

The Effect of Tetraphenylphosphonium Chloride on Phase Behavior and Nanoscale Structures in a Mixture of D₂O and 3-Methylpyridine

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The effects of adding an “inversely antagonistic” salt, tetraphenylphosphonium chloride (PPh₄Cl), to a binary mixture of deuterated water and 3-methylpyridine were investigated by visual inspection and small-angle neutron scattering. With increasing salt concentration, the two-phase region shrinks and a charge density wave structure is induced, as in the case of adding a “normally antagonistic” salt, sodium tetraphenylborate (NaBPh₄), to the binary mixture. The concentration range of the periodic structure is narrower than that in the case of adding NaBPh₄, and no ordered lamellar structure is observed in the present study.

It has been known that the phase behaviors of binary mixtures of water and an organic solvent change with the addition of a salt. In most cases, both cations and anions of salt are hydrophilic and attract water molecules, and the solubility of water and the organic solvent decreases with an increase in the salt concentration and the two-phase region is enhanced.¹⁻⁴ Various experiments have been performed to verify the existence of solvation clusters to explain the phase behavior, and the diameters of the clusters are shown to be on the order of several tens of angstroms.^{2,3}

Recently, some of the authors showed the opposite phase behavior in a deuterated water (D₂O)/3-methylpyridine (3MP) binary mixture upon the addition of an antagonistic salt, sodium tetraphenylborate (NaBPh₄). NaBPh₄ is composed of hydrophilic cations and hydrophobic anions,⁵⁻⁷ and they are distributed heterogeneously in the mixture because they either attract water or 3MP molecules. This phase behavior can be explained as follows: the solvation clusters of D₂O and 3MP should attract electrostatically, and the NaBPh₄ molecules behave as surfactants.⁸ In addition, the authors discovered a nanometer-scale periodic structure in the one-phase region. When the salt concentration was lower than 60 mmol L⁻¹, a broad single peak profile was observed by small-angle neutron scattering (SANS).^{5,6} When the salt concentration was increased above 60 mmol L⁻¹ in water-rich mixtures, the SANS profiles drastically changed to multipeak profiles. This was the first observation of an ordered lamellar structure induced by the preferential solvation of an antagonistic salt.⁷

In this study, we tried to confirm the effect of preferential solvation on a D₂O/3MP mixture in the presence of a different kind of antagonistic salt, tetraphenylphosphonium chloride (PPh₄Cl) (referred to as “inversely antagonistic” salt), composed of hydrophobic cations and hydrophilic anions. The phase behavior observed by visual inspection indicates that the effect

of adding the “inversely antagonistic” salt is the same as that of adding the “normally antagonistic” salt, NaBPh₄. The charge density wave (CDW) structure⁹ is also confirmed in the present study; however, the concentration range is narrower than that in the previous case, and the lamellar structure is not found in the measured composition range.

D₂O (99.9% isotopic purity) purchased from EURISO-TOP was mixed with 3MP (99.5% purity) and PPh₄Cl (98% purity) purchased from Aldrich without further purification.¹⁰ The volume fraction of 3MP, φ_{3MP} , was varied between 0.05 and 0.55 for visual inspection and was set at 0.09, 0.35, and 0.54 for SANS measurements. The concentration of PPh₄Cl, C_{salt} , was 5, 13, and 18 mmol L⁻¹ for the visual inspection, while it was fixed at 85 mmol L⁻¹ for the SANS measurement.

In order to visually investigate the phase behavior, the temperature of the centrifuge tubes containing the samples was controlled by a heat bath, with an accuracy of $\pm 1.0^\circ\text{C}$, and monitored by a thermocouple.

SANS measurements were performed using the NG7-30m SANS instrument at the National Institute of Standards and Technology (NIST) Center for Neutron Research (NCNR).¹¹ The wavelength of the incident neutron beam was 6 Å, with a resolution of 12.4%, and the scattered neutrons were collected by a two-dimensional ³He detector placed 1.0 and 6.5 m from the sample position. Each sample was kept in a titanium cell with quartz windows. The sample thickness was selected as 2 mm. A temperature-controlled chamber was used to regulate the temperature T with an accuracy of $\pm 0.1^\circ\text{C}$. The momentum transfer, $Q = 4\pi \sin\theta/\lambda$, ranged over 7.6×10^{-3} and $5.2 \times 10^{-1} \text{ \AA}^{-1}$, where λ and 2θ are the incident neutron wavelength and the scattering angle, respectively. The observed two-dimensional data were azimuthally averaged and corrected for transmission, background scattering, and sample thickness to obtain absolute intensities.¹² The calculated incoherent scattering intensity was subtracted from the absolute intensity data.

The phase diagram obtained by the visual inspection is shown in Figure 1. In the D₂O/3MP binary mixture, cloud points are observed between 37 and 67 °C depending on φ_{3MP} . When 5 mmol L⁻¹ of PPh₄Cl is added to the binary mixture, the cloud points are raised and the two-phase region shrinks. As we increase C_{salt} , the two-phase region shrinks further and disappears above $C_{salt} = 20 \text{ mmol L}^{-1}$. This behavior is similar to our previous observation for the mixture of D₂O, 3MP, and NaBPh₄.⁵ This evidence indicates that preferential solvation of the cations and anions of an antagonistic salt increases the solubility of D₂O and 3MP, irrespective of the type of salt.

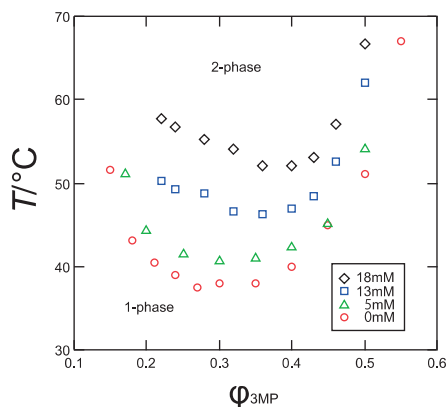


Figure 1. Phase diagram obtained by visual inspection. Open circles indicate cloud points of the binary mixture of D₂O and 3MP. Open triangles, squares, and diamonds correspond to those of ternary mixtures with $C_{\text{salt}} = 5, 13,$ and 18 mmol L^{-1} , respectively. Errors are hidden within the size of plot characters.

Scattering intensities of the samples for $C_{\text{salt}} = 85 \text{ mmol L}^{-1}$ measured by SANS are depicted in Figure 2. For better visualization, the profiles at higher temperatures are shifted by multiplying with 2.5 for $T = 31 \text{ }^\circ\text{C}$, 5 for $T = 54 \text{ }^\circ\text{C}$, and 10 for $T = 73 \text{ }^\circ\text{C}$. At this salt concentration, the two-phase region shown in Figure 1 disappears. However, for all the 3MP volume fractions, the scattering intensities increase with increasing temperature. This result indicates that concentration fluctuations exist in the one-phase region and increase with increasing temperature. The absolute intensities from the sample with $\phi_{3\text{MP}} = 0.35$ are about 10 times larger than those from the other samples, which means that the former is closer to the critical concentration.

As shown by the dashed lines in Figure 2, the SANS profiles are fitted with the Ornstein–Zernike formula:¹³

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

where I_0 is proportional to the osmotic compressibility, and ξ is the correlation length. The profiles from the samples with $\phi_{3\text{MP}} = 0.35$ and 0.54 are explained well by eq 1. The fitting parameters for these samples are shown in Table 1. On the other hand, the results of fitting to eq 1 are not very good in the case of the sample with $\phi_{3\text{MP}} = 0.09$, as shown by the dashed line for the profile at $T = 73 \text{ }^\circ\text{C}$. The small shoulder observed around $Q = 0.1 \text{ } \text{\AA}^{-1}$ suggests that a periodic structure coexists with the concentration fluctuation. Following the previous results for ternary mixtures with NaBPh₄, we apply the formula proposed by Onuki and Kitamura:⁹

$$I_{\text{OK}} = \frac{I_{\text{OK}0}}{1 + [1 - \gamma_p^2 / (1 + \lambda_D^2 Q^2)] \xi^2 Q^2} \quad (2)$$

where the nondimensional parameter γ_p indicates the degree of solvation asymmetry between the cations and the anions, which is related to the Gibbs free energy transfer,⁹ and λ_D is the Debye screening length, which is set as $10.4 \text{ } \text{\AA}$. In the case of an antagonistic salt, $\gamma_p > 1$, and the peak position corresponding to the repeat distance in the CDW structure is calculated as

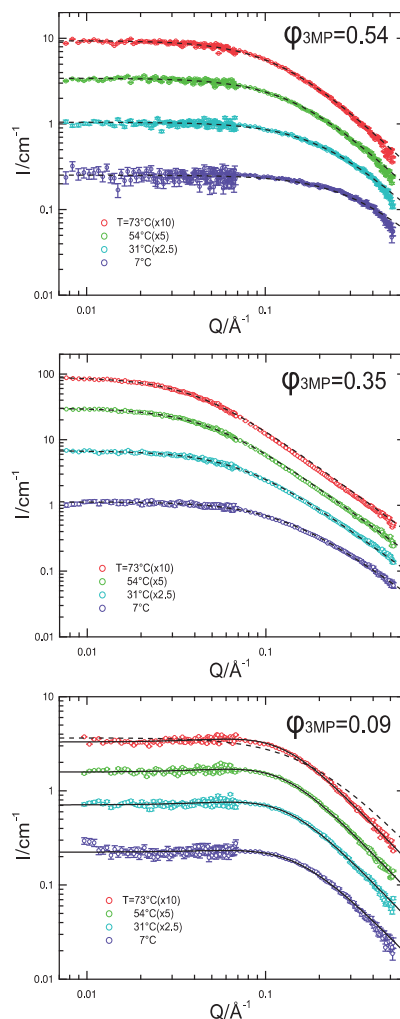


Figure 2. Temperature dependence of the SANS profiles for the samples with $\phi_{3\text{MP}} = 0.54$ (upper), 0.35 (middle), and 0.09 (lower). The salt concentration was fixed at 85 mmol L^{-1} . For better visualization, the data at higher temperature are shifted by a multiplication factor of 2.5 for $T = 31 \text{ }^\circ\text{C}$, 5 for $T = 54 \text{ }^\circ\text{C}$, and 10 for $T = 73 \text{ }^\circ\text{C}$, respectively. Error bars represent ± 1 standard deviation.

Table 1. Fit results for the samples with $\phi_{3\text{MP}} = 0.54$ and 0.35 ^a

T / $^\circ\text{C}$	$\phi_{3\text{MP}} = 0.54$		$\phi_{3\text{MP}} = 0.35$	
	I_0/cm^{-1}	$\xi/\text{\AA}$	I_0/cm^{-1}	$\xi/\text{\AA}$
7	0.252 ± 0.002	3.02 ± 0.08	1.133 ± 0.005	7.92 ± 0.09
31	0.420 ± 0.002	4.69 ± 0.07	2.716 ± 0.009	13.24 ± 0.09
54	0.687 ± 0.003	6.70 ± 0.08	6.081 ± 0.014	20.19 ± 0.08
73	0.942 ± 0.004	8.27 ± 0.08	9.005 ± 0.020	24.23 ± 0.09

^aError bars represent ± 1 standard deviation.

$$Q_m = \frac{\sqrt{\gamma_p - 1}}{\lambda_D} \quad (3)$$

Eq 2 well explains the SANS profiles from the sample with $\phi_{3\text{MP}} = 0.09$, as shown by the solid lines in Figure 2. The best-fit parameters are summarized in Table 2. The calculated Q_m 's are about $0.06 \text{ } \text{\AA}^{-1}$ at all the temperatures observed. The fact that

Table 2. Fit results for the sample with $\varphi_{3MP} = 0.09^a$

$T/^\circ\text{C}$	$I_{\text{OKO}}/\text{cm}^{-1}$	$\xi/\text{\AA}$	γ_p
7	0.223 ± 0.002	5.5 ± 0.1	1.38 ± 0.05
31	0.283 ± 0.002	6.4 ± 0.1	1.42 ± 0.03
54	0.316 ± 0.002	6.7 ± 0.1	1.40 ± 0.02
73	0.329 ± 0.002	6.8 ± 0.1	1.40 ± 0.02

^aError bars represent ± 1 standard deviation.

the SANS profiles can be explained by eq 2 suggests that the CDW structure is also induced in the water-rich mixture of D₂O and 3MP upon the addition of an “inversely antagonistic” salt. Furthermore, the concentration fluctuation increases with increasing temperature, as is the case with “normally antagonistic” salts.⁵ However, the characteristic repeat distance in the CDW structure is unchanged with temperature, unlike the case with the “normally antagonistic” salts.

The present results indicate that the solvation effect of “inversely antagonistic” salts on a mixture of D₂O and 3MP is similar to that of the “normally antagonistic” salts. The electrostatic force between a cluster of 3MP molecules attracted by hydrophobic cations and a cluster of D₂O molecules attracted by hydrophilic anions decreases the interfacial tension between the solvents. From this experimental evidence, we could generalize that the surface activities of antagonistic salts follow the same trend as that in the case of surfactants.

The ability to form a long-range periodic structure could also be the general case for these kinds of salts. However, the regularity of the structure might depend on the type of salt and interaction with the solvent molecules. In the case of NaBPh₄ at $\varphi_{3MP} = 0.09$, the typical value of the degree of solvation asymmetry γ_p is around 2,⁷ which is two times larger than that for PPh₄Cl. In the present case, the heterogeneous distribution of ions may not be distinct and the microphase separation of D₂O and 3MP is weak. Thus, the composition range of the structure⁹ in the ternary mixture with PPh₄Cl is narrower than that with NaBPh₄.

There are two possible reasons why the lamellar phase in the present mixture is not observed. One is that the observed conditions do not cover the range of the lamellar phase. The other is that the lamellar phase is intrinsically absent in the mixture with PPh₄Cl. As described in a previous paper, the lamellar structure is stabilized by the balance between the entropic effect of the ions and the electrostatic double-layer repulsion.⁷ This balance is easily disturbed by the size difference between the ions and the solubilities of the ions in the solvents. Thus, it is possible that the delicate balance required to stabilize the lamellar structure is disrupted in the present mixture.

We confirmed that the solvation effect of an “inversely antagonistic” salt, PPh₄Cl, causes shrinkage of the two-phase region in a mixture of D₂O and 3MP, as was the case with a “normally antagonistic” salt, NaBPh₄.^{5–7} A periodic structure,

which could be interpreted as the CDW structure, was also formed in a water-rich mixture. However, the composition range of the periodic structure was narrower than that in the case of NaBPh₄ addition, and the lamellar structure was not observed. This might be caused by the difference in the solvation strength of the cations and anions in the solvents. This aspect should be investigated in more detail in future.

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