The Adsorption Behaviour of Ionic Surfactants and their Mixtures with Nonionic Polymers and with Polyelectrolytes of Opposite Charge at the Air-Water Interface

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Supporting Information

Nonionic surfactants

Eqn 4 in the main paper is

$$\sum_{i=1}^{c} \left[x_i^\alpha \frac{\gamma_i^\alpha}{\gamma_i^{\alpha\beta}} \exp\left[\frac{A_i}{RT}(\sigma - \sigma_i) \right] \right] = 1 \tag{1}$$

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where c is the number of components. Setting all the partial molar areas to A and taking the case of a nonionic surfactant we obtain

$$x_w^\alpha \frac{\gamma_w^\alpha}{\gamma_w^{\alpha\beta}} \exp\left[\frac{A}{RT}(\sigma - \sigma_w)\right] + x_s^\alpha \frac{\gamma_s^\alpha}{\gamma_s^{\alpha\beta}} \exp\left[\frac{A}{RT}(\sigma - \sigma_s)\right] = 1 \tag{2}$$

Using the same substitutions that led to Eqn 7 in the main paper in Eqn 2 we obtain

$$\exp\left[\frac{A}{RT}(\sigma - \sigma_w)\right] + x_s^\alpha \frac{\gamma_s^\alpha}{\gamma_s^{\alpha\beta}} \exp\left[\frac{A}{RT}(\sigma - \sigma_s)\right] = 1 \tag{3}$$

Rearranging this equation gives

$$\ln\left(1 - \exp\left[\frac{A}{RT}(\sigma - \sigma_w)\right]\right) - \frac{A\sigma}{RT} = \ln x_s^\alpha + \ln\left(\frac{\gamma_s^\alpha}{\gamma_s^{\alpha\beta}}\right) - \frac{A\sigma_s}{RT} \tag{4}$$

Below the CMC, x_s is equal to the overall surfactant concentration and above the CMC it is equal to the CMC. Figure 1 shows the linear relationship between the left hand side of Eqn 4 with respect to $ln x_s$ for four nonionic surfactants, $C_{12}E_6$, $C_{12}E_8$, $C_{10}E_4$, and TX100. The limiting areas per molecule for the first three compounds are respectively 59, 68, and 45 Å^2 and compare well with values of 55 and 63 for $C_{12}E_6$ and $C_{12}E_8$.[1] The value of 45 Å^2 for $C_{10}E_4$ is close to the NR value of 44 Å^2 for $C_{12}E_4$. The value for the area TX100 is 58 Å^2, which agrees with the value of 58.7 Å^2 per molecule obtained by Szymczyk and Janczuk.[2]

Since the surface activity coefficient is unity over this range γ_s^α for the bulk phase must also be constant up to the CMC. Since the activity coefficient in the micelle at the CMC is unity γ_s^α can then be determined from the CMC using

$$x_s^\alpha \gamma_s^\alpha = x_s^{\text{micelle}} \gamma_s^{\text{micelle}} \text{ at } x_s^\alpha = cmc \tag{5}$$

which becomes
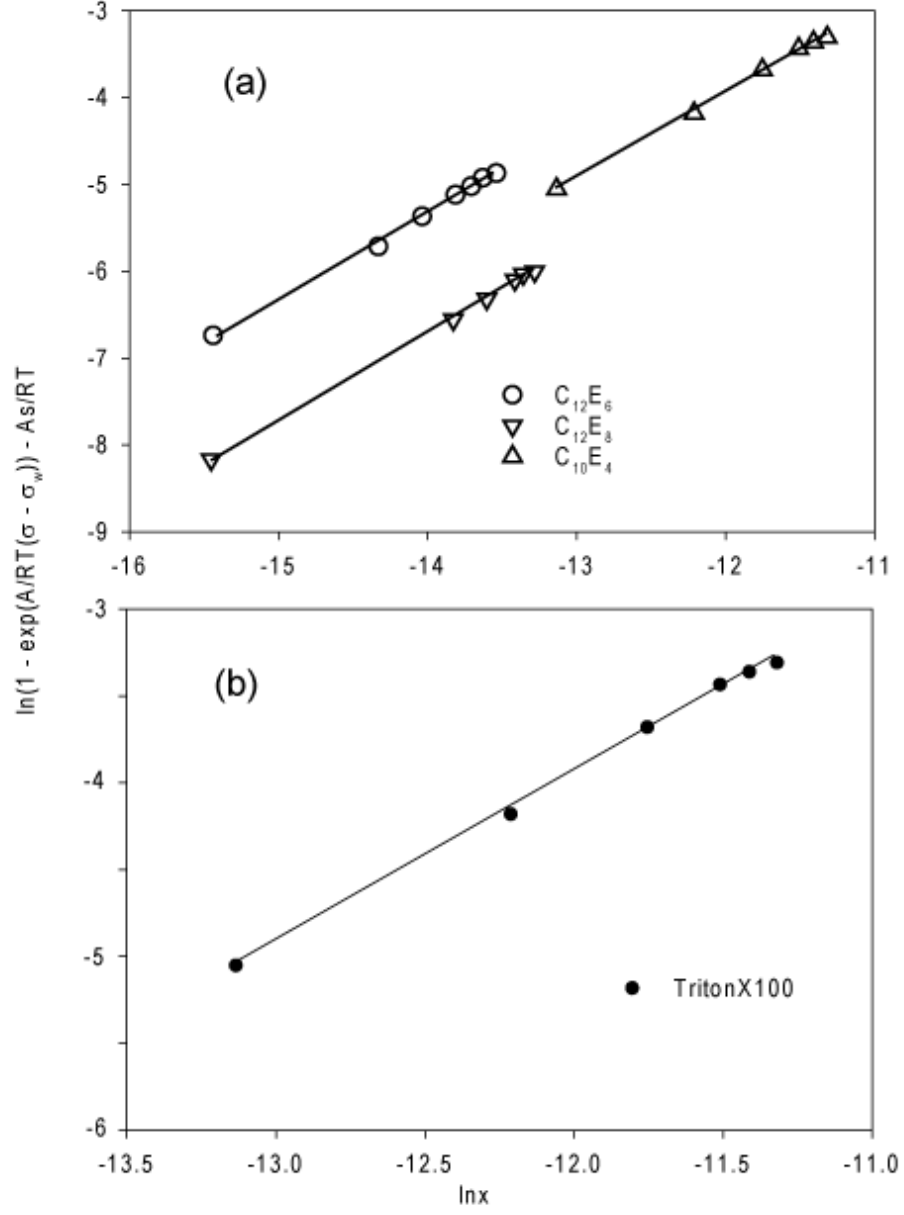
$$\gamma_s^\alpha = \frac{1}{cmc} \tag{6}$$

Figure 1: The linear plot of Eqn 4 for (a) $C_{12}E_6$, $C_{12}E_8$ and $C_{10}E_4$ at 25 ^oC using experimental data from Nikas et al[3] and (b) for TX100 at 25 ^oC using experimental data from Szymczyk and Janczuk.[2] The slopes for the fits were constrained to 1 and the resulting values of A were 59, 68 and 45 $Å^2$ for $C_{12}E_6$, $C_{12}E_8$ and $C_{10}E_4$ respectively, and 58 $Å^2$ for TX100.

Using this relation Eqn 3 reduces to

$$\exp\left[\frac{A}{RT}(\sigma - \sigma_w)\right] + \frac{x_s^\alpha}{cmc}\exp\left[\frac{A}{RT}(\sigma - \sigma_s)\right] = 1 \tag{7}$$

or

$$\sigma_w - \sigma = \pi = \frac{RT}{A}ln\left[1 + \frac{x_s^\alpha}{cmc}\exp\left[\frac{A}{RT}(\sigma_w - \sigma_s)\right]\right] \tag{8}$$

This is identical with the Szyskowski equation

$$\sigma_w - \sigma = \frac{RT}{A}ln\left[1 + bx_s^\alpha\right] \tag{9}$$

with the parameter b given by

$$b = \frac{1}{cmc}exp\left[\frac{A(\sigma_w - \sigma_s)}{RT}\right] \tag{10}$$

Determination of the Surface Excess

It follows from Eqns 14 to 10 and the Langmuir-Szyskowsi equation that the surface excess, Γ, is given by

$$\Gamma = \frac{RT}{A}\left(\frac{bx_s^\alpha}{1 + bx_s^\alpha}\right) = \frac{RT}{A}\left(\frac{b'a_s^\alpha}{1 + b'a_s^\alpha}\right) \tag{11}$$

where b' is given by

$$b' = exp\left[\frac{A(\sigma_w - \sigma_s)}{RT}\right] \tag{12}$$

For a 1:1 ionic surfactant Eqn 11 from the main paper similarly gives the surface excess as

$$\Gamma_s = \frac{RT}{A}\left(\frac{b'(a_\pm^\alpha)^2}{1 + b'(a_\pm^\alpha)^2}\right) \tag{13}$$

Either the absolute or the relative surface excess can therefore be determined from the value of $a_\pm^s$.

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Adsorption Isotherm in the Presence of Salt

When the dissolved salt has a common ion with the surfactant, e g. Na^+ in SDS and NaCl, then the molar fraction of counter ion must be modified and Eqn 11 in the main paper becomes

$$\sigma_w - \sigma = \pi = \frac{RT}{A}ln\left[1 + x_s^\alpha(x_s^\alpha + x_{NaCl})\left(\gamma_\pm^\alpha\right)^2\exp\left[\frac{A}{RT}(\sigma_w - \sigma_s)\right]\right] \quad (14)$$

and the activity coefficient at the cmc for surfactant + salt (e g NaCl) is

$$\gamma_\pm^\alpha = \frac{1}{2}\left[\frac{1}{cmc(cmc + x_{NaCl})}\right]^{\frac{1}{2}} \quad (15)$$

Similarly, Eqn 8 of the main paper becomes

$$\ln\left(1 - \exp\left[\frac{A}{RT}(\sigma - \sigma_w)\right]\right) - \frac{A\sigma}{RT} = \ln x_s^\alpha + 2\ln\left(\frac{\gamma_\pm^\alpha}{\gamma_\pm^{\alpha\beta}}\right) - \frac{A\sigma_s}{RT} + \ln\left(x_s + x_{NaCl}\right) \quad (16)$$

which gives a linear relationship of the left hand side with $\ln x_s$ but with a slope of unity. The last term on the right hand side is almost constant because the mole fraction of surfactant is negligible compared with that of NaCl for normal salt concentrations.

Alternatively, the following argument shows that we can also use the original Eqn 8 from the main part of the paper, which is

$$\ln\left(1 - \exp\left[\frac{A}{RT}(\sigma - \sigma_w)\right]\right) - \frac{A\sigma}{RT} = 2\ln x_s^\alpha + 2\ln\left(\frac{\gamma_\pm^\alpha}{\gamma_\pm^{\alpha\beta}}\right) - \frac{A\sigma_s}{RT} \quad (17)$$

If we apply this to the situation where there is added electrolyte with a common ion, for example, when the common ion in SDS and NaCl is Na^+ the total area, A^*, is

$$A^* = (n_w + n_{SDS^-} + n_{Cl^-} + n_{Na_{SDS}^+} + n_{Na_{NaCl}^+})A \quad (18)$$

where n is the molar concentration of the adsorbed species. The salt makes a negligible contribution and we can write

$$A^* = (n_w + n_{SDS^-} + n_{Na^+_{SDS}})A \tag{19}$$

which will be approximately double the area obtained by applying the more accurate Eqn 16. The two different plots are compared in Fig 2 of the main paper.

Weakly Interacting Systems and Added Electrolyte

For P-S systems and taking SDS and NaCl as example, the activity coefficient of the surfactant below the CAC (Eqn 18 in the main paper) becomes

$$\gamma_\pm = \frac{\gamma^c_\pm}{3} \left[\frac{1}{cac(cac + x_{NaCl})} \right]^{\frac{1}{2}} \tag{20}$$

The two limiting components of the activity between the CAC and T_3 are fixed points at the CAC and T_3. At these points the concentration is

$$x^t_s = x^t_s(x^t_s + x_{NaCl}) \tag{21}$$

where x^t_s equals either cac or T_3. Neglecting the small difference between T_3 and cmc, the effects of electrolyte cancel out the denominator of Eqn 20 to a good approximation and the activity is then identical to Eqn 20 in the main paper, i e

$$a^t_s = \left(\frac{\gamma^c_\pm}{3} \right)^{\frac{x^t - T_3}{cac - T_3}} \left(\frac{1}{2} \right)^{\frac{x^t - cac}{T_3 - cac}} \tag{22}$$

The cancellation of terms leading to Eqn 22 arises because electrical neutrality requires that the attachment of a surfactant ion to neutral polymer must involve an associated counterion. They also seem to imply that electrolyte has no effect on the ST of P-S systems. However,

electrolyte does have a strong effect through the modification of the σ_s and A parameters of the surfactant by electrolyte. That Eqn 22 and Eqn 20 of the main paper are the same indicates that there is no additional effect of electrolyte when neutral polymer is present. These equations have not been used in the present work.

Strongly Interacting Systems and Electrolyte

Above T_1 and when there is no ST peak the activity is given by Eqn 29 in the main paper, but similarly to Eqn 22, this is determined by the activities at the two limiting points, T_1 and T_3, and these approximately cancel for the same reasons, i e the equation is approximately unchanged. When there is phase separation, however, the concentration of surfactant monomer occurs (in Eqns 28 and 31) and should be replaced by Eqn 21. The mean activity coefficient is correspondingly given by Eqn 20.

The effect of added electrolyte on the CAC is known to be large (see e g Nizri et al[4]). However, this interaction has no effect on the ST because the resulting complex does not adsorb. Added electrolyte does affect the region between the CAC and T_1 but it cannot easily be expressed. For this region we have used a Langmuir isotherm in the form

$$x_s^{complex} = \left[\frac{k\frac{x^t}{T_1 - x^t}}{\left(1 + k\frac{x^t}{T_1 - x^t}\right)} \right] \tag{23}$$

where k is the binding constant. We represent the effect of added electrolyte by replacing x and T_1 by

$$x_\pm^t = \left[x^t(x^t + x_{NaCl}) \right]^{\frac{1}{2}} \tag{24}$$

$$T_\pm = \left[T_1(T_1 + x_{NaCl}) \right]^{\frac{1}{2}} \tag{25}$$

However, there are several inconsistencies in using this approach. In the end, provided the results are treated as semi-quantitative these approximations are probably unimportant because most of the effects of electrolyte can be subsumed empirically into the constant k.

References

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