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Spectroscopic study of water-NaCl-benzene mixtures at high temperatures and pressures

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Near-infrared and ultraviolet spectra of water-NaCl-benzene mixtures have been measured in the 473–573 K and 100–400 bar range and 373–498 K and 50–300 bar range, respectively. Concentrations of water in the benzene-rich phase and benzene in the water-rich phase were estimated from integrated intensities of the absorption bands. It is found that addition of NaCl in the aqueous phase suppresses transfer of water into the benzene-rich phase, and the relative decrease in water solubility in benzene exhibits good correlation with an increase in density of the aqueous NaCl solution relative to that of neat water. The salting-out constant for the water-NaCl-benzene system, which is estimated from a relative decrease in benzene solubility in the aqueous phase by addition of sodium chloride, increases significantly with increasing temperature. It is suggested that the effect of sodium chloride on the water-benzene mutual solubilities can be explained by ion-induced electrostriction of the aqueous phase. © *2005 American Institute of Physics.*
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I. INTRODUCTION

Mutual solubility of water and hydrocarbons is very small at ambient temperature. However, it increases remarkably with increasing temperature under pressure, and finally water and hydrocarbons become completely miscible with each other at sufficiently high temperatures. For example, water and benzene form a homogeneous mixture with any mixing ratio at temperatures and pressures higher than 570 K and 200 bar respectively.[1,2] The mutual solubility is also influenced by addition of salt. It is known that hydrocarbons are less soluble in a salt solution than in pure water. This effect of salt, called salting-out effect, has been extensively studied near the ambient condition.[3–10] On the other hand, only a few studies on the ternary water-salt-hydrocarbon mixtures at high temperatures and pressures have been reported to our knowledge. It has been shown that addition of salt into water-hydrocarbon mixtures causes shift of the one-phase critical curve to higher temperatures and higher pressures,[11,12] and decrease in the mutual miscibility of water and hydrocarbons.[13] Nevertheless, solubility property of the water-salt-hydrocarbon mixtures at high temperatures has remained largely unknown, only one paper[14] being reported so far to our knowledge. A high-temperature solubility property of such ternary mixtures is important in various research areas. It is useful for gaining insight into the salt effect from the viewpoint of basic science, and in addition, for understanding various geochemical processes involved in mineral formation, and for the assessment and treatment of contamination of seawater by industrial pollution. This paper deals with *in situ* spectroscopic measurements of water-NaCl-benzene mixtures at high temperatures and pressures, aiming to elucidate the salt effect on the mutual solubilities at various temperatures and pressures. The *in situ* spectroscopic method is particularly useful for obtaining volumetric concentrations of components in each phase of the coexisting water-rich and hydrocarbon-rich phases of the mixtures.[15–17]

II. EXPERIMENTAL METHOD AND RESULTS

The experimental setup and the high-pressure cell used in the present study have been described previously.[18] Deionized water with electric conductivity of less than 0.2 μS^{-1} was used, and guaranteed reagent grade benzene and sodium chloride from Nacalai Tesque Inc. and Wako Pure Chemical Industry Inc., respectively, were used as received. Aqueous sodium chloride solutions of 0.5 and 1.0 mol/kg concentrations, which were sufficiently low to avoid precipitation at the present experimental condition,[19] were prepared and put in the cell with benzene. The initial volume ratios of the sodium chloride solution and benzene were 1:3 and 3:1 for measurements of a benzene-rich phase and a water-rich phase, respectively.

Near-infrared spectra of the benzene-rich phase were measured in the 5500–7800 cm^{-1} range with a Perkin-Elmer System 2000 Fourier-transform spectrometer 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 473–573 K range and pressures in the 100–400 bar range. Ultraviolet spectra in the 220–300 nm range of the water-rich phase of the mixtures were measured at temperatures in the 373–498 K range and pressures in the 50–300 bar range with a JASCO V-550 spectrometer with 2 nm spectral bandwidth. At higher temperatures, ultraviolet absorption of benzene dissolved in water becomes too strong to measure with reasonable accuracy, which is due to the increase in solubility of benzene in water, even using the shortest path length of the cell as mentioned in the following.

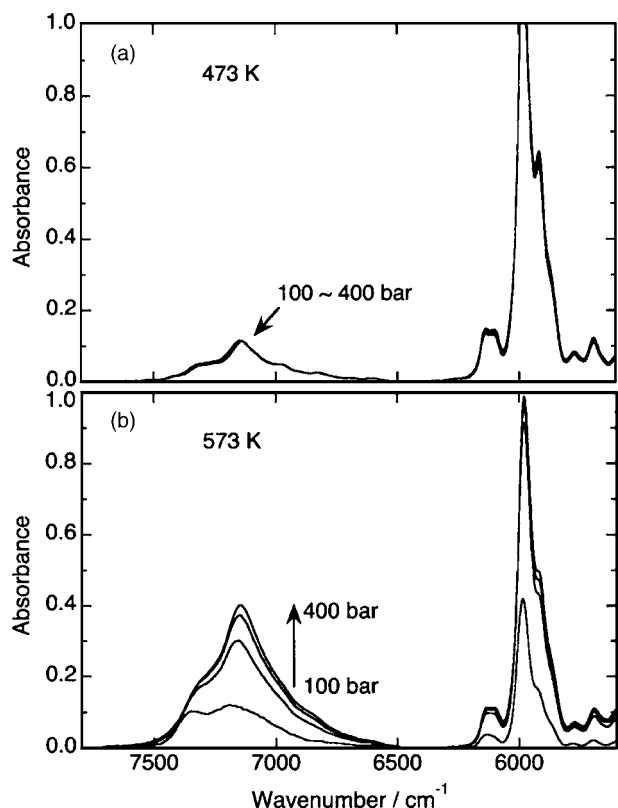[a)]Electronic mail: sikawa@sci.hokudai.ac.jp

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FIG. 1. Near-infrared absorption of the benzene-rich phase of water-NaCl (1.0 mol/kg) benzene mixtures at (a) 473 K and (b) 573 K and at pressures in the 100–400 bar range.

FIG. 2. Effect of NaCl concentrations in aqueous phase on near-infrared absorption of water dissolved in the benzene-rich phase.

The optical path length of the cell was 1.46 or 1.59 mm for the near-infrared measurements and 0.34 mm for the ultraviolet measurements. These values were determined by comparison of the absorption intensity of a near-infrared band of benzene at room temperature with that measured using an ordinary liquid cell of known path length. Uncertainty of the path length thus obtained may be less than a few percent. The sample temperature was measured with a Chromel-Alumel thermocouple inserted directly into the sample fluid and controlled by a digital controller with an accuracy of ±1 K, and the sample pressure was measured with a pressure transducer of a semiconductor strain gage and controlled within ±0.5 bar. Each of the experimental temperature-pressure points was attained at slow enough rate, and the phase equilibrium of the sample fluid was confirmed by the spectrum that remained unchanged for at least an hour.

A. Observed near-infrared spectra

Figure 1 shows typical spectra of the benzene-rich phase of the ternary mixtures with 1.0 mol/kg sodium chloride concentration in the aqueous phase. The absorption centered at around 7200 cm^{-1} is assigned to the OH-stretching overtone transition of water and that around 6000 cm^{-1} is assigned to the CH-stretching overtone transition of benzene. At 473 K, the absorption intensity varies only a little with pressure in the 100–400 bar range, while it exhibits significant pressure dependence at 573 K. This difference in the pressure dependence at the two different temperatures is con-
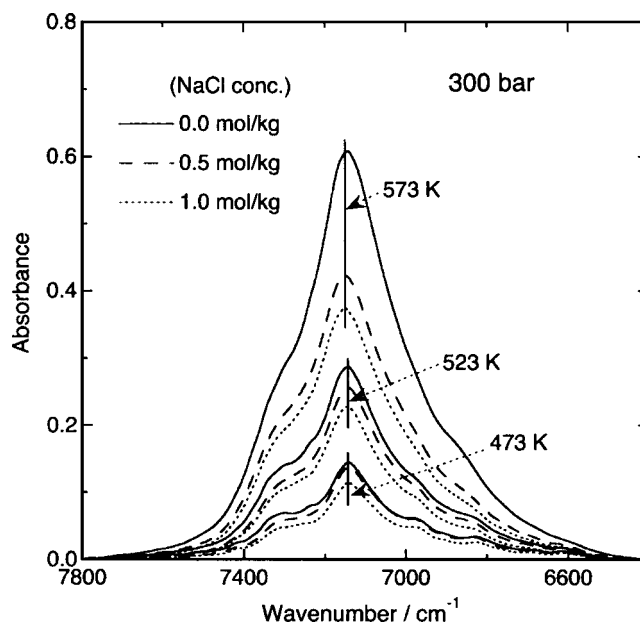
sistent with that observed for water-benzene binary mixtures,[20] and indicates that water solubility in benzene increases remarkably with increasing pressure at 573 K. Effect of salt on the absorption is shown in Fig. 2. Obviously, the absorption intensity decreases with increasing sodium chloride concentration, indicating that the transfer of water molecules from the aqueous phase into the benzene-rich phase is suppressed by sodium chloride dissolved in the aqueous phase. In spite of this, the absorption profile is almost independent of the salt concentration. This fact suggests that the benzene-rich phase does not contain sodium chloride, otherwise the absorption profile would change to some extent owing to an influence of ions on water molecules. This point will be discussed further in the latter section.

B. Observed ultraviolet spectra

Figure 3(a) shows examples of ultraviolet absorption of benzene in the 1.0 mol/kg sodium chloride solution at 473 K and pressures in the 50–300 bar range. The absorption is assigned to a π-π^* transition, and the structure with some peaks is attributed to the vibrational progressions originated from totally symmetric ring-breathing mode of benzene. The absorption intensity increases only slightly with increasing pressure, which is the case at all the temperatures in the present measurements. This small pressure dependence and the progression profile of the benzene absorption are almost the same as observed for water-benzene binary mixtures.[17] Figure 3(b) displays effect of salt on the absorption intensity at two temperatures, 423 and 498 K. Obviously the intensity decreases by addition of sodium chloride, indicating that benzene solubility in the salt solution is smaller than that in neat water. It should also be noticed that the absorption increases remarkably with increasing temperature in contrast to the small pressure dependence.
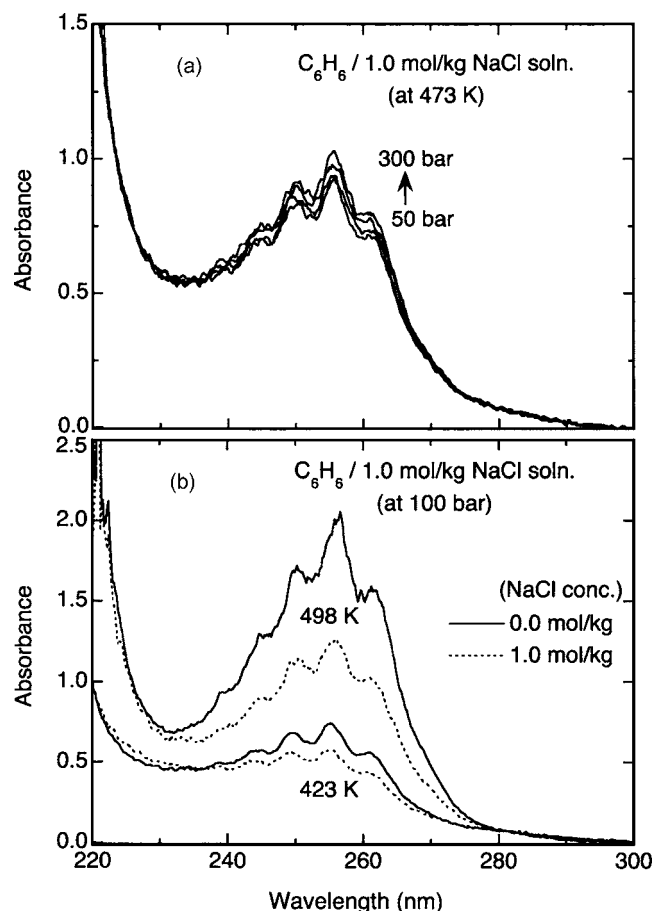
FIG. 3. Ultraviolet absorption of benzene dissolved in 1.0 mol/kg NaCl solution; (a) at 473 K and at pressures in the 50–300 bar range. (b) Effect of NaCl concentration on the absorption at 423 and 498 K and at 100 bar.

III. DISCUSSION

A. Estimation of concentrations

Concentrations of water in the benzene-rich phase were obtained from observed band intensities of the OH-stretching overtone transition in the same way as in the previous work.[17] The integration was performed over the 6400–7800 cm^{-1} range, and the resulting integrated intensity,

$$A_{\mathrm{obs}} = l^{-1} \int (I_0/I) d\nu,$$

where l denotes the sample thickness, was divided by the molar absorption intensity, A^m, to estimate the molar concentration of water as

$$(C_W/\mathrm{mol\ l}^{-1}) = 10^3 (A_{\mathrm{obs}}/\mathrm{cm}^{-2})/(A^m/\mathrm{cm\ mol}^{-1}),$$

where the following empirical expression for A^m was used:[17]

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

The resulting values of the water concentrations are plotted in Fig. 4. Uncertainty of the absolute values of the water concentrations obtained by this method is rather hard to estimate at present. Nevertheless it may be less than 20%, and
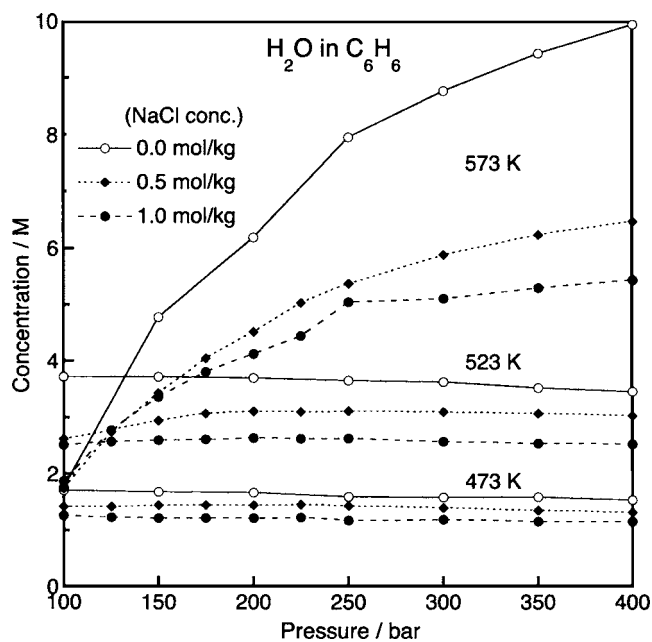

FIG. 4. Concentrations of water in the benzene-rich phase of the water-NaCl-benzene mixtures plotted against pressure.

that of the relative change of the concentrations with temperature and pressure will be significantly smaller.[17]

Concentrations of benzene in the aqueous phase were obtained from the ultraviolet absorption intensities. The integration was performed over the 230–280 nm range with a baseline connecting the both ends of absorption, and the concentration was estimated from the intensity ratio to the water-benzene binary mixtures, for which the benzene solubility in water has previously been determined.[17] This is based on the assumption that the molar absorption intensity of benzene is not affected by sodium chloride in the aqueous solution, which may be supported by the fact that the band profile of the benzene absorption changes little by addition of sodium chloride as seen in Fig. 3. The resulting values of the benzene concentration are plotted in Figs. 5 and 6. Uncertainty of the benzene concentrations thus obtained may be less than 10% including uncertainty of the optical path length mentioned before. The solubility of benzene in the 1.0 mol/kg sodium chloride solution increases slightly with increasing pressure at each temperature as seen in Fig. 5, which is in contrast to a slight decrease in water solubility in benzene at the two lower temperatures shown in Fig. 4. This opposite direction of the pressure dependence has been suggested to be caused by difference in molecular size and difference in the thermal compressibility of water and benzene on the basis of a cavity-based solvation model.[17] Dependence of the benzene solubility in the aqueous phase on sodium chloride concentration is displayed in Fig. 6. It is found that the relative decrease in solubility is larger for benzene in the aqueous phase than for water in the benzene-rich phase at similar temperatures.

B. Effect of salt on solubility of water in benzene

Obviously the concentrations of water in the benzene-rich phase decrease with increasing sodium chloride concen-
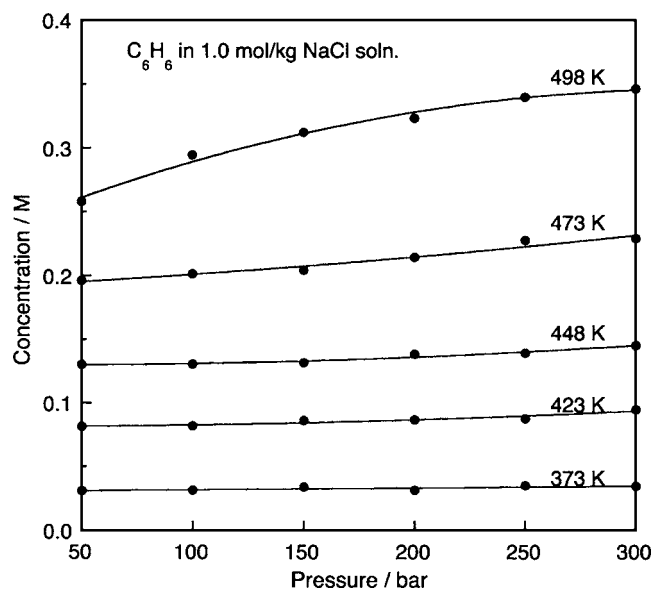
FIG. 5. Concentrations of benzene in the 1.0 mol/kg NaCl solution plotted against pressure.

FIG. 7. Relative volume change on mixing for the water-benzene binary system (open circle) and for the water-NaCl-benzene ternary system (filled circle). Figures in the parentheses denote NaCl concentration in a mol/kg unit in the aqueous phase.

tration in the aqueous phase, indicating that the salt suppresses transfer of water molecules into the benzene-rich phase. The water concentrations at 473 and 523 K vary only slightly with pressure, which is a common feature of mixtures in the two-phase region,[17,20] but those at 573 K exhibit remarkably large increase with increasing pressure. Actually, binary water-benzene mixtures without sodium chloride form homogeneous phase at pressures above 200 bar at 573 K, and the water concentrations do not provide solubility but depend on experimental condition such as initial filling ratio of water and benzene in the cell. A phase behavior of the ternary water-sodium chloride-benzene system is not known at present. However, the fact that the water band profile changes little by addition of sodium chloride as seen in Fig. 2 suggests that the benzene-rich phase does not involve the
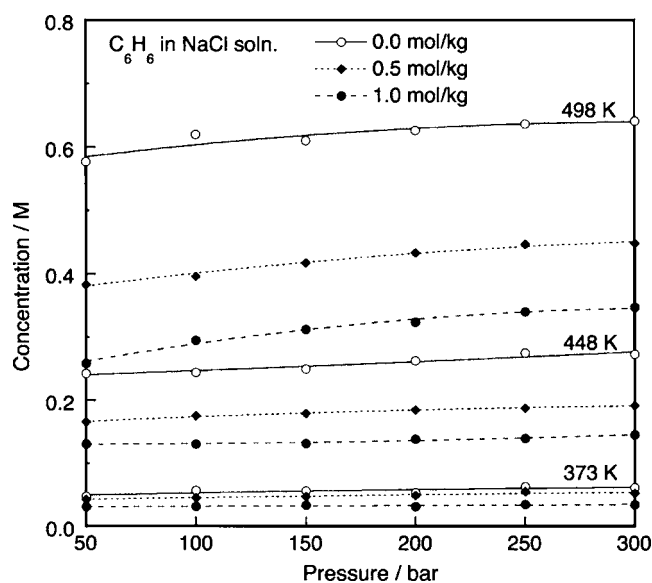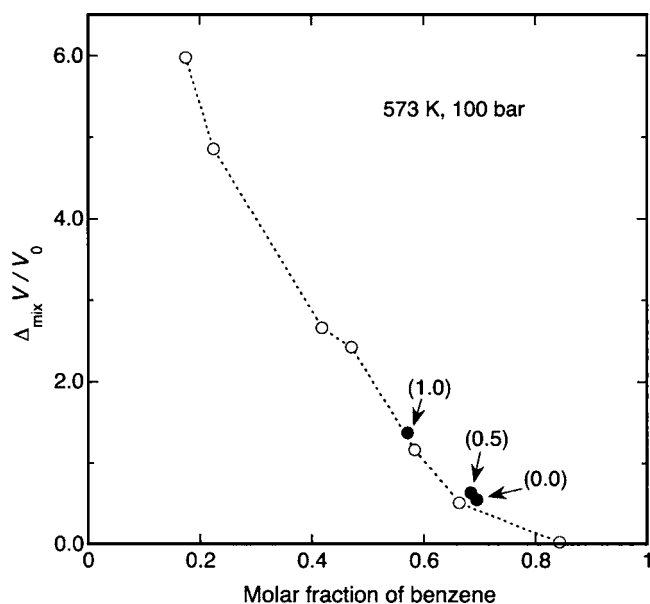
salt, and the ternary mixtures are not in the homogeneous phase in the present temperature-pressure range.

The suggestion mentioned above is supported by the volumetric behavior of the benzene-rich phase, where the concentration of benzene can be estimated from the intensity of the C–H-stretching overtone band by a method as described in the previous paper.[16] By the use of the water and benzene concentrations, C_W and C_B, respectively, the density (in g cm^{-3}) of the benzene-rich phase is given by

$$\rho_{mix} = (C_W M_W + C_B M_B)/1000,$$

where M_W and M_B are the molar weights of water and benzene, respectively. The average density before mixing is estimated by

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

where ρ_W and ρ_B denote densities of neat water and neat benzene, respectively, which are taken from literature.[21,22] Then the relative volume change on mixing is given by

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

The resulting values together with the previous results for water-benzene mixtures[16] are plotted in Fig. 7. It is found that the present results for the ternary mixtures are in good agreement with those for the binary mixtures. This fact indicates that the volumetric behavior of the benzene-rich phase is the same for the ternary and binary mixtures, and then supports the assumption that sodium chloride does not transfer into the benzene-rich phase in the present temperature range.

The fact that the transfer of water into the benzene-rich phase is suppressed by sodium chloride in the aqueous phase should be explained by a solvation of ions, which strongly

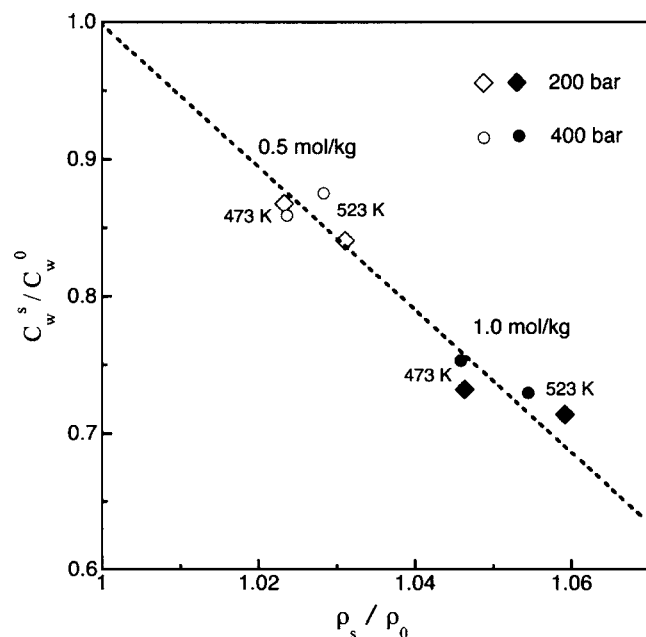FIG. 6. Concentrations of benzene in the NaCl solutions with different NaCl concentrations.

FIG. 8. Correlation between the relative decrease in water concentration in the benzene-rich phase and relative increase in density of the aqueous solution by addition of sodium chloride at 473 and 523 K and at 200 and 400 bar.

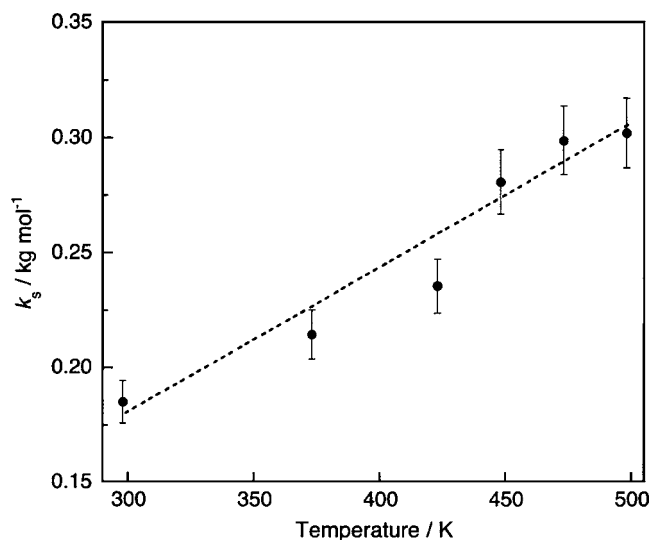FIG. 9. Plot of the salting-out constants for the water-NaCl-benzene system against temperature. The value at 298 K, 0.185±0.010, is an average of literature values (Ref. 3).

attract water molecules and make a barrier to the water transfer higher. This inference may be supported by a correlation between a relative decrease of the water concentration in benzene, C_W^s/C_W^0, and a relative increase in the density of water, ρ_s/ρ_0, where suffixes s and 0 denote the systems with and without salt, respectively. The former is simply given by a ratio of the water concentrations observed in the present study and the latter is estimated from experimental densities of water and sodium chloride solution at the same temperatures and pressures.[19] It should be noted here that the density of the salt solution ρ_s is distinctly larger than a simple average density of water and sodium chloride, which is attributed to the electrostriction effect.[23] A good correlation is found between the concentration ratio C_W^s/C_W^0 and the density ratio ρ_s/ρ_0 as shown in Fig. 8. Therefore it is suggested that the suppression of water transfer into the benzene-rich phase is explained by electrostriction of the water-rich phase by the dissolved ions.

C. Effect of salt on solubility of benzene in the aqueous phase

The decrease in solubility of hydrocarbons in water by addition of salt, which is known as the salting-out effect, has been extensively studied around ambient temperatures. However, it remains largely unknown how the salting-out effect varies as the temperature rises. A quantitative discussion of the salting-out effect is usually based on the Setschenow equation,[3]

$$\log(S_0/S) = k_s m_s,$$

where S_0 and S denote solubilities of benzene into neat water and salt solution, respectively, m_s indicates molality of salt in the salt solution, and k_s is the Setschenow or salting-out constant. It should be noticed here that the salt concentration is given in molality (mol/kg) instead of molarity (mol/l), the latter of which is sometimes used to describe the salting-out effect near the ambient condition.[3–8] The reason for the use of molality in the present study is that the salt concentration in molality is independent of thermal expansion of the solution, while that in molarity varies with temperature and is difficult to estimate at high temperatures. The estimated values of the Setschenow constant are plotted against temperature in Fig. 9, where the value at each temperature is the average over different pressures, because the present experimental data are not precise enough to discuss such a small pressure dependence. It is obvious that the salting-out constant increases as temperature rises or, in other words, the degree of salting-out effect becomes larger at higher temperatures. It has been reported that the apparent molar volume of NaCl(aq) becomes negatively larger as the temperature rises.[19] This means that the electrostriction effect becomes stronger as the temperature rises, and seems to be parallel to the present observation of the stronger salting-out effect at higher temperatures.

IV. CONCLUSION

In conclusion, both the solubilities of water in benzene and benzene in water decrease by addition of sodium chloride in the water phase, and degree of the decrease becomes larger as temperature rises, which can be explained by the increase in the electrostriction effect with increasing temperature.

ACKNOWLEDGMENTS

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