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Citation	The Journal of Chemical Physics, 117(4), 1682-1685 https://doi.org/10.1063/1.1488580
Issue Date	2002
Doc URL	http://hdl.handle.net/2115/1397
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Type	article
File Information	JCP117-4.pdf



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Infrared study of anomalous volume behavior of water–benzene mixtures in the vicinity of the critical region

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(Received 6 July 2001; accepted 1 May 2002)

Volume behavior of water–benzene mixtures at temperatures and pressures in the 473–623 K and 100–350 bar ranges, respectively, has been studied by infrared *in situ* measurements. The densities of the benzene-rich phase were estimated from the spectroscopically determined concentrations of water and benzene and compared with the average densities before mixing, which were calculated using literature densities of neat water and neat benzene at the same temperature and pressure. Anomalously large volume change for mixing has been found in the vicinity of the critical region of the water–benzene mixtures. © 2002 American Institute of Physics.
[DOI: 10.1063/1.1488580]

I. INTRODUCTION

Water–hydrocarbon mixtures at high temperatures and pressures have received much attention in various research areas from basic chemical physics to industrial applications. Although the mutual solubility of water and hydrocarbons is very poor at room temperature, it increases significantly with increasing temperature under pressure. Water and benzene, for example, becomes completely miscible at any mixing ratio at temperatures and pressures above 570 K and 200 bar, respectively.^{1–3} Thermodynamic properties of such mixtures have been widely studied,^{4–8} being indispensable to design various industrial plants and processes, such as petrochemical plants^{4,5} and hydrothermal destruction of toxic waste chemicals.^{9–11} The wide range variation of the solubility will be useful to a study of intermolecular interaction of water with hydrocarbons, which is important for understanding biomolecular phenomena such as formation and stability of native structures of proteins.^{12,13} From these viewpoints, it is intriguing how the water and hydrocarbon molecules mix with each other at high temperature and pressure. However, a molecular level structure of the water–hydrocarbon mixtures remains largely unknown.

In recent articles,^{14–16} we have shown that infrared *in situ* measurements are useful to a molecular level study of the water–hydrocarbon mixtures at high temperatures and pressures. The infrared OH stretching absorption of HDO dissolved in the hydrocarbon-rich phase, being a measure of water concentration, varies remarkably with temperature and pressure. The temperature–pressure dependence of the water concentration is properly understood by making reference to the phase diagram of the mixture. Figure 1 shows a pressure–temperature phase diagram for water–benzene mixtures. With increasing temperature at constant pressures, in the experimental ranges of 473–648 K and 100–350 bar, water concentration in hydrocarbons increases remarkably and reaches maximum near the one-phase critical curve, and then steeply decreases at higher temperatures (cf. Fig. 6 in Ref.

15). On the other hand, pressure dependence of the water concentration depends significantly on the temperature. At temperatures below the liquid–liquid–gas three-phase critical end point, the water concentration is almost independent of pressure. On the contrary, at temperatures higher than the critical end point, the water concentration increases by an order of magnitude as the pressure increases from 100 to 350 bar (cf. Fig. 4 in Ref. 15). Such remarkable temperature–pressure dependence of the water concentration is considered to be a characteristic feature of the mixture in the vicinity of the critical region.

Very recently, we measured near-infrared absorption bands of benzene, toluene, and ethylbenzene in their mixtures with water.¹⁷ It has been found that the absorption intensities of these bands show a similar temperature–pressure dependence to that of the water concentration mentioned above. Therefore, it is interesting to examine how the overall density of the hydrocarbon-rich phase varies with temperature and pressure. The infrared *in situ* measurements are particularly useful for such a study on the density behavior of one of the two coexisting phases.

This article deals with the temperature and pressure dependence of the density, or the volume property, of the benzene-rich phase in the vicinity of the critical region of the water–benzene mixtures, aiming to obtain a further insight into the critical behavior of the water–hydrocarbon mixtures.

II. EXPERIMENTAL METHOD AND RESULTS

The experimental setup and the high-pressure cell have been described elsewhere.¹⁵ In brief, the cell is made of ni-monic alloy 80A (anticorrosion Ni-base superalloy) and the windows are colorless sapphire cylinders. The effective aperture for the optical transmission is 6 mm and the optical path length is 1 mm. The temperature and pressure of the sample fluid are measured with a thermocouple and a semiconductor strain gauge, respectively. Water specimen was a mixture of H₂O and D₂O with a molar ratio of 1:20, and ratios of the isotopic species are estimated to be 1:40:400 for H₂O, HDO, and D₂O. Therefore, contribution of H₂O to the

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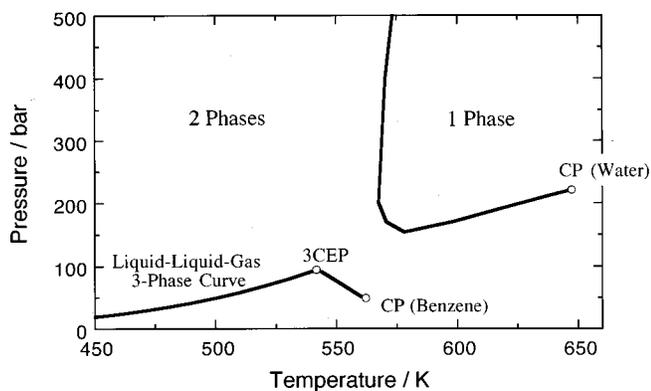


FIG. 1. Pressure-temperature phase diagram for water-benzene mixtures. CP: critical point, 3CEP: three-phase critical end point.

OH stretching absorption can be approximately neglected and the observed OH bands are assigned exclusively to HDO. Thus the OH bands become free from the complication due to overlap of the symmetric and antisymmetric OH stretching absorption, which is inevitable when neat H_2O is used.

Figure 2 shows examples of the observed OH absorption bands at 473 and 598 K. The peak at around 3648 cm^{-1} and the shoulder at around 3580 cm^{-1} , which are clearly seen in the spectra at 473 K, are assigned to hydrogen-bond-free and hydrogen-bonded OH groups, respectively.¹⁴ A small band at about 3910 cm^{-1} is assigned to a combination band of D_2O and excluded from estimation of the integrated intensities of

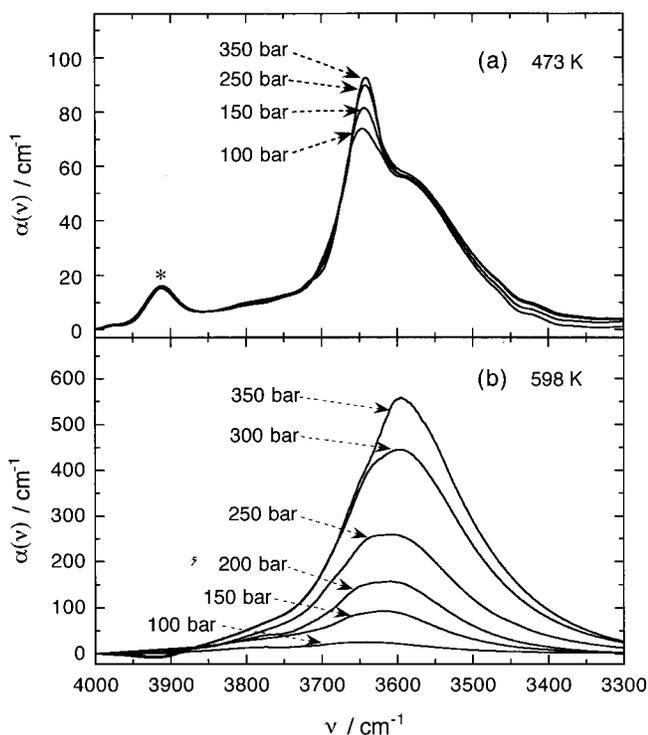


FIG. 2. Infrared OH stretching absorption of HDO in benzene at 473 and 598 K. A band marked with * is assigned to a combination transition of D_2O .

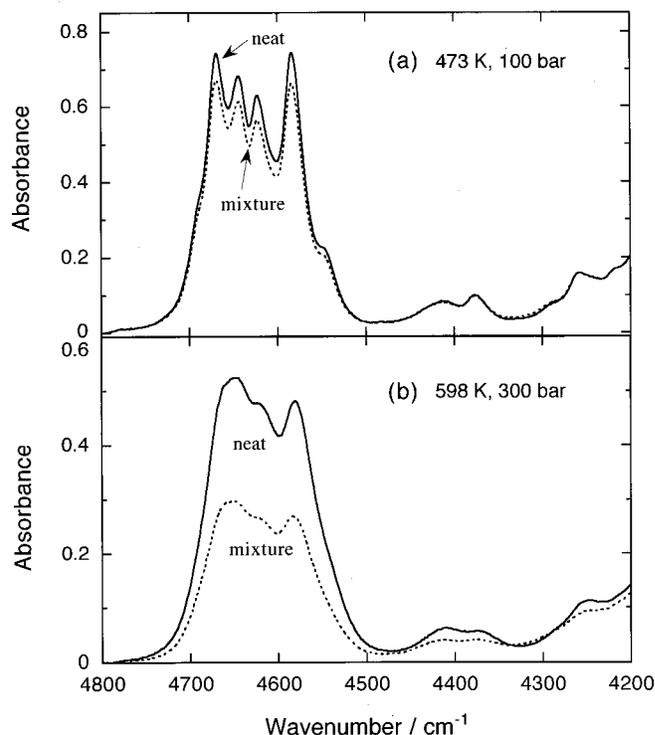


FIG. 3. Near-infrared spectra of benzene at 473 and 598 K for neat benzene (solid line) and the benzene-rich phase of the water-benzene mixture (broken line).

the OH absorption. The corresponding D_2O absorption at higher temperatures has been canceled out by using D_2O -saturated benzene, instead of neat benzene which was used for the 473 K spectra, as reference for obtaining the absorption band of HDO. In the low-temperature range, 373–533 K, the two component bands could be separated from each other and the intensity ratio of the hydrogen-bonded band to the hydrogen-bond-free band increased with increasing temperature.¹⁴ This fact indicates that the rate of increase in water solubility in benzene is large enough to surmount the entropy effect which is unfavorable to water-water association. At 598 K, these two bands seem to merge into a single band, which may indicate rapid exchange between the hydrogen-bond-free and hydrogen-bonded states of the OH groups within a hydrogen-bonded water cluster in benzene.^{15,16} A difference in the vertical scale between Figs. 2(a) and 2(b) indicates that the water concentration in benzene increases by several times as the temperature goes up from 473 to 598 K at the higher pressures. At 473 K, a small pressure dependence can be seen near the band maximum, but integrated intensity as a measure of the water concentration is roughly independent of pressure in the 100–350 bar range. On the contrary, the water concentration increases by an order of magnitude in the same pressure range at 598 K, and the steepest increase occurs in the vicinity of the one-phase critical curve.¹⁵

Figure 3 shows observed near-infrared bands of benzene, which are assigned to combination transitions. The peak positions and the band profiles of neat benzene and water-benzene mixture are very similar to each other. This fact suggests that these combination transitions are little affected

by the environmental condition of the benzene molecules, and we may assume that the molar absorption intensity is the same for neat benzene and water–benzene mixtures. The molar absorption intensity, A_{neat}^m , for the neat benzene has been estimated from the integrated intensity using the literature density data at the same temperature and pressure.¹⁸ The resulting A_{neat}^m values were found to be almost independent of temperature and pressure in the 473–648 K and 100–350 bar ranges, respectively, and we obtained $A_{\text{neat}}^m = (2.15 \pm 0.05) \times 10^5 \text{ cm mol}^{-1}$ for the absorption in the 4470–4800 cm^{-1} range.¹⁷ This value is consistent with the previously reported molar absorption intensity of $2.19 \times 10^5 \text{ cm mol}^{-1}$ in the 4493–4763 cm^{-1} range at 298 K and 1 bar.¹⁹ These facts support the above-mentioned assumption for the molar absorption intensity. Then, we have obtained concentration of benzene in the benzene-rich phase from the absorption intensity divided by the above-mentioned value of A_{neat}^m .

The molar absorption intensity of the OH stretching band of water, on the other hand cannot be directly measured. It varies significantly with states of the water molecules, mainly depending on hydrogen bond or hydrogen-bond-like interaction.²⁰ It is known that the peak position of the OH band is also sensitive to the hydrogen bonding and shifts to lower frequency as the hydrogen bond strengthens then a relationship between the molar absorption intensity and the peak frequency will be useful for estimation of the molar absorption intensity. In the previous study,¹⁵ we derived an empirical relationship between the molar absorption intensity and the peak frequency of the OH band using the data of gas, liquid and solid water, and estimated the molar concentration of water in benzene. The uncertainty of the estimated water concentration may be in the 10%–20% range.¹⁷ Although it is based on rather crude approximations, we make use of the results since any other reliable methods are not available at present.

III. DISCUSSION

Using the water and benzene concentrations, C_W and C_B , respectively, obtained from the infrared intensities,^{15,17} we estimate densities of the benzene-rich phase by

$$\rho_{\text{mix}} = C_W M_W + C_B M_B,$$

where M_W and M_B denote the molar weights of water and benzene, respectively. The resulting densities are plotted against pressure at each temperature in Fig. 4(a).

At 473 and 523 K, which are below the three-phase critical end point temperature, 543 K,²¹ the densities increase slightly with increasing pressure. At higher temperatures, on the contrary, the densities make a significant increase, and show the steepest rise at 548 K in the lower pressure range, which is near the three-phase critical end point. These features bear a remarkable resemblance to the pressure-dependent change in the water concentration observed in the previous studies.¹⁵

To characterize the mixing state of the water–benzene mixtures, we make a comparison between average densities before mixing and the experimental densities of the mixtures. The average density before mixing, ρ_0 , is given by

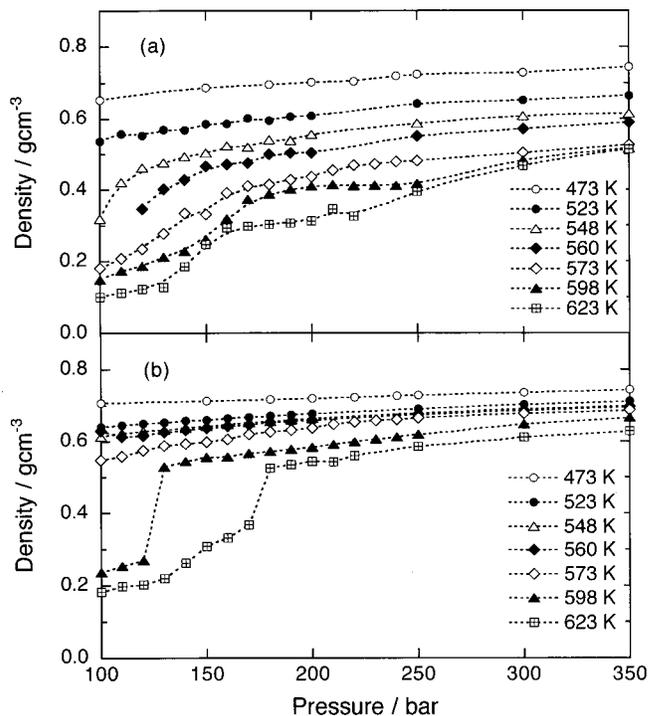


FIG. 4. Experimental (a) and calculated (b) densities of the benzene-rich phase of the water–benzene mixtures.

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

where, ρ_W and ρ_B are the densities of neat D_2O water^{22,23} and neat benzene,¹⁸ respectively, and C_W and C_B are experimental molar concentrations mentioned above. The resulting ρ_0 values are plotted in Fig. 4(b). If the molar volumes of the neat components were additive, the average densities before mixing would agree with the experimental densities of the mixtures at the same temperature and pressure. Obviously, this is not the case for the water–benzene mixtures as seen in Fig. 4. All the experimental densities are smaller than the average densities before mixing at the same temperatures and pressures. This fact indicates that water dissolution in benzene gives rise to increase in partial molar volumes of water and/or benzene. The discrete jumps in the calculated densities at 598 and 623 K are caused by the gas-to-liquid transition of neat water. Except for the jumps, the temperature-pressure-dependence of the calculated densities is milder than that of the experimental densities. At the lower temperatures, the calculated densities are only slightly dependent on the pressure and temperature. On the contrary, the experimental densities of the mixtures decrease significantly with increasing temperature and steeply increase with increasing pressure at temperatures higher than the three-phase critical end point temperature.

These intriguing properties of the mixtures can be clearly represented by a relative volume change for mixing given by

$$\frac{\Delta_{\text{mix}} V}{V_0} = \frac{\rho_0}{\rho_{\text{mix}}} - 1$$

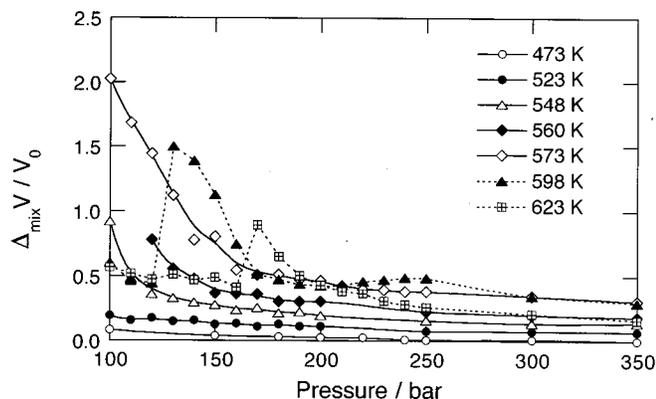


FIG. 5. Relative volume change for mixing for the benzene-rich phase of the water-benzene mixtures.

and the resulting values are plotted against pressure in Fig. 5. At 473 and 523 K, the volume change for mixing is small and slightly decreases with increasing pressure and about 1% at 473 K and 350 bar. This is like an ordinary volume behavior of a liquid mixture in the region far from the critical condition. At the higher temperatures, the volume change for mixing becomes anomalously large particularly in the low-pressure region. At 573 K and 100 bar, it reaches about 2, which means three times swelling of the fluid. The jumps at 598 and 623 K are due to the jumps in the calculated densities mentioned above, which are caused by the gas-to-liquid transition of neat water. This fact indicates that the dissolution of liquid water into the supercritical benzene give rise to distinctly larger swelling than the dissolution of gas water. The similar jumps would be observed at lower temperatures in the pressure range below 100 bar, if we could extend the experimental pressure range to lower than 100 bar.

The anomalously large volume change for mixing may indicate that the density of the supercritical benzene or the hydrocarbon-rich phase changes from a liquid-like condition to a gas-like condition by dissolution of water. This volume behavior is probably characteristic of water-hydrocarbon mixtures in the vicinity of the critical region. It may have some relation to the large excess molar volumes of fluid mixtures of carbon dioxide with ethene²⁴ and sulfur hexafluoride²⁵ observed at about room temperature and near

the critical pressures of the component fluids. These properties of AB binary mixtures in the vicinity of the critical region should be explained by the difference among the three types of intermolecular interaction, A-A, B-B, and A-B, and their magnitudes relative to thermal kinetic energy.

ACKNOWLEDGMENTS

This work was supported by the Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan (No. 13440169) and by the Research Fellowships of the Japan Society for the Promotion of Science for Young Scientist to S. F.

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