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Microheterogeneity of ethanol–water binary mixtures observed at the cluster level

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Abstract

The microscopic structures in ethanol–water binary mixtures were examined by analyzing the mass spectra of clusters generated through fragmentation of liquid droplets. From the effects of temperature and mixing ratios on the cluster structures, we have demonstrated that the ethanol–water binary mixtures have microscopic phase separation at the cluster level in wide mixing ratios: 10 vol.%<[EtOH]<90 vol.%. In this region, ethanol-rich clusters whose molecular composition is independent of the mixing ratio were observed at lower temperatures, and the ethanol-rich clusters interacted with water molecules with increasing temperature. Furthermore, we would like to present the mechanism for the formation of ethanol-rich clusters, induced by the contact with water molecules.

Keywords: Microheterogeneity; Cluster; Phase separation; Ethanol; Mixture

1. Introduction

Small alcohols such as methanol, ethanol and propanol are miscible with water at any mixing ratio. However, their binary mixtures deviate far from the ideal mixing, as shown by the anomalous thermodynamics or physicochemical properties changing nonlinearly with alcohol–water mixing ratio [1–3]. Accordingly, as a representative model system for non-ideal mixtures, an alcohol–water binary mixture has been widely studied through experimental and theoretical approaches such as mass spectrometry [2–8], neutron diffraction [9–11], X-ray diffraction [5,12,13], X-ray emission [14], Raman spectroscopy [15], molecular dynamic simulation [16], etc; as a result, microheterogeneous structures of alcohol–water binary mixtures at the molecular level became to be generally accepted. In the studies on microscopic structure of alcohol–water binary mixtures, we paid special attention to the experimental evidence on “microscopic phase separation” and “incomplete mixing”.

The microscopic phase separation was presented for ethanol–water binary mixtures by Nishi *et al* [15]. They observed an isosbestic point on low-frequency Raman spectra of ethanol–water binary solutions with varying mixing ratios. This indicated that the association state of molecules is mainly two in these binary solutions: the ethanol aggregate state and the water aggregate state. Interestingly, they suggested that the interactions between the ethanol aggregates and the water aggregates are weak to lead microscopic phase separation. Nishi also had mass spectrometric analysis of clusters in ethanol–water binary mixtures, and observed that the essential cluster structure in the solutions is maintained in wide ethanol mole fractions: 0.2–0.8 [5]. On the other hand, the incomplete mixing was suggested for methanol–water binary mixtures by Soper *et al.* on the basis of neutron diffraction experiments [9]. They noted that the local structure of water in a concentrated methanol–water solution is surprisingly close to its counterpart in pure water, and concluded that anomalous thermodynamics of alcohol–water binary mixtures arises from incomplete mixing at the molecular level. These reports have suggested that alcohol and water cannot be mixed at the molecular level, and that alcohol-rich and water-rich clusters coexist in the binary mixtures.

Such microheterogeneity influences solvation for a hydrophobic solute molecule. We have reported that preferential solvation is promoted by the microheterogeneity of binary mixed solvent [4,17,18]. As an industrial application of the microheterogeneity in ethanol–water binary mixtures, one of the authors (K. M.) has designed an advanced methodology to isolate ethanol from ethanol–water binary mixtures through

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ultrasonic atomization without heating [19,20]. The ultrasonic atomization for ethanol–water binary mixtures generates nanometer or less size droplets (mist particles), and it was confirmed that ethanol was concentrated in the resulting mist particles. We think that the ethanol-rich clusters in the mixtures will be preferentially transferred from the liquid to the gas phase due to the microscopic phase separation.

Here we would like to focus on such microheterogeneous structures in ethanol–water binary mixtures. By means of the mass spectrometry for clusters isolated through fragmentation of liquid droplets, we measured mass spectra of clusters in ethanol–water binary mixtures with varying mixing ratios and temperature. Our results indicate that ethanol-rich clusters and water-rich clusters coexist showing microscopic phase separation in wide mixing ratios. Moreover, here we would like to suggest that water molecules promote self-association of ethanol molecules as a result of balance of interactions, working at the same time in the condensed liquid phase. The molecular self-association in a mixture is generally promoted to complement a loss of stabilization energy induced by contacts with unfavorable molecules. The relationship among the relative interactions in a solution controls microscopic structure in the solution. We call this a "complementary relationship" [2,21,22]. The complementary relationship has been observed for the cluster formation in other binary mixtures [2] and electrolyte solutions [21,22], too. The clustering in alcohol–water mixtures is one of the examples for clustering inherent in multi-component solutions.

2. Experimental and methods

The microscopic structures of ethanol–water binary mixtures were analyzed through the mass spectrometry for clusters isolated from liquid droplets. The principle of this specially designed mass spectrometry has been reported previously [2,23]. The mass spectrometer consists of a four-stage differentially pumped vacuum chamber, a heated nozzle for sample injection, and a quadruple mass filter (EXTREL C50). Sample solutions are continuously injected into the vacuum chamber at a flow rate of 0.1 cm^3/min. When a part of a nozzle is heated, a constant flow of liquid droplets is generated due to the increase in the pressure inside the nozzle caused by the vaporization of a part of a solution. The nozzle temperature (T_{NZ}) to generate a constant flow of liquid droplets is depending on the ethanol–water mixing ratio; for example, $125 \leq T_{NZ} \leq 195$ °C for pure water and $90 \leq T_{NZ} \leq 130$ °C for 90 vol.% ethanol. When the T_{NZ} is lower and higher than these appropriate temperature regions, the thermal energy is not enough to generate a constant flow of liquid droplets, and is enough to break hydrogen-bonded clusters, respectively. Owing to the pressure gradient, the liquid droplets are led to the second and then the third chamber, which leads to fragmentation of the liquid droplets into clusters via adiabatic expansion. During the fragmentation process, the weakly interacting molecules are vaporized as monomeric molecules. The resulting clusters are ionized by an electron impact at 30 eV, and then analyzed by a quadruple mass filter.

Ethanol with special grade (>99.5%, Wako) was used. Water was purified using Milli-RX 12 and Milli-Q SP. TOC (Millipore) filters. The ethanol–water binary mixtures were prepared by measuring both volume and weight. The ethanol vol.% (mole fraction of ethanol, X_{EtOH}) in the prepared sample is as follows: 0 (0), 5(0.016), 10 (0.0329), 20 (0.0705), 30 (0.116), 40 (0.169), 50 (0.235), 60 (0.315), 70 (0.416), 90 (0.737), 95 (0.857), 100 (1).

3. Results and discussion

3.1. Mass spectrometric analysis of clusters

Mass spectra of clusters generated from various ethanol–water binary mixtures were measured at various temperatures. The temperature effect on the cluster structures observed through the mass spectrometry was strongly dependent on the ethanol–water mixing ratio. Here we would like to classify the ethanol–water binary mixtures into three regions on the basis of the observed cluster structures.

3.1.1. (1) $0 \leq [EtOH] \leq 10$–20 vol.%

In this region the microscopic structures were mainly composed of the hydrogen-bonding network of water molecules, and the hydrogen-bonding network was identical with the one in pure water. Figs. 1 and 2 show mass spectra of clusters generated from pure water and an ethanol–water binary mixture of [EtOH] = 5 vol.%, respectively.

At [EtOH] = 0 vol.% (pure water), the mass spectra of clusters could be measured at the nozzle temperatures (T_{NZ}) between 125 and 195 °C. The mass spectra observed at T_{NZ} = 125, 150, 175 and 195 °C are shown in Fig. 1a, b, c and d, respectively. At T_{NZ} = 125 °C, water clusters $H^+(H_2O)_n$ are observed only in smaller mass numbers (≤~500 amu). With the increase of the nozzle temperature from 125 to 150 °C, the water clusters with the relatively larger mass numbers are also formed, and the signal intensities are remarkably increased. With further increase of the nozzle temperature, the signal intensities are decreased, and most of the water clusters are decomposed at T_{NZ} = 195 °C. This temperature effect will be reasonably explained by the thermodynamic property of water droplets generated through the heated nozzle. At $T_{NZ} \leq 125$ °C, the thermal energy of the water droplets is too small to fragment the water droplets into clusters completely. This will lead to formation of the relatively small water clusters. Since the thermal energy is enough to fragment the water droplets into water clusters at T_{NZ} = 150 °C, formation of the water clusters attains a maximum around T_{NZ} = 150 °C. At $T_{NZ} > 150$ °C, the excess thermal energy is used for the breaking of the hydrogen bonds in the water clusters. At T_{NZ} = 195 °C, water clusters hardly exist, because most of the hydrogen bonds in the water clusters will be broken. This corresponds to the vaporization of water droplets. From this temperature dependence, the temperature of the water droplets can be roughly estimated to be 90–100 °C lower than the T_{NZ}.

The mass distribution of water clusters $H^+(H_2O)_n$ observed herein Fig. 1-b is in good agreement with the previously