Precipitation of water from aqueous mixtures with addition of hydrophilic ions

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We examine phase separation in aqueous mixtures at fixed amounts of hydrophilic monovalent ions. When water is the minority component, preferential solvation can stabilize water domains enriched with ions. This ion-induced precipitation occurs in wide ranges of the temperature and the average composition where the solvent would be in one-phase states without ions. The volume fraction of such water domains is decreased to zero as the interaction parameter \( \chi \) (dependent on the temperature) is decreased toward a critical value for each average composition.

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In fluid mixtures containing water, phase separation behavior can be drastically changed by a small amount of a salt \([1]\). More strikingly, many groups have observed long-lived heterogeneities (sometimes extending over a few micrometers) in one-phase states \([2]\) and a third phase visible as a thin plate at a liquid-liquid interface in two-phase states \([3]\). Very recently, mesophases with lamellar or onion structures have been found for an antagonistic salt composed of hydrophilic and hydrophobic ions \([4]\). Dramatic ion effects are ubiquitous in various soft matters. For example, in polyelectrolytes, the phase behavior sensitively depend on the degree of ionization and the composition for mixture solvents \([5]\) and large-scale heterogeneities have been observed \([6]\). In these phenomena, the solvation interaction among ions and polar molecules should play a major role together with the Coulomb interaction among charges \([7]\). Recently some theoretical efforts have been made to elucidate the solvation effects in phase transitions in electrolytes and polyelectrolytes \([8][9]\). In this Letter, we consider hydrophilic monovalent ion pairs such as Na\(^+\) and Cl\(^-\) in a binary mixture of water and a less polar component (oil or alcohol) and examine ion-induced precipitation.

Neglecting the electrostatic interaction but accounting for the solvation interaction, we first consider a binary mixture in a cell with a fixed volume \( V \). Here ions constitute the third component with density \( n(r) \). The volume fractions of water, oil, and ions are written as \( \phi(r) \) and \( \phi'(r) \), and \( v_1n(r) \), respectively, where \( v_1 \) is the ionic volume. If the two solvent species have the same molecular volume \( v_0 \), their densities are \( \phi/v_0 \) and \( \phi'/v_0 \). The space-filling condition reads \( \phi + \phi' + v_1n = 1 \). The ion volume fraction is assumed to be small or \( v_1n \ll 1 \), which is easily satisfied for small ions with \( v_1 \ll v_0 \). In this Letter we thus set \( \phi' = 1 - \phi \), which simplifies the calculations.

When the ions have a strong preference of water over oil, we set up the free energy as

\[
\frac{F}{T} = \int dr \left[ \frac{f(\phi)}{T} + \frac{C}{2} \nabla \phi^2 + n \ln(nv_0) - gn\phi \right],
\]

where \( C \) is a positive constant and \( g \) is a positive parameter representing the ion preference of water. The space integral is within the cell. The Boltzmann constant will be set equal to unity and then the temperature \( T \) represents the thermal energy of a particle. The free energy density \( f(\phi) \) is taken to be the simple form,

\[
v_0f/T = \phi \ln \phi + (1 - \phi) \ln(1 - \phi) + \chi \phi(1 - \phi),
\]

where \( \chi \) is the interaction parameter dependent on \( T \) and its mean-field critical value is 2 without ions. We fix the total particle numbers of the three components as

\[
\bar{n} = \int dr n/v, \quad \bar{\phi} = \int dr \phi/V,
\]

In equilibrium the homogeneity of the ion chemical potential \( \delta F/\delta n \) yields

\[
n = \bar{n}e^{\phi\phi}/\langle e^{\phi\phi} \rangle,
\]

where \( \langle e^{\phi\phi} \rangle = \int dr e^{\phi\phi}/V \) is the space average of \( e^{\phi\phi} \). Substitution of Eq.(4) into \( F \) in Eq.(1) gives

\[
\frac{F}{T} = \int dr \left[ \frac{f(\phi)}{T} + C \frac{1}{2} \nabla \phi^2 \right] + V\bar{n} \ln(\bar{n}v_0/\langle e^{\phi\phi} \rangle).
\]

In equilibrium the chemical potential difference \( h = \delta F/\delta \phi \) for the composition is also homogeneous. Here,

\[
h = f' - TC\nabla^2 \phi - Tgn,
\]

where \( f' = \partial f/\partial \phi \). Around a planar interface varying along the \( z \) axis, we obtain \( TC(d\phi/dz)^2 = 2H(\phi) \), where

\[
H(\phi) = f(\phi) - f(\phi_\alpha) - T(n - n_\alpha) - h(\phi - \phi_\alpha).
\]

We suppose coexistence of a water-rich phase \( \alpha \) and an oil-rich phase \( \beta \) with \( \Delta \phi = \phi_\alpha - \phi_\beta > 0 \). The compositions and the ion densities in the two phases are written as \( \phi_\alpha, \phi_\beta, n_\alpha, \) and \( n_\beta \), respectively. The volume fraction of the phase \( \alpha \) is denoted by \( \gamma_\alpha \). Since that of the phase \( \beta \) is \( \gamma_\beta = 1 - \gamma_\alpha \), we have

\[
\gamma_\alpha = (\bar{\phi} - \phi_\beta)/\Delta \phi = (\bar{n} - n_\beta)/\Delta n,
\]

where \( \Delta n = n_\alpha - n_\beta \). From Eq.(4) the ratio of the bulk ion densities is written as \( n_\alpha/n_\beta = \exp(g\Delta \phi) \gg 1 \) from
Eq.(4), where we assume $g\Delta \phi \gg 1$. Neglecting the surface free energy, we express $F$ as

$$\frac{F}{V} = \gamma_0 f_0 + \gamma_\beta f_\beta - T\bar{n}\log((\gamma_0 e^{\phi_0} + \gamma_\beta e^{\phi_\beta})/\bar{n}v_0),$$

(9)

where $f_\alpha = f(\phi_\alpha)$ and $f_\beta = f(\phi_\beta)$. We minimize this $F$ with respect to $\gamma_0$, $\phi_\alpha$, and $\phi_\beta$ at fixed $\phi$ to obtain

$$h = f'_\alpha - T\bar{g}_n = f'_\beta - T\bar{g}_n, \quad (10)$$

$$f_\alpha - f_\beta - T\bar{n} = h\Delta \phi, \quad (11)$$

where $f'_\alpha = f'(\phi_\alpha)$ and $f'_\beta = f'(\phi_\beta)$. These equations also follow from Eqs.(6) and (7).

Our main finding is that there appears a precipitation branch of $\phi = \phi_\alpha \approx 1$ in the region $\chi < 2$ for $g \gg 1$. In Eq.(10) we set $f'_\alpha \approx \bar{v}_0^{-1}T[-\log(1 - \phi_0) - \chi]$ to obtain

$$1 - \phi_0 \approx A_\alpha \exp[-gG(\phi_\beta)], \quad (12)$$

where $A_\alpha = \exp(\chi + \bar{v}_0 f'_\beta/T)$. Here we introduce

$$G(\phi) = -v_0[f(\phi) + (1 - \phi)f'(\phi)]/T$$

$$= -\log \phi - \chi(1 - \phi)^2, \quad (13)$$

where the second line follows from Eq.(2). By setting $f_\alpha \approx 0$ in Eq.(11) we also find $v_0 n_\alpha = G(\phi_\beta)$. Outside the spinodal curve without ions, we notice $dG/d\phi = -v_0(1 - \phi)\partial^2 f/\partial \phi^2 < 0$, which leads to $G(\phi) > 0$ from $G(1) = 0$. Thus the right hand side of Eq.(12) is small or $\phi_\alpha \approx 1$ for large $g$. The equation for $\phi_\beta$ is given by

$$v_0n_\alpha = G(\phi_\beta) = v_0\bar{n}\Delta \phi/[\bar{\phi} - \phi_\beta + e^{-g\Delta \phi}\Delta \phi], \quad (14)$$

where we may set $\Delta \phi \approx 1 - \phi_\beta$. As $\gamma_\alpha = (\bar{\phi} - \phi_\beta)/\Delta \phi$ decreases to zero, $\phi_\alpha$ and $n_\alpha$ increase up to $\phi$ and $v_0\bar{n}e^{\phi_g(1 - \phi)}$, respectively. Remarkably, $\phi_\alpha$ and $\phi_\beta$ depend on $\phi$. From the second line of Eq.(13), the precipitation branch exists only for $\chi > \chi_p(\bar{\phi})$. The lower bound is

$$\chi_p = [-\log(1 - \bar{\phi}) - v_0\bar{n}e^{\phi_g(1 - \bar{\phi})}]/(1 - \bar{\phi})^2, \quad (15)$$

where $\gamma_\alpha \to 0$ as $\chi \to \chi_p$.

To easily understand the mathematics, let us focus on the case $\gamma_\alpha \ll 1$, where $f_\alpha \approx 0$ and $f_\beta \approx f(\bar{\phi}) - f'_\beta(1 - \bar{\phi})\gamma_\alpha$ in Eq.(9). Treating $\gamma_\alpha$ as an order parameter, we write the deviation $\Delta F = F(\gamma_\alpha) - F(0)$ of the free energy from the one-phase value $F(0)$ as

$$\Delta F/TV \approx A_\gamma \gamma_\alpha - \bar{n}log(1 + B_1\gamma_\alpha), \quad (16)$$

where $A_\gamma = 1 - \bar{v}_0^{-1}T\bar{g}_n(1 - \bar{\phi})$ and $B_1 = e^{g\Delta \phi} - 1 \approx e^{g\Delta \phi}$. For $w \equiv \bar{n}B_1/A_\gamma > 1$, $\Delta F$ has a negative minimum given by $-TV A_\gamma (\log w + w - 1)/B_1 < 0$ attained at

$$\gamma_\alpha = (w - 1)/B_1 \equiv v_0\bar{n}/G(\bar{\phi}) - e^{-g(1 - \bar{\phi})}, \quad (17)$$

which is consistent with Eq.(14) in the limit $\phi_\beta \to \bar{\phi}$. The condition $w > 1$ is equivalent to $\chi > \chi_p$ for $g \gg 1$.

Figure 1 gives the phase diagrams in the $\phi$-$\chi$ plane with $\bar{\alpha} = 6 \times 10^{-4}\bar{v}_0^{-1}$ and $g = 11$. In the first case of $\bar{\phi} = 0.35$, $\phi_\alpha$ changes continuously and is minimum at $\chi = 2.05$, where $\chi_p = 0.687$ and the maximum of $n_\alpha$ is $0.381v_0^{-1}$ at $\chi = \chi_p$. In the second case of $\bar{\phi} = 0.46$, where $\chi_p = 1.834$ and $n_\alpha = 0.0842v_0^{-1}$ at $\chi = \chi_p$, we find that $\phi_\alpha$ changes discontinuously along a hysteresis loop in the range $1.953 < \chi < 1.967$. In equilibrium, $F$ is minimized and the resultant discontinuous transition

![FIG. 2: $\chi = \chi_p(\bar{\phi})$ for $v_0\bar{n} = 4 \times 10^{-4}$, $2 \times 10^{-4}$, and $5 \times 10^{-5}$. Precipitation occurs for $\bar{\phi} < \phi_p$ (arrows). Shown also are the coexistence and spinodal curves without ions.](image-url)
is at $\chi = 1.957$. In Fig.2, we display curves of $\chi = \chi_p(\bar{\phi})$ for three values of $\bar{n}$ with $g = 10$. Each curve assumes a minimum at small $\bar{\phi}$ far away from the coexistence curve without ions. With increasing $\bar{\phi}$, the precipitation branch shrinks and disappears as $\bar{\phi} \rightarrow \phi_p$, where $\phi_p$ is a critical composition less than 0.5. As functions of $\bar{\phi}$ and $\chi$, we show $\gamma_o$ in Fig.3 in the continuous case of $g = 10$ and $\phi_o$ in Fig.4 in the discontinuous case of $g = 11$.

Without the electrostatic interaction, the surface tension of our system is expressed as the integral

$$
\sigma = \frac{1}{2} \int_{\phi_\beta}^{\phi_o} d\phi H(\phi)^{1/2},
$$

(18)

where $C$ is assumed to be a constant. In Fig.5, we display the function $[2H(\phi)v_0/T]^{1/2}$ for $g = 11$. Here $H(\phi) \approx f''(\phi_\beta)(\phi - \phi_\beta)^2/2$ as $\phi \rightarrow \phi_\beta$ with $f'' = d^2 f/d\phi^2$. Thus we obtain $\sigma \sim TC(\Delta \phi)^2/2\xi$, where $\xi = (f''/CT)^{-1/2}$ is the correlation length at $\phi = \phi_\beta \equiv \bar{\phi}$.

Including the electrostatic interaction, we next consider aqueous mixtures containing a hydrophilic monovalent salt. The cation and anion densities are written as $n_1$ and $n_2$, whose total amounts are fixed as

$$
\int dn_1 = \int dn_2 = V\bar{n}/2.
$$

(19)

The electric potential $\Phi$ satisfies the Poisson equation $\nabla \cdot \varepsilon \nabla \Phi = -4\pi e(n_1 - n_2)$, where the dielectric constant $\varepsilon(\phi)$ can depend on $\phi$. The free energy $F$ reads

$$
F = \int dr \left[ \frac{f(\phi)}{T} + \frac{C}{2} |\nabla \phi|^2 + \frac{\varepsilon |\nabla \Phi|^2}{8\pi T} \right] + \sum_{i=1,2} \left[ n_i \ln(n_i v_0) - g_i n_i \phi \right].
$$

(20)

The ion chemical potentials due to solvation, written as $\mu_{sol}^i(\phi)$, strongly depend on $\phi$. The interaction terms

$$(\propto g_i)$$

in $F$ follow for the linear forms $\mu_{sol}^i(\phi) = \mu_{i0} - T g_i \phi$ (where the first terms are irrelevant constants). This linear dependence is adopted to gain the physical consequences in the simplest manner. For each ion species $i$, the solvation-chemical-potential difference between the two phases is given by $\Delta \mu_{sol}^i = T g_i \Delta \phi$, which is the Gibbs transfer free energy in electrochemistry [11]. In aqueous solutions, $g_i \gg 1$ for hydrophilic small ions, while $g_i < 0$ for hydrophobic ions [8, 11]. We minimize $F$ with respect to $n_i$ under Eq.(19) to obtain

$$
n_i = n_i^0 \exp[g_i \phi + e \Phi/T],
$$

(21)

where $- i = 1, +$ is for $i = 2$, and $n_i^0 = \bar{n}/[2 \int dr \exp(g_i \phi + e \Phi/T)]$. The composition profile is determined by the homogeneity of $\delta F/\delta \phi$. Here we neglect the image interaction, whose role is reduced compared to that of the solvation interaction for not small ion densities [8, 12].

For $g_1 = g_2 = g$, we have $n_1 = n_2 = n/2$ and $\Phi = 0$,
so $F$ in Eq.(20) reduces to $F$ in Eq.(1). For $g_1 \neq g_2$, an electric double layer appears at the interface with a potential difference $\Delta \Phi = (g_1 - g_2)\Delta \phi/2e$ across it, but the bulk phase relations (10) and (11) still hold with

$$g = (g_1 + g_2)/2.$$  

In Fig.6, we give numerical results for $g_1 = 15$, $g_2 = 7$, $\bar{\phi} = 0.35$, and $v_0\bar{n} = 6 \times 10^{-4}$. The space unit is $a = v_0^{1/3}$. We suppose a spherical water-rich droplet with radius $d$ placed at the center of a spherical cell with radius $\tilde{R} = 600a$. Then $\gamma_C = (d/R)^3$. The dielectric constant is of the form $\varepsilon = 40(1 + \phi)$. We also set $aC = \chi$ and $e^2/T = 120a$. In the left, the droplet disappears at $d = 26.0a$, where $\varepsilon$ in Eq.(17) is 1.08. This critical radius follows if the bulk free energy $\Delta F$ in Eq.(9) is equated with the minums of the surface free energy $4\pi\sigma d^2$. In the right, we set $\chi = 1.7$ to display the profiles of $\Phi(r)$, $\phi(r)$, $n_1(r)$, and $n_2(r)$. We obtain $\phi_\alpha = 0.993$ and $n_\alpha = 0.352v_0^{-1}$ within the droplet and $\phi_\beta = 0.349$ and $n_\beta = 2.55 \times 10^{-4}v_0^{-1}$ outside it. In Fig.6, the potential $\Phi(r)$ relaxes with the Debye length $\kappa^{-1} = 11.8a$ and is well fitted to the one-dimensional solution of the nonlinear Poisson-Boltzmann equation (dotted line) with $\Delta \Phi = 3T/e$ [3]. Here $n_\alpha$ and $n_\beta$ are the bulk values of $n = n_1 + n_2$.

In future we should explain the experimental findings of large-scale heterogeneities [2]. We note that one-phase states are metastable outside the spinodal curve with ions ($\chi < 1/2\bar{\phi}(1 - \bar{\phi}) - \bar{\phi}^2v_0\bar{n}/2$) in Fig.1. Thus precipitation from a one-phase state should be triggered by some impurities and/or hydrophilic walls. We also note that the wetting transition of aqueous mixtures is much influenced by the ion-induced precipitation mechanism.

Experiments are informative, where the temperature, the water volume fraction, and the salt amount are varied. We mention an experiment by Leunissen et al. [13], where micron-sized water droplets containing ions formed a crystal in an oil with low dielectric constant ($\varepsilon_{oil} = 4 - 10$) without a surfactant. Graaf et al. [14] ascribed its origin to the screened Coulomb interaction among droplets. We also propose experiments of the salting-out effect of polyelectrolytes in water-alcohol [5], where the degree of ionization much increases with accumulation of water around the polymers [10].

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