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X-ray diffraction studies on methanol–water, ethanol–water, and 2-propanol–water mixtures at low temperatures

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Abstract

X-ray diffraction measurements over a range from ambient to freezing point temperatures have been made on methanol–water, ethanol–water, and 2-propanol–water mixtures, whose compositions are around mole fractions of the structural transition of solvent clusters at 25 °C, i.e. ~0.3, ~0.2, and ~0.1, respectively. The present results showed that the structure of dominant clusters formed in the mixtures at 25 °C is still kept at low temperatures, except that O· · ·O hydrogen bonds formed in the mixtures are gradually ordered with lowering temperature. At the freezing point temperatures, ice I_h is crystallized in methanol–water and ethanol–water mixtures below the mole fraction of structural transition. Above the mole fraction of structural transition, methanol–water mixtures are kept in the metastable liquid state, but ethanol hydrate is crystallized in ethanol–water mixtures. In the case of 2-propanol–water mixtures, ice I_h is crystallized from the mixtures at all the mole fractions (0.05, 0.1, and 0.2) investigated because microheterogeneity in 2-propanol–water mixtures at 25 °C is most enhanced among the three alcohol–water mixtures. From the present results, it was concluded that the structure of dominant clusters formed in the mixtures at the ambient temperature is reflected into that of frozen alcohol–water mixtures.
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Keywords: Alcohol–water mixtures; Low temperatures; X-ray diffraction; Structure

1. Introduction

Aqueous alcohol solutions, such as ethanol–water and propanol–water mixtures, are widely utilized as a solvent for chemical reaction and various analytical techniques, such as solvent extraction and chromatography [1]. On the other hand, solid–liquid phase transition for alcohol–water mixtures with temperature has so far been investigated by using various techniques, such as calorimetry [2–4] and dielectric relaxation [5]. Formation of clathrate hydrate has been often discussed on the basis of these results. Takaizumi et al. [3,4] performed differential scanning calorimetry (DSC) on aqueous solutions of methanol (M), ethanol (E), 1-propanol (1pr), 2-propanol (2pr), and *tert*-butanol (tbu) to observe freezing process of them with lowering temperature. They pointed out that an inflection point appears in the solid–liquid phase diagrams for all the alcohol–water mixtures at alcohol mole fractions of x_M=0.3, x_E=0.17, x_{1pr}=0.1, x_{2pr}=0.13, and x_{tbu}=0.03, respectively. In addition, they proposed that the structure of solid phase changes at the inflection point, i.e. stable ice is crystallized from the mixtures below the inflection point, while peritectic or eutectic alcohol hydrate is formed above the inflection point.

On the other hand, to clarify the structure of predominant clusters formed in alcohol–water mixtures at 25 °C on the molecular level, we have made X-ray diffraction experiments on aqueous mixtures of methanol [6], ethanol [7–9], 1-propanol [10], and 2-propanol [11] over the whole alcohol mole fraction range. These results showed that structural transition of predominant clusters from tetrahedral-like structure of water to hydrogen-bonded alcohol chains takes place at $x_M \approx 0.3$, $x_E \approx 0.2$, $x_{1pr} \approx 0.1$, and $x_{2pr} \approx 0.1$, respectively, where various thermodynamic parameters,

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such as heat of mixing and partial molar volume, show anomalies at 25 °C. Hence, we concluded that the structural transition of solvent clusters at the respective mole fractions is responsible for the anomalies of various thermodynamic parameters at 25 °C.

The coincidence between the inflection points observed at the ambient and low temperatures suggests that the structure of solid phase for alcohol–water mixtures at low temperatures is strongly related to that of the corresponding liquid phase at ambient temperature. Thus, it is of great interest to elucidate the freezing process of alcohol–water mixtures at the molecular level by X-ray diffraction.

In the present investigation, in order to clarify structure of alcohol–water mixtures at low temperatures, X-ray diffraction measurements have been performed over a range from ambient to freezing temperatures on methanol–water, ethanol–water, and 2-propanol–water mixtures around the above inflection points. On the basis of the results obtained, the structure of the frozen alcohol–water mixtures and effects of hydrophobic group on the freezing process of the mixtures are discussed at the molecular level.

2. Experimental

2.1. Sample solutions

Methanol, ethanol, and 2-propanol (Wako, Grade for a high performance liquid chromatography) were dried with thermally activated 4-Å molecular sieves for several days. Doubly distilled water was used for preparation of all sample solutions. Methanol–water mixtures at methanol mole fractions of x_M=0.2, 0.3, and 0.4, ethanol–water mixtures at ethanol mole fractions of x_E=0.1, 0.2, and 0.3, and 2-propanol–water mixtures at 2-propanol mole fractions of x_{2pr}=0.05, 0.1, and 0.2 were prepared by weighing alcohols and distilled water, respectively. Densities of the mixtures at 25 °C were measured with an electronic

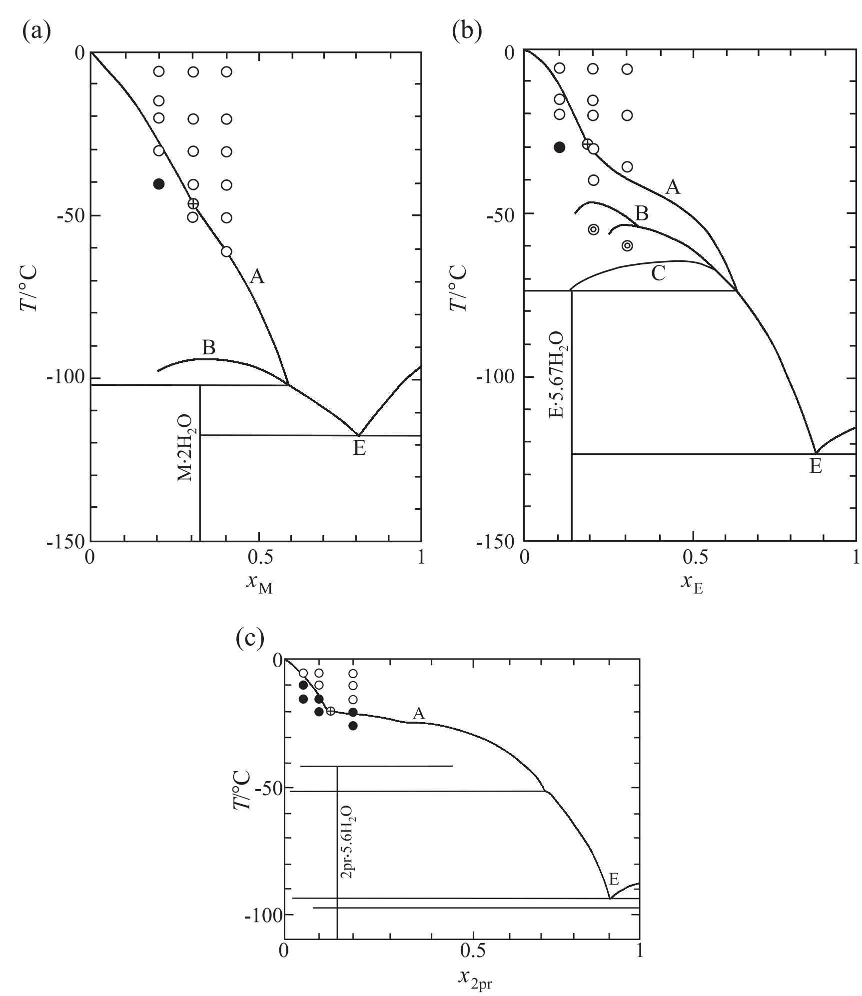

Fig. 1. Solid–liquid phase diagrams for (a) methanol–water, (b) ethanol–water, and (c) 2-propanol–water mixtures [3,4]. The composition, temperature, and state for sample mixtures in the present X-ray measurements are given by circles, except for mixtures at 25 °C; opened, filled, and double circles represent supercooled solution, crystallization of ice I_h, and crystallization of alcohol hydrate, respectively. (A) Solid phase firstly formed from supercooled liquid, (B) solid phase firstly formed from supercooled liquid, except for ice, (C) intermediate compound, and (E) eutectic point. The crossed circle gives an inflection point observed in the DSC experiments [3,4].

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