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Membrane formation by preferential solvation of ions in mixture of water, 3-methylpyridine, and sodium tetrphenylborate

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The structure and dynamics of a ternary system composed of deuterium oxide (D2O), 3-methylpyridine (3MP), and sodium tetraphenylborate (NaBPh4) are investigated by means of small-angle neutron scattering (SANS) and neutron spin echo (NSE) techniques. In the SANS experiments, a structural phase transition is confirmed between a disordered-phase and an ordered-lamellar-phase upon variation of the composition and/or temperature of the mixture. The characteristic lengths of the structures is on the sub-micrometer scale. A dispersion relation of the structure is measured through NSE experiments, which shows that the relaxation rate follows a cubic relation with momentum transfer. This implies that the dynamics of the system are determined predominantly by membrane fluctuations. The present results indicate that 3MP-rich domains are microscopically separated from bulk water in the presence of NaBPh4, and that the layers behave as membranes. These results are interpreted that preferential solvation of salt in each solvent induces a microphase separation between the solvents, and the periodic structure of 3MP-rich domains is stabilized by the long-range electrostatic interaction arising from Na+ ions in D2O-rich domains. © 2013 AIP Publishing LLC.

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I. INTRODUCTION

Binary mixtures of water and organic solvents have been investigated for the study of phase separation and associated critical phenomena.1 From experiments, it is known that the two-phase region of a binary mixture expands when a hydrophilic salt such as NaCl or NaBr is added.2–5 It is well known that the interfacial energy between water and an organic solvent increases with the addition of a hydrophilic salt,6 and this could be a factor in salt-induced phase separation. Thus, the effect of a hydrophilic salt on a mixture of water and an organic solvent is opposite to that of surfactant molecules,7 which serve to increase the mutual solubility of water and the organic solvent by decreasing the interfacial energy.

Recently, we investigated the effect of the salt, sodium tetrphenylborate (NaBPh4), which is composed of the hydrophilic cation Na+ and hydrophobic anion BPh4−, on a mixture of deuterium oxide (D2O) and 3-methylpyridine (3MP). Figure 1 shows the phase diagrams of D2O/3MP/NaBPh4 drawn from our previous and present experiments. The binary mixture of D2O and 3MP shows closed-loop-type phase separation. When an antagonistic salt, NaBPh4, is dissolved in the D2O and 3MP mixture, the two-phase region shrinks as the amount of salt increases, and it disappears above 15 mmol/L;8 thus, the mutual solubility of D2O and 3MP decreases in the presence of NaBPh4 on the macroscopic scale. This result implies that the antagonistic salt can act as a surface-active agent in the D2O and 3MP mixture. Moreover, a periodic structure with a characteristic length scale of hundreds to thousands of angstroms was observed by means of small-angle neutron scattering (SANS), even far from the phase separation point. In the D2O-rich mixture in particular, an ordered-lamellar-phase (Lα phase) was found at a NaBPh4 concentration of ≈85 mmol/L.9

These experimental observations are explained in the framework of the theory proposed by Onuki and Kitamura.6,12,13 In their model, a charge-density-wave structure is induced by coupling the solvation effect and critical concentration fluctuations. In addition, they showed that hydrophilic and hydrophobic ions tend to adsorb near the interface between the water and the organic solvent. These ions act as an electric double layer at the interface, and reduce the interfacial tension between the water and the organic solvent.13

Although pairs of hydrophilic and hydrophobic ions play the role of a surface-active agent under certain conditions, the details of the formation mechanisms of a salt-induced ordered structure have not yet been clarified. As shown in Fig. 1(c), the composition and temperature ranges for the ordered-lamellar-structure are very narrow, suggesting that these structures are formed under a delicate balance among various interactions.

In the present study, we focused on the static and dynamic structures of the ordered-lamellar-structure in the mixture of D2O/3MP/NaBPh4 to understand how the ordered structure is stabilized. Neutron scattering techniques were employed to study the system because of the good scattering contrast

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between D$_2$O and 3MP. The SANS results indicate various kinds of nanoscale structures are formed depending on conditions, and neutron spin echo (NSE) experiments confirm the membrane picture by measuring the collective dynamics of the system on the nanosecond timescale.

II. EXPERIMENTS

D$_2$O (deuterium oxide, 99.9% purity, EURISO-TOPI, 3MP (3-methylpyridine, 99.5% purity, Aldrich), and NaBPh$_4$ (sodium tetraphenylborate, 99.5% purity, Aldrich) were mixed without further purification. The volume fraction of 3MP, $\phi_{3MP}$, indicates the volume fraction of 3MP, and the vertical axis is the temperature. The symbols in (a) and (b) show the cloud point obtained in previous research, while the symbol in (c) shows the phase transition point of the disordered-phase and the ordered-lamellar-phase investigated through the present SANS measurements. The dotted lines are visual guides. Error bars are of a value $\pm 1$ K, which is the ambiguity in the estimation of the cloud point and the phase transition point.

III. RESULTS

A. SANS studies with changing $C_{salt}$

Figure 2(a) shows the SANS profiles of D$_2$O/3MP/NaBPh$_4$ with changing $C_{salt}$ at $\phi_{3MP} = 0.09$ and $T = 280.5$ K. When the concentration of NaBPh$_4$ is below 1 mmol/L, the SANS profile shows a monotonic decrease with increasing $Q$. The SANS profiles from binary D$_2$O/3MP are explained by employing the Ornstein–Zernike function, which describes the concentration fluctuations of binary mixtures:

$$I_{OZ}(Q) = \frac{I_0}{1 + \xi^2 Q^2}. $$

In addition, the van der Waals radius of BPh$_4^-$ ion is evaluated as $4.9$ Å. It is noted that 3MP is a weak base, and some molecules accept D$_2$O as added. The base dissociation constant of 3MP, $K_b$, is $4.78 \times 10^{-9}$ (p$K_b = 8.32$). Additionally, we measured the pD value of a solution with $\phi_{3MP} = 0.09$ to be $9.43$. According to these facts, the ratio of 3MPD$^+$ to 3MP, [3MPD$^+$/[3MP], is evaluated as $1.78 \times 10^{-4}$ at 298.2 K. Therefore, in the present paper, we neglect the effect of the conjugated acid on the neutron scattering length density or electrostatic interactions between membranes.

The SANS measurements were performed using the NG3- and NG7-30 m SANS instruments at the National Institute of Standards and Technology (NIST) Center for Neutron Research (NCNR). The wavelength of the incident neutron beam was $6$ Å with a resolution of $14.2$ % for NG3 and $12.4$ % for NG7, and the scattered neutrons were collected with a two-dimensional $^3$He detector placed at specific distances from the sample position: $1.3$ m and $5.0$ m for NG3, and $1.0$ m and $6.5$ m for NG7. The samples were kept in titanium cells with quartz windows. The sample thickness was $2$ mm. A temperature-controlled chamber was used to regulate the sample temperature $T$ with an accuracy of $\pm 0.1$ K. The momentum transfer, $Q = 4\pi \sin \theta / \lambda$, was covered in the range from $8.6 \times 10^{-3}$ Å$^{-1}$ to $5.5 \times 10^{-1}$ Å$^{-1}$, where $\lambda$ and $2\theta$ are the incident neutron wavelength and the scattering angle, respectively. The observed two-dimensional data were averaged azimuthally, and then corrected for transmission, background scattering, and the sample thickness to obtain absolute intensities in units of cm$^{-1}$. The estimated incoherent scattering intensity was subtracted from the absolute intensity data.

The NSE experiments were carried out with the NG5-NSE spectrometer at the NCNR and the iNSE spectrometer at the research reactor JRR-3 of the Japan Atomic Energy Agency. The measured spatial and time domains for NG5-NSE were from $3 \times 10^{-2}$ Å$^{-1}$ to $2.5 \times 10^{-1}$ Å$^{-1}$ and from $0.05$ ns to $15$ ns, respectively, and those for iNSE were from $2 \times 10^{-2}$ Å$^{-1}$ to $1.5 \times 10^{-1}$ Å$^{-1}$ and from $0.16$ ns to $16$ ns, respectively. The sample was kept in a standard titanium cell with quartz windows for the NG5-NSE experiments, and in a quartz cell with a thickness of $4$ mm for the iNSE experiments. The sample temperature $T$ was regulated in a temperature-controlled chamber with an accuracy better than $0.1$ K. The DAVE software package was used for data reduction of the NG5-NSE data.
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IP: 129.6.122.135 On: Mon, 19 May 2014 18:41:53

Kitamura.12 On the basis of the Ginzburg–Landau theory, they derived the following function to explain the charge-density-wave structure:

\[
I_{Ok}(Q) = \frac{I_0}{1 + \left[1 - \frac{\gamma_p}{\xi} \left(Q^2/\lambda_D^2 + 1\right)\right]} \xi^2 Q^2, \tag{2}
\]

where \(I_0\) and \(\xi\) are the same parameters as in Eq. (1). The term \(\lambda_D\) denotes the Debye screening length,23 and \(\gamma_p(\gamma_p \geq 0)\) is a dimensionless parameter concerning the difference between the solubilities of cations and anions in water. It should be noted that Eq. (2) is equivalent to Eq. (1) when \(\gamma_p = 0\). When an antagonistic salt is dissolved in the mixture of water and 3MP, \(\gamma_p\) increases to more than 1, and a peak due to the periodicity of a charge distribution (charge-density-wave structure) appears at finite \(Q\). The peak position for \(\gamma_p > 1\) is calculated as

\[
Q_m = \frac{2\pi}{d} = \frac{\sqrt{\gamma_p - 1}}{\lambda_D}, \tag{3}
\]

where \(d\) indicates the characteristic mean repeat distance. The dashed lines in Fig. 2(a) for \(C_{salt} = 5\) mmol/L and 300 mmol/L indicate the fitting results according to Eq. (2). We found that the SANS profiles from the disordered-phase are explained well by Eq. (2) for \(C_{salt} = 5\) mmol/L, but not for \(C_{salt} = 300\) mmol/L at high \(Q\). Table I summarizes the fit parameters derived from Eq. (2) for the mixture at \(C_{salt} = 0\) mmol/L, 1 mmol/L, 5 mmol/L, and 300 mmol/L.

The fitting result obtained using Eq. (2) shows a slight deviation from the SANS profile for \(C_{salt} = 300\) mmol/L at \(Q \geq 0.3\) Å\(^{-1}\). This deviation should reflect the influence of the form factor of the molecular arrangement near the interfaces of the system on a scale of 10 Å to 20 Å. We assume that a thin layer, composed mainly of 3MP, constitutes the internal structure. Here, we employ a model scattering function for the sponge structure of a surfactant solution.24–27 The model scattering function for the sponge structure of a surfactant solution is given as25, 27

\[
I_{L3}(Q) = \frac{\phi_{3MP} + \phi_{BPh}}{\pi r_d^2 \delta} P_{L3}(Q) S_{L3}(Q), \tag{4}
\]

with the form factor derived from randomly oriented disks of membranes

\[
P_{L3}(Q) = 4\pi r_d^2 \Delta \rho \left[1 - \cos(\delta Q) \exp(-\delta^2 Q^2/2)]/Q^2\right] \left[r_d^2 Q^2 + 2\exp(-r_d^2 Q^2/6)\right], \tag{5}
\]

where \(\phi_{3MP}\) and \(\phi_{BPh}\) are the volume fractions of 3MP and NaBPh4, respectively, \(\Delta \rho\) is the density difference, \(S_{L3}(Q)\) denotes the form factor of the molecular arrangement near the interfaces of the system on a scale of 10 Å to 20 Å. We assume that a thin layer, composed mainly of 3MP, constitutes the internal structure.
and the structure factor
\[ S_L(Q) = 1 + \frac{C_1 \arctan(\xi \omega Q/2)}{Q} + \frac{C_2}{1/\xi^2 + (Q - 2\pi/d)^2} \approx 1 + \frac{C_1 \pi}{2Q} + \frac{C_2}{1/\xi^2 + (Q - 2\pi/d)^2}, \] (6)

where \( r_d \) the radius of gyration of a disk membrane, \( \Delta \rho \) the difference in scattering length density distribution between membrane and bulk water, \( \delta \) the thickness of membrane, \( \xi_{io} \) the inside–outside correlation length, which reflects the membrane scale, and \( \xi \), the correlation length of cells. The terms \( C_1 \) and \( C_2 \) are constants. In the fitting procedure, the term \( \arctan(\xi \omega Q/2) \) in Eq. (6) was approximated as \( \pi/2 \) by assuming that the value of \( \xi_{io} \) is sufficiently large. As shown in Fig. 2(b), the SANS profile for the mixture at \( C_{salt} = 300 \) mmol/L is well explained by Eq. (4) including the high-\( Q \) region, with the fitting parameters being \( d = 92 \pm 1 \) Å, \( \delta = 16 \pm 1 \) Å, \( r_d = 6.7 \pm 0.7 \) Å, \( \xi_c = 25.0 \pm 0.8 \) Å, and \( \Delta \rho = (47.7 \pm 0.8) \times 10^{10} \) cm\(^{-2}\).

The SANS profiles obtained from the ordered-lamellar-phase are analyzed according to the model scattering function for lamellar structures in surfactant systems, as proposed by Nallet et al., \(^{28}\)

\[ I_{La}(Q) = \frac{2\pi P_{La}(Q) S_{La}(Q)}{dQ^2}, \] (7)

with the form factor of the membrane
\[ P_{La}(Q) = \frac{2(\Delta \rho)^2}{Q^2} \left[ 1 - \cos(\delta Q) \exp \left( -\frac{1}{2} \tau^2 Q^2 \right) \right], \] (8)

and the structure factor
\[ S_{La}(Q) = 1 + 2 \sum_{n=1}^{N-1} \left( 1 - \frac{n}{N} \right) \cos \left( \frac{dnQ}{1 + 2\Delta Q^2d^2q(n)} \right) \times \exp \left[ -\frac{\Delta Q^2d^2n^2 + 2d^2g(n)Q^2}{2(1 + 2\Delta Q^2d^2q(n))} \right] \times \frac{1}{\sqrt{1 + 2\Delta Q^2d^2q(n)}}, \] (9)

where \( \tau \) denotes the membrane thickness distribution, which could be fixed at \( \delta/4 \) as the cases of surfactant membranes. \(^{28,29}\) \( N \) the number of layers, and \( \Delta Q \) the instrumental resolution. The value of \( N \) is fixed at 500 since \( S_{La}(Q) \) is almost independent of \( N \) when \( N \) is larger than a certain value, i.e., \( N \approx 100. \) \(^{30}\) The correlation function of fluctuating membranes \( g(n) \) is given by
\[ g(n) = \frac{\eta}{4\pi^2} \left[ \ln(\pi n) + 0.5772 \right], \] (10)

\[ \eta = \frac{Q_m^2 k_b T}{8\pi \sqrt{K B}}, \] (11)

where \( \eta \) represents the Caillé parameter, which reflects the regularity of membranes. \(^{31}\) \( Q_m \) denotes the position of the first-order Bragg peak, \( k_b \) the Boltzmann constant, \( K \) the bulk bending modulus (\( K = \kappa/d \), where \( \kappa \) denotes the bending modulus for a single membrane), and \( B \) the layer compressibility at constant surfactant and oil chemical potentials (i.e., at constant 3MP and salt chemical potentials, in the present case). A smaller value of \( \eta \) indicates better periodicity of the lamellar structure. The width of the instrumental resolution function \( \Delta Q \) is given by\(^{29}\)

\[ \Delta Q^2 = \frac{Q^2}{8\ln 2} \left( \frac{\Delta \lambda}{\lambda} \right)^2 + \frac{(2\pi)^2}{12\lambda^2} \left( \frac{R_1^2}{L_1^2} + \frac{R_2^2}{L_2^2} + \frac{(\Delta R)^2}{L_2^2} \right), \] (12)

where \( R_1 \) and \( R_2 \) denote the radii of the source and sample aperture (50.00 mm and 12.70 mm, respectively), \( \Delta \lambda \) the detector resolution (5 mm), \( L_1 \) and \( L_2 \) the incident and scattered flight path lengths, respectively, and \( L' = L_1L_2/(L_1 + L_2) \). These parameters are defined for the experimental setup of the SANS measurements. Although Eq. (7) was proposed to explain the lamellar structure in surfactant systems, it has been applied to investigate the structural features of the present system. \(^9\) The fitting results according to Eq. (7) are shown in Fig. 2(a) with solid lines for the SANS profiles of the samples with NaBPh\(_4\) concentration between 60 mmol/L and 250 mmol/L, and the curves reproduce the experimental results well. The fit parameters \( d, \eta, \) and \( \delta \) are summarized in Table II.

From the analyses performed using Eqs. (4) and (7), the existence of membrane structures is confirmed in both the sponge phase and ordered-lamellar-phase. Here, it could be reasonable to speculate that the D\(_2\)O-rich and 3MP-rich domains behave as bulk water and membranes, respectively. Since BPh\(_4^-\) is hydrophobic,\(^{32}\) most BPh\(_4^-\) ions should exist in 3MP-rich domains rather than in bulk water. The 3MP-rich membranes are stacked regularly, and the nanostructures, i.e., sponge structure and ordered-lamellar-structure, are generated.

Figure 3 shows the \( C_{salt} \) dependence of the fit parameters, \( d, \eta, \) and \( \Delta \rho \) for the mixture of D\(_2\)O/3MP/NaBPh\(_4\) (\( \phi_{3MP} = 0.09 \)) and T is around 281 K. The temperature is 281.8 K for the mixture at \( C_{salt} = 85 \) mmol/L and 280.5 K in the other cases. Here, we confirmed that the effect of the temperature difference, i.e., 281.8 K and 280.5 K, on the SANS profile at \( C_{salt} = 85 \) mmol/L is negligible. In Figs. 3(a), 3(c), and 3(d), the data for the sponge phase derived from Eq. (4) are also shown as open symbols. The characteristic maximum value of the mean

<table>
<thead>
<tr>
<th>( C_{salt} ) (mmol/L)</th>
<th>( d (\text{Å}) )</th>
<th>( \eta )</th>
<th>( \delta (\text{Å}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>157.3 ± 0.2</td>
<td>0.44 ± 0.01</td>
<td>14 ± 4</td>
</tr>
<tr>
<td>75</td>
<td>194.3 ± 0.3</td>
<td>0.19 ± 0.01</td>
<td>16 ± 2</td>
</tr>
<tr>
<td>85</td>
<td>195.6 ± 0.2</td>
<td>0.20 ± 0.01</td>
<td>16 ± 3</td>
</tr>
<tr>
<td>120</td>
<td>172.2 ± 0.2</td>
<td>0.20 ± 0.01</td>
<td>16 ± 2</td>
</tr>
<tr>
<td>140</td>
<td>156.7 ± 0.2</td>
<td>0.23 ± 0.01</td>
<td>15 ± 2</td>
</tr>
<tr>
<td>160</td>
<td>145.4 ± 0.3</td>
<td>0.38 ± 0.01</td>
<td>15 ± 5</td>
</tr>
<tr>
<td>180</td>
<td>140.9 ± 0.1</td>
<td>0.41 ± 0.01</td>
<td>14 ± 3</td>
</tr>
<tr>
<td>200</td>
<td>141.8 ± 0.2</td>
<td>0.48 ± 0.01</td>
<td>14 ± 3</td>
</tr>
<tr>
<td>250</td>
<td>123.8 ± 0.4</td>
<td>0.65 ± 0.01</td>
<td>13 ± 4</td>
</tr>
</tbody>
</table>
repeat distance, \(d\), is observed at \(C_{\text{salt}} \approx 85\) mmol/L. On the other hand, \(\eta\) has its minimum around \(C_{\text{salt}} = 75\) mmol/L to 140 mmol/L. Figure 3(d) shows the \(C_{\text{salt}}\) dependence of \(\delta/d\). Here, \((\delta/d)_{\text{calc}}\) is evaluated by assuming that the membranes are composed of 3MP and BPh\(_4^-\) ions, and that the morphology of the sponge and ordered-lamellar-structure follows the ideal dilution relation:

\[
(\delta/d)_{\text{calc}} = \phi_{3\text{MP}} + \phi_{\text{BPh}^-}.
\]

In Eq. (13), the volume fraction of Na\(^+\) in 3MP-rich domains is ignored, since this magnitude is sufficiently small compared with that of BPh\(_4^-\).\(^{32}\) The magnitudes of \(\delta/d\) and \((\delta/d)_{\text{calc}}\) are close enough, and this result supports the idea that the membranes are composed of 3MP-rich domains and ions. A small discrepancy between \(\delta/d\) and \((\delta/d)_{\text{calc}}\) may originate from the partial mixing of D\(_2\)O and 3MP molecules. Figure 3(e) shows the \(C_{\text{salt}}\) dependence of \(\Delta \rho\) and \(\Delta \rho_{\text{calc}}\), which is evaluated from

\[
\Delta \rho_{\text{calc}} = \rho_{\text{D}_2\text{O}} - \left( \frac{\phi_{3\text{MP}}}{\phi_{3\text{MP}} + \phi_{\text{BPh}^-}} \rho_{3\text{MP}} + \frac{\phi_{\text{BPh}^-}}{\phi_{3\text{MP}} + \phi_{\text{BPh}^-}} \rho_{\text{BPh}^-} \right),
\]

where \(\rho_{\text{D}_2\text{O}}(6.4 \times 10^{10}\text{cm}^{-2})\), \(\rho_{3\text{MP}}(1.4 \times 10^{10}\text{cm}^{-2})\), and \(\rho_{\text{BPh}^-}(2.1 \times 10^{10}\text{cm}^{-2})\) denote the scattering length densities of D\(_2\)O, 3MP, and BPh\(_4^-\) ions, respectively, for 6 Å neutrons. The coincidence of \(\Delta \rho\) and \(\Delta \rho_{\text{calc}}\) suggests that strong scattering occurs because of the spatial distribution between bulk water composed of D\(_2\)O-rich domains and the membrane composed of 3MP-rich domains and BPh\(_4^-\) ions.

In this manner, the fitting results give a reasonable set of structural parameters, and they validate the application of the aforementioned models to the system. Because the Nallet model originally assumes a regular stacking of surfactant layers in water, the fitting results confirm the picture that planar 3MP-rich domains are stacked regularly in water.

\[\text{FIG. 3.} \quad C_{\text{salt}}\text{ dependence of the fit parameters, } d, \eta, \text{ and } \Delta \rho \text{ for the mixture of D}_2\text{O/3MP/NaBPh}_4\; (\phi_{3\text{MP}} = 0.09). \text{ The temperature is 281.8 K for the mixture at } C_{\text{salt}} = 85\text{ mmol/L and 280.5 K in the other cases. The open and closed symbols indicate the data in the disordered-phase and the ordered-lamellar-phase, respectively. Error bars represent } \pm 1\text{ standard deviation. (a) The mean repeat distance } d. \text{ The solid line is a visual guide. (b) The Caillé parameter } \eta. \text{ The solid line is a visual guide for the data at } 75\text{ mmol/L } \leq C_{\text{salt}} \leq 140\text{ mmol/L}, \text{ where } \eta \text{ shows relatively small values. (c) The membrane thickness } \delta. \text{ (d) The } C_{\text{salt}}\text{ dependence of } \delta/d. \text{ The dashed line indicates the estimated values, } (\delta/d)_{\text{calc}}, \text{ according to Eq. (13). (e) The scattering length density difference between the membrane and the bulk water, } \Delta \rho. \text{ The dashed line indicates the values of } \Delta \rho_{\text{calc}} \text{ according to Eq. (14).}\]
This indicates that the values of \( \eta \) slightly decreases at \( T \approx 281.8 \) K. This behavior is similar to that of the smectic density-wave structure and sponge structure) and ordered-lamellar-structure. On the other hand, \( d \) increases with decreasing \( \phi_{3\text{MP}} \) at \( T = 281.8 \) K. This behavior is similar to that of the smectic lamellar structure in surfactant systems, which follows the ideal dilution relation. \[^{33}\] Figure 6(b) shows the \( \phi_{3\text{MP}} \) dependence of \( \eta \) at \( T = 281.8 \) K. \( \eta \) reaches a minimum value around a certain value of \( \phi_{3\text{MP}} \): \( \phi_{3\text{MP}} = 0.1 \) in this sample. It is noteworthy that this tendency is also observed in some surfactant mixtures. In the mixture of water/octane/nonionic poloxymethylene surfactant \((C_{12}E_3)\), for example, the minimum \( \eta \) value is observed at around \( \phi = 0.5 \) (where \( \phi \) denotes the volume fraction of oil) since the layer compressibility \( B \) attains a maximum value at \( \phi = 0.5 \) in this system. \[^{34}\] Figure 6(c) shows the \( \phi_{3\text{MP}} \) dependence of \( \delta/d \). With increasing \( \phi_{3\text{MP}} \), \( \delta/d \) slightly increases at \( T = 281.8 \) K, whereas, slightly decreases at \( T = 340.8 \) K. The magnitudes of \( \delta/d \) and \((\delta/d)_{\text{calc}}\) derived from Eq. \( (13) \) are of the same order for the mixture at \( \phi_{3\text{MP}} = 0.09, 0.10, 0.12, \) and 0.13 (see Fig. 6(c)).

**C. NSE studies with changing \( T \) and \( \phi_{3\text{MP}} \)**

As shown above, the disordered-structure (i.e., charge-density-wave structure and sponge structure) and ordered-lamellar-structure are observed in the mixture of \( D_2\text{O}/3\text{MP} \) upon the addition of \( \text{NaBPh}_4 \). So far, the dynamical behaviors of surfactant monolayers or bilayers have been investigated both theoretically and experimentally. \[^{35} - {44}\] The stability of such membranes has been discussed considering the bending elastic properties through the Helfrich bending Hamiltonian. \[^{45}\] We compare the dynamical properties of the newly discovered nanostructures in \( D_2\text{O}/3\text{MP}/\text{NaBPh}_4 \) with the theory for surfactant membranes.

The dynamical properties of the system were investigated by means of NSE. Figure 7(a) shows the normalized intermediate correlation function \( I(Q, t)/I(Q, 0) \) for the mixture at
$C_{\text{salt}} = 85 \text{ mmol/L}$, $\phi_{\text{3MP}} = 0.09$, and $T = 293.2 \text{ K}$, which is the ordered-lamellar-phase of the system. In the case of a fluctuating surfactant membrane, the intermediate correlation function $I(Q, t)/I(Q, 0)$ is expressed by using the stretched exponential function as follows:

$$I(Q, t) = \exp[-(\Gamma t)^{2/3}], \quad (15)$$

where $\Gamma$ denotes the relaxation rate. Figure 7(b) shows the $Q$ dependence of $\Gamma$. The single membrane fluctuation model proposed by Zilman and Granek (ZG)\textsuperscript{39} gives the $Q^3$ relation of $\Gamma$ as

$$\Gamma = 0.025 \gamma_k \left( \frac{k_B T}{\kappa_{\text{NSE}}} \right)^{1/2} \frac{k_B T}{\eta_{\text{vis}}} Q^3, \quad (16)$$

where $\kappa_{\text{NSE}}$ and $\eta_{\text{vis}}$ denote the bending modulus of the membrane and the viscosity of the surrounding medium, respectively. The factor $\gamma_k$ originates from the averaging over the angle between the wave vector and the membrane surface in the calculation of $I(Q, t)$. In the present analysis, we set $\gamma_k = 1$ for simplicity. For the value of $\eta_{\text{vis}}$, we used the following values for the viscosity of $D_2O$: $1.676 \text{ mPa} \cdot \text{s} (283.2 \text{ K})$, $1.250 \text{ mPa} \cdot \text{s} (293.2 \text{ K})$, $1.110 \text{ mPa} \cdot \text{s} (298.2 \text{ K})$, $0.786 \text{ mPa} \cdot \text{s} (313.2 \text{ K})$, $0.651 \text{ mPa} \cdot \text{s} (323.2 \text{ K})$, $0.535 \text{ mPa} \cdot \text{s} (335.1 \text{ K})$, and $0.474 \text{ mPa} \cdot \text{s} (343.2 \text{ K})$.\textsuperscript{46} Throughout the observed $Q$ range (i.e., $3.0 \times 10^{-2} \text{ Å}^{-1} \leq Q \leq 2.5 \times 10^{-1} \text{ Å}^{-1}$) and temperature range (i.e., $283.2 \text{ K} \leq T \leq 343.2 \text{ K}$), $I(Q, t)/I(Q, 0)$ is well fitted by Eq. (15), and $\Gamma$ follows Eq. (16).

It should be noted that the $Q$ dependence of $\Gamma$ shows a slight deviation from Eq. (16) around $Q = 0.07 \text{ Å}^{-1}$ due to the so-called de Gennes narrowing. At the length scales of the inter-layer distance, the relative motion of the membranes becomes slower, and the apparent $\Gamma$ becomes smaller. The appropriate $Q$ range of the ZG model is limited by the inter-lamellar distance (low-$Q$ limit) and the membrane thickness (high-$Q$ limit). Further, it is noted that the ZG model is based on the assumption that a membrane fluctuates freely without being affected by long-range intermembrane interactions. In the present system, the long-range electrostatic repulsion dominates the lamellar structure, as will be shown in Sec. IV. Nonetheless, the dynamical properties in this system can also be described well by Eqs. (15) and (16). This fact may suggest that the principal behavior of the membrane fluctuation of this
system in both the sponge phase and ordered-lamellar-phase is less affected by the existence of a long-range intermembrane interaction.

Figure 8 shows the temperature dependence of $\kappa_{\text{NSE}} / k_B T$ according to Eq. (16) for the mixtures of $C_{\text{salt}} = 85$ mmol/L at various $\phi_{3\text{MP}}$ from 0.09 to 0.13. $\kappa_{\text{NSE}} / k_B T$ decreases with increasing temperature. Here, it is noted that the value of $\kappa_{\text{NSE}}$ according to Eq. (16) in surfactant systems deviates from the actual value because of the difference between the viscosity of water $\eta_{\text{vis}}$ and the effective viscosity of bulk water near membranes: in many cases, $\kappa_{\text{NSE}}$ approaches the reasonable value when $\eta_{\text{vis}}$ is substituted with $\eta_{\text{eff}} \approx 3 \eta_{\text{vis}}$. Similarly, the values of $\kappa_{\text{NSE}} / k_B T$ in the present case may deviate from the reasonable values. In addition, the long-range electrostatic repulsion between membranes can suppress their fluctuation, and this increases the value of $\kappa_{\text{NSE}}$ from the actual value.

IV. DISCUSSION

In this study, we showed that an antagonistic salt NaBPh$_4$ in a mixture of D$_2$O and 3MP induces nanostructures, i.e., the disordered-structure and the ordered-lamellar structure. Around $T = 281$ K, the SANS profile at $C_{\text{salt}} = 5$ mmol/L is explained by the function describing the charge-density-wave structure (Eq. (2)), and the profile at $C_{\text{salt}} = 300$ mmol/L is modeled by the scattering function of the sponge phase of surfactant solutions (Eq. (4)). The boundary between D$_2$O-rich and 3MP-rich domains is vague in the charge-density-wave phase, whereas the boundary is sharp and membranes are formed in the sponge phase. In addition, the SANS profiles for the mixture at 60 mmol/L $\leq C_{\text{salt}} \leq 250$ mmol/L are well explained by the model function of a lamellar structure in surfactant mixtures$^{28}$ (see Eq. (7)). In both the sponge phase and the ordered-lamellar-phase, 3MP-rich domains exist as planar membranes and their dynamics are well explained as fluctuating membranes.

Figure 9(a) describes the scattering length density distribution obtained to describe the SANS profile for D$_2$O/3MP/NaBPh$_4$ at $C_{\text{salt}} = 85$ mmol/L, $\phi_{3\text{MP}} = 0.09$, and $T = 281.8$ K (left), and the schematic illustration of the system, indicating the membrane structure mainly composed of 3MP according to the results of SANS and NSE measurements (right). The vertical axis indicates the temperature dependence of $\delta$, $d$, and the distribution of ions. In (b) and (c), the scale of the membrane thickness $\delta$ and the van der Waals radius of BPh$_4^-$ ion (4.9 Å, see Sec. II) are expanded to three times their original size to facilitate visualization. Additionally, the ionic radius of Na$^+$ (0.95 Å$^{23}$) is expanded to eight times its original size. In (c), the dipole moment arising from Na$^+$ and BPh$_4^-$ ion pairs, and the electrostatic repulsion between membranes, $P_{\text{ele}}$, are also described.

In this section, we discuss the origin of the planar membrane formation and the lamellar structure that does not contain any surfactant molecules or polymers.
A. Formation mechanisms of the membrane

According to the theoretical consideration of Onuki and Kitamura, a pair of hydrophilic and hydrophobic ions tends to adsorb at the interface between domains of water and organic solvent.\textsuperscript{23,24} Then, macrophase separation is inhibited to satisfy the charge neutrality in each domain. This expectation is consistent with the experimental result, which shows that the two-phase region in the mixture of D\textsubscript{2}O/3MP/NaBPh\textsubscript{4} shrinks with an increasing amount of NaBPh\textsubscript{4} (see Fig. 1). Therefore, a certain number of Na\textsuperscript{+} and BPh\textsubscript{4}\textsuperscript{-} ion pairs should adsorb around the interface between D\textsubscript{2}O-rich and 3MP-rich domains; the majority of Na\textsuperscript{+} ions are distributed in D\textsubscript{2}O-rich domains, whereas BPh\textsubscript{4}\textsuperscript{-} ions are distributed in 3MP-rich domains.

As shown in Table I, the magnitudes of $I_0$ and $\xi$ increase with increasing $C_{salt}$. This indicates that the contrast between D\textsubscript{2}O-rich and 3MP-rich domains and/or the number of separated domains increases with increasing salt concentration. In other words, microphase separation is enhanced with increasing $C_{salt}$ in contrast to the fact that macrophase separation is suppressed. The microphase separated domains are stretched owing to the entropic effect of ions, that is, the translational entropy of Na\textsuperscript{+} and BPh\textsubscript{4}\textsuperscript{-} ions distributed around the interface between D\textsubscript{2}O-rich and 3MP-rich domains increases with increasing interfacial area. In the present case, the stretched 3MP-rich domain behaves as a membrane.

B. The stabilization of the ordered-lamellar-structure

As shown in Fig. 9, the membrane surfaces are negatively charged because of the BPh\textsubscript{4}\textsuperscript{-} ions in 3MP-rich domains. This picture is analogous to ionic surfactant membranes, and the intermembrane interaction free energy per unit surface area could be assumed following for that of ionic surfactant mixtures:\textsuperscript{23,33,52}

$$f_{int} = f_{hyd} + f_{ele} + f_{vdW} + f_{Hel},$$

(17)

where $f_{hyd}$ denotes the free energy arising from the hydration structures of surface charges, $f_{ele}$ the free energy of the electrostatic interaction (so-called electrostatic double-layer repulsion\textsuperscript{23}), $f_{vdW}$ the free energy of the van der Waals interaction, and $f_{Hel}$ the free energy arising from the steric interaction (Helfrich interaction\textsuperscript{45}).

It is reasonable to neglect the effect of $f_{hyd}$ when $d$ is larger than 30 Å, because this effect is known as short-ranged.\textsuperscript{53}

$f_{ele}$ is evaluated from the electrostatic pressure between neighboring membranes, $P_{ele}$, arising from the “entropic” effect of Na\textsuperscript{+} ions in D\textsubscript{2}O-rich domains, as\textsuperscript{23,33}

$$P_{ele} = \frac{k_B T \pi \sigma^2 \ell_B}{2 [1 + \pi \ell_B \sigma (d - \delta)]^2},$$

(18)

$$f_{ele} = -\frac{1}{2} \int_{-\infty}^{d} P_{ele} d(d)$$

$$\approx \frac{k_B T \pi \sigma^2}{4 [1 + \pi \sigma \ell_B (d - \delta)]},$$

(19)

where $\ell_B$ denotes the Bjerrum length ($\ell_B \approx 7$ Å), $\sigma$ the surface density of BPh\textsubscript{4}\textsuperscript{-} ions, and $\alpha$ a dimensionless parameter, which is set to $\alpha = 1$ if all Na\textsuperscript{+} ions are dissociated and exist only in water-rich domains (otherwise $0 \leq \alpha < 1$). By assuming that all BPh\textsubscript{4}\textsuperscript{-} ions exist at the interface between D\textsubscript{2}O-rich domains and 3MP-rich domains, $\sigma$ is given by

$$\sigma = \frac{1}{2} C_{salt} N_A d,$$

(20)

where $N_A$ denotes Avogadro’s number. The $C_{salt}$ and temperature dependence of $\sigma$ according to Eq. (20) is shown in Fig. 11. If we set $\alpha = 1$, for simplicity, the typical value of $f_{ele}$ is evaluated as $f_{ele} = 2.3 \times 10^{-24}$ J Å\textsuperscript{-2} for the mixture at $C_{salt} = 85$ mmol/L, $\phi_{3MP} = 0.09$, and $T = 281.8$ K. Figure 10 shows the $d$ dependence of $f_{ele}$ evaluated from Eq. (19) for the mixture at $C_{salt} = 60$ mmol/L, 85 mmol/L, or 140 mmol/L, $\phi_{3MP} = 0.09$, and $T = 280.5$ K. $\alpha$ is set to 1 for simplicity. Here, the factor $1/d$ represents the number of the membranes per unit length. The results show that $f_{ele}$ decreases with increasing $d$, that is, $P_{ele}$ acts as a repulsive interaction.

$f_{vdW}$ is approximately given as

$$f_{vdW} \approx \frac{-k_B T}{12\pi} \left\{ \frac{1}{(d - \delta)^2} + \frac{1}{(d + \delta)^2} - \frac{2}{d^2} \right\}.$$  

(21)

The typical value is $f_{vdW} = -1.1 \times 10^{-28}$ J Å\textsuperscript{-2} for the mixture at $C_{salt} = 85$ mmol/L, $\phi_{3MP} = 0.09$, and $T = 281.8$ K. That is, the magnitude of $f_{vdW}$ is sufficiently small compared with that of $f_{ele}$.

$f_{Hel}$ arises from the entropic confinement of a fluctuating membrane by neighboring membranes.\textsuperscript{35} In the case of the lamellar structure including an ionic surfactant, this effect can usually be neglected, since the electrostatic interaction between membranes suppresses the undulation.\textsuperscript{23,33} Similarly, it should be reasonable to neglect the effect of $f_{Hel}$ for the ordered-lamellar-structure in the present case. This idea is confirmed by the temperature dependence of $d$ (see Fig. 5(a)):

if the steric interaction between membranes is dominant, the opposite behavior, i.e., the increase in $d$ with $T$, should be observed. Other evidence is provided by the magnitude of

\[ \text{FIG. 10. The } d \text{ dependence of } f_{ele} \text{ evaluated from Eq. (19) for the mixture at } C_{salt} = 60 \text{ mmol/L, 85 mmol/L, or 140 mmol/L, } \phi_{3MP} = 0.09, \text{ and } T = 280.5 \text{ K. } \alpha \text{ is set to 1 for simplicity.} \]
the Caillé parameter. If the steric interaction is dominant, the Caillé parameter $\eta_{\text{Hel}}$ could be given by

$$\eta_{\text{Hel}} = \frac{4}{3} \left( 1 - \frac{\delta}{d} \right)^2 \approx 1.0 \text{ to } 1.1. \quad (22)$$

This value is approximately twice as large as the present experimental results (see Fig. 3).

In this manner, it is interpreted that the electrostatic repulsion between membranes is the prime factor for stabilizing the long-range periodic structure in ordered-lamellar-phase. Additionally, it is pointed out that the “intramembrane interactions,” i.e., the osmotic pressure arising from BPh$_4^-$ ions in the 3MP-rich domains, $P_{\text{osm}}$, or the dipole-dipole interaction arising from Na$^+$ and BPh$_4^-$ ion pairs around the interface between D$_2$O-rich and 3MP-rich domains, $P_{\text{dipole}}$, may also affect the morphology of the ordered-lamellar-structure. If we assume that $P_{\text{osm}}$ and $P_{\text{dipole}}$ result in decrease $d$, and their magnitudes increase with increasing $C_{\text{salt}}$, the decrease of $d$ above $C_{\text{salt}} = 85 \text{ mmol}/\text{L}$ (see Fig. 3(a)) is explained. In future, the distributions of Na$^+$ and BPh$_4^-$ ions in the mixture should be investigated experimentally to discuss the details of the effect of $P_{\text{osm}}$ and $P_{\text{dipole}}$.

Figure 11(a) shows the $C_{\text{salt}}$ dependence of $\sigma$ according to Eq. (20) for the mixture at $\phi_{\text{3MP}} = 0.09$ around $T = 281$ K. $\sigma$ has a maximum around $C_{\text{salt}} = 250 \text{ mmol}/\text{L}$. This result suggests that the number of BPh$_4^-$ ions in 3MP-rich domains is saturated at $C_{\text{salt}} > 250 \text{ mmol}/\text{L}$. The value of $\sigma$ in the ordered-lamellar-phase spans the range between $2.5 \times 10^{-3} \text{ Å}^{-2}$ and $1.0 \times 10^{-2} \text{ Å}^{-2}$, which is comparable with that of the surface density of surfactant molecules in typical surfactant membranes.

Figure 11(b) shows the temperature dependence of $\sigma$ at $C_{\text{salt}} = 85 \text{ mmol}/\text{L}$ and $\phi_{\text{3MP}} = 0.09, 0.10, 0.12, \text{ and } 0.13$. $\sigma$ increases with decreasing temperature for all the samples. The inset of Fig. 11(b) exhibits the $\phi_{\text{3MP}}$ dependence of $\sigma$ at two different temperatures: the open and closed symbols indicate the data for $T = 340.8$ K (disordered-phase) and $T = 281.8$ K (ordered-lamellar-phase), respectively. At $T = 340.8$ K, $\sigma$ is almost independent of $\phi_{\text{3MP}}$ with a value of about $\sigma = 2.6 \times 10^{-3} \text{ Å}^{-2}$. On the other hand, $\sigma$ increases with decreasing $\phi_{\text{3MP}}$ at $T = 281.8$ K.

V. CONCLUSION

In the present study, we investigated the structural properties of the disordered-phase and ordered-lamellar-phase in the mixture of D$_2$O/3-methylpyridine (3MP)/NaBPh$_4$. The SANS results for the ordered-lamellar-phase were well explained by the product of the structure factor $S(Q)$ of the lamellar structure and the form factor $P(Q)$ of the planar membrane. The fit parameter, the difference in scattering length density distribution between membrane and bulk water $\Delta \rho$, is almost constant at $4.9 \times 10^{10} \text{ cm}^{-2}$; this corresponds to the difference in the scattering length densities of D$_2$O ($\rho_{\text{D}_2\text{O}} = 0.6 \times 10^{10} \text{ cm}^{-2}$) and 3MP ($\rho_{\text{3MP}} = 1.4 \times 10^{10} \text{ cm}^{-2}$). These results indicate that 3MP-rich domains behave as membranes in the bulk water, D$_2$O. The intermediate scattering functions measured using NSE supported the description of membrane structure for both the disordered-phase and the ordered-lamellar-phase: this is well explained by the stretched exponential function with the stretching exponent $\beta = 2/3$, and the decay rate is proportional to the cube of momentum transfer.

On the basis of the SANS and NSE results, we showed that the 3MP-rich domains are stretched as a membrane owing to the solvation effects of Na$^+$ and BPh$_4^-$, and the periodicity of the ordered-lamellar-structure is stabilized mainly by the effects of the electrostatic interactions between neighboring membranes.

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11Strong light scattering is observed in the ordered-lamellar-phase due to the existence of μm-sized structure. Note that similar light scattering is also observed in the mixture for 0 < φ_{3MP} ≤ 0.04 below 318 K, even though the ordered-lamellar-structure is not confirmed by SANS. The detailed structure in these conditions should be clarified in future studies.


22According to our microscopic observation in D2O/3MP/NaBPh4 at φ_{3MP} = 0.09 and T = 283.2 K, the ordered-lamellar-phase was not confirmed when C_{NaBH4} ≤ 50 mmol/L.


