrying out adsorption and aggregation studies of surfactants in mixed solvents. Due to this reason, surfactant behavior is being studied in binary mixtures of solvents with a renewed interest in the last four years.[95-120] In view of this, in chapter 6 surface tension and conductance studies of CPC were made in water + glycerol medium in the absence and presence of NaCl.

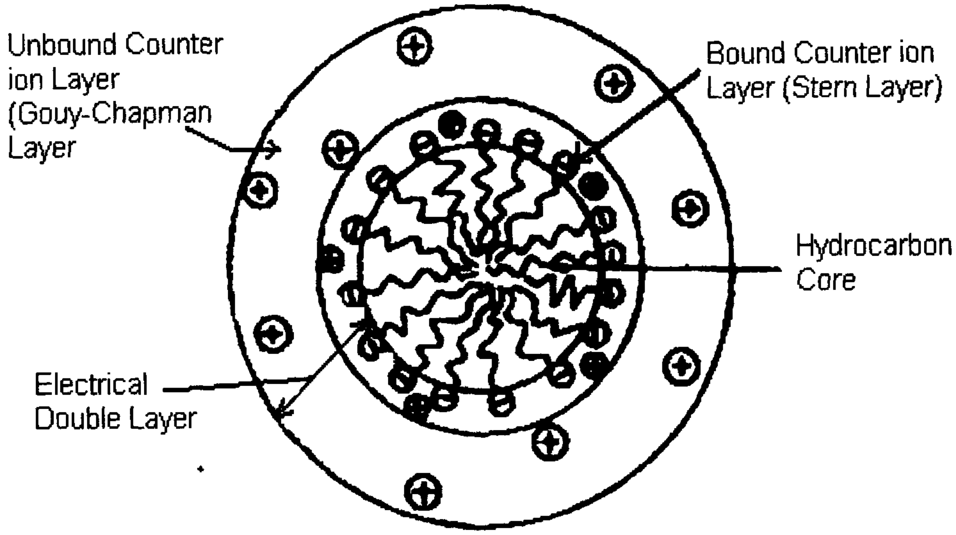

Figure 1.1 - A schematic representation of a spherical ionic micelle showing bound counter ions and the electrical double layer.

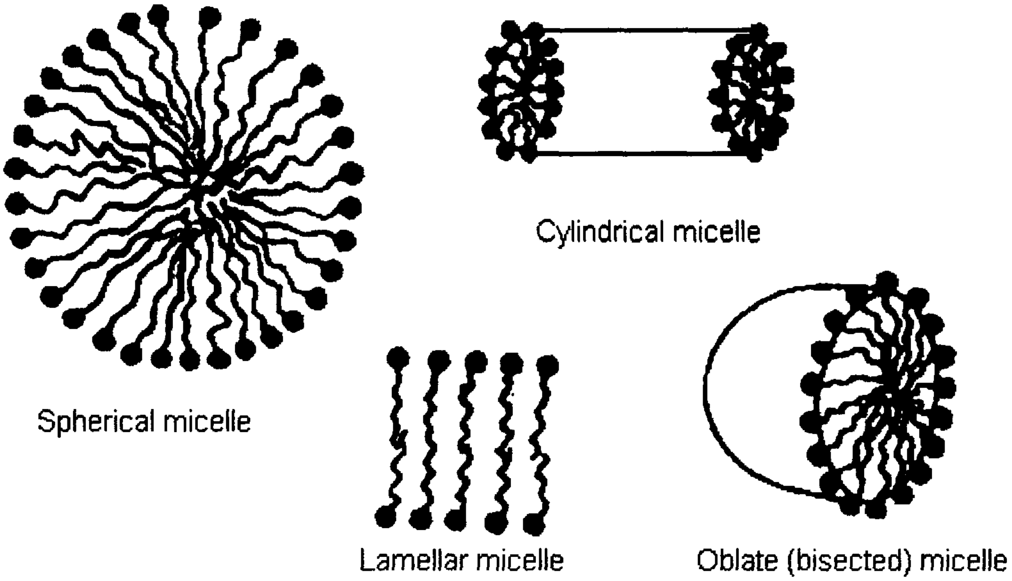

Figure 1.2 - Schematic representation of different shapes of micelles

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CHAPTER 2

Experimental Techniques

2. 1 Surface Tension Measurement

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

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

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

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

The recommended sample vessel made up of Corning glass was used for holding the liquid or solution. This sample vessel is also cleaned thoroughly with acetone and water. The dry sample vessel is also flamed off with a Bunsen burner to make it free from any surface-active substance. The solution is taken in the cooled sample vessel up to the recommended height. The sample vessel containing the solution is then placed in the steel jacket of the tensiometer. The steel jacket is maintained at the required temperature using Haake DC 10 circulation bath. The supplied temperature sensor senses the temperature of the solution. The recommended immersion speed, search speed and immersion depth were selected. The entire operation of the tensiometer is controlled by the microprocessor. The instrument is attached to a PC and the surface tension values are displayed on the monitor screen. Ten surface tension values taken at an interval of 1 second and an average of these values were displayed on the screen. This particular tensiometer has a resolution of 0.01 mN m^{-1}. The reproducibility of the measured surface tension values of the solutions was found to be within ±1 mN m^{-1}. A schematic diagram of the Wilhelmy Plate method is shown in Fig. 2.1.

2.2 Electrical Conductance Measurement

Conductance measurements were made at 1 kHz using Wayne Kerr B905 Automatic Precision Bridge. This LCR meter has 0.01 nS resolution and measures conductance with an accuracy of 0.05 %. It has an averaging facility and averages 2 ('Average' 1) to 128 ('Average' 9) measurements in a time span of about 670 ms to 36 s, respectively. We have used throughout the 'Average' 9 option. The bridge works basically on the principle of Ohm's law. Matching currents are passed through the standard resistor and the solution under test. The corresponding two voltages produced, whose values depend upon the impedances at the standard resistor and the test solution, are measured, resolved and computed to give the desired information on the display. All functions of the instrument are under the direct control of a microprocessor. A dip-type conductivity cell having platinized platinum elecrtrodes was used. The cell constant was determined using standard KCl solution. The desired temperature for the solution under test is maintained with the help of Haake D8 circulation bath.

2.3 Viscosity

Viscosity was measured by using a Cannon-Ubbelohde type viscometer having viscometer constant $3.51\text{x}10^{-3}$ cSt s^{-1}.

2. 4 Density Measurement and Weighing

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

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

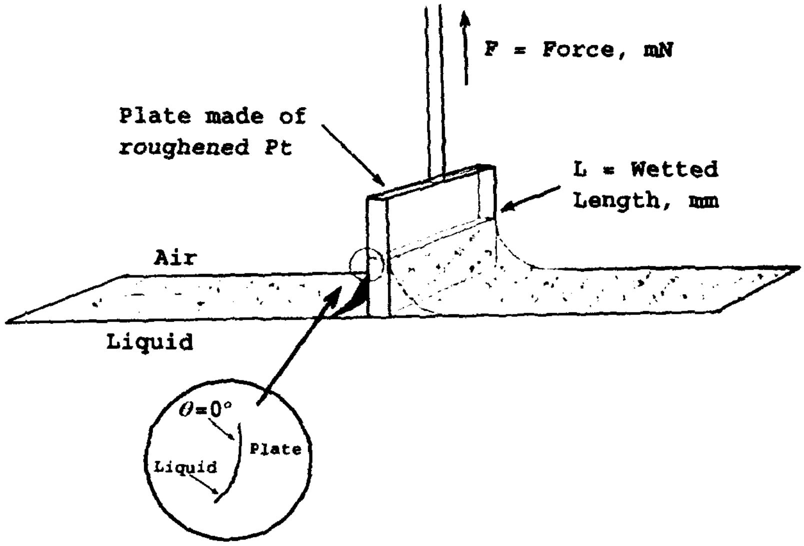

Figure 2.1 - Schematic diagram of Wilhelmy Plate.

CHAPTER 3

Adsorption and Aggregation Behaviours of Cetylpyridinium Chloride in Aqueous Lithium Chloride, Sodium Chloride and Potassium Chloride Media

3.1 INTRODUCTION

As mentioned in the scope of the work section in chapter 1, scattered works indicate that co-ions, depending upon its nature, can produce perceivable changes in the values of micellization parameters.[1-3] We report here the results of the surface tension and conductance measurements of cetylpyridinium chloride (CPC) in aqueous LiCl, NaCl and KCl media at different temperatures. Micellization characteristics of CPC in water[3-7] in the temperature range from 288 to 333 K and in aqueous NaCl[6,7] and NaBr[7] solutions at 303 K have been reported. We intended to investigate the micellization behaviour of CPC in aqueous LiCl, NaCl and KCl solutions at temperatures $\leq$ 303 K and at low concentration region of electrolytes. However, we could not carry out measurements below 295 K as we faced solubility problem for CPC in electrolyte solutions at temperatures less than 295 K.

3.2 EXPERIMENTAL

CPC (Fluka, > 98.0 %), LiCl (SRL, 99 %), NaCl (Merck, 99.5 %) and KCl (Merck, 99.5 %) were used as received. Double distilled water having conductance 2.3 μS and surface tension 72 mN m^{-1} at 25 °C was used throughout for preparing solutions. Surface tension measurements were made by the Wilhelmy plate method using K11 Krüss Tensiometer. Conductance measurements were made using B905 Wayne Kerr Automatic Precision Bridge. During surface tension and conductance measurements, temperature of the solutions was controlled using Haake DC10 circulation bath. Density of the solutions, whenever needed for converting molal to molar concentration units, was measured using Anton Paar DMA 5000 density meter.

3.3 RESULTS AND DISCUSSION

Surface tension, γ, values of CPC in aqueous LiCl, NaCl and KCl solutions are presented in Tables 3.1 – 3.3 and Figs. 3.1 – 3.3 in the form of γ versus logc plots, c is the concentration of CPC in mol kg^{-1}. The cmc values of CPC determined from these plots are given in Table 3.4. Specific conductivity, κ, values of CPC in the three electrolyte solutions are presented in Tables 3.5 – 3.7 and Figs. 3.4 – 3.6. The cmc values of CPC determined from κ versus c plots are also given in Table 3.4. Values of cmc obtained from γ and κ data are in agreement. The reported values of cmc of CPC in water at different temperatures[3-7] and in aqueous NaCl solution[6] at 303 K are in agreement with the present values. The variation of cmc with electrolyte concentration is depicted in Fig. 3.7. From Table 3.4 and Fig. 3.7 it is clear that the co-ions chosen for study in this work do not have any effect on the cmc of CPC. The variation of cmc with temperature is shown in Fig. 3.8 and the cmc minimum for CPC in water in the presence and absence of electrolyte appears to occur around 298 K. Others[6] data also indicate cmc minimum at 298 K for CPC in water.

From the cmc values of CPC in electrolyte solutions we determined the counter ion binding constant, β, by using the Corrin–Harkins (CH) equation[8]

$$\ln X_{cmc} = A - \beta_{CH} \ln X_c \tag{3.1}$$

where X_c is the mole fraction of the counter ion near the cmc and X_{cmc} represents the cmc in mole fraction unit. Equation (3.1) can be derived from the mass action model for micellization. The CH plot of $\ln X_{cmc}$ versus $\ln X_c$ is shown in Fig. 3.9. β_{CH} represents the counter ion binding constant determined from the slope of the Corrin-

Harkin equation. The values of β_{CH} obtained from the CH plots drawn using the cmc values from κ and γ data are given in Table 3.8. Values of counter ion binding constant were also determined from the κ data using the slope – ratio method, which are also listed in Table 3.8. The counter-ion binding constant determined from the slope – ratio method is denoted by β_{κ}. We can get values of β_{κ} at each electrolyte concentration, whereas from the CH plot method we get only an overall value for β in a chosen range of electrolyte concentration. Since aggregation number is known to vary with change in the concentration of added electrolyte, β_{CH} is expected to vary with C resulting in nonlinearity of CH plot. However, the linearity of CH plot envisages that in the presence of an added electrolyte both aggregation number and the amount of counter ion binding to the micelle vary in such a manner that β_{CH} remains constant. No regular trend is observed in the variation of β_{κ} with electrolyte concentration and with temperature. By using κ data of CPC up to 0.2444 mol kg^{-1} we have earlier reported[4] $\beta_{\kappa} = 0.72$ for CPC in water at 298 K. Molinero et al.[9] also reported $\beta_{\kappa} = 0.77$ for CPC in water at 298 K. However, the value of β_{κ} is found to be dependent on the upper concentration limit of CPC used for finding the slope above cmc. For instance, when κ data of CPC up to 0.01 mol kg^{-1} were used, we found that $\beta_{\kappa} = 0.61$ and by using κ data up to 0.002 mol kg^{-1} the value of β_{κ} for CPC in water decreased further to 0.54 at 298 K. The value of β_{κ} equal to 0.55 is in agreement with the β_{κ} value reported recently by Chatterjee et al.[6] for CPC in water.

The parameter A of Eq. (3.1) is equal to $\Delta G_m^0/RT$, where ΔG_m^0 is the free energy change due to micellization per mole of surfactant at the chosen standard state. ΔG_m^0 is also given by the expression

$$\Delta G_m^0 = RT(1 + \beta_\kappa)\ln X_{cmc} \tag{3.2}$$

The standard state for expressing the free energy change of micellization depends upon the concentration unit used for representing counterion concentration and cmc in Eqs. (3.1) and (3.2). The value of ΔG_m^0 obtained by using mole fraction unit for concentration is nearly 10 to 15 kJ mol^{-1} more than the value calculated using molar unit for concentration. From the A parameter of Eq. (3.1) we get an overall value for ΔG_m^0 in the chosen range of electrolyte concentration, whereas from Eq. (3.2) ΔG_m^0 can be calculated at different electrolyte concentrations. Both the values of ΔG_m^0 calculated from A and Eq. (3.2) using molar unit of concentration (standard state refers to hypothetical standard state of unit molar concentration) are given in Table 3.9. The ΔG_m^0 values of CPC in water and in NaCl solution are in agreement with the corresponding values reported by Chatterjee et al.[6].

Surface excess values of CPC at the air-water interface near its cmc, Γ_{cmc}, in the presence of the three electrolytes were calculated from the respective surface tension data using the expression[10]

$$\Gamma_{cmc} = -\frac{1}{RT}\left[\frac{1}{1+\frac{c_0}{c_0+c_e}}\right]\left(\frac{d\gamma}{d\ln c}\right)_{cmc} \tag{3.3}$$

where c, c_e, c_0, R and T represent the surfactant concentration, electrolyte concentration, cmc, gas constant, and absolute temperature, respectively. In the absence of electrolyte, i.e., for CPC in water, Eq. (3.3) becomes

$$\Gamma_{cmc} = -\frac{1}{2RT}\left(\frac{d\gamma}{d\ln c}\right)_{cmc} \tag{3.4}$$

The computed values of Γ_{cmc} for CPC in water and in the different electrolyte solutions are given in Table 3.10. The value of Γ_{cmc} (1.70×10^{-6} mol m^{-2}) for CPC in water at 303 K is in agreement with the reported[5] value (1.73×10^{-6} mol m^{-2}). The variation of Γ_{cmc} with electrolyte concentration does not, however, follow a regular trend. The effect of temperature on Γ_{cmc} is found to be not significant in the range from 295 to 303 K. The surface area, A_0, covered per molecule of CPC at the air – water interface is calculated from the relation

$$A_0 = 1/(N_A\Gamma_{cmc}) \tag{3.5}$$

where N_A represents the Avogadro number. A_0 is found to be equal to 0.85 nm^2 for CPC in water at 298 K which is about 63 % more than the surface area covered per sodium dodecylsulfate (SDS) molecule (0.52 nm^2).[11] Larger surface area covered by CPC at the air – water interface compared to that by SDS is visualized as due to the presence of pyridine ring in the hydrocarbon tail of the CPC molecule and this pyridine ring of the adsorbed CPC molecule appears to reside just at the interface. With the addition of electrolyte Γ_{cmc} of CPC increases, which is a trend generally observed for ionic surfactants.[11] Added electrolyte thus enhances the adsorption of CPC at the air – water interface thereby decreasing the surface area coverage per molecule of CPC. The enhancement of adsorption by the addition of electrolytes can be explained as due to their salting out effect. The difference in the hydration of the co-ions (Li^+, Na^+, and K^+), however, does not seem to have any influence over this salting out effect of electrolytes. Moreover, added electrolytes also tend to decrease the area per CPC molecule by better screening of electrostatic repulsion between the ionic heads as a result of increase in the number of counter ions in the Stern and diffuse layers.

In order to estimate the aggregation number, n, of CPC in electrolyte solutions, we applied the mixed electrolyte model[12] for analyzing the conductance data. We did the data fitting using this model at 25 °C only. This model is based on the Debye-Hückel-Onsager approach and the molar conductance, Λ, of the surfactant solution is given by the expression

$$\Lambda = \left[\Lambda_1^0 - \frac{A_1 I^{1/2}}{1+B_0 a_1}\right]\frac{c_0}{c} + \left[\Lambda_n^0 - \frac{A_n I^{1/2}}{1+B_0 a_n}\right]\frac{n(1-\beta)c_n}{c} \qquad (3.6)$$

where c_n is the molar concentration of micelle, a_i's and Λ_i^0's correspond to the effective ionic sizes and limiting equivalent conductances, respectively of monomer (i = 1) and micelle (i = n). I is the ionic strength and

$$B_0 = \left[\frac{8\pi N_A {e_0}^2}{10^3 \varepsilon k_B T}\right]^{1/2} I^{1/2} \qquad (3.7)$$

$$A_i = \frac{2.801\text{x}10^6 |z_+ z_-| q \Lambda_i^0}{(\varepsilon T)^{3/2}(1+q^{1/2})} + \frac{41.25(|z_+|+|z_-|)}{\eta(\varepsilon T)^{1/2}} \qquad (3.8)$$

$$q = \frac{(\lambda_+^0 + \lambda_-^0)|z_+ z_-|}{(|z_+| + |z_-|)(|z_+|\lambda_-^0 + |z_-|\lambda_+^0)} \tag{3.9}$$

In the above Eqs (3.6) – (3.8), k_B is the Boltzman constant, ε is the dielectric constant of water, e_0 is the elementary charge, and η is the viscosity of water. λ_+^0 and λ_-^0 are the limiting ionic equivalent conductivities of cationic and anionic species of effective charges z_+ and z_-, respectively. The analysis of the conductance data using Eq. (3.6) was done by presuming spherical geometry for the CPC micelle. The details of the data fitting are described elsewhere.[4,14-17] According to this method, to compute the values of c_0, n and β from Eq. (3.6), we first require the values of r_1 (radius of the CP ion), r_n (radius of the micelle), r_c (radius of the counter ion), a_1, a_n, A_1, A_n, Λ_1^0, Λ_n^0, λ_+^0, λ_-^0, and I. The value of r_1 was estimated approximately by using Tanford relation.[13] According to Tanford relation the volume of cetyl chain, v, is given by

$$v = 27.4 + 26.9n_c \tag{3.10}$$

n_c in Eq. (3.10) refers to the number of carbon atoms in the cetyl chain (equal to 16). To this volume we added the volume of pyridinium ring, v_p. Thus, the volume of the CP ion, v_{cp}, was calculated as

$$v_{cp} = v + v_p \tag{3.11}$$

Based on the reported[18] length of the pyridinium ring, its approximate volume was calculated to be equal to 92 Å^3. We thus obtained $v_{cp} \approx 549.8$ Å^3. Presuming this volume to be spherical, an effective radius of CP ion was calculated as

$$r_1 = \left[\frac{3v_{cp}}{4\pi}\right]^{1/3} \tag{3.12}$$

r_1 was found to be equal to 5.08 Å. r_n was calculated using the relation, $r_n = n^{1/3}r_1$. The value of Λ_1^0 of CPC in water or electrolyte solution at 25 °C is taken from the literature[4] as equal to 86.60 x 10^{-4} S m^2 eq^{-1}. The value of λ_+^0 of CP ion was calculated by subtracting from Λ_1^0 the literature[19] value of λ_-^0 of Cl^- (76.4 x 10^{-4} S m^2 eq^{-1} at 25 °C). The value of λ_+^0 for the micelle (λ_{+mic}^0) was computed using the Stokes–Einstein relation

$$\lambda_{+mic}^0 = \frac{z_n e_0 F}{6\pi\eta r_n} \tag{3.13}$$

where F is the Faraday constant. The charge on the micelle is $z_+ = z_n = n(1-\beta)$. The value of Λ_n^0 was calculated by adding the value of λ_-^0 of Cl^- to λ_{+mic}^0.. The values of a_1 and a_n were determined by adding the Stokes ionic radius[19] of Cl^- (1.21 Å) to r_1 and r_n, respectively. The values of A_1 and A_n were calculated from the Eqs. (3.8) and (3.9) by making appropriate substitutions for z_+, λ_+^0 and Λ_i^0 (i = 1 or n). At 25 °C, the values of ε and η were taken as 78.3 and 8.9 x 10^{-3} P, respectively. For fitting the conductivity data to Eq. (3.6) an iterative least-squares method was used by writing a computer program on the basis of the Newton – Raphson method. Shanks and Franses[12] used four different models for the calculation of I and concluded that ionic micelles do not contribute to I. This conclusion made by Shanks and Franses was found to be true in our earlier works.[4,14-17] Therefore, during data fitting I was calculated as I = c (in the absence of electrolyte) and $I = c + c_e$ (in the presence of electrolyte of concentration c_e) when $c < c_0$ and $I = c_0$ (in the absence of electrolyte) and I = $c_0 + c_e$ (in the presence of electrolyte of concentration c_e) when $c > c_0$.

In the present case while fitting the data for a particular electrolyte concentration, rather than determining all the three parameters (c_0, β and n) from iteration, we fed the values of c_0 and β from Tables 3.4 and 3.8 and kept them constant during iteration. We therefore determined the value of n only by iteration. The computed values of n at 298 K are given in Table 3.11. At 0.01 and 0.02 mol kg^{-1} electrolyte concentrations we could not obtain realistic values for n, because the changes in κ caused by the addition of CPC to the electrolytes of these two concentrations are found to be very less. Molinero et al.[9] obtained micellar aggregation numbers of CPC in water and in aqueous KCl solution at 298 K from fluorescence quenching measurements by using tris(4,7-diphenyl-1,10-phenanthroline) ruthenium(II) dichloride as probe and 9-methylanthracene as quencher. Molinero et al.[9] reported that (i) aggregation number of CPC in the absence of KCl varied from 18 to 55 when the concentration of CPC was varied from 0.004 to 0.15 mol dm^{-3}, (ii) in the presence of KCl at constant [CPC] = 0.01 mol dm^{-3} the aggregation number of CPC varied from 49 to 64 when the KCl concentration was varied from 0.01 to 0.03 mol dm^{-3}, and (iii) the aggregation number of CPC remained constant at 64 above 0.03 mol dm^{-3} KCl up to 0.08 mol dm^{-3}. By applying the mixed electrolyte model to the conductance data of CPC in water at 298 K we reported[4] earlier aggregation number equal to 54 ± 5 for CPC. Varade et al.[7] reported from SANS measurements aggregation number of CPC at 303 K equal to 104 in water and 113, 131 and 229 in 0.1, 0.5 and 1.0 mol dm^{-3}

NaCl solutions, respectively ([CPC] = 0.25 mol dm^{-3}). From Table 3.11 it is apparent that in NaCl solution above $5x10^{-4}$ mol kg^{-1}, the n values of CPC obtained from the mixed electrolyte model are comparable to the aggregation numbers reported by Varade et al.[7]. On the other hand, in LiCl and KCl solutions, excluding $5.2x10^{-4}$ mol kg^{-1} electrolyte concentration, the n values derived from the mixed electrolyte model are found to be comparable to the aggregation numbers reported by Molinero et al.[9]. In the light of the aggregation numbers estimated in the present study and those reported by others[7,9], co-ions of the added electrolytes appear to have an influence on the aggregation number of CPC similar to the case reported[2] for SDS in the presence of various electrolytes containing different co-ions.

3.4 CONCLUSIONS

Critical micelle concentration values of CPC in aqueous LiCl, NaCl and KCl solutions were determined at 295, 298 and 303 K from their surface tension and electrical conductance data and the co-ions are found to have no influence on cmc. Cmc of CPC passes through a minimum around 298 K. Both temperature and co-ion do not have any significant effect on the surface density of CPC calculated at the cmc. The surface area covered per CPC molecule at the air–water interface is equal to 0.85 nm^2, which is about 63 % higher than that of sodium dodecyl sulfate molecule indicating location of pyridine ring of the adsorbed CPC molecule at the interface. Values of counter-ion binding constant were determined from the CH plots and the slope – ratio method. CH plot provides an overall value of counter-ion binding constant, whereas that obtained from the slope – ratio method showed a dependence on electrolyte concentration. The effect of coion on the counterion binding constant is also found to be negligible. Standard free energy of micellization for CPC was also computed and has almost same value at a particular electrolyte concentration in the case of all the three electrolytes. Values of aggregation number of CPC in the presence of electrolytes were estimated from the conductance data using the mixed electrolyte model. In the presence of more than 5.2×10^{-4} mol kg^{-1} NaCl, aggregation number of CPC is higher than that in the presence of LiCl and KCl thereby envisaging a likely effect of coion on aggregation number.

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Table 3.1a - Surface Tension (γ) values of CPC in aqueous Lithium Chloride solution at 295 K

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
		[LiCl] = 0.0 mol kg^{-1}			
0	72.7	0.2873	49.8	0.7745	40.8
0.0228	68.4	0.3263	47.3	0.8469	40.5
0.0454	68.4	0.3645	46.6	0.9160	40.2
0.0677	63.7	0.4020	45.6	0.9821	40.0
0.0897	61.4	0.4476	44.9	1.0454	40.5
0.1115	58.6	0.4921	43.2	1.1060	40.7
0.1331	57.3	0.5355	43.5	1.1642	41.0
0.1650	56.0	0.5778	42.4	1.2200	40.8
0.2066	53.8	0.6191	42.2	1.2736	40.8
0.2474	51.5	0.6987	41.5		
		[LiCl] = 3.2 x 10^{-4} mol kg^{-1}			
0.0227	63.6	0.7003	43.3	1.0549	41.5
0.0864	58.4	0.7684	42.0	1.1140	42.0
0.2228	53.3	0.8504	41.5	1.1687	41.8
0.3456	50.0	0.8776	42.0	1.2323	41.8
0.4638	47.7	0.9049	42.2	1.2779	41.9
0.6366	44.7	0.9822	42.1	1.3277	41.9
		[LiCl] = 5.2 x 10^{-4} mol kg^{-1}			
0.0285	61.2	0.5706	44.3	0.9177	41.9
0.1094	55.1	0.6419	42.1	0.9701	41.5
0.1664	53.2	0.7274	42.0	1.0414	41.7
0.2900	49.4	0.7607	41.7	1.0842	41.7
0.3851	46.6	0.8226	41.9		
0.4850	45.3	0.8559	41.5		
		[LiCl] = 1.3 x 10^{-3} mol kg^{-1}			
0.0467	56.8	0.4385	42.4	0.7371	41.3
0.0886	53.2	0.5144	41.4	0.7697	41.3
0.1773	49.2	0.5691	41.5	0.8350	41.6

Table 3.1a - Continued

[CPC/ mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
[LiCl] = 1.3 x 10^{-3} mol kg^{-1}					
0.2332	47.0	0.6157	41.1	0.8770	41.3
0.3079	45.7	0.6578	40.8	0.9283	41.1
0.3686	44.1	0.7091	41.4	0.9842	41.2
[LiCl] = 5.2 x 10^{-3} mol kg^{-1}					
0.0270	50.0	0.2252	40.7	0.3693	39.6
0.0631	46.5	0.2522	40.3	0.3964	39.8
0.1081	43.9	0.2793	40.1	0.4369	39.8
0.1621	41.8	0.3108	39.6	0.4685	39.6
0.1982	41.3	0.3378	39.5	0.5225	39.7
[LiCl] = 0.01 mol kg^{-1}					
0.0044	53.9	0.1186	41.9	0.2459	39.3
0.0351	46.5	0.1361	40.7	0.2635	39.2
0.0483	45.7	0.1581	40.1	0.2767	39.1
0.0615	44.6	0.1713	39.4	0.2986	39.4
0.0834	43.0	0.1932	39.1	0.3250	39.3
0.1010	41.8	0.2196	39.3		
[LiCl] = 0.02 mol kg^{-1}					
0.0086	49.3	0.0813	40.6	0.1455	38.3
0.0257	45.5	0.0941	40.0	0.1583	38.5
0.0428	43.2	0.1027	39.3	0.1711	38.3
0.0513	42.6	0.1155	38.5	0.1882	38.5
0.0727	41.0	0.1326	38.3	0.2096	38.6

Table 3.1b - Surface Tension (γ) values of CPC in aqueous Lithium Chloride solution at 298 K

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
[LiCl] = 0.0 mol kg^{-1}					
0	72.0	0.2314	55.8	0.7566	43.1
0.0058	71.5	0.2623	54.9	0.8312	42.7
0.0117	71.0	0.2926	53.2	0.9024	41.9
0.0233	69.9	0.3323	52.3	0.9704	41.8
0.0348	68.2	0.3711	51.2	1.0354	41.3
0.0463	67.5	0.4185	50.0	1.0977	41.8
0.0690	65.8	0.4647	48.8	1.1573	41.7
0.0915	63.3	0.5096	47.5	1.2145	41.6
0.1137	61.3	0.5534	47.3	1.2693	41.7
0.1356	60.8	0.5961	46.4	1.3220	41.6
0.1681	58.7	0.6377	46.0	1.3727	41.7
0.2000	58.1	0.6783	45.0	1.4214	41.6
[LiCl] = 3.2 x 10^{-4} mol kg^{-1}					
0.0179	64.3	0.5136	43.0	0.9513	38.9
0.0849	57.3	0.5940	42.6	0.9960	38.8
0.2054	51.2	0.6565	41.2	1.0495	39.2
0.2724	48.7	0.7146	40.4	1.1031	39.2
0.3394	47.1	0.7816	39.3	1.1389	38.9
0.4020	45.0	0.8441	38.8	1.1612	39.3
0.4600	43.0	0.8888	39.0		
[LiCl] = 5.2 x 10^{-4} mol kg^{-1}					
0.1171	49.9	0.4013	42.1	0.8069	38.6
0.1463	47.8	0.4432	41.6	0.8738	38.5
0.1798	46.5	0.5059	40.9	0.9365	38.5
0.2508	45.0	0.5811	40.2	1.0243	38.5
0.2968	43.4	0.6438	39.2	1.0786	38.6
0.3512	42.7	0.7065	38.5	1.1580	39.0

Table 3.1b – Continued

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
[LiCl] = 1.3 x 10^{-3} mol kg^{-1}					
0.0217	59.0	0.3686	42.1	0.7328	39.0
0.0781	52.4	0.4206	41.0	0.7892	38.8
0.1214	49.6	0.4684	39.7	0.8370	38.8
0.1605	47.8	0.5204	39.6	0.9020	39.2
0.2168	45.7	0.5551	39.4	0.9410	39.4
0.2949	43.8	0.6028	38.7	0.9975	39.4
[LiCl] = 5.2 x 10^{-3} mol kg^{-1}					
0.0288	54.2	0.1358	45.3	0.2963	41.4
0.0453	53.0	0.1564	45.0	0.3168	41.5
0.0700	47.7	0.1934	43.6	0.3374	41.6
0.0905	48.0	0.2222	42.7	0.3621	41.3
0.1029	47.8	0.2428	41.3		
0.1193	45.8	0.2592	41.6		
[LiCl] = 0.01 mol kg^{-1}					
0.0165	56.6	0.1772	39.9	0.2926	38.9
0.0371	49.7	0.2019	39.6	0.3173	38.2
0.0824	44.1	0.2225	38.8	0.3462	38.3
0.1071	43.1	0.2431	38.2	0.3709	38.2
0.1319	40.3	0.2555	38.9	0.3997	38.1
0.1525	40.2	0.2761	38.2		
[LiCl] = 0.02 mol kg^{-1}					
0.0154	54.3	0.1003	41.2	0.1620	37.4
0.0270	48.5	0.1080	41.1	0.1774	37.5
0.0386	47.7	0.1196	39.0	0.1928	38.0
0.0501	46.5	0.1311	37.6	0.2160	37.7
0.0617	44.4	0.1388	37.4	0.2275	37.6
0.0810	43.1	0.1466	37.6		

Table 3.1c - Surface Tension (γ) values of CPC in aqueous Lithium Chloride solution at 303 K

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
[LiCl] = 0.0 mol kg^{-1}					
0	71.5	0.2084	53.1	1.0049	40.3
0.0166	69.6	0.2847	50.5	1.1163	40.2
0.0331	66.7	0.3589	48.5	1.2226	40.2
0.0495	64.8	0.5016	45.3	1.3242	40.0
0.0820	61.4	0.6370	43.6	1.4215	40.1
0.1141	58.3	0.7657	42.1	1.5147	40.3
0.1459	55.7	0.8882	40.3	1.6897	40.6
[LiCl] = 3.2 x 10^{-4} mol kg^{-1}					
0.0416	55.9	0.5773	41.7	1.0067	38.5
0.1755	49.7	0.6928	40.1	1.0622	38.8
0.2355	47.5	0.8406	38.9	1.2067	38.7
0.3371	46.3	0.8867	38.6	1.2885	38.6
0.4295	43.4	0.9559	38.5		
[LiCl] = 5.2 x 10^{-4} mol kg^{-1}					
0.0590	55.9	0.5760	41.0	0.9024	40.1
0.1497	50.1	0.6530	40.2	0.9614	40.5
0.2313	48.4	0.7029	40.3	0.9888	39.8
0.3084	46.9	0.7483	40.1	1.0385	40.2
0.3900	44.7	0.7800	40.4	1.0839	40.1
0.4853	43.6	0.8480	39.9	1.1202	40.3
[LiCl] = 1.3 x 10^{-3} mol kg^{-1}					
0.0428	56.3	0.3467	42.4	0.6555	39.2
0.1140	50.1	0.4276	41.3	0.6794	39.3
0.1567	48.1	0.5104	40.5	0.7268	39.0
0.1995	46.8	0.5796	39.2	0.7600	39.5
0.2744	44.5	0.6080	39.4	0.8170	39.5

Table 3.1c – Continued

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
		[LiCl] = 5.2 x 10^{-3} mol kg^{-1}			
0.0331	51.1	0.2457	39.6	0.4111	38.1
0.0709	46.6	0.2882	38.6	0.4582	38.3
0.1228	43.2	0.3118	38.7	0.5055	38.6
0.1748	41.2	0.3449	38.2	0.5517	38.3
0.2221	40.3	0.3733	38.5		
		[LiCl] = 0.01 mol kg^{-1}			
0.0133	51.8	0.1328	39.5	0.2611	38.1
0.0398	46.0	0.1682	38.8	0.2744	38.7
0.0575	43.8	0.1947	37.9	0.3054	38.2
0.0885	41.3	0.2169	38.1	0.3319	38.3
0.1106	40.1	0.2434	37.9	0.3496	38.3
		[LiCl] = 0.02 mol kg^{-1}			
0.0192	47.2	0.1197	37.8	0.2107	37.5
0.0479	42.3	0.1388	37.2	0.2346	37.5
0.0814	39.7	0.1580	37.2	0.2777	37.6
0.1053	38.0	0.1724	37.2		

Table 3.2a - Surface Tension (γ) values of CPC in aqueous Sodium Chloride solution at 295 K

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
[NaCl] = 3.2 x 10^{-4} mol kg^{-1}					
0.0173	63.7	0.5375	44.8	1.0447	41.1
0.0477	59.9	0.6199	42.7	1.0837	40.9
0.1257	55.9	0.6893	43.1	1.1574	41.0
0.2167	52.4	0.7413	42.0	1.2006	41.0
0.2948	50.3	0.8410	40.6	1.2744	40.9
0.3641	48.4	0.9016	41.3	1.4217	40.9
0.4508	47.2	0.9797	40.7		
[NaCl] = 5.2 x 10^{-4} mol kg^{-1}					
0.0133	66.5	0.5040	45.8	0.8843	42.0
0.0752	58.7	0.5482	45.5	0.9550	42.4
0.1282	56.5	0.5880	44.7	1.0257	42.2
0.2564	52.0	0.6278	43.6	1.0919	42.3
0.3360	50.7	0.7161	43.2	1.1849	41.9
0.4377	46.5	0.8222	42.2	1.2954	42.2
[NaCl] = 1.3 x 10^{-3} mol kg^{-1}					
0.0132	62.7	0.4564	41.8	0.7987	40.6
0.0483	56.6	0.5793	40.2	0.8513	40.8
0.1141	50.5	0.6187	40.2	0.8952	40.6
0.1887	47.9	0.6627	39.8	0.9609	40.8
0.2501	46.3	0.6934	40.6	1.0048	40.8
0.3159	45.2	0.7372	40.4	1.0884	40.6
0.3774	43.5	0.7591	40.3	1.1806	40.8
[NaCl] = 5.2 x 10^{-3} mol kg^{-1}					
0.0123	57.0	0.2247	38.8	0.4045	38.8
0.0327	51.0	0.2492	38.4	0.4453	38.6
0.0654	46.6	0.2738	38.0	0.4862	38.7
0.0981	44.7	0.3023	38.5	0.5148	38.9

Table 3.2a – Continued

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC/ mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
		[NaCl] = 5.2 x 10^{-3} mol kg^{-1}			
0.1553	41.2	0.3350	38.3		
0.2002	39.7	0.3718	38.6		
		[NaCl] = 0.01 mol kg^{-1}			
0.0174	51.5	0.1692	39.2	0.2864	38.2
0.0434	47.6	0.1909	38.7	0.3081	38.0
0.0651	44.9	0.2126	38.2	0.3428	38.6
0.0868	43.6	0.2430	38.1		
0.1389	40.4	0.2647	38.5		
		[NaCl] = 0.02 mol kg^{-1}			
0.0130	50.5	0.1128	38.7	0.1909	37.6
0.0260	47.1	0.1258	38.4	0.1995	38.4
0.0390	44.9	0.1388	38.0	0.2299	38.2
0.0521	43.0	0.1562	37.5	0.2776	37.9
0.0781	40.8	0.1648	38.1		
0.0954	39.8	0.1735	38.1		

Table 3.2b - Surface Tension (γ) values of CPC in aqueous Sodium Chloride solution at 298 K

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
		[NaCl] = 3.2 x 10^{-4} mol kg^{-1}			
0.0083	66.7	0.5368	46.1	0.8754	41.6
0.0248	63.9	0.5988	45.1	0.9084	41.7
0.0578	57.9	0.6566	44.0	0.9497	41.3
0.0950	56.8	0.6937	43.3	0.9952	41.3
0.1363	53.4	0.7268	43.1	1.0366	41.5
0.1858	53.7	0.7556	43.0	1.0902	41.1
0.2560	52.1	0.7845	42.1	1.1275	40.9
0.2973	51.5	0.8136	42.4	1.1614	41.2
0.3882	49.1	0.8341	41.5	1.2059	41.1
0.4708	46.7	0.8549	41.5		
		[NaCl] = 5.2 x 10^{-4} mol kg^{-1}			
0.0164	68.9	0.4500	46.4	0.8100	41.7
0.0573	62.3	0.4950	45.7	0.8592	41.4
0.1146	57.7	0.5441	44.7	0.9001	41.3
0.1555	55.4	0.5728	43.8	0.9369	41.3
0.1882	54.3	0.6055	43.5	0.9656	41.2
0.2373	52.3	0.6383	43.2	1.0025	41.3
0.2987	50.8	0.6710	42.9	1.0351	41.3
0.3355	48.1	0.7241	42.3	1.0924	41.4
0.3968	47.1	0.7651	41.4		
		[NaCl] = 1.3 x 10^{-3} mol kg^{-1}			
0.0204	65.8	0.4539	42.7	0.7115	40.4
0.0654	56.7	0.5071	41.9	0.7525	40.4
0.1350	52.4	0.5439	41.8	0.8057	40.5
0.2004	49.4	0.5766	40.9	0.8424	40.7
0.2536	47.7	0.6052	40.9	0.8792	40.5
0.3149	45.7	0.6339	40.4	0.9652	40.4
0.3926	44.3	0.6667	40.3		

Table 3.2b – Continued

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
		[NaCl] = 5.2 x 10^{-3} mol kg^{-1}			
0.0228	53.5	0.2048	40.4	0.3050	39.1
0.0501	48.0	0.2322	39.6	0.3323	39.1
0.1275	43.2	0.2504	39.3	0.3505	38.9
0.1502	41.7	0.2686	38.9	0.3869	39.2
0.1775	40.9	0.2867	39.2	0.4188	39.6
		[NaCl] = 0.01 mol kg^{-1}			
0.0153	56.6	0.1649	39.9	0.2722	38.9
0.0345	49.7	0.1879	39.6	0.2952	38.2
0.0767	44.1	0.2070	38.8	0.3221	38.3
0.0997	43.1	0.2262	38.2	0.3451	38.2
0.1227	41.8	0.2377	38.9	0.3719	38.1
0.1419	41.0	0.2569	38.2		
		[NaCl] = 0.02 mol kg^{-1}			
0.0176	50.7	0.1146	37.2	0.2116	36.2
0.0397	45.1	0.1367	36.2	0.2293	36.3
0.0661	40.9	0.1587	36.1	0.2601	36.6
0.0882	38.9	0.1808	36.3		

Table 3.2c - Surface Tension (γ) values of CPC in aqueous Sodium Chloride solution at 303 K

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
[NaCl] = 3.2 x 10^{-4} mol kg^{-1}					
0.0269	62.3	0.6720	43.9	1.2006	40.3
0.0851	57.4	0.7349	43.2	1.2636	41.0
0.1523	56.4	0.8110	41.8	1.3351	41.3
0.2196	53.4	0.9007	41.1	1.3756	41.0
0.3226	50.1	0.9947	40.8	1.4518	40.9
0.4301	48.5	1.0664	40.0	1.5456	41.2
0.5511	45.9	1.1290	40.6	1.6263	40.9
[NaCl] = 5.2 x 10^{-4} mol kg^{-1}					
0.0351	59.5	0.5797	43.0	0.9663	40.3
0.1010	54.7	0.6719	41.9	1.0055	40.4
0.1669	51.8	0.7158	40.9	1.0406	40.3
0.2371	49.3	0.7509	41.2	1.1110	40.7
0.3294	47.1	0.7993	40.3	1.1814	40.7
0.3952	45.9	0.8431	40.5		
0.4918	43.4	0.9177	40.6		
[NaCl] = 1.3 x 10^{-3} mol kg^{-1}					
0.0244	57.2	0.3828	44.6	0.7575	40.4
0.0896	50.9	0.4398	43.6	0.8431	40.1
0.1344	49.1	0.5132	41.9	0.8878	40.3
0.1751	48.5	0.5621	40.8	0.9326	40.5
0.2159	47.2	0.6069	40.9	0.9938	39.9
0.2688	46.2	0.6598	40.4	1.0224	40.2
0.3217	44.9	0.7045	40.3	1.0995	40.2
[NaCl] = 5.2 x 10^{-3} mol kg^{-1}					
0.0170	56.3	0.1787	42.7	0.3277	39.0
0.0511	49.2	0.2171	41.0	0.3490	39.7
0.0723	48.1	0.2426	40.3	0.4000	39.5

Table 3.2c – Continued

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
[NaCl] = 5.2 x 10^{-3} mol kg^{-1}					
0.0936	47.0	0.2639	40.0	0.4298	39.6
0.1319	45.4	0.2766	39.8	0.4682	39.5
0.1490	43.8	0.3021	39.6	0.4937	39.6
[NaCl] = 0.01 mol kg^{-1}					
0.0209	53.6	0.1793	39.0	0.3044	38.3
0.0417	50.1	0.2002	38.6	0.3336	38.5
0.0792	44.9	0.2252	38.0	0.3545	38.5
0.1043	43.7	0.2419	38.4	0.3795	38.4
0.1418	41.3	0.2586	38.5	0.4379	38.5
0.1543	40.7	0.2794	38.3		
[NaCl] = 0.02 mol kg^{-1}					
0.0118	50.7	0.1141	39.0	0.2084	37.6
0.0315	46.0	0.1219	37.8	0.2360	37.7
0.0472	44.5	0.1376	37.7	0.2713	37.3
0.0669	43.1	0.1494	37.4	0.3303	37.7
0.0787	41.2	0.1691	37.3		
0.1023	40.2	0.1888	37.5		

Table 3.3a - Surface Tension (γ) values of CPC in aqueous Potassium Chloride solution at 295 K

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
[KCl] = 3.2 x 10^{-4} mol kg^{-1}					
0.0087	60.0	0.4694	43.4	1.0950	41.0
0.0435	54.7	0.6345	41.8	1.2167	40.9
0.0956	52.4	0.7432	41.2	1.2862	41.3
0.1608	49.1	0.8474	40.9	1.3471	40.5
0.2173	47.5	0.9343	40.9		
0.3303	45.2	0.9822	40.4		
[KCl] = 5.2 x 10^{-4} mol kg^{-1}					
0.0488	60.2	0.4883	45.5	0.8835	41.1
0.0932	57.0	0.5327	44.2	0.9723	41.2
0.2131	50.5	0.5948	43.5	1.0654	41.5
0.2930	49.9	0.6615	42.5	1.1543	41.3
0.3818	47.6	0.7991	41.4	1.2520	41.5
[KCl] = 1.3 x 10^{-3} mol kg^{-1}					
0.0139	62.8	0.3064	46.1	0.6964	41.0
0.0929	54.2	0.3621	44.6	0.7381	41.2
0.1161	52.6	0.4457	42.5	0.8125	41.1
0.1811	49.9	0.5617	41.2	0.8728	41.2
[KCl] = 5.2 x 10^{-3} mol kg^{-1}					
0.0211	51.7	0.2410	38.9	0.4016	38.8
0.0507	48.0	0.2663	38.6	0.4608	38.9
0.1015	44.0	0.2959	38.6	0.5116	39.3
0.1268	42.8	0.3170	38.8	0.5454	39.1
0.1818	40.8	0.3636	38.8	0.5918	39.2
[KCl] = 0.01 mol kg^{-1}					
0.0325	50.6	0.1716	38.8	0.2968	38.8
0.0696	45.4	0.2134	38.8	0.3340	39.2

Table 3.3a – Continued

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
		[KCl] = 0.01 mol kg^{-1}			
0.0928	42.5	0.2226	38.7	0.3664	39.1
0.1391	40.4	0.2690	38.9		
		[KCl] = 0.02 mol kg^{-1}			
0.0088	50.9	0.0836	39.5	0.1497	38.6
0.0352	43.1	0.0969	39.4	0.1629	38.9
0.0484	41.7	0.1145	38.4	0.1761	38.8
0.0660	41.1	0.1233	38.9	0.1893	38.8
0.0704	40.4	0.1365	38.8	0.2025	38.9

Table 3.3b - Surface Tension (γ) values of CPC in aqueous Potassium Chloride solution at 298 K

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
[KCl] = 3.2 x 10^{-4} mol kg^{-1}					
0.0546	59.0	0.6957	42.3	0.9775	41.3
0.1455	54.4	0.7411	41.5	1.0595	41.4
0.2274	51.9	0.7775	41.2	1.1094	41.5
0.3228	49.2	0.7956	41.4	1.1822	41.3
0.4638	46.3	0.8730	41.3		
0.6046	43.7	0.9139	41.0		
[KCl] = 5.2 x 10^{-4} mol kg^{-1}					
0.0401	54.9	0.3925	44.5	0.7135	40.6
0.1338	49.0	0.4504	43.8	0.7714	40.6
0.1739	48.0	0.5040	43.0	0.8383	40.7
0.2542	46.7	0.5708	42.1	0.8829	40.9
0.3032	45.3	0.6467	41.5	0.9365	40.7
0.3389	45.2	0.6868	40.5	1.0123	41.0
[KCl] = 1.3 x 10^{-3} mol kg^{-1}					
0.0200	59.1	0.2780	45.2	0.5700	40.0
0.0300	55.8	0.3200	44.5	0.6100	39.7
0.0700	53.4	0.3620	42.4	0.6990	39.4
0.0970	51.5	0.4000	42.1	0.7581	39.7
0.1310	50.3	0.4400	42.1	0.8100	38.9
0.1730	48.8	0.4800	40.6	0.8600	39.5
0.2200	47.2	0.5300	40.2	0.9099	39.3
[KCl] = 5.2 x 10^{-3} mol kg^{-1}					
0.0100	56.1	0.2100	40.6	0.4500	38.2
0.0300	52.4	0.2400	38.9	0.4890	38.0
0.0800	46.0	0.2670	38.8	0.5400	38.5
0.1200	43.8	0.3700	38.7	0.5700	38.7
0.1700	41.3	0.4100	38.2		

Table 3.3b – Continued

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
		[KCl] = 0.01 mol kg^{-1}			
0.0089	56.4	0.1821	37.3	0.3419	37.2
0.0266	47.6	0.2131	37.2	0.3774	38.2
0.0533	43.4	0.2353	37.0	0.4218	37.5
0.1110	39.2	0.2797	37.2		
0.1554	37.6	0.3108	37.2		
		[KCl] = 0.02 mol kg^{-1}			
0.0133	52.6	0.0667	41.1	0.1378	38.8
0.0222	50.0	0.0845	39.6	0.1511	38.4
0.0356	45.9	0.0978	38.6	0.1600	38.6
0.0489	43.4	0.1111	38.3	0.1733	38.6
0.0578	42.0	0.1200	38.7	0.1911	38.4

Table 3.3c - Surface Tension (γ) values of CPC in aqueous Potassium Chloride solution at 303 K

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
[KCl] = 3.2 x 10^{-4} mol kg^{-1}					
0.0793	57.2	0.6676	41.5	0.9305	39.2
0.1676	51.6	0.7551	40.4	0.9929	39.5
0.3129	48.2	0.8095	39.7	1.0723	39.5
0.4923	44.3	0.8553	39.7	1.1223	39.8
0.5966	43.2	0.8929	39.6	1.1809	39.7
[KCl] = 5.2 x 10^{-4} mol kg^{-1}					
0.0394	61.2	0.5604	43.1	1.0200	40.2
0.1182	55.0	0.6260	42.0	1.0990	40.1
0.2321	50.9	0.6830	41.4	1.1866	40.5
0.3240	47.9	0.7705	40.3	1.2741	40.2
0.4115	46.0	0.8626	40.0		
0.4816	44.5	0.9369	40.0		
[KCl] = 1.3 x 10^{-3} mol kg^{-1}					
0.0134	61.6	0.4957	41.1	0.8843	39.8
0.1072	52.9	0.5851	39.6	0.9245	39.8
0.1786	48.7	0.6207	39.4	0.9647	39.9
0.2680	46.1	0.6564	39.7	1.0179	39.6
0.3260	44.3	0.7234	39.4	1.0762	40.1
0.4198	42.0	0.8084	39.4		
[KCl] = 5.2 x 10^{-3} mol kg^{-1}					
0.0363	48.5	0.2315	38.6	0.3767	37.9
0.0998	43.5	0.2860	37.7	0.3994	37.7
0.1679	40.1	0.3132	37.4	0.4267	38.1
0.1997	39.4	0.3586	37.7	0.4765	37.8

Table 3.3c – Continued

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
		[KCl] = 0.01 mol kg^{-1}			
0.0350	47.2	0.1707	37.1	0.3546	37.4
0.0657	43.2	0.2320	37.1	0.3852	37.8
0.0876	41.3	0.2758	37.3	0.4246	37.9
0.1357	38.5	0.3195	37.3		
		[KCl] = 0.02 mol kg^{-1}			
0.0125	50.1	0.0961	38.2	0.2255	37.2
0.0251	45.7	0.1211	37.3	0.2548	37.5
0.0459	42.3	0.1337	37.1	0.2840	37.9
0.0668	40.1	0.1629	37.1	0.3091	37.7
0.0835	39.5	0.1921	37.1		

Table 3.4 - Critical Micelle Concentrations of CPC in Aqueous Electrolyte Solutions at Different Temperatures Determined from Surface Tension and Conductance (in parentheses) Data

		Concentration of Electrolyte / mol kg^{-1}						
Electrolyte	T/K	0	3.2x10^{-4}	5.2x10^{-4}	1.3x10^{-3}	5.2x10^{-3}	0.01	0.02
		cmc x 10^{4}/mol kg^{-1}						
LiCl	295	9.55	8.10	7.50	5.40	3.09	1.88	1.33
			(8.50)	(8.00)	(6.10)	(2.90)	(1.92)	(1.30)
	298	8.91	8.32	7.08	5.75	2.66	1.74	1.29
			(8.40)	(7.20)	(5.90)	(2.80)	(2.00)	(1.30)
	303	9.44	8.91	7.24	5.96	3.31	2.00	1.40
			(9.00)	(7.90)	(6.40)	(3.50)	(2.20)	(1.45)
NaCl	295		8.70	8.13	5.96	2.66	2.00	1.26
			(8.90)	(8.20)	(5.90)	(3.00)	(2.20)	(1.28)
	298		8.41	7.50	6.13	2.63	1.88	1.34
			(8.40)	(7.30)	(5.90)	(2.80)	(1.90)	(1.50)
	303		9.17	8.03	6.17	3.10	2.11	1.50
			(8.90)	(8.10)	(6.10)	(2.92)	(2.10)	(1.38)
KCl	295		7.94	7.50	5.60	2.51	1.74	1.12
			(8.20)	(7.50)	(5.90)	(2.40)	(1.76)	(1.11)
	298		7.59	7.08	5.50	2.66	1.68	1.06
			(7.90)	(7.00)	(5.70)	(2.85)	(1.80)	(1.10)
	303		8.41	7.94	6.17	2.90	1.78	1.12
			(8.60)	(8.20)	(6.50)	(3.00)	(2.10)	(1.25)

Table 3.5a – Specific Conductance (κ) values of CPC in aqueous Lithium Chloride solution at 295 K

[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}
[LiCl] = 3.2 x 10^{-4} mol kg^{-1}					
0	47.507	0.7100	113.19	1.0300	132.04
0.1480	61.184	0.8030	120.70	1.1200	135.78
0.3380	78.468	0.8450	123.65	1.2200	139.50
0.4720	90.884	0.9020	126.64	1.2700	141.64
0.6270	105.11	0.9370	128.33		
[LiCl] = 5.2 x 10^{-4} mol kg^{-1}					
0	75.036	0.4900	116.30	0.9124	146.85
0.1268	86.190	0.6083	126.87	1.0475	152.00
0.2366	94.765	0.6674	131.79	1.1403	155.63
0.3042	100.99	0.7519	138.66	1.2501	159.66
0.3971	108.61	0.8026	141.91	1.3345	162.90
[LiCl] = 1.3 x 10^{-3} mol kg^{-1}					
0	149.27	0.3840	181.40	0.6720	203.12
0.0790	155.33	0.4580	187.79	0.7290	205.59
0.1180	158.67	0.5260	193.67	0.7970	207.87
0.2030	165.71	0.5590	196.18	0.8420	209.59
0.2770	171.90	0.5930	198.94	0.9380	212.84
0.3300	175.97	0.6330	201.17		
[LiCl] = 5.2 x 10^{-3} mol kg^{-1}					
0	556.94	0.1950	575.89	0.3550	586.91
0.0230	559.65	0.2350	579.65	0.3890	587.79
0.0630	563.63	0.2630	582.32	0.4290	588.97
0.1030	567.33	0.2970	584.83	0.4750	590.43
0.1370	571.00	0.3190	585.59	0.5270	591.79

Table 3.5a – Continued

[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}
		[LiCl] = 0.01 mol kg^{-1}			
0	830.75	0.0954	839.18	0.2438	848.74
0.0159	831.58	0.1272	842.09	0.2650	849.58
0.0371	832.52	0.1802	846.46	0.3127	851.24
0.0477	834.39	0.1961	847.39	0.3497	852.49
0.0742	837.20	0.2173	848.33	0.3921	853.22
		[LiCl] = 0.02 mol kg^{-1}			
0	2026.5	0.0838	2035.0	0.1624	2039.9
0.0157	2027.7	0.0995	2036.1	0.1886	2041.0
0.0262	2030.1	0.1205	2037.4	0.2148	2041.8
0.0419	2030.7	0.1362	2038.9	0.2410	2042.5
0.0576	2033.2	0.1519	2039.3	0.2514	2042.9

Table 3.5b – Specific Conductance (κ) values of CPC in aqueous Lithium Chloride solution at 298 K

[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}
[LiCl] = 3.2 x 10^{-4} mol kg^{-1}					
0	54.518	0.4680	96.821	0.8588	132.51
0.0496	62.016	0.5175	101.42	0.9083	135.25
0.1046	64.139	0.5671	106.03	0.9413	137.09
0.1762	70.257	0.6276	111.84	1.0019	139.77
0.2918	80.726	0.6717	116.40	1.0789	143.08
0.3469	85.568	0.7267	121.77		
0.3909	89.605	0.7762	126.36		
[LiCl] = 5.2 x 10^{-4} mol kg^{-1}					
0	78.770	0.3132	112.37	0.7074	150.83
0.0216	82.054	0.3780	118.96	0.7722	155.08
0.0702	87.827	0.4644	125.47	0.8261	157.94
0.1242	93.369	0.5400	133.88	0.8747	160.42
0.1836	99.278	0.5940	139.49	0.9395	163.27
0.2646	107.28	0.6318	143.07	0.9989	165.95
[LiCl] = 1.3 x 10^{-3} mol kg^{-1}					
0	159.46	0.2981	188.51	0.6956	220.05
0.0276	161.33	0.3533	193.80	0.7508	222.02
0.0497	163.71	0.4417	201.71	0.8004	225.21
0.0939	168.08	0.4858	206.16	0.8391	226.05
0.1546	174.19	0.5576	212.69	0.9053	228.67
0.2319	181.75	0.6017	215.61		
[LiCl] = 5.2 x 10^{-3} mol kg^{-1}					
0	585.75	0.2068	605.21	0.4304	616.61
0.0224	586.28	0.2460	608.76	0.5031	618.59
0.0503	589.42	0.3019	612.11	0.5478	620.06
0.1118	595.38	0.3410	613.36	0.6148	624.03
0.1565	599.35	0.3801	614.72		

Table 3.5b – Continued

[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}
		[LiCl] = 0.01 mol kg^{-1}			
0	1007.0	0.1210	1017.6	0.3081	1026.6
0.0055	1008.0	0.1431	1020.3	0.3356	1027.6
0.0275	1010.0	0.1706	1021.7	0.3631	1028.2
0.0660	1012.9	0.2091	1024.1	0.3741	1028.6
0.0770	1014.0	0.2366	1025.0	0.4016	1029.1
0.0990	1015.1	0.2751	1025.9	0.4401	1029.9
		[LiCl] = 0.02 mol kg^{-1}			
0	2136.1	0.0852	2146.8	0.1598	2153.1
0.0107	2137.1	0.1066	2149.5	0.1758	2154.0
0.0320	2140.3	0.1119	2151.0	0.1971	2155.2
0.0533	2143.2	0.1332	2152.0	0.2237	2156.4
0.0639	2145.4	0.1492	2152.6	0.2557	2157.3

Table 3.5c – Specific Conductance (κ) values of CPC in aqueous Lithium Chloride solution at 303 K

[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}
		[LiCl] = 3.2 x 10^{-4} mol kg^{-1}			
0	54.593	0.6789	123.12	1.0935	156.81
0.1509	69.493	0.7693	132.63	1.1840	159.88
0.2640	80.571	0.8598	141.49	1.2820	164.58
0.3998	94.368	0.9201	146.84	1.3725	168.89
0.6110	116.04	1.0031	151.61		
		[LiCl] = 5.2 x 10^{-4} mol kg^{-1}			
0	92.458	0.6143	159.37	1.0401	188.32
0.0655	99.543	0.7208	169.19	1.0974	190.92
0.1557	109.49	0.7699	173.19	1.1793	194.51
0.3031	126.28	0.8027	175.75	1.2612	198.22
0.4342	139.24	0.8436	178.32		
0.5324	149.23	0.9009	181.33		
		[LiCl] = 1.3 x 10^{-3} mol kg^{-1}			
0	172.50	0.4088	213.63	0.7543	243.18
0.0461	176.91	0.4549	219.08	0.8061	245.52
0.1152	183.68	0.5182	226.03	0.8636	247.88
0.1670	189.06	0.5873	232.74	0.9384	251.29
0.2707	199.09	0.6449	237.05	0.9845	252.98
0.3513	207.65	0.6737	238.94		
		[LiCl] = 5.2 x 10^{-3} mol kg^{-1}			
0	629.93	0.1978	651.06	0.4284	669.72
0.0330	633.98	0.2582	657.13	0.4834	672.01
0.0714	637.97	0.3076	661.71	0.5273	674.03
0.1099	641.94	0.3515	665.35	0.5822	675.75
0.1483	645.75	0.3955	668.16		

Table 3.5c – Continued

[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}
[LiCl] = 0.01 mol kg^{-1}					
0	1088.4	0.1102	1103.1	0.2466	1115.2
0.0105	1092.9	0.1417	1106.5	0.2939	1117.1
0.0420	1094.5	0.1837	1109.9	0.3463	1118.3
0.0577	1096.9	0.2047	1111.7	0.3778	1119.2
0.0735	1098.5	0.2257	1113.2	0.4145	1121.1
[LiCl] = 0.02 mol kg^{-1}					
0	2293.6	0.1076	2304.6	0.1946	2312.0
0.0154	2295.9	0.1281	2306.4	0.2049	2312.9
0.0512	2298.1	0.1434	2307.6	0.2407	2315.2
0.0717	2301.0	0.1537	2308.6	0.2817	2318.5
0.0973	2304.3	0.1742	2310.2	0.3073	2319.9

Table 3.6a – Specific Conductance (κ) values of CPC in aqueous Sodium Chloride solution at 295 K

[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}
[NaCl] = 3.2 x 10^{-4} mol kg^{-1}					
0	37.957	0.6436	94.813	0.9887	118.86
0.1346	49.529	0.7255	102.24	1.0705	121.96
0.2458	59.325	0.7723	105.55	1.1465	124.74
0.3803	71.875	0.8074	108.72	1.2167	127.38
0.5266	84.626	0.8600	112.52	1.3161	131.21
0.6026	91.623	0.9185	115.62	1.4389	135.43
[NaCl] = 5.2 x 10^{-4} mol kg^{-1}					
0	64.652	0.5953	114.50	0.9803	140.78
0.1261	74.210	0.7003	123.23	1.0853	144.88
0.2381	83.867	0.7493	127.49	1.1273	146.60
0.3642	94.679	0.8123	132.83	1.2043	149.42
0.4832	104.59	0.8823	136.55	1.2673	151.53
[NaCl] = 1.3 x 10^{-3} mol kg^{-1}					
0	157.05	0.4211	193.94	0.7982	216.77
0.0492	161.57	0.4812	199.13	0.8748	219.46
0.0984	166.11	0.5413	204.06	0.9404	221.75
0.1531	171.10	0.5905	208.02	1.0278	224.72
0.2680	181.21	0.6507	210.83		
0.3609	189.69	0.7053	213.22		
[NaCl] = 5.2 x 10^{-3} mol kg^{-1}					
0	577.35	0.1831	593.65	0.3662	605.83
0.0431	580.32	0.2262	597.15	0.3985	606.67
0.0754	583.30	0.2423	598.46	0.4631	608.55
0.0969	585.34	0.2585	600.08	0.5223	610.19
0.1293	588.47	0.3016	602.85		
0.1616	591.25	0.3339	604.16		

Table 3.6a – Continued

[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}
		[NaCl] = 0.01 mol kg^{-1}			
0	1132.1	0.1408	1144.1	0.2867	1151.3
0.0209	1134.3	0.1668	1146.1	0.3180	1152.1
0.0573	1136.3	0.1981	1148.3	0.3701	1154.3
0.0990	1139.2	0.2294	1149.5	0.4066	1155.2
0.1251	1142.4	0.2554	1151.1		
		[NaCl] = 0.02 mol kg^{-1}			
0	2226.8	0.0865	2238.7	0.1831	2243.2
0.0102	2230.2	0.1068	2240.8	0.2086	2243.8
0.0356	2232.7	0.1374	2241.3	0.2340	2244.7
0.0661	2236.6	0.1628	2242.9	0.2595	2245.2

Table 3.6b – Specific Conductance (κ) values of CPC in aqueous Sodium Chloride solution at 298 K

[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}
[NaCl] = 3.2 x 10^{-4} mol kg^{-1}					
0	44.814	0.6018	103.68	1.1753	141.21
0.0281	47.025	0.7312	116.28	1.2652	144.71
0.0731	51.984	0.8773	127.50	1.3776	149.29
0.1969	63.690	0.9448	131.06	1.4844	153.50
0.2925	73.175	1.0179	134.20		
0.4444	88.036	1.0741	136.64		
[NaCl] = 5.2 x 10^{-4} mol kg^{-1}					
0	73.593	0.3264	106.08	0.6829	140.76
0.0786	81.028	0.3929	112.82	0.7796	147.92
0.1028	83.915	0.4533	118.85	0.8702	152.66
0.1934	92.846	0.5198	125.21	0.9548	156.33
0.2659	100.13	0.5741	130.22	1.0454	160.14
[NaCl] = 1.3 x 10^{-3} mol kg^{-1}					
0	168.11	0.3288	201.19	0.6297	227.52
0.0279	170.45	0.4012	208.35	0.6854	230.16
0.0669	173.93	0.4458	212.57	0.7578	233.26
0.0892	176.59	0.5015	218.00	0.8024	234.59
0.1226	181.09	0.5294	220.94	0.8414	236.34
0.1393	183.28	0.5517	223.25	0.8859	237.40
0.2341	191.80	0.5907	225.61	0.9305	239.61
0.2898	196.83	0.6130	227.02		
[NaCl] = 5.2 x 10^{-3} mol kg^{-1}					
0	623.61	0.1918	642.75	0.3776	654.05
0.0420	627.06	0.2397	647.25	0.4375	655.93
0.0779	630.62	0.2577	648.82	0.4735	656.97
0.1019	633.13	0.2757	650.60	0.5274	658.54
0.1618	639.61	0.3057	651.54	0.5514	659.38

Table 3.6b – Continued

[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}
		[NaCl] = 0.01 mol kg^{-1}			
0	1203.4	0.1079	1217.6	0.2427	1226.7
0.0108	1206.7	0.1564	1222.5	0.2589	1227.3
0.0431	1208.3	0.1780	1224.2	0.2696	1227.6
0.0701	1213.6	0.2049	1225.2	0.2858	1228.1
0.0917	1215.0	0.2265	1226.1		
		[NaCl] = 0.02 mol kg^{-1}			
0	2359.7	0.1269	2371.0	0.2689	2378.5
0.0203	2363.9	0.1421	2373.8	0.2994	2379.3
0.0304	2364.1	0.1725	2375.1	0.3146	2380.3
0.0558	2365.4	0.1979	2375.7	0.3501	2380.9
0.0710	2366.9	0.2080	2376.2	0.4313	2383.3
0.0964	2369.3	0.2283	2377.1		
0.1167	2370.7	0.2436	2378.4		

Table 3.6c – Specific Conductance (κ) values of CPC in aqueous Sodium Chloride solution at 303 K

[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}	[CPC/ mmol kg^{-1}	κ x 10^{4}/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}
[NaCl] = 3.2 x 10^{-4} mol kg^{-1}					
0	44.292	0.6825	117.28	1.0444	146.09
0.1425	58.591	0.7300	122.42	1.1215	149.89
0.2790	74.318	0.8071	130.38	1.2816	157.60
0.3799	85.081	0.8427	133.33	1.3646	161.35
0.4807	95.761	0.8723	135.85	1.4180	164.02
0.5816	106.35	0.9376	140.28		
[NaCl] = 5.2 x 10^{-4} mol kg^{-1}					
0	75.353	0.6134	141.99	1.0514	174.49
0.1461	91.016	0.6791	149.28	1.1682	179.82
0.2629	103.31	0.7667	157.49	1.2849	184.90
0.3579	113.44	0.8470	163.14	1.3433	187.94
0.4455	123.30	0.8981	166.13		
0.5404	133.61	0.9857	170.59		
[NaCl] = 1.3 x 10^{-3} mol kg^{-1}					
0	183.05	0.3570	222.94	0.7463	253.61
0.0541	188.85	0.4056	227.82	0.7895	256.08
0.0811	192.16	0.4759	234.08	0.8544	258.14
0.1244	198.09	0.5300	240.06	0.9625	263.05
0.1893	204.54	0.5895	244.79	1.0274	264.37
0.2704	213.23	0.6598	249.09	1.1300	269.78
[NaCl] = 5.2 x 10^{-3} mol kg^{-1}					
0	682.00	0.2065	707.20	0.4298	719.90
0.0391	686.40	0.2456	710.10	0.4632	722.30
0.0726	687.60	0.2735	713.20	0.4911	723.00
0.1116	695.40	0.3516	716.00	0.5525	725.10
0.1507	698.50	0.3907	718.90	0.6027	726.90

Table 3.6c – Continued

[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}
		[NaCl] = 0.01 mol kg^{-1}			
0	1324.8	0.1547	1344.3	0.3300	1355.2
0.0258	1332.5	0.1856	1349.3	0.3867	1357.2
0.0412	1332.9	0.2114	1350.8	0.4382	1358.7
0.0670	1334.9	0.2629	1352.9		
0.1083	1338.7	0.2887	1353.8		
		[NaCl] = 0.02 mol kg^{-1}			
0	2590.2	0.0846	2599.7	0.1481	2605.6
0.0159	2592.2	0.0952	2601.0	0.1640	2606.3
0.0264	2593.6	0.1058	2602.2	0.1798	2607.4
0.0370	2595.4	0.1217	2604.5	0.2063	2608.7
0.0688	2597.7	0.1322	2605.1	0.2221	2609.3

Table 3.7a – Specific Conductance (κ) values of CPC in aqueous Potassium Chloride solution at 295 K

[CPC] / mmol kg^{-1}	$\kappa \times 10^4$/ S m^{-1}	[CPC] / mmol kg^{-1}	$\kappa \times 10^4$/ S m^{-1}	[CPC] / mmol kg^{-1}	$\kappa \times 10^4$/ S m^{-1}
[KCl] = 3.2×10^{-4} mol kg^{-1}					
0	48.265	0.4891	92.111	0.8814	125.56
0.0544	53.398	0.5615	99.027	0.9599	128.83
0.0966	58.243	0.6823	109.46	0.9961	130.43
0.1691	64.871	0.7245	114.05	1.0323	132.15
0.2597	72.453	0.7728	117.76	1.0685	133.18
0.3200	77.898	0.8211	121.71	1.1168	135.01
0.4046	84.828	0.8452	123.57	1.1952	138.02
[KCl] = 5.2×10^{-4} mol kg^{-1}					
0	77.897	0.6114	132.87	1.1179	160.24
0.0724	85.857	0.6918	139.35	1.2144	164.64
0.2253	99.202	0.8526	150.19	1.2787	166.78
0.3701	112.98	0.9571	154.47	1.4315	172.66
0.5068	123.86	1.0697	158.34		
[KCl] = 1.3×10^{-3} mol kg^{-1}					
0	183.31	0.5228	229.68	0.9237	247.56
0.0645	190.56	0.5800	233.94	1.0024	250.92
0.1934	201.61	0.6803	238.44	1.1169	253.84
0.2865	210.71	0.7662	241.54	1.2529	259.20
0.3724	216.93	0.8378	246.03		
[KCl] = 5.2×10^{-3} mol kg^{-1}					
0	691.83	0.2585	716.95	0.6118	727.67
0.0431	698.81	0.3189	720.98	0.6893	730.46
0.1293	706.18	0.4136	722.34		
0.1896	714.60	0.4998	725.79		

Table 3.7a – Continued

[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}
		[KCl] = 0.01 mol kg^{-1}			
0	1464.7	0.1500	1476.1	0.2690	1481.4
0.0259	1465.4	0.1655	1477.2	0.2949	1481.9
0.0621	1468.4	0.1862	1478.5	0.3311	1483.1
0.0828	1470.2	0.2069	1479.2		
0.1242	1473.7	0.2328	1480.0		
		[KCl] = 0.02 mol kg^{-1}			
0	2635.0	0.0872	2642.2	0.1635	2646.0
0.0327	2637.7	0.1035	2643.5	0.1853	2647.0
0.0545	2639.4	0.1144	2644.2	0.2180	2648.0
0.0599	2639.5	0.1362	2644.8		
0.0763	2641.3	0.1471	2645.4		

Table 3.7b – Specific Conductance (κ) values of CPC in aqueous Potassium Chloride solution at 298 K

[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}
[KCl] = 3.2 x 10^{-4} mol kg^{-1}					
0	53.399	0.4065	95.043	0.9798	141.34
0.0446	58.115	0.4788	102.25	1.0299	143.44
0.0557	59.705	0.5512	108.91	1.0911	147.44
0.0724	61.901	0.6292	116.18	1.1968	151.84
0.1336	67.475	0.6959	122.82	1.2803	155.22
0.2283	77.369	0.8240	133.13		
0.3230	86.572	0.9074	137.98		
[KCl] = 5.2 x 10^{-4} mol kg^{-1}					
0	82.190	0.4084	125.49	0.9004	163.64
0.0615	87.848	0.4922	133.47	0.9564	166.31
0.1119	94.237	0.5761	141.37	1.0179	168.91
0.1790	101.53	0.6600	149.37	1.1744	175.11
0.2517	110.07	0.7551	156.37		
0.3300	117.84	0.8278	160.36		
[KCl] = 1.3 x 10^{-3} mol kg^{-1}					
0	207.19	0.3186	237.54	0.7041	266.98
0.0168	208.65	0.3521	240.56	0.7599	269.21
0.0782	215.30	0.3912	244.59	0.8158	271.52
0.1341	220.72	0.4415	248.83	0.8884	274.41
0.1900	225.88	0.5029	254.22	0.9610	276.71
0.2291	229.83	0.5532	258.97		
0.2738	234.31	0.6370	264.43		
[KCl] = 5.2 x 10^{-3} mol kg^{-1}					
0	755.59	0.2017	772.85	0.4034	785.82
0.0392	757.79	0.2409	776.82	0.4594	787.07
0.0785	760.93	0.2634	779.23	0.4987	788.54
0.1009	763.33	0.2970	781.42	0.5323	789.79

Table 3.7b – Continued

[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}
		[KCl] = 5.2 x 10^{-3} mol kg^{-1}			
0.1345	766.37	0.3250	782.99		
0.1737	769.61	0.3642	784.04		
		[KCl] = 0.01 mol kg^{-1}			
0	1442.9	0.1563	1462.0	0.3125	1469.9
0.0485	1451.2	0.1724	1463.9	0.3610	1471.4
0.0700	1454.0	0.2155	1466.4	0.3933	1472.5
0.0916	1454.8	0.2532	1467.8	0.4256	1474.1
0.1132	1457.7	0.2802	1468.8		
		[KCl] = 0.02 mol kg^{-1}			
0	2797.4	0.0737	2808.7	0.1579	2815.1
0.0105	2801.2	0.0947	2811.4	0.1737	2815.6
0.0421	2805.1	0.1158	2813.2	0.1947	2816.4
0.0526	2807.5	0.1316	2814.2	0.2263	2817.3
0.0632	2808.1	0.1421	2814.6	0.2421	2817.8

Table 3.7c – Specific Conductance (κ) values of CPC in aqueous Potassium Chloride solution at 303 K

[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}
		[KCl] = 3.2 x 10^{-4} mol kg^{-1}			
0	55.446	0.5542	111.84	1.0790	155.37
0.0365	59.632	0.6489	120.89	1.1591	159.65
0.1240	68.232	0.7656	132.55	1.2247	163.07
0.1823	74.081	0.8239	138.19	1.2684	165.25
0.2771	83.811	0.8968	144.84	1.3121	167.32
0.3792	94.619	0.9624	148.86	1.3704	170.19
0.4667	103.07	1.0207	152.43		
		[KCl] = 5.2 x 10^{-4} mol kg^{-1}			
0	90.261	0.6114	154.58	1.1179	188.53
0.0724	99.602	0.6918	161.75	1.2144	194.16
0.2253	114.50	0.8526	176.20	1.2787	196.28
0.3701	131.50	0.9571	180.94	1.4315	204.29
0.5068	144.13	1.0697	186.79		
		[KCl] = 1.3 x 10^{-3} mol kg^{-1}			
0	212.67	0.5228	266.19	0.9237	289.46
0.0645	221.20	0.5800	271.05	1.0024	293.94
0.1934	233.37	0.6803	279.13	1.1169	296.95
0.2865	243.71	0.7662	281.88	1.2529	303.52
0.3724	250.60	0.8378	286.56		
		[KCl] = 5.2 x 10^{-3} mol kg^{-1}			
0	800.09	0.2585	829.06	0.6118	845.79
0.0431	806.28	0.3189	834.40	0.6893	849.14
0.1293	814.21	0.4136	837.86		
0.1896	825.30	0.4998	842.66		

Table 3.7c – Continued

[CPC] / mmol kg^{-1}	$\kappa \times 10^4$/ S m^{-1}	[CPC] / mmol kg^{-1}	$\kappa \times 10^4$/ S m^{-1}	[CPC] / mmol kg^{-1}	$\kappa \times 10^4$/ S m^{-1}
		[KCl] = 0.01 mol kg^{-1}			
0	1589.8	0.1292	1604.8	0.2636	1616.2
0.0310	1594.1	0.1551	1608.7	0.2946	1617.5
0.0569	1595.9	0.1758	1610.2	0.3308	1618.5
0.0827	1599.0	0.1913	1612.6	0.3515	1619.6
0.1034	1602.4	0.2326	1615.2	0.3773	1619.9
		[KCl] = 0.02 mol kg^{-1}			
0	3090.7	0.1152	3105.4	0.1937	3109.2
0.0576	3096.9	0.1309	3106.7	0.2199	3111.0
0.0785	3099.6	0.1518	3107.3	0.2461	3111.9
0.0995	3103.0	0.1780	3108.4	0.2879	3113.6

Table 3.8 - Values of Counter Ion Binding Constant for CPC Micelles in Aqueous Electrolyte Solutions at Different Temperatures Derived from CH Plots (β_{CH}) and the Slope – Ratio Method (β_{κ}).

Electrolyte	T/K	β_{CH} a)	Concentration of Electrolyte / mol kg^{-1}					
			$3.2\text{x}10^{-4}$	$5.2\text{x}10^{-4}$	$1.3\text{x}10^{-3}$	$5.2\text{x}10^{-3}$	0.01	0.02
			β_{κ}					
LiCl	295	0.66 (0.63)	0.55	0.55	0.56	0.68	0.66	0.63
	298	0.65 (0.65)	0.48	0.52	0.56	0.63	0.68	0.63
	303	0.64 (0.63)	0.53	0.54	0.56	0.55	0.67	0.27
NaCl	295	0.67 (0.69)	0.57	0.54	0.57	0.63	0.62	0.76
	298	0.64 (0.66)	0.57	0.55	0.60	0.68	0.74	0.61
	303	0.66 (0.64)	0.54	0.54	0.58	0.64	0.71	0.58
KCl	295	0.71 (0.69)	0.52	0.56	0.59	0.74	0.60	0.53
	298	0.67 (0.68)	0.51	0.56	0.58	0.65	0.65	0.74
	303	0.68 (0.72)	0.47	0.53	0.57	0.65	0.72	0.64

a) Values of β were determined from Eq. (3.1) by substituting cmc values obtained from κ and γ (those in the parentheses) data separately.

Table 3.9 - Values of ΔG_m^0 of CPC in Aqueous Electrolyte Solutions at Different Temperatures Determined from Equations (3.1) and (3.2)

Electrolyte	T/K	$-\Delta G_m^0$/ kJ mol^{-1} from Eq. (3.1)	Concentration of Electrolyte / mol kg^{-1}						
			0	3.2×10^{-4}	5.2×10^{-4}	1.3×10^{-3}	5.2×10^{-3}	0.01	0.02
			$-\Delta G_m^0$/ kJ mol^{-1} from Eq. (3.2)						
LiCl	295	44.0	42.3	42.2	42.4	43.7	50.1	51.2	51.8
	298	45.4	42.9	40.7	42.4	44.3	49.3	52.2	52.4
	303	45.1	43.4	42.5	43.3	44.7	46.7	52.3	50.8
NaCl	295	45.3		42.5	42.0	44.1	48.5	49.4	56.0
	298	45.1		43.2	43.2	45.4	50.8	54.3	51.1
	303	45.3		43.1	43.2	45.4	50.2	53.8	51.4
KCl	295	45.6		41.5	42.9	44.7	52.7	49.7	49.2
	298	45.9		41.7	43.6	45.0	49.8	51.7	56.6
	303	47.4		41.0	42.9	44.9	50.4	54.1	53.7

Table 3.10 - Surface Density of CPC at the Air – Water Interface in the Presence and Absence of Electrolytes at Different Temperatures

		Concentration of Electrolyte / mol kg^{-1}						
Electrolyte	T/K	0	3.2x10^{-4}	5.2x10^{-4}	1.3x10^{-3}	5.2x10^{-3}	0.01	0.02
		Γ_{cmc} x 10^6/ mol m^{-2}						
LiCl	295	1.78	2.63	1.97	2.33	1.71	2.03	1.93
	298	1.96	2.34	2.23	2.38	2.82	2.57	2.73
	303	1.70	1.88	2.13	1.93	2.11	1.90	2.06
NaCl	295		2.35	2.40	1.85	2.41	2.20	2.42
	298		2.28	2.53	2.37	2.14	2.18	2.75
	303		2.27	2.07	1.87	1.84	2.64	2.71
KCl	295		2.11	2.20	2.71	2.65	2.63	1.97
	298		2.43	2.07	2.60	2.82	2.17	2.97
	303		1.72	2.42	2.46	2.02	2.49	2.80

Table 3.11 - Aggregation Numbers of CPC in Aqueous Electrolyte Solutions at 298 K

Electrolyte	Concentration of Electrolyte / mol kg^{-1}			
	$3.2x10^{-4}$	$5.2x10^{-4}$	$1.3x10^{-3}$	$5.2x10^{-3}$
	Aggregation Number			
LiCl	43	103	55	40
NaCl	45	92	90	158
KCl	45	83	47	72

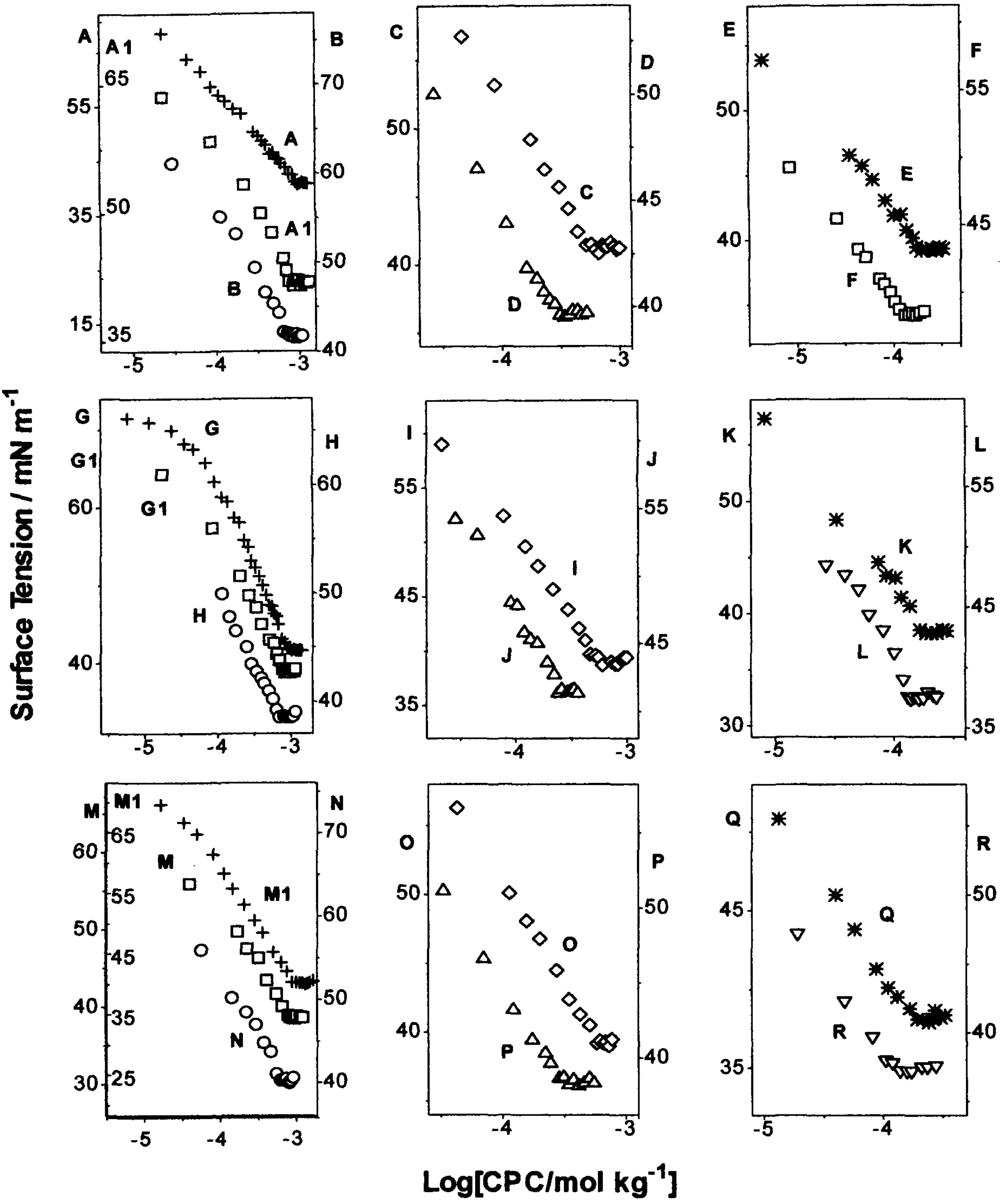

Figure 3.1. Variation of surface tension with logarithm of CPC concentration in aqueous LiCl solutions at 295 K (top row), 298 K (middle row) and 303 K (bottom row). LiCl concentrations in mol kg^{-1} are: 0 (A, G and M1), 3.2x10^{-4} (A1, G1 and M), 5.2x10^{-4} (B, H and N), 1.3x10^{-3} (C, I and O), 5.2x10^{-3} (D, J and P), 0.01 (E, K and Q) and 0.02 (F, L and R).

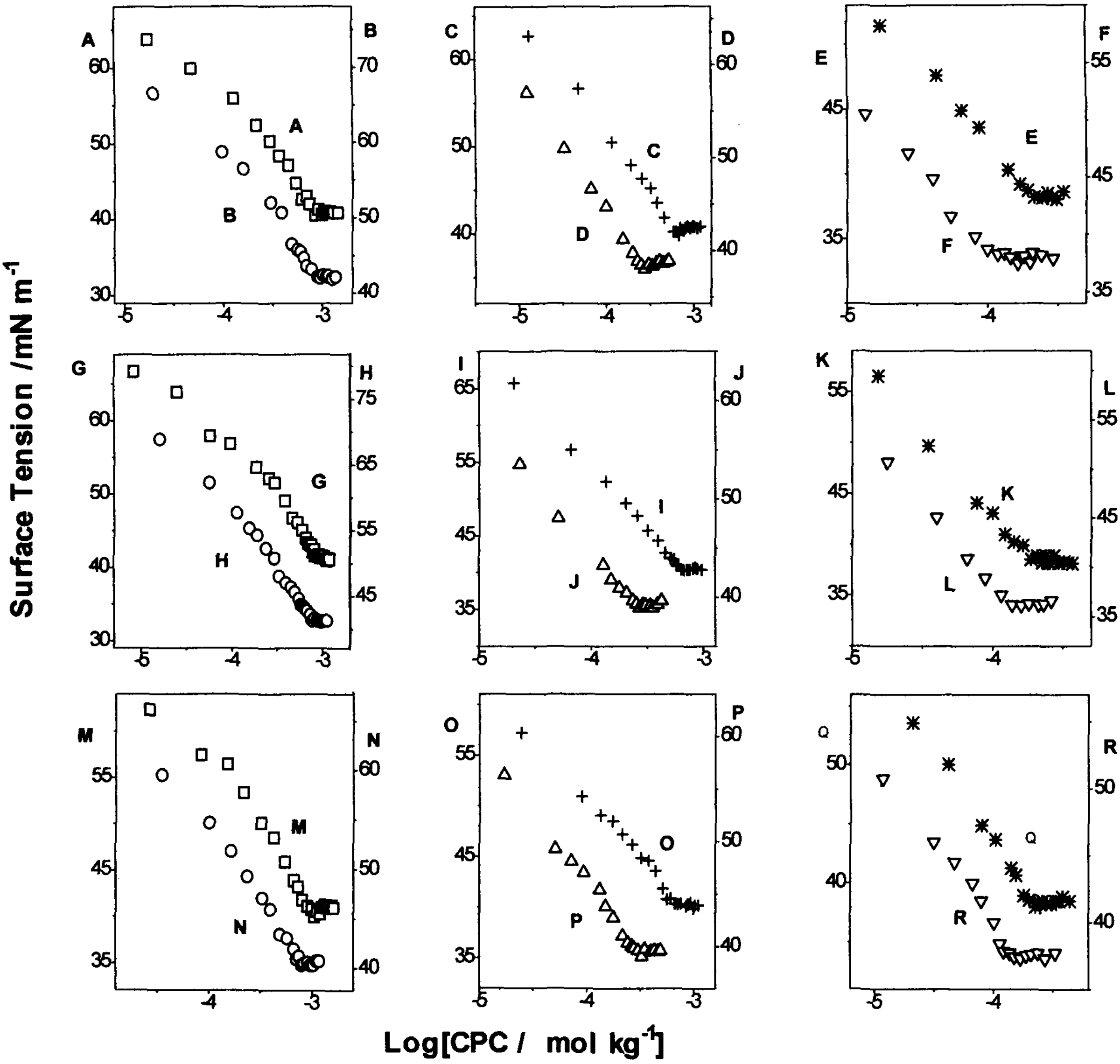

Figure 3.2. Variation of surface tension with logarithm of CPC concentration in aqueous NaCl solutions at 295 K (top row), 298 K (middle row) and 303 K (bottom row). NaCl concentrations in mol kg^{-1} are: 3.2x10^{-4} (A, G and M), 5.2x10^{-4} (B, H and N), 1.3x10^{-3} (C, I and O), 5.2x10^{-3} (D, J and P), 0.01 (E, K and Q) and 0.02 (F, L and R).

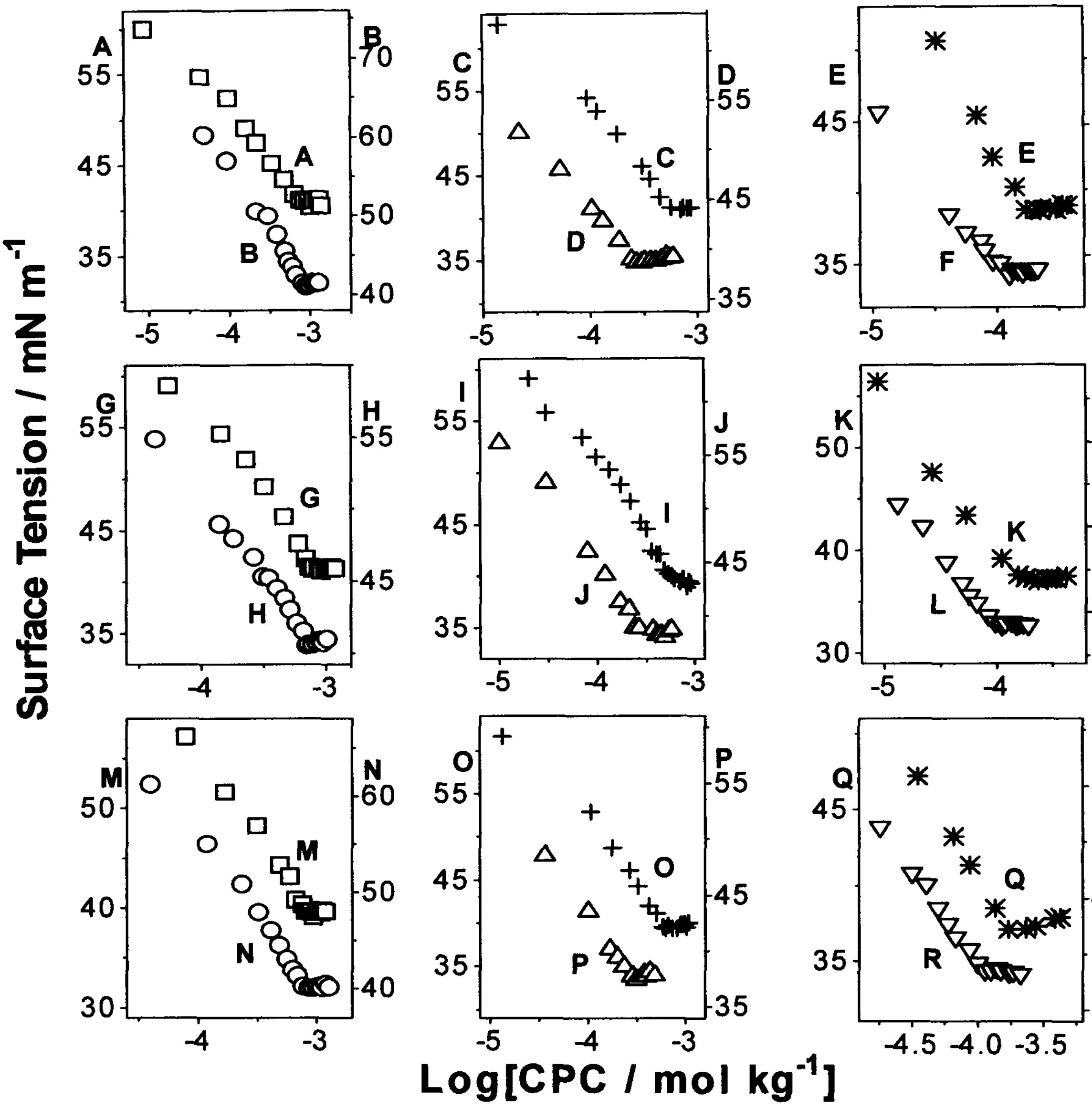

Figure 3.3. Variation of surface tension with logarithm of CPC concentration in aqueous KCl solutions at 295 K (top row), 298 K (middle row) and 303 K (bottom row). KCl concentrations in mol kg^{-1} are: 3.2x10^{-4} (A, G and M), 5.2x10^{-4} (B, H and N), 1.3x10^{-3} (C, I and O), 5.2x10^{-3} (D, J and P), 0.01 (E, K and Q) and 0.02 (F, L and R).

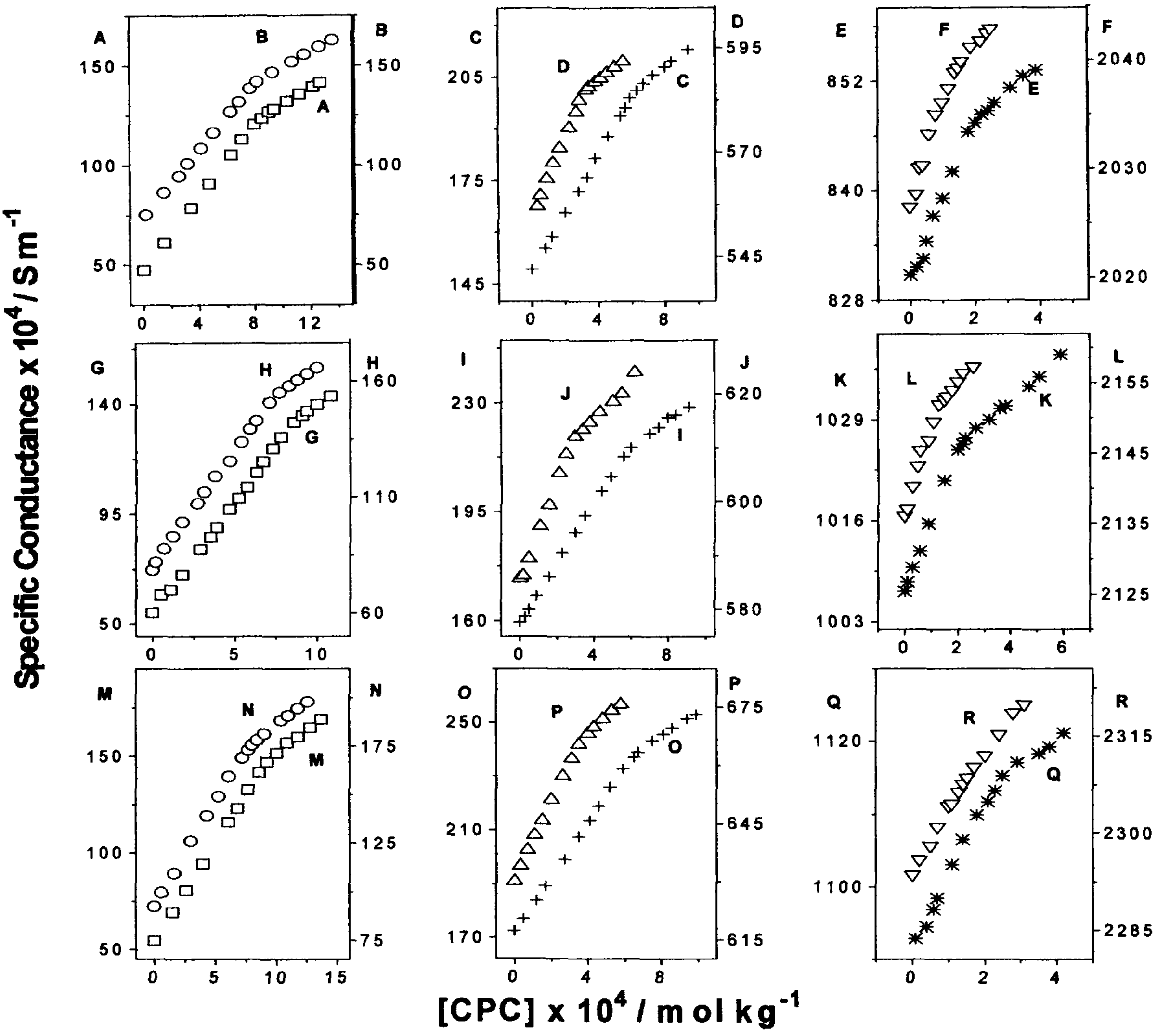

Figure 3.4. Variation of specific conductance with CPC concentration in aqueous LiCl solutions at 295 K (top row), 298 K (middle row) and 303 K (bottom row). LiCl concentrations in mol kg^{-1} are: 3.2×10^{-4} (A, G and M), 5.2×10^{-4} (B, H and N), 1.3×10^{-3} (C, I and O), 5.2×10^{-3} (D, J and P), 0.01 (E, K and Q) and 0.02 (F, L and R).

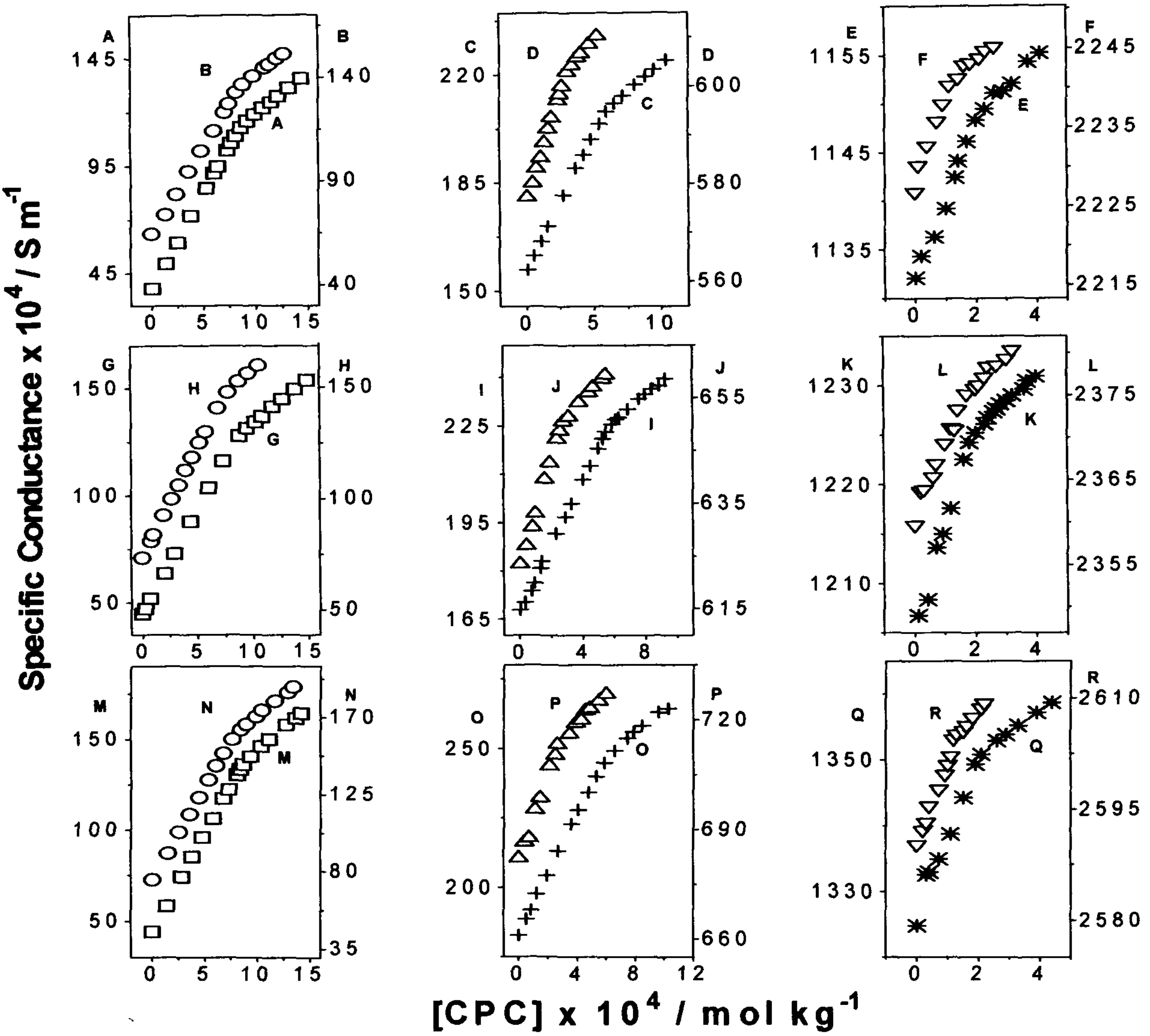

Figure 3.5. Variation of specific conductance with CPC concentration in aqueous NaCl solutions at 295 K (top row), 298 K (middle row) and 303 K (bottom row). NaCl concentrations in mol kg^{-1} are: 3.2×10^{-4} (A, G and M), 5.2×10^{-4} (B, H and N), 1.3×10^{-3} (C, I and O), 5.2×10^{-3} (D, J and P), 0.01 (E, K and Q) and 0.02 (F, L and R).

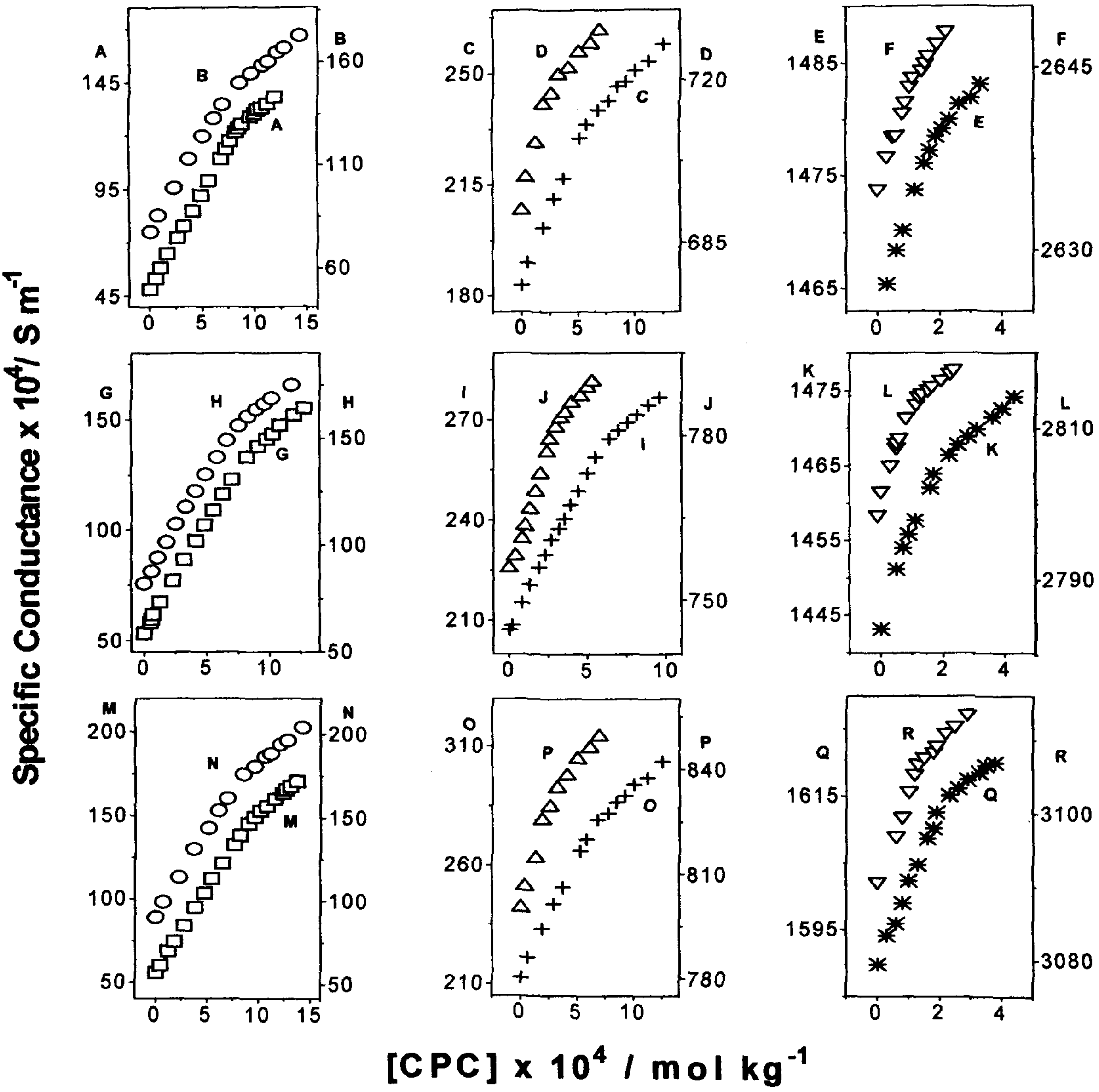

Figure 3.6. Variation of specific conductance with CPC concentration in aqueous KCl solutions at 295 K (top row), 298 K (middle row) and 303 K (bottom row). KCl concentrations in mol kg^{-1} are: 3.2x10^{-4} (A, G and M), 5.2x10^{-4} (B, H and N), 1.3x10^{-3} (C, I and O), 5.2x10^{-3} (D, J and P), 0.01 (E, K and Q) and 0.02 (F, L and R).

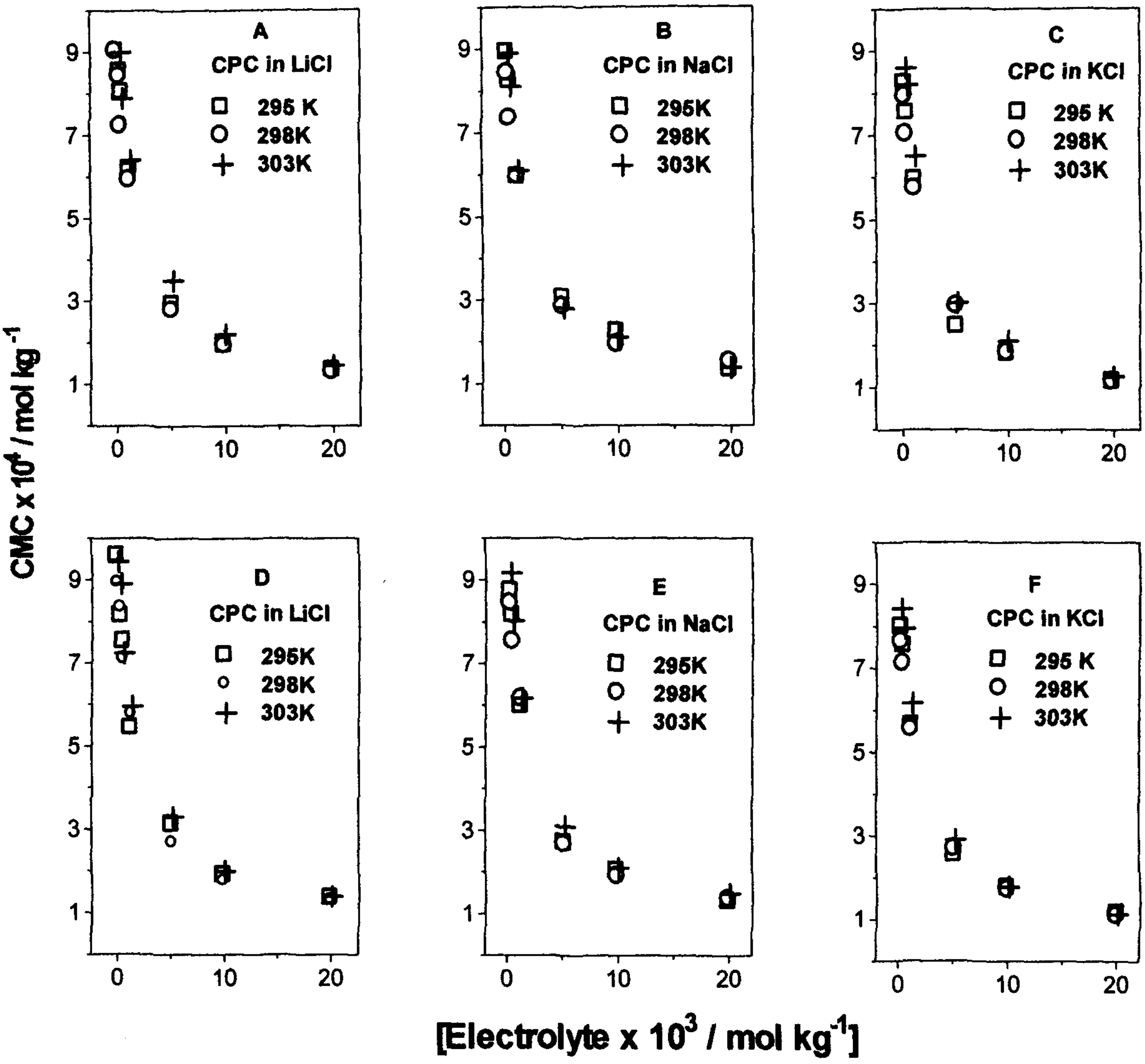

Figure 3.7. Variation of cmc (from κ: A – C; from γ: D – F) of CPC as a function of electrolyte concentration.

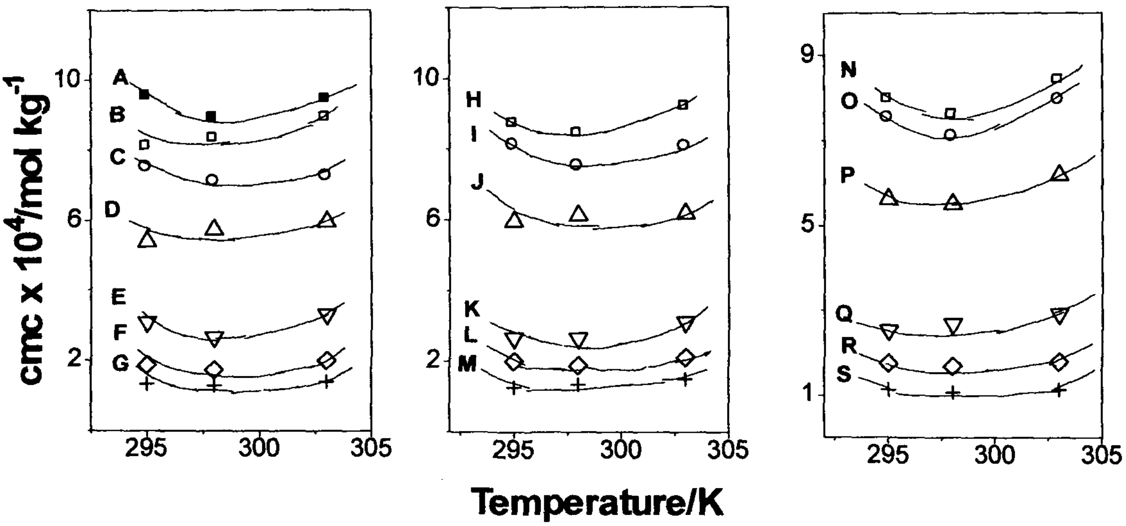

Figure 3.8. Variation of cmc (from γ) of CPC as a function of temperature (A: in H_2O; B – G: in LiCl; H – M: in NaCl and N – S: in KCl).

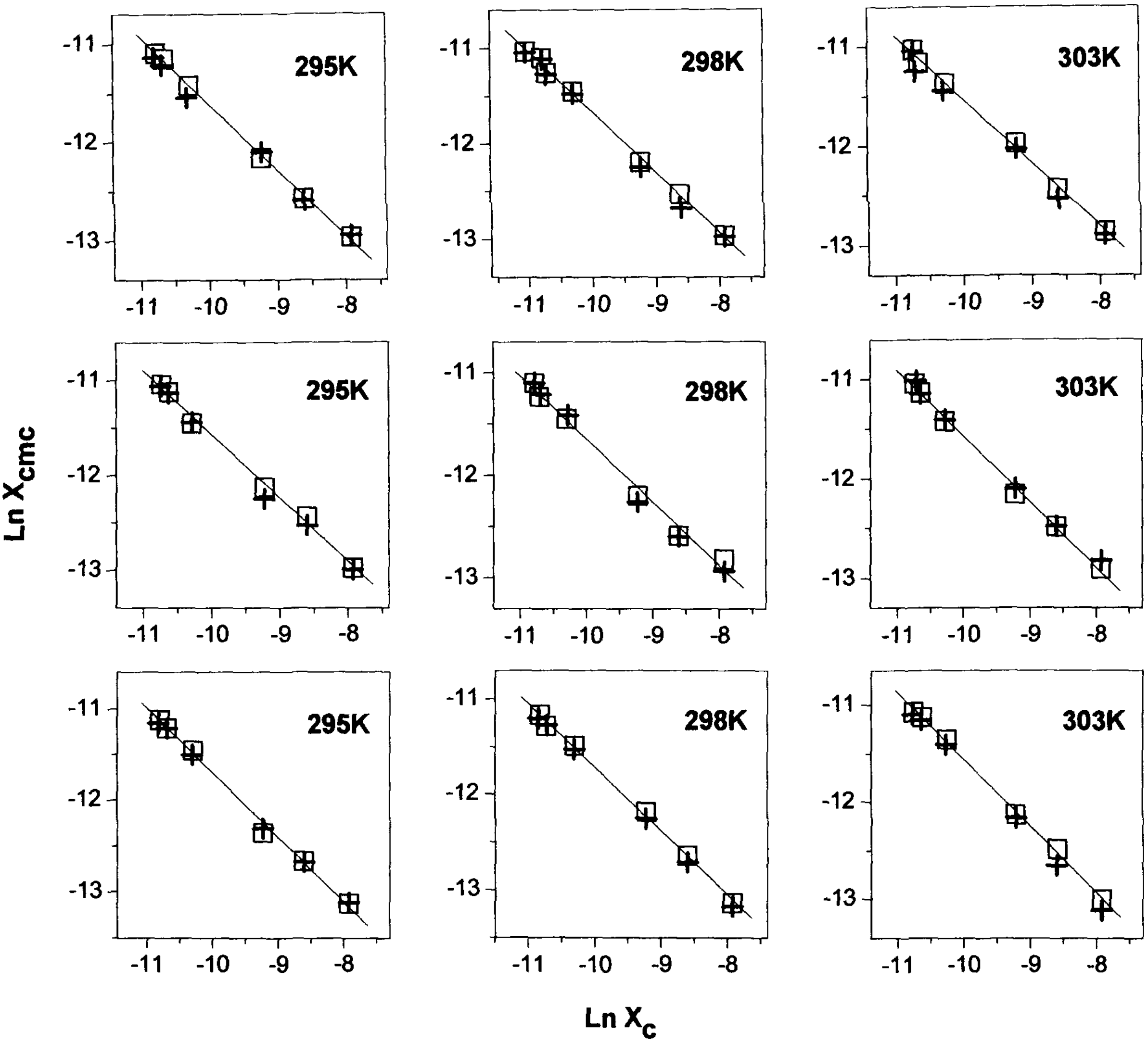

Figure 3.9. Variation of logarithm of cmc of CPC with logarithm of counter ion concentration (top row – in LiCl; middle row – in NaCl; bottom row – in KCl; □ : from κ and + : from γ).

CHAPTER 4

Adsorption and Aggregation Behaviours of Cetylpyridinium Chloride in Aqueous Sodium Salicylate and Sodium Benzoate Solutions

4.1 INTRODUCTION

We presented in chapter 3 the results of surface tension and conductance measurements on CPC in the presence of aqueous LiCl, NaCl and KCl solutions. These systems consisted of three different coions and one counter ion. The results indicated that the chosen coions do not have any effect on the cmc of CPC, but a probable influence of coions on the aggregation number of CPC was noticed when the conductance data was analyzed by applying the mixed electrolyte model (MEM) of Shanks and Franses.[1] In this chapter, we present the results of surface tension and conductance measurements of CPC by varying the counter ions. The systems chosen for study are CPC + sodium salicylate (NaSal) and CPC + sodium benzoate (NaBen) in aqueous medium. Thus the chosen systems consist of mixed coions (CP^+ and Na^+) and mixed counter ions (Cl^- + Sal^- and Cl^- + Ben^-). NaSal and NaBen are important electrolytes due to their hydrotropic property. Moreover, CPC + NaSal and cetyltrialkylammonium chloride/bromide (CTAC/CTAB) + NaSal systems exhibit viscoelasticity due to formation of worm-like micelles and hence these systems have been extensively studied by different groups.[2-14] Solubilization study of NaBen in CPC micelles is reported,[15] but NaBen does not induce viscoelasticity in CPC. Similarly, if the hydroxyl group of sodium hydroxyl benzoate is in the meta or para position,[16] then also viscoelasticity is not induced in CPC or CTAC or CTAB surfactant. Thus, the specificity of hydroxyl group in the ortho position in NaSal plays a decisive role in the formation of worm-like micelles.[14] Even salicylate is reported to bind as a coion to an anionic surfactant.[17]

Counter ion binding behaviour of salicylate ion to the CPC or CTAC or CTAB micelles is mainly responsible for the viscoelasticity of these micellar systems.

The counter ion binding behaviour of salicylate and benzoate ions to CPC micelles in aqueous medium in the concentration region where viscosity behaviour is Newtonian has not been fully explored to the best of our knowledge. The objective of this study is therefore to investigate the adsorption and aggregation behaviours of CPC + NaSal and CPC + NaBen systems in the Newtonian concentration region.

4.2 EXPERIMENTAL

CPC (Aldrich, > 99.0 %), NaSal (Fluka, > 99.5 %) and NaBen (Fluka, > 99.5 %) were used without purifying further. Millipore water was used for preparing the solutions. Surface tension and conductance measurements were made at 25 °C as described in chapter 2. Viscosity was measured by using a Cannon-Ubbelohde type viscometer having viscometer constant 3.51×10^{-3} cSt s^{-1}

4.3 RESULTS AND DISCUSSION

Surface tension, conductance and cmc. The measured surface tension (γ) values of CPC + NaSal and CPC + NaBen aqueous systems at 25 °C are given in Tables 4.1 and 4.2, respectively. Specific conductance (κ) values up to 0.001 mol kg^{-1} salt concentrations are listed in Tables 4.3 and 4.4 for CPC + NaSal and CPC + NaBen systems, respectively. Although we measured conductance at salt concentrations higher than 0.001 mol kg^{-1}, in those regions the variations in specific conductance (κ) with CPC concentration were found to be not significant and hence the data were not taken into consideration. Surface tension and conductance isotherms are shown in Figs. 4.1 – 4.4. The values of critical micelle concentration (cmc) determined from the surface tension and conductance isotherms are listed in Table 4.5.

The variation of cmc with the concentration of added salt is shown in Fig. 4.5. In Fig. 4.5 the cmc values of CPC + NaCl aqueous system at 25 °C (data from chapter 3) are also shown for comparison sake. It is clear from Fig. 4.5 that at a particular salt concentration the cmc in the presence of three salts follows the order NaSal < NaBen < NaCl. By adding 0.3 mol kg^{-1} of NaSal and NaBen, the cmc of CPC decreased from 9×10^{-4} (cmc with no salt) to $\sim 7 \times 10^{-7}$ and 3×10^{-6}, respectively. Thus, salicylate counter ion has a significantly larger tendency to decrease the cmc of CPC. The hydroxyl group in salicylate has therefore remarkable influence on the micellization of CPC.

Counter ion binding. The Corrin – Harkins (CH) equation is generally used to evaluate the counter ion binding constant, β. This equation can be written as

$$\ln c_0 = A - \beta_{CH} \ln(c_0 + c_e) \tag{4.1}$$

In Eq. (4.1), the concentrations are expressed in molal unit instead of mole fraction unit. The terms c_0 and c_e represent cmc and concentration of added electrolyte, respectively and A is a constant related to the standard free energy of micellization. The term $c_0 + c_e$ gives the total concentration of free counter ion. In Fig. 4.6a we have shown the CH plots for the systems under study as well as for CPC + NaCl aqueous system and it may be seen that a sharp deviation from linearity occurs in the presence of NaSal and NaBen, especially at low salt concentrations. Therefore, CH relation given by Eq. (4.1) is not applicable to the present systems. Although

CH equation has been used to evaluate β in surfactant systems containing mixed counter ions,[4] it is actually derived for surfactant systems containing single counter ion only. Since the systems under study have mixed counter ions, chloride and salicylate or chloride and benzoate, the CH equation needs to be modified. The micellization equilibrium can be represented in the presence of two counter ions as

$$nS^{+} + m_1C_1^{-} + m_2C_2^{-} \rightleftharpoons M^{z_n+} \qquad (4.2)$$

where S and M represent surfactant monomer with one positive charge and micelle with z_n positive charges, respectively. C_1 is the counter ion (chloride) from the surfactant molecule and C_2 is the added counter ion (salicylate or benzoate). The positive charge on the micelle, $z_n = n - m_1 - m_2$. Using the mass-action model and the thermodynamic relation between the equilibrium constant and the free energy change, we can write

$$\ln[S] = \left[\frac{\ln[M]}{n} + \frac{\Delta G^0_{mic}}{nRT}\right] - \frac{m_1}{n}\ln[C_1] - \frac{m_2}{n}\ln[C_2] \qquad (4.3)$$

ΔG^0_{mic} refers to the standard free energy of micellization. Considering the equilibrium (4.2) at a surfactant concentration, c, which is slightly above cmc, we can write Eq. (4.3) as

$$\ln c_0 \approx \frac{\Delta G^0_m}{RT} - \beta_1\ln[c_0 + (c - c_0)(1 - \beta_1)] - \beta_2\ln[c_e - (c - c_0)(\qquad \beta_2)] \qquad (4.4)$$

The commonly used approximation that ln[M]/n is negligible in comparison to $\Delta G^0_m/(RT)$ when c is slightly above c_0 has been applied in Eq. (4.4). ΔG^0_m (= $\Delta G^0_{mic}/n$) is the standard free energy of micellization per mole of surfactant monomer. β_1 (= m_1/n) and β_2 (= m_2/n) represent counter ion binding constants of the surfactant for C_1 and C_2 counter ions, respectively. The total counter ion binding constant (β) of the surfactant is given by $\beta = \beta_1+\beta_2$. Since we considered the equilibrium (4.2) at a surfactant concentration slightly above cmc, Eq. (4.4) can be reduced, by approximating $(c - c_0) \approx 0+$, to

$$\ln c_0 \approx \frac{\Delta G_m^0}{RT} - \beta_1 \ln c_0 - \beta_2 \ln c_e \tag{4.5}$$

Eq. (4.5) can also be rearranged to the form

$$\ln c_0 = A' - B \ln c_e \tag{4.6}$$

where $A' = \Delta G_m^0/[(1+\beta_1)RT]$ and $B = \beta_2/(1+\beta_1)$. Thus, we get Eq. (4.6) in place of CH equation for a surfactant system containing mixed counter ions and we call it as the modified CH equation. Eq. (4.6) is applicable only when $c_e > 0$ and the added electrolyte contains counter ion different from that in the surfactant molecule. It is interesting to note that in the high concentration region of electrolyte where $c_0 + c_e \approx c_e$ the CH equation becomes similar to the modified CH equation. However, it is pertinent to note that in case of mixed counter ions the slope of the CH plot (when c_e is high) or modified CH plot does not correspond to β.

In Fig. 4.6b, we have shown the plot of $\ln c_0$ versus $\ln c_e$ for CPC + NaSal and CPC + NaBen aqueous systems and the linearity of the plots envisages the applicability of Eq. (4.6) instead of Eq. (4.1). From the least-squares fitting we got the values $A' = -15.14$ and -13.67 and $B = 0.663$ and 0.659 for CPC + NaSal and CPC + NaBen systems, respectively. Similar B values for the two systems indicate that the hydroxyl group of salicylate does not have much influence on B. Since $\beta_2 = B(1+\beta)/(1+B)$, the values of β_2 as well as β_1 can be determined if we know the value of β. Using the value of B from Fig. 4.6b, we get $\beta_2 = (0.398 \pm 0.001)(1+\beta)$ for Sal^- and Ben^-. Therefore, β must be more than 0.66, otherwise value of β_2

becomes unacceptable since it exceeds β value. The value of B thus provides a lower limit to the value of β and not the value of β. Thus, in surfactant systems consisting of mixed counter ions, the modified CH equation explains the variation of cmc with concentration of added salt, but does not provide the value of β. Since $\beta > 0.66$ in CPC + NaSal and CPC + NaBen, both salicylate and benzoate increase the counter ion binding to the CPC micelle because β is equal to 0.66 when the counter ion is chloride alone (obtained from the CH plot for CPC + NaCl; data from chapter 3). Because of the presence of mixed counter ions the slope – ratio method of determining β from conductance data is not applicable. This was realized from the fact that the values of β obtained from the slope – ratio method varied between 0.2 (salt concentration 2×10^{-4} mol kg^{-1}) to 0.35 (salt concentration 0.001 mol kg^{-1}) and these values of β are not acceptable in view of the above conclusion that β must be more than 0.66. The relation between β_2 and β therefore reveals that the majority of the counter ion bound to the micelle is salicylate or benzoate. For instance, if $\beta = 0.8$, $\beta_2 = 0.72$ and $\beta_1 = 0.08$. Therefore, the added salicylate or benzoate ions predominantly bind to the micelle suppressing the binding of chloride. Preferential binding of salicylate or benzoate ions to the CPC micelle may be explained by the two-site binding model reported for salicylate ion.[13,14] According to this model, both hydrophobic and electrostatic factors play role in the binding of these organic ions to the cationic micelle. Due to hydrophobic interaction salicylate or benzoate ion penetrates into the micelle and orients such that their hydrophilic functional groups project outward.[13,14] Some of the salicylate and benzoate ions also bind to the cationic micelle due to electrostatic interaction and reside at the micellar surface. The present study reveals that salicylate and benzoate ions bind almost equally to the CPC micelle and consequently the amount of counter ion binding is not responsible for the viscoelasticity, which is observed in CPC + NaSal and not in CPC + NaBen.

Free energy. The standard free energy of micellization per mole of ionic surfactant, ΔG^0_m, has two components, one for the transfer of ionic monomer and the other for the transfer of counter ions from the bulk to the micellar phase. These two components are evaluated using the relations $\Delta G^0_{hc} = RT\ln X_{cmc}$ and $\Delta G^0_{el} = \beta RT\ln X_{cmc}$. ΔG^0_{hc} is the standard free energy change due to transfer of one mole of hydrocarbon chain of the surfactant from the bulk to the micellar phase which also includes a free energy term due to repulsive interaction between the head groups. ΔG^0_{el} is the standard free energy change due to the transfer of counter ions from the bulk to the micellar interface and it includes free energy term due to electrostatic interactions between the head groups and counter ions. Since we do not know the correct value of β for the systems under study, we evaluated only ΔG^0_{hc} for CPC in the presence of NaSal and NaBen, which are given in Table 4.5 and also presented in Fig. 4.7. The difference between the values of ΔG^0_{hc} for CPC in the presence of NaSal and NaBen is found to be -3.5 ± 0.5 kJ mol^{-1}. Thus, the ortho hydroxyl group in NaSal has a favouring influence on the aggregation of CPC to the extent of 3.5 kJ mol^{-1}.

Viscosity. We measured the viscosity of aqueous solution of CPC as a function of NaSal concentration to ensure that the systems studied show Newtonian viscous behaviour (Table 4.6). From Fig. 4.8 it is clear that in the concentration range of CPC and NaSal covered in this study the systems have low viscosity. It is also apparent from Fig. 4.8 that the viscosity of CPC + NaSal system becomes very high only when the CPC concentration crosses a threshold value (about 0.005 mol kg^{-1}). When the CPC concentration is below this threshold value, viscosity does not reach high values just by increasing the concentration of NaSal.

Surface Excess. To evaluate surface excess of systems containing mixed counter ions no accurate expression is available. Before obtaining an expression for the surface excess of an ionic surfactant in the presence of two counter ions, we first look at the expressions available for the surface excess of ionic surfactants in the absence of added counter ion and in the presence of added salt contributing same counter ion as that of the surfactant molecule. We consider the dissociation of an ionic surfactant in the premicellar concentration region as

$$SC_1 \rightarrow S^+ + C_1^- \tag{4.7}$$

For simplicity, 1:1 ionic surfactant is taken as an example. The Gibbs adsorption isotherm can be written for SC_1 as

$$d\gamma = -RT(\Gamma_s d\ln c + \Gamma_{c1} d\ln c) \tag{4.8}$$

where Γ_s and Γ_{c1} are the surface excesses of surfactant monomer and counter ion, respectively. The surfactant concentration c is less than c_0. Prosser and Franses[17] treated the adsorbed layer at the air – solution interface to be electroneutral. For a electrically neutral adsorbed layer ($\Gamma_s = \Gamma_{c1} = \Gamma$), Eq. (4.8) rearranges to

$$\Gamma = -[1/(2RT)](d\gamma/d\ln c) \tag{4.9}$$

However, the adsorbed layer may not be electroneutral. For example, the amount of surface excess calculated from Eq. (4.9) for sodium di-n-octylsulphosuccinate was reported to be half the value measured by the radiotracer method.[18] Therefore, counter ions may either be partially adsorbed or may not be adsorbed. Considering $\Gamma_{c1} = \beta_{1ad}\Gamma_s$, where β_{1ad} is the binding constant for the counter ion C_1 at the air – solution interface, Eq. (4.9) becomes

$$\Gamma = -\frac{1}{RT(1+\beta_{1ad})}\left(\frac{d\gamma}{d\ln c}\right) \tag{4.10}$$

In Eq. (4.10) if we substitute $\beta_{1ad} = 1$, i.e., when the adsorbed layer is electroneutral, we get back Eq. (4.9). If $\beta_{1ad} = 0$, i.e., when the counter ions do not adsorb, we get the conventional form of equation for Γ as

$$\Gamma = -\frac{1}{RT}\left(\frac{d\gamma}{d\ln c}\right) \tag{4.11}$$

For example, the reported[19] experimental value of surface excess for sodium dodecylsulphate (SDS) measured by the radiotracer method was found to lie in between the values calculated from Eqs. (4.9) and (4.11) implying thereby that β_{1ad} for SDS lies between 0 and 1. Some of the ionic models[20-22] for adsorption takes into account the counter ion binding by considering β_{1ad} taking up value between 0 and 1. Measurement of surface excess using the Neutral Impact Collision Ion Scattering Spectroscopic (NICISS) technique reported recently[23] also indicated presence of counter ions in the adsorption layer.

In the presence of an added electrolyte MC_1, which contribute same counter ion as that of the surfactant molecule (e.g., CPC + NaCl), and presuming electoneutrality of the adsorbed layer, Prosser and Franses[17] derived the relation for Γ as

$$\Gamma = -\frac{1}{RT}\left[\frac{1}{1+\frac{c_o}{c_o+c_e}}\right]\left(\frac{d\gamma}{d\ln c}\right)_{c_e} \tag{4.12}$$

Eq. (4.12) also reduces to Eq. (4.9) in the absence of electrolyte, i.e., when $c_e = 0$. Instead of electroneutrality of adsorbed layer, if we consider partial counter ion binding ($0 < \beta_{1ad} < 1$), it can be shown that

$$\Gamma = -\frac{1}{RT}\left[\frac{1}{1+\frac{\beta_{1ad}c_o}{c_o+c_e}}\right]\left(\frac{d\gamma}{d\ln c}\right)_{c_e} \tag{4.13}$$

Now, let us consider the case of a surfactant system with mixed counter ions. For this, we take surfactant SC_1 in the presence of an electrolyte MC_2 of concentration c_e. The Gibbs adsorption isotherm for this system can be written as

$$d\gamma = -RT(\Gamma_s d\ln c + \Gamma_{c1} d\ln c + \Gamma_{c2} d\ln c_e) \tag{4.14}$$

Γ_{c2} is the surface excess of the counter ion from the added electrolyte and the adsorption of the coion M^+ has been neglected. Presuming again electroneutrality of the adsorption layer, we can write

$$\Gamma_s = \Gamma_{c1} + \Gamma_{c2} = \Gamma \tag{4.15}$$

In writing Eq. (4.15) we have considered that $\Gamma_{c1} = \beta_{1ad}\Gamma_s$, $\Gamma_{c2} = \beta_{2ad}\Gamma_s$ and $\beta_{1ad} + \beta_{2ad} = 1$, where β_{1ad} and β_{2ad} are the binding constants of counter ions C_1 and C_2 at the adsorption layer, respectively. At constant c_e, Eq. (4.14) takes the form

$$\Gamma = -\frac{1}{RT(1+\beta_{1ad})}\left(\frac{d\gamma}{d\ln c}\right)_{c_e} \tag{4.16}$$

In Eq. (4.16), Γ appears to be independent of β_{2ad}, but the value of the slope $d\gamma/d\ln c$ will be dependent on β_{2ad} or adsorption of C_2 and hence Γ is indirectly dependent on β_{2ad}. At a particular concentration of added salt containing a different counter ion, the value of $d\gamma/d\ln c$ can be determined experimentally and therefore the surface excess of CPC can be evaluated from Eq. (4.16) if the value of β_{1ad} is known. We calculated Γ at cmc (Γ_{cmc}) for CPC in the presence of NaSal and NaBen by arbitrarily assigning the values 0, 0.5 and 1 for β_{1ad}. The values of Γ_{cmc} evaluated thus are presented in Table 4.7. The dependence of Γ_{cmc} on salt concentration is shown in Fig. 4.9. The trend in the variation of Γ_{cmc} with salt concentration is same at all the chosen values of β_{1ad}. The surface excess of CPC in the presence of NaSal is higher than in the presence of NaBen. Both NaSal and NaBen decreases Γ_{cmc} initially up to about 0.002 ± 0.001 mol kg^{-1} salt concentration. Thereafter, Γ_{cmc} increases with further addition of salt. This increase is steeper in the case of NaSal. Γ_{cmc} attains maximum value around 0.1 mol kg^{-1} NaSal and around 0.02 mol kg^{-1} NaBen. On increasing NaSal concentration above 0.1 mol kg^{-1}, Γ_{cmc} decreases. In the case of NaBen, Γ_{cmc} decreases from 0.02 to 0.15 mol kg^{-1} salt concentration only and thereafter remains almost constant. These results show that the ortho hydroxyl group in NaSal has profound influence on the adsorption behaviour of CPC.

4.4 CONCLUSIONS

Among benzoate and salicylate counter ions, the latter has a significantly larger tendency to decrease the cmc of CPC. The ortho hydroxyl group in NaSal has a favouring influence on the aggregation of CPC to the extent of 3.5 kJ mol^{-1}. A modified Corrin – Harkins equation has been derived, which accounts successfully for the change in cmc of CPC with concentrations of NaSal and NaBen. The slope of the modified CH equation does not provide the value of the total counter ion binding constant (β), but gives us information about the lower limit to the value of β, which is found to be 0.66. The addition of salicylate and benzoate counter ions increased the value of β for CPC. Salicylate and benzoate ions predominantly bind to the CPC micelle suppressing the binding of chloride. This study revealed that salicylate and benzoate ions bind almost equally to the CPC micelle and consequently the amount of counter ion binding is not responsible for the viscoelasticity phenomenon. An adsorption isotherm was derived to estimate the surface excess of CPC in the presence of mixed counter ions by taking into account the adsorption of counter ions at the air – solution interface. Using this adsorption isotherm and choosing arbitrary values for the constant of binding of chloride ion at the adsorption layer (β_{1ad}), surface excess of CPC was evaluated in the presence of salicylate and benzoate ions. The results show that the ortho hydroxyl group in NaSal has profound influence on the adsorption behaviour of CPC. Thus, this study provides a new approach to explain the influence of mixed counter ions on the adsorption and micellization behaviours of ionic surfactants.

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Table 4.1 - Surface Tension (γ) values of CPC in aqueous Sodium Salicylate solution at 298 K

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
		[NaSal] = 0.0 mol kg^{-1}			
0.0020	72.1	0.1165	64.0	1.5861	42.9
0.0039	71.8	0.1931	60.7	1.8237	43.3
0.0063	71.3	0.3063	56.8	2.0798	43.2
0.0090	71.3	0.4541	52.6	2.3510	43.1
0.0121	70.9	0.5986	49.5	2.8557	42.9
0.0157	70.8	0.7399	46.2	3.3155	43.1
0.0196	70.5	0.8780	43.9	3.9332	42.8
0.0274	69.8	1.0131	43.6	4.6459	42.6
0.0469	68.4	1.1779	43.1	5.1123	42.4
0.0779	66.1	1.3697	43.0		
		[NaSal] = 2.0 x 10^{-5} mol kg^{-1}			
7.1x10^{-4}	72.7	0.0323	56.5	0.3630	38.1
0.0014	71.8	0.0435	54.4	0.4261	37.2
0.0021	70.8	0.0574	52.4	0.5001	37.3
0.0028	69.7	0.0851	49.3	0.5726	37.5
0.0042	67.9	0.1261	46.1	0.6436	37.8
0.0085	64.6	0.1802	43.3	0.7130	38.0
0.0141	61.3	0.2334	41.3	0.7809	38.5
0.0225	58.5	0.2989	39.2		
		[NaSal] = 5.0 x 10^{-5} mol kg^{-1}			
5.2x10^{-4}	72.3	0.0238	52.4	0.2769	36.2
0.0010	70.4	0.0321	50.2	0.3139	36.3
0.0016	68.8	0.0423	48.2	0.3504	36.3
0.0021	67.5	0.0627	45.2	0.3953	36.6
0.0031	65.1	0.0930	42.2	0.4393	36.6
0.0052	62.2	0.1229	40.2	0.4826	36.9
0.0083	59.4	0.1623	38.0	0.5251	36.9

Table 4.1 – Continued

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
[NaSal] = 5.0 x 10^{-5} mol kg^{-1}					
0.0125	56.4	0.2011	36.6		
0.0176	54.3	0.2393	36.1		
[NaSal] = 1.0 x 10^{-4} mol kg^{-1}					
5.2x10^{-4}	68.7	0.0175	48.1	0.1612	35.0
0.0010	66.3	0.0236	46.4	0.1901	35.1
0.0015	63.9	0.0318	44.3	0.2188	35.3
0.0021	62.0	0.0420	42.0	0.2564	35.4
0.0031	59.7	0.0623	39.2	0.2935	35.5
0.0052	56.5	0.0824	37.6	0.3391	35.9
0.0083	53.5	0.1023	35.9	0.3839	36.1
0.0124	50.8	0.1319	35.3		
[NaSal] = 2.0 x 10^{-4} mol kg^{-1}					
4.0x10^{-4}	67.8	0.0137	47.2	0.1007	35.1
8.1x10^{-4}	65.5	0.0185	45.1	0.1160	35.1
0.0012	63.9	0.0240	43.2	0.1387	34.7
0.0016	61.8	0.0304	41.6	0.1612	34.8
0.0024	59.3	0.0383	40.2	0.1907	34.6
0.0040	56.0	0.0541	37.8	0.2198	35.0
0.0064	52.9	0.0698	35.9	0.2556	35.1
0.0097	49.8	0.0853	35.3	0.2908	35.1
[NaSal] = 3.0 x 10^{-4} mol kg^{-1}					
9.2x10^{-4}	64.0	0.0201	41.0	0.0782	34.9
0.0018	59.8	0.0238	39.6	0.0926	34.9
0.0037	54.6	0.0274	38.6	0.1106	34.7
0.0055	50.9	0.0311	37.8	0.1462	34.0
0.0073	47.8	0.0365	36.7	0.1992	34.6

Table 4.1 – Continued

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
[NaSal] = 3.0 x 10^{-4} mol kg^{-1}					
0.0092	46.2	0.0438	35.7	0.2861	34.7
0.0128	43.7	0.0529	35.5		
0.0165	42.1	0.0638	34.9		
[NaSal] = 5.0 x 10^{-4} mol kg^{-1}					
2.4 x10^{-4}	62.1	0.0076	42.7	0.0759	34.6
4.8x10^{-4}	59.1	0.0100	40.7	0.1066	34.3
7.1x10^{-4}	57.4	0.0123	40.4	0.1406	34.2
0.0010	55.7	0.0151	39.1	0.1735	34.2
0.0014	53.5	0.0184	38.1	0.1896	34.2
0.0019	52.0	0.0222	36.6	0.2477	34.2
0.0024	50.6	0.0259	35.7	0.2846	34.5
0.0033	47.9	0.0306	35.4	0.3202	34.2
0.0043	46.9	0.0398	34.8		
0.0057	44.3	0.0535	34.7		
[NaSal] = 0.001 mol kg^{-1}					
1.3x10^{-4}	69.3	0.0057	45.6	0.0320	34.9
2.6x10^{-4}	62.7	0.0074	43.2	0.0369	34.5
5.2x10^{-4}	59.5	0.0095	41.6	0.0441	34.4
0.0010	58.0	0.0120	39.8	0.0513	34.3
0.0018	54.6	0.0171	36.8	0.0608	34.3
0.0028	51.4	0.0221	35.6	0.0701	34.3
0.0041	48.3	0.0270	34.9	0.0838	34.2
[NaSal] = 0.003 mol kg^{-1}					
1.8x10^{-4}	62.4	0.0030	43.2	0.0141	35.8
2.6x10^{-4}	58.2	0.0042	41.2	0.0158	35.5
3.5x10^{-4}	55.7	0.0056	39.4	0.0192	35.8
5.3x10^{-4}	54.6	0.0072	37.9	0.0209	35.1

Table 4.1 – Continued

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
		[NaSal] = 0.003 mol kg^{-1}			
8.8x10^{-4}	51.2	0.0089	36.6	0.0259	35.0
0.0014	48.4	0.0106	36.3	0.0325	34.9
0.0021	45.8	0.0124	36.2	0.0406	34.3
		[NaSal] = 0.005 mol kg^{-1}			
4.9x10^{-5}	73.4	0.0029	42.5	0.0150	34.8
9.9x10^{-5}	73.0	0.0036	40.9	0.0178	34.7
2.0x10^{-4}	65.3	0.0045	39.6	0.0214	34.4
4.0x10^{-4}	54.9	0.0055	39.0	0.0250	34.5
6.9x10^{-4}	52.6	0.0074	37.0	0.0286	34.4
0.0011	50.1	0.0093	35.9	0.0321	34.2
0.0016	46.7	0.0112	35.7	0.0373	33.9
0.0022	44.2	0.0122	35.4		
		[NaSal] = 0.010 mol kg^{-1}			
3.8x10^{-5}	73.0	0.0024	42.3	0.0095	36.1
7.5x10^{-5}	73.4	0.0030	40.2	0.0109	36.0
1.5x10^{-4}	70.2	0.0037	38.6	0.0123	35.9
3.0x10^{-4}	69.8	0.0044	37.6	0.0144	35.3
4.5x10^{-4}	65.0	0.0051	37.2	0.0165	35.4
7.5x10^{-4}	54.8	0.0059	36.8	0.0192	35.2
0.0011	48.8	0.0066	36.4	0.0233	34.6
0.0014	46.0	0.0073	36.7		
0.0019	44.7	0.0088	36.5		
		[NaSal] = 0.015 mol kg^{-1}			
4.3x10^{-5}	73.0	0.0012	45.4	0.0083	36.7
8.7x10^{-5}	72.8	0.0016	42.8	0.0099	35.7
1.7x10^{-4}	72.4	0.0020	41.7	0.0116	35.4

Table 4.1 – Continued

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
		[NaSal] = 0.015 mol kg^{-1}			
3.5x10^{-4}	65.4	0.0025	40.3	0.0140	35.2
5.2x10^{-4}	57.3	0.0032	39.3	0.0165	35.3
6.1x10^{-4}	54.6	0.0040	37.9	0.0197	34.6
7.8x10^{-4}	48.9	0.0049	37.6	0.0228	34.7
0.0010	47.4	0.0066	36.6	0.0267	34.1
		[NaSal] = 0.02 mol kg^{-1}			
7.9x10^{-5}	72.8	0.0021	40.9	0.0051	37.8
2.4x10^{-4}	70.0	0.0024	40.6	0.0056	37.2
4.0x10^{-4}	64.6	0.0028	40.4	0.0062	37.3
6.3x10^{-4}	57.4	0.0031	39.4	0.0069	37.1
8.7x10^{-4}	50.6	0.0035	39.2	0.0077	37.0
0.0012	45.9	0.0038	38.7	0.0092	36.5
0.0015	43.4	0.0042	37.9	0.0107	36.3
0.0018	42.4	0.0046	37.9		
		[NaSal] = 0.05 mol kg^{-1}			
5.3x10^{-5}	72.9	0.0013	44.5	0.0030	39.5
1.6x10^{-4}	73.1	0.0014	42.5	0.0033	38.8
3.2x10^{-4}	70.3	0.0016	41.7	0.0036	39.0
4.7x10^{-4}	64.3	0.0018	40.9	0.0040	38.5
6.3x10^{-4}	60.1	0.0020	40.7	0.0044	37.9
7.9x10^{-4}	55.7	0.0022	41.0	0.0049	37.8
9.5x10^{-4}	51.7	0.0025	40.1	0.0054	37.9
0.0011	47.3	0.0028	39.7	0.0064	37.4
		[NaSal] = 0.10 mol kg^{-1}			
3.7x10^{-5}	72.4	7.2x10^{-4}	52.7	0.0054	39.2
7.4x10^{-5}	71.8	9.4x10^{-4}	47.3	0.0037	39.0
1.1x10^{-4}	69.4	0.0012	44.9	0.0042	38.5

Table 4.1 – Continued

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
[NaSal] = 0.10 mol kg^{-1}					
1.5x10^{-4}	67.6	0.0015	41.7	0.0050	38.5
2.0x10^{-4}	65.7	0.0018	40.7	0.0064	37.7
2.7x10^{-4}	62.2	0.0020	40.1	0.0086	37.4
3.5x10^{-4}	59.6	0.0024	39.6	0.0107	36.9
5.0x10^{-4}	57.3	0.0028	39.3		
[NaSal] = 0.15 mol kg^{-1}					
4.8x10^{-5}	71.8	6.1x10^{-4}	46.6	0.0022	39.7
9.6x10^{-5}	70.0	7.1x10^{-4}	44.8	0.0026	39.2
1.4x10^{-4}	65.1	8.1x10^{-4}	42.9	0.0031	38.8
1.9x10^{-4}	61.7	9.0x10^{-4}	42.1	0.0037	38.7
2.6x10^{-4}	57.9	0.0011	42.2	0.0044	38.3
3.4x10^{-4}	54.2	0.0013	42.0	0.0054	38.0
4.2x10^{-4}	50.3	0.0016	40.5	0.0072	37.6
5.2x10^{-4}	48.2	0.0019	40.2		
[NaSal] = 0.20 mol kg^{-1}					
4.7x10^{-5}	68.5	6.7x10^{-4}	44.8	0.0036	39.2
9.5x10^{-5}	65.4	0.0010	41.5	0.0042	38.7
1.4x10^{-4}	62.8	0.0012	41.2	0.0048	38.6
1.9x10^{-4}	58.6	0.0015	39.9	0.0056	38.5
2.5x10^{-4}	53.0	0.0018	39.6	0.0064	38.4
3.1x10^{-4}	50.8	0.0022	39.9	0.0073	38.2
3.9x10^{-4}	47.8	0.0026	39.4	0.0091	37.9
4.8x10^{-4}	46.3	0.0030	39.1	0.0119	37.3
[NaSal] = 0.25 mol kg^{-1}					
3.7x10^{-5}	69.7	5.5x10^{-4}	45.9	0.0026	39.3
7.5x10^{-5}	68.6	6.3x10^{-4}	44.4	0.0030	39.7

Table 4.1 – Continued

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
		[NaSal] = 0.25 mol kg^{-1}			
1.1x10^{-4}	66.3	7.8x10^{-4}	43.8	0.0034	39.4
1.5x10^{-4}	62.7	9.3x10^{-4}	43.2	0.0040	39.1
2.0x10^{-4}	61.2	0.0011	43.2	0.0045	38.6
2.6x10^{-4}	58.9	0.0014	42.1	0.0051	38.3
3.3x10^{-4}	55.9	0.0017	40.1	0.0063	38.0
4.0x10^{-4}	49.0	0.0020	39.5	0.0092	37.5
4.8x10^{-4}	46.7	0.0023	39.9		
		[NaSal] = 0.32 mol kg^{-1}			
4.5x10^{-5}	66.3	4.9x10^{-4}	46.2	0.0016	40.9
9.0x10^{-5}	64.7	5.7x10^{-4}	45.4	0.0020	40.2
1.4x10^{-4}	62.0	6.6x10^{-4}	44.0	0.0025	39.7
1.8x10^{-4}	58.7	7.5x10^{-4}	43.4	0.0030	39.7
2.3x10^{-4}	55.7	8.4x10^{-4}	42.6	0.0037	39.2
2.9x10^{-4}	53.2	0.0010	41.9	0.0046	39.1
3.5x10^{-4}	49.0	0.0012	41.2	0.0064	38.7
4.2x10^{-4}	47.1	0.0014	40.6	0.0090	37.7

Table 4.2 - Surface Tension (γ) values of CPC in aqueous Sodium Benzoate solution at 298 K

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
		[NaBen] = 1.0 x 10^{-4} mol kg^{-1}			
0.0010	71.6	0.0502	56.4	0.5525	40.0
0.0020	71.2	0.0697	54.3	0.6400	40.3
0.0030	70.0	0.1086	51.3	0.7260	40.4
0.0049	68.2	0.1663	48.6	0.8104	40.7
0.0089	65.4	0.2234	46.3	0.9098	40.9
0.0148	63.1	0.2984	44.2	1.0070	41.5
0.0227	60.8	0.3724	42.4	1.1335	41.7
0.0345	58.3	0.4633	40.3		
		[NaBen] = 2.0 x 10^{-4} mol kg^{-1}			
0.0009	71.3	0.0463	53.4	0.4772	39.4
0.0018	69.5	0.0644	50.8	0.5424	39.5
0.0027	67.6	0.1003	48.0	0.6225	39.9
0.0046	65.2	0.1536	44.9	0.7012	39.8
0.0082	62.3	0.2063	43.3	0.7784	40.3
0.0137	59.6	0.2756	40.9	0.8542	40.6
0.0210	57.4	0.3438	39.5	0.9287	40.8
0.0319	55.5	0.4110	39.3	1.0019	41.0
		[NaBen] = 3.0 x 10^{-4} mol kg^{-1}			
0.0011	69.2	0.0635	48.6	0.3957	39.0
0.0022	66.3	0.0809	47.2	0.4961	39.1
0.0044	63.2	0.1026	45.7	0.6138	39.3
0.0088	60.3	0.1456	43.0	0.7661	39.8
0.0154	56.9	0.1882	41.5	0.9134	40.0
0.0242	54.0	0.2304	40.1	1.0560	40.1
0.0352	52.0	0.2723	39.0		
0.0483	50.1	0.2931	39.0		

Table 4.2 – Continued

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
[NaBen] = 5.0 x 10^{-4} mol kg^{-1}					
2.6x10^{-4}	70.5	0.0069	56.4	0.0996	40.5
5.2x10^{-4}	67.3	0.0095	54.8	0.1231	38.9
7.8x10^{-4}	66.0	0.0121	53.8	0.1461	38.2
0.0010	65.3	0.0157	52.0	0.1686	37.8
0.0013	63.9	0.0208	50.3	0.1950	37.9
0.0018	62.5	0.0259	49.4	0.2292	37.9
0.0023	61.5	0.0360	47.0	0.2623	38.1
0.0033	60.0	0.0460	45.5	0.3023	38.3
0.0044	58.6	0.0609	43.6	0.3407	38.2
0.0054	57.8	0.0804	41.8	0.3776	38.1
[NaBen] = 0.001 mol kg^{-1}					
1.9x10^{-4}	66.7	0.0097	52.4	0.0742	39.8
3.9x10^{-4}	65.3	0.0120	51.2	0.0883	38.7
7.8x10^{-4}	63.4	0.0151	49.6	0.1057	38.1
0.0012	62.2	0.0189	48.5	0.1227	37.8
0.0019	60.2	0.0227	47.5	0.1459	37.6
0.0027	58.8	0.0302	45.8	0.1684	37.9
0.0039	57.2	0.0377	44.2	0.1934	37.3
0.0054	55.3	0.0488	42.3	0.2235	37.4
0.0074	54.1	0.0598	41.2	0.2525	37.5
[NaBen] = 0.003 mol kg^{-1}					
1.3x10^{-4}	71.7	0.0071	49.7	0.0458	38.0
2.6x10^{-4}	66.8	0.0092	47.9	0.0529	37.7
3.9x10^{-4}	65.0	0.0112	46.7	0.0600	37.6
6.5x10^{-4}	62.6	0.0137	45.4	0.0693	37.6
9.1x10^{-4}	60.2	0.0163	44.1	0.0784	37.3
0.0014	58.1	0.0213	42.4	0.0917	37.0

Table 4.2 – Continued

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
[NaBen] = 0.003 mol kg^{-1}					
0.0019	56.6	0.0263	40.7	0.1133	36.8
0.0030	54.5	0.0312	39.5	0.1340	37.0
0.0040	53.0	0.0361	38.5		
0.0056	51.0	0.0410	38.0		
[NaBen] = 0.005 mol kg^{-1}					
1.0x10^{-4}	67.3	0.0051	50.4	0.0648	36.3
2.1x10^{-4}	63.0	0.0062	49.2	0.0788	36.3
4.1x10^{-4}	62.7	0.0076	47.8	0.0958	36.4
8.3x10^{-4}	59.9	0.0096	45.9	0.1120	36.6
0.0012	58.2	0.0137	44.0	0.1426	36.2
0.0019	55.9	0.0216	39.9	0.1710	35.9
0.0025	55.2	0.0314	37.9	0.2098	35.9
0.0033	53.3	0.0409	37.1	0.2556	35.7
0.0041	52.2	0.0521	36.9	0.3051	35.7
[NaBen] = 0.010 mol kg^{-1}					
5.4x10^{-5}	71.5	0.0022	53.2	0.0275	37.3
1.1x10^{-4}	68.2	0.0032	51.0	0.0323	37.0
1.6x10^{-4}	63.8	0.0042	49.2	0.0370	37.0
2.1x10^{-4}	64.4	0.0063	46.1	0.0425	36.9
3.0x10^{-4}	61.4	0.0084	44.0	0.0479	36.6
4.1x10^{-4}	60.7	0.0115	41.5	0.0550	36.5
6.2x10^{-4}	58.9	0.0156	39.4	0.0635	36.2
9.4x10^{-4}	58.2	0.0196	38.2		
0.0015	55.3	0.0236	37.6		

Table 4.2 – Continued

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
[NaBen] = 0.015 mol kg^{-1}					
$4.7\text{x}10^{-5}$	72.2	0.0026	50.7	0.0212	37.0
$9.3\text{x}10^{-5}$	68.4	0.0035	48.6	0.0246	36.7
$1.4\text{x}10^{-4}$	64.3	0.0053	44.7	0.0280	36.6
$1.9\text{x}10^{-4}$	61.5	0.0072	42.9	0.0321	36.6
$2.6\text{x}10^{-4}$	60.0	0.0081	42.1	0.0369	36.4
$3.5\text{x}10^{-4}$	59.8	0.0099	40.7	0.0432	36.1
$6.3\text{x}10^{-4}$	57.9	0.0125	38.9	0.0508	35.9
0.0011	55.9	0.0160	37.6		
0.0017	53.1	0.0178	37.6		
[NaBen] = 0.02 mol kg^{-1}					
$4.3\text{x}10^{-5}$	72.2	0.0023	49.8	0.0205	37.1
$8.7\text{x}10^{-5}$	69.8	0.0032	47.9	0.0236	36.6
$1.3\text{x}10^{-4}$	65.2	0.0049	44.5	0.0267	36.5
$1.7\text{x}10^{-4}$	62.3	0.0066	41.9	0.0305	36.6
$2.6\text{x}10^{-4}$	59.6	0.0083	40.4	0.0350	35.8
$4.3\text{x}10^{-4}$	57.5	0.0108	38.4	0.0408	35.4
$6.9\text{x}10^{-4}$	57.0	0.0132	37.7	0.0478	35.3
0.0011	53.6	0.0157	37.4		
0.0016	51.9	0.0181	37.0		
[NaBen] = 0.05 mol kg^{-1}					
$3.7\text{x}10^{-5}$	73.0	0.0010	52.2	0.0100	38.1
$7.5\text{x}10^{-5}$	70.6	0.0014	49.5	0.0121	37.4
$1.1\text{x}10^{-4}$	64.3	0.0020	47.3	0.0149	37.6
$1.5\text{x}10^{-4}$	62.0	0.0027	45.3	0.0176	37.0
$2.1\text{x}10^{-4}$	58.7	0.0035	43.2	0.0210	36.7
$2.8\text{x}10^{-4}$	57.0	0.0049	40.5	0.0243	36.5
$4.3\text{x}10^{-4}$	55.5	0.0064	39.0	0.0282	36.2

Table 4.2 – Continued

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
		[NaBen] = 0.05 mol kg^{-1}			
6.6x10^{-4}	52.9	0.0078	38.6	0.0333	36.0
		[NaBen] = 0.10 mol kg^{-1}			
3.7x10^{-5}	72.3	7.0x10^{-4}	49.9	0.0060	38.6
7.3x10^{-5}	71.5	0.0010	48.8	0.0074	38.5
1.1x10^{-4}	67.3	0.0014	46.1	0.0088	38.2
1.5x10^{-4}	62.3	0.0018	44.6	0.0109	37.8
2.0x10^{-4}	59.4	0.0024	42.8	0.0136	37.1
2.6x10^{-4}	56.1	0.0031	41.2	0.0170	37.0
3.3x10^{-4}	55.1	0.0038	40.0	0.0216	36.3
4.8x10^{-4}	52.0	0.0045	39.4	0.0280	36.3
		[NaBen] = 0.15 mol kg^{-1}			
5.0x10^{-5}	71.8	9.4x10^{-4}	47.4	0.0056	39.3
9.9x10^{-5}	67.2	0.0013	44.8	0.0064	39.0
1.5x10^{-4}	60.4	0.0018	44.1	0.0073	39.0
2.0x10^{-4}	56.5	0.0024	42.5	0.0082	39.0
2.7x10^{-4}	53.5	0.0030	41.4	0.0092	38.8
3.5x10^{-4}	53.4	0.0036	40.7	0.0111	38.6
4.5x10^{-4}	51.3	0.0042	39.7	0.0139	37.9
6.4x10^{-4}	50.5	0.0049	39.5		
		[NaBen] = 0.20 mol kg^{-1}			
3.9x10^{-5}	70.1	9.1x10^{-4}	50.5	0.0053	39.9
7.8x10^{-5}	67.4	0.0011	47.9	0.0061	39.6
1.2x10^{-4}	64.1	0.0015	46.0	0.0068	39.4
1.6x10^{-4}	61.3	0.0018	45.2	0.0076	38.9
2.0x10^{-4}	60.3	0.0024	43.9	0.0083	38.9
2.8x10^{-4}	58.6	0.0031	41.2	0.0098	38.8

Table 4.2 – Continued

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
		[NaBen] = 0.20 mol kg^{-1}			
4.4x10^{-4}	56.5	0.0038	40.9	0.0120	38.2
6.7x10^{-4}	52.4	0.0045	40.2		
		[NaBen] = 0.25 mol kg^{-1}			
3.7x10^{-5}	71.1	7.0x10^{-4}	48.8	0.0052	40.7
7.3x10^{-5}	69.4	9.9x10^{-4}	47.7	0.0059	40.8
1.1x10^{-4}	66.0	0.0014	45.9	0.0066	40.6
1.5x10^{-4}	61.8	0.0018	45.2	0.0080	39.8
2.0x10^{-4}	58.4	0.0024	43.3	0.0101	39.4
2.6x10^{-4}	55.4	0.0030	42.0	0.0122	38.9
3.3x10^{-4}	53.8	0.0037	41.3		
4.8x10^{-4}	52.0	0.0045	40.8		
		[NaBen] = 0.31 mol kg^{-1}			
4.2x10^{-5}	68.0	8.1x10^{-4}	49.6	0.0045	41.2
8.4x10^{-5}	62.1	0.0011	48.0	0.0050	41.3
1.3x10^{-4}	60.1	0.0016	45.9	0.0055	41.1
1.7x10^{-4}	58.1	0.0021	44.5	0.0062	41.1
2.3x10^{-4}	55.5	0.0026	43.0	0.0071	40.5
3.1x10^{-4}	54.6	0.0032	42.0	0.0087	40.1
3.9x10^{-4}	53.0	0.0036	41.9	0.0111	39.5
5.6x10^{-4}	51.7	0.0040	41.7		

Table 4.3 – Specific Conductance (κ) values of CPC in aqueous Sodium Salicylate solution at 298 K

[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}
[NaSal] = 0.0 mol kg^{-1}					
0	1.9914	0.3374	39.117	0.8941	93.850
0.0161	5.1118	0.4070	46.020	0.9477	97.333
0.0428	8.6701	0.4819	53.733	1.0172	101.31
0.0696	11.784	0.5783	63.125	1.0975	105.20
0.0964	14.782	0.6533	70.602	1.1564	108.07
0.1446	19.527	0.7710	82.420	1.2206	110.77
0.1821	23.514	0.8192	87.053	1.2741	113.29
0.2303	28.652	0.8567	90.525		
0.2731	33.024	0.8727	92.167		
[NaSal] = 2.0 x 10^{-4} mol kg^{-1}					
0	18.069	0.0537	22.045	0.1199	27.081
0.0021	17.517	0.0614	22.732	0.1268	27.584
0.0053	17.800	0.0690	23.332	0.1353	28.151
0.0094	18.105	0.0766	23.964	0.1438	28.712
0.0146	18.546	0.0840	24.521	0.1520	29.275
0.0208	19.097	0.0914	25.047	0.1602	29.833
0.0279	19.709	0.0986	25.581	0.1683	30.382
0.0360	20.366	0.1058	26.060	0.1841	31.511
0.0459	21.329	0.1129	26.586	0.1994	32.592
[NaSal] = 3.0 x 10^{-4} mol kg^{-1}					
0	21.050	0.0279	23.420	0.0749	27.230
0.0009	21.080	0.0329	23.850	0.0818	27.680
0.0027	21.330	0.0388	24.320	0.0894	28.170
0.0053	21.510	0.0446	24.820	0.0969	28.630
0.0089	21.860	0.0503	25.290	0.1043	29.100
0.0132	22.220	0.0559	25.770	0.1115	29.540

Table 4.3 – Continued

[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}
[NaSal] = 3.0 x 10^{-4} mol kg^{-1}					
0.0176	22.600	0.0623	26.240	0.1258	30.350
0.0227	23.020	0.0687	26.750	0.1396	31.160
[NaSal] = 5.0 x 10^{-4} mol kg^{-1}					
0	41.458	0.0147	42.858	0.0455	45.300
0.0007	41.534	0.0181	43.188	0.0522	45.318
0.0014	41.659	0.0216	43.506	0.0589	46.117
0.0021	41.721	0.0250	43.820	0.0722	46.898
0.0035	41.828	0.0285	44.078	0.0853	47.684
0.0049	41.951	0.0319	44.321	0.0983	48.489
0.0063	42.065	0.0353	44.537	0.1174	49.595
0.0091	42.361	0.0387	44.786	0.1362	50.934
0.0119	42.615	0.0421	45.046		
[NaSal] = 0.001 mol kg^{-1}					
0	81.747	0.0091	82.587	0.0300	84.142
0.0004	81.812	0.0105	82.688	0.0328	84.323
0.0007	81.842	0.0123	82.824	0.0362	84.585
0.0015	81.953	0.0141	82.969	0.0397	84.786
0.0022	82.044	0.0159	83.151	0.0431	84.861
0.0033	82.144	0.0181	83.327	0.0465	85.017
0.0044	82.220	0.0202	83.483	0.0532	85.415
0.0055	82.280	0.0223	83.624	0.0598	85.747
0.0066	82.356	0.0248	83.795	0.0664	86.099
0.0077	82.466	0.0272	83.951	0.0728	86.386

Table 4.4 – Specific Conductance (κ) values of CPC in aqueous Sodium Benzoate solution at 298 K

[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}
		[NaBen] = 2.0 x 10^{-4} mol kg^{-1}			
0	15.087	0.2623	39.206	0.6403	70.015
0.0057	15.604	0.3041	43.058	0.6870	73.315
0.0170	16.649	0.3455	46.944	0.7330	76.552
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
0.0619	20.806	0.4267	54.077	0.8672	85.245
0.0951	23.837	0.4666	57.221	0.9536	90.378
0.1336	27.273	0.5060	60.203	1.0377	95.296
0.1770	31.280	0.5449	63.146	1.1195	100.23
0.2199	35.326	0.5930	66.701		
		[NaBen] = 3.0 x 10^{-4} mol kg^{-1}			
0	23.845	0.2062	43.672	0.5222	69.023
0.0073	24.484	0.2339	46.397	0.5738	72.704
0.0217	25.873	0.2615	49.042	0.6249	76.220
0.0434	27.961	0.2889	51.481	0.6880	80.483
0.0649	30.042	0.3230	54.185	0.7502	84.624
0.0935	32.713	0.3568	56.869	0.8115	88.584
0.1219	35.496	0.3903	59.406	0.8720	92.485
0.1502	38.210	0.4303	62.408	0.9316	96.137
0.1783	40.907	0.4699	65.283		

Table 4.4 – Continued

[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}
[NaBen] = 5.0 x 10^{-4} mol kg^{-1}					
0	40.795	0.0444	45.014	0.1793	57.802
0.0024	40.888	0.0524	45.712	0.1994	59.457
0.0048	41.212	0.0614	46.620	0.2191	61.082
0.0071	41.441	0.0727	47.684	0.2481	63.256
0.0107	41.757	0.0838	48.765	0.2763	65.299
0.0154	42.198	0.0948	49.872	0.3127	67.835
0.0212	42.758	0.1057	50.964	0.3479	70.220
0.0271	43.275	0.1165	51.975	0.3902	73.078
0.0329	43.847	0.1378	53.923	0.4307	75.996
0.0386	44.446	0.1587	55.875	0.4772	78.995
[NaBen] = 0.001 mol kg^{-1}					
0	78.909	0.0276	81.480	0.1224	90.175
0.0009	78.959	0.0344	82.139	0.1374	91.281
0.0018	79.060	0.0428	82.854	0.1522	92.308
0.0035	79.171	0.0511	83.603	0.1738	93.767
0.0052	79.347	0.0593	84.393	0.1949	95.131
0.0079	79.583	0.0675	85.128	0.2221	96.922
0.0105	79.910	0.0755	85.968	0.2548	98.788
0.0139	80.288	0.0835	86.768	0.2862	100.88
0.0174	80.509	0.0915	87.624	0.3162	102.72
0.0225	81.007	0.1071	89.047	0.3507	104.87

Table 4.5 - Critical Micelle Concentration Values of CPC in Aqueous NaSal and NaBen Solutions at 25 °C from Surface Tension and Conductance (in the parentheses) Data

[NaSal] / mol kg^{-1}	Cmc x 10^4/ mol kg^{-1}	ΔG^0_{hc} / kJ mol^{-1}	[NaBen] / mol kg^{-1}	Cmc x 10^4 / mol kg^{-1}	ΔG^0_{hc} / kJ mol^{-1}
0.0	8.971 (8.875)	-27.3			
2 x 10^{-5}	4.263 -	-29.2			
5 x 10^{-5}	2.186 -	-30.8			
1 x 10^{-4}	1.259 -	-32.2	1 x 10^{-4}	5.690	-28.5
2 x 10^{-4}	0.817 (0.818)	-33.3	2 x 10^{-4}	3.828 (4.577)	-29.4
3 x 10^{-4}	0.518 (0.612)	-34.4	3 x 10^{-4}	2.612 (3.210)	-30.4
5 x 10^{-4}	0.326 (0.346)	-35.5	5 x 10^{-4}	1.545 (1.886)	-31.7
0.001	0.262 (0.280)	-36.1	0.001	1.012 (1.135)	-32.7
0.003	0.094	-38.6	0.003	0.428	-34.9
0.005	0.089	-38.8	0.005	0.338	-35.5
0.010	0.043	-40.6	0.010	0.217	-36.5
0.015	0.040	-40.7	0.015	0.151	-37.4
0.020	0.028	-41.6	0.020	0.141	-37.6
0.050	0.015	-43.1	0.050	0.067	-39.5
0.100	0.014	-43.3	0.100	0.049	-40.3
0.150	0.010	-44.2	0.150	0.042	-40.6
0.200	0.009	-44.5	0.201	0.040	-40.8
0.251	0.008	-44.8	0.250	0.038	-41.2
0.316	0.007	-45.0	0.305	0.031	-41.4

Table 4.6 - Experimental Values of Viscosity of CPC + NaSal System in Aqueous Medium at 25 °C

[CPC] = 7 x 10^{-7} mol kg^{-1}		[CPC] = 9 x 10^{-4} mol kg^{-1}		[CPC]/[NaSal] = 1	
[NaSal] / mol kg^{-1}	Viscosity / cP	[NaSal] / mol kg^{-1}	Viscosity / cP	[NaSal] / mol kg^{-1}	Viscosity / cP
0	0. 895	0	0. 896	0.001	0.927
0.01	0. 899	0.01	1.001	0.005	2.85
0.05	0. 909	0.05	1.013	0.01	30.4
0.10	0. 926	0.10	1.035		
0.20	0. 959	0.20	1.032		
0.25	0. 977	0.25	1.006		

Table 4.7 - Calculated Surface Excess Values of CPC in Aqueous NaSal and NaBen Solutions at 298 K

[NaSal] / mol kg^{-1}	$\beta_{\mathrm{lad}} = 0$	$\beta_{\mathrm{lad}} = 0.5$	$\beta_{\mathrm{lad}} = 1$	[NaBen] / mol kg^{-1}	$\beta_{\mathrm{lad}} = 0$	$\beta_{\mathrm{lad}} = 0.5$	$\beta_{\mathrm{lad}} = 1$
	Γ_{cmc} x 10^6 / mol m^{-2}				Γ_{cmc} x 10^6 / mol m^{-2}		
0.0	3.39	2.26	1.69				
2 x 10^{-5}	3.22	2.15	1.61	1 x 10^{-4}	3.01	2.01	1.51
5 x 10^{-5}	3.02	2.01	1.51	2 x 10^{-4}	2.73	1.82	1.37
1 x 10^{-4}	2.84	1.90	1.42	3 x 10^{-4}	2.79	1.86	1.39
2 x 10^{-4}	2.72	1.81	1.36	5 x 10^{-4}	2.55	1.70	1.27
3 x 10^{-4}	2.59	1.72	1.29	0.001	2.58	1.72	1.29
5 x 10^{-4}	2.57	1.71	1.28	0.003	2.78	1.85	1.39
0.001	2.66	1.78	1.33	0.005	2.84	1.90	1.42
0.003	2.45	1.63	1.23	0.010	2.87	1.92	1.44
0.005	2.94	1.96	1.47	0.015	2.91	1.94	1.46
0.010	3.21	2.14	1.60	0.020	2.87	1.92	1.44
0.015	3.24	2.16	1.62	0.050	2.87	1.91	1.43
0.020	3.09	2.06	1.54	0.100	2.37	1.58	1.19
0.050	5.22	3.48	2.61	0.150	2.21	1.47	1.11
0.100	5.82	3.88	2.91	0.201	2.37	1.58	1.18
0.150	4.64	3.10	2.32	0.250	2.33	1.55	1.16
0.200	3.56	2.37	1.78	0.305	2.28	1.52	1.14
0.251	3.73	2.49	1.87				
0.316	2.86	1.90	1.43				

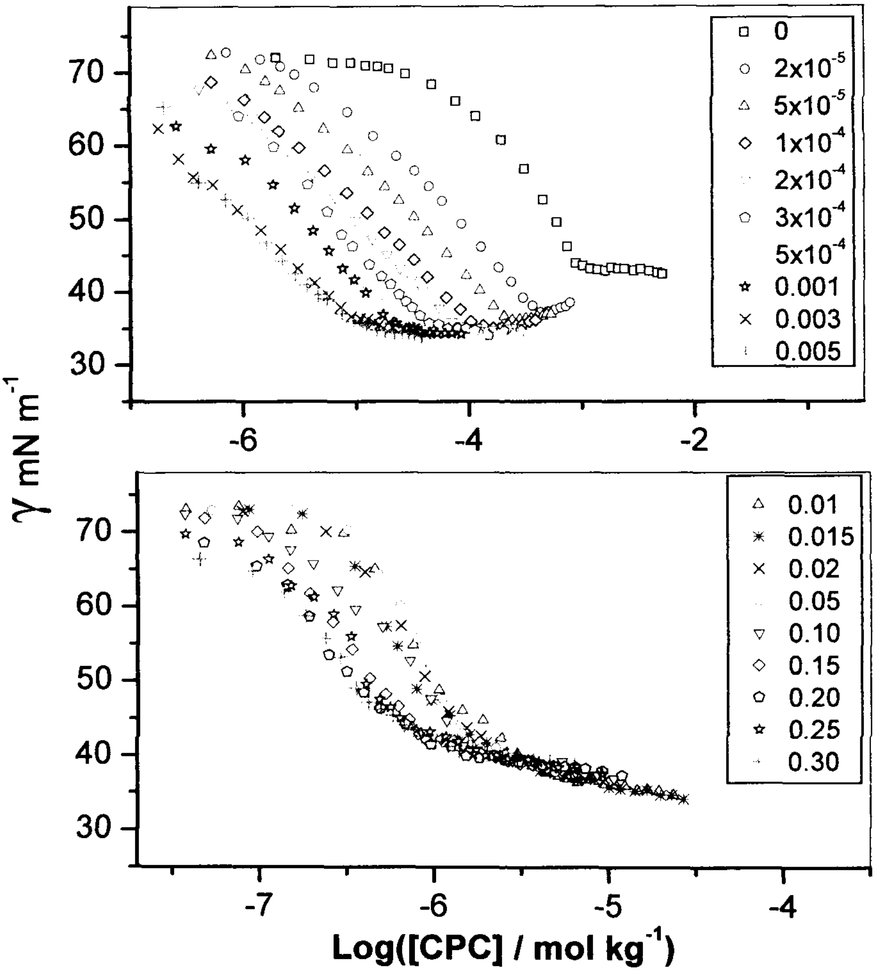

Fig. 4.1. Variation of surface tension of CPC + NaSal with CPC concentration in aqueous medium at 25 °C. Each plot corresponds to a particular concentration of NaSal as indicated in the insets.

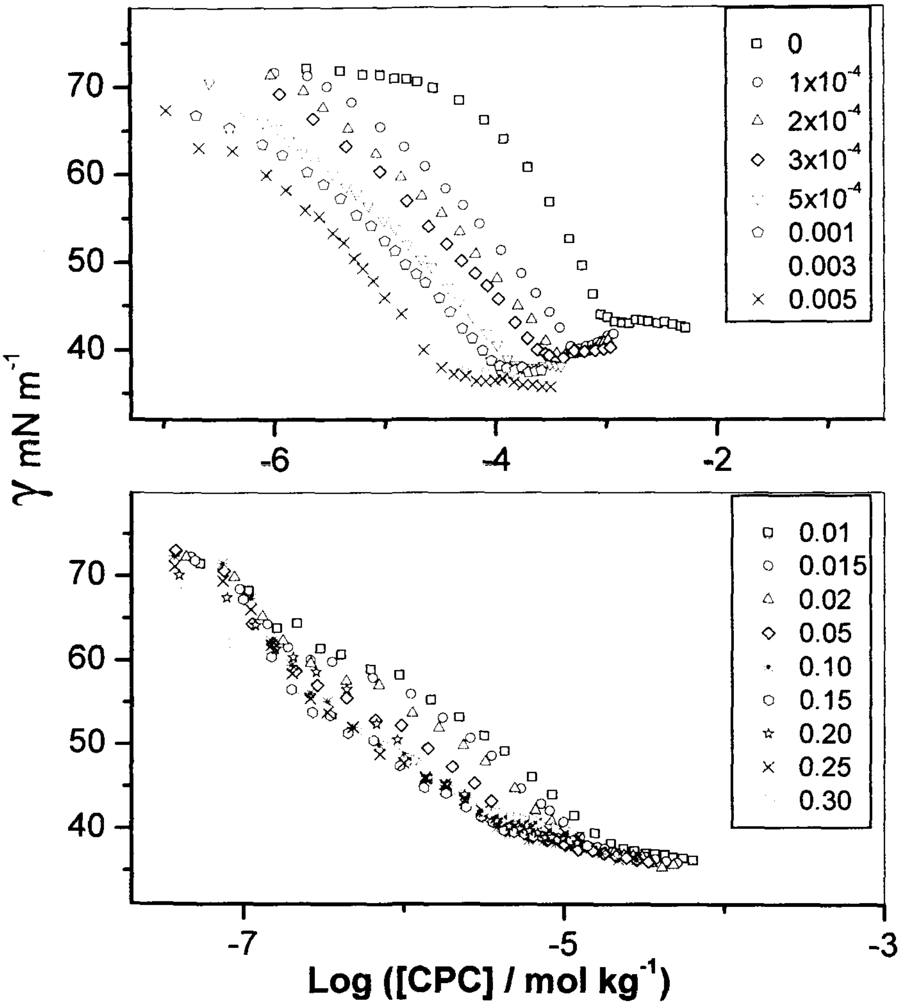

Fig. 4.2. Variation of surface tension of CPC + NaBen with CPC concentration in aqueous medium at 25 °C. Each plot corresponds to a particular concentration (in mol kg^{-1}) of NaBen as indicated in the insets.

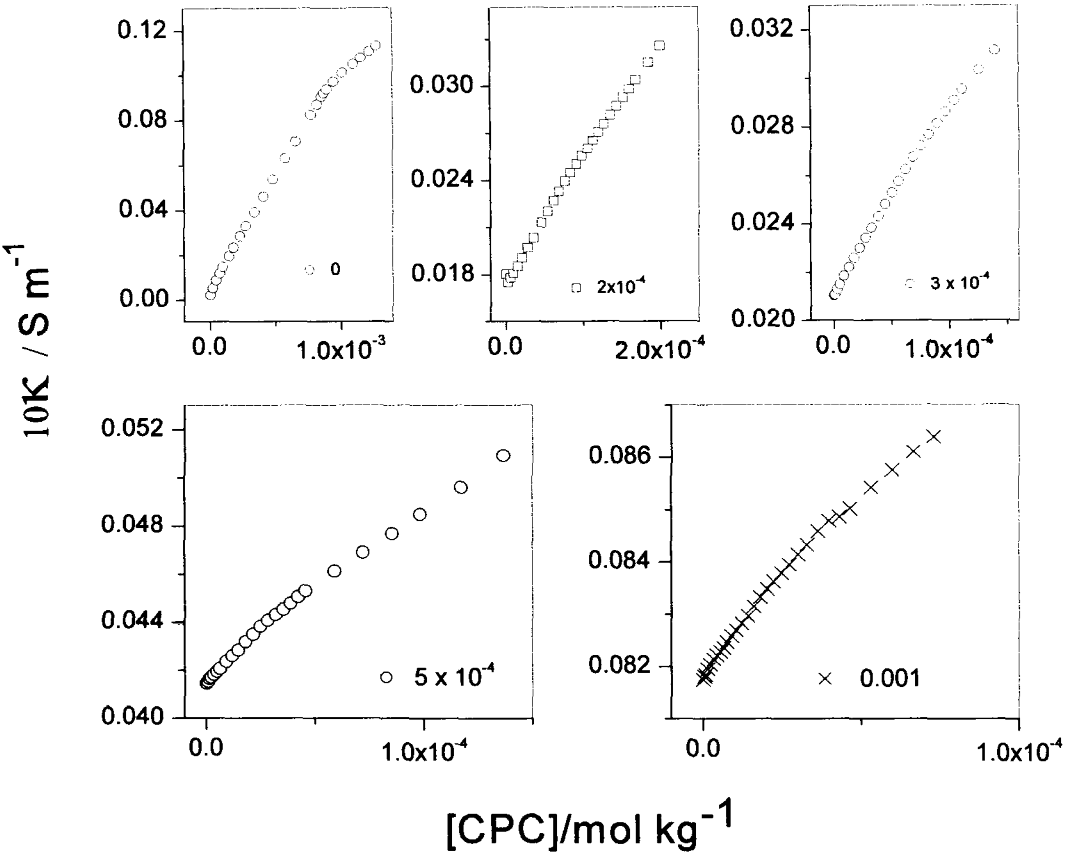

Fig. 4.3. Conductance isotherms of CPC + NaSal at 25 °C. Salt concentrations in mol kg^{-1} are indicated in the insets.

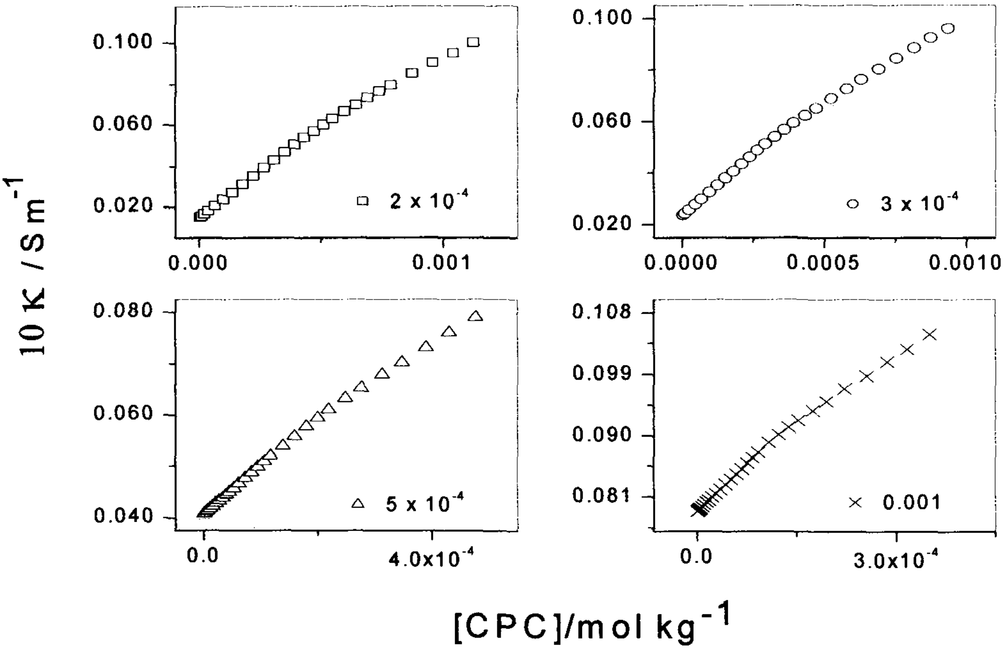

Fig. 4.4. Conductance isotherms of CPC + NaBen at 25 °C. Salt concentrations in mol kg^{-1} are indicated in the insets.

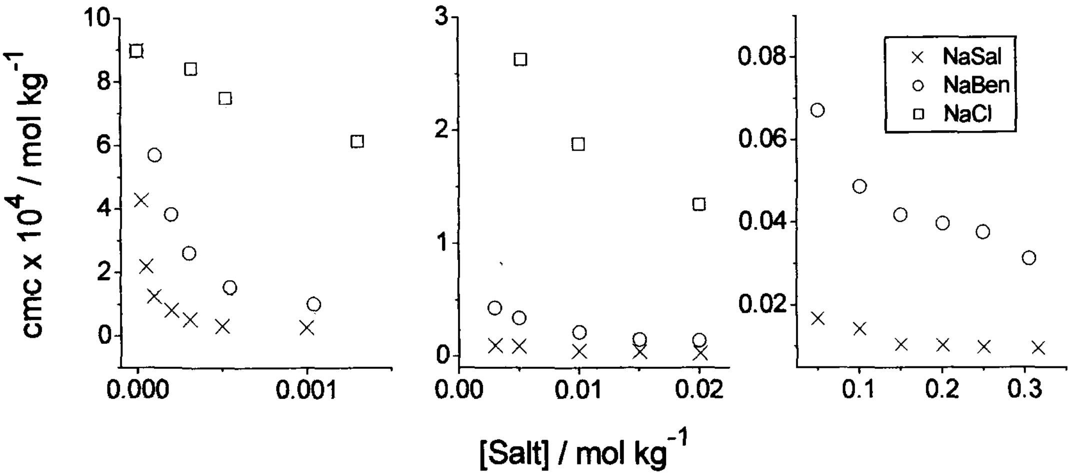

Fig. 4.5. Variation of cmc of CPC with salt (indicated in the inset) concentration at 25 °C.

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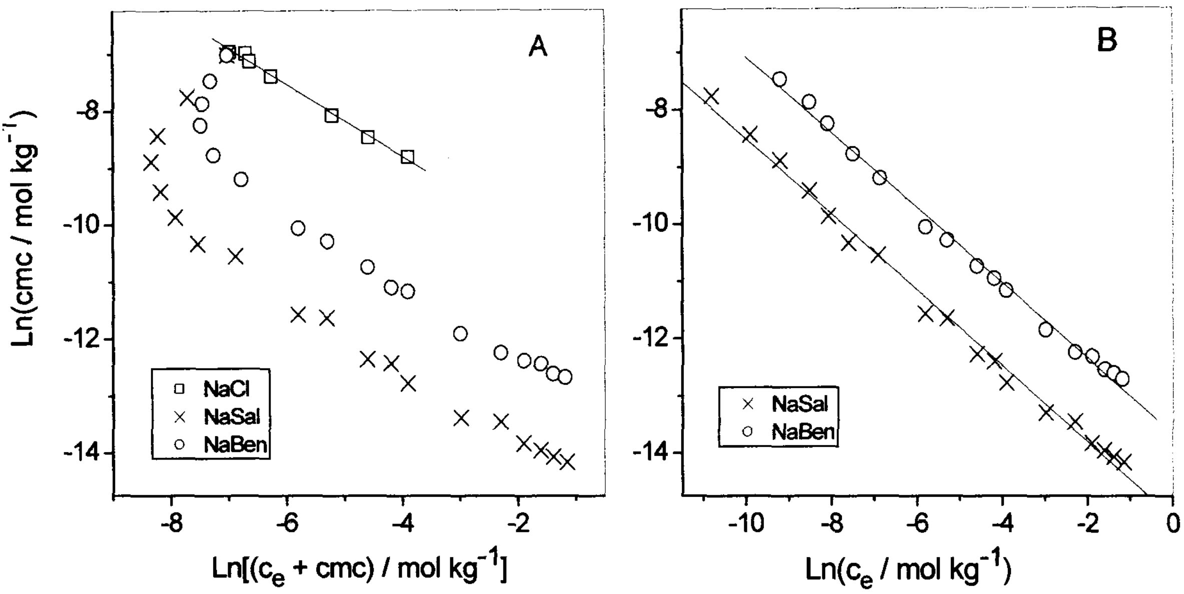

Fig. 4.6. (a) CH plots for CPC + NaCl, CPC + NaSal and CPC + NaBen systems (layer A) and (b) modified CH plots for CPC + NaSal and CPC + NaBen (layer B) systems at 25 °C

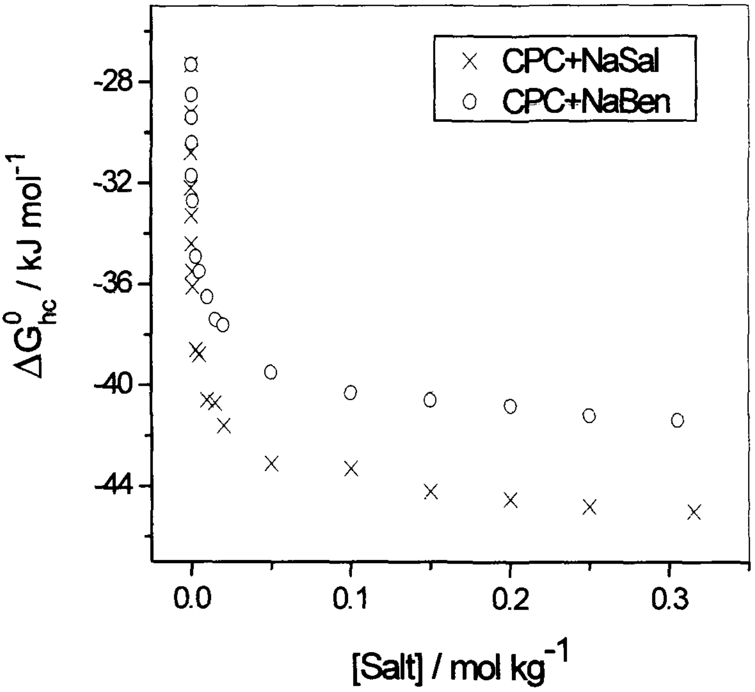

Fig. 4.7. Variation of ΔG^0_{hc} of CPC with concentration of NaSal and NaBen in aqueous medium at 25 °C

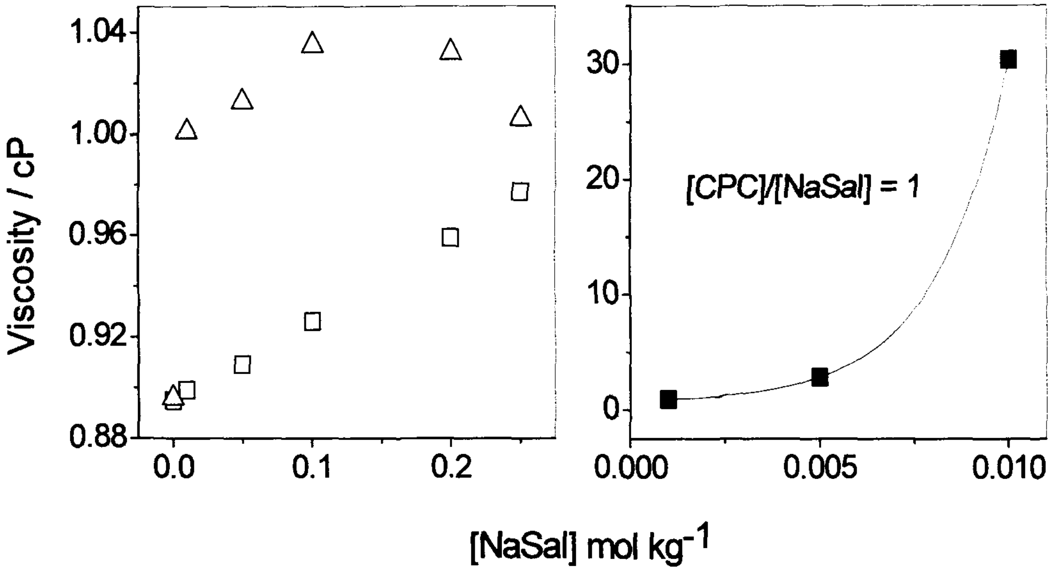

Fig. 4.8. Viscosity of aqueous solution of CPC as a function of NaSal concentration at 25 °C. Concentration of CPC = 7 x 10^{-7} (open square) and 9 x 10^{-4} (open triangles) mol kg^{-1}.

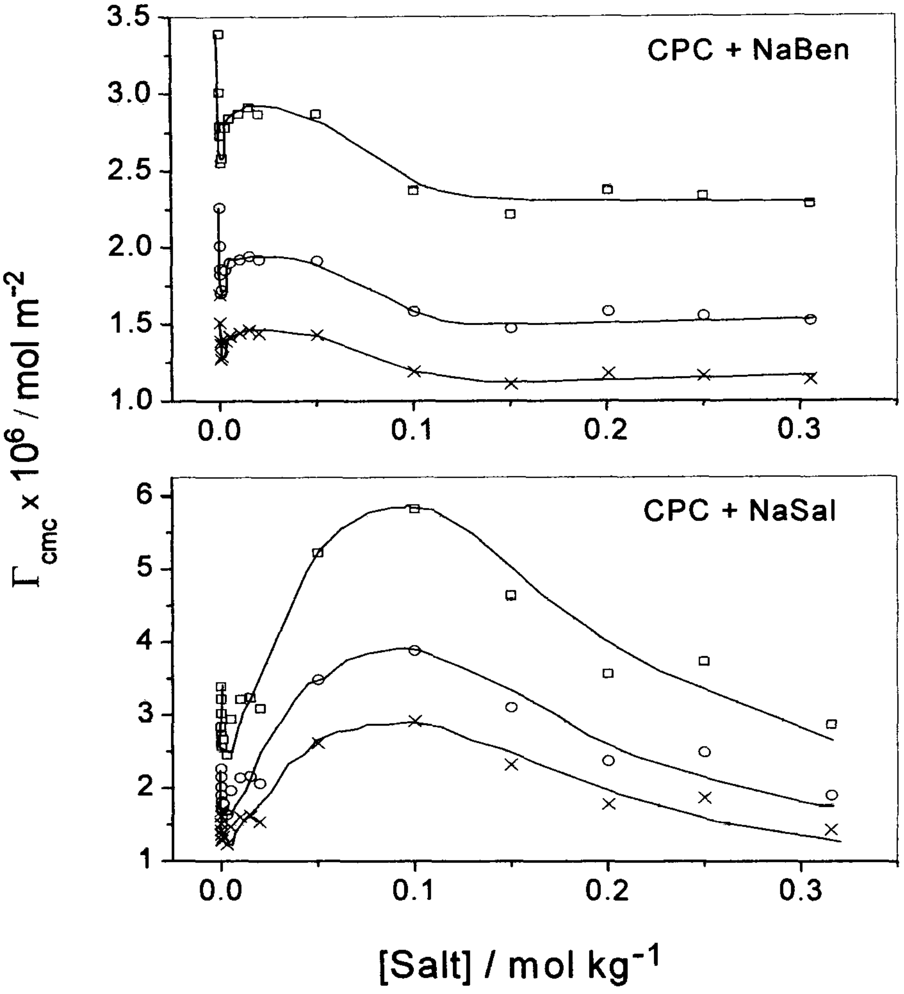

Fig. 4.9. Surface excess of CPC in aqueous medium as a function NaSal and NaBen concentration calculated for $\beta_{1ad} = 0$ (open squares), 0.5 (open circles) and 1 (crosses) at 25 °C. Lines are drawn to guide the eyes.

CHAPTER 5

Adsorption and Aggregation Behaviours of Cetylpyridinium Chloride in Aqueous Sodium Bromide and Tetrabutylammonium Bromide Solutions

5.1 INTRODUCTION

We studied the adsorption and aggregation behaviours of CPC in aqueous medium in the presence of different coions in chapter 3 and in the presence of different coions and counter ions in chapter 4. In continuation of our effort to study the adsorption and micellization characteristics of CPC in the presence of electrolytes, in this chapter we have made surface tension and conductance measurements of aqueous solutions of CPC at 30 °C in the presence of different pairs of coions and counter ions. The systems studied are CPC + NaBr (coion pair: $CP^+ + Na^+$; counter ion pair: $Cl^- + Br^-$) and CPC + TBAB (coion pair: $CP^+ + TBA^+$; counter ion pair: $Cl^- + Br^-$). TBAB represents tetrabutylammonium bromide. We chose the salts NaBr and TBAB in view of the following reasons: (1) Bromide counterion is reported to influence the micellization of cationic surfactants differently from chloride counterion.[1-4] (2) TBAB is a surface active electrolyte[5] and its effect on SDS is different from other electrolytes.[6-9] TBAB induces clouding in SDS and produces sphere-to-rod shape transition of SDS micelles at much lower concentration than that of other electrolytes.[6-9] It is therefore worthwhile to study the influence of this bulky coion on the aggregation and micellization of CPC and compare it with that of NaBr.

5.2 EXPERIMENTAL

CPC (Aldrich, > 99.0 %), NaBr (Merck, > 99.5 %) and TBAB (Aldrich, 99%) were used as received. Millipore water was used for preparing the solutions. Surface tension and conductance measurements were made as described in chapter

2. Temperature of the solutions was maintained at 30 °C by using Haake DC10 circulation bath.

5.3 RESULTS AND DISCUSSION

Surface tension and conductance. Surface tension, γ, values of CPC in aqueous NaBr and TBAB solutions at 303 K are given in Tables 5.1a and 5.1b, respectively. The plots of γ versus log c (c is the concentration of CPC) are shown in Fig. 5.1. It can be seen from Fig. 5.1 that the surface tension values of CPC in aqueous NaBr and TBAB solutions are almost same up to 0.02 mol kg^{-1} electrolyte concentration. Above 0.02 mol kg^{-1} electrolyte concentration, surface tension of CPC in NaBr and TBAB solutions are almost same if the CPC concentration is more than 0.003 mmol kg^{-1}, but below this CPC concentration surface tension in TBAB solution becomes lower than in NaBr solution. Such surface tension behaviour of CPC in TBAB solution is due to surface activity of TBAB. The experimental values of specific conductivity, κ, of CPC at 303 K in aqueous NaBr and TBAB media are presented in Table 5.2a and 5.2b, respectively. The plots of κ versus c are shown in Fig. 5.2.

Critical micelle concentration. The cmc (c_0) values obtained from surface tension and conductance data are listed in Table 5.3. Values of cmc obtained from γ and κ data are in agreement. The variation of cmc with electrolyte concentration is shown in Fig. 5.3. In Fig. 5.3, we have also shown the variation of cmc of CPC with NaCl concentration (data from chapter 3). It is clear from Fig. 5.3 that bromide counterion decreases cmc of CPC more than chloride counterion as reported[4] by others also. This indicates that the added bromide counterions replace the chloride counterions at the micellar surface. Similar conclusion was made by Aswal and Goyal[1,2] from small angle neutron scattering (SANS) experiments on cetyltrimethylammonium chloride (CTAC) + KBr system. Lower hydration of bromide compared to chloride is considered to be the reason for enhancement of micellization in the presence of bromide. From Fig. 5.3 it is clear that the coions, sodium and tetrabutylammonium (TBA^+) ions, do not have any effect on the cmc of CPC.

Counter ion binding constant. The counter ion binding constant, β, of an ionic surfactant is commonly determined by using the Corrin-Harkins (CH) relation (equation (4.1)). Since the systems under study have mixed counter ions, chloride and bromide, the CH relation as such is not applicable. This has been pointed out in the preceding chapter for the CPC + NaSal and CPC + NaBen. The CH plots for the CPC + NaBr and CPC + TBAB systems are shown in Fig. 5.4. Deviation from linearity at low electrolyte concentration (c_e) can be observed in Fig. 5.4 as it was observed in the case of CPC + NaSal and CPC + NaBen systems (chapter 4). However, the deviation at low electrolyte concentration in CPC + NaBr and CPC + TBAB systems is not so prominent as in CPC + NaSal and CPC + NaBen systems. Nevertheless, the CH relation is applicable when the system has single counter ion only. Therefore, we used the modified CH equation derived in chapter 4, which is of the form

$$\ln c_0 = A' - B \ln c_e \qquad (5.1)$$

where $A' = \Delta G^0_m/[(1+\beta_1)RT]$ and $B = \beta_2/(1+\beta_1)$. β_1 and β_2 are the binding constants for the chloride and bromide counter ions, respectively. The other terms involved in

Eq. (5.1) are defined in chapter 4. Eq. (5.1) is applied to the systems under study by plotting $\ln c_0$ verus $\ln c_e$ in Fig. 5.5. The values of B determined from Fig. 5.5 were found to be 0.62 and 0.61 in the cases of NaBr and TBAB. Thus, the value of B is not influenced by the Na^+ or TBA^+ coions. Since $\beta_2 = B(1+\beta)/(1+B)$, the values of β_2 as well as β_1 can be determined if we know the value of β. Using the value of B from Fig. 5.5, we get $\beta_2 = 0.38(1+\beta)$. Therefore, β must be more than 0.61, otherwise value of β_2 becomes unacceptable as it exceeds β value. As pointed out in chapter 4, the value of B provides the lower limit to the value of β. It may be noted that the lower limit to the value of β for chloride and bromide combination of counter ions is less than that for the mixture of chloride and salicylate or benzoate counter ions.

Mixed electrolyte model. In order to estimate β of CPC in the presence of chloride and bromide counter ions, we applied the mixed electrolyte model (MEM) to the conductance data. The details of the MEM are described in chapter 3. At 30 °C, the value of Λ_1^0 of CPC in water or electrolyte solution was estimated from the experimental κ data by extrapolation and was taken as equal to 114.9×10^{-4} S m^2 eq^{-1}. The value of λ_+^0 of CP ion at 30 °C was calculated by subtracting from Λ_1^0 the literature[10] value of λ_-^0 of Cl^- (85.4×10^{-4} S m^2 eq^{-1}). For dielectric constant (ε) and viscosity (η) at 30 °C we substituted the values 76.6 and 8.0×10^{-3} P, respectively. Presuming the micelle to be spherical, the value of λ_+^0 for the cationic micelle (λ_{+mic}^0) was computed using the Stokes–Einstein relation

$$\lambda_{+mic}^0 = \frac{z_n e_0 F}{6\pi\eta r_n} \qquad (5.2)$$

where F is the Faraday constant. The charge on the micelle is $z_+ = z_n = n(1\text{-}\beta)$, where n is the aggregation number. In the case of ionic surfactant solution containing single counter ion, the value of Λ_n^0 is calculated by adding the value of λ_-^0 of the counter ion to λ_{+mic}^0. In the present system, the cationic micelle consists of mixed counter ions, chloride and bromide. Since the difference (1.8×10^{-4} S m^2 eq^{-1}) in the values of λ_-^0 of Cl^- and Br^- (87.2×10^{-4} S m^2 eq^{-1})[10] is not much, we took the value of λ_-^0 approximately as equal to the average of the λ_-^0 values of Cl^- and Br^- (= 86.25×10^{-4} S m^2 eq^{-1}) and this average value was added to λ_{+mic}^0 to get the value of Λ_n^0. Similarly, since the Stokes ionic radii of Cl^- (1.21 Å) and Br^- (1.18 Å) are very close[10], the values of a_1 and a_n were determined by adding an average Stokes ionic radius value (1.195 Å) to r_1 and r_n, respectively. The ionic strength of the surfactant solution was determined as explained in chapter 3. The data fitting was done by iterating the values of cmc, β and n till best fits were obtained, unlike in chapter 3 wherein cmc and β were kept constant and only n was obtained by iteration. The best-fit values of these three parameters are given in Table 5.4. The cmc values obtained from the MEM are comparable with the cmc values given in Table 5.3. By this analysis we get β corresponding to each electrolyte concentration and, by taking an average (β_{av}) of such β values in each electrolyte media, we got $\beta_{av} = 0.73$ in NaBr and 0.74 in TBAB solutions. Using this average value of β, we obtained $\beta_2 = 0.66$ and $\beta_1 = 0.08$. Therefore, added bromide ion replaces chloride from CPC micelle and preferentially binds to the micelle. The evaluation of β, β_1 and β_2 thus confirms the replacement of bound chloride ions from the CPC micelle by bromide ions as inferred above to account for larger decrease in cmc on addition of bromide.

For comparison sake, the values of cmc, β and n of CPC in aqueous NaCl solution at 30 °C were also computed from the MEM by using the κ data given in chapter 3. The value of β_{av} for CPC in NaCl medium was found to be 0.66, which indicates that bromide binds more than chloride to the cetylpyridinium micelle. Similar observation has been reported from the SANS[1-4] and counter ion trapping studies[11,12] on CTAC, CTAB (cetyltrimethylammonium bromide) and CPC. This provides support to the above method of analyzing the data on surfactant systems containing mixed counter ions using the modified CH equation and the MEM. The values of n in the presence of NaBr and TBAB are comparable and are higher than the n values in the presence of NaCl. Higher values of n in the presence of bromide counterion compared to those in the presence of chloride counterion are in agreement with the results reported[4] from SANS study.

Free energy of micellization. The standard free energy of micellization, ΔG_m^0, per mole of monomer of CPC in the presence of electrolytes was calculated from the relation

$$\Delta G_m^0 = RT(1 + \beta)\ln X_{cmc} \qquad (5.3)$$

The standard state refers to the hypothetical standard state of unit mole fraction. X_{cmc} is the value of cmc in mole fraction unit. R and T represent the gas constant and absolute temperature, respectively. The values of ΔG_m^0 evaluated from Eq. (5.3) by using values of β_{av} are given in Table 5.5. The values of ΔG_m^0 are almost same in aqueous NaBr and TBAB media.

Surface excess. The values of surface excess, Γ_{cmc}, for CPC at the air-water interface near its cmc in the presence of NaBr and TBAB were calculated from the respective surface tension data using the expression[13,14]

$$\Gamma_{cmc} = -\frac{1}{RT}\left[\frac{1}{1+\frac{c_o}{c_o+c_e}}\right]\left(\frac{d\gamma}{d\ln c}\right)_{cmc} \qquad (5.4)$$

Eq. (5.4) has been applied by presuming that (i) the effect of chloride and bromide counter ions on the adsorption of CP^+ at the air – solution interface is same and (ii) the adsorption layer is electrically neutral. The value of the slope, $d\gamma/d\ln c$, at the cmc was determined by least-squares fitting the γ versus lnc data near the cmc to a linear equation. The values of Γ_{cmc} for CPC as a function of electrolyte concentration at 30 °C are given in Table 5.6. Fig. 5.6 shows the trend in the variation of Γ_{cmc} with NaBr and TBAB concentration. Up to 0.02 mol kg^{-1} electrolyte concentration Γ_{cmc} of CPC increases almost equally in NaBr and TBAB solutions. Above 0.02 mol kg^{-1} electrolyte concentration, Γ_{cmc} of CPC remains constant in NaBr solution, but decreases in TBAB solution with further increase in TBAB concentration. Thus, TBA^+ coion affects the adsorption of CPC when its concentration exceeds 0.02 mol kg^{-1}. Such an effect of coion on the surface excess of ionic surfactant has also been reported in the cases of AOT and SDS by the butyrate coion.[14,15] TBAB is a surface active electrolyte[5] and the surface tension isotherm of aqueous TBAB solution at 30 °C is shown in Fig. 5.6. This surface tension isotherm was fitted to a polynomial and the surface excess of TBAB was calculated (Table 5.6 and Fig. 5.6). It is clear from Fig. 5.6 that TBA^+ ion adsorbs considerably at the air – water interface. Therefore, in TBAB solution adsorption of

CPC takes place on a surface that already contains adsorbed TBA^+ coions. The adsorbed TBA^+ coions do not have any influence on the adsorption of CPC up to 0.02 mol kg^{-1} TBAB. Therefore, up to 0.02 mol kg^{-1} electrolyte concentration salting-out effect of electrolyte seems to be responsible for the enhancement of surface excess of CPC with addition of TBAB or NaBr. Above 0.02 mol kg^{-1} TBAB, due to electrostatic and steric effects the adsorbed TBA^+ coions hinder the adsorption of CPC thereby causing decrease of surface excess of CPC with increase in TBAB amount.

Surface area. The surface area covered per molecule of CPC at the air-solution interface, A_0, was estimated from the relation

$$A_o = \frac{1}{N_A \Gamma_{cmc}} \tag{5.5}$$

where N_A represents the Avagadro number. The values of A_0 are also listed in Table 5.6. With the addition of electrolyte up to 0.02 mol kg^{-1}, surface area covered per CPC molecule decreases. This is because added electrolytes enhances the adsorption of CPC at the air- water interface thereby decreasing the surface area covered per surfactant molecule and secondly, due to the increase in the number of counter ions in the Stern and diffuse layers, the electrostatic interaction between the head groups are better screened causing the adsorbed CPC molecules to come closer.

Free energy of adsorption. The standard free energy of adsorption (ΔG^0_{ad}) at the air – solution interface was calculated using the relation

$$\Delta G^0_{ad} = \Delta G^0_m - \frac{\pi_{cmc}}{\Gamma_{cmc}} \tag{5.6}$$

In Eq. (5.6) the surface pressure, $\pi_{cmc} = \gamma_o - \gamma_{cmc}$. γ_o and γ_{cmc} refer to the surface tensions of solvent and the surfactant solution at the cmc. The computed values of ΔG^0_{ad} are given in Table 5.5. On the addition of electrolyte, the value of ΔG^0_{ad} for CPC decreases and hence explains the observed increase in the surface activity of CPC. The relative values of ΔG^0_m and ΔG^0_{ad} indicate that adsorption is more spontaneous than aggregation.

5.4 CONCLUSIONS

Bromide counterion decreases cmc of CPC more than chloride counterion. A modified form of Corrin-Harkins equation was used to describe the variation of cmc with added electrolyte concentration in the presence of mixed counter ions. From the slope of this equation the lower limit to the value of β can be known and binding constants of the individual counter ions (β_1 and β_2) can be determined provided β is known. It is demonstrated that the MEM can be applied to analyze the conductance data of surfactant solution containing chloride and bromide as mixed counter ions. The value of β obtained from the MEM was then used to determine β_1 and β_2. By this treatment we could show that (i) bromide preferentially binds to CPC micelle by replacing chloride counter ion, (ii) bromide binding is more than chloride and (iii) aggregation number of CPC is higher in the presence of bromide. These observations are in accordance with the reported results of SANS and counter ion trapping studies. Na^+ and TBA^+ coions do not have any effect on the cmc of CPC, but TBA^+ affects the adsorption of CPC. In TBAB solution, adsorption of CPC takes place on a surface that already contains adsorbed TBA^+

coions and above 0.02 mol kg^{-1} TBAB the adsorbed TBA^+ hinders the adsorption of CPC due to electrostatic and steric effects.

5.5 REFERENCES

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Table 5.1a - Surface Tension (γ) values of CPC in aqueous Sodium Bromide solution at 303 K

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] x / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
[NaBr] = 0.0 mol kg^{-1}					
0	71.5	0.2084	53.1	1.0049	40.3
0.0166	69.6	0.2847	50.5	1.1163	40.2
0.0331	66.7	0.3589	48.5	1.2226	40.2
0.0495	64.8	0.5016	45.3	1.3242	40.0
0.0820	61.4	0.6370	43.6	1.4215	40.1
0.1141	58.3	0.7657	42.1	1.5147	40.3
0.1459	55.7	0.8882	40.3	1.6897	40.6
[NaBr] = 2.0 x10^{-4} mol kg^{-1}					
0.0124	67.1	0.2827	49.6	0.9130	40.6
0.0247	64.5	0.3326	47.9	0.9981	40.6
0.0431	61.8	0.3869	46.5	1.0802	40.7
0.0614	60.0	0.4400	45.3	1.1594	40.9
0.0855	57.7	0.4973	44.2	1.2358	40.9
0.1155	56.1	0.5683	42.5	1.3097	41.1
0.1509	54.3	0.6471	41.2	1.4500	41.5
0.1917	52.6	0.7328	40.2		
0.2376	49.9	0.8246	40.1		
[NaBr] = 3.0x10^{-4} mol kg^{-1}					
0.0024	71.2	0.1118	57.5	0.7574	41.4
0.0049	70.2	0.1504	55.3	0.8475	41.6
0.0098	68.7	0.1984	53.3	0.9368	41.7
0.0147	67.1	0.2938	49.6	1.0692	41.7
0.0244	65.1	0.3883	47.0	1.2429	42.2
0.0390	63.3	0.4819	44.6	1.4557	42.1
0.0585	61.1	0.5700	42.5	1.6638	42.2
0.0828	59.2	0.6664	41.2	1.8672	42.4

Table 5.1a – Continued

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC/ mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
[NaBr] = 5.0 x10^{-4} mol kg^{-1}					
0.0018	71.0	0.1280	55.4	0.8277	40.7
0.0037	70.7	0.1643	52.9	0.9614	40.8
0.0074	69.7	0.2364	49.9	1.0931	41.1
0.0147	67.9	0.3080	47.3	1.2552	41.1
0.0257	65.2	0.4143	44.6	1.3827	41.6
0.0404	62.8	0.5194	42.1	1.5083	41.6
0.0624	60.4	0.6233	40.6		
0.0916	58.2	0.7261	40.4		
[NaBr] = 0.001 mol kg^{-1}					
0.0020	70.8	0.1145	51.4	0.6013	39.3
0.0040	69.9	0.1459	49.5	0.6759	39.4
0.0079	67.9	0.1811	47.6	0.7867	39.6
0.0159	64.9	0.2200	45.9	0.8963	39.6
0.0278	61.5	0.2974	42.8	1.0405	40.0
0.0436	58.6	0.3743	40.5	1.2178	40.1
0.0633	55.7	0.4505	39.3		
0.0870	53.4	0.5262	39.2		
[NaBr] = 0.003 mol kg^{-1}					
0.0011	69.8	0.0540	49.6	0.2542	37.7
0.0022	68.7	0.0690	47.2	0.2955	37.6
0.0043	66.4	0.0861	45.8	0.3364	37.5
0.0087	62.8	0.1074	43.7	0.3972	37.4
0.0152	59.1	0.1498	40.5	0.4573	37.5
0.0216	56.7	0.1708	39.2	0.5364	37.6
0.0303	53.8	0.1918	38.4		
0.0411	51.6	0.2127	37.8		

Table 5.1a – Continued

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
[NaBr] = 0.005 mol kg^{-1}					
$8.0\text{x}10^{-4}$	69.0	0.0288	51.2	0.1404	37.3
0.0016	68.1	0.0383	49.2	0.1713	37.1
0.0032	65.7	0.0495	46.7	0.2020	37.3
0.0064	62.0	0.0621	44.8	0.2324	37.3
0.0096	59.6	0.0779	42.9	0.2776	37.1
0.0144	56.6	0.0936	41.1	0.3371	37.3
0.0208	53.9	0.1093	39.8	0.4101	37.2
[NaBr] = 0.01 mol kg^{-1}					
$6.9\text{x}10^{-4}$	67.9	0.0301	46.0	0.1467	36.5
0.0014	66.0	0.0410	43.0	0.1860	36.5
0.0027	62.8	0.0532	40.9	0.2249	36.3
0.0055	59.4	0.0667	38.5	0.2760	36.4
0.0096	54.9	0.0802	37.2	0.3264	36.3
0.0151	51.1	0.0936	36.7	0.4006	36.0
0.0219	48.3	0.1202	36.7	0.4731	36.3
[NaBr] = 0.02 mol kg^{-1}					
$5.2\text{x}10^{-4}$	65.6	0.0226	43.0	0.0872	36.0
0.0010	62.8	0.0297	40.8	0.1071	35.6
0.0021	60.0	0.0379	38.6	0.1268	35.7
0.0041	55.7	0.0470	36.8	0.1561	35.7
0.0072	52.1	0.0571	36.2	0.1947	35.3
0.0113	48.9	0.0672	36.3	0.2514	35.3
0.0165	45.8	0.0772	35.9		
[NaBr] = 0.05 mol kg^{-1}					
$1.3\text{x}10^{-4}$	66.2	0.0090	45.9	0.0423	35.3
$2.7\text{x}10^{-4}$	63.9	0.0116	43.5	0.0497	35.4
$5.3\text{x}10^{-4}$	61.3	0.0142	41.6	0.0571	35.3

Table 5.1a – Continued

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
		[NaBr] = 0.05 mol kg^{-1}			
0.0011	60.7	0.0168	40.4	0.0668	35.0
0.0021	57.3	0.0194	39.0	0.0787	35.0
0.0035	53.5	0.0246	37.2	0.0903	34.9
0.0050	50.8	0.0297	36.3	0.1085	34.5
0.0069	48.5	0.0348	35.6	0.1306	34.1
		[NaBr] = 0.10 mol kg^{-1}			
$1.2\text{x}10^{-4}$	66.4	0.0058	45.8	0.0325	33.9
$2.3\text{x}10^{-4}$	61.0	0.0077	43.5	0.0391	34.0
$4.7\text{x}10^{-4}$	58.6	0.0098	40.9	0.0478	33.8
$9.4\text{x}10^{-4}$	56.6	0.0121	39.3	0.0564	34.0
0.0016	54.5	0.0167	36.2	0.0691	33.9
0.0028	51.5	0.0212	34.8	0.0855	33.6
0.0042	48.4	0.0257	34.5	0.1054	33.5
		[NaBr] = 0.15 mol kg^{-1}			
$8.4\text{x}10^{-5}$	69.9	0.0055	43.7	0.0340	33.5
$1.7\text{x}10^{-4}$	63.4	0.0070	41.6	0.0402	33.4
$3.3\text{x}10^{-4}$	58.9	0.0086	39.7	0.0492	32.9
$6.7\text{x}10^{-4}$	57.6	0.0102	38.2	0.0580	33.1
0.0012	54.2	0.0135	36.1	0.0694	32.8
0.0020	51.5	0.0167	35.3	0.0805	32.9
0.0030	48.7	0.0215	34.2	0.0940	33.0
0.0042	46.0	0.0278	33.9		
		[NaBr] = 0.20 mol kg^{-1}			
$6.8\text{x}10^{-5}$	70.0	0.0039	46.0	0.0206	34.1
$1.4\text{x}10^{-4}$	64.2	0.0050	43.1	0.0244	33.7
$2.7\text{x}10^{-4}$	62.8	0.0062	41.4	0.0306	33.7
$5.4\text{x}10^{-4}$	61.4	0.0075	39.3	0.0368	33.5

Table 5.1a – Continued

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
		[NaBr] = 0.20 mol kg^{-1}			
9.5×10^{-4}	55.4	0.0089	37.9	0.0452	33.1
0.0015	52.8	0.0115	35.6	0.0545	33.0
0.0022	51.0	0.0141	35.1	0.0658	33.2
0.0030	48.4	0.0167	34.5	0.0767	32.8

Table 5.1b - Surface Tension (γ) values of CPC in aqueous Tetrabutylammonium Bromide solution at 303 K

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
[TBAB] = 3.0 x 10^{-4} mol kg^{-1}					
0.0026	71.5	0.1776	54.7	0.8151	41.9
0.0051	70.9	0.2780	50.4	0.9102	42.2
0.0102	69.9	0.3775	47.5	1.0045	42.2
0.0204	67.3	0.4761	44.7	1.1446	42.2
0.0357	64.9	0.5252	43.9	1.2830	42.4
0.0561	62.5	0.5740	43.2	1.4649	42.7
0.0866	60.1	0.6226	42.3	1.6883	42.7
0.1271	57.2	0.7193	41.6		
[TBAB] = 5.0 x 10^{-4} mol kg^{-1}					
0.0017	71.6	0.1208	55.3	0.6529	40.8
0.0035	70.5	0.1891	51.2	0.7171	40.9
0.0069	69.6	0.2569	48.5	0.8126	40.9
0.0139	67.5	0.3242	46.5	0.9070	41.1
0.0243	65.2	0.3909	44.3	1.0313	41.3
0.0382	62.6	0.4572	42.9	1.1538	41.5
0.0589	59.8	0.5229	41.8	1.3043	41.6
0.0865	57.5	0.5881	40.8		
[TBAB] = 0.001 mol kg^{-1}					
0.0019	70.1	0.0712	53.5	0.4978	38.9
0.0038	68.9	0.1010	50.6	0.5688	38.9
0.0075	66.4	0.1344	48.5	0.6392	39.0
0.0113	64.1	0.1714	46.6	0.7091	39.0
0.0150	62.4	0.2082	45.1	0.8130	39.3
0.0225	60.7	0.2814	42.1	0.9497	39.2
0.0338	58.3	0.3541	40.0	1.1508	39.2
0.0487	56.4	0.4262	38.4		

Table 5.1b – Continued

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
		[TBAB] = 0.003 mol kg^{-1}			
0.0011	69.1	0.0632	47.8	0.3265	37.2
0.0021	68.3	0.0820	45.3	0.3860	37.4
0.0042	65.5	0.1028	43.5	0.4642	37.5
0.0085	61.9	0.1235	41.9	0.5412	37.3
0.0148	58.6	0.1647	39.4	0.6171	37.4
0.0232	55.3	0.2057	37.8	0.7289	37.4
0.0338	52.5	0.2463	37.0	0.8742	37.5
0.0464	50.0	0.2866	37.4		
		[TBAB] = 0.005 mol kg^{-1}			
0.0010	67.9	0.0678	42.9	0.3098	36.6
0.0019	66.3	0.0851	40.8	0.3824	36.5
0.0039	63.4	0.1042	39.3	0.4539	36.8
0.0097	58.1	0.1233	37.6	0.5592	36.8
0.0175	53.7	0.1422	36.9	0.6960	36.8
0.0272	50.4	0.1800	36.5	0.8289	36.6
0.0388	47.5	0.2174	36.8		
0.0524	45.0	0.2546	36.8		
		[TBAB] = 0.01 mol kg^{-1}			
6.3×10^{-4}	65.8	0.0362	42.1	0.1675	35.8
0.0013	64.0	0.0461	40.0	0.2030	35.7
0.0025	61.3	0.0584	38.0	0.2497	35.8
0.0050	57.4	0.0707	36.5	0.2958	35.7
0.0088	53.4	0.0830	36.0	0.3636	35.7
0.0138	49.9	0.0952	36.0	0.4518	35.6
0.0200	47.1	0.1195	35.7		
0.0275	44.2	0.1436	35.9		

Table 5.1b – Continued

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
		[TBAB] = 0.02 mol kg^{-1}			
4.9x10^{-4}	62.4	0.0282	40.1	0.1298	35.3
9.8x10^{-4}	61.0	0.0360	38.4	0.1576	35.0
0.0020	59.0	0.0447	36.6	0.1850	35.2
0.0039	55.9	0.0543	36.1	0.2122	35.0
0.0068	52.9	0.0638	35.7	0.2479	35.0
0.0108	49.0	0.0734	35.5	0.3005	35.1
0.0156	45.7	0.0923	35.7	0.3689	34.9
0.0215	43.1	0.1111	35.2		
		[TBAB] = 0.05 mol kg^{-1}			
1.3x10^{-4}	57.9	0.0101	43.2	0.0586	34.3
2.7x10^{-4}	57.4	0.0128	41.5	0.0708	34.1
5.4x10^{-4}	56.5	0.0180	38.2	0.0851	33.9
0.0011	55.0	0.0232	36.3	0.1037	33.9
0.0021	52.7	0.0284	35.0	0.1218	33.8
0.0035	50.5	0.0335	34.5	0.1437	33.7
0.0054	48.0	0.0412	34.3		
0.0075	45.3	0.0487	34.2		
		[TBAB] = 0.10 mol kg^{-1}			
2.6x10^{-4}	53.7	0.0074	41.6	0.0390	32.7
5.1x10^{-4}	51.6	0.0094	40.0	0.0486	32.6
0.0010	50.7	0.0119	38.1	0.0603	32.5
0.0018	49.7	0.0144	37.2	0.0719	32.8
0.0028	47.3	0.0194	35.2	0.0855	32.4
0.0041	45.4	0.0244	34.1	0.1031	32.9
0.0056	43.7	0.0317	33.1	0.1203	32.2

Table 5.1b – Continued

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
[TBAB] = 0.15 mol kg^{-1}					
1.0×10^{-4}	50.0	0.0052	43.0	0.0310	33.5
2.1×10^{-4}	49.6	0.0068	41.2	0.0388	33.0
4.2×10^{-4}	49.2	0.0089	39.5	0.0464	32.6
8.3×10^{-4}	48.5	0.0109	38.2	0.0578	32.4
0.0015	47.7	0.0150	36.2	0.0688	32.4
0.0025	46.2	0.0190	34.9	0.0832	32.3
0.0037	44.8	0.0250	34.0		
[TBAB] = 0.20 mol kg^{-1}					
8.3×10^{-5}	48.4	0.0036	43.6	0.0176	35.7
1.7×10^{-4}	48.0	0.0049	41.9	0.0191	35.6
3.3×10^{-4}	47.3	0.0064	40.8	0.0207	35.4
6.6×10^{-4}	47.6	0.0080	39.6	0.0223	34.9
0.0012	46.4	0.0096	38.1	0.0238	34.8
0.0018	45.4	0.0128	37.0	0.0254	34.8
0.0026	44.6	0.0160	35.8	0.0284	33.9

Table 5.2a – Specific Conductance (κ) values of CPC in aqueous Sodium Bromide solution at 303 K

[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}
		[NaBr] = 0.0 mol kg^{-1}			
0	0.9238	0.5413	57.822	1.6764	136.31
0.0146	2.4038	0.6515	69.487	1.7985	141.75
0.0438	5.8502	0.7740	82.101	1.9189	147.06
0.0875	10.351	0.9083	95.360	2.0377	152.27
0.1453	16.501	1.0408	105.27	2.1550	157.38
0.2172	24.091	1.1714	112.43	2.2708	162.32
0.2886	31.522	1.3003	118.81	2.3850	167.14
0.3594	38.877	1.4274	124.86	2.4978	171.84
0.4438	47.800	1.5527	130.61		
		[NaBr] = 2.0 x10^{-4} mol kg^{-1}			
0	37.804	0.4660	87.039	1.2058	138.84
0.0087	38.815	0.5451	95.145	1.2740	141.99
0.0260	40.698	0.6229	103.03	1.3413	145.05
0.0519	43.473	0.6996	110.94	1.4730	151.10
0.0863	47.154	0.7752	117.00	1.6011	156.76
0.1289	51.467	0.8496	121.40	1.7258	162.34
0.1796	57.157	0.9229	125.27	1.8471	167.56
0.2381	63.225	0.9952	128.86	1.9653	172.61
0.3043	70.094	1.0664	132.33		
0.3858	78.449	1.1366	135.55		
		[NaBr] = 5.0 x10^{-4} mol kg^{-1}			
0	78.078	0.4676	133.19	0.7889	158.61
0.0622	85.532	0.5091	137.32	0.8185	160.67
0.1214	91.763	0.5489	142.11	0.8471	162.12
0.1779	98.843	0.5872	146.01	0.8747	162.97
0.2317	105.32	0.6240	148.88	0.9015	164.35

Table 5.2a – Continued

[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}
[NaBr] = 5.0 x10^{-4} mol kg^{-1}					
0.2831	111.29	0.6594	151.09	0.9274	166.05
0.3323	116.83	0.6936	153.38	0.9524	166.82
0.3794	122.82	0.7265	155.60	0.9767	167.64
0.4244	127.78	0.7582	157.38		
[NaBr] = 0.001 mol kg^{-1}					
0	130.69	0.3002	161.36	0.7332	189.79
0.0113	131.81	0.3436	165.86	0.7943	192.24
0.0340	133.91	0.3868	170.43	0.8550	194.64
0.0565	136.33	0.4297	174.91	0.9350	197.89
0.0902	139.66	0.4723	178.29	1.0141	201.08
0.1238	143.17	0.5147	180.46	1.0923	204.14
0.1683	147.48	0.5673	182.92	1.1888	207.91
0.2125	152.20	0.6196	184.95	1.2839	211.63
0.2565	156.75	0.6714	187.28	1.3777	214.96
[NaBr] = 0.003 mol kg^{-1}					
0	401.62	0.1313	413.75	0.3763	427.73
0.0039	401.91	0.1603	416.48	0.4087	429.12
0.0116	402.54	0.1925	419.24	0.4407	430.53
0.0192	403.30	0.2102	421.06	0.4721	431.15
0.0307	404.55	0.2277	422.33	0.5336	432.91
0.0459	405.42	0.2486	423.27	0.5933	434.44
0.0647	407.43	0.2761	424.27	0.6514	435.88
0.0834	409.15	0.3100	425.54		
0.1057	411.71	0.3434	426.79		
[NaBr] = 0.005 mol kg^{-1}					
0	715.17	0.1623	732.73	0.2656	737.63
0.0167	718.71	0.1701	733.18	0.2757	738.64

Table 5.2a – Continued

[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}
[NaBr] = 0.005 mol kg^{-1}					
0.0325	718.37	0.1797	733.99	0.2852	738.54
0.0475	720.31	0.1879	734.70	0.2942	739.25
0.0751	722.15	0.1957	734.80	0.3106	739.45
0.1001	726.20	0.2176	736.01	0.3254	740.56
0.1227	728.63	0.2309	736.72	0.3386	740.97
0.1434	730.75	0.2432	737.43	0.3506	741.37
0.1530	732.07	0.2548	737.43		
[NaBr] = 0.01 mol kg^{-1}					
0	1265.9	0.0739	1271.9	0.1733	1276.4
0.0030	1266.2	0.0826	1272.3	0.1898	1277.0
0.0090	1266.6	0.0912	1273.0	0.2063	1277.6
0.0150	1267.1	0.0999	1273.3	0.2280	1278.1
0.0239	1267.7	0.1085	1273.8	0.2496	1278.9
0.0328	1268.2	0.1199	1274.1	0.2709	1279.4
0.0446	1269.0	0.1312	1274.8	0.2972	1279.9
0.0564	1270.0	0.1453	1275.1	0.3232	1280.8
0.0651	1270.9	0.1593	1275.7		
[NaBr] = 0.02 mol kg^{-1}					
0	2475.4	0.0376	2478.5	0.0985	2482.6
0.0017	2475.6	0.0427	2479.1	0.1081	2483.0
0.0052	2475.4	0.0477	2479.5	0.1208	2483.4
0.0086	2476.0	0.0527	2480.1	0.1334	2483.6
0.0121	2476.2	0.0594	2480.5	0.1459	2484.2
0.0172	2476.6	0.0660	2480.5	0.1613	2484.6
0.0224	2477.2	0.0725	2481.1	0.1765	2484.8
0.0275	2477.5	0.0807	2481.7		
0.0326	2478.1	0.0889	2481.9		

Table 5.2a – Continued

[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}
		[NaBr] = 0.05 mol kg^{-1}			
0.0008	5912.3	0.0216	5920.1	0.0540	5928.9
0.0025	5913.7	0.0256	5921.6	0.0608	5929.9
0.0042	5914.2	0.0297	5923.0	0.0668	5930.8
0.0067	5915.2	0.0337	5923.5	0.0728	5931.8
0.0101	5915.7	0.0376	5925.0	0.0794	5933.3
0.0134	5917.2	0.0424	5926.4		
0.0175	5918.1	0.0478	5927.4		

Table 5.2b – Specific Conductance (κ) values of CPC in aqueous Tetrabutylammonuim Bromide solution at 303 K

[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}
[TBAB] = 5.0 x 10^{-4} mol kg^{-1}					
0	65.953	0.4877	121.66	0.8152	145.25
0.0657	73.608	0.5303	126.34	0.8450	146.96
0.1280	81.179	0.5712	130.37	0.8738	148.22
0.1871	87.927	0.6103	133.79	0.9016	149.61
0.2434	94.490	0.6479	136.27	0.9285	150.64
0.2969	100.55	0.6840	138.49	0.9544	152.25
0.3480	106.25	0.7187	140.37	0.9796	153.42
0.3967	111.61	0.7521	142.13	1.0039	154.02
0.4432	116.78	0.7842	143.77		
[TBAB] = 0.001 mol kg^{-1}					
0	139.19	0.2938	171.26	0.4943	188.17
0.0440	143.87	0.3229	174.33	0.5149	189.16
0.0856	148.65	0.3507	177.33	0.5348	190.15
0.1249	152.97	0.3773	180.07	0.5540	190.94
0.1622	156.93	0.4027	182.54	0.5724	191.65
0.1976	160.81	0.4270	184.41	0.5902	192.42
0.2313	164.37	0.4504	186.09	0.6073	193.36
0.2633	167.81	0.4728	187.23		
[TBAB] = 0.003 mol kg^{-1}					
0	308.18	0.1203	320.29	0.3203	334.49
0.0040	309.00	0.1391	322.09	0.3481	335.66
0.0119	309.38	0.1616	323.91	0.3756	336.44
0.0198	310.49	0.1839	325.92	0.4095	337.56
0.0316	311.55	0.2059	328.03	0.4429	338.67
0.0472	312.95	0.2278	329.62	0.5083	340.51
0.0628	314.56	0.2495	330.87	0.5719	342.52

Table 5.2b – Continued

[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}
[TBAB] = 0.003 mol kg^{-1}					
0.0821	316.61	0.2709	331.65	0.6338	344.26
0.1013	318.33	0.2958	332.82		
[TBAB] = 0.005 mol kg^{-1}					
0	539.20	0.1460	558.46	0.2456	563.01
0.0134	541.63	0.1614	558.66	0.2552	563.42
0.0385	546.82	0.1757	560.08	0.2642	563.52
0.0616	549.18	0.1892	560.79	0.2728	564.02
0.0829	552.29	0.2018	561.49	0.2810	564.23
0.1027	554.01	0.2137	561.90	0.2887	564.53
0.1209	556.37	0.2250	561.59		
0.1380	557.75	0.2356	562.08		
[TBAB] = 0.01 mol kg^{-1}					
0	1018.9	0.0587	1025.1	0.1567	1030.2
0.0021	1019.4	0.0686	1026.0	0.1715	1030.6
0.0062	1019.7	0.0785	1026.9	0.1862	1031.1
0.0103	1020.4	0.0882	1027.6	0.2025	1031.6
0.0164	1021.2	0.0979	1027.9	0.2186	1032.1
0.0225	1021.7	0.1076	1028.4	0.2363	1032.6
0.0307	1022.3	0.1191	1028.8	0.2537	1033.1
0.0387	1023.1	0.1305	1029.2	0.2710	1033.5
0.0488	1024.1	0.1437	1029.8		
[TBAB] = 0.02 mol kg^{-1}					
0	1798.6	0.0456	1803.4	0.1242	1808.5
0.0019	1799.1	0.0528	1803.7	0.1360	1809.1
0.0056	1799.6	0.0599	1804.7	0.1494	1809.8
0.0092	1799.9	0.0670	1805.1	0.1626	1810.2
0.0148	1800.4	0.0740	1805.6	0.1790	1810.9

Table 5.2b – Continued

[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}
		[TBAB] = 0.02 mol kg^{-1}			
0.0203	1801.1	0.0828	1806.2	0.1952	1811.3
0.0257	1801.7	0.0915	1806.7	0.2112	1811.8
0.0312	1802.1	0.1019	1807.1	0.2270	1812.6
0.0384	1802.7	0.1122	1807.8		
		[TBAB] = 0.05 mol kg^{-1}			
0	4102.3	0.0206	4125.7	0.0473	4137.3
0.0009	4103.6	0.0232	4127.5	0.0515	4138.4
0.0027	4108.1	0.0258	4130.4	0.0565	4137.9
0.0045	4109.3	0.0285	4132.0	0.0615	4139.2
0.0072	4113.6	0.0311	4133.6	0.0673	4139.8
0.0099	4118.0	0.0337	4133.7	0.0738	4141.0
0.0126	4120.8	0.0362	4134.9	0.0818	4139.2
0.0153	4123.2	0.0397	4135.9		
0.0179	4124.8	0.0431	4136.5		

Table 5.3 - Critical Micelle Concentration Values of CPC in Aqueous Electrolyte Solutions at 303 K from Surface Tension and Conductance (given in parentheses) Data

[NaBr] / mol kg^{-1}	Cmc x 10^4/ mol kg^{-1}	[TBAB] / mol kg^{-1}	Cmc x 10^4 / mol kg^{-1}
0.0	9. 44 (9.47)	-	-
2.0x10^{-4}	7.41 (7.52)	-	-
3.0x10^{-4}	6.61 -	3. 0x10^{-4}	6.56 -
5. 0x10^{-4}	6.16 (6.00)	5. 0x10^{-4}	5.65 (5.81)
0.001	4.42 (4.63)	0.001	4.36 (4.15)
0.003	2.00 (2.20)	0.003	2.40 (2.12)
0.005	1.41 (1.61)	0.005	1.45 (1.45)
0.01	0.89 (0.95)	0.01	0.82 (0.83)
0.02	0.52 (0.58)	0.02	0.54 (0.59)
0.05	0.30 (0.33)	0.05	0.29 (0.31)
0.10	0.20 -	0.10	0.22 -
0.15	0.17 -	0.15	0.19 -
0.20	0.12 -	0.20	0.15 -

Table 5.4 - Best-fit Values of Cmc, β and Aggregation Number of CPC in the Presence of NaBr, TBAB and NaCl at 30 °C Computed from MEM (σ denotes standard deviation in specific conductance)

[Salt] / mol kg^{-1}	10^4cmc / mol kg^{-1}	β	Agg. No.	Micelle radius, r_n / nm	$10^4 \lambda^0_{+mic}$ / S m^2 eq^{-1}	σ / mS m^{-1}
Medium = water						
0	9.0	0.66	32	1.62	68.92	0.20
Medium = Aqueous NaBr						
2×10^{-4}	7.3	0.72	57	1.96	83.41	0.23
5×10^{-4}	6.3	0.70	96	2.33	126.5	0.16
0.001	4.1	0.75	99	2.35	107.6	0.15
0.003	1.8	0.79	120	2.51	102.8	0.12
0.005	1.6	0.70	122	2.52	148.4	0.05
Medium = Aqueous TBAB						
5×10^{-4}	6.0	0.70	100	2.36	130.0	0.08
0.001	4.2	0.77	106	2.41	103.6	0.08
0.003	2.1	0.79	114	2.47	99.30	0.12
0.005	1.7	0.70	130	2.58	154.8	0.24
Medium = Aqueous NaCl						
3×10^{-4}	8.0	0.66	35	1.66	73.17	0.21
5×10^{-4}	7.5	0.67	40	1.74	77.63	0.15
0.001	5.4	0.67	49	1.86	88.87	0.13
0.005	2.8	0.65	54	1.92	100.6	0.12

Table 5.5 - Values of ΔG_m^0 and ΔG_{ad}^0 of CPC in Aqueous Electrolyte Solution at 303K

Electrolyte = NaBr			Electrolyte = TBAB		
[NaBr] mol kg^{-1}	ΔG_m^0 kJ mol^{-1}	ΔG_{ad}^0 kJ mol^{-1}	[TBAB] mol kg^{-1}	ΔG_m^0 kJ mol^{-1}	ΔG_{ad}^0 kJ mol^{-1}
0	-47.3	-66.0	0.0	-	-
2x10^{-4}	-48.3	-66.1	2x10^{-4}	-	-
3x10^{-4}	-48.8	-65.9	3x10^{-4}	-48.9	-65.5
5x10^{-4}	-49.1	-65.8	5x10^{-4}	-49.5	-65.9
0.001	-50.6	-66.4	0.001	-50.6	-65.8
0.003	-54.0	-67.7	0.003	-53.2	-66.6
0.005	-55.5	-67.9	0.005	-55.4	-68.1
0.01	-57.7	-69.0	0.01	-57.8	-70.2
0.02	-59.8	-70.7	0.02	-59.6	-71.3
0.05	-62.2	-73.2	0.05	-62.3	-74.7
0.10	-63.9	-75.1	0.10	-63.5	-78.0
0.15	-64.6	-76.0	0.15	-64.1	-79.2
0.20	-66.1	-77.5	0.20	-65.2	-82.4

Table 5.6 - Surface Excess (Γ_{cmc}) and Surface Area (A_0) per Molecule of CPC near CMC in presence of NaBr and TBAB, and Surface Excess (Γ) of TBAB at 303 K

For CPC in aqueous medium in the presence of electrolytes						For TBAB in water	
Electrolyte = NaBr			Electrolyte = TBAB				
[NaBr] mol kg^{-1}	Γ_{cmc} x 10^6 / mol m^{-2}	A_0/ nm^2	[TBAB] mol kg^{-1}	Γ_{cmc} x 10^6 /mol m^{-2}	A_0/ nm^2	[TBAB] mol kg^{-1}	Γ x 10^6/ mol m^{-2}
0.0	1.70	0.98	0.0	-	-	0.0	0
2x10^{-4}	1.74	0.96	-	-	-	-	-
3x10^{-4}	1.76	0.94	3x10^{-4}	1.78	0.93	3x10^{-4}	0
5x10^{-4}	1.85	0.90	5x10^{-4}	1.90	0.87	5x10^{-4}	0
0.001	2.05	0.81	0.001	2.13	0.78	0.001	0.04
0.003	2.48	0.67	0.003	2.56	0.65	0.003	0.35
0.005	2.82	0.59	0.005	2.77	0.60	0.005	0.50
0.01	3.08	0.54	0.01	2.93	0.57	0.01	0.70
0.02	3.27	0.51	0.02	3.10	0.54	0.02	0.90
0.05	3.27	0.51	0.05	3.02	0.55	0.05	1.16
0.10	3.32	0.50	0.10	2.65	0.63	0.10	1.36
0.15	3.27	0.51	0.15	2.46	0.68	0.15	1.48
0.20	3.27	0.51	0.20	2.09	0.79	0.20	1.56

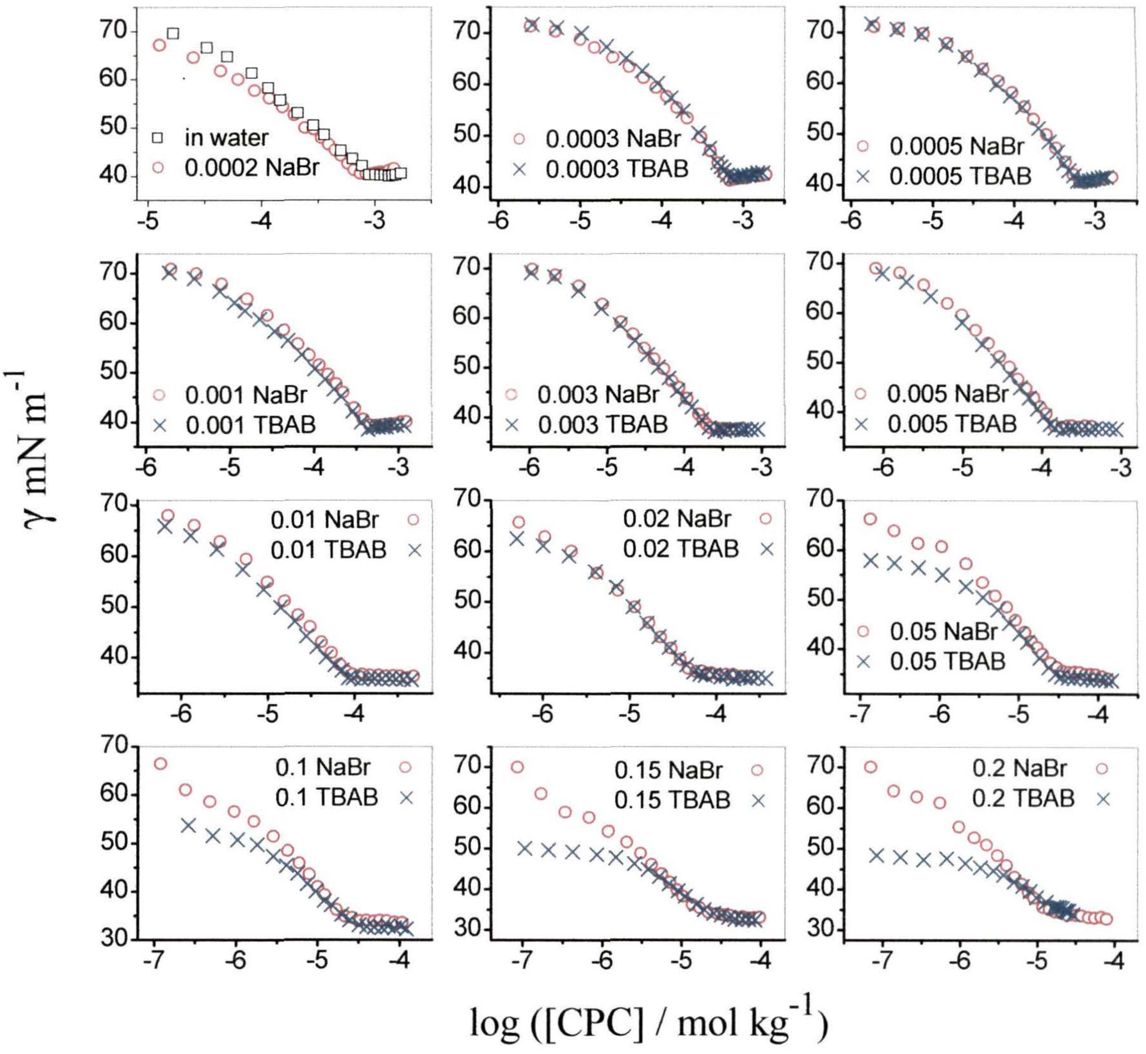

Figure 5.1. Surface tension isotherms of CPC in aqueous NaBr and TBAB solutions at 30 °C. Concentrations of NaBr and TBAB are indicated in the insets.

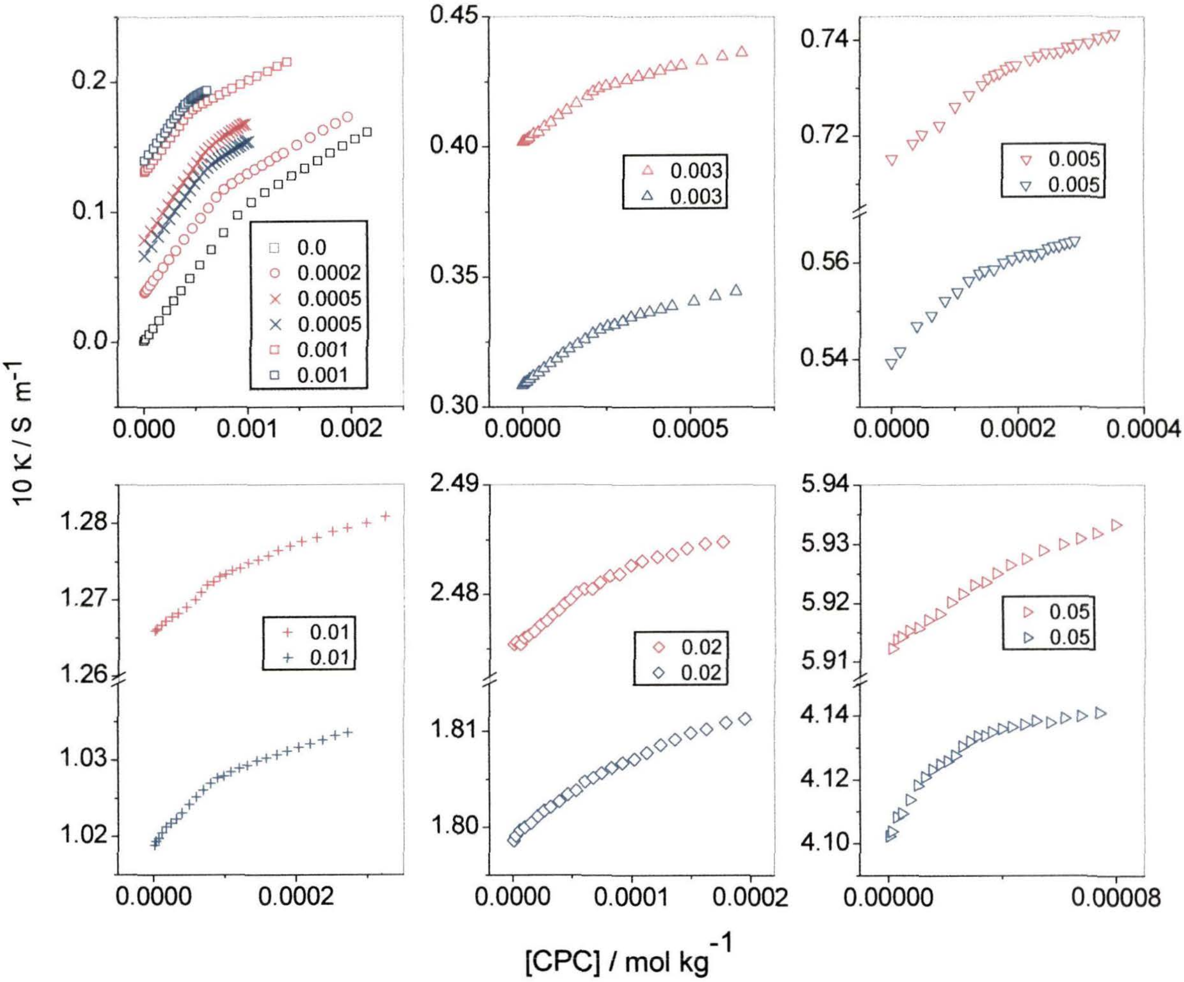

Figure 5.2. Specific conductivity isotherms for CPC in aqueous NaBr and TBAB solutions at 30 °C. Concentrations of NaBr (red symbols) and TBAB (blue symbols) are indicated in the insets. Black symbols correspond to water medium.

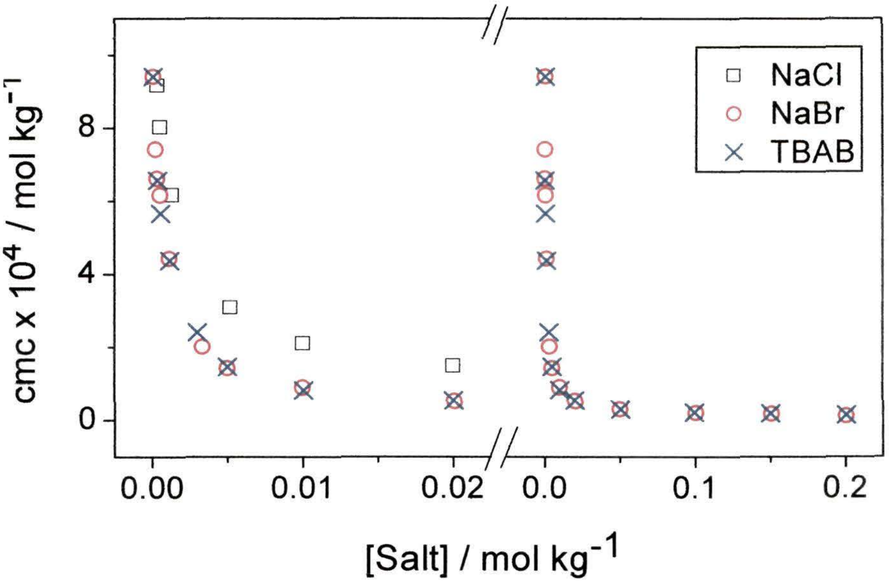

Figure 5.3. Variation of cmc of CPC with the concentration of added NaBr, TBAB and NaCl (data from ch. 3) at 30 °C

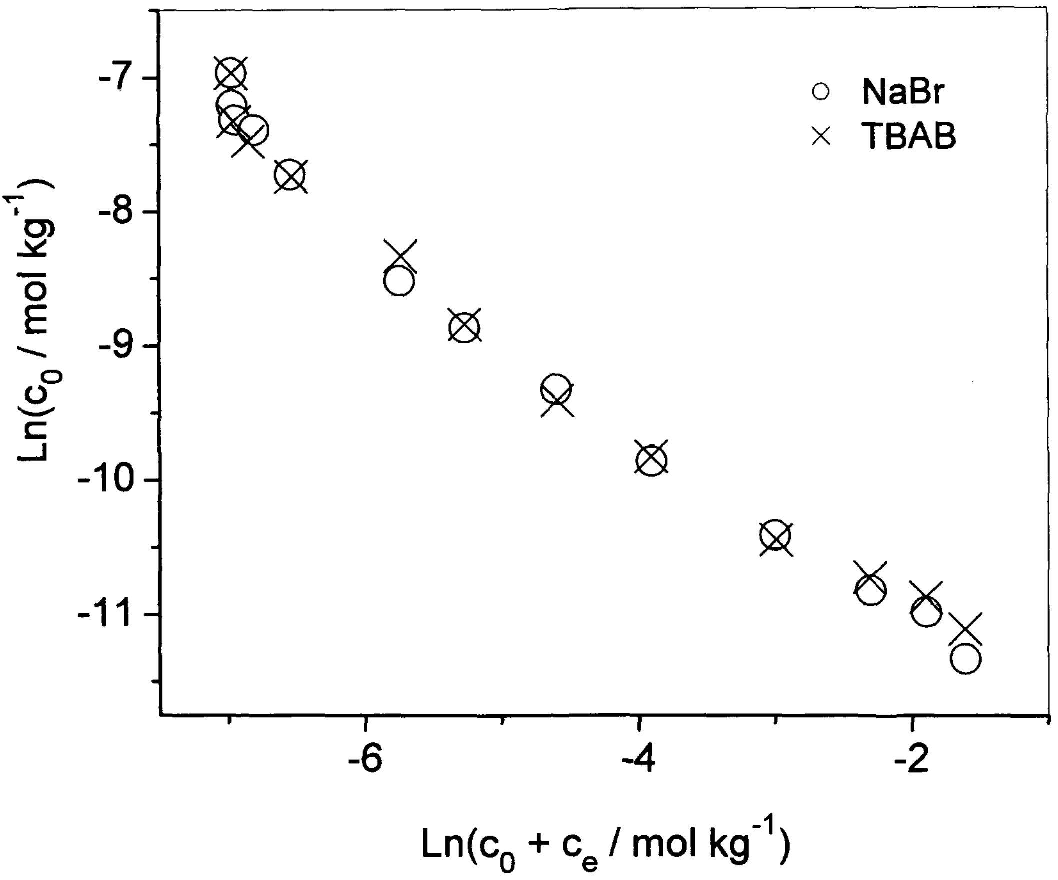

Fig. 5.4. CH plots for CPC + NaBr and CPC + TBAB aqueous systems at 30 °C.

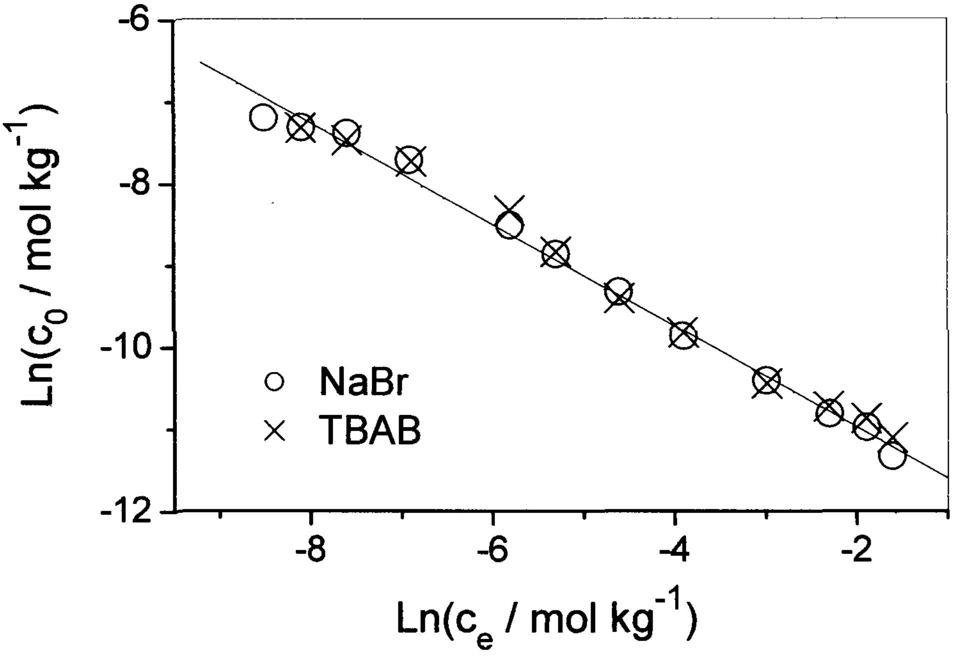

Fig. 5.5. Plots of $\ln c_0$ versus $\ln c_e$ at 30 °C for CPC in aqueous NaBr and TBAB media.

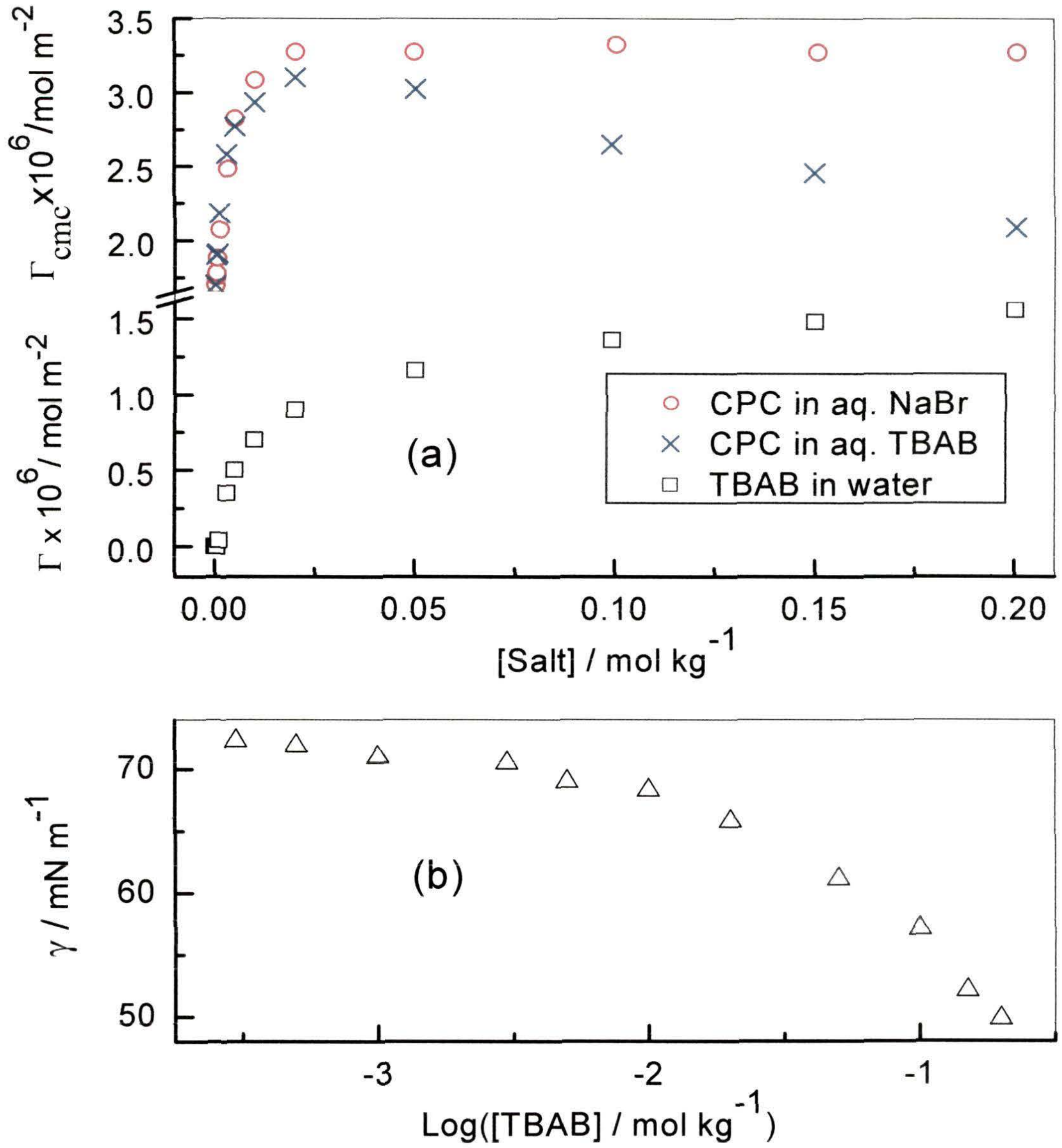

Figure 5.6. Plots of (a) surface excess of CPC at the cmc in aqueous medium as a function of NaBr and TBAB concentration and of TBAB in water and (b) surface tension isotherm of aqueous TBAB solution at 30 °C

CHAPTER 6

Adsorption and Aggregation Behaviours of Cetylpyridinium Chloride in the Presence of Sodium Chloride in Water + Glycerol Media

6.1 INTRODUCTION

Solvophobicity or solvophilicity of a solute is due to solute – solvent interactions. When the solutes are amphiphilic in nature, solvophobic interaction leads to two significant phenomena, viz. adsorption and aggregation. Thus, adsorption and aggregation of surfactants take place only in the presence of a solvent and therefore solvents play a decisive role in controlling the adsorption and micellization characteristics of surfactants. Mixing of solvents changes solvent quality, particularly polarity, and carrying out adsorption and aggregation studies of surfactants in mixed solvents provides knowledge of fundamental and practical importance. Owing to this reason, as already mentioned in chapter 1, micellization characteristics of surfactants in binary mixtures of solvents are being studied with a renewed interest during the last few years.[1-26]

Water + glycerol is one such mixed solvent medium in which micellization behaviours of a few surfactants have been studied. The systems studied in water + glycerol media are (i) dodecyltrimethylammonium bromide (DTAB),[3,11,27] cetyltrimethylammonium bromide (CTAB),[3,11,28] tetradecyltrimethylammonium bromide (TTAB),[3,11,14,27] cetylpyridinium bromide (CPB),[27] cetylpyridinium chloride (CPC),[29] sodium dodecylsulfate (SDS),[3,8,23] TX-100[3] and Brij 58.[28] In water + glycerol medium the counter ion binding constant (β) for the ionic surfactants is found to have no dependence on the glycerol amount while in all other mixed solvent media the value of β decreases with increase in the organic solvent content. This is a striking feature observed only in water + glycerol media irrespective of the ionic surfactant.

In all the cases reported till date values of β were determined from the conductance data by using the slope – ratio method except for one case where β was determined by the EMF method.[27] Another method commonly used for determining β is the Corrin – Harkins (CH) method, which has not been applied in water + glycerol media.

In view of the above, our main objective is to examine the unusual behaviour of β in water + glycerol medium by measuring surface tension and conductance of CPC in the presence of NaCl. The results of the measurements made at 25 °C are presented in this chapter.

6.2 EXPERIMENTAL

Glycerol (Aldrich, > 99.5 %), CPC (Aldrich, >99.0 %) and NaCl (Merck, 99.5 %) were used as supplied. Millipore grade water was used in preparing the solutions. Surface tension and conductance measurements at 25 °C were made as described in chapter 2. Density of water + glycerol system was measured using Anton Paar DMA 5000 Densitometer.

6.3 RESULTS AND DISCUSSION

Surface tension, conductance and cmc. Experimental values of surface tension (γ) at 25 °C as functions glycerol and NaCl amounts are listed in Tables 6.1a - g. Similarly, the specific conductance (κ) data are listed in Table 6.2a - g. For the purpose of determining critical micelle concentration (cmc), surface tension and specific conductance isotherms were drawn, which are shown in Figs. 6.1 – 6.5. The cmc values are given in Table 6.3. Fig. 6.6 displays the dependence of cmc on glycerol content in the absence and presence of NaCl, whereas Fig. 6.7 shows the variation of cmc with the concentration of added NaCl in water + glycerol media. The cmc of CPC increases with increase in glycerol content of the medium, which is a general trend in any water + polar organic solvent medium. To quantify the variation of cmc (c_0) with the amount of organic solvent, some groups[27,29] have used an empirical equation of the form

$$c_0 = c_{00}\exp(bw) \qquad (6.1)$$

where c_{00} is the cmc value in water, 'w' is the weight % of the organic solvent and 'b' is an empirical constant. In the present case Eq. (6.1) is not applicable as evident from the non-linearity of the plots of $\ln c_0$ versus w (Fig. 6.8). Instead, Eq (6.2) is found to be applicable (Fig. 6.6), which is given by

$$c_0 = y_0 + a\exp(bw) \qquad (6.2)$$

The least-squares fitted values of the three constants y_0, 'a' and 'b' as a function of NaCl concentration are given in Table 6.4. The application of Eq. (6.2) implies that cmc of CPC has two components; one component is dependent on the glycerol content while the other component (y_0) is independent of glycerol amount.

Counter ion binding constant. The counter ion binding constant calculated from the slope – ratio method is denoted by β_K and its values are given in Table 6.5. The Corrin-Harkins (CH) equation is written here as

$$\ln c_0 = A - \beta_{CH}\ln(c_0 + c_e) \qquad (6.3)$$

This equation has been described in the preceding chapters. The counter ion binding constant determined from the slope of Eq. (6.3) is denoted by β_{CH}. The CH plots are shown in Fig. 6.9 and the values of β_{CH} are given in Table 6.5. The striking feature of β_{CH} or β_K in water + glycerol medium is its negligible dependence on glycerol content. Similar observation was made by others[3,8,11,27,29] for different ionic surfactants in water + glycerol medium including for CPC[29] at 40 °C using the slope – ratio method. Generally in an aqueous organic solvent medium β_{CH} or β_K decreases with increase in the amount of organic solvent. Thus, water + glycerol media behave differently from other mixed solvents with respect to binding of counter ions to ionic micelle. A water-like environment around micellar surfaces may exist in water + glycerol medium as shown in Fig. 6.10 and that could be the probable reason for the unexpected constancy of β_{CH} or β_K as viewed by Palepu et al.[27] also.

Free energy of micellization. The free energy of micellization per mole of surfactant, ΔG_m^0, was calculated using the relation

$$\Delta G_m^0 = RT(1+\beta)\ln X_{cmc} \qquad (6.4)$$

X_{cmc} is the cmc in mole fraction unit. β is the counter ion binding constant determined from any method. In Eq. (6.4), for β we substituted the average of β_{CH} values in water + glycerol media, which was found to be 0.66. The values of ΔG_m^0 are listed in Table 6.6 and also shown in Fig. 6.11. The rate of decrease of ΔG_m^0 with addition of NaCl is almost same in water as well as water + glycerol media. The addition of glycerol does not favour micellization, which is attributed to the decrease in solvophobicity of CPC.

Quantification of solvophobicity is a difficult problem and still remains unsettled. Therefore, some empirical parameters are being used to express the solvophobic effect of a solvent medium. Gordon parameter (GP) is one such term and it is defined as $GP = \gamma_0/V^{1/3}$, where γ_0 and V refer to surface tension and molar volume of the solvent, respectively. Decrease in GP reflects a decrease in solvophobicity of a medium. Moya and coworkers[3,11] assessed the solvophobic effect of a variety of aqueous organic solvents with respect to different surfactants by using GP term. The values of GP for water + glycerol media are given in Table 6.7 and the correlation between ΔG_m^0 and GP is illustrated in Fig. 6.12. We recently proposed that the ratio of the solvent surface tension to the limiting surface tension at the cmc, $\gamma_0/\gamma_{\lim}$, can be used as a probable new scale to describe solvophobic effect[24] and applied it in water + formamide and water + propylene carbonate media.[25,26] However, in water + glycerol medium, like β_{CH}, $\gamma_0/\gamma_{\lim}$ also remains almost constant with increase in glycerol amount (Table 6.7 and Fig. 6.12) thereby rendering $\gamma_0/\gamma_{\lim}$ term not suitable for expressing solvophobicity.

Surface Excess and free energy of adsorption. Surface excess at the cmc (Γ_{cmc}) was evaluated from the relation

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

The description of the terms involved in Eq. (6.5) is given in the preceding chapters. The calculated values of Γ_{cmc} as a function of NaCl concentration, c_e, are given in Table 6.8 and the trend in the variation of Γ_{cmc} with c_e is displayed in Fig. 6.13. Γ_{cmc} increases on adding NaCl up to about 0.02 mol kg^{-1} and thereafter remains almost constant. In the cases of sodium bromide (cf. chapter 4), tetrabutylammonium bromide (cf. chapter 4) or sodium benzoate (cf. chapter 5) saturation in adsorption of CPC also occurs by adding ~ 0.02 mol kg^{-1} salt. By the addition of glycerol Γ_{cmc} decreases due to decrease in the solvophobicity or GP (Fig. 6.14), but the saturation point of adsorption remains almost same at 0.02mol kg^{-1} NaCl. Therefore, the electrolyte concentration required for saturating the air – solution interface by the adsorption of CPC is independent of the type of salt and the glycerol amount. The surface area, A_0 ($A_0 = 1/(N_A\Gamma_{cmc})$, N_A is the Avogadro number), of the adsorbed CPC molecule attains a minimum value of 0.62±0.01 nm^2 near the adsorption saturation.

The standard free energy of adsorption (ΔG^0_{ad}) at the air – solution interface was calculated using the relation

$$\Delta G^0_{ad} = \Delta G^0_m - \frac{\pi_{cmc}}{\Gamma_{cmc}} \tag{6.6}$$

The terms of Eq. (6.6) are defined in chapter 5. The computed values of ΔG^0_{ad} are given in Table 6.6. As expected the value of ΔG^0_{ad} for CPC decreases on addition of electrolyte and increases on addition of glycerol.

6.4 CONCLUSIONS

Critical micelle concentrations of CPC in water + glycerol media as functions of glycerol and NaCl concentrations were determined at 25 °C from the experimental data of surface tension and specific conductance. The variation in cmc follows the normal trend, i.e., increases with increase in glycerol content and decreases on adding NaCl. Empirical analysis of the exponential increase in cmc of CPC with weight per cent of glycerol is indicative of cmc having two components; one component being dependent while the other independent of glycerol amount. Counter ion binding constant determined from both slope – ratio and Corrin-Harkins methods showed no dependence on glycerol amount, thus confirming the unusual trend in the behaviour of β. This anomalous behaviour of β is viewed as due to existence of a water-like environment around micellar surfaces in water + glycerol medium. In water + glycerol medium the ratio of solvent surface tension to limiting surface tension at cmc is also independent of glycerol amount, whereas Gordon Parameter decreases with increase in glycerol content as in other aqueous organic solvents and represents solovophobicity of the medium. The air – solution interface becomes saturated by the adsorption of CPC when the concentration of added NaCl is about 0.02 mol kg^{-1} irrespective of the glycerol amount.

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Table 6.1a - Surface Tension (γ) values of CPC in Water + 10 % Glycerol medium in the presence of Sodium Chloride at 298 K

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
[NaCl] = 0.0 mol kg^{-1}					
0	72.2	0.1439	57.9	1.3027	43.4
0.0036	70.0	0.2010	56.0	1.6314	43.5
0.0072	67.7	0.2722	54.0	2.0798	43.2
0.0108	67.1	0.3431	51.9	2.5762	43.3
0.0144	66.1	0.4136	50.6	3.1739	42.9
0.0217	65.0	0.5538	47.7	3.7475	43.2
0.0361	63.3	0.6927	45.6	4.2986	43.0
0.0577	61.6	0.8987	43.6	5.8291	42.8
0.0937	60.2	1.1021	43.5	6.3021	42.8
[NaCl] = 0.001 mol kg^{-1}					
0	72.4	0.0766	55.8	0.5708	42.4
0.0032	68.3	0.1084	53.2	0.6932	42.5
0.0064	66.0	0.1528	52.3	0.8146	42.7
0.0096	64.6	0.2033	49.7	0.9948	42.5
0.0128	63.7	0.2600	48.4	1.2314	42.8
0.0192	61.7	0.3227	46.8	1.5217	42.5
0.0320	59.9	0.4473	44.2	2.1394	42.6
0.0511	57.9	0.5092	43.1	2.6245	42.5
[NaCl] = 0.005 mol kg^{-1}					
0	72.5	0.0913	48.8	0.4128	41.3
0.0033	65.2	0.1173	47.2	0.4763	40.9
0.0065	62.6	0.1497	45.5	0.6024	41.3
0.0098	60.5	0.1820	44.2	0.7895	41.1
0.0131	58.7	0.2143	43.1	1.0353	41.3
0.0196	57.1	0.2465	41.7	1.3368	41.0
0.0327	54.9	0.2786	41.4	1.9211	41.0
0.0522	52.2	0.3107	41.5	3.0203	41.2
0.0718	50.5	0.3554	41.0		

Table 6.1a – Continued

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
[NaCl] = 0.01 mol kg^{-1}					
0	73.0	0.0480	49.2	0.2538	40.8
0.0027	63.7	0.0639	47.7	0.3008	40.6
0.0053	60.9	0.0852	45.6	0.3528	40.6
0.0080	59.1	0.1117	43.7	0.4561	40.7
0.0107	57.3	0.1381	41.7	0.6602	41.0
0.0160	55.3	0.1645	41.0	0.9600	41.0
0.0214	53.8	0.1908	40.8	1.4431	40.7
0.0320	51.6	0.2171	40.8		
[NaCl] = 0.02 mol kg^{-1}					
0	72.8	0.0369	46.6	0.2106	39.8
0.0023	62.6	0.0461	45.0	0.2558	39.7
0.0046	59.0	0.0553	44.1	0.3458	39.7
0.0069	57.0	0.0691	42.3	0.4793	39.5
0.0092	55.2	0.0829	41.2	0.6982	39.6
0.0115	53.6	0.0966	40.6	1.1230	39.8
0.0139	52.4	0.1149	40.4	1.3699	39.7
0.0185	51.0	0.1378	40.1		
0.0277	48.7	0.1697	39.5		
[NaCl] = 0.05 mol kg^{-1}					
0	72.9	0.0299	44.0	0.2254	39.6
0.0019	60.9	0.0373	42.6	0.3701	39.1
0.0037	58.1	0.0448	41.1	0.5827	39.2
0.0056	54.8	0.0560	40.0	0.8583	38.9
0.0075	53.7	0.0708	39.7	1.1905	38.9
0.0112	50.5	0.0894	39.9	1.5099	38.5
0.0150	48.9	0.1153	39.8	1.8172	38.6
0.0224	46.2	0.1521	39.2	2.0548	38.6

Table 6.1a – Continued

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
[NaCl] = *0.10 mol* kg^{-1}					
0	72.6	0.0143	44.8	0.0965	38.7
0.0014	58.3	0.0200	42.5	0.1247	38.8
0.0029	54.8	0.0257	40.9	0.1527	38.7
0.0043	52.5	0.0314	40.1	0.2084	38.8
0.0057	51.3	0.0399	39.4	0.3185	38.3
0.0071	49.5	0.0513	39.0	0.5070	38.3
0.0086	48.1	0.0626	39.0	0.7675	37.8
0.0114	46.2	0.0768	38.7	1.2594	37.9
[NaCl] = 0.20 mol kg^{-1}					
0	73.3	0.0111	43.0	0.0718	38.2
0.0014	57.0	0.0139	41.3	0.0991	37.8
0.0028	53.6	0.0194	39.8	0.1535	37.8
0.0042	50.3	0.0249	38.9	0.2609	37.6
0.0055	47.8	0.0305	38.6	0.4184	37.5
0.0069	46.3	0.0387	38.8	0.6720	37.5
0.0083	44.8	0.0525	38.4		
[NaCl] = 0.30 mol kg^{-1}					
0	73.0	0.0147	39.6	0.1713	37.1
0.0012	52.9	0.0196	39.0	0.2657	37.2
0.0024	51.1	0.0244	38.6	0.4044	37.0
0.0037	48.3	0.0317	38.7	0.5843	36.8
0.0049	46.2	0.0415	38.0	0.8014	36.6
0.0061	44.6	0.0560	37.7	1.0103	36.8
0.0073	43.2	0.0754	37.7	1.4054	37.1
0.0098	41.6	0.0995	37.1		
0.0122	40.3	0.1235	37.4		

Table 6.1b - Surface Tension (γ) values of CPC in Water + 20 % Glycerol medium in the presence of Sodium Chloride at 298 K

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
		[NaCl] = 0.0 mol kg^{-1}			
0	71.6	0.1861	53.4	1.1528	43.0
0.0047	66.9	0.2323	52.6	1.4155	43.0
0.0093	65.0	0.2877	51.7	1.7603	42.9
0.0140	63.5	0.3612	49.9	2.1827	42.7
0.0187	62.6	0.4345	48.5	2.5960	43.2
0.0280	61.6	0.5257	47.6	3.0003	42.8
0.0467	60.0	0.6166	45.6	3.7832	42.9
0.0746	58.8	0.7070	44.4	4.5338	42.7
0.1025	57.6	0.7969	43.2	5.9455	42.4
0.1397	55.4	0.9757	42.3	7.2493	42.4
		[NaCl] = 0.001 mol kg^{-1}			
0	71.7	0.0784	55.2	0.5572	42.0
0.0030	66.8	0.1084	53.3	0.6729	42.4
0.0060	65.2	0.1384	52.0	0.8447	42.8
0.0091	63.3	0.1743	50.8	1.0704	41.9
0.0121	62.0	0.2160	49.5	1.3473	42.6
0.0181	60.6	0.2636	48.3	1.6722	42.5
0.0242	59.8	0.3228	46.7	1.9893	42.2
0.0362	58.4	0.3818	45.4	2.5012	42.6
0.0543	56.9	0.4405	44.4		
		[NaCl] = 0.005 mol kg^{-1}			
0	72.0	0.0768	50.2	0.3855	40.4
0.0030	64.3	0.1003	48.5	0.5001	41.7
0.0059	62.5	0.1239	47.1	0.6138	41.1
0.0089	60.5	0.1473	46.0	0.7825	41.0
0.0118	59.2	0.1766	44.5	1.0042	41.0
0.0178	58.0	0.2058	43.6	1.3832	41.3

Table 6.1b – Continued

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
[NaCl] = 0.005 mol kg^{-1}					
0.0296	55.1	0.2408	42.5	1.9060	40.8
0.0414	53.6	0.2814	41.5		
0.0591	51.4	0.3278	40.6		
[NaCl] = 0.01 mol kg^{-1}					
0	72.1	0.0392	50.2	0.1896	40.7
0.0025	63.2	0.0489	49.4	0.2185	40.6
0.0049	60.4	0.0636	47.5	0.2570	40.9
0.0074	59.1	0.0782	46.5	0.3048	40.0
0.0098	57.1	0.0976	45.3	0.3999	40.1
0.0147	55.4	0.1171	43.5	0.5878	39.9
0.0196	54.5	0.1365	42.7	0.8639	39.9
0.0294	52.2	0.1607	41.3	1.2218	40.8
[NaCl] = 0.02 mol kg^{-1}					
0	71.9	0.0349	48.4	0.1517	40.0
0.0022	62.1	0.0436	47.0	0.1817	39.5
0.0044	58.4	0.0566	45.3	0.2245	40.0
0.0065	58.4	0.0696	44.0	0.3096	39.7
0.0087	56.0	0.0826	42.1	0.5192	39.7
0.0131	53.9	0.0956	41.5	0.9256	40.1
0.0174	52.5	0.1129	40.5		
0.0262	50.1	0.1301	40.0		
[NaCl] = 0.05 mol kg^{-1}					
0	72.0	0.0179	48.1	0.1103	39.4
0.0018	59.8	0.0250	46.0	0.1385	38.9
0.0036	57.1	0.0322	44.0	0.1736	39.1
0.0054	55.4	0.0393	42.7	0.2435	39.6
0.0072	53.2	0.0464	41.5	0.3814	38.8

Table 6.1b – Continued

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
[NaCl] = 0.05 mol kg^{-1}					
0.0089	52.3	0.0571	40.2	0.5841	39.0
0.0107	51.2	0.0713	39.7		
0.0143	49.4	0.0890	39.7		
[NaCl] = 0.10 mol kg^{-1}					
0	72.6	0.0112	47.6	0.0503	39.3
0.0014	56.7	0.0140	46.0	0.0643	39.1
0.0028	55.4	0.0196	43.8	0.0837	39.2
0.0042	53.4	0.0252	42.2	0.1058	38.5
0.0056	51.8	0.0308	40.8	0.1334	39.1
0.0070	50.6	0.0364	39.8	0.2154	38.4
0.0084	49.2	0.0420	39.3	0.4815	38.5
[NaCl] = 0.20 mol kg^{-1}					
0	72.2	0.0101	44.4	0.0476	38.3
0.0013	53.6	0.0126	42.9	0.0626	38.4
0.0025	52.6	0.0151	41.2	0.0825	38.0
0.0038	49.8	0.0201	40.3	0.1072	37.9
0.0050	48.1	0.0251	39.1	0.1809	37.8
0.0063	46.8	0.0301	38.6	0.3017	37.4
0.0075	45.6	0.0376	38.7	0.5361	37.5
[NaCl] = 0.30 mol kg^{-1}					
0	72.3	0.0092	42.7	0.0552	37.7
0.0012	53.6	0.0115	41.7	0.0735	37.7
0.0023	50.0	0.0139	40.3	0.0962	37.6
0.0035	48.2	0.0162	39.8	0.1640	37.3
0.0046	48.0	0.0208	38.9	0.2750	37.2
0.0058	45.7	0.0277	38.5	0.4266	36.7
0.0069	44.1	0.0392	38.0	0.6359	37.0

Table 6.1c - Surface Tension (γ) values of CPC in Water + 30 % Glycerol medium in the presence of Sodium Chloride at 298 K

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
[NaCl] = 0.0 mol kg^{-1}					
0	70.8	0.1589	55.0	1.3582	43.0
0.0047	66.2	0.2240	53.2	1.7042	43.1
0.0094	64.5	0.2981	51.2	2.1278	43.1
0.0141	63.1	0.3719	50.0	2.7045	43.0
0.0188	62.4	0.4637	48.8	3.4971	43.1
0.0281	61.2	0.6461	46.3	4.9807	42.8
0.0469	59.6	0.8267	44.4	6.9828	42.6
0.0750	58.1	1.0055	42.7		
0.1123	56.5	1.1827	42.5		
[NaCl] = 0.001 mol kg^{-1}					
0	70.6	0.0749	55.2	0.6005	43.0
0.0031	65.8	0.1059	53.5	0.7200	42.0
0.0063	63.6	0.1431	52.0	0.8386	42.1
0.0094	61.8	0.1864	50.9	1.0147	42.1
0.0125	61.1	0.2358	49.5	1.2461	42.2
0.0188	60.0	0.2972	48.2	1.5863	42.4
0.0312	58.3	0.4192	45.5	2.0273	42.1
0.0499	56.6	0.5403	43.6	2.5595	42.7
[NaCl] = 0.005 mol kg^{-1}					
0	71.6	0.0610	51.6	0.3401	41.5
0.0028	65.1	0.0831	50.7	0.4479	41.1
0.0056	62.2	0.1107	48.7	0.6079	41.1
0.0083	60.6	0.1382	47.7	0.8130	41.2
0.0111	59.6	0.1712	46.0	1.0711	41.2
0.0167	57.5	0.2040	44.9	1.4237	41.3
0.0278	56.0	0.2423	43.6	1.9104	41.4
0.0444	53.5	0.2858	42.6		

Table 6.1c – Continued

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
		[NaCl] = 0.01 mol kg^{-1}			
0	71.7	0.0294	53.0	0.1994	41.3
0.0025	62.2	0.0441	50.7	0.2379	40.5
0.0049	59.5	0.0587	49.4	0.2859	40.6
0.0074	59.0	0.0782	47.8	0.3812	40.5
0.0098	58.6	0.0977	46.3	0.5227	40.2
0.0123	56.0	0.1220	44.8	0.7547	40.4
0.0147	56.3	0.1463	43.5	0.9820	40.2
0.0196	54.3	0.1705	42.3	1.4231	40.4
		[NaCl] = 0.02 mol kg^{-1}			
0	71.6	0.0451	47.3	0.2193	39.6
0.0023	61.3	0.0586	45.2	0.2635	39.3
0.0045	57.6	0.0721	44.8	0.3513	39.7
0.0068	55.8	0.0901	42.8	0.4817	39.8
0.0090	55.3	0.1080	41.3	0.6952	39.6
0.0136	53.7	0.1304	39.9	0.9043	39.8
0.0226	50.8	0.1527	40.0		
0.0316	49.1	0.1838	39.7		
		[NaCl] = 0.05 mol kg^{-1}			
0	71.5	0.0219	48.0	0.0874	39.4
0.0018	60.5	0.0292	45.0	0.1055	39.5
0.0037	55.3	0.0365	44.2	0.1272	39.2
0.0055	53.6	0.0438	43.3	0.1560	39.3
0.0073	53.0	0.0547	41.3	0.2275	39.2
0.0110	50.8	0.0656	40.3	0.4038	38.8
0.0146	49.5	0.0765	39.4	0.6443	38.6

Table 6.1c – Continued

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
[NaCl] = 0.10 mol kg^{-1}					
0	70.5	0.0145	47.2	0.0894	39.3
0.0015	57.7	0.0203	45.6	0.1123	39.0
0.0029	57.0	0.0261	43.7	0.1408	39.0
0.0044	52.4	0.0319	41.6	0.2255	39.0
0.0058	51.6	0.0376	41.2	0.3643	38.7
0.0073	49.9	0.0463	39.5	0.6332	38.4
0.0087	50.1	0.0549	39.4		
0.0116	48.0	0.0693	39.1		
[NaCl] = 0.20 mol kg^{-1}					
0	72.0	0.0103	44.4	0.0487	38.8
0.0013	55.2	0.0128	42.9	0.0640	38.7
0.0026	55.0	0.0154	42.9	0.0843	38.3
0.0039	51.0	0.0205	40.4	0.1096	38.4
0.0051	48.8	0.0257	39.4	0.1599	37.9
0.0064	46.3	0.0308	39.1	0.2591	37.9
0.0077	46.5	0.0385	38.9	0.4048	37.9
[NaCl] = 0.30 mol kg^{-1}					
0	71.7	0.0083	44.1	0.0415	38.0
0.0010	55.7	0.0104	42.4	0.0560	37.9
0.0021	52.8	0.0125	42.1	0.0765	37.8
0.0031	47.9	0.0167	40.3	0.1174	37.1
0.0042	48.3	0.0208	38.7	0.1982	37.3
0.0052	46.5	0.0250	38.7	0.3168	37.1
0.0063	44.5	0.0312	38.4	0.4325	37.1

Table 6.1d - Surface Tension (γ) values of CPC in Water + 40 % Glycerol medium in the presence of Sodium Chloride at 298 K

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
[NaCl] = 0.0 mol kg^{-1}					
0	70.1	0.2004	53.9	1.6411	42.6
0.0048	64.8	0.2762	52.3	1.9880	42.5
0.0096	63.4	0.3705	50.4	2.4122	42.4
0.0144	62.8	0.4642	49.2	2.9890	42.6
0.0192	61.5	0.6504	46.8	3.7803	42.8
0.0288	60.7	0.8346	45.0	4.5355	42.7
0.0575	58.6	1.0170	43.2	5.9469	42.4
0.0957	57.3	1.1976	41.8		
0.1434	55.5	1.3763	42.0		
[NaCl] = 0.001 mol kg^{-1}					
0	70.4	0.1877	51.5	1.2802	41.8
0.0039	63.7	0.2486	50.1	1.5638	42.1
0.0116	62.9	0.3243	48.5	1.9116	42.5
0.0269	58.9	0.3998	47.1	2.2524	42.4
0.0423	57.3	0.5497	44.5	2.7177	42.3
0.0654	55.9	0.6242	44.0	3.3601	42.3
0.0960	54.0	0.7721	42.0		
0.1343	53.0	0.9917	41.7		
[NaCl] = 0.005 mol kg^{-1}					
0	70.7	0.1084	49.5	0.7064	40.8
0.0030	62.2	0.1503	47.5	0.9337	40.7
0.0060	59.2	0.1921	46.2	1.2673	40.9
0.0121	57.5	0.2397	45.3	1.6991	40.8
0.0242	55.0	0.2989	43.4	2.1165	41.1
0.0362	54.1	0.3579	42.7	2.6193	41.0
0.0543	52.0	0.4166	41.7		
0.0784	50.7	0.5333	40.7		

Table 6.1d – Continued

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
		[NaCl] = 0.01 mol kg^{-1}			
0	70.2	0.0786	47.7	0.3541	40.0
0.0025	61.0	0.0982	47.4	0.4491	40.0
0.0049	58.0	0.1226	45.9	0.6366	40.4
0.0099	57.6	0.1469	45.0	0.9119	40.5
0.0148	54.1	0.1809	43.7	1.2679	40.3
0.0246	53.1	0.2196	42.4	1.6964	40.7
0.0394	52.3	0.2582	41.4		
0.0590	50.2	0.3062	40.2		
		[NaCl] = 0.02 mol kg^{-1}			
0	70.8	0.0498	48.4	0.2420	40.1
0.0023	60.4	0.0633	47.4	0.2862	40.2
0.0045	60.0	0.0813	46.1	0.3740	40.1
0.0091	56.4	0.1038	44.3	0.5474	39.9
0.0136	55.1	0.1262	43.2	0.8018	40.0
0.0181	53.2	0.1531	41.3	1.1310	39.8
0.0272	52.6	0.1798	40.5		
0.0362	50.5	0.2066	40.2		
		[NaCl] = 0.05 mol kg^{-1}			
0	70.9	0.0351	45.1	0.1088	39.7
0.0020	59.6	0.0429	44.4	0.1242	39.6
0.0039	57.1	0.0507	43.2	0.1473	39.7
0.0078	54.3	0.0585	44.0	0.1780	39.5
0.0117	53.5	0.0701	42.2	0.2162	39.6
0.0195	51.1	0.0817	41.4	0.3299	39.1
0.0273	49.0	0.0933	40.6	0.6258	39.4

Table 6.1d – Continued

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
[NaCl] = 0.10 mol kg^{-1}					
0	70.4	0.0182	47.2	0.0784	38.8
0.0015	57.3	0.0212	46.8	0.0994	38.9
0.0030	55.9	0.0272	45.8	0.1292	38.9
0.0045	53.9	0.0333	43.5	0.1884	38.8
0.0061	51.6	0.0393	42.4	0.3053	38.5
0.0076	49.1	0.0453	41.7	0.5332	38.4
0.0091	50.4	0.0544	39.4		
0.0121	48.4	0.0634	39.6		
[NaCl] = 0.20 mol kg^{-1}					
0	70.4	0.0158	44.4	0.0525	38.6
0.0013	54.7	0.0184	42.9	0.0656	38.2
0.0026	51.7	0.0211	41.4	0.0838	38.3
0.0040	52.2	0.0237	41.6	0.1097	38.1
0.0053	48.8	0.0289	39.9	0.1612	37.8
0.0066	48.8	0.0342	39.0	0.2880	37.8
0.0079	45.2	0.0394	38.8		
0.0132	43.3	0.0447	38.5		
[NaCl] = 0.30 mol kg^{-1}					
0	71.0	0.0130	43.5	0.0427	38.5
0.0009	55.4	0.0149	43.8	0.0537	37.9
0.0019	55.0	0.0186	41.7	0.0684	37.9
0.0028	49.5	0.0223	41.3	0.0867	37.8
0.0037	49.0	0.0260	40.8	0.1230	37.6
0.0056	46.7	0.0297	40.0	0.1947	37.2
0.0075	46.2	0.0353	38.5	0.3340	37.0

Table 6.1e - Surface Tension (γ) values of CPC in Water + 50 % Glycerol medium in the presence of Sodium Chloride at 298 K

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
[NaCl] = 0.0 mol kg^{-1}					
0	70.2	0.3017	52.7	2.0211	42.4
0.0066	65.7	0.4057	51.1	2.4994	42.7
0.0132	63.9	0.5222	49.7	2.9677	42.7
0.0264	61.8	0.6509	48.6	3.6517	42.9
0.0527	59.4	0.9062	46.0	4.3148	42.8
0.0922	57.5	1.1588	44.0	5.1678	43.0
0.1448	55.8	1.4085	42.3	6.1871	42.8
0.2103	54.2	1.6556	42.7		
[NaCl] = 0.001 mol kg^{-1}					
0	69.4	0.1096	55.4	1.0425	43.0
0.0042	62.7	0.1599	53.9	1.2800	41.9
0.0085	61.5	0.2268	51.6	1.6688	41.9
0.0127	60.4	0.3101	51.3	2.0489	42.2
0.0169	58.3	0.4755	48.2	2.4207	42.5
0.0253	57.0	0.6394	46.1	2.7845	42.3
0.0422	56.1	0.7207	45.3	3.4889	42.4
0.0675	56.7	0.8823	43.9		
[NaCl] = 0.005 mol kg^{-1}					
0	70.0	0.0686	53.2	0.6466	41.6
0.0031	60.7	0.0996	52.5	0.7651	41.4
0.0062	59.2	0.1368	49.1	0.9990	41.4
0.0094	57.9	0.1739	48.4	1.2854	41.7
0.0125	56.3	0.2232	47.3	1.5656	41.4
0.0187	56.3	0.2845	47.0	2.0013	41.6
0.0312	56.5	0.4063	44.3	2.5252	41.6
0.0437	55.8	0.5270	42.8		

Table 6.1e – Continued

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
		[NaCl] = 0.01 mol kg^{-1}			
0	69.9	0.0549	50.9	0.3011	42.7
0.0025	59.7	0.0748	50.2	0.3497	42.1
0.0050	57.6	0.0947	49.9	0.4461	41.3
0.0075	56.0	0.1195	48.2	0.6364	41.0
0.0100	55.8	0.1442	47.6	0.8695	40.9
0.0150	56.2	0.1738	46.8	1.1871	40.9
0.0250	53.5	0.2132	45.1	1.5382	40.9
0.0400	54.2	0.2524	44.7	1.8774	40.8
		[NaCl] = 0.02 mol kg^{-1}			
0	69.5	0.0433	51.1	0.2736	40.9
0.0022	58.0	0.0605	49.6	0.3156	40.3
0.0043	56.4	0.0821	48.2	0.3991	40.2
0.0065	56.8	0.1078	45.1	0.5229	40.1
0.0087	54.1	0.1335	45.4	0.7255	40.4
0.0130	53.5	0.1634	43.8	1.0018	40.1
0.0217	52.1	0.1974	42.3	1.3819	40.2
0.0303	51.3	0.2314	41.9		
		[NaCl] = 0.05 mol kg^{-1}			
0	69.6	0.0239	48.6	0.1389	39.8
0.0017	58.1	0.0341	47.4	0.1657	39.7
0.0034	59.0	0.0477	44.5	0.1991	39.9
0.0051	53.4	0.0613	44.2	0.2653	40.0
0.0068	52.2	0.0782	43.5	0.3961	39.3
0.0103	51.1	0.0985	42.9	0.5879	39.6
0.0171	49.0	0.1187	41.1	0.8965	39.7

Table 6.1e – Continued

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
		[NaCl] = 0.10 mol kg^{-1}			
0	70.0	0.0175	47.3	0.1013	38.9
0.0015	57.4	0.0233	46.8	0.1299	39.2
0.0029	54.5	0.0320	44.7	0.1868	38.9
0.0044	55.6	0.0407	42.1	0.2991	38.7
0.0058	51.5	0.0494	41.2	0.4638	38.5
0.0087	48.9	0.0610	41.0	0.6768	38.8
0.0117	48.4	0.0783	40.0	0.9329	38.4
		[NaCl] = 0.20 mol kg^{-1}			
0	69.5	0.0214	44.8	0.0693	39.2
0.0013	55.5	0.0268	43.2	0.0852	38.8
0.0027	54.4	0.0321	43.5	0.1063	38.7
0.0054	52.8	0.0374	42.1	0.1326	38.7
0.0080	50.7	0.0428	42.2	0.2106	38.2
0.0107	49.6	0.0507	39.5	0.3384	38.0
0.0161	47.6	0.0587	39.7	0.4633	37.9
		[NaCl] = 0.30 mol kg^{-1}			
0	69.8	0.0114	46.3	0.0508	38.9
0.0009	55.0	0.0132	42.4	0.0658	38.4
0.0019	54.2	0.0151	44.3	0.0844	38.2
0.0028	52.4	0.0189	43.6	0.1396	37.8
0.0038	51.3	0.0227	40.4	0.2301	37.6
0.0057	47.7	0.0264	40.8	0.4048	37.6
0.0076	48.8	0.0321	39.1		
0.0095	47.6	0.0396	38.8		

Table 6.1f - Surface Tension (γ) values of CPC in Water + 60 % Glycerol medium in the presence of Sodium Chloride at 298 K

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
		[NaCl] = 0.0 mol kg^{-1}			
0	68.5	0.2722	53.2	2.0752	42.1
0.0085	62.3	0.3568	52.5	2.3906	42.1
0.0171	61.6	0.4747	51.0	2.8571	42.3
0.0342	60.0	0.6089	50.0	3.4666	42.2
0.0683	57.9	0.7757	48.3	4.3555	42.4
0.1024	55.7	1.1063	46.9	5.4953	42.6
0.1535	56.0	1.4331	44.6	6.8520	42.7
0.2044	55.2	1.7560	43.0	8.1386	42.4
		[NaCl] = 0.001 mol kg^{-1}			
0	68.6	0.3205	50.0	1.8212	42.1
0.0065	62.3	0.4094	49.6	2.0577	42.2
0.0129	60.9	0.4979	48.9	2.4077	42.2
0.0387	57.9	0.5987	48.7	2.8656	42.3
0.0516	57.5	0.7241	46.8	3.5343	42.4
0.0773	56.3	0.8487	46.4	4.3936	42.7
0.1159	54.9	1.0959	44.8	5.4192	42.7
0.1672	53.5	1.3404	43.3		
0.2312	53.0	1.5821	41.9		
		[NaCl] = 0.005 mol kg^{-1}			
0	68.7	0.1854	49.3	1.1483	41.5
0.0049	62.6	0.2435	48.5	1.3309	41.2
0.0098	58.6	0.3207	48.5	1.6012	41.5
0.0196	57.1	0.3976	47.5	1.9551	41.7
0.0294	56.4	0.4932	46.2	2.4721	41.7
0.0490	53.5	0.5884	45.0	3.1371	41.6
0.0685	52.8	0.6829	43.7	3.6185	41.5

Table 6.1f – Continued

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
		[NaCl] = 0.005 mol kg^{-1}			
0.0978	52.1	0.7770	42.8		
0.1368	51.2	0.9636	41.9		
		[NaCl] = 0.01 mol kg^{-1}			
0	68.7	0.1498	49.5	0.7517	41.1
0.0044	60.3	0.1848	47.9	0.9195	41.1
0.0088	57.9	0.2285	47.0	1.1677	40.9
0.0177	56.5	0.2807	45.0	1.4925	41.0
0.0354	55.5	0.3415	45.3	1.9668	40.9
0.0618	53.0	0.4106	43.9	2.5764	41.0
0.0883	50.3	0.4966	42.7	3.3039	41.3
0.1147	50.8	0.5821	41.5		
		[NaCl] = 0.02 mol kg^{-1}			
0	68.0	0.0841	51.2	0.5326	40.4
0.0032	60.7	0.1098	49.9	0.6558	40.4
0.0065	60.4	0.1419	47.9	0.7776	40.6
0.0130	56.8	0.1803	47.0	0.9579	40.4
0.0195	57.6	0.2313	45.9	1.1937	39.8
0.0324	54.4	0.2821	44.0	1.5381	40.3
0.0454	53.2	0.3453	42.5	1.9806	40.3
0.0647	51.8	0.4081	40.8	2.4050	40.1
		[NaCl] = 0.05 mol kg^{-1}			
0	69.1	0.0795	46.8	0.3266	40.1
0.0031	56.3	0.1039	46.1	0.3741	40.1
0.0061	57.1	0.1282	44.1	0.4332	40.0
0.0123	55.3	0.1524	43.3	0.5505	39.9
0.0184	53.7	0.1826	42.4	0.7812	39.8
0.0307	51.9	0.2128	40.6	1.1179	39.6

Table 6.1f – Continued

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
		[NaCl] = 0.05 mol kg^{-1}			
0.0429	50.5	0.2428	40.6		
0.0612	48.8	0.2788	40.3		
		[NaCl] = 0.10 mol kg^{-1}			
0	68.4	0.0563	44.9	0.2369	39.4
0.0024	55.2	0.0704	44.6	0.2734	39.3
0.0047	53.8	0.0890	43.2	0.3188	39.3
0.0094	53.2	0.1123	41.9	0.4090	39.2
0.0141	52.9	0.1355	40.4	0.4982	39.0
0.0235	50.3	0.1587	39.6	0.5863	39.0
0.0329	48.1	0.1817	39.3		
0.0423	47.4	0.2093	39.1		
		[NaCl] = 0.20 mol kg^{-1}			
0	68.6	0.0285	46.0	0.1447	39.1
0.0018	53.8	0.0391	44.9	0.1656	38.6
0.0036	51.8	0.0533	43.8	0.1933	38.8
0.0071	51.3	0.0710	41.7	0.2209	38.5
0.0107	49.3	0.0886	40.4	0.2553	38.7
0.0143	48.9	0.1062	39.6	0.3235	38.6
0.0214	47.4	0.1237	38.8	0.3909	38.6
		[NaCl] = 0.30 mol kg^{-1}			
0	68.8	0.0241	46.3	0.1106	38.4
0.0015	56.2	0.0301	44.9	0.1283	38.5
0.0030	54.9	0.0391	43.5	0.1519	38.5
0.0060	53.8	0.0511	40.5	0.1753	38.3
0.0091	51.6	0.0631	40.3	0.2045	38.3
0.0121	49.0	0.0780	39.1	0.2623	38.4
0.0181	48.1	0.0928	38.7	0.3195	38.4

Table 6.1g - Surface Tension (γ) values of CPC in Water + 70 % Glycerol medium in the presence of Sodium Chloride at 298 K

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
[NaCl] = 0.0 mol kg^{-1}					
0	67.9	0.5349	53.0	3.8786	41.6
0.0112	62.9	0.7115	51.6	4.6792	41.7
0.0224	61.9	0.9312	50.7	5.4624	42.0
0.0449	60.7	1.3668	47.9	6.6058	41.7
0.0897	58.4	1.7973	46.2	7.7132	41.9
0.1568	56.0	2.2230	44.7	9.1365	41.9
0.2461	54.9	2.6439	43.0	10.835	42.1
0.3797	54.0	3.2665	41.7		
[NaCl] = 0.001 mol kg^{-1}					
0	67.1	0.2328	50.9	1.6814	44.7
0.0073	58.5	0.3196	50.6	2.0877	43.2
0.0146	58.4	0.4348	48.5	2.6189	41.8
0.0292	56.1	0.5637	47.9	3.1386	41.7
0.0584	56.1	0.7062	47.7	3.6470	41.7
0.0876	54.8	0.8479	47.6	4.2673	41.7
0.1312	54.5	1.1289	45.9	4.8713	41.9
0.1748	52.3	1.4067	45.5	5.4597	41.9
[NaCl] = 0.005 mol kg^{-1}					
0	67.5	0.1955	50.9	1.6610	41.3
0.0058	58.8	0.3437	49.5	1.8721	41.3
0.0116	56.9	0.4570	48.0	2.1842	41.4
0.0231	56.7	0.5696	45.9	2.5925	41.2
0.0462	56.0	0.9036	45.6	3.0906	41.3
0.0692	53.9	1.0136	45.3	3.6708	41.5
0.1152	54.0	1.2319	43.8	4.4164	41.8
0.1497	50.9	1.4477	42.2	5.1317	41.5

Table 6.1g – Continued

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
		[NaCl] = 0.01 mol kg^{-1}			
0	68.1	0.1843	47.0	1.7822	40.9
0.0049	55.5	0.2420	46.3	2.1281	40.8
0.0097	55.1	0.3188	45.4	2.5500	40.8
0.0195	54.8	0.4142	45.1	2.9608	41.2
0.0390	53.1	0.6971	43.0	3.5958	41.5
0.0681	51.4	0.8831	43.1	4.2050	41.1
0.0972	49.7	1.1581	41.0		
0.1360	47.6	1.4285	40.7		
		[NaCl] = 0.02 mol kg^{-1}			
0	67.9	0.2535	47.3	0.9061	40.6
0.0078	58.3	0.3142	46.9	1.0500	40.9
0.0155	56.6	0.3897	46.4	1.2627	40.5
0.0310	55.3	0.4647	44.9	1.4719	40.7
0.0619	54.0	0.5393	43.6	1.7454	40.6
0.0850	51.4	0.6135	42.2	2.0131	40.6
0.1158	49.8	0.6873	42.6	2.4038	40.8
0.1542	48.7	0.7607	41.9		
		[NaCl] = 0.05 mol kg^{-1}			
0	67.9	0.1139	49.2	0.5252	40.2
0.0036	60.1	0.1564	47.9	0.5935	40.0
0.0072	58.3	0.2057	45.9	0.7291	39.8
0.0143	58.0	0.2619	44.5	0.8631	39.8
0.0286	54.4	0.3248	42.5	1.0614	39.8
0.0500	52.3	0.3873	41.9	1.3847	39.6
0.0784	51.1	0.4564	40.3	1.6992	39.7

Table 6.1g – Continued

[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}	[CPC] / mmol kg^{-1}	γ / mN m^{-1}
[NaCl] = 0.10 mol kg^{-1}					
0	67.7	0.1094	46.5	0.3543	39.4
0.0061	57.7	0.1396	44.3	0.4015	39.6
0.0122	55.3	0.1697	43.5	0.4601	39.7
0.0244	53.7	0.1997	43.3	0.5183	39.6
0.0427	51.7	0.2356	41.2	0.6339	39.7
0.0609	48.4	0.2713	40.9	0.7482	39.4
0.0852	48.1	0.3070	40.3		
[NaCl] = 0.20 mol kg^{-1}					
0	67.6	0.0679	46.9	0.2481	39.2
0.0026	58.4	0.0887	45.1	0.2786	39.3
0.0052	56.8	0.1094	44.2	0.3192	39.5
0.0105	55.6	0.1353	42.6	0.3595	39.4
0.0209	53.2	0.1610	41.4	0.4097	39.4
0.0366	51.2	0.1867	40.3	0.4595	39.2
0.0523	48.8	0.2175	39.0	0.5584	39.1
[NaCl] = 0.30 mol kg^{-1}					
0	67.7	0.0662	44.8	0.2056	39.0
0.0022	60.8	0.0838	43.4	0.2315	38.8
0.0044	57.6	0.1013	43.0	0.2658	39.0
0.0089	54.7	0.1188	40.6	0.2999	38.6
0.0177	50.5	0.1363	39.7	0.3424	38.9
0.0310	48.5	0.1580	39.4	0.4267	38.8
0.0486	46.9	0.1797	39.2		

Table 6.2a – Specific Conductance (κ) values of CPC in Water + 10 % Glycerol medium in the presence of Sodium Chloride at 298 K.

[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}
		[NaCl] = 0.0 mol kg^{-1}			
0	3.2682	0.5209	46.265	1.3585	95.164
0.0241	4.7340	0.6137	53.608	1.4901	99.755
0.0481	6.9834	0.7060	61.313	1.6420	104.74
0.0960	12.397	0.7977	68.441	1.8138	110.69
0.1438	16.580	0.8888	74.650	2.0047	116.10
0.2152	22.602	0.9794	79.764	2.2139	122.48
0.2863	28.024	1.0695	83.969	2.6234	134.97
0.3570	33.231	1.1590	87.899	3.0214	145.47
0.4275	39.083	1.2480	91.214		
		[NaCl] = 0.001 mol kg^{-1}			
0	111.19	0.3006	135.65	0.8653	170.08
0.0190	112.82	0.3563	139.93	0.9720	173.60
0.0379	114.73	0.4117	144.17	1.0955	177.27
0.0757	118.17	0.4853	149.85	1.2352	181.53
0.1135	121.10	0.5585	155.23	1.4079	186.63
0.1511	124.15	0.6313	160.13	1.7467	196.36
0.1886	127.07	0.7037	163.51	2.0772	205.47
0.2447	131.45	0.7758	166.96		
		[NaCl] = 0.005 mol kg^{-1}			
0	523.61	0.2187	551.48	0.7992	570.60
0.0184	533.24	0.2547	553.97	0.9354	574.31
0.0367	537.20	0.2907	556.03	1.1035	578.47
0.0551	539.35	0.3265	558.18	1.2689	582.43
0.0734	540.57	0.3622	560.87	1.5925	589.91
0.0916	541.99	0.4155	562.28	1.9065	597.29
0.1099	543.71	0.4863	564.04	2.2115	604.52
0.1463	546.10	0.5741	565.85		
0.1825	548.59	0.6785	567.81		

Table 6.2a – Continued

[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}
		[NaCl] = 0.01 mol kg^{-1}			
0	982.40	0.1096	991.39	0.3843	1001.7
0.0122	982.88	0.1338	992.86	0.4431	1002.3
0.0245	984.06	0.1580	994.03	0.5014	1003.9
0.0367	986.99	0.1820	995.50	0.5594	1005.6
0.0489	987.87	0.2060	996.67	0.6515	1008.0
0.0610	988.65	0.2420	997.55	0.7654	1010.8
0.0732	989.34	0.2778	998.53		
0.0854	990.02	0.3253	999.90		
		[NaCl] = 0.02 mol kg^{-1}			
0	1943.2	0.0778	1948.5	0.1989	1953.3
0.0112	1940.7	0.0889	1948.8	0.2426	1954.3
0.0223	1944.5	0.1000	1949.0	0.3077	1956.5
0.0334	1945.4	0.1110	1950.0	0.3938	1958.2
0.0445	1946.7	0.1220	1950.8	0.5005	1960.6
0.0557	1947.6	0.1441	1951.5	0.6060	1962.7
0.0667	1948.1	0.1660	1952.2	0.8135	1967.8

Table 6.2b – Specific Conductance (κ) values of CPC in Water + 20 % Glycerol medium in the presence of Sodium Chloride at 298 K.

[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}
		[NaCl] = 0.0 mol kg^{-1}			
0	5.0293	0.5888	42.976	1.2303	75.300
0.0249	6.7762	0.7092	50.254	1.3700	79.793
0.0746	10.148	0.8289	57.319	1.5547	85.103
0.1241	13.762	0.8766	60.154	1.7376	89.826
0.1982	18.426	0.9241	62.819	1.9637	95.692
0.2721	23.330	0.9715	65.185	2.4079	106.38
0.3701	29.602	1.0189	67.336	2.8416	116.73
0.4676	35.580	1.1131	71.203	3.2652	126.09
		[NaCl] = 0.001 mol kg^{-1}			
0	97.340	0.3352	118.74	0.8586	144.22
0.0188	98.484	0.4086	123.16	0.9644	147.19
0.0376	99.931	0.4633	126.42	1.1042	150.88
0.0752	102.40	0.5179	129.09	1.2426	154.33
0.1126	104.77	0.5723	132.95	1.4136	158.45
0.1686	108.16	0.6264	135.87	1.7491	166.25
0.2243	111.53	0.6983	138.88	2.0763	173.52
0.2799	115.26	0.7697	141.46	2.3954	180.69
		[NaCl] = 0.005 mol kg^{-1}			
0	419.34	0.1985	428.88	0.4966	439.36
0.0133	419.69	0.2378	431.03	0.5604	440.83
0.0267	419.81	0.2640	432.21	0.6365	442.22
0.0533	420.88	0.2900	433.48	0.7372	444.31
0.0798	422.19	0.3161	434.42	0.8619	446.74
0.1063	423.60	0.3550	435.84	1.1073	451.35
0.1327	425.01	0.3938	436.82	1.3474	455.99
0.1591	426.59	0.4453	438.15		

Table 6.2b – Continued

[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}
[NaCl] = 0.01 mol kg^{-1}					
0	791.53	0.1312	801.45	0.3309	808.59
0.0120	793.14	0.1431	802.87	0.3773	809.47
0.0240	795.00	0.1667	804.09	0.4466	810.99
0.0359	796.27	0.1903	804.88	0.5382	812.45
0.0479	797.30	0.2139	805.80	0.6517	814.26
0.0598	797.98	0.2374	806.44	0.7639	816.37
0.0837	798.81	0.2608	806.93	0.9847	820.28
0.1075	800.13	0.2959	807.86		
[NaCl] = 0.02 mol kg^{-1}					
0	1519.5	0.1384	1525.8	0.3997	1530.1
0.0093	1520.5	0.1567	1526.1	0.4704	1531.3
0.0186	1520.8	0.1749	1526.3	0.5580	1532.4
0.0371	1521.7	0.2022	1526.9	0.6446	1534.0
0.0649	1522.5	0.2294	1527.2	0.7304	1536.2
0.0833	1523.1	0.2655	1527.7	0.8992	1538.8
0.1017	1524.3	0.3015	1528.3		
0.1201	1525.1	0.3463	1529.2		

Table 6.2c – Specific Conductance (κ) values of CPC in Water + 30 % Glycerol medium in the presence of Sodium Chloride at 298 K.

[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}
[NaCl] = 0.0 mol kg^{-1}					
0	2.6327	0.5763	32.481	1.6809	72.127
0.0365	4.3463	0.6826	37.698	1.8811	75.843
0.0730	8.4668	0.7882	43.066	2.1450	80.937
0.1456	12.247	0.8933	47.907	2.4052	85.602
0.2181	15.855	0.9979	52.747	2.7256	91.361
0.2902	18.505	1.1019	57.167	3.3502	101.51
0.3622	22.036	1.2053	60.580	3.9544	111.57
0.4338	25.431	1.3424	64.217		
0.5052	28.917	1.4785	67.659		
[NaCl] = 0.001 mol kg^{-1}					
0	90.539	0.4358	111.69	1.1687	134.62
0.0184	91.312	0.5250	115.53	1.3042	137.08
0.0552	93.023	0.6136	119.63	1.4385	139.35
0.0918	94.822	0.7018	123.28	1.6045	142.05
0.1467	97.658	0.7894	126.24	1.7687	144.85
0.2013	100.47	0.8765	128.56	2.0914	150.11
0.2738	104.41	0.9630	130.52		
0.3460	107.72	1.0662	132.67		
[NaCl] = 0.005 mol kg^{-1}					
0	319.78	0.2515	331.79	0.7396	343.42
0.0169	320.58	0.3011	333.53	0.8349	345.12
0.0338	321.21	0.3506	335.56	0.9295	344.79
0.0675	322.63	0.3999	337.07	1.0545	348.51
0.1012	324.57	0.4490	338.10	1.1783	350.62
0.1347	326.02	0.5142	339.69	1.3311	352.58
0.1682	327.76	0.5790	340.90	1.6311	357.05
0.2016	329.24	0.6596	341.90		

Table 6.2c – Continued

[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}
		[NaCl] = 0.01 mol kg^{-1}			
0	645.10	0.1628	652.39	0.3796	657.91
0.0117	645.89	0.1859	653.51	0.4247	658.69
0.0234	646.03	0.2089	654.49	0.4695	659.18
0.0468	646.96	0.2318	655.22	0.5364	660.16
0.0701	647.94	0.2547	655.76	0.6249	661.43
0.0934	648.82	0.2775	656.15	0.7344	662.70
0.1166	650.09	0.3117	656.84	0.8426	664.37
0.1397	651.17	0.3457	657.42		
		[NaCl] = 0.02 mol kg^{-1}			
0	1238.0	0.1102	1246.1	0.3484	1251.3
0.0111	1238.6	0.1321	1247.0	0.4124	1252.2
0.0221	1240.0	0.1540	1248.1	0.4759	1253.1
0.0332	1241.4	0.1758	1248.6	0.5600	1254.5
0.0442	1242.4	0.1975	1249.0	0.6640	1255.7
0.0553	1243.3	0.2301	1249.5	0.7669	1257.2
0.0663	1244.2	0.2625	1249.8		
0.0883	1245.2	0.3055	1250.6		

Table 6.2d – Specific Conductance (κ) values of CPC in Water + 40 % Glycerol medium in the presence of Sodium Chloride at 298 K.

[CPC] / mmol kg^{-1}	$\kappa \times 10^4$/ S m^{-1}	[CPC] / mmol kg^{-1}	$\kappa \times 10^4$/ S m^{-1}	[CPC] / mmol kg^{-1}	$\kappa \times 10^4$/ S m^{-1}
[NaCl] = 0.0 mol kg^{-1}					
0	3.1239	0.8769	31.016	2.0039	55.730
0.0359	4.2920	1.0133	35.741	2.1637	58.116
0.1075	5.8849	1.1486	39.178	2.3535	61.020
0.2144	9.4499	1.2830	42.544	2.5411	64.217
0.3206	13.496	1.4163	45.499	2.7882	68.822
0.4613	18.707	1.5486	47.340	3.0317	72.685
0.6009	22.990	1.6799	50.450	3.3312	76.166
0.7394	27.889	1.8427	53.637	3.6253	80.233
[NaCl] = 0.001 mol kg^{-1}					
0	60.306	0.6095	78.894	1.5297	99.110
0.0326	62.389	0.7352	82.033	1.6782	101.08
0.0977	63.161	0.8598	84.966	1.8255	102.75
0.1948	66.632	0.9836	90.305	1.9714	104.10
0.2914	69.272	1.1065	91.146	2.1161	106.37
0.3555	72.959	1.2285	93.600	2.2595	108.52
0.4830	76.298	1.3798	95.746	2.4016	109.92
[NaCl] = 0.005 mol kg^{-1}					
0	247.46	0.4384	260.00	1.0347	268.05
0.0262	248.17	0.5143	260.84	1.1557	269.79
0.0784	249.71	0.5899	261.91	1.2757	271.12
0.1303	251.28	0.6650	263.56	1.3946	272.34
0.2080	254.17	0.7397	264.28	1.5594	274.39
0.2852	256.59	0.8387	264.77	1.7222	276.25
0.3620	258.55	0.9371	266.98	1.8830	278.18

Table 6.2d – Continued

[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}
[NaCl] = 0.01 mol kg^{-1}					
0	464.26	0.3060	471.50	0.8517	478.93
0.0238	465.29	0.3524	472.67	0.9624	480.39
0.0713	466.02	0.4217	473.50	1.0938	482.64
0.1186	467.24	0.4906	474.58	1.2239	484.16
0.1657	468.27	0.5591	475.31	1.3951	485.82
0.2126	469.78	0.6499	477.02	1.5638	488.51
0.2594	470.52	0.7400	477.90		
[NaCl] = 0.02 mol kg^{-1}					
0	894.15	0.1939	900.70	0.6814	905.25
0.0195	895.47	0.2322	900.80	0.7544	906.57
0.0585	896.79	0.2704	901.48	0.8268	907.15
0.0780	897.67	0.3841	902.26	0.8988	907.55
0.0974	898.01	0.4593	903.00	0.9702	908.08
0.1167	898.65	0.5339	903.93		
0.1554	899.53	0.6079	904.42		

Table 6.2e – Specific Conductance (κ) values of CPC in Water + 50 % Glycerol medium in the presence of Sodium Chloride at 298 K.

[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}
[NaCl] = 0.0 mol kg^{-1}					
0	2.9215	1.2666	29.440	2.8546	51.154
0.0481	3.2214	1.4486	34.331	3.1088	54.527
0.1441	6.0770	1.6291	36.096	3.4433	55.158
0.2874	8.8916	1.8083	37.389	3.8545	59.225
0.4771	12.985	1.9860	38.954	4.2581	63.914
0.6652	16.660	2.2063	42.654	4.6544	66.632
0.8984	22.126	2.4245	47.355	5.0435	73.927
1.0832	24.914	2.6406	50.166	5.4257	74.430
[NaCl] = 0.001 mol kg^{-1}					
0	38.048	0.8918	56.228	2.3356	74.855
0.0339	39.540	1.0518	59.396	2.5687	77.036
0.1015	40.815	1.2102	59.641	2.7983	79.490
0.2024	41.592	1.3670	62.027	3.0805	82.238
0.3360	43.749	1.5532	64.662	3.3576	86.051
0.4685	48.685	1.7372	68.725	3.6296	87.577
0.5999	50.811	1.9192	71.668	3.8968	90.554
0.7303	52.102	2.0990	72.416		
[NaCl] = 0.005 mol kg^{-1}					
0	170.77	0.5224	179.98	1.2556	188.28
0.0254	171.40	0.5953	182.61	1.3698	189.65
0.0760	172.12	0.6678	183.51	1.5055	191.31
0.1515	173.36	0.7398	184.06	1.6840	192.57
0.2266	175.13	0.8352	184.49	1.8598	194.59
0.3012	175.68	0.9299	185.64	2.0760	195.40
0.3754	176.88	1.0238	186.39	2.2883	197.17
0.4491	179.75	1.1403	187.59		

Table 6.2e – Continued

[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}
		[NaCl] = 0.01 mol kg^{-1}			
0	320.90	0.3774	327.13	1.0332	334.08
0.0226	321.34	0.4643	328.46	1.1555	335.62
0.0676	322.34	0.5505	328.80	1.2764	336.85
0.1124	322.95	0.6360	330.40	1.4355	338.05
0.1792	323.10	0.7209	330.73	1.5921	339.94
0.2457	325.47	0.8260	331.61	1.7464	340.43
0.3117	325.78	0.9301	333.49	1.8983	341.19
		[NaCl] = 0.02 mol kg^{-1}			
0	618.56	0.3678	622.91	0.9269	626.82
0.0561	619.19	0.4217	623.74	1.0279	627.94
0.0933	619.39	0.4931	624.08	1.1444	630.24
0.1489	620.81	0.5639	624.47	1.2756	631.12
0.2041	621.20	0.6517	625.06	1.4368	631.85
0.2590	621.78	0.7386	625.74		
0.3135	622.22	0.8247	626.04		

Table 6.2f – Specific Conductance (κ) values of CPC in Water + 60 % Glycerol medium in the presence of Sodium Chloride at 298 K.

[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}
[NaCl] = 0.0 mol kg^{-1}					
0	1.6149	1.5723	23.309	3.8747	42.980
0.0577	2.3358	1.8439	27.216	4.2729	44.318
0.1727	4.2614	2.1129	30.054	4.6652	48.225
0.3444	6.4823	2.3793	32.183	5.1474	50.567
0.5717	10.112	2.6432	35.741	5.6207	52.992
0.7972	13.003	2.9564	36.988	6.0855	55.466
1.0208	16.500	3.2660	40.150	6.5419	57.676
1.2979	20.801	3.5721	41.064		
[NaCl] = 0.001 mol kg^{-1}					
0	24.398	1.2299	41.592	3.1143	57.812
0.0385	25.131	1.4094	44.124	3.3727	59.132
0.1151	25.959	1.5873	46.284	3.6274	60.795
0.2296	27.097	1.7634	48.269	3.9405	62.486
0.3812	28.955	1.9379	49.482	4.2482	64.114
0.5315	31.868	2.1451	51.476	4.5504	65.728
0.6807	33.501	2.3499	53.055	4.8473	67.136
0.8656	36.669	2.5860	54.644		
1.0486	38.873	2.8521	56.189		
[NaCl] = 0.005 mol kg^{-1}					
0	109.91	0.8468	116.93	2.1706	125.75
0.0361	110.64	0.9839	118.13	2.3604	127.39
0.1081	111.25	1.1200	119.22	2.5791	127.76
0.2156	112.30	1.2886	119.88	2.8254	129.93
0.3224	112.80	1.4555	121.13	3.0681	130.95
0.4286	113.75	1.6207	122.12	3.3071	131.37
0.5691	115.39	1.7844	122.88	3.6009	132.63
0.7085	115.95	1.9786	124.06		

Table 6.2f – Continued

[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^{4}/ S m^{-1}
[NaCl] = 0.01 mol kg^{-1}					
0	206.65	0.6181	213.32	1.5620	219.48
0.0264	206.86	0.7182	214.37	1.7240	220.85
0.0789	207.94	0.8176	214.85	1.9065	221.90
0.1573	208.48	0.9162	215.86	2.0863	222.86
0.2353	208.88	1.0384	216.29	2.2635	223.86
0.3128	209.62	1.1593	217.19	2.4380	224.62
0.4154	211.31	1.2791	217.70		
0.5171	212.07	1.4214	218.97		
[NaCl] = 0.02 mol kg^{-1}					
0	399.90	0.4048	405.10	1.1106	410.40
0.0229	400.21	0.4928	405.73	1.2341	410.64
0.0685	401.00	0.5802	406.45	1.3765	412.61
0.1139	401.21	0.6668	407.18	1.5368	413.47
0.1817	402.76	0.7741	407.66	1.6948	413.84
0.2491	403.56	0.8804	408.86	1.8890	415.21
0.3161	404.14	0.9856	409.07	2.0796	415.94

Table 6.2g – Specific Conductance (κ) values of CPC in Water + 70 % Glycerol medium in the presence of Sodium Chloride at 298 K.

[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}
[NaCl] = 0.0 mol kg^{-1}					
0	0.7982	2.1423	16.750	5.2089	31.982
0.0786	1.2318	2.5123	19.495	5.6169	33.364
0.2354	2.3807	2.8787	21.489	6.1537	35.168
0.4693	3.7575	3.2414	24.830	6.6824	36.468
0.7791	6.4217	3.6007	25.759	7.2033	38.392
1.0863	8.9972	3.9564	27.500	7.8437	39.677
1.3910	11.124	4.3787	28.966	8.4723	41.609
1.7685	13.902	4.7962	30.676	9.0896	43.262
[NaCl] = 0.001 mol kg^{-1}					
0	14.451	1.6946	27.328	4.1442	40.606
0.0488	14.988	1.9654	29.264	4.4672	41.643
0.1460	15.740	2.2330	31.514	4.7854	42.659
0.2911	16.566	2.4975	33.370	5.0990	43.506
0.4831	18.100	2.7589	34.798	5.4081	44.584
0.6737	18.890	3.0173	36.290	5.7127	45.499
0.9097	20.664	3.2727	37.413	6.0129	46.245
1.1433	22.996	3.5671	37.526	6.3088	47.174
1.4206	24.965	3.8575	39.556		
[NaCl] = 0.005 mol kg^{-1}					
0	55.177	1.1729	64.031	2.9236	73.623
0.0431	55.769	1.3753	65.674	3.1822	74.347
0.1290	56.170	1.5757	67.483	3.4735	75.403
0.2571	56.854	1.7741	68.490	3.7604	76.249
0.4267	58.741	1.9704	69.751	4.1128	77.427
0.5949	60.071	2.2035	70.866	4.4587	78.610
0.7618	61.230	2.4338	71.746	4.7981	79.471
0.9684	61.729	2.6615	72.753	5.1314	80.654

Table 6.2g – Continued

[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}	[CPC] / mmol kg^{-1}	κ x 10^4/ S m^{-1}
		[NaCl] = 0.01 mol kg^{-1}			
0	111.38	1.0836	118.83	2.8221	127.84
0.0330	111.75	1.2671	121.19	3.0388	128.54
0.0988	112.64	1.4483	121.06	3.2522	129.18
0.1969	113.41	1.6273	123.33	3.4623	130.06
0.3268	114.30	1.8041	124.16	3.7206	130.66
0.4556	114.96	2.0078	124.86	3.9741	131.78
0.6150	116.36	2.2086	125.88	4.2229	132.22
0.7729	116.93	2.4067	126.63		
0.9290	117.80	2.6021	126.93		
		[NaCl] = 0.02 mol kg^{-1}			
0	220.85	0.7418	225.64	1.8113	229.76
0.0263	221.00	0.8654	226.44	1.9918	230.51
0.0788	221.37	0.9877	227.18	2.1697	231.23
0.1571	222.37	1.1088	227.71	2.3448	231.52
0.2608	222.53	1.2288	227.87	2.5601	231.80
0.3636	223.47	1.3712	228.00	2.7715	232.76
0.4909	224.48	1.5119	229.04	2.9790	232.97
0.6170	225.07	1.6510	229.45		

Table 6.3 - Critical Micelle Concentration values of CPC in Water Glycerol media in the presence of NaCl at 25 °C. The values given in parentheses are those obtained by conductance method.

[NaCl] / mol kg^{-1}	Wt % Glycerol						
	10	20	30	40	50	60	70
	CMC x 10^4 / mol kg^{-1}						
0	9.11	9.50	10.4	12.2	14.0	20.9	32.9
	(9.27)	(9.96)	(10.9)	(12.3)	(14.5)	(21.3)	(33.1)
0.001	5.80	6.13	7.10	9.22	11.8	16.5	28.2
	(6.09)	(6.52)	(7.30)	(9.52)	(12.4)	(17.4)	(28.2)
0.005	2.90	3.09	3.55	5.10	6.69	10.4	18.5
	(3.20)	(3.11)	(3.64)	(4.98)	(6.84)	(10.7)	(18.7)
0.01	1.69	1.95	2.36	3.16	4.21	6.72	13.9
	(1.87)	(1.94)	(2.31)	(3.26)	(4.26)	(6.75)	(14.8)
0.02	1.09	1.25	1.39	1.91	3.28	4.58	9.44
	(1.22)	(1.26)	(1.41)	(1.91)	(3.85)	(4.51)	(9.68)
0.05	0.60	0.62	0.78	1.10	1.63	2.60	5.40
	-	-	-	-	-	-	-
0.10	0.37	0.40	0.51	0.72	1.02	1.78	3.64
	-	-	-	-	-	-	-
0.20	0.20	0.27	0.28	0.42	0.70	1.26	2.24
	-	-	-	-	-	-	-
0.30	0.17	0.21	0.24	0.41	0.42	0.87	1.79

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

[NaCl] / mol kg^{-1}	y_0 x 10^4 / mol kg^{-1}	a x 10^5 / mol kg^{-1}	b	R^2 (R= correlation coefficient)
0	8.85	1.65	0.071	0.998
0.001	5.69	1.98	0.067	0.997
0.005	2.61	1.38	0.068	0.999
0.01	1.86	0.33	0.084	0.997
0.02	1.15	0.33	0.079	0.994
0.05	0.59	0.17	0.081	0.998
0.10	0.37	0.11	0.081	0.999
0.20	0.16	0.19	0.067	0.999
0.30	0.18	0.04	0.085	0.996

Table 6.5 - Values of Counterion Binding Constant for CPC in Water Glycerol media at 25 °C Derived from the CH Plots (β_{CH}) and the Slope – Ratio Method (β_{κ})

Wt % Glycerol	β_{CH}	[NaCl] / mol kg^{-1}	β_k						
			Wt % Glycerol						
			10	20	30	40	50	60	70
0[a]	0.66	0	0.60	0.58	0.58	0.50	0.52	0.57	0.58
10	0.69	0.001	0.61	0.61	0.62	0.51	0.50	0.58	0.56
20	0.67	0.005	0.66	0.60	0.61	0.58	0.54	0.50	0.55
30	0.67	0.01	0.65	0.66	0.62	0.46	0.45	0.43	0.51
40	0.65	0.02	0.66	0.60	0.65	0.62	0.47	0.50	0.53
50	0.65								
60	0.62								
70	0.64								

a) Data from chapter 3

Table 6.6 - Calculated Values of ΔG^{o}_{m} and ΔG^{o}_{ad} of CPC + Water + Glycerol System in Presence of NaCl at 25 °C

[NaCl] / mol kg^{-1}	Wt % Glycerol							
	0$^{a)}$	10	20	30	40	50	60	70
				ΔG^{o}_{m} / kJ mol^{-1}				
0	-45.4	-45.0	-44.4	-43.6	-42.5	-40.9	-39.2	-36.6
0.001	-47.0	-46.8	-46.5	-45.2	-43. 7	-41.6	-40.2	-37.3
0.005	-50.4	-49.7	-49.3	-48.1	-46.1	-43.9	-42.1	-39.0
0.01	-51.8	-51.9	-51.2	-49.7	-48.1	-45.8	-43.9	-40.2
0.02	-53.2	-53.7	-53.1	-51.9	-50.1	-46.8	-45.4	-41.8
0.05		-56.2	-56.0	-54.3	-52.4	-49.7	-47.8	-44.1
0.10		-58.2	-57.8	-56.0	-54.1	-51.6	-49.3	-45.7
0.20		-60.6	-59.4	-58.5	-56.4	-53.1	-50.8	-47.7
0.30		-61.4	-60.5	-59.2	-56.9	-55.2	-52.3	-48.7
				ΔG^{o}_{ad} / kJ mol^{-1}				
0	-60.5	-61.6	-62.5	-63.2	-63.6	-62.8	-62.0	-60.9
0.001	-60.7	-62.0	-60.4	-60.5	-60.3	-61.2	-62.6	-62.1
0.005	-65.2	-62.6	-62.5	-62.0	-61.5	-60.2	-58.4	-57.7
0.01	-66.4	-64. 8	-64.1	-63.5	-62.1	-60.5	-58.5	-63.9
0.02	-67.0	-66.3	-65.6	-65.3	-63.8	-61.1	-59.8	-56.2
0.05		-68.1	-68.5	-67.6	-66.0	-63.6	-61.7	-58.5
0.10		-70.4	-70.5	-69.3	-67.8	-66.0	-63.7	-60.0
0.20		-72.8	-72.5	-72.1	-70.7	-67.6	-65.7	-62.2
0.30		-74.0	-73.7	-73.2	-71.8	-69.8	-66.7	-63.2

a) Data from chapter 3

Table 6.7 - Values of Density, Molar Volume, Gordon Parameter and Ratio of Solvent Surface Tension to Limiting Surface Tension for Water + Glycerol Medium at 25 °C

Weight % Glycerol	Density x 10^{-3}/ kg m^{-3}	Molar Volume x 10^6/ m^3 mol^{-1}	γ_0 / mN m^{-1}	γ_{lim} / mN m^{-1}	GP / J m^{-3}	γ_0/γ_{lim}
0	0.99704	18.05	72.3	43.4	2.76	1.67
10	1.02070	19.18	72.2	43.6	2.70	1.66
20	1.04549	20.52	71.6	43.4	2.62	1.67
30	1.07096	22.15	70.8	43.3	2.52	1.64
40	1.09698	24.20	70.1	42.9	2.42	1.64
50	1.12366	26.80	69.2	42.8	2.31	1.61
60	1.15086	30.24	68.5	42.6	2.20	1.61
70	1.17807	34.98	67.7	42.1	2.07	1.61

Table 6.8 - Surface Excess (Γ_{cmc}) of CPC near CMC in Water + Glycerol medium in presence of NaCl at 25 °C

[NaCl] / mol kg^{-1}	Weight % Glycerol							
	0[a)]	10	20	30	40	50	60	70
	Γ_{cmc} x 10^6 / mol m^{-2}							
0	1.96	1.72	1.61	1.49	1.43	1.36	1.31	1.25
0.001	2.37	1.95	2.12	1.95	1.78	1.51	1.32	1.21
0.005	2.14	2.36	2.35	2.19	2.01	1.87	1.86	1.62
0.01	2.18	2.40	2.44	2.29	2.27	2.10	2.11	1.31
0.02	2.75	2.52	2.55	2.40	2.32	2.23	2.20	2.18
0.05		2.68	2.59	2.44	2.39	2.32	2.29	2.22
0.10		2.67	2.58	2.45	2.42	2.29	2.28	2.28
0.20		2.73	2.53	2.41	2.34	2.28	2.23	2.27
0.30		2.64	2.54	2.41	2.48	2.27	2.33	2.26

a) Data from chapter 3

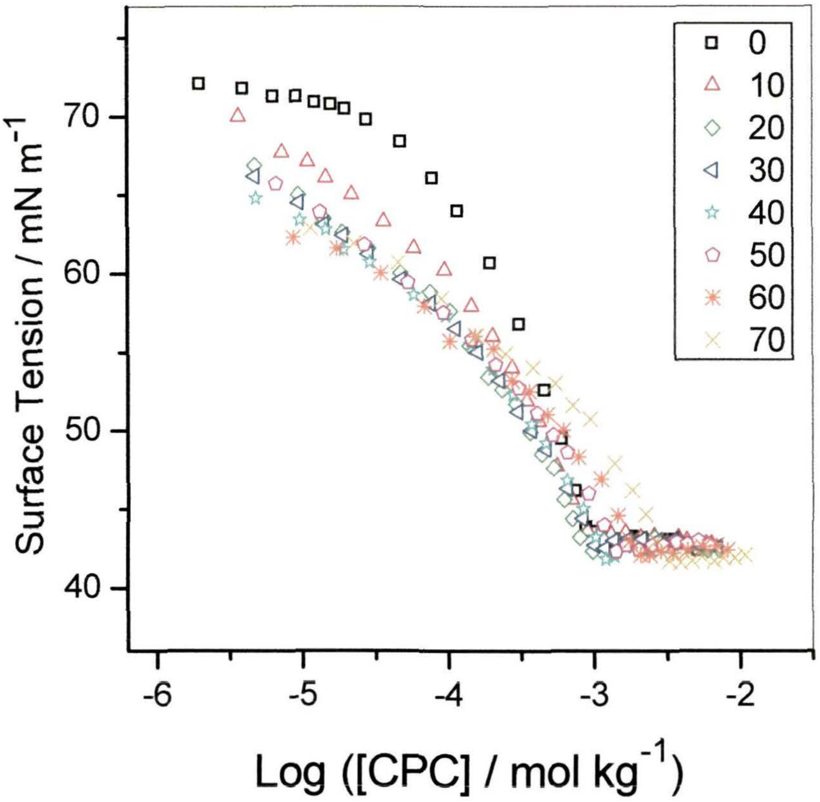

Fig. 6.1. Surface tension of water + glycerol + CPC system at 25 °C as a function of CPC concentration at fixed water per cent of glycerol (given in the inset).

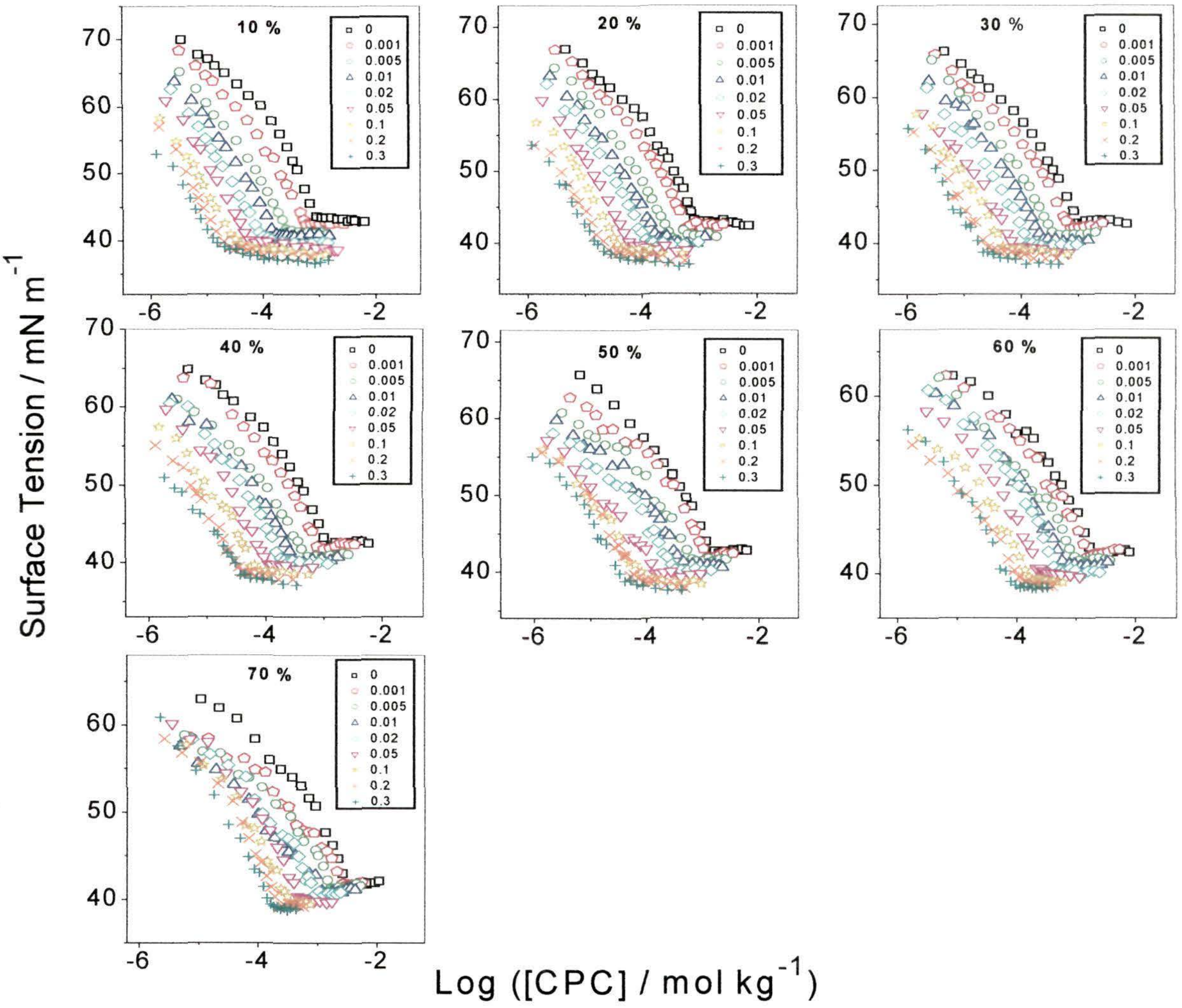

Fig. 6.2. Surface tension of water + glycerol +CPC system at 25 °C as a function of CPC concentration in the presence of NaCl and at fixed weight per cent of glycerol (indicated in each layer). The concentrations of NaCl in mol kg^{-1} are indicated in the insets.

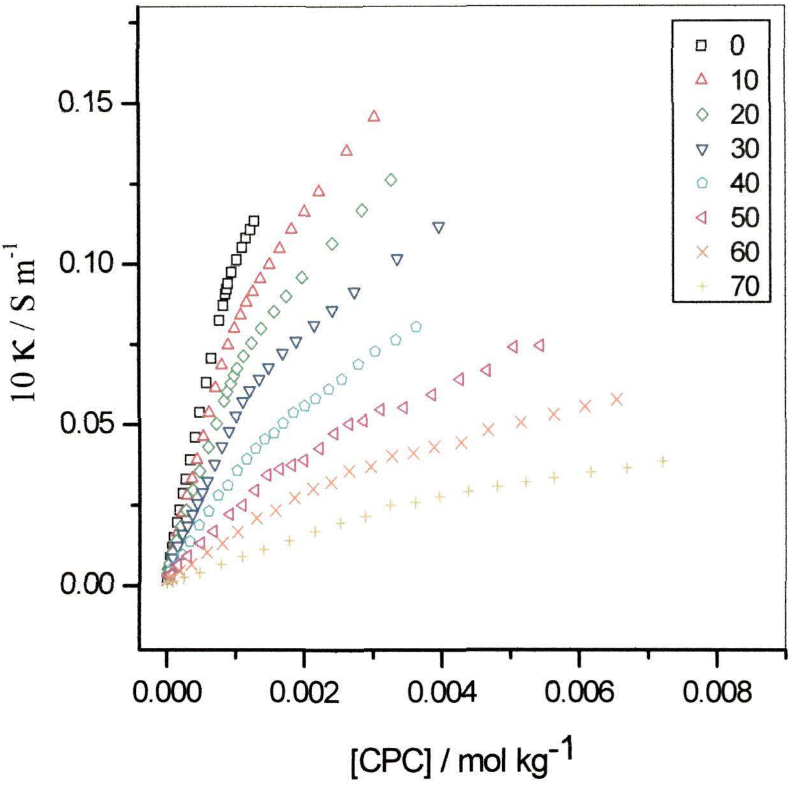

Fig. 6.3. Specific conductance of CPC in water + glycerol medium at 25 °C as a function of CPC concentration at fixed weight per cent of glycerol (indicated in the inset).

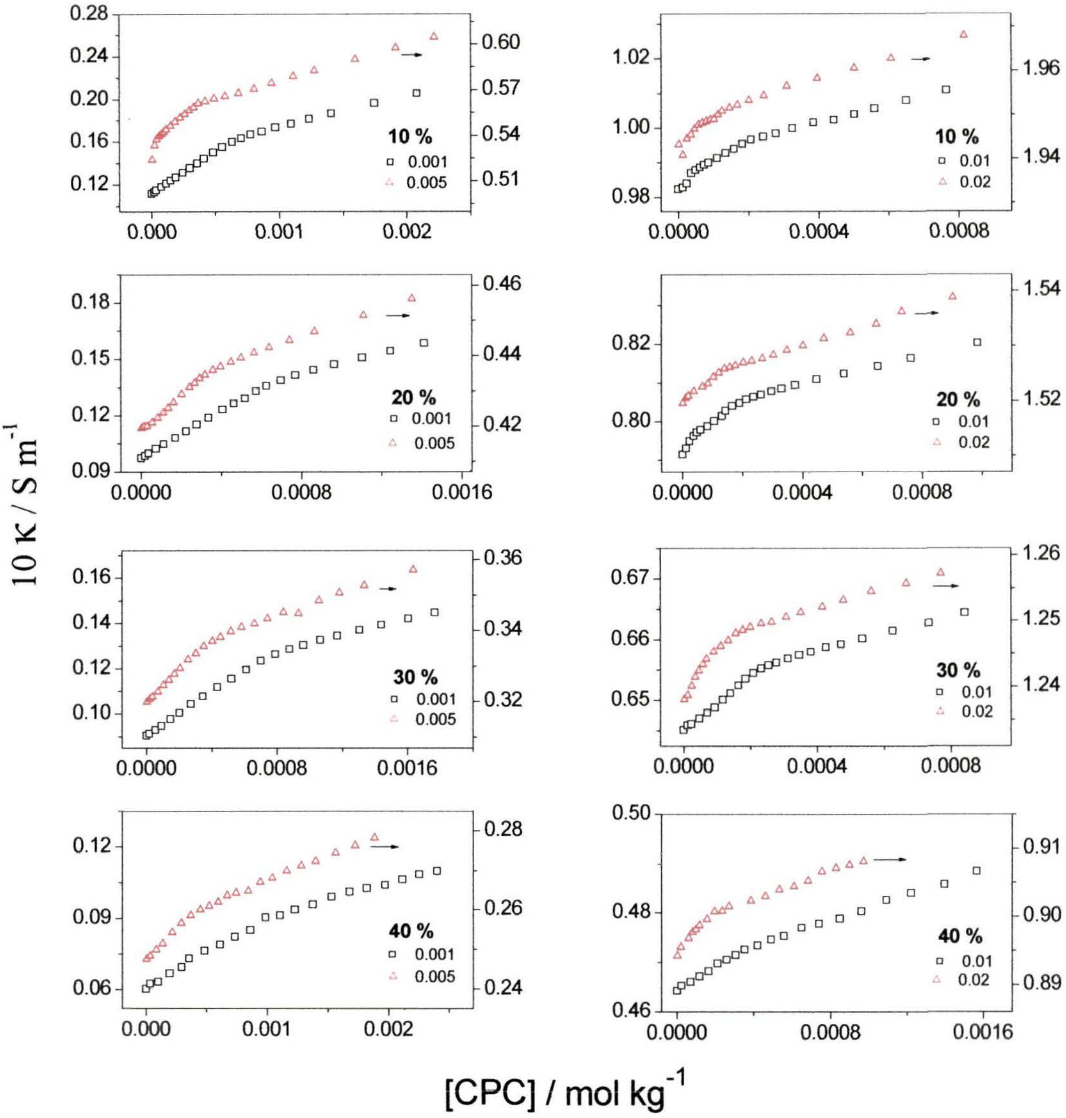

Fig. 6.4. Specific Conductance of CPC in water + glycerol medium at 25 °C as a function of CPC concentration in the presence of NaCl. The weight per cents of glycerol and concentrations of NaCl are indicated in the insets.

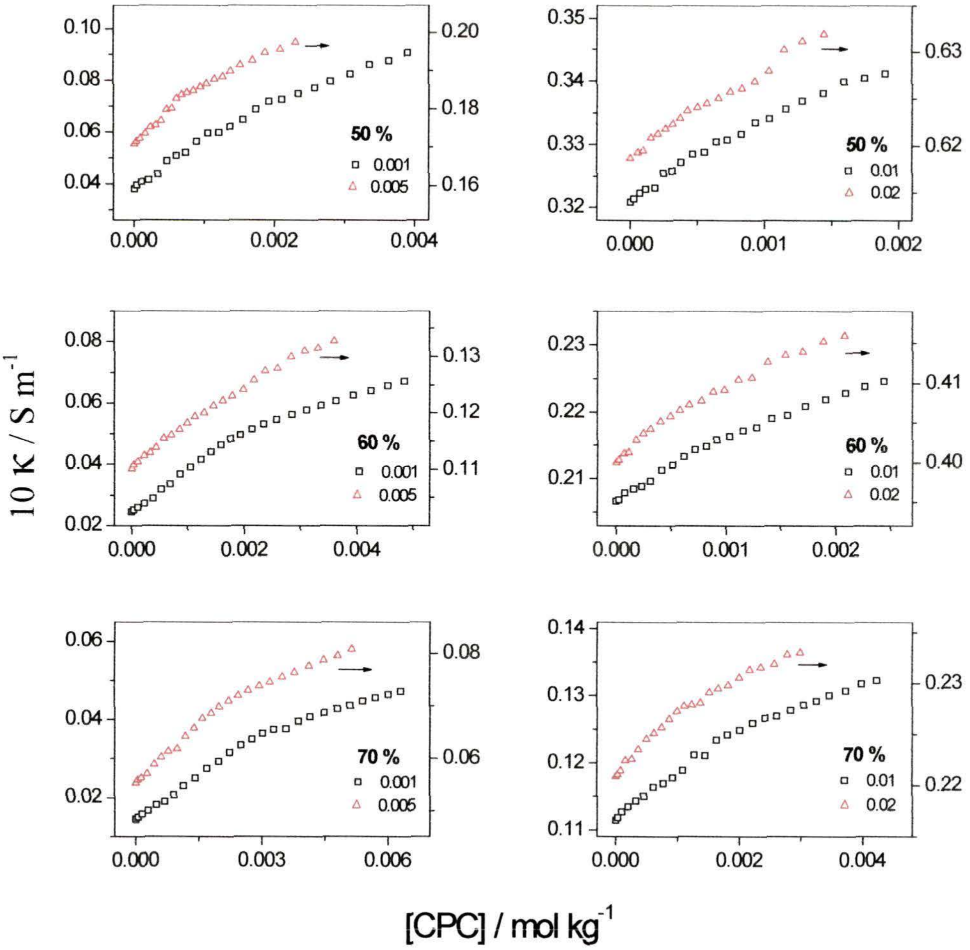

Fig. 6.5. Specific Conductance of CPC in water + glycerol system at 25 °C as a function of CPC concentration in the presence of NaCl. The weight per cents of glycerol and concentrations of NaCl are indicated in the insets.

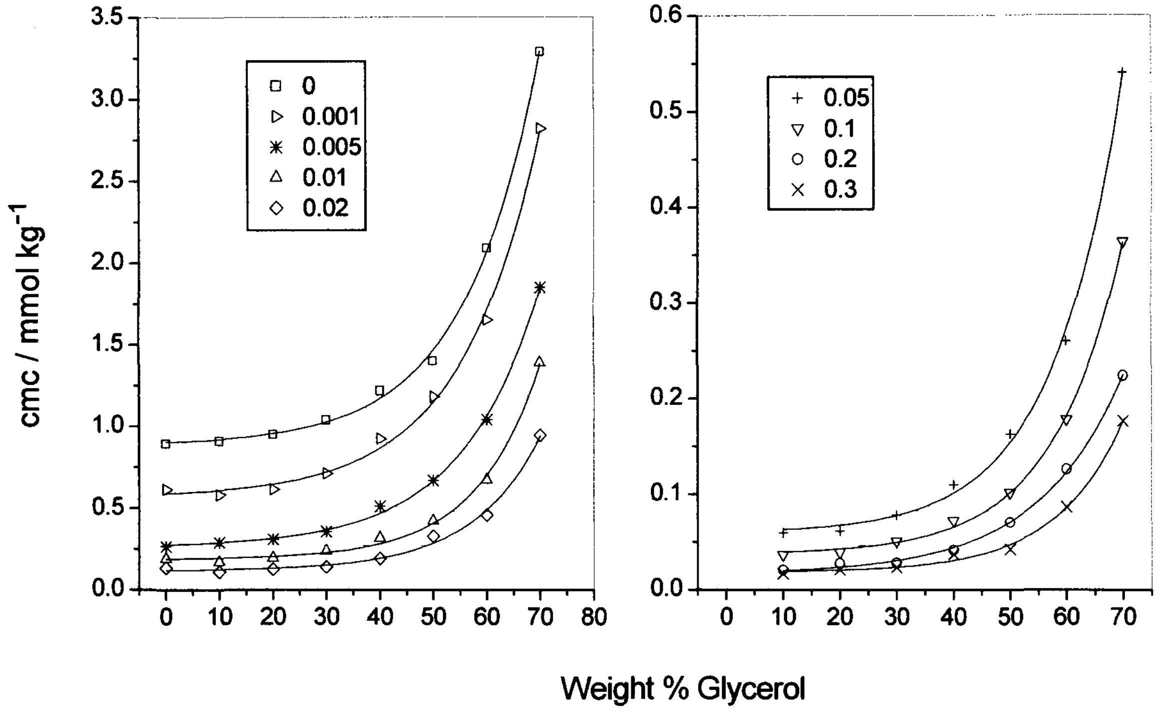

Fig. 6.6. Cmc values of CPC in water + glycerol medium at 25 °C as a function of glycerol content at fixed concentrations of NaCl (indicated in the insets). The lines represent the simulated values of cmc from Eq. (6.2).

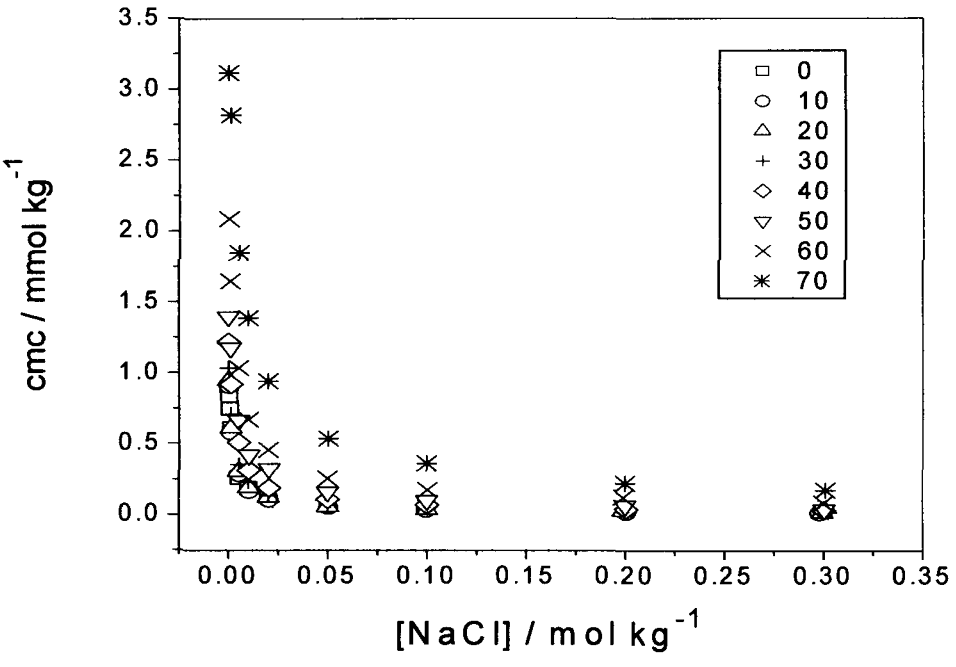

Fig. 6.7. Cmc values of CPC in water + glycerol medium at 25 °C as a function of NaCl concentration at fixed weight per cent of glycerol (indicated in the insets).

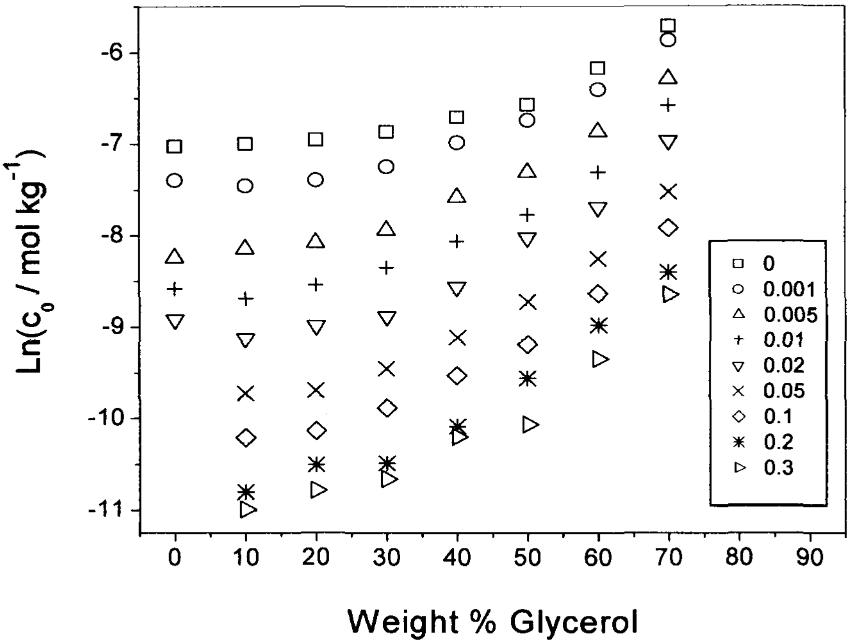

Fig. 6.8. Plots of logarithm of cmc of CPC in water + glycerol medium at 25 °C as a function of glycerol content at fixed concentrations of NaCl (indicated in the insets).

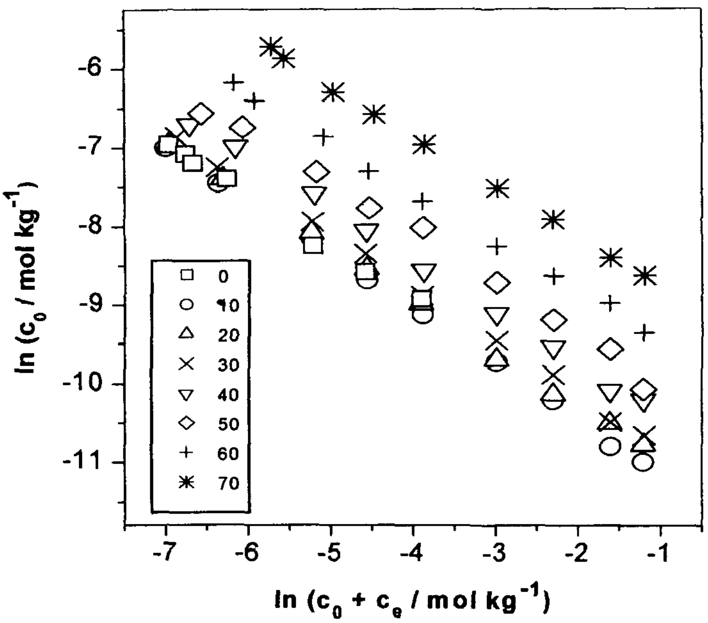

Fig. 6.9. CH plots for CPC in water + glycerol medium at 25 °C

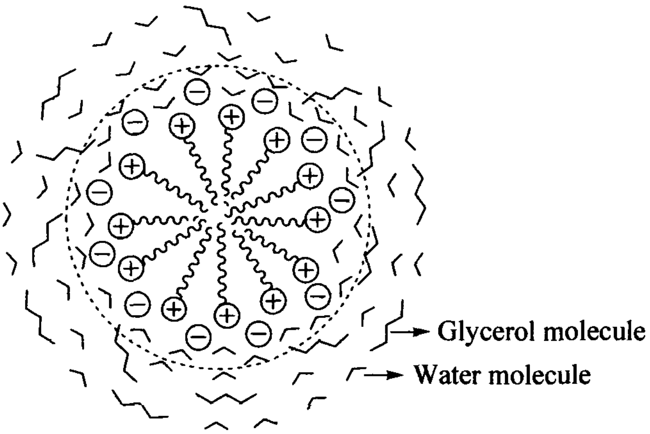

Fig. 6.10. A schematic representation of the micellar surface with water-like stern layer. Most of the hydrogen-bonded glycerol molecules are in the diffuse layer

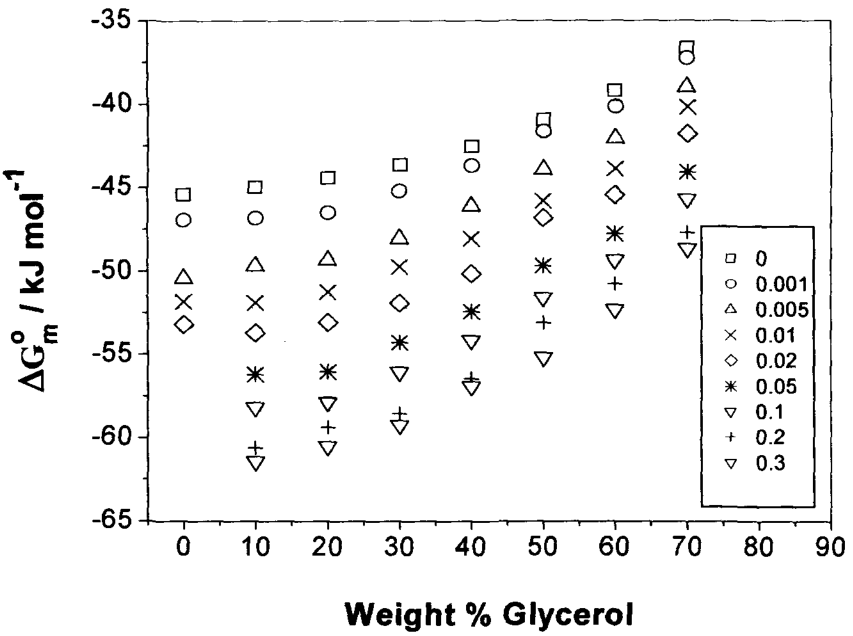

Fig. 6.11. Plots of standard free energy of micellization of CPC in water + glycerol medium at 25 °C as a function of glycerol content at fixed concentrations of NaCl (indicated in the insets).

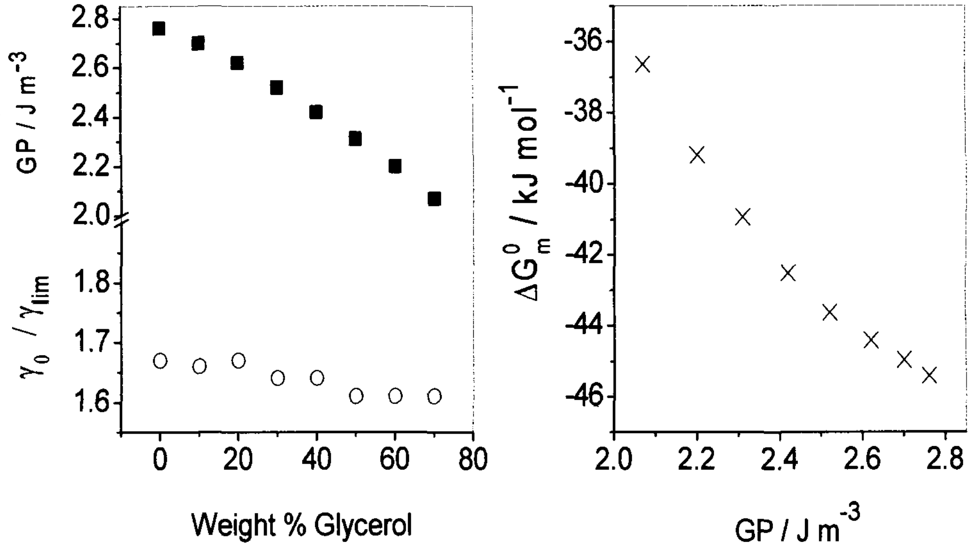

Fig. 6.12. Variation of Gordon parameter and ratio of solvent surface tension to limiting surface tension with weight per cent of glycerol, and of ΔG^o_m with Gordon parameter.

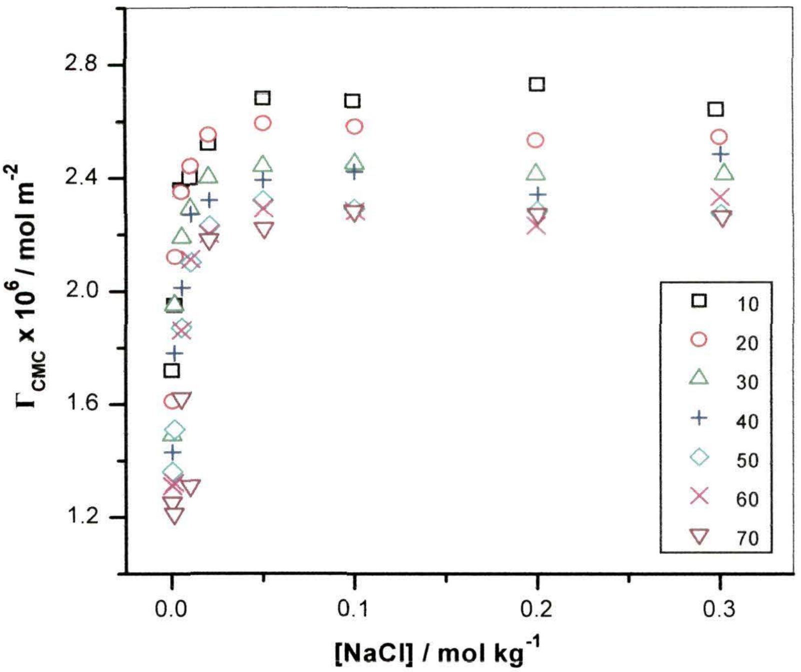

Fig. 6.13. Variation of surface excess of CPC at cmc in water + glycerol media at 25 °C with NaCl concentration.

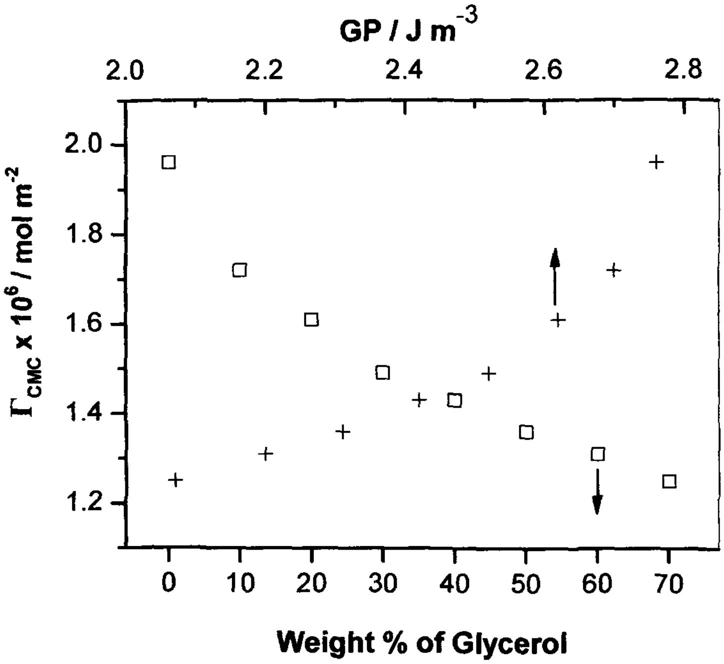

Fig. 6.14. Variation of surface excess of CPC with weight per cent of glycerol and Gordon parameter

CURRICULUM VITAE

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Research Publications

1. Electrical Conductance Behaviour of Oil-in-Water Microemulsions Stabilized by Sodium Dodecyl Sulfate and 1-Butanol.

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

   Langmuir **2003**, *19*, 7276-7281

2. Micellization of Cetylpyridinium Chloride in Aqueous Lithium Chloride, Sodium Chloride and Potassium chloride Media.

   T. Mukhim and K. Ismail.

   J. Surface Sci. Technol., vol. *21*, No. 3-4, pp. 113-127, **2005**.

3. Effect of Tetrabutylammonium Coion and Mixed Counterions on the Adsorption and Aggregation Behaviors of Cetylpyridinium Chloride.

   T. Mukhim, J. Dey, S. Das and K. Ismail.

   Langmuir (communicated).

Seminars / Symposia / Conferences attended

1. Seventy Second Annual Session of the National Academy of Sciences, India, held at the North-Eastern Hill University, Shillong. (October 25 to 27, 2002)
2. Workshop on Challenges in Higher Education organized by Lady Keane College in collaboration with MCTA Unit, Lady Keane College, on 30th May 2005.
3. Workshop on Disaster Management organized by National Disaster Management Authority (Govt. of India), New Delhi, Govt. of Meghalaya; NEC and Lady Keane College on 10th and 11th June 2008.
4. Ninety sixth Indian Science Congress held at North Eastern Hill University, Shillong, 3rd to 7th January 2009.

Place: Shillong
Date: 22nd April 2010

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