Infrared study of water–benzene mixtures at high temperatures and pressures

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Abstract
Infrared spectra of water–benzene mixtures have been measured at temperatures
and pressures in the 473–648 K and 100–350 bar ranges, which extend over the
two- and one-phase regions of the mixtures. Molar concentrations of water and
benzene in the benzene-rich phase were estimated from absorption intensities
of the OH stretching band of HDO and combination bands of benzene,
respectively. Using these results, densities of the benzene-rich phase were
estimated and compared with the average densities before mixing which were
calculated from literature densities of the neat liquids at the same temperature
and pressure. An anomalously large volume change for mixing has been found
in the vicinity of the critical region of the mixture.

1. Introduction

Water and hydrocarbons are almost immiscible or only poorly miscible at room temperature.
However, their mutual solubilities increase with increasing temperature under pressure. Water
and benzene, for example, become completely miscible at temperatures and pressures above
570 K and 200 bar [1–3], as seen in the pressure–temperature phase diagram shown in figure 1.

Such a wide range variation of the solubility as a function of temperature and pressure will
be useful to a study of solubility phenomena in terms of intermolecular interaction. In addition,
the water–hydrocarbon mixtures at high temperatures and pressures have been given much
attention over a wide range of industry including oil refineries, the petrochemical industry [4, 5]
and environment-protecting technology where hydrothermal oxidation reactions are applied
for the destruction of toxic waste chemicals [6, 7]. For these applications, knowledge of
the thermodynamic properties of the mixtures is indispensable and they have been widely
studied [4, 5, 8–10]. However, the molecular level structure of water–hydrocarbon mixtures
remains largely unknown.

Recently, we have shown that infrared *in situ* measurements are useful for a molecular level
study of water–hydrocarbon mixtures at high temperatures and pressures [11–13]. The infrared
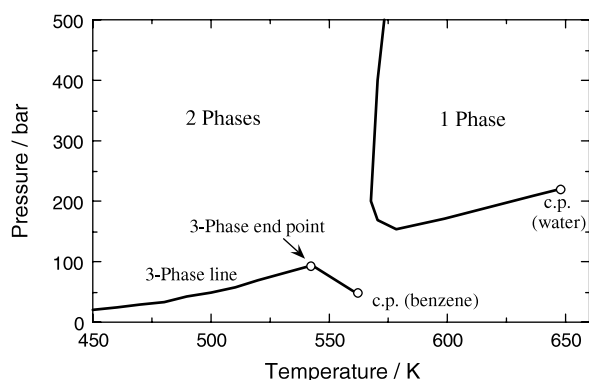
Figure 1. The pressure–temperature phase diagram for water–benzene mixtures.
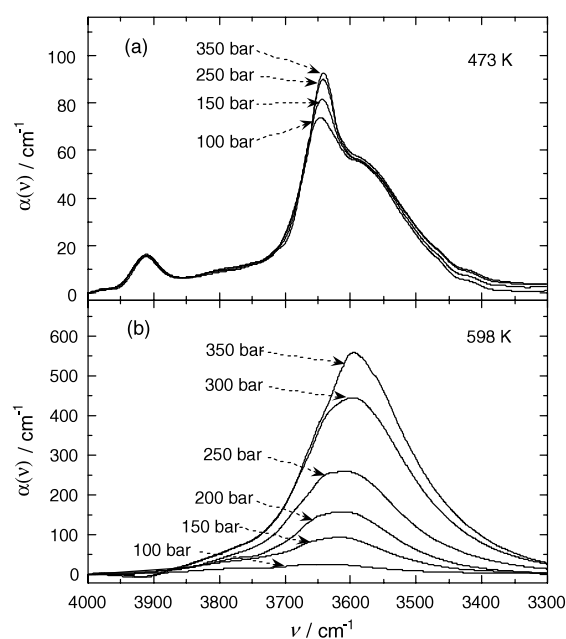

Figure 2. Infrared absorption of HDO in the benzene-rich phase at 473 and 598 K.

OH stretching absorption intensity, as a measure of water concentration in the hydrocarbon-rich phase, shows remarkable temperature–pressure dependence. Examples of the observed spectra are shown in figure 2.

A peak and a shoulder, at around 3648 and 3580 cm^{-1}, respectively, seen in the spectra at 473 K, are assigned to hydrogen-bond-free and hydrogen-bonded OH groups, respectively. The previous band shape analysis showed that the ratio of the hydrogen-bonded species to the hydrogen-bond-free species increases with increasing temperature in the 373–533 K range at 100 bar [11]. This indicates that the rate of increase in water concentration with increasing temperature is large enough to surmount the entropy effect that is unfavourable to the hydrogen-bonded association. The difference in vertical scale between the spectra at 473 and 598 K indicates that the water concentration increases by several times as the temperature goes up from 473 to 598 K at the higher pressures. Moreover, the two component bands seem to merge
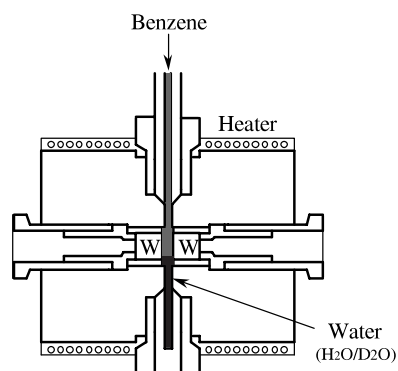
Figure 3. A schematic diagram of the high-pressure cell.

into a single band at 598 K. This fact suggests that interchange between the hydrogen-bond-free and hydrogen-bonded states of the OH groups in the hydrogen-bonded water clusters becomes rapid enough at the higher temperatures [12].

In this paper, we have studied the volume behaviour of the benzene-rich phase of the water–benzene mixtures. The densities of the benzene-rich phase are obtained from spectroscopically determined concentrations of water and benzene as a function of temperature and pressure. The water concentrations are estimated from infrared absorption intensities of the OH stretching bands of HDO in benzene. The concentrations of benzene are obtained from near-infrared absorption intensities of benzene. Such observation of the one phase in the two-phase coexistence region has become possible for the first time with *in situ* infrared measurements.

2. Experimental details

The detail of the high-pressure cell has been described elsewhere [12]. The cell body is made of nimonic alloy 80 A and the windows are colourless sapphire cylinders. The effective aperture for the optical transmission is 6 mm and the optical path length of the sample fluid is 1 mm. The water specimen was a mixture of H_2O and D_2O with a molar ratio of 1:20 and, as a result, the ratios of the isotopic species were H_2O:HDO:D_2O = 1:40:400. Consequently, the observed OH absorption bands can be assigned only to HDO to a good approximation, and are free from complication due to overlap of the symmetric and antisymmetric OH stretching absorptions. A small amount of the water specimen is put in the cell, and then compressed liquid benzene is transmitted into the cell with a syringe pump for liquid chromatography. The level of the water–benzene interface was adjusted to slightly below the optical axis to measure the benzene-rich phase, as shown schematically in figure 3. Spectral measurements were performed with a BOMEM DA3 Fourier transform spectrometer at sample temperatures in the 473–648 K (± 0.5 K) range and pressure in the 100–350 bar (± 1 bar) range. Each of the experimental temperature–pressure points was attained at a slow enough rate, and the phase equilibrium of the mixture was confirmed by a spectrum that was unchanged for at least an hour. The sample was not agitated, to avoid emulsification.

3. Results and discussion

Figure 4 shows examples of near-infrared absorption bands of benzene in neat benzene and in the benzene-rich phase of the water–benzene mixture. The absorption in the 4470–4800 cm^{-1}
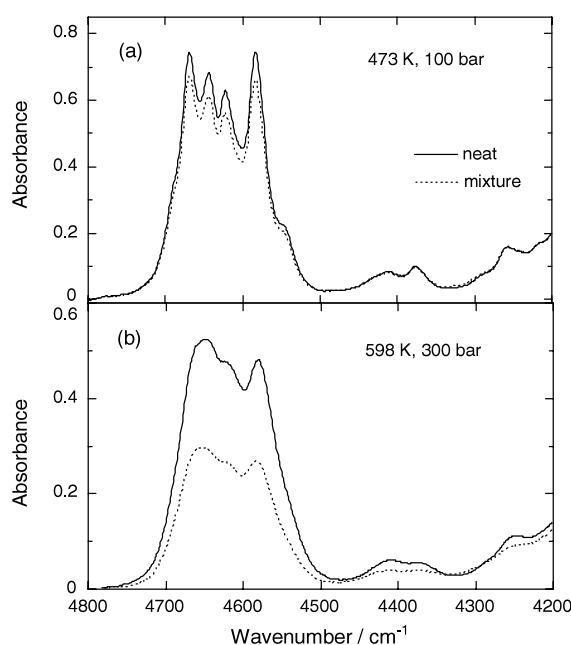
Figure 4. Near-infrared absorption of benzene.

range is assigned to combination transitions of benzene. The band profiles for the two temperatures look rather different. This is explained by the difference in broadening of the component bands due to the vibrational and/or reorientational relaxation which is accelerated by the thermal motion of the molecules.

The reduction in absorbance from neat benzene to the mixtures is due to the decrease of the benzene concentration, which is caused by dissolution of water into the benzene-rich phase. To estimate the benzene concentration in the benzene-rich phase, we need the molar absorption intensity of benzene. Using the integrated intensity combined with the literature density of neat benzene at the same temperature and pressure, we have estimated the molar absorption intensity of neat benzene. The resulting values are almost independent of temperature and pressure as shown in figure 5, and we have obtained $A_{neat}^m = (2.15 \pm 0.05) \times 10^5$ cm mol^{-1} [13]. This value is consistent with the previously reported absorption intensity of 2.19×10^5 cm mol^{-1} in the 4493–4763 cm^{-1} range at 298 K and 1 bar [14]. In addition, the peak position and band profile for the mixture look very similar to those for the neat liquid as seen in figure 4. These facts indicate that the molar absorption intensity of that band is little affected by the condition of the surrounding benzene molecules. Therefore, we assume that the concentration of benzene in the benzene-rich phase, C_B, can be estimated from the absorption intensity of the mixture, A_{mix}, divided by the A_{neat}^m-value:

$$C_B = A_{mix}/A_{neat}^m. \tag{1}$$

The resulting values are plotted against pressure in figure 6.

Figure 7 shows plots of the integrated intensities of the OH stretching bands of HDO against pressure for each temperature. The temperature–pressure dependence of the intensity can be properly understood by referring to the phase diagram shown in figure 1. At constant temperatures lower than the three-phase end-point temperature, 542.6 K, the intensity as a measure of the water concentration is approximately independent of pressure. On the other
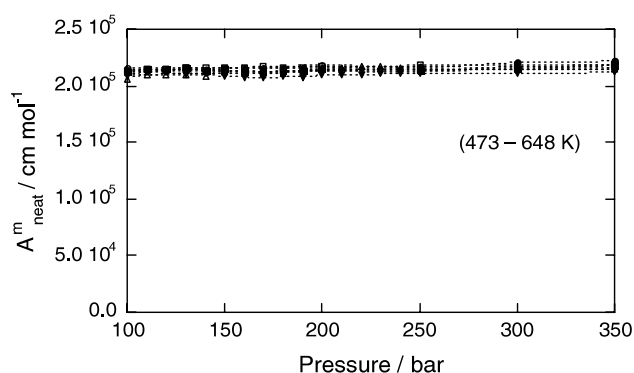
Figure 5. Plots of the molar absorption intensity of neat benzene against pressure at various temperatures.
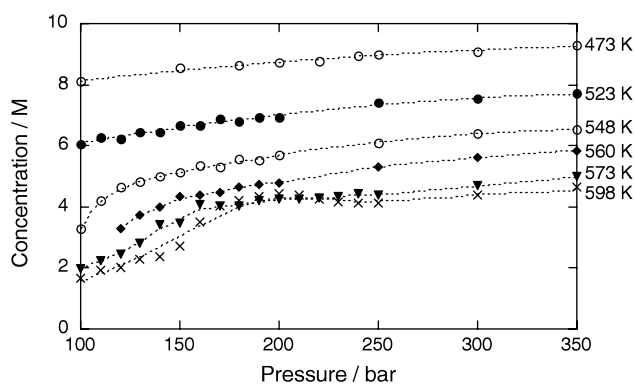

Figure 6. The molar concentration of benzene in the benzene-rich phase of the water–benzene mixtures.

hand, at temperatures higher than the three-phase end point, the water concentration exhibits remarkable pressure dependence. It increases by an order of magnitude as the pressure rises from 100 to 350 bar. The temperature-dependent change of the intensity at constant pressure is clearly shown by other plots in figure 8. It is found that, at constant pressure, the water concentration increases with increasing temperature up to a certain temperature, and then decreases steeply at higher temperatures. The turning of the concentration occurs near the temperature where a constant-pressure line crosses the extended line of the three-phase equilibrium curve or the two-phase critical curve on the phase diagram shown in figure 1. These remarkable temperature and pressure dependences of the water concentration are considered to be characteristic features of the water–hydrocarbon mixtures in the vicinity of the critical region.

The molar absorption intensity of the OH stretching band of water, in contrast to that of benzene, varies significantly with the state of the water molecules. It is particularly sensitive to the hydrogen bonding. To estimate the water concentration in benzene, we have proposed an empirical relationship between the molar absorption intensity A^m and the peak wavenumber v_0 or the first band moment, both of which are sensitive to the strength of the hydrogen bonding.
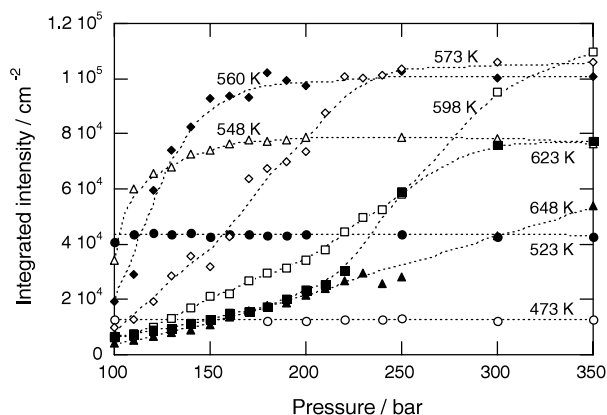
Figure 7. Integrated intensities of HDO in the benzene-rich phase plotted against pressure.
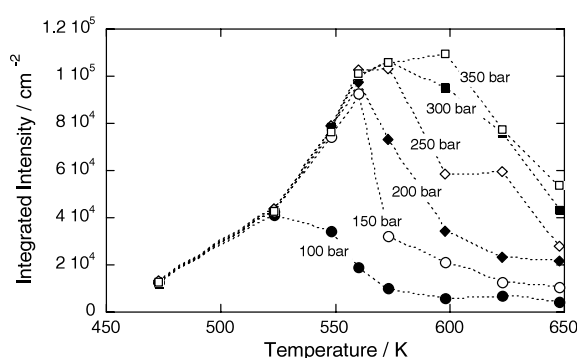

Figure 8. Integrated intensities of HDO in the benzene-rich phase plotted against temperature.

The results are as follows [12]:

$$A^m = A_0^m / \Theta \tag{2}$$

$$\Theta = 9n/(n^2 + 2)^2 \tag{3}$$

$$A_0^m / (10^6 \, \text{cm} \, \text{mol}^{-1}) = 3.0 + 5.37 \times 10^{-2} (3707 - \nu_0 / \text{cm}^{-1})$$

$$+ 2.12 \times 10^{-4} (3707 - \nu_0 / \text{cm}^{-1})^2 \tag{4}$$

where Θ denotes the internal-field correction factor given by the refractive index n of the fluid mixture. It has been found that the values of Θ are in a rather narrow range, 0.82–0.90, for the present experimental conditions, and the temperature–pressure dependence of the water concentration has a close resemblance to that of the integrated absorption intensity shown in figure 7. The water concentrations obtained were in the 1–8 M range.

Making use of the benzene and water concentrations, C_B and C_W, respectively, we estimate densities of the benzene-rich phase by

$$\rho_{mix} = M_B C_B + M_W C_W \tag{5}$$

where M_B and M_W denote the molar weights of benzene (C_6H_6) and water (D_2O), respectively. The resulting densities are plotted against pressure at each temperature in figure 9(a). At 473 and 523 K, which are below the three-phase critical end-point temperature, the densities slightly increase with increasing pressure. At the higher temperatures, in contrast, the densities
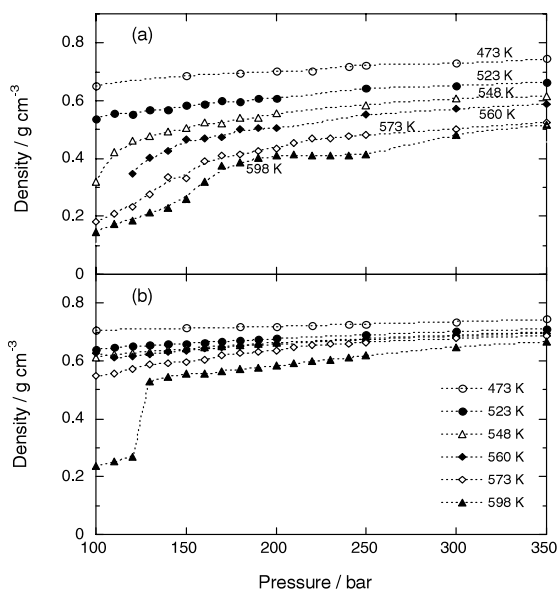
Figure 9. Experimental (a) and calculated (b) densities of the benzene-rich phase of the water–benzene mixtures.

increase significantly with pressure. The steepest increase in the lower-pressure range is found at 548 K which is near the three-phase end point. These features are similar to those seen in the temperature–pressure dependence of the water concentrations or the OH stretching band intensities shown in figure 7. This fact indicates that the behaviour of the density as well as that of the water concentration shows the near-criticality of the mixture.

The volume property of the water–benzene mixture can be characterized by comparison with average densities before mixing, which are given by the densities of neat D_2O water [15, 16] and neat benzene [17], ρ_W and ρ_B, respectively, with experimental molar concentrations as follows:

$$\rho_0 = (M_W C_W + M_B C_B)/[(M_W C_W/\rho_W) + (M_B C_B/\rho_B)]. \tag{6}$$

The resulting ρ_0-values are plotted in figure 9(b). If the molar volumes of the neat components were additive, the calculated densities would agree with the experimental densities. However, all the experimental densities are obviously smaller than the corresponding calculated densities at the same temperature and pressure, as seen in figure 9. This fact indicates that water dissolution in benzene gives rise to an increase in the partial molar volume of water and/or benzene. At the lower temperatures, the calculated densities are only slightly dependent on the pressure and the temperature. In contrast, the experimental densities of the mixtures decrease significantly with increasing temperature and steeply increase with increasing pressure particularly at 548 K. The jump of the calculated densities at 598 K seen in figure 9(b) is due to the gas-to-liquid transition of neat water. Except the jump, the temperature–pressure dependence of the calculated densities is significantly milder than that of the experimental densities.

To get further insight into the mixing state, we estimate the relative change in the volume for mixing by

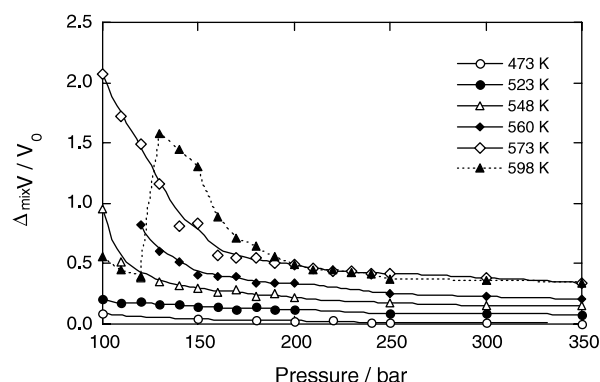$$\Delta_{mix}V/V_0 = \rho_0/\rho_{mix} - 1. \tag{7}$$

Figure 10. The relative volume change for mixing for the benzene-rich phase of the water–benzene mixtures.

The resulting values are plotted against pressure in figure 10. At 473 and 523 K, the volume change for mixing is small and slightly decreases with increasing pressure. This looks to be an ordinary volume behaviour of a liquid mixture at conditions far from the critical region. At the higher temperatures, in contrast, the volume change for mixing becomes anomalously large in the low-pressure region. It reaches about 2 at 573 K and 100 bar, which means a three-times swelling of the fluid.

The jump at 598 K is caused by the jump in the calculated densities mentioned above, which is due to the gas-to-liquid transition of the neat water. This indicates that the dissolution of liquid water into the supercritical benzene gives rise to distinctly larger swelling than the dissolution of steam. Unfortunately, the present experimental pressures are limited to being higher than 100 bar, and we could not find the maxima of the volume change at 548, 560 and 573 K. However, it is likely that jumps similar to that at 598 K would exist at pressures lower than 100 bar.

The anomalously large volume change for mixing occurs at temperatures higher than the critical temperature of benzene, and may indicate that the density of the supercritical benzene or the benzene-rich phase changes from a liquid-like condition to a gas-like condition on dissolution of water. These phenomena are probably characteristic of fluid mixtures in the vicinity of the critical region, and may be understood on the basis of the differences between intermolecular water–water, water–benzene and benzene–benzene interactions.

4. Conclusions

The volume change for mixing of water and benzene has been studied by means of infrared *in situ* measurements in the temperature–pressure range which extends over the two- and one-phase regions of the mixtures. The densities of the benzene-rich phase are estimated from the spectroscopically determined concentrations of water and benzene. The results are compared with the average densities before mixing which are calculated using literature densities of neat water and neat benzene at the same temperature and pressure. The anomalously large volume change for mixing has been obtained in the vicinity of the critical region of the water–benzene mixture. At 573 K and 100 bar, the supercritical fluid of benzene swells by about three times on dissolution of water. This may indicate a change in nature of the benzene-rich phase from the liquid-like condition to the gas-like condition. This is probably characteristic of fluid mixtures in the near-critical region, and could be observed for the first time in *in situ* infrared measurements on one phase in the two-phase coexistence region.

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