

Near-Infrared Study of Water and Water-Benzene Mixtures at High Temperatures and Pressures

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Near-infrared absorption of water and water-benzene mixtures has been measured at temperatures and pressures in the range of subcritical and supercritical condition of water. The molar absorption intensity of the OH stretching overtone transition of neat water was obtained. It decreases linearly with increasing pressure in the region of gas and gaslike density. Enthalpy for dimerization has been estimated to be 15 ± 3 kJ/mol from temperature dependence of the slopes. Molar absorption intensity in the liquidlike-density region exhibits a good correlation with the first band moment. Using this correlation, we have estimated concentrations of water in both the water-rich phase and the benzene-rich phase of the mixtures from the integrated absorption intensities of the OH stretching overtone band. Benzene concentrations were obtained from the CH stretching overtone band of benzene. From these concentrations, the densities of the both phases were estimated and compared with the average densities before mixing, which were calculated from literature densities of neat water and neat benzene. It is found that anomalously large volume expansion on the mixing occurs in the vicinity of the critical region of the mixtures. Furthermore, magnitude of the relative volume change increases with decreasing molar fraction of benzene in the present experimental range. It is suggested that dissolving a small amount of benzene in water induces a change in the fluid density from a liquid-like condition to a gas-like condition in the vicinity of the critical region.

1. Introduction

Water at high temperatures and pressures in the subcritical to supercritical region exhibits intriguing properties. With increasing temperature, water becomes a good solvent for nonpolar compounds such as hydrocarbons [1–3], which are usually thought of hydrophobic substances. For example, water and benzene become completely miscible at any mixing ratio at temperatures and pressures above 573 K and 200 bar, respectively, forming a homogeneous phase. Such water-hydrocarbon mixtures are important in a wide range of industries such as petrochemical industry, oil refineries, and an environment-protecting technology, and a number of thermodynamical data have been reported so far [4–7]. In contrast to those extensive studies on the thermodynamic properties, molecular-level structures of the high-temperature mixtures had remained largely unknown until quite recently.

We have recently shown that *in situ* infrared measurements are useful for obtaining molecular-level information of the high-temperature

mixtures. We have found that water concentration in aromatic hydrocarbons increases rapidly with increasing temperature, and the relative ratio of hydrogen-bonded dimeric water to monomeric water increases with increasing temperature up to 523 K at a constant pressure of 100 bar [8]. This fact indicates that the effect of the solubility increase on the monomer-dimer equilibrium is superior to the entropy effect that is unfavorable to water-water association. In addition, we have shown that a concept of the π -hydrogen bonding is useful to understand interaction between water and aromatic hydrocarbons even at the high temperatures [9]. Moreover, using the concentrations of both water and hydrocarbons, we have found anomalous volumetric behavior of the mixtures in the vicinity of the critical region [10]. These findings have been obtained for the first time by the *in situ* spectroscopic measurements of one phase, the hydrocarbon-rich phase, of the two coexisting fluid phases.

These infrared measurements, however, were restricted to the hydrocarbon-rich phase of the mixtures. We could not study water and the

water-rich phase due to too heavy infrared absorption of water. We then attempted to study both the water-rich and hydrocarbon-rich phases as well as neat water using near-infrared absorption of the overtone OH stretching transition, which has some advantage over the fundamental absorption. Intensity of the overtone band is two orders of magnitude smaller than the fundamental band, and the integrated intensity can be obtained with much less uncertainty using an easily controlled optical pathlength. In addition, the effect of hydrogen bonding on the absorption intensity is much milder for the overtone band than for the fundamental band, the latter of which increases remarkably with increasing hydrogen-bond strength. Therefore, it is possible to study water and water-hydrocarbon mixtures in the wide range of density from gaslike to liquidlike condition. This paper reports our recent near-infrared measurements of neat water and both the water-rich and benzene-rich phases of the water-benzene mixtures. Some of the results have been published elsewhere [11, 12]. Concentrations of both water and benzene are estimated from respective integrated intensities of near-infrared absorption bands, and the volumetric behavior of the mixtures is discussed.

2. Experimental Methods

2.1. Apparatus and procedure Figure 1 shows a schematic of the high-temperature-pressure cell.

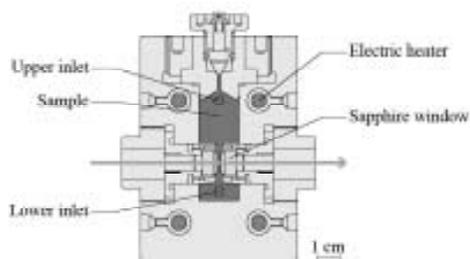


Fig. 1. Schematic of the high-temperature-pressure cell.

The cell body is made of Hastelloy, a nickel-based superalloy, and the maximum operating temperature and pressure are 773 K and 500 bar, respectively. The windows are colorless sapphire with an effective aperture for optical transmission of 6 mm, and are pressed against optically polished flat surfaces of window plugs for a pressure seal by the unsupported area principle. The optical path length of a sample is 1.46 mm. The cell is heated by rod-shaped electric heaters that are inserted into holes bored in the cell body, and the sample temperature is measured with a chromel-alumel

thermocouple. The cell has three sample inlets. The one on the top is for initial filling of sample liquids and the two on the side are for transmitting compressed liquids into the cell with a syringe pump for liquid chromatography. The upper one of the two side inlets is for hydrocarbons and the lower one for water. Pressure of the sample is measured with a pressure transducer of a semiconductor strain gage, which is set between the cell and the pump.

Near infrared transmission spectra were measured with a Perkin-Elmer System 2000 Fourier-transform spectrometer, which was equipped with a near-infrared source and a near-infrared detector. Spectral measurements were performed with 2 cm^{-1} resolution at sample temperatures in the 373–673 K range and pressures in the 20–400 bar range. Each of the experimental temperature-pressure points was attained at a slow enough rate, and the phase equilibrium of a sample fluid was confirmed by a spectrum that remained unchanged for at least an hour. The samples were neat water and water-benzene mixtures with various mixing ratios.

2.2. Observed Spectra Figure 2 displays the observed spectra of the near-infrared OH-stretching overtone transition of neat water at pressures in the 20 to 400 bar range and at a constant temperature of 673 K, where an inset figure shows the spectra at lower pressures on an expanded scale. The rotational fine structure is clearly observed at the lowest two pressures, but gradually collapses to a smooth envelop with P, Q and R branches as the pressure increases. At the higher pressures, the P, Q and R branches merge into a single band.

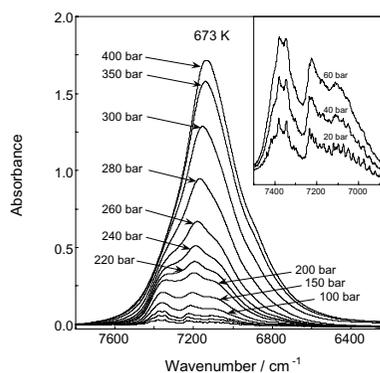


Fig. 2. Observed near-infrared OH-stretching overtone absorption of water at various pressures and 673 K. (Reproduced from Ref. 11 with permission. Copyright (2003) American Institute of Physics).

However, the R branch does not completely fade out even at 400 bar, but remains as a slight bump on the higher-wavenumber side of the band. Thus the absorption band still retains rotational features to a certain extent at 673 K and 400 bar, where the density is 29 mol/l. This fact indicates that an appreciable proportion of the molecules rotate quite freely, although they undergo frequent collisions with other molecules. The spectra of water have usually been decomposed to symmetric components with Lorentzian and/or Gaussian profiles to estimate the ratios of the different hydrogen bonded states of water molecules. However, such a method is not useful for analysis of the present spectrum. A contribution of the free molecules exhibiting the remnant of the P, Q and R branches is difficult to separate from the heavily overlapping components bands. Therefore, to discuss the state of hydrogen bonding in water, we use the integrated intensity and the first moment of the absorption bands.

Figure 3 shows observed near-infrared spectra of the water-rich phase (a) and the benzene-rich phase (b) of the water-benzene mixtures at a constant pressure of 200 bar. These spectra were obtained using samples with initial volumetric water/benzene ratios of 4.5 : 1.5 (a) and 1.5 : 4.5 (b), respectively.

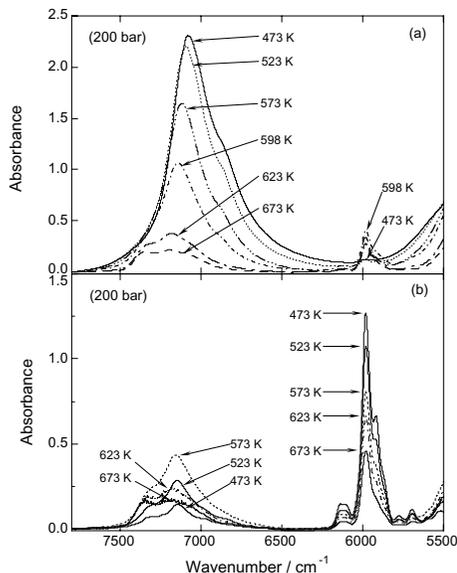


Fig. 3. Near-infrared spectra of (a) the water-rich phase and (b) the benzene-rich phase of the water-benzene mixtures.

In addition to the OH-stretching overtone

absorption of water around 7100 cm⁻¹, the CH-stretching overtone absorption of benzene is observed at around 6000 cm⁻¹. The absorption of water in the water-rich phase (a) decreases with increasing temperature, while the absorption of benzene as a solute increases. A detailed description of these spectral variations was given in the previous paper [12]. For the spectra of the benzene-rich phase (b), the benzene absorption decreases monotonously with increasing temperature. On the other hand, the absorption of water as a solute initially increases with increasing temperature up to 573 K, and then decreases at higher temperatures.

3. Discussion

3.1 Molar absorption intensities of neat water The integrated intensities of the OH stretching overtone absorption bands of neat water have been estimated in the frequency range of 6200 to 7800 cm⁻¹. The molar absorption intensities, A^m , are obtained from the integrated intensities divided by the molar concentration of water C_w [13]:

$$A^m = \frac{1}{C_w l} \int \ln(I_0/I) d\nu, \quad (1)$$

where l denotes the sample thickness, 0.146 cm, and I and I_0 transmission spectra of the cell with and without sample, respectively. To exclude effect of reflection at a fluid-window interface and allow for the overlapping with another band at lower frequency, a base line for integration was drawn by connecting the signal levels of the both ends of the range.

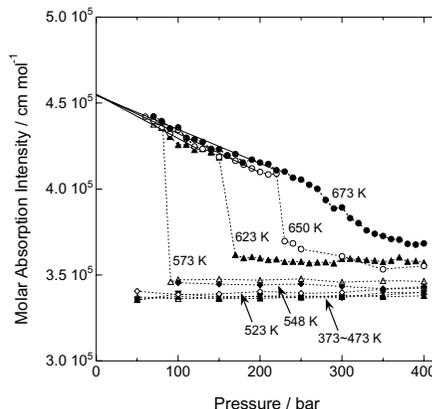


Fig. 4. Effect of pressure on the molar absorption intensity of the OH overtone band of water at various temperatures. (Reproduced from Ref. 11 with permission. Copyright (2003) American Institute of Physics).

For spectra recorded at pressures below 50 bar that exhibit a distinct rotational fine structure, the intensities were inaccurate due to uncertainty in the position of the baseline and are excluded from the following discussion.

The resulting molar absorption intensities decrease with increasing pressure as shown in Fig. 4. The discrete jumps at 573 and 623 K are due to the gas-to-liquid transition. At 650 K, which is slightly above the critical temperature, 647.1 K [13], the intensities are extremely sensitive to pressure at around the critical point and we have obtained a quasi-discrete jump. The intensities at 673 K, on the other hand, vary smoothly with pressure. The decrease of the molar absorption intensities with increasing pressure is attributed to the effect of hydrogen bonding. This is in contrast to the pressure dependence of the OH stretching fundamental absorption intensity, which shows a remarkable increase as the hydrogen bonds strengthen [14].

The approximately linear decrease of the intensity in the low-pressure region is attributed to a pressure-induced shift of the monomer-dimer equilibrium. The observed molar absorption intensity is given by an average of those of the free molecules, A_m , and the dimers, A_d ,

$$A = (1 - x) A_m + x A_d, \quad (2)$$

where x denotes a mole fraction of water molecules forming the dimers. In the range of $x \ll 1$, x is approximately given by $\square KP$ [11] where K and P denote the equilibrium constant and the total pressure, respectively. Then, Eq. (2) becomes

$$A = A_m + \square KP (A_d - A_m). \quad (3)$$

Least squares fitting was performed for the plots of the three higher temperatures with constraint of the same intercept. A value of $A_m = (4.55 \pm 0.02) \times 10^5$ cm/mol is obtained from the intercept. Assuming A_m and A_d to be constant, the temperature dependence of the slope, $s_A = 2K(A_d - A_m)$, provides enthalpy change for the dimerization,

$$\Delta H = -R \frac{\partial \ln K}{\partial (1/T)} = -R \frac{\partial \ln[-s_A]}{\partial (1/T)} \quad (4)$$

where R is the gas constant. From the plots of $\ln[-s_A]$ against inverse temperature, we obtained a ΔH value of 15 ± 3 kJ mol⁻¹. This is in good agreement with the previously reported result, 16.65 ± 3.77 kJ mol⁻¹, which was obtained from analysis of the absorption intensity of the OH stretching fundamental transition [14].

At present, the equilibrium constant K can not be experimentally determined, since the value of A_d is unavailable and seems difficult to measure. Nevertheless, a rough estimation of A_d is possible by use of a matrix isolation study and theoretical calculations. Using the result, we estimate the equilibrium constant K to be 9×10^{-4} , 10×10^{-4} , 11×10^{-4} bar⁻¹ at 673, 650, and 623 K, respectively, and the molar fraction of dimerization, x , is estimated to be 0.18, 0.20, and 0.22, at 100bar [11]. Therefore, roughly 20% of water molecules take part in the dimerization at 100 bar in the above temperature range.

In addition to the molar absorption intensity of the OH stretching transition, the position of the band center provides another measure of hydrogen bond strength. It is well known that the band center shifts to lower wavenumber as the hydrogen bonds strengthen. Since the overtone band concerned in the present study is not symmetrical, we take the first moment, the center of gravity of the band,

$$\bar{\nu} = \int \nu \ln(I_0/I) d\nu / \int \ln(I_0/I) d\nu, \quad (5)$$

as the band center. The resulting first moments at densities in liquid and liquid-like regions show a good correlation with the molar absorption intensities, and the relationship is given by the following expression [12]

$$(A^m/\text{cm mol}^{-1}) = 7.4108 \times 10^7 - 2.1260 \times 10^4 (\bar{\nu}/\text{cm}^{-1}) + 1.5317 (\bar{\nu}/\text{cm}^{-1})^2 \quad (6)$$

Since both the quantities are mainly determined by the hydrogen-bonding state of water molecules, we have assumed that the relationship can be applied to aqueous mixtures in which the molar absorption intensity is determined by the hydrogen-bonding state. From the first moment of the band, which can be obtained from the observed absorption profile without knowledge of concentration, the molar absorption intensity is given by the relationship (6). Then the water concentration in the aqueous mixtures can be estimated from the observed absorption intensity divided by the molar absorption intensity. This spectroscopic method is particularly useful to estimate the water concentration in one phase of the two-phase coexistence region of aqueous mixtures such as water-hydrocarbon mixtures at high temperatures and pressures, where only *in situ* spectroscopic measurements provide reliable information without disturbing the equilibrium.

3.2 Estimates of concentrations in the mixtures.

Form the observed integrated band intensities of the mixtures, A_{obs} , the molar concentration of water is given by

$$(C_W / \text{mol l}^{-1}) = 10^3 \times (A_{\text{obs}} / \text{cm}^{-2}) / (A^m / \text{cm mol}^{-1}) \quad (7)$$

An integration range of the benzene bands was taken to be 5824–6064 cm^{-1} , and the benzene concentrations, C_B , were obtained by directly comparing the absorption intensities of mixtures and neat benzene, using literature data of concentrations of neat benzene at the same temperature and pressure [15].

3.3. Volumetric behavior of the mixtures

Densities of the mixtures are readily given from concentrations of water and benzene as,

$$\rho_{\text{mix}} = (C_W M_W + C_B M_B) \quad (8)$$

where M_W and M_B are molar weights of water and benzene, respectively. To elucidate volumetric properties of the mixtures, we have estimated relative volume change on the mixing given by,

$$\frac{\Delta_{\text{mix}} V}{V_0} = \frac{V_{\text{mix}} - V_0}{V_0} = \frac{\rho_0}{\rho_{\text{mix}}} - 1 \quad (9)$$

where ρ_0 is an average density before mixing given by,

$$\rho_0 = \frac{C_W M_W + C_B M_B}{(C_W M_W / \rho_W) + (C_B M_B / \rho_B)} \quad (10)$$

where ρ_W and ρ_B denote densities of neat water and neat benzene, respectively. The resulting values of the relative volume change are plotted against pressure at each temperature in Fig. 5.

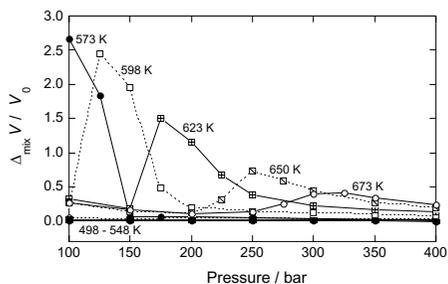


Fig. 5. Relative volume change on the mixing for the water-rich phase of the mixtures.

At temperatures below 548 K, the relative volume change is very small, a few hundredths, and slightly decreases with increasing pressure. This is similar to the volumetric behavior of ordinary liquid mixtures at temperatures and pressures far from the critical condition. On the other hand, at the higher temperatures in the two-phase and the one-phase regions, the relative volume change is anomalously large particularly at low pressures. At 573 K and 100 bar, for example, the relative volume change reaches about 2.7, which means 3.7 times volume expansion on the mixing. The jumps at 598 K and 623 K are due to the jumps in the calculated densities by the gas-to-liquid transition of water.

Figure 6 shows a contour map of the relative volume change on the P-T phase diagram, where variations in the relative volume change are expressed by gradation. The darker region indicates higher degree of the volume expansion. It is found that the anomalously large volume expansion occurs in a narrow region, which is enclosed by an extended line of the three-phase equilibrium curve and the one-phase critical curve, and the gas-liquid equilibrium curve of water. The volume change is particularly large in the area immediately above the vapor pressure curve of water. This fact suggests that the dissolution of benzene, which itself is in the supercritical condition, induces a density change of the water-rich phase from a liquid-like condition to a gas-like condition.

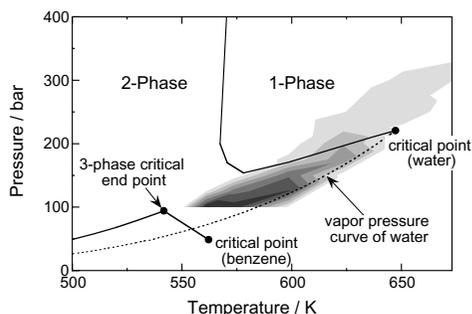


Fig. 6. Contour map of the relative volume change on the pressure-temperature phase diagram of the water-benzene mixtures. The darker region indicates higher degree of the volume expansion.

3.4. Composition dependence of the relative volume change To elucidate a relationship between the volumetric behavior of the water-rich phase and that of the benzene-rich phase, we have examined how the relative volume change varies with the molar fraction of benzene. Near-infrared

measurements have been performed for samples with different initial volume ratios of water and benzene, which were set at 5.5:0.5, 5.0:1.0, 4.0:2.0, 0.5:5.5, 1.0:5.0, and 1.5:4.5, respectively, while the results described so far in this paper are of the sample with the initial ratio of 4.5:1.5. The observed spectra have been treated in the same way as described in the experimental section and the values of the relative volume changes are estimated at various temperatures and pressures. The results have indicated that the pressures at which the maximum volume change occurs at each temperature are the same for all the samples, although the magnitudes of the relative volume change vary with composition. Figure 7 shows plots of the maximum values at a few temperatures against molar fraction of benzene. It is found that the magnitude of the relative volume change on the mixing increases with decreasing molar fraction of benzene, except at 650 K and 250 bar where the plots exhibit a little decrease at the lowest benzene fraction. These facts suggest that dissolving a small amount of benzene in liquid water at a pressure, slightly above the vapor pressure, induces a transition in the fluid density from liquid-like to gas-like condition.

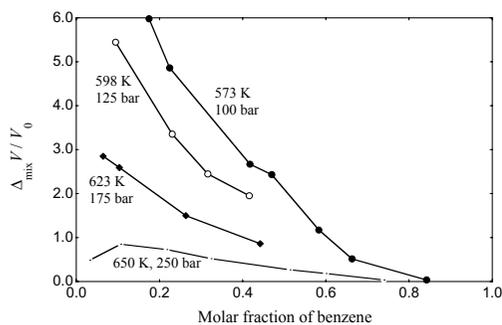


Fig. 7. Plots of the relative volume change of the water-benzene mixtures against molar fraction of benzene.

We have recently found a similar volumetric behavior to that in Fig. 5 for binary mixtures of water with toluene, ethylbenzene [16] and hexane [17] in the hydrocarbon-rich phase. Therefore, the anomalously large volume expansion on mixing should be characteristic of water-hydrocarbon mixtures in the vicinity of the critical region.

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