The Interpretation of Surface Tension Data for Solutions of Ionic Surfactants in the Presence of Electrolyte

Denver G. Hall, Brian A. Pethica, and Kozo Shinoda*
Unilever Research, Port Sunlight Laboratory, Port Sunlight, Wirral, Merseyside, England L62 4XN
**Department of Chemistry, Faculty of Engineering, Yokohama National University, Minami-ku, Yokohama 233*

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An improved method is presented for interpreting surface tension data on solutions of an ionic surfactant to which has been added an electrolyte whose co-ion has the same valence as the surfactant ion. Adequate account is taken of co-ion adsorption and of deviations from ideality of the solution. When a monolayer of surfactant ions is formed and the distributions of free surfactant ions and co-ions in the region adjacent to it are determined predominantly by electrostatic repulsion, it is shown that the separate contributions to the total Gibbs excess of surfactant ions from the monolayer and the adjacent region can be obtained. Finally some experimental data are re-examined and a simple explanation is given for the minimum reported to occur in co-ion adsorption as the surfactant ion concentration is increased at constant co-ion concentration.

In a previous paper Shinoda and Nakayama[1)] described a method based on the Gibbs adsorption isotherm of interpreting surface tension data for a solution of an ionic surfactant plus electrolyte. This method was applied to suitable data then available to determine amounts adsorbed. Later, Lucassen-Reynders[2)] suggested that it should be modified to include co-ion adsorption. In both papers ideal behaviour of the bulk solution was assumed. In this paper a more rigorous analysis is given in which both co-ion adsorption and solution non-ideality are allowed for. Tajima, Muramatsu and Sasaki[3—6)] have also considered this problem but from a viewpoint somewhat different and, in our opinion, less illuminating than that described below.

Theory

We let subscripts 1—4 refer to water, surfactant ions, counterions and co-ions respectively and take as our starting point the Gibbs adsorption isotherm which, for the system of interest, at equilibrium at constant T and p can be written as

$$\mathrm{d}\sigma = -\Gamma_2 RT\mathrm{d}\ln m_2 f_2 - \Gamma_3 RT\mathrm{d}\ln m_3 f_3 - \Gamma_4 RT\mathrm{d}\ln m_4 f_4 \qquad (1)$$

where σ is the surface tension, Γ_2—Γ_4 are the surface excesses of species 2—4 referred to the dividing surface for which $\Gamma_1=0$, m_2—m_4 are the molalities of species 2—4, f_2—f_4 are the corresponding bulk ionic activity coefficients and the ionisation of water is considered to be negligible.

In the case that the valence of 3 is z_3 whereas species 2 and 4 are both monovalent, the electrical neutrality conditions for the interface and the bulk solutions enable us to write

$$\left.\begin{aligned} z_3\Gamma_3 &= \Gamma_2 + \Gamma_4 \\ z_3 m_3 &= m_2 + m_4 \end{aligned}\right\} \qquad (2\text{a, b})$$

Eliminating Γ_3 from Eq. (1) we obtain

$$\mathrm{d}\sigma = -\Gamma_2 RT\mathrm{d}\ln m_2 - \frac{(\Gamma_2+\Gamma_4)}{z_3}RT\mathrm{d}\ln m_3 - \Gamma_4 RT\mathrm{d}\ln m_4 - \Gamma_2 RT\mathrm{d}\ln\gamma_2 - \Gamma_4 RT\mathrm{d}\ln\gamma_4 \qquad (3)$$

where

$$\left.\begin{aligned} \ln\gamma_2 &= \ln f_2 + \frac{\ln f_3}{z_3} \\ \ln\gamma_4 &= \ln f_4 + \frac{\ln f_3}{z_3} \end{aligned}\right\} \qquad (4\text{a, b})$$

From Eqs. (2), (3), and (4) after elementary manipulation we obtain

$$\frac{1}{RT}\left(\frac{\partial\sigma}{\partial m_2}\right)_{m_4} = -\left[\frac{\Gamma_2}{m_2}+\frac{\Gamma_2+\Gamma_4}{z_3(m_2+m_4)}+\Gamma_2\left(\frac{\partial\ln\gamma_2}{\partial m_2}\right)_{m_4} + \Gamma_4\left(\frac{\partial\ln\gamma_4}{\partial m_2}\right)_{m_4}\right]$$

$$\frac{1}{RT}\left(\frac{\partial\sigma}{\partial m_4}\right)_{m_2} = \frac{1}{z_3RT}\left(\frac{\partial\sigma}{\partial m_3}\right)_{m_2} = -\left[\frac{\Gamma_4}{m_4}+\frac{\Gamma_2+\Gamma_4}{z_3(m_2+m_4)}+\Gamma_2\left(\frac{\partial\ln\gamma_2}{\partial m_4}\right)_{m_2} + \Gamma_4\left(\frac{\partial\ln\gamma_4}{\partial m_4}\right)_{m_2}\right]$$

$$\frac{1}{RT}\left(\frac{\partial\sigma}{\partial m_2}\right)_{m_3} = -\frac{1}{RT}\left(\frac{\partial\sigma}{\partial m_4}\right)_{m_3} = -\left[\frac{\Gamma_2}{m_2}-\frac{\Gamma_4}{m_4}-\Gamma_2\left(\frac{\partial\ln\gamma_2}{\partial m_2}\right)_{m_3} + \Gamma_4\left(\frac{\partial\ln\gamma_4}{\partial m_2}\right)_{m_3}\right] \qquad (5\text{a, b, c})$$

A considerable simplification results when it is legitimate to write

$$\gamma_2 = \gamma_4 \qquad (6)$$

As under these circumstances and at constant T and p, γ_2, and γ_4 depend only on m_3.

For the case that a monolayer of adsorbed surfactant is present we write

$$\Gamma_2 = \Gamma_2^{\mathrm{m}} + \Gamma_2^{\mathrm{s}} \qquad (7)$$

where Γ_2^{m} is the amount of surfactant ion in the monolayer and Γ_2^{s} is the contribution to Γ_2 from the region adjacent to the monolayer. Also we suppose that Γ_2^{s} and Γ_4 are determined primarily by electrostatic repulsion due to the monolayer and that, as a consequence of this, the distribution of surfactant ions in the region adjacent to the monolayer is sufficiently like that of the co-ions to enable us to write

$$\frac{\Gamma_2{}^{\mathrm{s}}}{m_2} = \frac{\Gamma_4}{m_4} \tag{8}$$

If we now define the quantity α by

$$\alpha = -2\frac{(\Gamma_2{}^{\mathrm{s}}+\Gamma_4)}{\Gamma_2{}^{\mathrm{m}}}, \tag{9}$$

assume that $\gamma_2=\gamma_4$ and put $\beta=(\partial\ln\gamma_2/\partial m_3)$ Eqs. (5a, b, and c) become respectively

$$\frac{1}{RT}\left(\frac{\partial\sigma}{\partial\ln m_2}\right)_{m_4} = -\Gamma_2{}^{\mathrm{m}}\left[1-\frac{\alpha m_2}{2(m_2+m_4)} + (1-\alpha/2)\left(\frac{m_2}{z_3(m_2+m_4)}+m_2\beta\right)\right] \tag{10a}$$

$$\frac{1}{RT}\left(\frac{\partial\sigma}{\partial\ln m_3}\right)_{m_2} = -\Gamma_2{}^{\mathrm{m}}\left[(1-\alpha/2)\left(\frac{1}{z_3}+m_3z_3\beta\right)-\frac{\alpha}{2}\right] \tag{10b}$$

$$\frac{1}{RT}\left(\frac{\partial\sigma}{\partial\ln m_2}\right)_{m_3} = -\Gamma_2{}^{\mathrm{m}} \tag{10c}$$

Discussion

Equation (10c) is the main result of this paper. It shows that even for non ideal solutions $\Gamma_2{}^{\mathrm{m}}$, the amount of adsorbed surfactant present in the monolayer, can be obtained directly from measurements of the variation of surface tension with surfactant concentration at constant counterion concentration provided that Eqs. (7) and (8) are valid. These two equations are closely related. When species 2 and 4 distribute similarly with respect to each other and with respect to species 3,[7] (γ_2 is equal to γ_4), whereas Eq. (8) holds when species 2 and 4 distribute similarly with respect to the monolayer and is unlikely to be valid when Eq. (7) is invalid. According to Debye-Hückel theory, Eq. (7) must hold when m_3 is small and there is no significant ion association.

The concentration at which equating γ_2 and γ_4 leads to significant errors cannot be estimated from experimental data on surfactant solutions because insufficient data are available. However, freezing-point depression measurements[8] and EMF measurements[9–11] indicate that, below their critical micelle concentrations, most 1: 1 ionic surfactants do not associate significantly and are reasonably well-behaved 1: 1 electrolytes. If this is so, the value of m_3 at which Eq. (6) ceases to be a good approximation may be similar to corresponding values for mixtures of simple 1: 1 electrolytes. The activity coefficients of such mixtures can be described quite well by the expression[12]

$$\ln\gamma_2 = \frac{-A\sqrt{m_3}}{1+\sqrt{m_3}} + B_{22}m_2 + B_{24}m_4 \tag{11}$$

where A, given by the Debye-Hückel limiting law, is the same for all 1: 1 electrolytes, the Bs are empirical constants and $B_{24}=B_{42}$. At constant m_3 the sum of the last two terms of Eq. (5c) is given by $\Gamma_2(B_{22}-B_{24})-\Gamma_4(B_{44}-B_{42})$. Typical values of $(B_{22}-B_{24})$ are of the order 0.3 kg mol^{-1}.[13] Such values lead to errors in Γ_2 and $\Gamma_2{}^{\mathrm{m}}$ which are proportional to m_2 and which can be expected to be of the order 3% when $m_2=0.1$ mol kg^{-1}. When $\gamma_2=\gamma_4$, Eq. (11) becomes

$$\ln\gamma_2 = \ln\gamma_4 = \frac{-A\sqrt{m_3}}{1+\sqrt{m_3}} + Bm_3 \tag{12}$$

where $B=B_{22}=B_{24}=B_{44}$. From Eq. (12) we find that

$$\beta = \frac{-A}{2(1+\sqrt{m_3})}\left(\frac{1}{\sqrt{m_3}}-\frac{1}{1+\sqrt{m_3}}\right) + B \tag{13}$$

Since $A=2.342$ kg$^{1/2}$ mol$^{-1/2}$ at 298 K, whereas B is typically of order 0.4 kg mol^{-1}, it is evident that the final term of Eq. (13) can be ignored when m_3 is small. Also the term $m_2\beta$, which is always $\ll m_3\beta$, decreases with increasing m_3 at constant m_2. When $m_3=0.1$ mol kg^{-1}, $m_3\beta\simeq0.21$; whereas when $m_3=0.01$ mol kg^{-1}, $m_3\beta\simeq0.10$. Consequently, the activity terms in Eqs. (10) and (5) are not negligible when $m_3>0.01$ mol kg^{-1}, although that in Eq. (10a) is negligible when $m_3\gg m_2$.

Less information is available for mixtures of 2: 1 eelctrolytes with a common divalent ion than for mixtures of 1: 1 electrolytes. The errors which arise through equating γ_2 and γ_4 can be expected to be somewhat greater in this case than in that above.

No direct experimental evidence for the conditions under which Eq. (8) ceases to be a good approximation appears to be available and it is not obvious how such evidence can be obtained. However when Eq. (8) is valid, the dependence of σ on m_2 and m_3 should be independent of the nature of the co-ion, provided that it has the same valence as the surfactant ion and does not form part of the monolayer. The experimental data of Matuura *et al.*[14] suggest that this may be so. Whether or not it is provides an indirect test of Eq. (8).

When $m_4\gg m_2$ and Eq. (8) is valid, $\Gamma_2\simeq\Gamma_2{}^{\mathrm{m}}$. This result can be expected to hold when $m_4\gg m_2$ even if Eq. (8) is not valid, provided that $\Gamma_2{}^{\mathrm{s}}$ is determined primarily by electrostatic effects. Hence experimental values of Γ_2 in the presence of excess salt are essentially values of $\Gamma_2{}^{\mathrm{m}}$. The results of Brooks and Pethica[15] reinforce this conclusion. They found that the π *vs.* A curves obtained directly for insoluble monolayers of long chain surfactants at the *n*-heptane/aqueous NaCl interface are independent of chain length for a given head group. Also the curves are the same as the π *vs.* A curves for the shorter chain length homologues obtained from application of the Gibbs adsorption isotherm to the appropriate interfacial tension data. Such agreement can be regarded as confirming the Gibbs equation. Alternatively it is strong evidence that $\Gamma_2=\Gamma_2{}^{\mathrm{m}}$ under the conditions concerned.*

Equations (10b and c) show that the surface tensions of the solutions of interest behave as if the solutions were ideal and as if the surface phase were a charged phase[1,16] consisting of $\Gamma_2{}^{\mathrm{m}}$ mol per unit area of surfactant ion and $\Gamma_2{}^{\mathrm{m}}[(1-\alpha/2)[1/z_3+m_3z_3\beta]-\alpha/2]$ mol per unit area of counterion. Hence the above theory enables the data for the air-solution interface considered previously[1] to be reinterpreted as in Table 1.

The values of α for the hydrocarbon surfactants are considerably smaller when deviations from solution

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* Although the equation used by Brooks and Pethica to obtain Γ_2 contains the approximation $\Gamma_4=0$, the errors attributable to this approximation are less than the experimental errors in this particular case.

TABLE 1.

Compound	$\Gamma_2{}^{\mathrm{m}} \times 10^6$ mol m^{-2}	$-\frac{1}{RT}\left(\frac{d\sigma}{d \ln m_3}\right)_{m_2} \times$ 10^6 mol m^{-2}	$z_3 m_3 \beta$	α	Ref
$C_7F_{15}CO_2H$	4.0	1.8	−0.10	0.47	1
$C_7F_{15}CO_2K$	3.9	2.0	−0.15	0.37	1
$(C_7F_{15}CO_2)_2Ba$	3.3	1.0	−0.13	0.10	1
$C_{11}H_{23}CO_2K$	4.2	2.9	−0.21	0.11	17
$C_{12}H_{25}NH_3Cl$	5.2	3.5	−0.21	0.13	17
$C_{12}H_{25}SO_4Na$	4.4	3.2	−0.21	0.07	17

ideality are taken into account than they are when such deviations are ignored. These values show that the negative adsorptions of co-ions, although small, are not negligible and should be allowed for when interpreting accurate data rigorously. Somewhat surprisingly, the values of α for the two monovalent fluorocarbon surfactants are considerably bigger than those of the hydrocarbon surfactants despite the similar values of $\Gamma_2{}^{\mathrm{m}}$.

Subsequent to the work of Shinoda and Nakayama, Tajima *et al.*[3–6] have examined the adsorption of sodium dodecyl sulphate (SDS) at the air/solution interface in the presence of NaCl, both by measuring surface tension and by direct measurement of adsorption using radiotracers. An interesting feature of this work is the observed minimum in Γ_4 as m_2 is increased at constant m_4. This is precisely what one expects from the above theory as Eqs. (8) and (9) enable us to write

$$\Gamma_4 = \frac{-\Gamma_2{}^{\mathrm{m}} \alpha m_4}{2(m_2+m_4)} \tag{14}$$

which shows that Γ_4 can be expected to decrease initially as $\Gamma_2{}^{\mathrm{m}}$ increases; when $\Gamma_2{}^{\mathrm{m}}$ and α are both close enough to their limiting values to be essentially independent of m_2 the rate of increase of Γ_4 becomes smaller as m_4 becomes larger. An equally simple alternative explanation of this behaviour is difficult to envisage.

Also of interest is the increase in saturation adsorption of surfactant as m_4 is increased. We have from Eq. (9)

$$\Gamma_2 = \Gamma_2{}^{\mathrm{m}}\left[1-\frac{\alpha}{2}\,\frac{m_2}{m_2+m_4}\right] \tag{15}$$

which shows that Γ_2 increases with increasing m_2 more slowly than does $\Gamma_2{}^{\mathrm{m}}$ and that when $\Gamma_2{}^{\mathrm{m}}$ is constant, Γ_2 should decrease with increasing m_2. If we assume that $\Gamma_2{}^{\mathrm{m}}$ and α have attained their limiting values at the surfactant critical micelle concentration (CMC) and are both independent of m_4, we can use Eq. (15) to calculate the change in Γ_2 at the CMC as m_4 is increased. The results of such a calculation agree well with experiment when $\Gamma_2{}^{\mathrm{m}}$ is taken as 4.33×10^{-6} mol m^{-2} and α is taken as 0.56. However, this value of α is much larger than that shown in Table 1. Consequently we conclude that only a small proportion of the increase in saturation adsorption of surfactant with increasing m_4 is due to the effect described by Eq. (15).

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