Nonionic and ionic surfactants at an interface

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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.

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 $\gamma$ dependent on the adsorbed surfactant density $\Gamma$. 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 $\epsilon_\alpha$ 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 $\Gamma$ 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 $z_{in} = \int_0^L dz [\psi(z) - \psi_\beta]/\Delta \psi$ 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 $\psi_\alpha$ and $\psi_\beta$ 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 $n_\alpha$ and $n_\beta$. The phase $\alpha$ is more polar or water-rich, while the phase $\beta$ is less polar or oil-rich. Then,

$$\Gamma = \int_0^L dz \left[ n(z) - n_\alpha - \frac{\Delta n}{\Delta \psi} (\psi(z) - \psi_\alpha) \right]$$

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 $\gamma \equiv \gamma_0 - TT$, where $\gamma_0$ is the surface tension without doping [2,9]. For electrolyte systems [8] there is also an electrostatic contribution,

$$\gamma \equiv \gamma_0 - TT - \frac{1}{8\pi} \int dz |\nabla \Phi|^2,$$

where $\epsilon$ is the dielectric constant and $\Phi$ 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 \( \phi_{1} = v_1 n_1 \), 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,

\[
\phi_A = (1 - N_1 c_1)/2 + \psi, \quad \phi_B = (1 - N_1 c_1)/2 - \psi. \tag{3}
\]

Here \( 2\psi = \phi_A - \phi_B \) is the composition difference of the solvent. We may set \( \phi_A \equiv 1/2 + \psi \) and \( \phi_B \equiv 1/2 - \psi \) 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 \( \bar{f}_{\text{nond}} \) of the form,

\[
\frac{a^3}{2T} \bar{f}_{\text{nond}} = \phi_A \ln \phi_A + \phi_B \ln \phi_B + \chi \phi_A \phi_B + \frac{C}{2} |\nabla \psi|^2 + c_1 \ln c_1 - g_1 c_1 \psi - c_1 \ln Z_{\text{am}}, \tag{4}
\]

where \( \chi \) 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 \( Z_{\text{am}} \) is the partition function of a rod-like dipole with its center at the position \( r \). We assume that the surfactant molecules take a rod-like shape with length \( 2\ell \) considerably longer than \( a \). It is given by the following integral on the surface of a sphere with radius \( \ell \),

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

where \( u \) is the unit vector along the rod direction and \( d\Omega \) represents the integration over the angles of \( u \). The two ends of the rod are at \( r + \ell u \) and \( r - \ell u \) under the influence of the solvent potentials given by \( T w_a \psi(r + \ell u) \) and \( -T w_a \psi(r - \ell u) \), respectively. It is instructive to examine the case in which \( \psi(r) \) varies slowly. That is, if the expansion \( \psi(r + \ell u) - \psi(r - \ell u) \approx 2\ell \nabla \psi \) is used, the last term in eq. (4) becomes \( -\frac{\ell a^3}{2} |\nabla \psi|^2 c_1 \). 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

\[
n_L = 3C/[4a^3(\ell w_a)^2]. \tag{6}
\]

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, \( Z_{\text{am}} \) becomes

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

where we have replaced \( \psi(r \pm \ell u) \) 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

\[
Z_{\text{am}}(z) \equiv 1 + (1 - |z|/\ell)[\cos(\psi(\Delta \psi) - 1)], \tag{8}
\]

for \( |z| < \ell \), while \( Z_{\text{am}} = 1 \) for \( |z| > \ell \). Furthermore, in the dilute limit \( N_1 c_1 \ll 1/\psi_0 \), we have \( c_1(z) = c_{1a} Z_{\text{am}}(z) \) for \( z < 0 \) and \( c_1(z) = c_{1b} Z_{\text{am}}(z) \) for \( z > 0 \), where \( c_{1a} \) and \( c_{1b} = e^{-g_1 \Delta \psi} c_{1a} \) are the bulk surfactant densities, leading to \( \Gamma \equiv \ell a^{-3} (c_{1a} + c_{1b})[\cos(\psi(\Delta \psi) - 1)]/2 \). However, the steric effect due to finite surfactant volume becomes important with increasing \( \Gamma \).

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

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

\[
h = \ln(\phi_A \phi_B) - 2\psi - C \nabla^2 \psi - g_1 c_1 + h_{\text{am}}. \tag{10}
\]

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

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

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

\[
\frac{c_{1a}(z)}{c_{1a}} \to \left[ 1 - 4\psi^2 \right]^{N_1/2} \left[ 1 - 4\psi^2 \right]^{N_1/2} Z_{\text{am}}(z)^{\psi_0 \psi}, \tag{12}
\]

In our model, if \( N_1 \) is large and if \( \psi_0 \) 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 \( \psi \approx 0 \). This leads to \( \Gamma \sim c_{1a}(1 - 4\psi^2)^{-N_1/2} \) for \( Z_{\text{am}} = 1 \). For our choice \( \chi = 3 \) in our figures, we have \( \psi_0 = 0.429 \) and \( (1 - 4\psi^2)^{-1} = 3.79 \). However, the first factor in eq. (12) tends to unity near the critical point.

The grand potential \( \Omega \) is given by the space integral of \( \omega = \int \bar{f}_{\text{nond}} - T a^{-3}(\psi + \psi_0) \). In equilibrium, \( \Omega \) is minimized as a functional of \( \psi \) and \( c_1 \) under given boundary conditions. For an interface, \( \omega(z) \) should tend to a common limit \( \omega_\infty \) as \( z \to \pm \infty \) (see the appendix) and the surface tension is expressed as \( \gamma = \int dz[\omega(z) - \omega_\infty] \). Here
it is convenient to introduce $\eta \equiv a^3 f_{non}/T - \nu_1 c_1 + c_1 = a^3 \omega/T + h \psi + c_1$. Use of eq. (9) yields

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

(13)

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

$$\gamma = \frac{T}{a^3} \int dz \left[ \eta(z) - \eta_a - h(\psi(z) - \psi_0) - c_1(z) + c_1 a \right],$$

(14)

where $h = (\eta_a - \eta_\beta - c_1 a + c_1 \Gamma)/(\psi_a - \psi_\beta)$ with $\eta_a$, $\eta_\beta$, $c_1 a$, and $c_1 \Gamma$ 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 $\psi_0(z) = \lim_{\psi \to 0} \psi(z)$ be the interface profile without surfactant and $\delta \psi = \psi - \psi_0$ be the deviation due to $c_1$. Then $\eta(z) - \eta_a = \partial^2 \psi/dz^2 = \partial^2 \psi_0/dz^2 = \cdots$ up to first order in $\delta \psi$ and $c_1$, because of the interface equation $\ln(1 + 2\psi_0)/\left(1 - 2\psi_0\right) - 2\chi \psi_0 - \partial^2 \psi_0/dz^2 = 0$ without surfactant. Hence $a^3 \Delta \psi^2/T$ is nearly the integral of $-c_1(z) + c_1 a - h(\psi(z) - \psi_0)$ with $h = (c_1 \beta - c_1 a)/\Delta \psi$, leading to eq. (2).

In all the figures to follow, we will set $C = \chi^2$, $\chi = 3$, and $\ell = 2.5a$, where $\gamma_0 = 0.497T a^{-2}$ at $c_1 = 0$. In eq. (6) we have the critical density $n_c = 0.36w_{\alpha}^{-1}$. The interface width $\xi$ is about $5a \sim 2\ell$. In fig. 1, we present $c_1(z) = a^2 n_1(z)$, $(\gamma_0 - \gamma)a^2/T$, and $\Gamma a^2$, where $g_1 = 4$ and $w_{\alpha} = 10$. With increasing $c_1 a$, the peak of $c_1(z)$ grows, $\Gamma$ increases, and $\gamma$ 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 $c_1 a < 10^{-4}$ and the steric effect is relevant for larger $c_1 a$, so that eq. (2) holds only for very small $c_1 a$; in fact, $(\gamma_0 - \gamma)/TT \sim 1.3$ at $c_1 a = 10^{-4}$. See the argument below eq. (12). For $N_1 = 1$, eq. (2) nicely holds for $c_1 a < 3 \times 10^{-4}$ and $\Gamma \propto c_1 a$ at any $c_1 a$.

**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 nonvalent 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 $f = f_{non} + f_{ion}$ is the sum of $f_{non}$ in eq. (4) and the following new part:

$$f_{ion} = T n_2 \ln(1 - g_2 \psi) + \frac{\varepsilon(\psi)}{8\pi} \nabla \Phi^2 + n \mu_{im},$$

(15)

where $n = n_1 + n_2$. We define $c_1 = a^2 n_1$ 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 $\varepsilon_c$ and $\varepsilon_1$ are positive constants. The parameters $g_1$ in eq. (4) and $g_2$ in eq. (15) can arise from the solvation (ion-dipole) interaction and can be very large in aqueous solutions [7,8]. The differences $\Delta \mu_{\alpha \beta} = T g_1 \Delta \psi$ are the so-called Gibbs transfer free energies per particle from phase $\alpha$ to phase $\beta$ for ion species $i$ [10]. For water-nitrobenzene mixtures at room temperature, $\Delta \mu_{\alpha \beta}/T$ 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 $\Phi$ arises from the charge density,

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

(16)
The electric field $E = -d\Phi/dz$ around an interface reads
\begin{equation}
\frac{e}{T} E(z) = \frac{4\pi \varepsilon_0}{1 + \varepsilon_1 \psi(z)/\varepsilon_c} \int_{-\infty}^{z} dz' \left[ n_1(z') - n_2(z') \right],
\end{equation}
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 $\Phi_0 = 0$ without loss of generality.

The image potential $\mu_{im}$ acts on each ion [12,13], which arises from inhomogeneous $\varepsilon$. For moderate inhomogeneity and in the 1D case, it is expressed in the following Cauchy integral [8]:
\begin{equation}
\mu_{im}(z) = TA_0 \frac{\varepsilon_1}{\varepsilon_c} \int \frac{dz' e^{z/z'} \psi(z')}{\pi} \frac{dz'}{z - z'},
\end{equation}
where $A$ represents the charge strength,
\begin{equation}
A = \frac{\pi e^2}{4a_0^2}, T = \frac{\pi e T_B}{4a},
\end{equation}
and $\kappa = [4\pi n e^2/\varepsilon_c T]^{1/2}$ is the Debye wave number [12]. The factor $e^{-2z/z'}$ 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 $\kappa$ as the space-dependent ion density $n(z) = n_1(z) + n_2(z)$.

Again we assume homogeneity of the chemical potentials $\nu_{1tot} = \delta F/\delta n_1$, $\nu_{2tot} = \delta F/\delta n_2$, and $\nu_{htot} = a^3 \delta F/\delta \psi$. From $F = \int d\mathbf{r} (f_{ion} + f_{ion})$ they are
\begin{equation}
\nu_{1tot} = v_1 + e\Phi/T + \mu_{im}/T, \\
\nu_{2tot} = \ln c_2 + 1 - g_2 \psi - e\Phi/T + \mu_{im}/T, \\
\nu_{htot} = h - g_{2c} \psi + h_{im}/T, \\
\end{equation}
where $v$ 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 $\mu_{im}$ in eq. (18). The $h_{im}(z)$ in eq. (20) arises from the image interaction and is obtained by the right-hand side of eq. (18) if $\psi$ is replaced by $n = n_1 + n_2$.

Since the counterion volume fraction is neglected, $c_2$ around an interface is written as
\begin{equation}
\frac{c_2(z)}{c_{2a}} = \exp \left[ g_2 (\psi(z) - \psi_a) + \frac{e}{T} \Phi(z) - \frac{1}{T} \mu_{im}(z) \right].
\end{equation}
In our previous work [8], we examined the image factor $F_{im}(z) \equiv \exp[-\mu_{im}(z)/T]$ in various cases. Let us consider it in the $\alpha$ region with $z_{in} - z > \xi$, where $z_{in}$ is the interface position and $\xi$ is the interface thickness. Then, $F_{im}(z) \cong \exp[-De^{-2\alpha(z_{in}-z)/(z_{in}-z)}].$

However, its effect on the ionic surfactants is diminished when the amphiphilic interaction is strong or for $w_1 \Delta \psi \gg 1$. These aspects will be illustrated in figs. 5 and 6 for $A = 4$ and 10.

From the charge neutrality in the bulk regions $\alpha$ and $\beta$, we require $c_{1a} = c_{2a}$ and $c_{1b} = c_{2b}$. Then we find
\begin{equation}
\ln(c_{1a}/c_{1b}) = (g_1 + g_2) \Delta \psi/2 + S_t, \\
e(\Phi_\alpha - \Phi_\beta)/T = (g_1 + g_2) \Delta \psi/2 + S_t,
\end{equation}
where $\Phi_\alpha - \Phi_\beta$ is called the Galvani potential difference. The $S_t$ stems from the surfactant volume fraction $N_1 c_{1a}$,
\begin{equation}
S_t = \frac{N_1}{4} \ln \left[ \frac{(1 - N_1 c_{1a})^2 - 4\beta_0^2}{(1 - N_1 c_{1a})^2 - 4\beta_0^2} \right] - \frac{N_1^2}{4} \chi \Delta c_1,
\end{equation}
with $\Delta c_1 = c_{1a} - c_{1b}$. Here $S_t \to 0$ as $N_1 \to 0$. Note that $\Phi(z)$ changes on the scale of the Debye screening length, $\kappa^{-1}$ in the phase $\alpha$ and $\kappa^{-1}$ in the phase $\beta$. As a result, $\Phi$ changes from $\Phi_\alpha$ to $\Phi_\beta$ on the spatial scale of $\kappa^{-1}$. We consider the grand potential density $\omega = \frac{T}{a^3} \langle h_{tot}(\psi) + \nu_{tot} + \mu_{tot} \rangle$. With the aid of eq. (20) we have $\omega = (T a^3 (\eta_0 - \eta_\beta - \eta_0 + c_{2a}/\kappa^2) - a^3 \Delta \psi/2 \mu_{im}/T).$

Again we assume a spherical charge distribution $\gamma = \frac{T}{a^3} \int dz' \left[ \psi(z') \psi(z) - c(z) - A_0 \right] - \frac{1}{8\pi \kappa^2} \int \int \int \left[ \nabla \Phi', \nabla \Phi, \Phi' \Phi \right] dz' dz dz' \int \int \int \left[ \nabla \Phi', \nabla \Phi, \Phi' \Phi \right] dz' dz dz'$,
\begin{equation}
\end{equation}
where $\gamma = \eta_0 - \eta_\beta - \eta_0 + c_{2a}/\kappa^2$ and $\gamma = \eta_0 - \eta_\beta - \eta_0 + c_{2a}/\kappa^2$ with $c_{2a}$ and $c_{2b}$ 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 $c_1 = 0.8 c_2$. The dielectric constant of the phase $\alpha$ is twice larger than that of the phase $\beta$ 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 $\phi_\alpha, \phi_\beta$, and $\eta_{1c1} = 1 - \phi_\alpha - \phi_\beta$ (top), $c_1$ and $c_2$ (middle), and $\psi/T$ with $\Phi_\alpha = 0$ (bottom). In the left plates, the cations are more hydrophilic than the cationic surfactant, where $g_1 = 4$ and $g_2 = 10$ leading to $\Gamma = 0.12 a^{-2}$ and $\gamma = 0.317 T a^{-2}$ at $c_{1a} = 10^{-3}$. In the right plates, the surfactant cations are hydrophilic and the counternions are hydrophobic, where $g_1 = -g_2 = 8$ leading to $\Gamma = 0.155 a^{-2}$ and $\gamma = 0.159 T a^{-2}$ at $c_{1a} = 3.6 \times 10^{-4}$. The distribution of the ionic surfactant $c_1$ is narrower than that of the counternions $c_2$. This gives rise to a peak of $\Phi$, at which the right-hand side of eq. (17) vanishes.

ii) In fig. 3, we show $\gamma_\alpha, \gamma_\beta$, and $\Gamma$ as functions of $c_{1a}$ at $w_1 = 12$, where $\gamma_\beta$ is the first term on the right-hand side of eq. (26). The Lifshitz-point $c_{1a} = a^3 n_L = 2.5 \times 10^{-3}$ for $C = 9a^3$ is marked by an arrow (top). For small $c_{1a}$, 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 $\Gamma$ even at small $c_{1a}$.
 iii) In fig. 4, we show $\gamma$, $\gamma_1$, and $\Gamma$ vs. $g_2$ at $w_a = 12$ and $g_1 = 8$ to demonstrate the above trend, where $\Gamma$ and $\gamma_0 - \gamma$ are markedly enhanced for negative $g_2$.

 iv) In figs. 5 and 6, we set $w_a = 15$, where $\Gamma$ 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 $\gamma_1 = 0.491T/a^2 \cong 0 - 7T$. There are virtually no ions in the region $\beta$. The distribution of $c_2$ in the region $\alpha$ is broad changing on the scale of $\kappa^{-1}$, where $\kappa_a = 0.046/a$. Note that $\Phi(z)$ is constant in the region $\beta$ displayed in fig. 5. However, it should tend to $\Phi_\beta(\cong 0)$ here) for $z - z_{\alpha} \gg \kappa_\beta^{-1} \sim 10^3a$.

 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 order $a$. See the discussion around eq. (22). With $A = 10$, the image interaction is amplified and $\Gamma$ 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.

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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), $\phi_A$, and $\phi_B$. 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 $\alpha$ (left) or $\beta$ (right) depending on $g_2$.

Fig. 3: $\gamma a^2/T$, $\gamma_1 a^2/T$, and $\Gamma a^2$ as functions of $c_{1\alpha}$ with $N_1 = 5$, $\chi = 3$, and $w_a = 12$, where $\gamma$ is calculated from eq. (26) and $\gamma_1$ 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 $\Gamma a^2$ as functions of $g_2$ with $\chi = 3$, $w_a = 12$, and $g_1 = 8$, where $\gamma_1$ is the first term on the right-hand side of eq. (26). The counterions are hydrophobic for $g_2 < 0$ and hydrophilic for $g_2 > 0$. 

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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 $\Gamma$ 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 $\varepsilon/T = w_0 \Delta \psi$ and $N_I$. It is decreased as $A \sim \ell_0/a$ 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 $\chi$ at large $w_0$ 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.

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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

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

(A.1)

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

$$h_{int} = \frac{a^3}{T} \frac{\delta F_{int}}{\delta \psi'}, \quad \nu_{int} = \frac{a^3}{T} \frac{\delta F_{int}}{\delta c'_K},$$

(A.2)

with $K = 1, 2$. Here $F_{int} = \int d\tau [-Tn_1 \ln Z_{am} + n\mu_{im}]$ is the sum of the amphiphilic and image free energies, so $h_{int} = h_{am} + h_{im}$ and $\nu_{int} + \ln Z_{am} = \nu_{2int} \equiv \mu_{im}$ (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 $\psi$ and $c_K$. Then $\int dz [h_{int} \psi' + \nu_{int} c_1' + \nu_{2int} c_2'] = 0$ and integration of eq. (A.1) gives $\omega(\infty) = \omega(-\infty)$.

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