Multilamellar Structures Induced by Hydrophilic and Hydrophobic Ions Added to a Binary Mixture of D_2O and 3-Methylpyridine

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(Received 15 March 2009; published 14 October 2009)

A phase transition is observed between a one-phase disordered phase and an ordered phase with multilamellar (onion) structures in an off-critical mixture of D_2O and 3-methylpyridine (3MP) containing 85 mM of a salt in the absence of a surfactant. The salt consists of hydrophilic cations and hydrophobic anions that interact asymmetrically with the solvent composition fluctuations inducing mesophases. The structure factor of the composition distribution obtained from small-angle neutron scattering has a peak at an intermediate wave number in the disordered phase and multiple peaks in the ordered phase. Lamellar layers forming onions are composed of solvation-induced charged membranes swollen by D_2O. The onion phase is realized only for small volume fractions of 3MP (in D_2O-rich solvent).

DOI: 10.1103/PhysRevLett.103.167803 PACS numbers: 61.20.Qg, 64.75.Cd, 81.16.Dn, 82.45.Gj

Binary mixtures of water and organic solvents have been used extensively to study the universal aspects of their critical behavior and phase separation dynamics. However, the unique ion effects in such mixtures, where preferential hydration around each ion should affect the composition fluctuations, has not yet been studied in detail [1,2]. The addition of even small concentrations of salts composed of small hydrophilic ions to the above-mentioned mixtures can drastically change their phase behavior [3–7]. Many groups exhibit long-lived heterogeneities (occasionally extending over a few micrometers) in the one-phase state [8,9] and a third phase visible as a thin plate forms at a liquid-liquid interface in the two-phase state [10]. These observations were reproduced in different experiments using high-purity solvents and salts, and therefore, they should be regarded as ion-induced supramolecular aggregates. Although it has not yet been understood clearly, the solvation (ion-dipole) interaction among ions and polar molecules should play a major role in these phenomena together with the Coulombic interaction among charges [1,2].

Recently, the solvation effect on phase behavior was theoretically studied in polar mixtures, including the case of antagonistic ion pairs composed of hydrophilic and hydrophobic ions [11]. Such cations and anions interact differently with composition fluctuations, leading to a charge-density-wave phase for sufficiently large solvation asymmetry even at low salt concentrations. In a small-angle neutron scattering (SANS) experiment, Sadakane *et al.* [12] found a peak at an intermediate wave number $Q_m(\sim 0.1\ \text{Å}^{-1})$ in a near-critical mixture of D_2O and 3-methylpyridine (3MP) containing 100 mM sodium tetraphenylborate ($NaBPh_4$). The volume fraction of 3MP, denoted by ϕ_{3MP}, was chosen to be 0.35, 0.42, and 0.54. This salt dissociates into hydrophilic Na^+ and hydrophobic $BPh_4{}^-$. The $BPh_4{}^-$ acquires strong hydrophobicity such that the salt is more soluble in pure 3MP than in pure D_2O despite the hydrophilic nature of Na^+ [13]. Furthermore, the mixture exhibited colors that changed dramatically on approaching criticality at low salt concentrations ($\sim$10 mM), indicating the emergence of large-scale heterogeneities. No distinct mesophases appeared in the same solvent when hydrophilic salts such as NaCl were added [14].

In this Letter, we again use the system of D_2O + 3MP + $NaBPh_4$. We purchased D_2O with isotopic purity of 99.9% from EURISO-TOP and 99.5% purity 3MP and 99.5% purity $NaBPh_4$ from Aldrich. These chemicals were mixed without further purification. Hereafter, we report the observation of multilamellar (onion) structures for small ϕ_{3MP}. Detailed measurements were carried out for $\phi_{3MP} =$ 0.08, 0.09, 0.11, and 0.14 in the temperature range $283\ \text{K} \le T \le 343\ \text{K}$. The concentration of $NaBPh_4$ was fixed at 85 mM. Without the salt, the mixtures in the measured composition and temperature ranges remained homogeneous in one-phase states with small composition fluctuation, because the lower critical solution temperature is at $T = 310$ K and $\phi_{3MP} = 0.30$. Upon the addition of

$NaBPh_4$, onions appeared spontaneously from these disordered states.

To understand this mesophase formation, we consider the number densities of D_2O, 3MP, and $NaBPh_4$, denoted by n_D, n_{3MP}, and n_{salt}. At $\phi_{3MP} = 0.09$, we found that

$$n_D/n_{3MP} \cong 54.3, \qquad n_{3MP}/n_{salt} \cong 10.6. \tag{1}$$

Thus $n_{salt} \ll n_{3MP} \ll n_D$. The molecular volumes of D_2O and 3MP (inverse densities of the pure components) were 28 and 168 Å^3, respectively. The volume fraction of $NaBPh_4$ was less than 2% and the observed SANS intensity was mostly due to the composition distribution of the solvent. In addition in surfactant mixtures, spontaneous onion formation (without the application of a shear flow) was observed at small surfactant concentrations in water-rich solvents [15–18].

Figure 1 shows the temperature dependence in the optical microscopic images. These images were captured using a Nikon Optiphot2-Pol with CCD camera. The thickness of the sample was 90 μm and the sample temperature was controlled within an accuracy better than 0.1 K using a Linkam TH-99 hot stage. The sample composition was $\phi_{3MP} = 0.09$. At $T = 323$ K [Fig. 1(a)], the entire area is homogeneous without visible structures. As we decreased T below 318 K, small droplets emerged from the entire sample and they grew in size [Fig. 1(b)]. In (c), T is further lowered to 293 K and the space is nearly filled with deformed droplets having diameters of approximately 20 μm. The left-hand side panel of Fig. 1(b′) shows a magnified view of (b), while the right-hand side panel shows the corresponding Maltese cross pattern obtained under crossed Nicoles using polarized light. This pattern arises from inhomogeneous composition distributions with spherical symmetry. Such patterns have been observed in polymer spherulites [19] and onions of surfactant systems [16–18]. Thus, our result indicates that the onion structure is formed below T_L, where $T_L = 318$ K is the transition temperature.

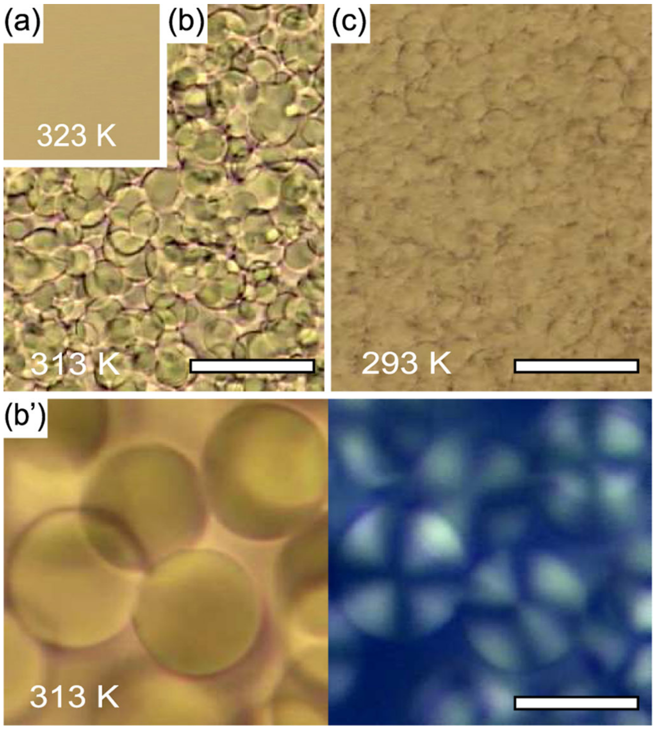

FIG. 1 (color online). Optical microscopic images obtained from the sample of $\phi_{3MP} = 0.09$: (a) $T = 323$ K (disordered), (b) $T = 313$ K (onion), and (c) $T = 293$ K (onion). Scale bars in (b) and (c) are 100 μm. (b′) A magnified view of (b) (left) and a birefringent image of the same region (right) with the scale bar being 20 μm.

SANS experiments were performed at SANS-J, JRR-3M at the Japan Atomic Energy Agency. A 6.0 Å incident neutron beam was mechanically selected with a wavelength resolution of 13%, and the scattered neutrons were detected at distances of 2.5 and 10 m from the sample position. Each sample was kept in 2 mm thick quartz cell and placed in a temperature-controlled chamber with an accuracy better than 0.1 K. The measured wave number Q ranged between 6×10^{-3} Å^{-1} and 1.3×10^{-1} Å^{-1} and the observed two-dimensional data were azimuthally averaged. Figure 2 shows the SANS intensity vs Q from the sample of $\phi_{3MP} = 0.09$. By varying T, it was found that the system was in the disordered phase for $T > T_L$ and in the ordered phase for $T < T_L$. At the lowest temperature 283 K, a pronounced Bragg peak is observed at $Q_m = 3.4 \times 10^{-2}$Å^{-1}, a second one is observed at 6.8×10^{-2} Å^{-1}, and a slight shoulder is observed at around 1.0×10^{-1} Å^{-1} (although this is not clearly seen in the figure). The same behavior was found for all the SANS data below T_L, indicating the formation of aligned lamellae. This is further evidence of the onion formation below T_L.

Our SANS profile at $T = 283$ K can be well fitted to the formula for lyotropic lamellae given by Nallet *et al.* [20] in the range $Q > 3 \times 10^{-2}$ Å^{-1}, as shown by the solid curve of $T = 283$ K in Fig. 2(a). The spatial distribution of the scattering density profile is reconstructed as shown in Fig. 2(b), yielding the mean repeat distance $d = 174.8$ Å and the membrane thickness $\delta = 16.2$ Å. The scattering density difference in their formula is $\Delta\rho = (4.57 \pm 0.02) \times 10^{10}$ cm^{-2}, which is almost equal to that between 3MP and D_2O.

In the disordered phase above T_L, the intensity exhibits a broad peak at $Q_m \sim 0.07$ Å^{-1}, with Q_m shifting slightly to lower values as $T \rightarrow T_L$. It may fairly be fitted to the theoretical mean-field intensity $I_{OK}(Q)$ [solid curves for $T = 343$ and 318 K in Fig. 2(a)] [11]. Its inverse is of the form

$$I_{OK}(0)/I_{OK}(Q) = 1 + \left[1 - \frac{\gamma_p^2}{1 + \lambda^2 Q^2}\right]\xi^2 Q^2, \tag{2}$$

where γ_p indicates the degree of solvation asymmetry between cations and anions. For $\gamma_p = 0$ it follows the Ornstein-Zernike form. For $\gamma_p > 1$ the structure factor

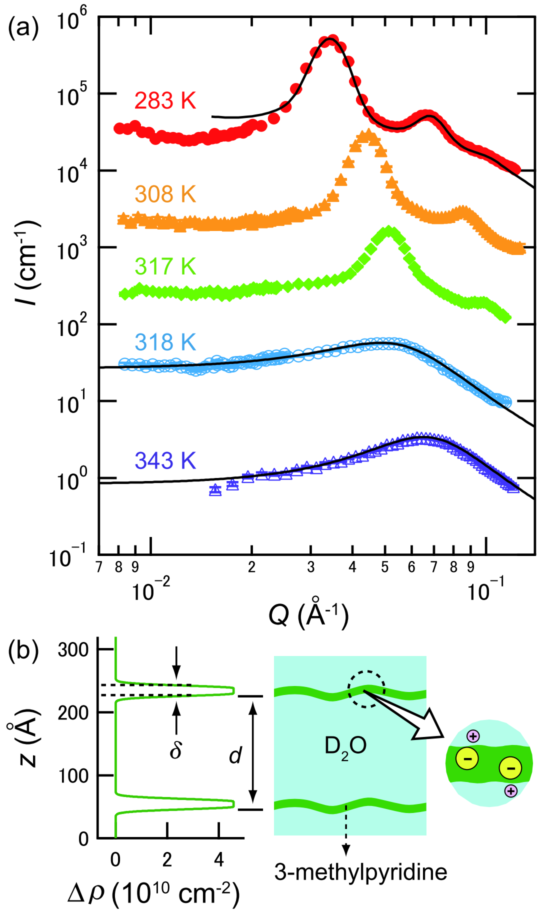

FIG. 2 (color online). (a) Temperature dependence of SANS intensity from a sample of $\phi_{3MP} = 0.09$. The first-order transition occurs slightly below $T = 318$ K. The data at lower temperatures are shifted by multiplying 10 for better visualization. (b) Scattering density distribution at $T = 283$ K estimated from the formula in Ref. [20] (left) and schematic picture of the distribution of the ingredients (right). The vertical axis indicates the distance normal to the layers.

has a peak at an intermediate wave number. In the present case γ_p is treated as an adjustable parameter given by 2.32 at $T = 333$ K and by 1.96 at $T = 320$ K. Slightly below T_L, the system was phase separated into an ordered phase in an upper region and a disordered phase in a lower region. The data of $T < T_L$ in Fig. 2(a) are those from the upper region. The transition is, thus, a first-order one. The same T_L was obtained with decreasing and increasing T around the transition. The mass density of D_2O is 1.11 g/cm^3 and that of 3MP is 0.96 g/cm^3; therefore, the ordered phase contains more 3MP than the coexisting disordered phase. In this case the mass density difference between the two phases is less than 10 mg/cm^3. As T was further lowered, the onion droplets increasingly swelled with D_2O. As a result, the lamellar spacing increased as will be shown in Fig. 3. At low temperatures below 293 K, the entire cell was filled with swollen onions.

Figure 3 shows the temperature dependence of $d = 2\pi/Q_m$. For $\phi_{3MP} = 0.09$, d increases considerably with decreasing T in the range 293 K $< T < T_L$ because of the swelling of the onions taking place on a time scale of 1 min. For $\phi_{3MP} = 0.14$, d varies very weakly in the entire temperature range. Above 330 K, the dependence of d on ϕ_{3MP} is weak. The transition temperature T_L decreases with increasing ϕ_{3MP}, and reaches 318 and 303 K for $\phi_{3MP} = 0.09$ and 0.11, respectively. However, the system remained in the disordered phase for $\phi_{3MP} \geq 0.14$. The figure shows that the transition occurs for $d \sim 130$ Å.

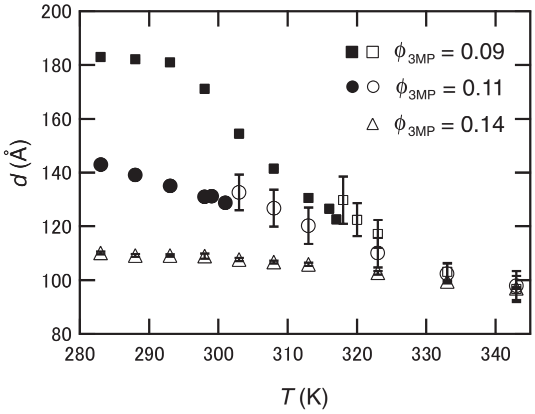

FIG. 3. Repeat distance d vs temperature T for $\phi_{3MP} = 0.14$ (triangle), 0.11 (circle), and 0.09 (square). Open symbols indicate data of the disordered phase while filled symbols indicate data of the onion phase. No onion appears for $\phi_{3MP} = 0.14$.

Figure 4 shows an ultra-small-angle neutron scattering (USANS) spectrum observed at PNO spectrometer in JRR-3M ($2 \times 10^{-5} < Q < 5 \times 10^{-4}$ Å^{-1}) together with the data obtained at SANS-J in the focusing-SANS mode (the lowest Q is expanded down to 3×10^{-4} Å^{-1} [21]). The measurement was carried out at $T = 298$ K for the sample of $\phi_{3MP} = 0.09$. The low-Q profile obeys the Porod law in the range of $1 \times 10^{-4} < Q < 5 \times 10^{-3}$ Å^{-1}. It should arise from the interfaces of the onion droplets in the range $R^{-1} \ll Q \ll Q_m$, where R is the

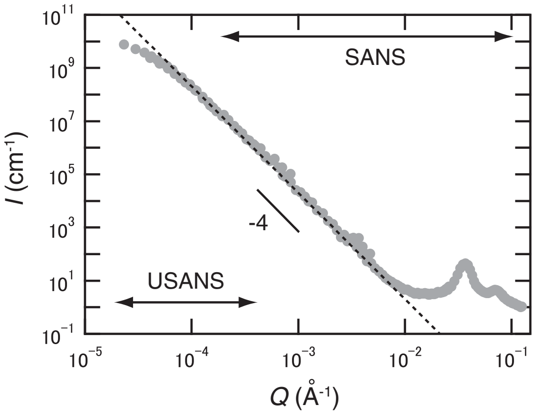

FIG. 4. Connected USANS profile obtained at PNO and SANS-J over a wide range of Q at $T = 298$ K and $\phi_{3MP} = 0.09$. The Porod tail $\propto Q^{-4}$ from onion surfaces can be observed in the range $1 \times 10^{-4} < Q < 5 \times 10^{-3}$ Å^{-1}.

droplet radius. Each onion is composed of approximately 1000 concentric lamellae provided the droplet interior is filled with layers. The estimated value of R from this data analysis is consistent with the observation by optical microscopy, although a more precise data analysis is needed here accounting for the effects of the resolution function and the polydispersity.

Now, we discuss the physical processes involved. In aqueous solutions, each Na^+ ion is known to be surrounded by a hydration shell composed of several water molecules [1,2]. This suggests that each BPh_4^- ion should be solvated by a certain number of 3MP molecules around it due to its strong hydrophobicity [13], although this solvation number $N_{3\mathrm{MP}}^s$ is currently not known. Equation (1) gives the particle number densities in the disordered phase at $\phi_{3\mathrm{MP}} = 0.09$. Then, the number density of the solvating 3MP molecules is $N_{3\mathrm{MP}}^s n_{\mathrm{salt}}$, while that of the free 3MP molecules is $n_{3\mathrm{MP}} - N_{3\mathrm{MP}}^s n_{\mathrm{salt}}$. In the onion phase, each onion should be composed of concentric thin membranes comprising BPh_4^- ions and solvating 3MP molecules. If all the BPh_4^- ions are trapped on the membranes, the areal density of BPh_4^- is given by

$$\sigma_a = n_s d = 92\ (\text{Å}^2). \tag{3}$$

Here, $d = 180$ Å is the spacing in case (c) shown in Fig. 1. On both sides of each membrane, Na^+ ions are localized within "counterion layers" with thickness of the order of the Debye screening length $\lambda = (4\pi n_{\mathrm{salt}} \ell_B)^{-1/2} \cong 15$ Å, where ℓ_B is the Bjerrum length in $\mathrm{D_2O}$ ($\sim$7 Å). The segregation of charge and composition in this manner should significantly lower the solvation free energy. However, the mechanism leading to the onion structure remains to be investigated in future, where the electrostatic energy due to the deformation of the charged membranes should be crucial as a new aspect.

We also argue why the lamellar structure is formed in the window composition range $0.05 < \phi_{3\mathrm{MP}} < 0.12$. When lamellae are formed, trapped 3MP molecules can simultaneously interact with a number of BPh_4^- ions on the plane, thus achieving high solvation. If $\phi_{3\mathrm{MP}}$ is less than the lower bound, the number density of 3MP should be too small to trigger the aggregation of BPh_4^- ions. If $\phi_{3\mathrm{MP}}$ is increased above the upper bound, 3MP molecules would be sufficiently abundant outside the thin membrane regions. This would eventually lead to the destruction of the membranes with increasing $\phi_{3\mathrm{MP}}$, where the delocalization of BPh_4^- ions can increase their translational entropy without an increase in the solvation free energy.

In summary, we have realized an onion structure in a $\mathrm{D_2O}$-3MP mixture with a low concentration of 3MP by adding a small amount of an antagonistic salt composed of hydrophilic and hydrophobic ions without a surfactant. In previous experiments [3–7], hydrophilic salts have mostly been used, and many problems have remained unresolved. As demonstrated in this Letter, the effects of adding an antagonistic salt are quite significant in soft matter. We predict that its addition decreases the surface tension of a macroscopic liquid-liquid interface to zero [22], leading to emulsification; this also explains our previous experiment [12].

This work was supported by Grant-in-Aid for Scientific Research on Priority Area "Soft Matter Physics" from the Ministry of Education, Culture, Sports, Science and Technology of Japan. One of the authors (K. S.) was supported by the JSPS (19-3802). We would like to thank Dr. D. Yamaguchi at the JAEA for assisting us in the SANS experiment.

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