

## Adsorption characteristics of sodium dodecylsulfate and cetylpyridinium chloride at air/water, air/formamide and air/water–formamide interfaces

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### ARTICLE INFO

#### Article history:

Received 7 December 2011

Received in revised form 26 January 2012

Accepted 17 February 2012

Available online 25 February 2012

#### Keywords:

Adsorption model

Ionic surfactant

Counterion

Surface density

Surface potential

### ABSTRACT

The adsorption model developed by Kralchevsky and co-workers, the Kralchevsky–Danov–Broze–Mehreteab (KDBM) model, has been applied to fit the surface tension data in the submicellar region of sodium dodecylsulfate (SDS) and cetylpyridinium chloride (CPC) in water, water + 50 wt.% formamide (FA) and FA media. The KDBM model satisfactorily fits the surface tension data and from the fitting surface density of surfactant monomer ( $\Gamma_1$ ), surface density of counterion ( $\Gamma_2$ ) and electrostatic potential at the air–solution interface were evaluated. The value of  $\Gamma_1$  decreases as the FA content in the medium increases due to decreasing solvophobicity, but the value of  $\Gamma_2$  does not follow this trend. For both SDS and CPC the maximum value of the counterion binding constant ( $\Gamma_2/\Gamma_1$ ) is almost same (about 0.8) in water and FA, but much low (about 0.3–0.5) in 50% FA. In all the three media, on increasing the concentration of SDS or CPC the surface potential passes through a maximum in the low concentration region.

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### 1. Introduction

The interfacial properties like surface tension and adsorption of surfactant solutions determine and control the performance of surfactant systems in many practical applications. Understanding of the interfacial behavior of surfactants at the air–liquid interfaces is therefore important. The theoretical description of electrical phenomena occurring at the interface during adsorption of ionic surfactants is rather complicated and attempts are still being made to improve it. Two types of adsorption models have been developed to describe the adsorption phenomena, viz., nonionic or pseudo-nonionic models and ionic models [1,2]. In nonionic models the surface charge is ignored, whereas ionic models account for the surface charge and its electric double layer. Nonionic models and their modifications are however employed to describe the adsorption characteristics of ionic surfactants also [2–5]. Kralchevsky and co-workers [6–10] developed an ionic model to estimate at the air–solution interface (i) the surface density of ionic surfactant monomer, (ii) the surface density of counterion, and (iii) the surface potential. We have termed this model as Kralchevsky–Danov–Broze–Mehreteab (KDBM) model. Although ionic models which account for counterion adsorption

were developed by Kalinin and Radke [11] and by Warszynski et al. [12], the KDBM model is considered to be superior because in this model surfactant and counterion adsorption isotherms are made thermodynamically compatible by applying the Euler condition [6]. This thermodynamically sound model has been applied hitherto to explain the adsorption characteristics of only sodium dodecylsulfate (SDS) in the absence and presence of additives in aqueous medium [6–10,13]. The objective of this work is to apply the KDBM model to analyze the adsorption characteristics of SDS and cetylpyridinium chloride (CPC) surfactants at air/water, air/formamide and air/water–formamide interfaces since to the best of our knowledge such calculations in organic and aqueous organic media have not yet been undertaken.

### 2. Theoretical basis of the KDBM model

Applying the treatment of Borwankar and Wasan [14] in the Gibbs adsorption isotherm and using the Poisson–Boltzmann equation for a planar surface, Kralchevsky et al. [6] obtained a set of equations, which can be written for a 1:1 surfactant as

$$2Q = \left( \frac{8\sqrt{a_2}}{\kappa_c} \right) \left[ \cosh \left( \frac{\Phi_0}{2} \right) - 1 \right] \quad (1)$$

$$\Gamma_1 - \Gamma_2 = \left( \frac{4}{\kappa_c} \right) \sqrt{a_2} \sinh \left( \frac{\Phi_0}{2} \right) \quad (2)$$

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The term  $Q$  introduced by Kralchevsky et al. [6] is given by the expression

$$Q = \left(\frac{1}{\kappa_c}\right) \int_0^{\Phi_0} \left\{ \sum_i a_i [\exp(-Z_i \Phi) - 1] \right\}^{1/2} d\Phi \quad (3)$$

$\Gamma_i$  is the surface density of species  $i$  having charge  $z_i$  and  $Z_i = z_i/z_1$  ( $i=1$  and 2 represent surfactant monomeric ion and counterion, respectively). In Eqs. (1)–(3),  $a_i$  refers to the bulk activity of  $i$  and  $\kappa_c$  is computed from the expression

$$\kappa_c^2 = \frac{2F^2 z_1^2}{\varepsilon_0 \varepsilon RT} \quad (4)$$

where  $F$  is the Faraday constant,  $\varepsilon_0$  is the permittivity of free space,  $\varepsilon$  is the dielectric constant of the solvent,  $T$  is the absolute temperature and  $R$  is the gas constant. In Eq. (3),

$$\Phi = \frac{z_1 e_0 \Psi}{k_B T} \quad (5)$$

where  $e_0$  is the charge of the electron,  $k_B$  is the Boltzmann constant and  $\Psi$  is the electrostatic potential.  $\Phi_0$  and  $\Psi_0$  represent reduced potential and surface potential at the subsurface, respectively. The subsurface is identified as the boundary surface between the Stern layer and the diffuse layer. The dependence of  $a_{0i}$  (activity of  $i$  at the subsurface) on  $a_i$  is given by the relation

$$a_{0i} = a_i \exp(-Z_i \Phi_0) \quad (6)$$

To take into account the adsorption of counterions, Kralchevsky et al. [6] considered the adsorption constant  $K$ , which appears in the different adsorption isotherms, to have a linear dependence on the concentration of counterions at the subsurface and represented  $K$  as

$$K = K_1 + K_2 a_{02} \quad (7)$$

where  $K_1$  and  $K_2$  are constants that are related to the respective free energies of adsorption. Using Eq. (7) counterion adsorption can be described [6,7], irrespective of the surfactant adsorption isotherm, by the Stern isotherm of the form

$$\frac{\Gamma_2}{\Gamma_1} = \frac{K_2 a_{02}}{K_1 + K_2 a_{02}} \quad (8)$$

Eq. (7) is a necessary condition for thermodynamic compatibility of the Stern isotherm of counterion adsorption with the surfactant adsorption isotherms [6].

### 3. Materials and methods

Sodium dodecylsulfate (Aldrich), cetylpyridinium chloride (Sigma) and formamide (FA; Fluka) were used as supplied. Surface tension measurements were made by the Wilhelmy plate method using K11 Krüss tensiometer as described elsewhere [15]. Haake DC10 circulation bath was used for maintaining the temperature at 25 °C. Milli-Q grade water was used for preparing aqueous solutions.

### 4. Method of computation

A computer program was written for least-squares fitting the surface tension data to the KDBM model using an iteration method. In this program, activity values of a surfactant in a given solution were computed using the Debye–Hückel equation,

$$\log \gamma_{\pm} = -A_1 |z_+ z_-| \sqrt{I} \quad \text{and} \quad a_i = c_i \gamma_{\pm} \quad (9)$$

$c_i$  is the bulk concentration of  $i$  and  $\gamma_{\pm}$  is the average activity coefficient term. The ionic strength,  $I$ , is given by the equation,  $I = (1/2) \sum_i c_i z_i^2$ .  $A_1$  is calculated from the expression,

$$A_1 = \frac{e_0 F^2}{4.606 \pi (2RT \varepsilon_0 \varepsilon)^{3/2}} \quad (10)$$

For computing the adsorption of surfactant monomer, we used the Frumkin adsorption isotherm, which is written as [6]

$$\left(\frac{\Gamma_1}{\Gamma_{\infty} - \Gamma_1}\right) \exp\left(-\frac{2A_K \Gamma_1}{RT}\right) = K a_{01} \quad (11)$$

$\Gamma_{\infty}$  refers to the limiting value of surface density and  $A_K$  is an interaction parameter. Kolev et al. [7] have shown that both Frumkin and van der Waals models provide equally good fits. It may be noted that on the right hand side of Eq. (11)  $a_{01}$  is used instead of the bulk activity  $a_1$ , which is in accordance with the approach developed by Borwankar and Wasan [14]. To start the computation, an initial set of trial values were fed for  $\Phi_0$ ,  $\Gamma_{\infty}$ ,  $K_1$ ,  $K_2$  and  $A_K$ . Using these initial approximate values, surface activities were calculated from Eq. (6), values of  $\Gamma_1$  were calculated from Eq. (11) and the values of  $\Gamma_2$  were calculated from Eq. (8). Substituting these values of  $\Gamma_1$  and  $\Gamma_2$  in Eq. (2), new values of  $\Phi_0$  were computed numerically, which were used again to calculate  $a_{01}$ ,  $a_{02}$ ,  $\Gamma_1$  and  $\gamma$ . The cycle continues till consistent values of  $\Phi_0$  were obtained. After this, surface tension values were calculated using the relation

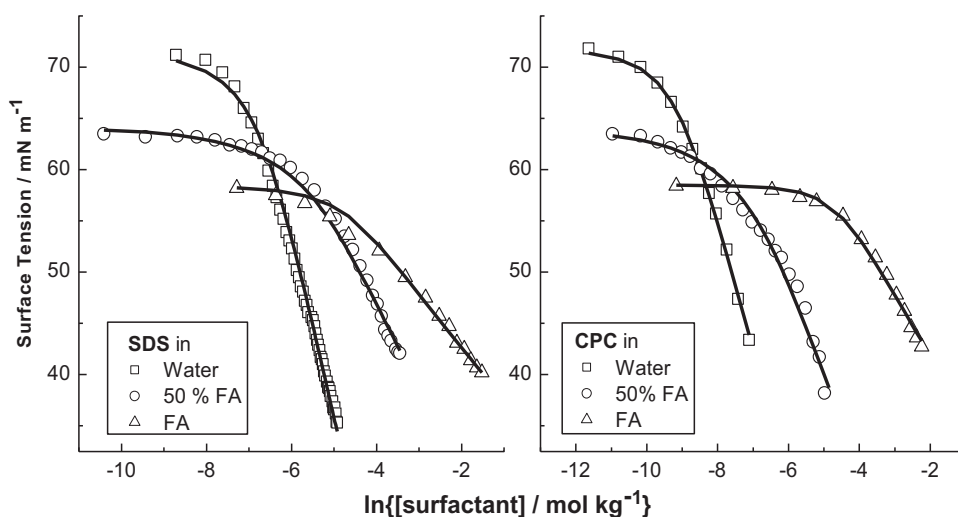
$$\gamma = \gamma^0 + RT \Gamma_{\infty} \ln\left(\frac{1 - \Gamma_1}{\Gamma_{\infty}}\right) + A_K \Gamma_1^2 - 2QRT \quad (12)$$

$\gamma^0$  is the surface tension of the solvent and  $\gamma$  is the surface tension of the surfactant solution. The values of  $2Q$  were computed from Eq. (1). These calculated values of surface tension were compared with the experimental values and the standard deviation was computed. If the fitting is not good, then a new set of values were obtained for  $\Gamma_{\infty}$ ,  $K_1$ ,  $K_2$  and  $A_K$  by minimizing the square of the deviation. The segment of the computer program for minimizing the square of the deviation so as to obtain the new set of values for  $\Gamma_{\infty}$ ,  $K_1$ ,  $K_2$  and  $A_K$  is written on the basis of the Newton–Raphson method and is similar to the procedure used by us earlier [16]. Once again the process of computing  $\Gamma_1$ ,  $\Gamma_2$  and consistent values of  $\Phi_0$  was continued. In this manner the computation was repeated till minimum standard deviation was achieved.

### 5. Results and discussion

Experimental values of surface tension in the premicellar concentration region for SDS and CPC in water, 50 wt.% FA and pure FA are shown in Fig. 1. Computed values of the parameters of the KDBM model for SDS and CPC in the different media are listed in Table 1. The agreement between the experimental and calculated values of surface tension is quite good as apparent from Fig. 1.

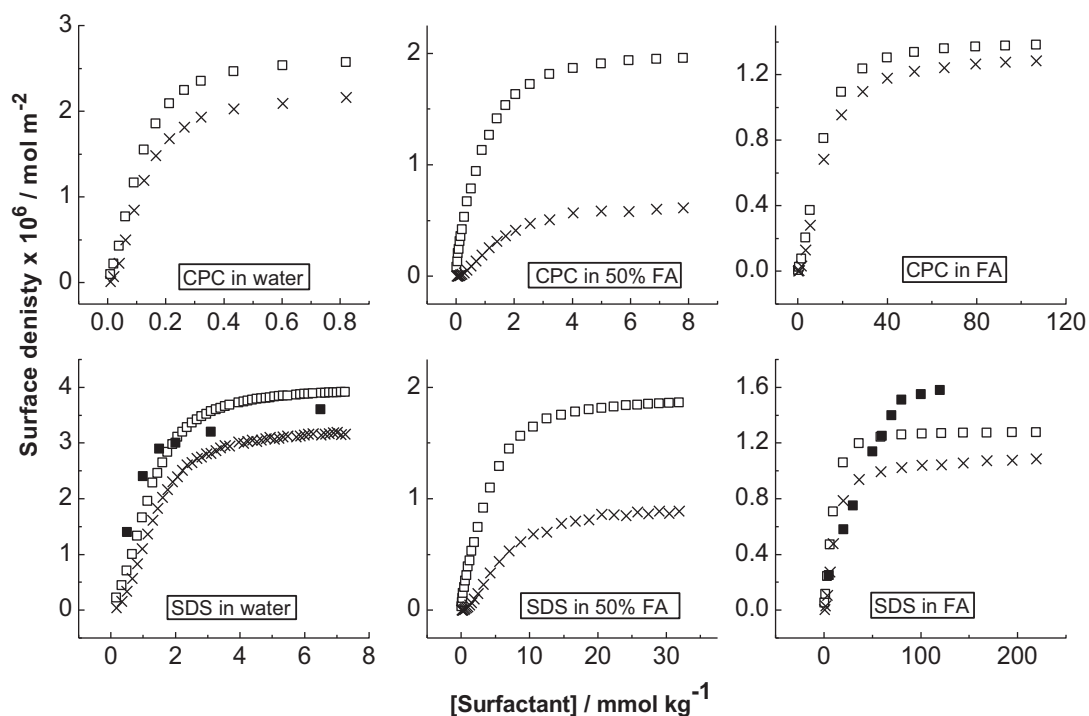
For SDS in water, the value  $4.01 \mu\text{mol m}^{-2}$  of  $\Gamma_{\infty}$  (Table 1) is comparable with the values 3.92 computed by Prosser and Franses [2] from the Frumkin model, 4.4 reported by Kralchevsky et al. [6] and 3.69 determined from the neutron reflection method [17,18]. The reported [15,19] maximum value of surface density of SDS in water calculated directly from the Gibbs adsorption isotherm varies from 3.2 to 3.5  $\mu\text{mol m}^{-2}$ . It may be noted that the maximum value of the surface density calculated from the Gibbs adsorption isotherm by using surface tension data is actually equal to the adsorption at the critical micelle concentration and it is different from  $\Gamma_{\infty}$ .  $\Gamma_{\infty}$  is a parameter of the adsorption isotherm and its value depends on the model used for the isotherm. In Fig. 2, we have shown the reported experimental values of surface density of SDS in water measured by the direct radiotracer [19] and the neutron reflection methods [17,18], which are comparable to



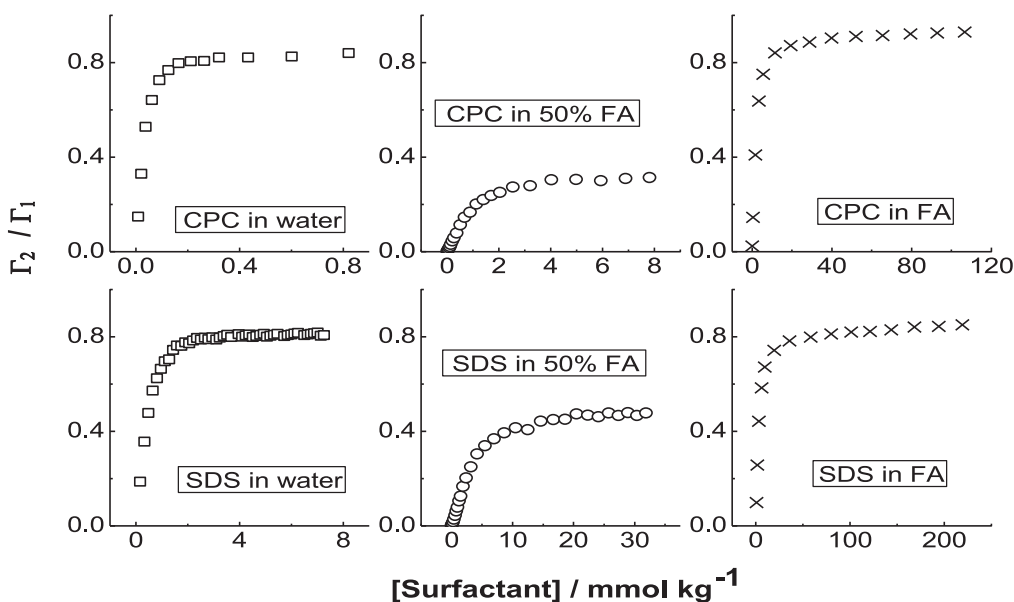
**Fig. 1.** Plots of experimental (symbols) and calculated (solid lines) surface tension of SDS and CPC versus concentration of respective surfactants at 25 °C in water, 50 wt.% FA and FA media.

**Table 1**  
Least-squares fitted values of the parameters of the KDBM model for ionic surfactants at 25 °C (percentage of FA in water is by weight;  $\sigma$  refers to standard deviation in  $\gamma$ ).

Medium	$\Gamma_{\infty}$ ( $\times 10^6$ mol m $^{-2}$ )	$\left(\frac{2A_k}{RT}\right)$ ( $\times 10^{-4}$ m $^2$ mol $^{-1}$ )	$K_1$ (m $^3$ mol $^{-1}$ )	$K_2$ (m $^6$ mol $^{-2}$ )	$-\Delta G_{ad}^0$ (kJ mol $^{-1}$ )	$-\Delta G_{cad}^0$ (kJ mol $^{-1}$ )	$\sigma$ (mN m $^{-1}$ )
Surfactant = SDS							
Water	4.01	18.1	150	0.390	31	6.7	0.76
50% FA	1.92	16.1	50	0.020	27	-0.7	0.60
FA	1.27	8.1	0.5	0.01	14	8.0	0.64
Surfactant = CPC							
Water	2.62	0.32	7170	71	39	9.0	0.31
50% FA	2.00	0.12	2000	0.27	35	-3.3	0.97
FA	1.40	0.08	0.1	0.01	10	12.3	0.39



**Fig. 2.** Variation of surface density (i) of the dodecylsulfate and cetylpyridinium ions (open squares) and (ii) of the respective counterions (crosses) with the concentration of surfactants in water, 50 wt.% FA and FA at 25 °C. Solid squares indicate reported values in water [17–19] and FA [18].



**Fig. 3.** Variation of the counterion binding constant at the air–solution interface with the concentration of respective surfactants in water (open squares), 50 wt.% FA (open circles) and FA (crosses) at 25 °C.

the values of  $\Gamma_1$  computed from the KDBM model. In 50 wt.% FA, the value of  $\Gamma_\infty$  for SDS decreases to  $1.92 \mu\text{mol m}^{-2}$  and in FA it decreases further to  $1.28 \mu\text{mol m}^{-2}$ . The surface density of SDS in FA was measured at 6 °C recently by Wang and Morgner [18] using a vacuum-based spectroscopic method known as the neutral impact collision ion scattering spectroscopy (NICISS) and these experimental values (shown in Fig. 2) are comparable to the values of  $\Gamma_1$  computed from the KDBM model. The experimental value of maximum surface density measured by Wang and Morgner [18] is equal to  $1.58 \mu\text{mol m}^{-2}$  which is also comparable to the value of  $\Gamma_\infty$  of SDS in FA computed from the KDBM model. The decrease in  $\Gamma_\infty$  due to addition of FA is expected and it is attributable to the decrease in solvophobicity of SDS towards the medium. Similar trend in the variation of  $\Gamma_\infty$  with the addition of FA has been observed in the case of CPC (Table 1) also. Thus, KDBM model gives acceptable values of surface density of both SDS and CPC in water, water + FA and FA media.

The term  $A_K$  or  $2A_K/RT$  is related to the interaction between the hydrocarbon tails of the ionic surfactant at the interface and its positive value signifies attraction. As the FA content in the medium increases, the solvophobicity of a surfactant decreases causing the surface density of the surfactant to decrease. Since surface area is inversely proportional to surface density, as the solvophobicity decreases the surface area per mole of surfactant increases causing thereby increase in the separation and reduction in the interaction between the hydrocarbon tails of the surfactant. This explains why  $A_K$  decreases as the FA amount in the medium increases. Similarly, lower surface density of CPC than SDS shows that at the interface the surface area of pyridinium head group is more than that of sulfate head group and this causes larger separation and less interaction between the cetyl tails compared to that between the dodecyl tails. Accordingly, CPC has lower values for  $A_K$  than SDS as observed from the KDBM model (Table 1).

The values of surface density for surfactant monomers and counterions as a function of surfactant concentration are shown in Fig. 2. In Fig. 3 we have plotted the counterion binding constant, which is equal to the moles of counterion bound or adsorbed per mole of the adsorbed surfactant monomer ( $\Gamma_2/\Gamma_1$ ), versus surfactant concentration. In the case of both SDS and CPC,  $\Gamma_1$  is lowest in FA, while  $\Gamma_2$  has almost same value in water and FA and lowest value in 50 wt.% FA. Thus, solvophobicity of the solvent controls the

adsorption of the solvophobic tails of surfactants and therefore  $\Gamma_1$  for both dodecylsulfate and cetylpyridinium ions decreases as the amount of FA increases in the medium. On the other hand,  $\Gamma_2$  for sodium and chloride counterions is controlled by the Columbic interaction. Steric hindrance due to solvation of the counterions also influences  $\Gamma_2$ . Lower values of  $\Gamma_2$  in 50% FA than in water or FA envisage that the solvation spheres of counterions are larger in the mixed solvent and this is probably due to hydrogen-bonded structures between water and FA. In fact, computational and structural studies [20–22] of water + FA system have indicated formation of a common hydrogen bond network due to hydrogen bonding between FA and water molecules. Therefore, in 50% FA probably steric factor suppresses the adsorption of counterions.

The term  $K_1$  is related to the standard free energy of adsorption of surfactant monomer ( $\Delta G_{ad}^0$ ) and  $K_2/K_1$  is related to the standard free energy of adsorption of counterion ( $\Delta G_{cad}^0$ ) [6]. Kralchevsky et al. [6] related  $K_1$  to  $\Delta G_{ad}^0$  by the expression

$$K_1 = \left( \frac{\delta_1}{\Gamma_\infty} \right) \exp \left[ \frac{-\Delta G_{ad}^0}{RT} \right] \quad (13)$$

where  $\delta_1$  is approximately equal to the thickness of the adsorption layer. An approximate value of  $\delta_1$  was estimated in the following manner. The length of the tail ( $d$ ) in angstroms was calculated from the expression [23]

$$d = 1.5 + 1.265n_c \quad (14)$$

The term  $n_c$  in Eq. (14) is equal to the number of carbon atoms in the surfactant tail. We then considered  $\delta_1 \approx d + d_h$ , where  $d_h$  is the diameter or length of the head group. Considering the radius of sulfate ion as  $2.3 \text{ \AA}$  [24], we obtained a value of  $2.13 \text{ nm}$  for  $\delta_1$  of SDS, which is in good agreement with the value of about  $2 \text{ nm}$  used by Kralchevsky et al. [6]. To estimate the value of  $\delta_1$  for CPC we added the length of pyridinium ring to  $d$ . Evans et al. [25] estimated the length of the pyridinium ring as equal to  $5.6 \text{ \AA}$  and by adding this to  $d$  we obtained a value of  $2.7 \text{ nm}$  for  $\delta_1$  of CPC. By using the values of  $\delta_1$  so estimated we evaluated  $\Delta G_{ad}^0$  whose values are given in Table 1. In water and 50% FA,  $\Delta G_{ad}^0$  of CPC is more negative, which indicate higher adsorption of CPC than SDS in these media. In fact, in these two media, at a given surfactant concentration adsorption of CPC is found to be more than SDS. For example, in water at

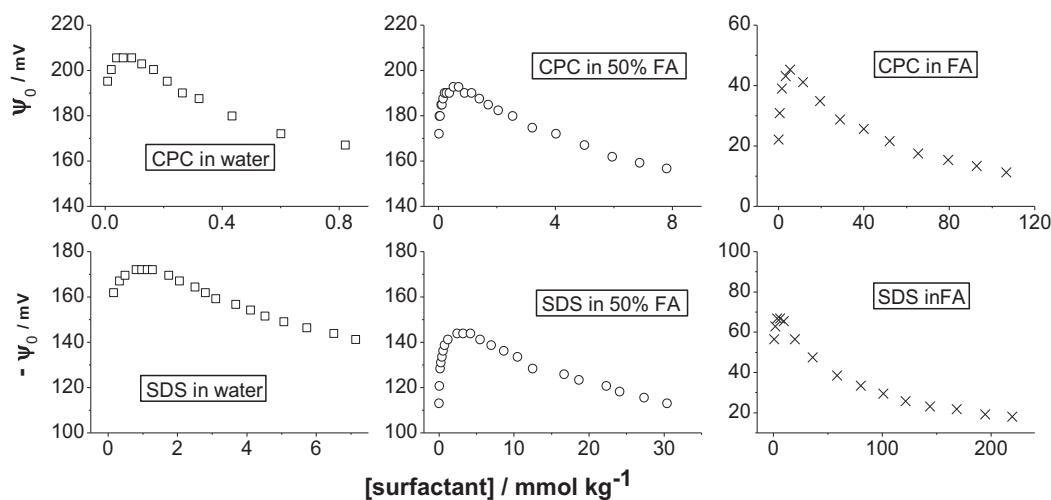


Fig. 4. Plots of surface potential versus concentration of the respective surfactants in water, 50 wt.% FA and FA at 25 °C.

$7.5 \times 10^{-4} \text{ mol kg}^{-1}$  surfactant concentration, the surface density values of CPC and SDS are 2.56 and  $1.22 \mu\text{mol m}^{-2}$ , respectively. Similarly, in 50% FA at  $0.006 \text{ mol kg}^{-1}$  surfactant concentration, the surface density values of CPC and SDS are 1.90 and  $1.35 \mu\text{mol m}^{-2}$ , respectively. In FA, the difference in the values of  $\Delta G_{ad}^0$  of CPC and SDS is less and accordingly these two surfactants have almost same surface density values. Furthermore, Kralchevsky et al. [6] related  $K_2/K_1$  to  $\Delta G_{cad}^0$  by an expression similar to Eq. (13) as

$$\frac{K_2}{K_1} = \left( \frac{\delta_2}{r_\infty} \right) \exp \left[ \frac{-\Delta G_{cad}^0}{RT} \right] \quad (15)$$

where  $\delta_2$  is the thickness of the Stern layer and can be approximately equated to the diameter of the solvated counterion. In aqueous medium, Kralchevsky et al. [6] considered  $\delta_2 \approx 0.7 \text{ nm}$ . For estimating  $\Delta G_{cad}^0$  in water, we used this value of  $\delta_2$  in the case of both SDS and CPC since sodium and chloride ions have almost same hydrated radii [24]. In water + FA and FA media, we made a representative calculation for estimating  $\Delta G_{cad}^0$  by arbitrarily taking the value of  $\delta_2$  as 1 nm in view of the increase in partial molar volume of NaCl due to addition of FA to water [26]. The values of  $\Delta G_{cad}^0$  thus obtained are given in Table 1 and it is apparent from these values that in 50% water + FA medium the counterion binding is less favored than in water and FA media.

Variation of surface potential as a function of surfactant concentration pass through a maximum (Fig. 4) in all the three media. For SDS in water, Kralchevsky et al. [6] also obtained a maximum in the plot of surface potential versus surfactant concentration and their values of surface potential are in good agreement with those of the present study. The appearance of surface potential maximum is described [6] as due to the competition of two effects: (i) an increase in surface potential due to increase in surface charge, which in turn is caused by the increase in surfactant adsorption and (ii) decrease in surface potential with increase in ionic strength of the solution. In the low surfactant concentration region the first effect dominates, while in the higher surfactant concentration region the second effect is predominant. Surface potential decreases on addition of FA, which is due to decrease in surfactant adsorption. Nakahara et al. [27] measured the surface potential of SDS at air/solution interface by using an ionizing  $^{241}\text{Am}$  electrode. Despite differences in the reported [27] values of the surface potential ( $-80 \text{ mV}$ ) as well as SDS concentration ( $0.01 \text{ mmol kg}^{-1}$ ) at the maximum and those of the present study, it is pertinent to note that the trend in the variation of surface potential with SDS concentration observed by Nakahara et al. [27] is similar to that shown in Fig. 4.

## 6. Conclusions

The KDBM model fits satisfactorily the surface tension data in the submicellar region of ionic surfactants in aqueous, aqueous organic and polar organic media. Using this model, surface density of surfactant monomer, surface density of counterion and surface potential at the air–solution interface can be evaluated.

## Acknowledgments

The authors acknowledge the financial assistance received from the DST, New Delhi. S.C. acknowledges the fellowship from UGC.

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