Volumetric Behavior of Water–Alcohol Mixture at 673.15 K under high pressures. I. Methanol and Ethanol Solutions

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ABSTRACT

The densities of water-methanol and water-ethanol mixtures were measured with the laser-doppler type vibrating tube densimeter at 673.15 K in the pressure range of 25–40 MPa. The excess molar volumes V_m^E for all mixtures studied were evaluated from the experimental values, and the dependences of alcohol composition for V_m^E were fitted with Redlich-Kister equation. For all mixtures studied, V_m^E are positive deviations from the ideal mixtures in the whole composition range at 673.15 K. The composition dependences of V_m^E show maxima around 30–40 mol% of alcohol in water and the pressure dependences of V_m^E around 30 MPa at 673.15 K.

1. Introduction

It is generally agreed that water is an environmentally benign green solvent, and its high temperature and pressure region has recently attracted much attention in various industrial processes due to the wide tunability for its various solvent properties[1]. A water molecule has four hydrogen-bonding site, two of which are donors and others acceptors. Water molecules form the three-dimensional tetrahedral network structure by the effect of intermolecular hydrogen bonding which plays a dominant role for determining the solvent characteristic properties of aqueous solutions in sub- and supercritical region when a solute was introduced in aqueous solutions. Alcohols are also typical hydrogen-bonded fluids whose molecules have not only the hydrogen-bonding sites like water but also hydrophobic alkyl groups. For its amphiphilicity, the interactions between water and hydrophilic or hydrophobic group of alcohol have interested in the study of aqueous solutions. Alcohol molecules strongly affect the three-dimensional water structure, and the water-alcohol mixtures whose structure varies from bulk water are expected to very unique solvent depending on their composition for industrial green chemical applications.

For a better understanding of chemical and physical processes in fluids, it is

important to study the physical properties of fluids. Density is one of the most fundamental thermodynamic properties, and the nature of molecular transport in fluids depends on the density. The densities of water-alcohol mixtures have been studied exclusively and the structures of water-alcohol mixtures were discussed exclusively in terms of hydrogen-bonding structure[2–6]. At high temperature and pressure including sub- and supercritical region, however, there have been few studies[7–10] on the temperature and pressure dependences for water-alcohol mixtures. The discussion of the volumetric properties and the solvent structure for a series of water-alcohol mixtures at high temperatures and pressures will provide useful information about new reaction field and the design of new aqueous solvents in industrial processes.

In this study, the densities of water-methanol and water-ethanol mixtures were measured with the previously developed laser-doppler type vibrating tube densimeter at 673.15 K in the pressure range of 25-40 MPa. This is the first step of our volumetric study of water-alcohol mixtures at higher temperatures and pressures.

2. Experiment

The density measurement has been carried out at 673.15 K and 25, 30, 35, 40 MPa. The density determination is based on measuring the resonance frequency f (Hz) of the vibrating tube, through which the sample fluid flows continuously. The relationship between the density ρ (kg m^{-3}) of fluid and the resonance frequency f (Hz) of tube filled with fluid is given by

$$\rho = K_1 f^{-2} + K_2, \tag{1}$$

where K_1 (kg m^{-3} s^{-2}) and K_2 (kg m^{-3}) are instrument constants as a function of temperature and pressure. In this study, constants K_1 and K_2 are determined by the resonance frequencies of the three reference fluids of known densities: water, nitrogen, and carbon dioxide were chosen as reference fluids for calibration of the instrument. The equation of state for water is given by Wagner *et al.* [11] and that of nitrogen and carbon dioxide by Span *et al* [12, 13].

3. Results and discussions
3.1. Densities and excess molar volumes

Composition dependences of the experimental densities ρ of water-methanol and water-ethanol mixtures at 673.15 K and high pressures are shown in Fig. 1. The densities of water[11] and methanol[14] are also plotted in Fig. 1. As shown in Fig. 1, the densities of all the mixtures studied are increased with increasing pressures. For all the mixtures studied,
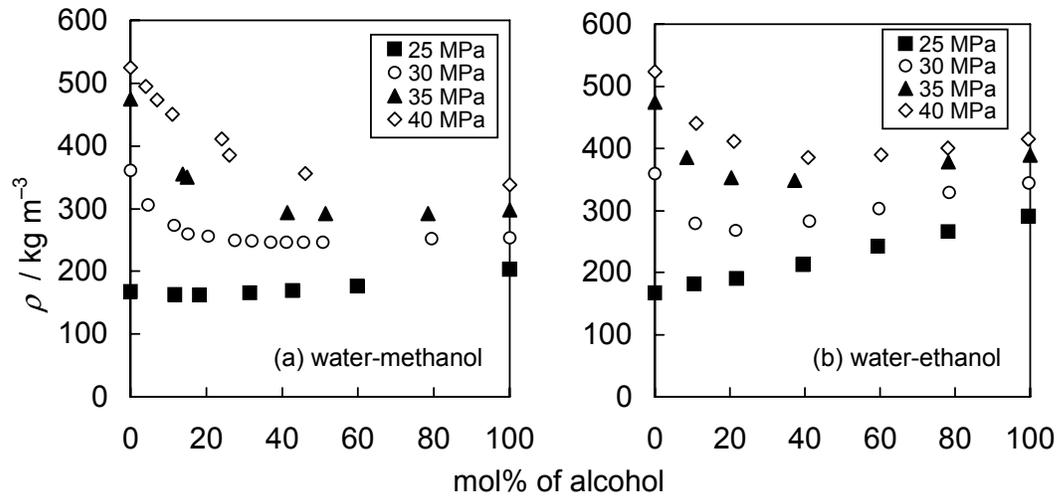
Fig. 1. Composition dependences of the densities ρ for (a) water-methanol and (b) water-ethanol mixtures at 673.15 K and high pressures.

the densities at 25 MPa slightly increased with increasing the alcohol composition in water. In the pressure range of 30–40 MPa, on the other hand, the densities decreased with increasing the alcohol composition in water-rich region and increased in alcohol-rich region.

To discuss the deviation of the volumetric behaviors of water-alcohol mixtures studied from those of ideal mixtures, the excess molar volumes of water-alcohol mixtures were estimated. The excess molar volume V_m^E (cm^3 mol^{-1}) is given as follows:

$$V_m^E = V_m - \left\{ X V_{m,A}^0 + \left(1 - X\right) V_{m,W}^0 \right\}, \tag{2}$$

$$V_m = \left\{ X M_A + \left(1 - X\right) M_W \right\} / \rho. \tag{3}$$

In equations (2) and (3), X is the mole fraction of alcohol in water, V_m is the molar volume of mixtures studied, and V_m^0 the molar volume of the pure component. M is the molecular weight, and the suffix A and W stand for alcohol (methanol or ethanol) and water, respectively. The composition dependences of V_m^E obtained by equation (2) were fitted with the Redlich-Kister equation[15] given by

$$V_m^E = X \left(1 - X\right) \left\{ A + B\left(1 - 2X\right) + C\left(1 - 2X\right)^2 \right\}, \tag{4}$$

where A, B, and C (cm^3 mol^{-1}) are the fitting coefficients.

The composition dependences of V_m^E and the fitting curve with the Redlich-Kister equation for all the water-alcohol mixtures studied are shown in Fig. 2. As shown in Fig. 2, the excess molar volumes of all the mixtures show the positive deviations in the whole composition range and the composition dependences of V_m^E show maxima around 30-40
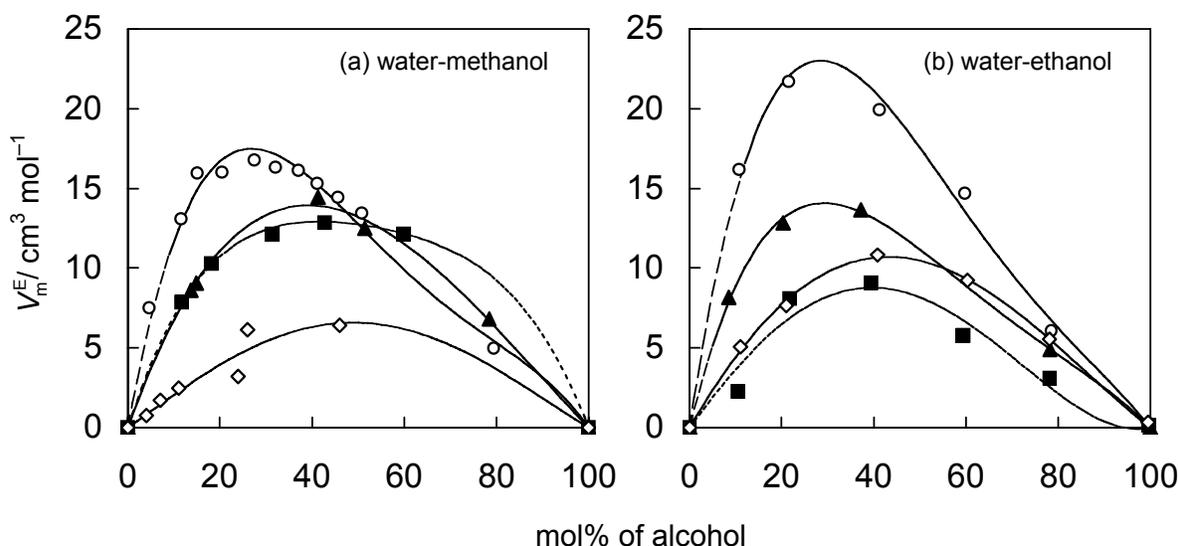
Fig. 2. Composition dependences of the excess molar volumes V_m^E for (a) water-methanol and (b) water-ethanol mixtures at 673.15 K and high pressures. Dotted lines (••••••) indicate the fitting curve of the Redlich-Kister equation at 25 MPa, short dashed lines (– – –) at 30 MPa, short dashed and dotted lines (– • – • –) at 35 MPa, and solid lines (——) at 40 MPa.

mol% of alcohol in water. In ambient condition, for example, the composition dependences of V_m^E for water-alcohol mixtures show the negative deviation from the ideal mixtures[2,3]. This negative deviation is caused by two factors. One is the strong hydrogen-bonded interaction between water and hydrophilic –OH group of alcohol molecules, and the other is the hydrophobic hydration[16]: water molecules surround and form a clathrate-like 'iceberg' structure around the hydrophobic alkyl group of alcohol molecule. In this study, however, although the hydrogen-bonded structure is found in hydrogen-bonded fluid like water and methanol and plays an important role at high temperatures and pressures[17–21], the effect of the structure enhancement of water around hydrophobic group is scarce. For all the water-alcohol mixtures studied, not only the hydrogen-bonded interaction between water and hydrophilic –OH group of alcohol molecules but also the effect of water molecules keeping away from the hydrophobic group of alcohol molecule is significant to the positive deviation of V_m^E.

In water-rich region, V_m^E of ethanol solutions are larger than methanol ones. In alcohol-rich region, on the other hand, the difference of V_m^E between two mixtures was not significant. These results indicate that the effect of the structural change for water-alcohol mixtures in water-rich region is larger than that in alcohol-rich region. In water-rich region, the magnitude of the effect of water molecules keeping away from the hydrophobic group of alcohol molecule depends on the length of alkyl group of alcohol molecules. At high

pressures, hydrogen bonds among molecules are strengthened and begin to condense. These concerted effects, the effect of water molecules keeping away from the hydrophobic group of alcohol molecule and compression effect, may give the maximum around 30 MPa for the pressure dependences of the excess molar volumes V_m^E at 673.15 K.

3.2. Contribution of water-alcohol interactions

The partial molar volumes of water $\overline{V_{m,W}}$ or alcohol (methanol or ethanol) $\overline{V_{m,A}}$ were roughly estimated from the fitting curve with Redlich-Kister equation to discuss the volume change of water-alcohol mixtures. To focus on the contribution of water–alcohol interactions on the volumetric behavior of water-alcohol mixtures, here we briefly examined the concentration and pressure dependences for the relative partial molar volumes of water $\overline{V_{m,W}}/V_{m,W}^0$ and alcohol $\overline{V_{m,A}}/V_{m,A}^0$ at 673.15 K ($V_{m,W}^0$ and $V_{m,A}^0$ are the molar volume of water and alcohol, respectively). The composition dependences of the relative partial molar volumes ($\overline{V_{m,W}}/V_{m,W}^0$ and $\overline{V_{m,A}}/V_{m,A}^0$) are exhibited in Figs. 3 and 4, respectively. For water-methanol mixtures as shown in Fig. 3, composition dependences of $\overline{V_{m,W}}/V_{m,W}^0$ and $\overline{V_{m,A}}/V_{m,A}^0$ at 30 and 35 MPa are more remarkable than those at 25 and 40 MPa. This indicates that the effect of water-methanol interaction is significant on the volumetric change at 30 and 35 MPa. For water-ethanol mixtures as shown in Fig. 4, composition dependences of the relative partial molar volumes for water-ethanol mixtures qualitatively agree with those for water-methanol mixtures.

As shown in Figs. 3 and 4, the relative partial molar volumes of all the components hardly show the composition dependences at 25 and 40 MPa. At 25 MPa, near the critical pressure of water, the displacement between water and alcohol molecules are larger than that at higher pressures because the partial molar volumes and thermal mobility of molecules in solution are enlarged. The effect of the thermal motions of molecules is more important than the effect of the interactions between water-alcohol molecules for the volume change of solutions at 25 MPa and 673.15 K. At 40 MPa and 673.15 K, on the other hand, hydrogen bonds among molecules are strengthened and then broken and all the molecules in solution begin to condense. The effect of water–alcohol interactions is also less important, but the compression effect plays a dominant role for the volume change of water-alcohol mixtures at 40 MPa and 673.15 K.

As compared Fig. 3(b) with Fig. 4(b), $\overline{V_{m,A}}/V_{m,A}^0$ of ethanol is larger than that of methanol in water-rich region at 30 and 35 MPa. This indicates that the effect of water-ethanol interaction seems to be larger than that of water–methanol interaction at 30 and 35 MPa at 673.15 K. The effect of the length of alkyl groups of alcohol molecules may be
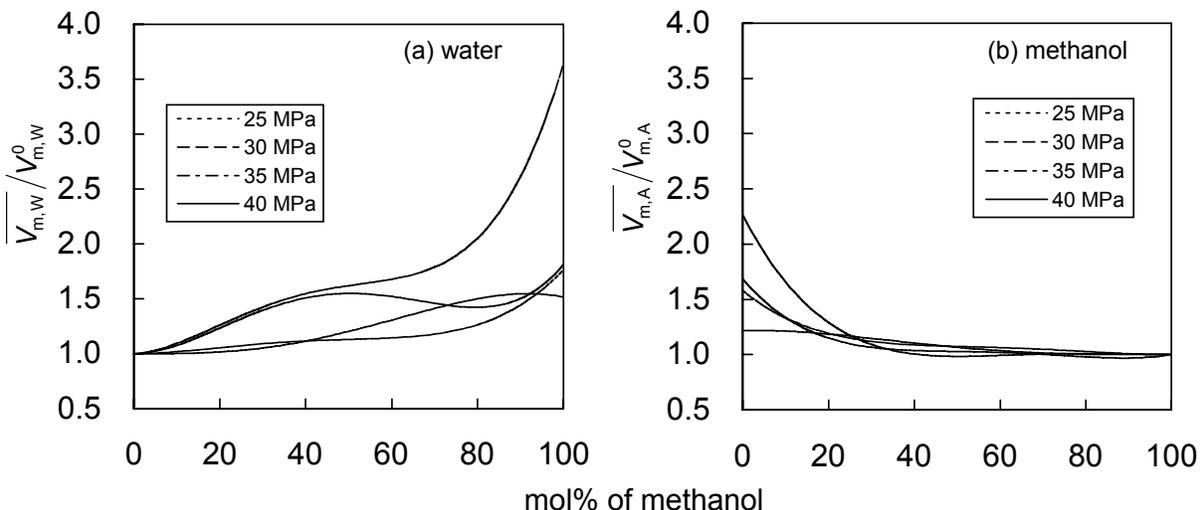
Fig. 3. Composition dependences of relative partial molar volumes for (a) water $\overline{V_{m,W}}/V_{m,W}^0$ and (b) methanol $\overline{V_{m,A}}/V_{m,A}^0$ in water-methanol mixtures at 673.15 K and high pressures. The lines indicate the same as Fig. 2.
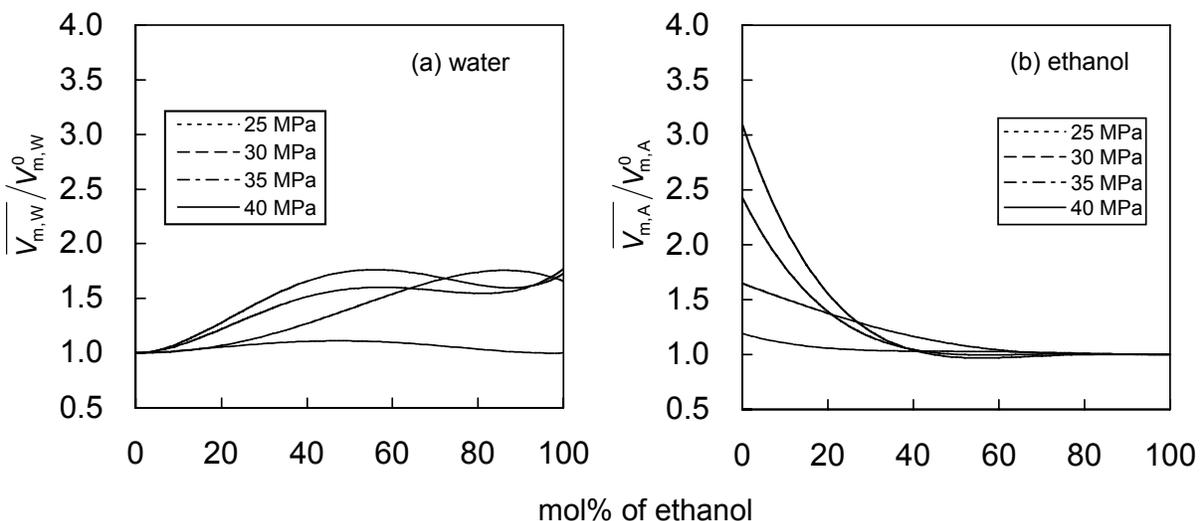
Fig. 4. Composition dependences of relative partial molar volumes for (a) water $\overline{V_{m,W}}/V_{m,W}^0$ and (b) ethanol $\overline{V_{m,A}}/V_{m,A}^0$ in water-ethanol mixtures at 673.15 K and high pressures. The lines indicate the same as Fig. 2.

significant to the volume change of water-alcohol mixtures. For detail discussions about the effect of the alkyl group of alcohols on the volume change at 673.15 K, we are preparing the density measurement in a series of water-alcohol mixtures.

4. Conclusion

In this paper, we reported the experimental densities ρ of methanol and ethanol aqueous solutions at 673.15 K in the pressure range of 25–40 MPa, and estimated the excess molar volumes V_m^E and fitted V_m^E with the Redlich-Kister equation. For all the solutions

studied, the concentration dependence of V_m^E gave the positive deviations from the ideal solution at all the experimental conditions. The concerted effects, the dispersion of water molecules around the hydrophobic group of alcohol molecule and compression effect, may give the maximum around 30–40 mol% of alcohol concentration and 30 MPa for the excess molar volumes at 673.15 K. Using the estimated $\overline{V_m^E}$ by the Redlich-Kister equation, the partial molar volumes of water $\overline{V_{m,W}}$ and alcohol $\overline{V_{m,A}}$ and the relative partial molar volumes $\overline{V_{m,W}}/V_{m,W}^0$ and $\overline{V_{m,A}}/V_{m,A}^0$ were roughly examined to discuss the contribution of the effect of water–alcohol interactions on the volume change of solutions 673.15 K. The comparison V_m^E between methanol and ethanol aqueous solutions indicated that the magnitude of water–methanol interactions were larger than that of ethanol solutions at 30–35 MPa and 673.15 K. The effect of thermal motions of molecules was significant at 25 MPa and compression effect became dominant at 40 MPa on the volume change of solutions at 673.15 K.

Based on the obtained results and discussion, we will then extend the PVT study to a wide variety of alcohol aqueous solution over a wide range of thermodynamic conditions and give useful information of solvent as a new reaction field for industrial green chemical and physical processes.

Acknowledgement

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