

Heterogeneity of acetonitrile–water mixtures in the temperature range 279–307 K studied by small-angle neutron scattering technique

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Abstract

At 279, 287, 298, and 307 K the heterogeneity of acetonitrile–water mixtures in a range of acetonitrile mole fraction x_{AN} from 0.2 to 0.6 has been evaluated in terms of Ornstein–Zernike correlation length, concentration and density fluctuations, and Kirkwood–Buff parameters obtained from small-angle neutron scattering (SANS) experiments. At 298 K the correlation lengths for CH_3CN-D_2O ($D=^2H$) and CD_3CN-H_2O mixtures have shown that the heterogeneity of acetonitrile–water mixtures at $x_{AN}=0.3$ and 0.4 is most enhanced in the mole fraction range examined. With decreasing temperature from 307 to 279 K, the correlation length and the fluctuations for CH_3CN-D_2O mixtures at $x_{AN}=0.3$ and 0.4 most significantly rise in the mole fraction range. The Kirkwood–Buff parameters have revealed that both acetonitrile–acetonitrile and water–water interactions in acetonitrile–water mixtures at the same mole fractions remarkably increase with decreasing temperature, whereas acetonitrile–water interactions decrease. According to all the parameters estimated, a change in mixing state of acetonitrile–water mixtures with lowering temperature was discussed.

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1. Introduction

Acetonitrile is miscible with water at any ratio under ambient conditions. However, acetonitrile–water mixtures are separated to acetonitrile-rich and water-rich phases either by cooling or addition of salts, such as NaCl. Indeed, the upper critical solution temperature (UCST) of acetonitrile–water mixtures has been found at 272 K when $x_{AN}=0.38$ [1]. So far, many researchers have measured various physicochemical properties of acetonitrile–water mixtures, such as partial molar volumes

[1] and viscosities [2], and reached a conclusion that acetonitrile and water molecules are not homogeneously mixed with each other at the molecular level even under ambient conditions.

Recently, small-angle X-ray and neutron scattering techniques have been often utilized to directly observe a mixing state of binary solutions at a mesoscopic level. Nishikawa et al. have made small-angle X-ray scattering (SAXS) measurements on acetonitrile–water mixtures at 273, 279, and 298 K and estimated the fluctuations and the Kirkwood–Buff parameters from the SAXS intensities [3]. It has been shown that both acetonitrile–acetonitrile and water–water interactions in the mixture at $x_{AN}=0.38$ are most enhanced with decreasing temperature in the entire x_{AN} range. In a SANS experiment, a mixture of deuterated and undeuterated solvent molecules gives high contrast with each other because of the largely different neutron scattering lengths (6.67 and -3.74 fm, respectively)

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of D and H atoms. Hence, a SANS technique is a powerful tool to elucidate a mixing state of binary solutions. We have made SANS measurements at 298 K on $\text{CH}_3\text{CN}-\text{D}_2\text{O}$ and $\text{NaCl}-\text{CH}_3\text{CN}-\text{D}_2\text{O}$ mixtures with varying x_{AN} and salt concentration [4,5] before the SAXS investigation. The results have revealed that the size of the clusters for $\text{CH}_3\text{CN}-\text{D}_2\text{O}$ mixtures at 298 K is most enhanced between $x_{\text{AN}}=0.3$ and 0.4 in the entire range of the mole fraction and that the size further increases when the NaCl concentration increases.

Based on both Bhatia–Thornton [6] and Kirkwood–Buff [7] theories, Almásy et al. have proposed a procedure for estimation of concentration and density fluctuations and Kirkwood–Buff parameters from SANS intensities for a binary solution [8]. They have also reported the parameter values for aqueous mixtures of 3-methylpyridine [8] and pyridine [9] determined from their SANS intensities. After the studies by Almásy et al. [8,9], Bakó et al. have estimated both fluctuations and Kirkwood–Buff parameters for $\text{CH}_3\text{CN}-\text{D}_2\text{O}$ and $\text{CD}_3\text{CN}-\text{H}_2\text{O}$ mixtures at 298 K as a function of x_{AN} [10]. It has been found that the fluctuations and the Kirkwood–Buff parameters for $\text{CH}_3\text{CN}-\text{D}_2\text{O}$ and $\text{CD}_3\text{CN}-\text{H}_2\text{O}$ at $x_{\text{AN}}=0.38$ are most enhanced in the entire mole fraction range as well as the SAXS investigation [3]. However, SANS experiments have not been made on acetonitrile–water mixtures as a function of temperature down to the UCST.

In the present investigation, to evaluate heterogeneity of acetonitrile–water mixtures in the temperature range 279–307 K, SANS experiments have been made on $\text{CH}_3\text{CN}-\text{D}_2\text{O}$ and $\text{CD}_3\text{CN}-\text{H}_2\text{O}$ mixtures by using SANS-U and SWAN spectrometers installed at a reactor and a pulsed neutron facility, respectively. First, the Ornstein–Zernike correlation lengths [11] for $\text{CD}_3\text{CN}-\text{H}_2\text{O}$ mixtures at 298 K in the mole fraction range of $0.2 \leq x_{\text{AN}} \leq 0.6$ have been estimated from their SANS intensities measured on SANS-U. For comparison, those for $\text{CH}_3\text{CN}-\text{D}_2\text{O}$ mixtures at 298 K in the same x_{AN} range have also been determined by reanalyzing the SANS intensities measured on SANS-U in the previous investigation [4,5]. Then, to clarify a change in the heterogeneity of acetonitrile–water mixtures with lowering temperature, SANS experiments using SWAN have been made on $\text{CH}_3\text{CN}-\text{D}_2\text{O}$ mixtures at 279, 287, 298, and 307 K. The Ornstein–Zernike correlation lengths, the fluctuations, and the Kirkwood–Buff parameters for the mixtures have been estimated and compared with those obtained from the SAXS experiments [3]. According to the present results, a change in mixing state of acetonitrile–water mixtures with decreasing temperature toward the UCST is discussed at the molecular level.

2. Experimental

2.1. Sample solutions

Acetonitrile (Wako Pure Chemicals, extra grade) was dried for several days on thermally activated 4 Å molecular sieves and then distilled under nitrogen gas atmosphere. Heavy water, D_2O , (Aldrich, D atom content of 99.9%) and acetonitrile- d_3 , CD_3CN , (Euriso-top, D atom content of 99.8%) were used without further purification. To avoid replacement of D atoms by H ones, $\text{CH}_3\text{CN}-\text{D}_2\text{O}$ mixtures at $x_{\text{AN}}=0.2, 0.25, 0.3, 0.4,$

0.5, and 0.6 were made up in a nitrogen-filled glove box. $\text{CD}_3\text{CN}-\text{H}_2\text{O}$ mixtures were prepared by mixing acetonitrile- d_3 and doubly distilled water at the same mole fractions. Densities of the sample solutions at 279, 287, 298, and 307 K were measured with an electronic densimeter (ANTON Paar K.G., DMA60 and DMA602) for analysis of SANS data.

2.2. SANS experiments

SANS experiments at 298 K were made on $\text{CD}_3\text{CN}-\text{H}_2\text{O}$ mixtures at $x_{\text{AN}}=0.2, 0.25, 0.3, 0.4, 0.5,$ and 0.6 using SANS-U spectrometer at a reactor JRR-3M in Japan Atomic Energy Agency (JAEA), Tokai, Japan. In the experiments, the sample solutions were kept into a quartz cell of 10 mm in width, 40 mm in height, and 2 mm in sample thickness and exposed to neutron beams (wavelength, $\lambda=7$ Å), whose size is 5 mm in diameter at the sample position, for 1.5 h. The sample temperature was controlled within ± 0.1 K during the measurements by circulation of thermostated water around a sample chamber. The distance between the sample position and the detector was set to 2 m, where the momentum transfer Q ($=4\pi\lambda^{-1}\sin\theta$) range of 0.02–0.14 Å⁻¹ was covered [12]. The transmission by a sample and a cell was measured with a ³He detector placed at a beam stopper position. The observed intensities were corrected for background by subtraction of intensities of an empty cell, and then normalized by dividing the intensities for each sample solution by those for a standard polyethylene sample, Lupolen [13].

When the sample temperatures were 279, 287, 298, and 307 K, SANS intensities for $\text{CH}_3\text{CN}-\text{D}_2\text{O}$ mixtures at $x_{\text{AN}}=0.2, 0.25, 0.3, 0.4, 0.5,$ and 0.6 were measured on SWAN spectrometer at a pulsed neutron facility (KENS) in High Energy Accelerator Research Organization (KEK), Tsukuba, Japan. The Q -range of 0.01–12 Å⁻¹ was covered with SWAN [14]. The sample solutions were kept in a quartz cell of 22 mm in width, 25 mm in height, and 2 mm in sample thickness. The sample temperature was controlled within ± 0.5 K by circulation of temperature-controlled silicone oil in a sample jacket. The neutron beam size at a sample position was 20×20 mm², and the wavelength range used was $\lambda=0.5$ –11.6 Å. The scattering intensities were accumulated for 4 h per sample. The observed intensities were corrected for background, absorption, and cell scattering. The transmission by a sample and a cell was measured with a ³He position sensitive detector placed at a beam stopper position. The correction for detector efficiencies and normalization to absolute units was made by dividing the intensities of each solution by those of vanadium [14].

The incoherent scattering was subtracted from the normalized intensities obtained on both SANS-U and SWAN. All parameter values required for the above corrections were taken from the literature [15].

3. Results and discussion

3.1. $\text{CH}_3\text{CN}-\text{D}_2\text{O}$ and $\text{CD}_3\text{CN}-\text{H}_2\text{O}$ mixtures at 298 K

Fig. 1 shows the normalized SANS intensities $I_{\text{corr}}(Q)$ for the $\text{CD}_3\text{CN}-\text{H}_2\text{O}$ mixtures at 298 K obtained on SANS-U, together

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