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Diffusion Coefficient of Benzene around the Gas–Liquid Critical Temperature

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Synopsis. The diffusion coefficients of benzene in a pressurized vessel has heen measured up to above the gas–liquid critical temperatures. The observed diffusion coefficients are compared with the calculated values from a simple hard-sphere approach.

It is very interesting to study transport properties of molecular liquids over a wide range of its density, including the supercritical region. Shimokawa and his co-workers[1,2] have already reported NMR studies of some organic liquids sealed in pressurized ampoules over a wide range of temperature up to above the gas–liquid critical point. In this note, we report experimental results on the diffusion coefficients of benzene around the critical point, measured by the NMR spin-echo method. The density of the sample was measured by the NMR one-dimensional projection method.[3]

Experimental

Experimental procedures were essentially the same as reported previously.[1] A cylindrical Pyrex glass ampoule was used for high temperature NMR measurements. The inner volume of the ampoule was 0.267 cm^3 and the inner height was 1.50 cm. 0.107 g of reagent grade benzene was sealed in the ampoule under vacuum. The sample density was 0.401 g cm^{-3}, when the sample occupied uniformly the whole volume of the ampoule. This value is a little larger than the critical density of benzene, 0.302 g cm^{-3}.[4] The ampoule was placed in a home-made high pressure high temperature NMR vessel in which an rf-coil and an internal heater were equipped. The vessel was pressurized by nitrogen gas up to about 150 atm in order to suppress the internal pressure of the sealed ampoule at high temperature. The estimated pressures of the sample in the ampoule from the Martin–Hou equation of state[4] are 65.4 atm at 300 °C and 110.9 atm at 350 °C. Field gradient coils were attached to the cooling jacket which covered the vessel. The whole ensemble was placed in the gap of an electric magnet of 0.898 T. The temperature of the sample was measured by an alumel-chromel thermocouple placed near the measuring coil, which was calibrated after measuring runs. During measurements the temperature was controlled within ±2 °C.

NMR measurements were made with a Bruker CXP spectrometer operating at 38.3 MHz for protons. The diffusion coefficient of the sample, D, can be determined from the Hahn spin-echo method with a steady field gradient, using the relation,[5]

$$\ln\frac{A_{\text{on}}}{A_{\text{off}}}=-\frac{2}{3}\gamma^2 DG^2\tau^3, \qquad (1)$$

where A_{on} and A_{off} are echo heights with and without the magnetic field gradient G. γ is the gyromagnetic ratio for the measuring nuclei, protons, and τ is the interval between the 90° and 180° pulses. Values of G were determined from the analysis of the echo shape[6] at two temperatures, room temperature and a high temperature above the critical point. Usual values of G in the present experiments were 0.6 to 0.7 gauss cm^{-1} and dependent on temperature. For intermediate temperatures interpolated values G were used. The diffusion coefficient of pure liquid benzene at room temperature was determined as $(1.96\pm0.10)\times10^{-9}$ m^2 s^{-1}, which is in reasonable agreement with the literature value, $(2.05\pm0.10)\times10^{-9}$ m^2 s^{-1}.[7,8]

The density of the sample in the container was measured in situ using the one-dimensional projection method[3] at each temperature. The distinction of the gas (low density) and liquid (high density) phases disappeared above 290 °C, and this temperature is in good agreement with the reported gas–liquid critical temperature of benzene, 288.9 °C.[4]

Results and Discussion

Figure 1 shows the observed diffusion coefficient of benzene near the critical temperature which is indicated by an arrow in the figure. Below the critical temperature the observed diffusion coefficient is an average value over the gas and liquid phases, since the NMR signals from the both phases were taken in the present experimental setup. A knee of the curve was found at the critical temperature, above which the sample occupied the volume of the ampoule uniformly and had a constant density. The experimental scatter becomes large with increasing temperature due to the low S/N ratio and the large fluctuation of temperature in the sample. The observed diffusion coefficient of benzene is of the order of 10^{-7} m^2 s^{-1} in the supercritical region, which is larger than its value at room temperature by a factor of 50.

The density- and temperature dependence of the diffusion coefficient may be estimated from a simple hard

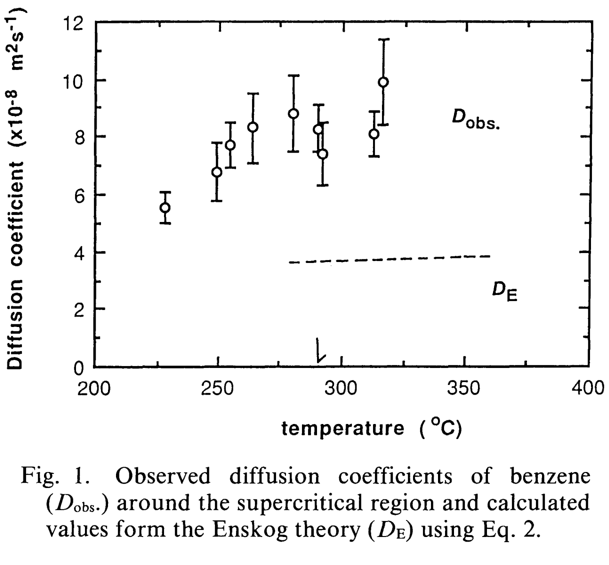

Fig. 1. Observed diffusion coefficients of benzene ($D_{\text{obs.}}$) around the supercritical region and calculated values form the Enskog theory (D_{E}) using Eq. 2.

sphere model for fluids. In the model based on the Enskog theory and the Carnahan–Stirling equation of state, the diffusion coefficient can be given by[9]

$$D_E=\frac{1}{16}\left(\frac{6}{\pi n y^2}\right)^{1/3}\left(\frac{\pi k T}{m}\right)^{1/2}\frac{(1-y)^3}{(1-y/2)}, \tag{2}$$

where n is the number density of molecules of mass m, k is the Boltzmann constant and T is the temperature. The packing fraction y is given by the relation

$$y=\sigma^3\left(\frac{\pi n}{6}\right), \tag{3}$$

where σ is the hard sphere diameter of a molecule. The value of y at room temperature can be calculated from the isothermal compressibility X_{th} for hard sphere fluids with the Carnahan–Stirling equation of states, using the relation[10]

$$nkT X_{\mathrm{th}}=(1-y)^4[2y(4-y)+(1-y)^4]^{-1}. \tag{4}$$

From the data of $X_{\mathrm{th}}=0.955\times10^{-9}\ \mathrm{Pa}^{-1}$[11] and $n=6.777\times10^{27}\mathrm{m}^{-3}$[12] at 20 °C, we have $y=0.457$ and then from Eq. 3 $\sigma=5.05\times10^{-10}$ m. This value of the molecular hard sphere diameter is close to the value deduced from a thermodynamical analysis by Kawai and Arakawa,[12] $\sigma=5.17\times10^{-10}$ m. With the present values for y and σ, we have calculated from Eq. 2 the diffusion coefficient, $D_{\mathrm{E}}=4.49\times10^{-9}\ \mathrm{m^2\,s^{-1}}$, which is larger than the observed value by a factor of about 2. Assuming that the hard-sphere diameter does not vary with temperature, we have a constant value for the packing fraction in the supercritical region in the present experimental conditions, i.e., $y=0.209$. Then, we can calculate values of D_{E} from Eq. 2, which is shown in Fig. 1 by the dotted line. Though the observed weak temperature dependence of D in the supercritical region is in agreement with the predicted proportionality to $T^{1/2}$, the calculated values of D are about 1/2 of the observed values. It is known that the effect of correlated motions neglected in the Enskog theory is important in the diffusion coefficient calculation. Alder and coworkers[13] have given correction factors to the Enskog diffusion coefficient D_{E}, based on molecular dynamics studies for hard-sphere fluids. The correction factor is about 0.6 in the dense liquid range ($y=0.5$) due to the backscattering effect and about 1.3 at intermediate densities ($y=0.3$) due to the vortex effect.[13] With such consideration, the observed D at room temperature is in reasonable agreement with the hard sphere value. The agreement is, however, still poor in the supercritical region. This discrepancy in the absolute values of D in the supercritical region seems to be attributed to the nonsphericity of benzene molecules.[14] It is interesting to compare the present results with those obtained in the previous experiments for toluene[1] and cyclopentane.[2] The present results for benzene is rather close to those of cyclopentane, which can be attributed probably to the molecular shape of each compound. More experimental data for various molecules and for a wider temperature range above the critical temperature will be needed to investigate such an effect on the diffusion coefficients of fluids near the critical temperature.

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