Small-Angle Neutron Scattering Study on Aggregation in Acetonitrile–D_2O and Acetonitrile–D_2O–NaCl Mixtures

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The salt-induced phase separation was, for the first time, directly observed at a molecular level by small-angle neutron scattering (SANS) experiments performed at room temperature on acetonitrile–D_2O and acetonitrile–D_2O–NaCl mixtures as a function of acetonitrile mole fraction, X_{AN}, and NaCl concentration, respectively. Aggregation or microheterogeneity in the acetonitrile–D_2O mixtures was most enhanced at X_{AN} = 0.3–0.4 with Debye correlation lengths L_D ~19 Å. In the acetonitrile–D_2O–NaCl mixtures at X_{AN} = 0.2 the aggregation increased with NaCl content and reached a plateau of L_D ~20 Å.

Microheterogeneity in acetonitrile–water mixtures has been an important subject in discussion of their physico-chemical properties such as self-diffusion coefficients[1,2] and Kirkwood–Buff parameters[3] for a long period. Another interesting subject of acetonitrile–water mixtures has been phase separation either by cooling or by addition of salts like NaCl. The phase separation of acetonitrile–water mixtures takes place over $\sim 0.2 < X_{AN} < \sim 0.8$ with an upper critical point of 272 K and X_{AN} = 0.38.[4] The salt-induced phase separation of aqueous acetonitrile mixtures has recently been applied to solvent extraction of water soluble compounds such as highly charged metalloporphyrins[5] that cannot be extracted into conventional solvents like chloroform. The detailed mechanism of the salt-induced phase separation, however, remains unknown at a molecular level, though some discussion on preferential solvation of Na^+ and Cl^- by acetonitrile was made from macroscopic viscosities and self-diffusion coefficients.[2] Recently, we have performed large-angle X-ray scattering (LAXS) and infrared spectroscopy measurements under an ambient condition on acetonitrile–water mixtures,[6] and it has been clarified that microheterogeneity occurs at $0.2 < X_{AN} < 0.6$, being consistent with the previous works.[1–3] However, the order of microheterogeneity could not be determined in the previous LAXS study.[6]

SANS technique can provide us mesoscopic structure information of fluctuation in density and/or concentration, and of the size and shape of aggregates formed in solutions as well as small-angle X-ray scattering (SAXS). In particular, SANS experiments would be more suitable than SAXS for acetonitrile–water mixtures because acetonitrile and water aggregates are highly contrasted by replacing H with D due to different scattering lengths of –3.74 and 6.67 fm, respectively.

In the present study, SANS measurements have been carried out at room temperature on acetonitrile–D_2O and acetonitrile–D_2O–NaCl mixtures in various X_{AN} and NaCl concentrations to determine the mesoscopic order of microheterogeneity or aggregates formed in both mixtures in terms of the Debye correlation length.[7]

Acetonitrile–D_2O mixtures at X_{AN} = 0.1, 0.2, 0.25, 0.3, 0.4, 0.5, 0.6, and 0.8 and acetonitrile–D_2O–NaCl mixtures at X_{AN} = 0.2 with different concentrations 0.149, 0.295, and 0.581 M (M = mol dm^{-3}) NaCl were prepared in a nitrogen-filled glove box. A phase diagram for acetonitrile–D_2O–NaCl mixtures at 298 K, as proved before the SANS measurements, indicates that NaCl-induced phase separation takes place over a wide X_{AN} range from 0.2 to 0.8. However, the salt concentration required for the phase separation depends on X_{AN}; the phase separation of the mixtures at X_{AN} = 0.2 occurs when the NaCl concentration exceeds ~1.4 M. In the present experiment, three homogeneous acetonitrile–D_2O–NaCl mixtures were prepared at NaCl content less than 1.4 M where the phase separation does not occur.

SANS measurements on acetonitrile–D_2O mixtures were made at 298.2 ± 0.1 K on SANS-U at a reactor JRR-3M in JAERI, Tokai, while acetonitrile–D_2O–NaCl mixtures at 296.2 ± 0.5 K on WINK at KENS in KEK, Tsukuba. The momentum transfer Q (= $4\pi\lambda^{-1}\sin\theta$; λ the wavelength, 2θ the scattering angle) range covered was 5×10^{-4}–0.5 with SANS-U[8] and 0.015–20 $Å^{-1}$ with WINK. The observed intensities on SAUS-U and WINK were corrected for background, absorption, and cell scattering and normalized by scattering of luporen and H_2O, respectively.[9,10]

In Figures 1 (a) and (b), the $I_{corr}(Q)$ values for the acetonitrile–D_2O and acetonitrile–D_2O–NaCl mixtures are plotted against

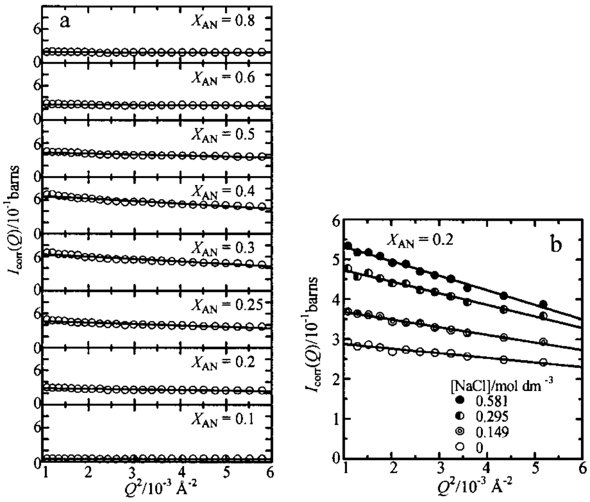

Figure 1. Plots of $I_{corr}(Q)$ against Q^2 values for (a) acetonitrile-D_2O mixtures at various X_{AN}s and (b) acetonitrile-D_2O-NaCl mixtures at X_{AN} = 0.2 and various NaCl concentrations. The observed values (circles) and least-squares fitted ones (solid lines) by eq (1).

Q^2, respectively. The SANS intensities for the acetonitrile–D_2O mixtures increase with a decrease in X_{AN} from 0.8, and are highest at X_{AN} = 0.3–0.4, suggesting that aggregation in the acetonitrile–D_2O mixtures is most enhanced at X_{AN} = 0.3–0.4. On the other hand, the SANS intensities for the acetonitrile–D_2O–NaCl mixtures gradually increase with increasing NaCl concentration. As shown in Figure 1, neutron scattering intensities, $I_{corr}(Q)$, in a small Q-range have a linear relation with Q^2 as described by

$$I_{corr}(Q) = I_0\left(1 - \frac{L_D{}^2}{6}Q^2\right), \tag{1}$$

where I_0 is the scattering intensity at Q = 0 $Å^{-1}$ and L_D is the Debye correlation length.[7,11] To make a quantitative analysis of aggregation in the present mixtures, the correlation length defined by Debye was calculated. The least-squares fitted values by using eq (1) are given by solid lines in Figure 1. The experimental intensities are well reproduced by eq (1), except for the acetonitrile–D_2O mixtures at X_{AN} = 0.25, 0.3, and 0.4, where the experimental intensities deviate from the straight lines, showing a multi-dispersive pattern,[12] i.e., aggregates of several dimension are probably formed at these compositions. Thus, L_D values at the compositions should be regarded as an average one of concentration fluctuations.

The L_D values determined for the acetonitrile–D_2O and acetonitrile–D_2O–NaCl mixtures are plotted against X_{AN} and NaCl concentration in Figures 2 (a) and (b), respectively. For the acetonitrile–D_2O mixture at X_{AN} = 0.2 the L_D value (15.2 ± 0.3 Å) obtained on WINK is in agreement with that (14.4 ± 0.4 Å) on SANS-U within experimental uncertainties.

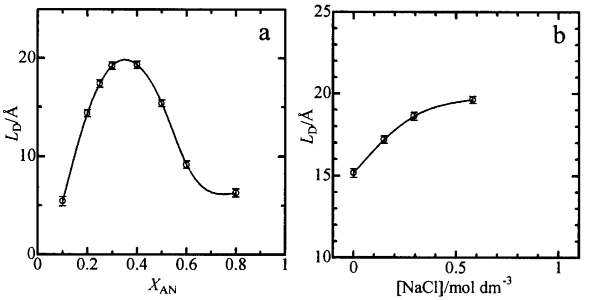

Figure 2. Debye correlation lengths L_D with the standard deviation of σ values as error bars for (a) acetonitrile-D_2O mixtures as a function of X_{AN} and (b) acetonitrile-D_2O-NaCl mixtures at X_{AN} = 0.2 as a function of NaCl concentration.

Figure 2 (a) shows that aggregation or microheterogeneity is most enhanced with L_D ~19 Å between X_{AN} = 0.3 and 0.4. These results are in good agreement with those from the previous LAXS study[6] and from the Kirkwood–Buff parameters that have concluded the largest acetonitrile–acetonitrile interaction at X_{AN} = 0.4.[3] It would be reasonable to conclude that the concentration fluctuations arise from microheterogeneity between acetonitrile and D_2O aggregates because acetonitrile molecules are contrasted with D_2O molecules in the present SANS measurements. The present results show the first direct evidence for aggregation or microheterogeneity at the mesoscopic scale for acetonitrile–water mixtures.

In Figure 2 (b) the L_D values rapidly increase with increasing NaCl concentration up to 0.295 M, suggesting enhancement of aggregation with NaCl concentration. However, they appear to have a plateau value of ~20 Å when the NaCl concentration exceeds 0.581 M. From these results, we can conclude that the size of aggregation in the acetonitrile–D_2O mixtures at X_{AN} = 0.2 becomes a critical value of L_D ~20 Å to initiate phase separation when the salt concentration reaches ~43% of the value required for phase separation.

We propose that two factors mainly contribute to the NaCl-induced phase separation of acetonitrile–water mixtures; preferential hydration to ions and microheterogeneity. In acetonitrile–water–NaCl mixtures both Na^+ and Cl^- are most likely to be preferentially solvated by water molecules, not by acetonitrile molecules as discussed in Reference 2, because both Gutmann's donor number (D_N = 18.0) and Mayer–Gutmann's acceptor number (A_N = 54.8) are larger for water than those (D_N = 14.1 and A_N = 19.3) for acetonitrile. In fact, our chemical analysis of both acetonitrile-rich and water-rich phases after phase separation indicated that most of added NaCl was found in the water-rich phase, while the NaCl content in the acetonitrile-rich phase was less than ~1.7%. Thus, the increased L_D values by increasing salt concentration should be caused by aggregation of water molecules around preferentially hydrated Na^+ and Cl^-. In the phase separation of acetonitrile–water mixtures by cooling, microheterogeneity may be enhanced by strengthened hydrogen bonds among water molecules at undercooled temperature, leading to the phase separation. It can be considered that the temperature of the phase separation is shifted to ambient because microheterogeneity is enhanced even at ambient temperature by hydration of Na^+ and Cl^-.

In the present findings on L_D for the acetonitrile–D_2O–NaCl mixtures, the L_D almost reaches a plateau value ~20 Å when [NaCl] ≥ 0.581 M, suggesting that the number of aggregates of this size increases until [NaCl] = ~1.4 M, where both water and acetonitrile aggregates fuse into large water-rich and acetonitrile-rich phases, respectively, resulting in phase separation. In this process, microheterogeneity caused by weak dipole–dipole interactions among water and acetonitrile molecules does play an important role to assist phase separation.

In solvent extraction for highly charged species such as metalloporphyrins by the salt-induced phase separation of acetonitrile–water mixtures, it is likely that the porphyrins would be surrounded by acetonitrile aggregates formed in acetonitrile–water mixtures. By addition of NaCl the acetonitrile aggregates are finally separated into the acetonitrile-rich phase from the water-rich phase; the porphyrins are extracted into the acetonitrile-rich phase.

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