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Surface Stoichiometry of Ionic Surfactants at Interfaces: A New Thermodynamic Model

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A new theoretical development based on the concept that the air−water interfacial layer of adsorbed ionic surfactant constitutes a nonautonomous phase is presented. This adsorbed layer can thus be described by a state function of variables whose values are dependent on the adjacent bulk phase. This thermodynamic analysis allows demonstration that, for a given interfacial amount of adsorbed ionic surfactant, a Corrin−Harkins-like relationship applies when varying the concentration of an inorganic salt having the same counterion in common with the ionic surfactant. Experimental validation of this analysis is done using the data of Tajima, who studied with a radiotracer method the effect of sodium chloride on the adsorption of sodium dodecyl sulfate (Na^+DS^-) at the air−water interface. The Corrin−Harkin-like relation, $\mathrm{Log}(a_{DS^-}) + \beta\,\mathrm{Log}(a_{Na^+}) = K$, is verified with excellent correlation coefficients for various amounts of adsorbed DS^- at the air−water interface. This result suggests that the behavior of the ionic surfactant layer at the air−water interface is similar to that of micelles. In particular, β may constitute a scale for quantifying the degree of counterion binding to the interfacial layer of surfactant. Finally, the presented model allows the concept of surface stoichiometry for the calculation of the surface area occupied by the polar headgroup of a ionic surfactant at an air−water interface to be introduced.

Introduction

Single-chain ionic surfactants form aggregates called micelles in water because the reduction of the hydrocarbon−water interface is energetically favored.[1,2] The critical micelle concentration (cmc) at which aggregation occurs reflects that hydrophobic interactions between the hydrocarbon chains of the surfactant molecules are balanced by hydration and electrostatic repulsive effects of the hydrophilic headgroups. In addition, it is also well recognized that surfactant properties strongly depend on counterion species.[3] From a theoretical point of view, considerable work has been devoted to rationalize the so-called "degree of counterion binding" to micelles, and various thermodynamic formalisms have been proposed for describing the behavior of ionic surfactant micelles.[4−8] Indeed, knowledge of the specific binding of counterions to ionic surfactant aggregates is of fundamental importance for a better understanding of micellization.

Another important property of ionic surfactants lies in their ability to adsorb at the air−water interface. Since the same fundamental molecular interactions must control aggregation at surfaces and in solution, the interfacial surfactant layer is likely to share many of the properties of micelles in solution. In particular, the concept of degree of counterion binding should be applicable to interfacial surfactant layers. This similarity between micelles and adsorbed films has already been outlined by several authors from thermodynamic studies[9] and neutron reflection experiments,[10] for example.

Adsorption of surfactants at the air−water interface is usually investigated by measuring the surface tension. The Gibbs equation allows the positive or negative surface excesses to be obtained.[11] However, the Gibbs equation can only apply to the study of neutral species. In particular, this formalism does not allow discrimination between the adsorption of an ionic surfactant and its counterion. Results from radiotracer experiments[12] have corroborated those obtained from tension measurements. More recently, the study of adsorption at the air−water interface using specular reflection of neutrons has provided a lot of structural information about the adsorption layer.[13] In particular, this method allowed determination of the amount of tosylate counterions bound to a monolayer of hexadecyltrimethylammonium cations.[13] To the best of our knowledge, the experimental determination of the "ionization degree" of an air−water interfacial layer of ionic surfactant remains limited to these last two methods. However, one could expect that some of the methods which are commonly used for the study of bulk micelles might be applied to interfacial layers. A well recognized method which bears evidence of the ionization of ionic surfactant micelles is based on the evolution of the cmc upon the addition of increasing amounts of an inorganic salt having the same counterion. The degree of counterion binding β can thus be graphically estimated from relation 1[8] which is similar to the regular Corrin−Harkins relation:[14]

$$\mathrm{Log}(\mathrm{cmc}\,\gamma_{\pm}) + \beta\,\mathrm{Log}((\mathrm{cmc} + C_s)\gamma_{\pm}) = K \qquad (1)$$

where $\gamma_{\pm}$ is the mean activity coefficient and C_s the concentration of added salt. This relation is a limiting case of the more general relation (2) linking the activities of surfactant ions, a_1, and counterions, a_2, in the presence of micelles:[8]

$$\mathrm{Log}(a_1) + \beta\,\mathrm{Log}(a_2) = K \qquad (2)$$

where a_1 and a_2 are respectively the activities of surfactant ions and counterions.

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Here, we will show for the first time that the behavior of an air−water interfacial layer of ionic surfactant can be described by Corrin−Harkins-like relations, which are similar to those established for ionized micelles. In the first part of this paper, we present a new theoretical development based on the thermodynamic concept that the air−water interfacial layer of ionic surfactant constitutes a no autonomous phase.[15] This adsorbed layer can thus be described by a state function of variables whose values are dependent on the adjacent solution phase. The theoretical demonstration as well as experimental validation will be developed by taking sodium dodecyl sulfate (Na^+DS^-) as a test ionic surfactant and Na^+X^- as an inorganic salt, with the Na^+ counterion in common. We demonstrate that for a given Γ_{DS^-} interfacial amount of adsorbed DS^-, the following relationship (3) applies when varying the inorganic salt concentration:

$$\mathrm{Log}(a_{DS^-}) + \beta\,\mathrm{Log}(a_{Na^+}) = K \tag{3}$$

where β and K are constants. Experimental validation of relation 3 is done using the published data of Tajima,[16] who studied with a radiotracer method the effect of sodium chloride on the adsorption of sodium dodecyl sulfate at the air−water interface. This theoretical demonstration as well as its experimental validation allowed us to introduce the concept of surface stoichiometry of the adsorbed surfactant layer, which is not possible in the Gibbs law formalism.

Results

The Gibbs energy G of an aqueous solution containing n_1 moles of Na^+DS^-, n_2 moles of Na^+X^-, and n_3 moles of water at constant pressure and temperature depends on n_1, n_2, n_3, and the air−water interfacial area A:

$$G = G(n_1,n_2,n_3,A) \tag{4}$$

and

$$dG = \mu_1\, dn_1 + \mu_2\, dn_2 + \mu_3\, dn_3 + \gamma\, dA \tag{5}$$

where μ_1, μ_2, and μ_3 are the chemical potentials of species and γ the superficial tension.

Since we are interested in studying the segregation of ionic species, it is more convenient to express the Gibbs energy G of the system as a function of the number of moles of each ionic or nonionic species (eq 6), which is purely formal.

$$G = G(n_{DS^-},n_{Na^+},n_{X^-},n_3,A) \tag{6}$$

The mass conservation and electroneutrality imposes that

$$n_{DS^-} = n_1 \quad \text{and} \quad n_{X^-} = n_2 \tag{7}$$

$$n_{Na^+} = n_1 + n_2 \tag{8}$$

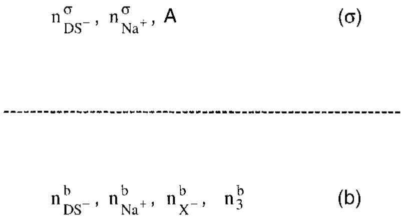
G is an extensive state function and

$$\begin{aligned} dG = \mu_{DS^-}\, dn_{DS^-} + \mu_{Na^+}\, dn_{Na^+} + \mu_{X^-}\, dn_{X^-} +{} \\ \mu_3\, dn_3 + \gamma\, dA \end{aligned} \tag{9}$$

where μ_{DS^-}, μ_{Na^+}, μ_{X^-}, and μ_3 represent the chemical potentials of species.

The problem is to find a structural model allowing description of the interfacial energy corresponding to the term $\gamma\, dA$. In the Gibbs model,[17] $\gamma\, dA$ is associated with neutral surface molecules (NaDS, NaX, H_2O) which are located in the interfacial region, in positive or negative excess with regard to a dividing surface (Gibbs plane S). The bulk concentration of species is taken as a reference for quantifying the surface excesses. The Gibbs plane is chosen so that the surface excess of solvent is zero, allowing the surface excesses of molecules to be determined and the Gibbs adsorption law to be obtained. This model does not introduce the notion of surface stoichiometry between the adsorbed ionic surfactant and its counterion.

SCHEME 1: Phase Separation Model for the Air−Water Interfacial Region of an Aqueous Solution of NaDS[a]



[a] (b) and (σ) represent the bulk phase and the interfacial layer of adsorbed surfactant respectively.

Since we are interested in quantifying the degree of counterion binding to an air−water interfacial layer of ionic surfactant, we propose here an alternative thermodynamic model. We associate to the energetic term $\gamma\, dA$ a "surface content" which is constituted of $n^{\sigma}_{DS^-}$ moles of DS^- anions and $n^{\sigma}_{Na^+}$ moles of Na^+ cations. Unlike Gibbs theory, $n^{\sigma}_{DS^-}$ and $n^{\sigma}_{Na^+}$ may be different in order to account for the possibility that amphiphilic DS^- adsorbs in excess at the air−water interfacial region, in association with only a fraction of strongly bounded Na^+ counterions. Since X^- is not amphiphilic, its concentration in the interfacial region is assumed to be zero because of electrostatic repulsion from the negatively charged interfacial layer of DS^-. Finally, water adsorption is not considered, which means that the air−water interface corresponds to the Gibbs plane.

The argument requires now to count in this plane the positive and negative charges and to associate them to the surface energy γ dA.

Mass conservation implies that

$$n_{Na^+} = n_1 + n_2 = n^{\sigma}_{Na^+} + n^{b}_{Na^+} \tag{10}$$

$$n_{DS^-} = n_1 = n^{\sigma}_{DS^-} + n^{b}_{DS^-} \tag{11}$$

$$n_{X^-} = n_2 = n^{b}_{X^-} \tag{12}$$

$$n_3 = n^{b}_{3} \tag{13}$$

where superscript b denotes the bulk region and superscript σ the interfacial region (Scheme 1). As a consequence of this separation, the Gibbs energy of the system can be formally divided in two contributions,

$$dG = \delta G^{\sigma} + \delta G^{b} \tag{14}$$

with

$$\delta G^{\sigma} = \mu_{DS^-}\, dn^{\sigma}_{DS^-} + \mu_{Na^+}\, dn^{\sigma}_{Na^+} + \gamma\, dA \tag{15}$$

$$\delta G^{b} = \mu_{DS^-}\, dn^{b}_{DS^-} + \mu_{Na^+}\, dn^{b}_{Na^+} + \mu_{X^-}\, dn^{b}_{X^-} + \mu_3\, dn^{b}_{3} \tag{16}$$

At this point, it must be pointed out that we do not take into account the existence of charged phases. Only mathematical variables have been associated. As a consequence and from a theoretical point of view, there is a priori no reason for G^{σ} and G^{b} to be state functions. Only experimental facts could validate this hypothesis. If it is true, then we will be able to obtain new theoretical information about the interfacial adsorption of ionic surfactants.

If G^σ and G^b are effectively state functions of the variables listed in eqs 15 and 16, we can write

$$\delta G^\sigma = dG^\sigma \tag{17}$$

$$\delta G^b = dG^b \tag{18}$$

In this hypothesis, G^σ and G^b are the free chemical energy of two nonautonomous phases in the formalism of Defay.[15]

It is interesting to emphasize that coherence of this model implies particular relations for G^σ and G^b, since these functions are defined from the chemical potentials of the global system. Indeed, we have

$$\mu_{DS^-} = \left(\frac{\partial G^\sigma}{\partial n^\sigma_{DS^-}}\right)_{n^\sigma_{Na^+},A} = \left(\frac{\partial G^b}{\partial n^b_{DS^-}}\right)_{n^b_{Na^+},n^b_{X^-},n_3} \tag{19}$$

$$\mu_{Na^+} = \left(\frac{\partial G^\sigma}{\partial n^\sigma_{Na^+}}\right)_{n^\sigma_{DS^-},A} = \left(\frac{\partial G^b}{\partial n^b_{Na^+}}\right)_{n^b_{DS^-},n^b_{X^-},n_3} \tag{20}$$

and

$$\mu_{NaDS} = \mu_{Na^+} + \mu_{DS^-} = \left(\frac{\partial G}{\partial n_1}\right)_{n_2,n_3,A} \tag{21}$$

Thus, G^σ and G^b are defined from the chemical potentials of the global system by the following relations:

$$\left(\frac{\partial G^\sigma}{\partial n^\sigma_{DS^-}}\right)_{n^\sigma_{Na^+},A} + \left(\frac{\partial G^\sigma}{\partial n^\sigma_{Na^+}}\right)_{n^\sigma_{DS^-},A} = \left(\frac{\partial G}{\partial n_1}\right)_{n_2,n_3,A} \tag{22}$$

$$\left(\frac{\partial G^b}{\partial n^b_{DS^-}}\right)_{n^b_{Na^+},n^b_{X^-},n_3} + \left(\frac{\partial G^b}{\partial n^b_{Na^+}}\right)_{n^b_{DS^-},n^b_{X^-},n_3} = \left(\frac{\partial G}{\partial n_1}\right)_{n_2,n_3,A} \tag{23}$$

The hypothesis of nonautonomous phases for region σ and region b also implies that the property of cross derivation is verified for the chemical potentials.[18]

$$\left(\frac{\partial \mu_{DS^-}}{\partial \mu_{Na^+}}\right)_{n^\sigma_{DS^-},A} = -\left(\frac{\partial n^\sigma_{Na^+}}{\partial n^\sigma_{DS^-}}\right)_{\mu_{Na^+},A} \tag{24}$$

The right-term in eq 24 allows definition of a surface stoichiometry β which is dependent on the Na^+ chemical potential.

$$\beta(\mu_{Na^+}) = \left(\frac{\partial n^\sigma_{Na^+}}{\partial n^\sigma_{DS^-}}\right)_{\mu_{Na^+},A} = \frac{n^\sigma_{Na^+}}{n^\sigma_{DS^-}} \tag{25}$$

Thus, for a transformation occurring with a constant interfacial adsorption of DS^- ($\Gamma_{DS^-} = n^\sigma_{DS^-}/A$), while the Na^+X^- concentration is varying, relation 24 predicts that

$$d\mu_{DS^-} = -\beta(\mu_{Na^+})\, d\mu_{Na^+} \tag{26}$$

If a_{DS^-} and a_{Na^+} are the activities of DS^- and Na^+ in the bulk, development of the chemical potentials in eq 26 leads to the following relation:

$$d \ln(a_{DS^-}) = -\beta(a_{Na^+})\, d \ln(a_{Na^+}) \tag{27}$$

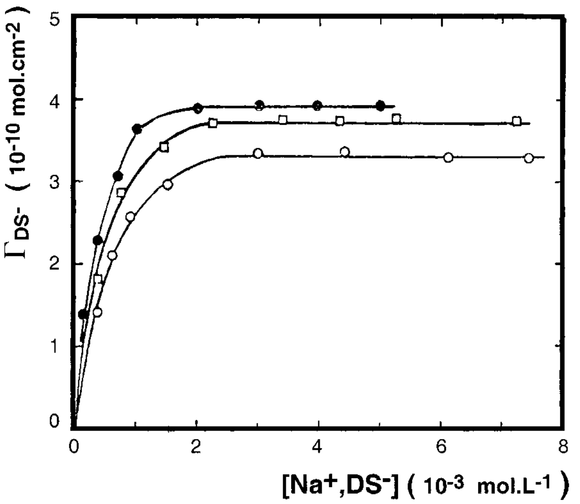


Figure 1. Adsorption isotherms of Na^+DS^- solutions in the presence of NaCl at 25 °C: ○ 1.0 × 10^{-3} M NaCl; □ 5.0 × 10^{-3} M NaCl; ● 10.0 × 10^{-3} M NaCl (from ref 16).

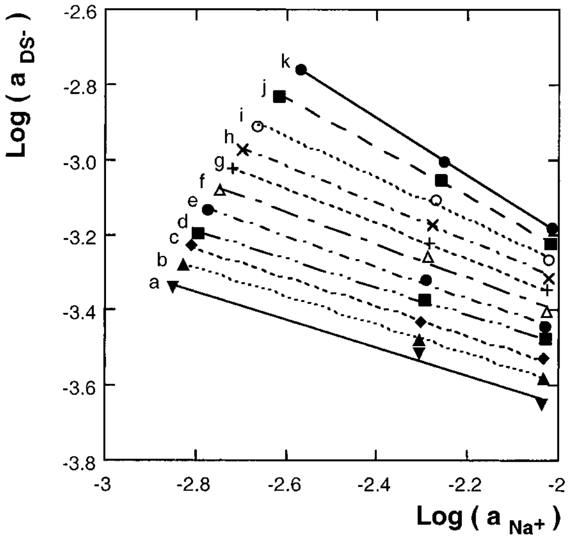


Figure 2. Plots of $\Gamma(a_{DS^-})$ as a function of Log(a_{Na^+}) taking Γ_{DS^-} equal to (a) 1.72, (b) 1.86, (c) 2, (d) 2.14, (e) 2.28, (f) 2.42, (g) 2.56, (h) 2.70, (i) 2.84, (j) 3.0, and (k) 3.14 × 10^{-10} mol cm^{-2}.

This relation can be easily integrated if one assumes that β is independent of a_{Na^+} for a given interfacial adsorption of DS^-. In this modelization, it is assumed that the surface stoichiometry β of the nonautonomous interfacial region phase σ is a constant. This could not be the case, and it is only the experiment which can validate this model. Under this assumption, integration of relation 27 gives

$$\text{Log}(a_{DS^-}) + \beta\, \text{Log}(a_{Na^+}) = K = \text{cste} \tag{3}$$

Relation 3, unlike Gibbs theory, predicts that a Corrin–Harkins-like relation exists for the interfacial layer of adsorbed ionic surfactant.

To check the validity of the theoretical relation (3), we have used the experimental results of Tajima,[16] who established the air–water interfacial adsorption isotherms of DS^- by using a radiotracer method (Figure 1) and studied the effect of added NaCl salt on the interfacial DS^- adsorption. From these isotherms, it is possible to determine for a given value of Γ_{DS^-} the equilibrium bulk concentration of Na^+DS^- when 1, 5, or 10 mM NaCl are present in the medium. Figure 2 represents the relation between Log(a_{DS^-}) and Log(a_{Na^+}) for various Γ_{DS^-} rang-

TABLE 1: Linear Fitting Parameters Obtained from the Corrin−Harkins-Like Plots of Figure 2

Γ_{DS^-} 10^{-10} mol cm^{-2}	β	K	correlation coefficient	curve in Figure 2
1.72	0.37	−4.40	0.99467	a
1.86	0.38	−4.36	0.99998	b
2.0	0.39	−4.32	0.99943	c
2.14	0.37	−4.22	0.9996	d
2.28	0.41	−4.27	0.9984	e
2.42	0.44	−4.28	0.9941	f
2.56	0.47	−4.29	0.9999	g
2.70	0.50	−4.33	0.999	h
2.84	0.55	−4.37	0.9967	i
3.00	0.654	−4.53	0.9996	j
3.14	0.76	−4.73	1	k

ing from 1.72 × 10^{-10} mol cm^{-2} to 3.14 × 10^{-10} mol cm^{-2}.[19] Activities are calculated assuming a mean $\gamma_\pm$ activity coefficient obtained from the extended law of Debye and Huckel:

$$\left(\mathrm{Log}(\gamma_\pm) = -\frac{0.509\sqrt{c_{\mathrm{Na^+}}}}{1 + 1.316\sqrt{c_{\mathrm{Na^+}}}}\right)$$

Despite the poor precision obtained in exploiting Tajima's data, a satisfying linear correlation is observed (Table 1), demonstrating the validity of eq 3. These experimental results show that the salt effect on the behavior of an air−water interfacial layer of adsorbed ionic surfactant can be described using Corrin−Harkins-like relations which are similar to the ones established for ionic micelles.

This observation suggests that the behavior of the surfactant layer at the air−water interface is similar to that of micellar aggregates. In particular, β may constitute a scale for quantifying the degree of counterion binding to the interfacial layer of surfactant. Moreover, the air−water interfacial layer of adsorbed amphiphiles presents the feature of a nonautonomous phase, and its behavior should be described from a state function depending on temperature, interfacial surface area, and content parameters. Finally, the linear relation between Log($a_{\mathrm{DS^-}}$) and Log($a_{\mathrm{Na^+}}$) indicates that the β degree of counterion binding does not depend on salt concentration for a given value of $\Gamma_{\mathrm{DS^-}}$. This behavior is formally the same as that reported for the ionization of micelles.

Figure 3 shows the evolution of β and K as $\Gamma_{\mathrm{DS^-}}$ increases from from 1.72 × 10^{-10} to 3.14 × 10^{-10} mol cm^{-2}. As $\Gamma_{\mathrm{DS^-}}$ increases, the negative charge of the air−water interface increases and electrostatic interactions with sodium counterions become stronger. As a consequence, the degree of counterion binding, β, increases as $\Gamma_{\mathrm{DS^-}}$ increases. It is noteworthy that for high values of $\Gamma_{\mathrm{DS^-}}$, one can find a β value which is very similar to that determined for SDS micelles ($\beta = 0.76$).[20] As a consequence, the structure of the interface between the bulk and the surface amphiphile layer should be very similar at premicellar concentrations to the micelle−bulk interface. Ionization of interfacial ionic surfactant layer agrees well with the recent study of Bain et al.,[10] who demonstrated, using neutron reflection studies, that 80% of counterions are bound to a monolayer of hexadecyltrimethylammonium tosylate at the air−water interface.

Another interesting consequence can be derived from the experimental validation of relation 3. Indeed, assuming in a classical way that U^σ is a homogeneous function of degree one in the variables,

$$dU^\sigma = T\,dS^\sigma + \mu_{\mathrm{DS^-}}\,dn^\sigma_{\mathrm{DS^-}} + \mu_{\mathrm{Na^+}}\,dn^\sigma_{\mathrm{Na^+}} + \gamma\,dA \quad (28)$$

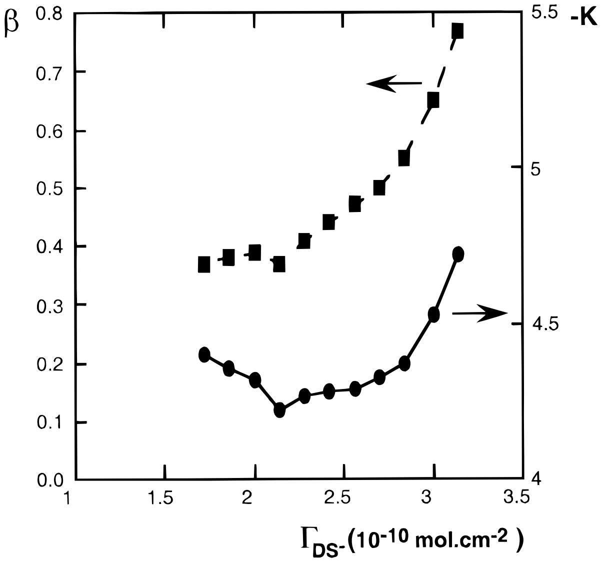


Figure 3. Evolution of β and K as a function of $\Gamma_{\mathrm{DS^-}}$.

a Gibbs−Duhem relation can be obtained in the following form at constant temperature:

$$0 = n^\sigma_{\mathrm{DS^-}}\,d\mu_{\mathrm{DS^-}} + n^\sigma_{\mathrm{Na^+}}\,d\mu_{\mathrm{Na^+}} + A\,d\gamma \quad (29)$$

that is,

$$d\gamma = -\frac{n^\sigma_{\mathrm{DS^-}}}{A}\,d\mu_{\mathrm{DS^-}} - \frac{n^\sigma_{\mathrm{Na^+}}}{A}\,d\mu_{\mathrm{Na^+}} \quad (30)$$

or

$$d\gamma = -\Gamma_{\mathrm{DS^-}}\,d\mu_{\mathrm{DS^-}} - \Gamma_{\mathrm{Na^+}}\,d\mu_{\mathrm{Na^+}} \quad (31)$$

In absence of added electrolyte and at low concentration C of NaDS, eq 31 reduces to relation 32.

$$d\gamma = -RT(\Gamma_{\mathrm{DS^-}} + \Gamma_{\mathrm{Na^+}})\,d\ln C \quad (32)$$

Since $\Gamma_{\mathrm{Na^+}} = \beta\Gamma_{\mathrm{DS^-}}$, as shown by relation 25, we finally obtain

$$\frac{d\gamma}{d\ln C} = -RT(1+\beta)\Gamma_{\mathrm{DS^-}} \quad (33)$$

Relation 33 gives a new interpretation for the physical signification of $d\gamma/d\ln C$. Indeed, in the Gibbs formalism, which does not separate the contributions of the ionic surfactant and its counterion, it is shown that

$$\frac{d\gamma}{d\ln C} = -2RT\Gamma_{\mathrm{NaDS(Gibbs)}} \quad (34)$$

Identification between relations 33 and 34 gives

$$2\Gamma_{\mathrm{NaDS(Gibbs)}} = (1+\beta)\Gamma_{\mathrm{DS^-}} \quad (35)$$

Relation 35 demonstrates that it is possible to introduce the notion of surface stoichiometry in the calculation of the surface area occupied by the polar headgroup of a ionic surfactant adsorbed at an air−water interface.

Conclusion

In conclusion, we have shown theoretical and experimental evidence that air−water interfacial layers of ionic surfactants present similar features to phases. Their behavior can be described from state functions depending on content parameters. The behavior of air−water interfacial ionic surfactant layers is similar to that of ionic micelles. In particular, the degree of counterion binding can be experimentally estimated from the air−water interfacial adsorption isotherms using Corrin−Harkins-like plots. This new approach may be of general interest for a better understanding of the behavior of amphiphilic ions at interfaces.

Finally, we have demonstrated for the first time that the concept of surface stoichiometry can be used in the calculation of the surface area occupied by the polar headgroup of a ionic surfactant at an air−water interface. This new model, which is complementary to the Gibbs law, should be extended to other interfaces, in particular solid−liquid and liquid−liquid interfaces.

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