

Nonionic and ionic surfactants at an interface

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received 7 February 2008; accepted in final form 14 April 2008
published online 26 May 2008

PACS 82.70.Uv – Surfactants, micellar solutions, vesicles, lamellae, amphiphilic systems,
(hydrophilic and hydrophobic interactions)

PACS 82.45.Gj – Electrolytes

PACS 68.05.-n – Liquid-liquid interfaces

Abstract – A Ginzburg-Landau theory is presented on surfactants in polar binary mixtures, which aggregate at an interface due to the amphiphilic interaction. They can be ionic surfactants coexisting with counterions. Including the solvation and image interactions and accounting for a finite-volume fraction of the surfactant, we obtain their distributions and the electric potential around an interface in equilibrium. The surface tension is also calculated. The distribution of the adsorbed ionic surfactant is narrower than that of the counterions. The adsorption is marked for hydrophilic and hydrophobic pairs of ionic surfactant and counterions

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Introduction. – Surfactant molecules can be trapped at an interface, reducing the surface tension and giving rise to mesoscopic structures, as their density in the bulk is increased [1,2]. Oil-water interfaces containing surfactants are usually treated as infinitesimally thin surfaces characterized by the surface tension γ dependent on the adsorbed surfactant density Γ . In this letter, we present a diffuse-interface model or a Ginzburg-Landau theory. Some authors presented Ginzburg-Landau free energies which include higher-order gradients of the composition or the surfactant density to describe dynamics of mesophase formation [3–6]. However, the gradient expansion in the free energy breaks down when the surfactants are strongly adsorbed onto an interface or when the trapping energy ϵ_a of a surfactant molecule much exceeds the thermal energy T . We will propose a model in which surfactant molecules are treated as rods and their two ends can stay in very different environments. In this letter, we examine only the equilibrium properties following from our model.

Moreover, surfactants can be ions or have charges in many important systems in biology and technology. The adsorption of surfactant and counterions in such cases has not yet been well studied. Hence we will treat ionic surfactants and counterions in binary mixtures, grafting the amphiphilic interaction onto our previous theory of electrolytes which accounts for the solvation effect [7,8].

We may define the excess adsorption Γ generally for doped particles such as surfactants and ions. For a diffuse

interface, we determine the interface position in terms of the order parameter $\psi(z)$ (the composition difference in this work) as $z_{\text{in}} = \int_0^L dz [\psi(z) - \psi_\beta] / \Delta\psi$ in a finite system in the region $0 < z < L$, where all the quantities change along the z -axis [9]. The $\psi(z)$ takes the two bulk values ψ_α and ψ_β with $\Delta\psi \equiv \psi_\alpha - \psi_\beta > 0$ on the two sides of the interface, while the bulk values of the doped-particle density $n(z)$ are denoted by n_α and n_β . The phase α is more polar or water-rich, while the phase β is less polar or oil-rich. Then,

$$\begin{aligned} \Gamma &= \int_0^L dz \left[n(z) - n_\alpha - \frac{\Delta n}{\Delta\psi} (\psi(z) - \psi_\alpha) \right] \\ &= \int_0^{z_{\text{in}}} dz [n(z) - n_\alpha] + \int_{z_{\text{in}}}^L dz [n(z) - n_\beta], \end{aligned} \quad (1)$$

where $\Delta n = n_\alpha - n_\beta$ and the integrands tend to zero far from the interface. At very small n , the surface tension decreases as $\gamma \cong \gamma_0 - T\Gamma$, where γ_0 is the surface tension without doping [2,9]. For electrolyte systems [8] there is also an electrostatic contribution,

$$\gamma \cong \gamma_0 - T\Gamma - \frac{1}{8\pi} \int dz \varepsilon |\nabla\Phi|^2, \quad (2)$$

where ε is the dielectric constant and Φ is the electric potential tending to constants far from the interface. We will derive eq. (2) including the amphiphilic interaction. The Boltzmann constant will be set equal to unity.

Nonionic surfactant in a binary mixture. – We first consider a polar binary mixture (water and oil) with

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a small amount of neutral surfactant. The water, oil, and surfactant densities are n_A , n_B , and n_1 , respectively. Assuming the same molecular size a for water and oil, their volume fractions are $\phi_A = a^3 n_A$, $\phi_B = a^3 n_B$, and $N_1 c_1 = v_1 n_1$, respectively, where v_1 is the surfactant molecular volume. We define the normalized surfactant density $c_1 = a^3 n_1$. Here the volume ratio $N_1 = v_1/a^3$ can be arbitrary. We assume the space-filling condition $\phi_A + \phi_B + N_1 c_1 = 1$; then,

$$\phi_A = (1 - N_1 c_1)/2 + \psi, \quad \phi_B = (1 - N_1 c_1)/2 - \psi. \quad (3)$$

Here $2\psi = \phi_A - \phi_B$ is the composition difference of the solvent. We may set $\phi_A \cong 1/2 + \psi$ and $\phi_B \cong 1/2 - \psi$ neglecting the surfactant volume fraction for $N_1 c_1 \ll 1/2 - |\psi|$. The free energy F is the space integral of its density f_{non} of the form,

$$\frac{a^3}{T} f_{\text{non}} = \phi_A \ln \phi_A + \phi_B \ln \phi_B + \chi \phi_A \phi_B + \frac{C}{2} |\nabla \psi|^2 + c_1 \ln c_1 - g_1 c_1 \psi - c_1 \ln Z_{\text{am}}, \quad (4)$$

where χ is the temperature-dependent coefficient, the coefficient C is positive, and g_1 represents the interaction between the surfactant and the composition difference. The last term represents the amphiphilic interaction, where Z_{am} is the partition function of a rod-like dipole with its center at the position \mathbf{r} . We assume that the surfactant molecules take a rod-like shape with length 2ℓ considerably longer than a . It is given by the following integral on the surface of a sphere with radius ℓ ,

$$Z_{\text{am}}(\mathbf{r}) = \int \frac{d\Omega}{4\pi} \exp[-w_a \psi(\mathbf{r} + \ell \mathbf{u}) + w_a \psi(\mathbf{r} - \ell \mathbf{u})], \quad (5)$$

where \mathbf{u} is the unit vector along the rod direction and $\int d\Omega$ represents the integration over the angles of \mathbf{u} . The two ends of the rod are at $\mathbf{r} + \ell \mathbf{u}$ and $\mathbf{r} - \ell \mathbf{u}$ under the influence of the solvation potentials given by $T w_a \psi(\mathbf{r} + \ell \mathbf{u})$ and $-T w_a \psi(\mathbf{r} - \ell \mathbf{u})$, respectively. It is instructive to examine the case in which $\psi(\mathbf{r})$ varies slowly. That is, if the expansion $\psi(\mathbf{r} + \ell \mathbf{u}) - \psi(\mathbf{r} - \ell \mathbf{u}) \cong 2\ell \mathbf{u} \cdot \nabla \psi$ is used, the last term in eq. (4) becomes $-\frac{2}{3} w_a^2 \ell^2 |\nabla \psi|^2 c_1$. This gradient form was assumed in the literature [3,4]. Together with the fourth term in eq. (4), the coefficient in front of $|\nabla \psi|^2$ vanishes for $n_1 = n_L$ (a Lifshitz point), where

$$n_L = 3C/[4a^3(\ell w_a)^2]. \quad (6)$$

For $n_1 > n_L$, a homogeneous solution is unstable at a finite wave number, leading to a mesophase. If $C \sim a^2$, we have $a^3 n_L \sim (a/\ell w_a)^2$, so n_L is small for $\ell w_a \gg a$.

The above gradient expansion cannot be used around an interface far from the critical point or for $\xi < 2\ell$. If a surfactant molecule is trapped at an interface with its hydrophilic (hydrophobic) end in the water-rich (oil-rich) region, the free energy decreases by $\epsilon_a = T w_a \Delta \psi$. Strong adsorption occurs for large $\epsilon_a/T = w_a \Delta \psi$. In the

one-dimensional (1D) case, where all the quantities vary along the z -axis, Z_{am} becomes

$$Z_{\text{am}}(z) = \int_{-\ell}^{\ell} \frac{d\zeta}{2\ell} \exp[-w_a \psi(z + \zeta) + w_a \psi(z - \zeta)], \quad (7)$$

where we have replaced $\psi(\mathbf{r} \pm \ell \mathbf{u})$ in eq. (5) by $\psi(z \pm \zeta)$ with $\zeta = \ell u_z$. In the thin-interface limit $\xi \ll \ell$, we place the interface at $z = 0$ to find

$$Z_{\text{am}}(z) \cong 1 + (1 - |z|/\ell)[\cosh(w_a \Delta \psi) - 1] \quad (8)$$

for $|z| < \ell$, while $Z_{\text{am}} = 1$ for $|z| > \ell$. Furthermore, in the dilute limit $N_1 c_1 \ll 1 - \psi_\alpha$, we have $c_1(z) = c_{1\alpha} Z_{\text{am}}(z)$ for $z < 0$ and $c_1(z) = c_{1\beta} Z_{\text{am}}(z)$ for $z > 0$, where $c_{1\alpha}$ and $c_{1\beta} = e^{-g_1 \Delta \psi} c_{1\alpha}$ are the bulk surfactant densities, leading to $\Gamma \cong \ell a^{-3} (c_{1\alpha} + c_{1\beta}) [\cosh(w_a \Delta \psi) - 1]/2$. However, the steric effect due to finite surfactant volume becomes important with increasing Γ .

In this letter, we are interested in the equilibrium interface profile in the 1D case. We require homogeneity of the surfactant chemical potential $T\nu_1 = (\delta F/\delta n_1)_\psi$ and the chemical potential difference $Th = a^3 (\delta F/\delta \psi)_{n_1}$ of the mixture. Some calculations give

$$\nu_1 = \ln(c_1/Z_{\text{am}}) - g_1 \psi - \frac{1}{2} N_1 \ln(\phi_A \phi_B) + \frac{1}{2} \chi N_1 (N_1 c_1 + 1) + 1 - N_1, \quad (9)$$

$$h = \ln(\phi_A/\phi_B) - 2\chi \psi - C \nabla^2 \psi - g_1 c_1 + h_{\text{am}}. \quad (10)$$

The h_{am} stems from the amphiphilic free energy $F_{\text{am}} = -T \int d\mathbf{r} n_1 \ln Z_{\text{am}}$. Its 1D form is

$$h_{\text{am}}(z) = w_a \int_{-\ell}^{\ell} \frac{d\zeta}{2\ell} X(z + \zeta) \times \left[e^{w_a [\psi(z+2\zeta) - \psi(z)]} - e^{w_a [\psi(z) - \psi(z+2\zeta)]} \right], \quad (11)$$

where $X(z) \equiv c_1(z)/Z_{\text{am}}(z)$. In the dilute limit $c_{1\alpha} \rightarrow 0$, $c_1(z)$ is expressed in terms of $\psi(z)$ as

$$\frac{c_1(z)}{c_{1\alpha}} \rightarrow \left[\frac{1 - 4\psi(z)^2}{1 - 4\psi_\alpha^2} \right]^{N_1/2} Z_{\text{am}}(z) e^{g_1 (\psi(z) - \psi_\alpha)}. \quad (12)$$

In our model, if N_1 is large and if ψ_α is close to $1/2$ far below the critical point, the first factor on the right-hand side of eq. (12) can be large in the interface region where $\psi \cong 0$. This leads to $\Gamma \sim c_{1\alpha} \xi (1 - 4\psi_\alpha^2)^{-N_1/2}$ even for $Z_{\text{am}} = 1$. For our choice $\chi = 3$ in our figures, we have $\psi_\alpha = 0.429$ and $(1 - 4\psi_\alpha^2)^{-1} = 3.79$. However, the first factor in eq. (12) tends to unity near the critical point.

The grand potential Ω is given by the space integral of $\omega = f_{\text{non}} - T a^{-3} (h\psi + \nu c_1)$. In equilibrium, Ω is minimized as a functional of ψ and c_1 under given boundary conditions. For an interface, $\omega(z)$ should tend to a common limit ω_∞ as $z \rightarrow \pm\infty$ (see the appendix) and the surface tension is expressed as $\gamma = \int dz [\omega(z) - \omega_\infty]$. Here

it is convenient to introduce $\eta \equiv a^3 f_{\text{non}}/T - \nu_1 c_1 + c_1 = a^3 \omega/T + h\psi + c_1$. Use of eq. (9) yields

$$\eta = \left(\frac{1}{2} + \psi\right) \ln \phi_A + \left(\frac{1}{2} - \psi\right) \ln \phi_B + N_1 c_1 - \chi \psi^2 - \frac{1}{4} \chi N_1^2 c_1^2 + \frac{1}{2} C(\psi')^2, \quad (13)$$

where $\psi' = d\psi/dz$. The γ can be expressed as

$$\gamma = \frac{T}{a^3} \int dz [\eta(z) - \eta_\alpha - h(\psi(z) - \psi_\alpha) - c_1(z) + c_{1\alpha}], \quad (14)$$

where $h = (\eta_\alpha - \eta_\beta - c_{1\alpha} + c_{1\beta})/(\psi_\alpha - \psi_\beta)$ with η_α , η_β , $c_{1\alpha}$, and $c_{1\beta}$ being the bulk values. The integrand in eq. (14) tends to zero far from the interface. We may then derive eq. (2) for small c_1 . Let $\psi_0(z) = \lim_{c_1 \rightarrow 0} \psi(z)$ be the interface profile without surfactant and $\delta\psi = \psi - \psi_0$ be the deviation due to c_1 . Then $\eta(z) - \eta_\alpha = C d/dz[\delta\psi d\psi_0/dz] + \dots$ up to first order in $\delta\psi$ and c_1 , because of the interface equation $\ln[(1 + 2\psi_0)/(1 - 2\psi_0)] - 2\chi\psi_0 - C d^2\psi_0/dz^2 = 0$ without surfactant. Hence $a^3 \Delta\gamma/T$ is nearly the integral of $-c_1(z) + c_{1\alpha} - h(\psi - \psi_\alpha)$ with $h = (c_{1\beta} - c_{1\alpha})/\Delta\psi$, leading to eq. (2).

In all the figures to follow, we will set $C = \chi a^2$, $\chi = 3$, and $\ell = 2.5a$, where $\gamma_0 = 0.497T a^{-2}$ at $c_1 = 0$. In eq. (6) we have the critical density $n_L = 0.36w_a^{-2}$. The interface width ξ is about $5a \sim 2\ell$. In fig. 1, we present $c_1(z) = a^3 n_1(z)$, $(\gamma_0 - \gamma)a^2/T$, and Γa^2 , where $g_1 = 4$ and $w_a = 10$. With increasing $c_{1\alpha}$, the peak of $c_1(z)$ grows, Γ increases, and γ decreases. The steric effect due to the surfactant volume fraction is apparent for $N_1 = 5$, while it is not for $N_1 = 1$. For $N_1 = 5$, the first factor in eq. (12) is crucial for $c_{1\alpha} < 10^{-4}$ and the steric effect is relevant for larger $c_{1\alpha}$, so that eq. (2) holds only for very small $c_{1\alpha}$; in fact, $(\gamma_0 - \gamma)/T\Gamma \sim 1.3$ at $c_{1\alpha} = 10^{-4}$. See the argument below eq. (12). For $N_1 = 1$, eq. (2) nicely holds for $c_{1\alpha} < 3 \times 10^{-4}$ and $\Gamma \propto c_{1\alpha}$ at any $c_{1\alpha}$.

Ionic surfactant and counterions in a binary mixture. – Previously, we treated nonamphiphilic ions, including the solvation and image interactions [7,8]. Here the first ion species with density n_1 is a cationic surfactant. The second species with density n_2 constitutes anionic counterions having no amphiphilic character. They are both monovalent with charges $\pm e$. We assume that the counterions are very small and their volume fraction is negligible. Then the relations in eq. (3) still hold.

For our complex ionic system, the total free-energy density $f = f_{\text{non}} + f_{\text{ion}}$ is the sum of f_{non} in eq. (4) and the following new part:

$$f_{\text{ion}} = T n_2 (\ln c_2 - g_2 \psi) + \frac{\varepsilon(\psi)}{8\pi} |\nabla \Phi|^2 + n \mu_{\text{im}}, \quad (15)$$

where $n = n_1 + n_2$. We define $c_1 = a^3 n_1$ and $c_2 = a^3 n_2$. The dielectric constant is assumed to be of the linear form $\varepsilon(\psi) = \varepsilon_c + \varepsilon_1 \psi$, where ε_c and ε_1 are positive constants. The parameters g_1 in eq. (4) and g_2 in eq. (15) can arise

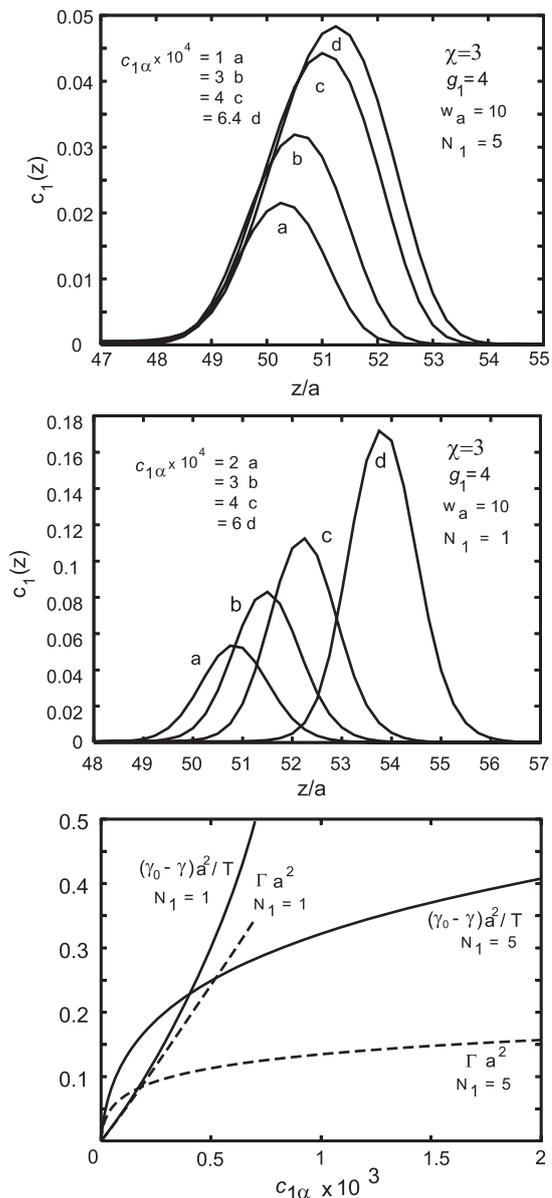


Fig. 1: Results for nonionic surfactants for $\chi = 3$, $g_1 = 4$, and $w_a = 10$: $c_1(z)$ for four values of $c_{1\alpha}$ for $N_1 = 5$ (top) and 1 (middle), while $(\gamma_0 - \gamma)a^2/T$ and Γa^2 vs. $c_{1\alpha}$ for $N_1 = 5$ and 1 (bottom). Here $\gamma_0 - \gamma \cong T\Gamma$ at small $c_{1\alpha}$.

from the solvation (ion-dipole) interaction and can be very large in aqueous solutions [7,8]. The differences $\Delta\mu_{\alpha\beta}^i = Tg_i \Delta\psi$ are the so-called Gibbs transfer free energies per particle from phase α to phase β for ion species i [10]. For water-nitrobenzene mixtures at room temperature, $\Delta\mu_{\alpha\beta}^i/T$ are of order 15 for monovalent metallic ions. Recently, Sadakane *et al.* [11] found periodic structures in a near-critical mixture containing strongly hydrophilic and hydrophobic ions, presumably, with $g_1 \sim -g_2 \sim 15$.

The electric potential Φ arises from the charge density,

$$-\nabla \cdot \varepsilon(\psi) \nabla \Phi = 4\pi e(n_1 - n_2). \quad (16)$$

The electric field $E = -d\Phi/dz$ around an interface reads

$$\frac{e}{T}E(z) = \frac{4\pi\ell_B}{1 + \varepsilon_1\psi(z)/\varepsilon_c} \int_{-\infty}^z dz' [n_1(z') - n_2(z')], \quad (17)$$

where the lower bound of the integration is pushed to $-\infty$. We define the Bjerrum length $\ell_B = e^2/\varepsilon_c T$ at $\varepsilon = \varepsilon_c$. We may set $\Phi_\alpha = 0$ without loss of generality.

The image potential μ_{im} acts on each ion [12,13], which arises from inhomogeneous ε . For moderate inhomogeneity and in the 1D case, it is expressed in the following Cauchy integral [8]:

$$\mu_{\text{im}}(z) = T A a \frac{\varepsilon_1}{\varepsilon_c} \int \frac{dz'}{\pi} \frac{e^{-2\kappa|z-z'|}}{z-z'} \frac{d\psi(z')}{dz'}, \quad (18)$$

where A represents the charge strength,

$$A = \pi e^2 / 4a\varepsilon_c T = \pi \ell_B / 4a, \quad (19)$$

and $\kappa = [4\pi n e^2 / \varepsilon_c T]^{1/2}$ is the Debye wave number [12]. The factor $e^{-2\kappa|z-z'|}$ in eq. (18) arises from the screening of the image potential by the other ions, so the image interaction is weakened with increasing the ion density. We take n in κ as the space-dependent ion density $n(z) = n_1(z) + n_2(z)$.

Again we assume homogeneity of the chemical potentials $T\nu_{1\text{tot}} = \delta F / \delta n_1$, $T\nu_{2\text{tot}} = \delta F / \delta n_2$, and $Th_{\text{tot}} = a^3 \delta F / \delta \psi$. From $F = \int d\mathbf{r} (f_{\text{non}} + f_{\text{ion}})$ they are

$$\begin{aligned} \nu_{1\text{tot}} &= \nu_1 + e\Phi/T + \mu_{\text{im}}/T, \\ \nu_{2\text{tot}} &= \ln c_2 + 1 - g_2\psi - e\Phi/T + \mu_{\text{im}}/T, \\ h_{\text{tot}} &= h - g_2c_2 + h_{\text{im}}/T, \end{aligned} \quad (20)$$

where ν_1 and h are given by eqs. (9) and (10). In taking the derivatives with respect to n_1 and n_2 , we neglect the n -dependence of μ_{im} in eq. (18). The $h_{\text{im}}(z)$ in eq. (20) arises from the image interaction and is obtained by the right-hand side of eq. (18) if ψ is replaced by $n = n_1 + n_2$.

Since the counterion volume fraction is neglected, c_2 around an interface is written as

$$\frac{c_2(z)}{c_{2\alpha}} = \exp \left[g_2(\psi(z) - \psi_\alpha) + \frac{e}{T}\Phi(z) - \frac{1}{T}\mu_{\text{im}}(z) \right]. \quad (21)$$

In our previous work [8], we examined the image factor $F_{\text{im}}(z) \equiv \exp[-\mu_{\text{im}}(z)/T]$ in various cases. Let us consider it in the α region with $z_{\text{in}} - z > \xi$, where z_{in} is the interface position and ξ is the interface thickness. Then,

$$F_{\text{im}}(z) \cong \exp[-D e^{-2\kappa_\alpha(z_{\text{in}}-z)} / (z_{\text{in}} - z)], \quad (22)$$

where $D = \ell_B \varepsilon_1 \Delta\psi / 4\varepsilon_c$. Here $D \sim \ell_B \sim Aa$ for $\varepsilon_1 \sim \varepsilon_c$ and $\Delta\psi \sim 1$. The image interaction can be crucial near an interface for $\xi < D < \kappa_\alpha^{-1}$, under which the image factor serves to repel the ions in the region $\xi < z_{\text{in}} - z < (2\kappa_\alpha)^{-1}$ in the α region. This ion depletion was used to explain an increase of γ of water-air interfaces with salt [12,13].

However, its effect on the ionic surfactants is diminished when the amphiphilic interaction is strong or for $w_a \Delta\psi \gg 1$. These aspects will be illustrated in figs. 5 and 6 for $A = 4$ and 10.

From the charge neutrality in the bulk regions α and β , we require $c_{1\alpha} = c_{2\alpha}$ and $c_{1\beta} = c_{2\beta}$. Then we find

$$\ln(c_{1\alpha}/c_{1\beta}) = (g_1 + g_2)\Delta\psi/2 + S_t, \quad (23)$$

$$e(\Phi_\alpha - \Phi_\beta)/T = (g_1 - g_2)\Delta\psi/2 + S_t, \quad (24)$$

where $\Phi_\alpha - \Phi_\beta$ is called the Galvani potential difference. The S_t stems from the surfactant volume fraction $N_1 c_1$,

$$S_t = \frac{N_1}{4} \ln \left[\frac{(1 - N_1 c_{1\alpha})^2 - 4\psi_\alpha^2}{(1 - N_1 c_{1\beta})^2 - 4\psi_\beta^2} \right] - \frac{N_1^2}{4} \chi \Delta c_1, \quad (25)$$

with $\Delta c_1 = c_{1\alpha} - c_{1\beta}$. Here $S_t \rightarrow 0$ as $N_1 \rightarrow 0$. Note that $\Phi(z)$ changes on the scale of the Debye screening length, κ_α^{-1} in the phase α and κ_β^{-1} in the phase β . As a result, Φ changes from Φ_α to Φ_β on the spatial scale of $\kappa_\alpha^{-1} + \kappa_\beta^{-1}$.

We consider the grand potential density $\omega = f - Ta^{-3}(h_{\text{tot}}\psi + \nu_{1\text{tot}}c_1 + \nu_{2\text{tot}}c_2)$. With the aid of eq. (20) we have $\omega = Ta^{-3}(\eta - h_{\text{tot}}\psi - c) + \varepsilon|\nabla\Phi|^2/8\pi - \rho\Phi$, where η is given by eq. (13) and $c = c_1 + c_2$. From $\omega(\infty) = \omega(-\infty)$ (see the appendix), we obtain

$$\begin{aligned} \gamma &= \frac{T}{a^3} \int dz [\eta(z) - h_{\text{tot}}\psi(z) - c(z) - A_\alpha] \\ &\quad - \frac{1}{8\pi} \int dz \varepsilon(\psi) |\nabla\Phi|^2, \end{aligned} \quad (26)$$

where $A_\alpha = \eta_\alpha - h_{\text{tot}}\psi_\alpha - c_\alpha$ and $h_{\text{tot}} = (\eta_\alpha - \eta_\beta - c_\alpha + c_\beta)/\Delta\psi$ with c_α and c_β being the bulk values of c . From this expression, eq. (2) follows at small $n = n_1 + n_2 = a^{-3}c$ if we use the argument below eq. (14).

We present some numerical results with $N_1 = 5$ and $\varepsilon_1 = 0.8\varepsilon_c$. The dielectric constant of the phase α is twice larger than that of the phase β at $\chi = 3$. We set $A = 4$ except in the left panel of fig. 6 where $A = 10$.

i) In fig. 2, we show the volume fractions ϕ_A , ϕ_B , and $N_1 c_1 = 1 - \phi_A - \phi_B$ (top), c_1 and c_2 (middle), and $e\Phi/T$ with $\Phi_\alpha = 0$ (bottom). In the left plates, the counterions are more hydrophilic than the cationic surfactant, where $g_1 = 4$ and $g_2 = 10$ leading to $\Gamma = 0.124a^{-2}$ and $\gamma = 0.317Ta^{-2}$ at $c_{1\alpha} = 10^{-3}$. In the right plates, the surfactant cations are hydrophilic and the counterions are hydrophobic, where $g_1 = -g_2 = 8$ leading to $\Gamma = 0.155a^{-2}$ and $\gamma = 0.159Ta^{-2}$ at $c_{1\alpha} = 3.6 \times 10^{-4}$. The distribution of the ionic surfactant c_1 is narrower than that of the counterions c_2 . This gives rise to a peak of Φ , at which the right-hand side of eq. (17) vanishes.

ii) In fig. 3, we show γ , γ_1 , and Γ as functions of $c_{1\alpha}$ at $w_a = 12$, where γ_1 is the first term on the right-hand side of eq. (26). The Lifshitz-point $c_{1\alpha} = a^3 n_L = 2.5 \times 10^{-3}$ for $C = 9a^2$ is marked by an arrow (top). For small $c_{1\alpha}$ eq. (2) holds, but the last electrostatic term in eq. (26) is not negligible. For a pair of hydrophilic and hydrophobic ions, a large electric double layer is formed at an interface [8], leading to a large Γ even at small $c_{1\alpha}$.

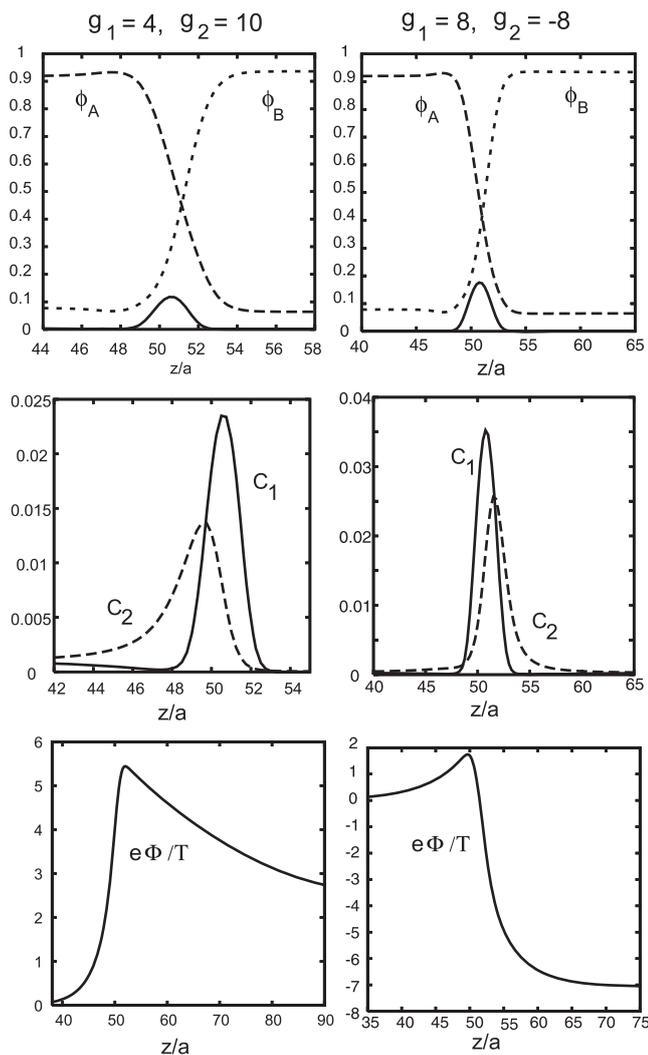


Fig. 2: Profiles for mixtures with cationic surfactant and anionic counterions with $N_1 = 5$, $w_a = 12$, and $A = 4$. Top: $N_1 c_1$ (solid line), ϕ_A , and ϕ_B . Middle: c_1 and c_2 . Bottom: $e\Phi/T$. Here $g_1 = 4$, $g_2 = 10$, and $c_{1\alpha} = 10^{-3}$ (left), while $g_1 = -g_2 = 8$ and $c_{1\alpha} = 3.6 \times 10^{-4}$ (right). The counterion distribution has a peak in the phase α (left) or β (right) depending on g_2 .

iii) In fig. 4, we show γ , γ_1 , and Γ vs. g_2 at $w_a = 12$ and $g_1 = 8$ to demonstrate the above trend, where Γ and $\gamma_0 - \gamma$ are markedly enhanced for negative g_2 .

iv) In figs. 5 and 6, we set $w_a = 15$, where Γ is appreciable even at $c_{1\alpha} = 10^{-5}$. In fig. 5, where $g_1 = g_2 = 10$, we have $\Gamma = 0.0090a^{-2}$ and $\gamma = 0.487T/a^2$, while $\gamma_1 = 0.491T/a^2 \cong \gamma_0 - T\Gamma$. There are virtually no ions in the region β . The distribution of c_2 in the region α is broad changing on the scale of κ_α^{-1} , where $\kappa_\alpha = 0.046/a$. Note that $\Phi(z)$ is constant in the region β displayed in fig. 5. However, it should tend to $\Phi_\beta (\cong 0$ here) for $z - z_{in} \gg \kappa_\beta^{-1} \sim 10^3 a$.

v) In the left panel of fig. 6, we increase A in eq. (19) to 10 with the other parameters being the same as in fig. 5. This is because the effect of the image interaction is rather weak at $A = 4$ [8], where D in eq. (22) is of

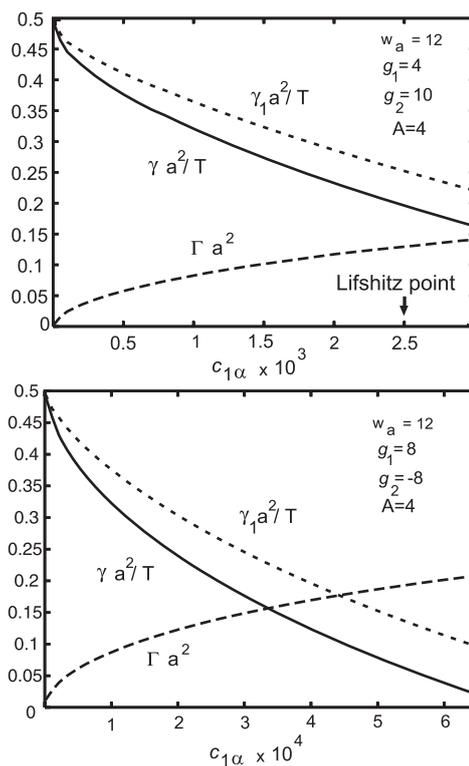


Fig. 3: $\gamma a^2/T$, $\gamma_1 a^2/T$, and Γa^2 as functions of $c_{1\alpha}$ with $N_1 = 5$, $\chi = 3$, and $w_a = 12$, where γ is calculated from eq. (26) and γ_1 is the first term on its right-hand side. The curves change on a scale of 10^{-3} for $g_1 = 4$ and $g_2 = 10$ (top) and on a scale of 10^{-4} for $g_1 = -g_2 = 8$ (bottom).

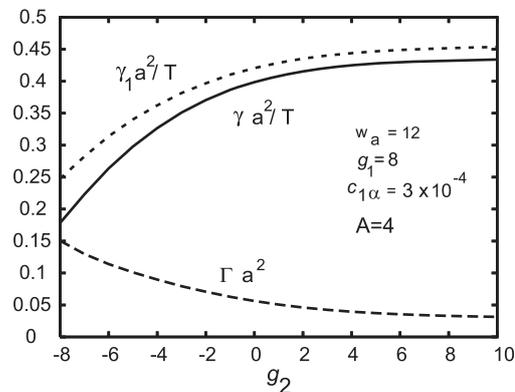


Fig. 4: $\gamma a^2/T$, $\gamma_1 a^2/T$, and Γa^2 as functions of g_2 with $\chi = 3$, $w_a = 12$, and $g_1 = 8$, where γ_1 is the first term on the right-hand side of eq. (26). The counterions are hydrophobic for $g_2 < 0$ and hydrophilic for $g_2 > 0$.

order a . See the discussion around eq. (22). With $A = 10$, the image interaction is amplified and Γ is decreased to $0.0049a^{-2}$ (55% of the value in fig. 5) with $\gamma = 0.491T/a^2$. See fig. 10 of our previous paper [8], where we set $A = 10$ to realize strong ion depletion in the more polar phase. However, the normalized potential $e\Phi/T$ is also amplified with increasing A from eq. (17) and the effect is very complicated.

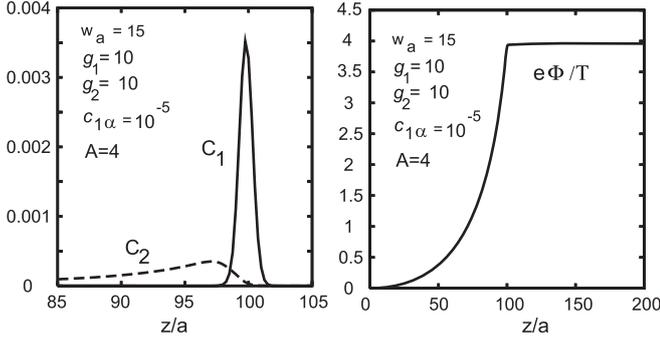


Fig. 5: c_1 and c_2 (left) and $e\Phi/T$ (right) with $w_a = 15$, $A = 4$, and $g_1 = g_2 = 10$, where $c_{1\alpha} = 10^{-5}$ is very small due to large w_a . The counterion distribution is wider than that of the ionic surfactant. There is no appreciable variation of Φ in the β region shown here, where the ion densities are nearly zero.

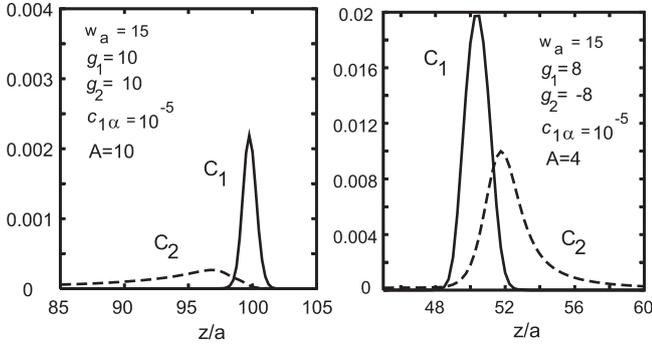


Fig. 6: c_1 and c_2 for $w_a = 15$ and $c_{1\alpha} = 10^{-5}$. Left: $A = 10$, where the electrostatic and image interactions are amplified from eqs. (17) and (18). Right: $g_1 = -g_2 = 8$ leading to enhanced adsorption. The other parameters in each panel are the same as in fig. 5.

vi) In the right panel of fig. 6, we consider the case of a hydrophilic and hydrophobic ion pair with $g_1 = -g_2 = 8$. The other parameters are the same as in fig. 5. Then Γ is increased to $0.071a^{-2}$ (8 times larger than the value in fig. 5) with $\gamma = 0.403T/a^2$.

Summary. – We have presented the continuum models of surfactants including the amphiphilic interaction explained around eqs. (4)–(8). They reasonably describe the adsorption of nonionic and ionic surfactants, though our numerical examples are still fragmentary. For ionic surfactants, included are also the electrostatic, solvation, and image interactions. The adsorption is extremely sensitive to $\varepsilon_a/T = w_a\Delta\psi$ and N_1 . It is decreased as $A \sim \ell_B/a$ is increased for a pair of hydrophilic ions from the left panels of figs. 5 and 6. It is also enhanced for hydrophilic and hydrophobic ion pairs, as shown in figs. 3 and 4 and the right panel of fig. 6.

Though we have set $\chi = 3$ in all the figures here, the changeover and the phase transition with decreasing χ at large w_a and g_i should be intriguing [8]. The phase transition of binary mixtures with salt can be

very complex at large g_i [7,8,11]. We should also study dynamics including the amphiphilic interaction in higher space dimensions.

This work was supported by Grants in Aid for Scientific Research and for the 21st Century COE project (Center for Diversity and Universality in Physics) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

APPENDIX

We consider a 1D equilibrium interface profile, $\psi = \psi(z)$, $c_1 = c_1(z)$, and $c_2 = c_2(z)$, for our ionic surfactant system. Use of eqs. (9), (10), and (18) gives

$$\frac{d}{dz} \left[\frac{a^3}{T} \omega - C(\psi')^2 + (c_1 - c_2) \frac{e\Phi}{T} - \frac{c}{T} \mu_{\text{im}} \right] = -h_{\text{int}}\psi' - \nu_{1\text{int}}c_1' - \nu_{2\text{int}}c_2', \quad (\text{A.1})$$

where $c = c_1 + c_2$, $\psi' = d\psi/dz$, $c_K' = dc_K/dz$, and

$$h_{\text{int}} = \frac{a^3}{T} \frac{\delta F_{\text{int}}}{\delta \psi}, \quad \nu_{K\text{int}} = \frac{a^3}{T} \frac{\delta F_{\text{int}}}{\delta c_K}, \quad (\text{A.2})$$

with $K = 1, 2$. Here $F_{\text{int}} = \int d\mathbf{r} [-Tn_1 \ln Z_{\text{am}} + n\mu_{\text{im}}]$ is the sum of the amphiphilic and image free energies, so $h_{\text{int}} = h_{\text{am}} + h_{\text{im}}$ and $\nu_{1\text{int}} + \ln Z_{\text{am}} = \nu_{2\text{int}} \cong \mu_{\text{im}}$ (see the discussion below eq. (20)). The F_{int} is invariant with respect to a shift of the interface position or with respect to $z \rightarrow z - \zeta$ in ψ and c_K . Then $\int dz [h_{\text{int}}\psi' + \nu_{1\text{int}}c_1' + \nu_{2\text{int}}c_2'] = 0$ and integration of eq. (A.1) gives $\omega(\infty) = \omega(-\infty)$.

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