

BINARY DIFFUSION COEFFICIENTS OF NAPHTHALENE AND BENZENE IN THE NEAR-CRITICAL REGION OF CARBON DIOXIDE

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Abstract

Binary diffusion coefficients in supercritical carbon dioxide were measured at pressures from 7 to 26 MPa and temperatures at 305.21 and 308.35 K for benzene by the Taylor dispersion technique with an uncoated capillary column, and for naphthalene by tracer response technique with a poly(ethylene glycol) coated capillary column. The critical slowing down of the binary diffusion coefficients was observed for both solutes in the near-critical region of carbon dioxide. The pressure showing the maximum decrement was not consistent with that showing the lowest value of PMV or the maximum value of the isothermal compressibility of carbon dioxide. The pressure showing the maximum decrease was thoroughly consistent with the pressure showing the maximum value of S_{10} , which was defined as the ratio of the latter half peak width to the frontal value of response curve. The background values were well represented with not only a correlation of D_{12}/T vs. CO_2 viscosity but also the Schmidt number correlation. The D_{12} datum showing the critical slowing down fully corresponded to that showing the deviation from both the correlations. Although it was reported by some workers using the Taylor dispersion method that binary diffusion coefficients tended to become zero as the pressure reached the critical pressure of carbon dioxide, it does not agree with the observation in this study.

Introduction

Although an anomaly in various physical properties near critical region has been well described [1], binary diffusion coefficients D_{12} have not been well understood. Some studies [2-5] on the critical anomaly in D_{12} measured by the Taylor dispersion method have been reported. Higashi et al. [6,7] also observed the decrease of diffusion coefficients by the capillary tube method. The authors [8] have demonstrated in the Taylor dispersion method that the mixture of the solute and CO_2 solvent does not attain to the supercritical state at most axial positions of the diffusion column when the relatively large amount of the solute is injected [3,4]. Clifford and Coleby [9] also concluded from the calculations for naphthalene in carbon dioxide that very large mass transfer reduction was caused by lowering of diffusion

coefficients and barycentric motion in the Taylor dispersion method. The critical anomaly in binary diffusion coefficients is still not clarified. In this study, D_{12} values for benzene in CO_2 by the Taylor dispersion method with an uncoated capillary column and naphthalene by a tracer response technique with a polymer coated capillary column were measured in the near critical region of carbon dioxide, and the anomalous decrease in D_{12} was examined.

Theory

When a tracer species is injected as a shot to a fully developed laminar flow in a cylindrical tube coated with thin polymer film, the averaged tracer concentration C_a can be described as follows [10]:

$$C_a(x,t) \approx \left(\frac{m}{p R^2} \right) \frac{1}{(1+k)\sqrt{4p at}} \exp\left(-\left(x - \frac{u_a}{1+k}t\right)^2 / 4at \right) \quad (1)$$

where

$$a = \frac{D_{12}}{1+k} + \frac{1+6k+11k^2}{(1+k)^3} \frac{u_a^2 R^2}{48D_{12}} \quad (2)$$

where k is the partition ratio, m is the injected amount of the tracer species, R is tube inner radius, and u_a is average velocity. In case of the Taylor dispersion measurements [11] k becomes zero, and eqs (1) and (2) reduce to eqs (3) and (4), respectively.

$$C_a(x,t) = \frac{m}{pR^2\sqrt{4pKt}} \exp\left(-\frac{(x-u_a t)^2}{4Kt} \right) \quad (3)$$

where

$$K = D_{12} + \frac{u_a^2 R^2}{48D_{12}} \quad (4)$$

In both cases of the tracer response technique and the Taylor dispersion method the root-mean-square error ϵ for the response curves measured ($C_{a,meas}$) and calculated ($C_{a,cal}$) at $x = L$ between t_1 and t_2 , given by eq 5, is minimized by choosing appropriate values of the D_{12} for the Taylor dispersion measurements or D_{12} and k for the tracer response technique:

$$\epsilon = \left[\frac{\int_{t_1}^{t_2} \{C_{a,meas}(L,t) - C_{a,cal}(L,t)\}^2 dt}{\int_{t_1}^{t_2} \{C_{a,meas}(L,t)\}^2 dt} \right]^{1/2} \quad (5)$$

where t_1 and t_2 are times at the frontal and the latter 10 % peak heights of measured response curve, respectively. Note that the fitting was regarded as acceptably good when $\epsilon < 0.02$, similarly to the fitting criterion [12,13].

Experimental Apparatus and Procedures

The experimental apparatus and the procedure for the Taylor dispersion [11,12] and the tracer response technique [10,13] were described elsewhere. Liquid benzene of 0.2 μL or benzene dissolved in supercritical carbon dioxide was injected to a diffusion column, made of stainless-steel tubing ($0.817 \pm 0.001 \text{ mm} \times 35.00 \text{ m}$). Naphthalene as a hexane solution at a concentration of 5 mg/mL was loaded through an injector to a poly(ethylene glycol) coated capillary column. In both cases the response signal was measured with an optical cell having a path length of 0.5 mm by scanning from 195 to 300 nm every 1.6 s at a resolution of 1 nm with a UV-Vis multidetector. D_{12} value was determined so that the fitting error between measured response curve and that calculated was minimized. We examined the effect of wavelength on the detector linearity, the peak distortion, and fitting error. As a result, response curve measured at 239 nm for benzene and 275 nm for naphthalene was used for the analysis. The pressure was maintained at the intended pressure within fluctuation $\pm 0.001 \text{ MPa}$ by a back pressure regulator (Model 880-81, JASCO, Japan) which was capable for controlling the pressure with a high frequency open-shut valve operated electromagnetically. The pressure fluctuation was directly measured by a pressure sensor and two Heise pressure gauges (Maximum pressures 10 MPa and 50 MPa). The pressure sensors were calibrated by the Heise pressure gauges. The pressure drop of the diffusion columns was measured to be less than 0.01 MPa with the pressure sensor and the pressure gauge. The temperature of the column which was immersed in the temperature controlled water bath, whose temperature was regulated within the fluctuation of $\pm 0.01 \text{ K}$.

Results and Discussion

Figure 1 shows (a) D_{12} vs. pressure, (b) D_{12} vs. CO_2 density, and (c) root-mean-square fitting error vs. CO_2 density, at 308.35 K and 305.21 K, together with D_{12} data reported in our previous study [14]. Note that CO_2 density was estimated by the equation of state by Pitzer and Schreiber [15]. In plot of D_{12} vs. pressure the D_{12} values at 308.35 K simply decrease with increasing pressure up to 8 MPa, and the values slightly decrease with pressure above 8 MPa. D_{12} data at 308.21 K abruptly decrease at 7.5 MPa, and thereafter D_{12} values jump and decrease gradually. The D_{12} data at 308.15 K in the previous study show similarly the sharp decrease at 7.5 MPa. The data at 308.35 K were almost consistent with those at 308.15 K except for the sharp decrease data. In plot of D_{12} vs. CO_2 density, the decrease of the D_{12} data is more evident. The differences between the observed D_{12} values and the background values designated by the solid line were estimated by the regression with the data showing no decrease. The density showing the minimum D_{12} value was not consistent with the density showing the maximum isothermal compressibility k_T of carbon dioxide at 305.21 K. The fitting error at 305.21 K was deviated and higher over the density range from 300 to 400 kg m^{-3} , and correspondingly the anomalous D_{12} decrease was observed. In the pressure or density region where the fitting error values are not deviated, those are less than 0.02 for the data at 308.35 K. This suggests that the response curves of the data showing the anomalous decrease are distorted. Moreover, although it has been reported in the literature [3-5] that the D_{12} values decrease toward zero as the pressure reaches the critical pressure, our data do not show the behavior.

In the tracer response technique with a polymer coated column two parameters: partition ratio k of solute in polymer phase to supercritical phase, and binary diffusion coefficient D_{12}

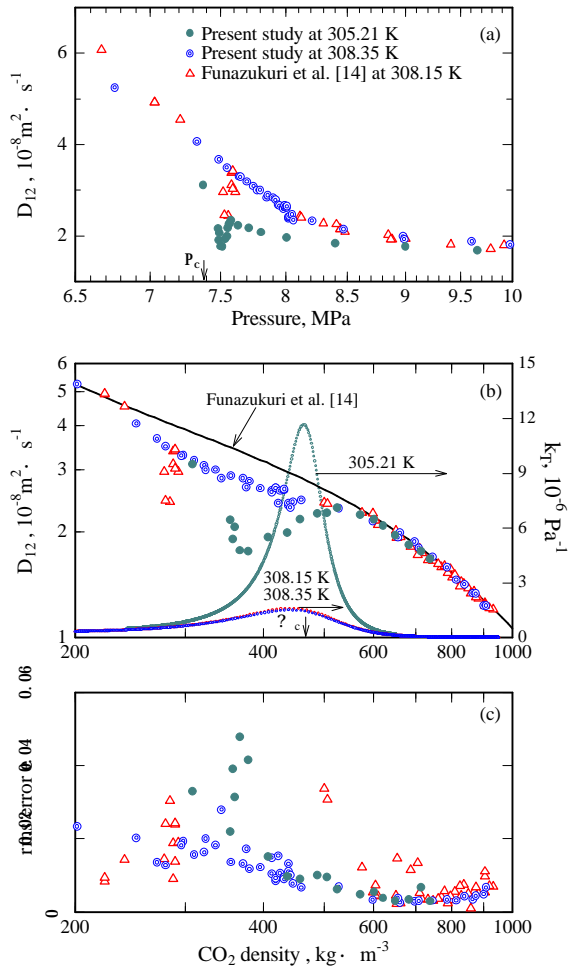


Figure 1. (a) D_{12} vs. pressure, (b) D_{12} vs. CO_2 density, and (c) root-mean-square fitting error for benzene.

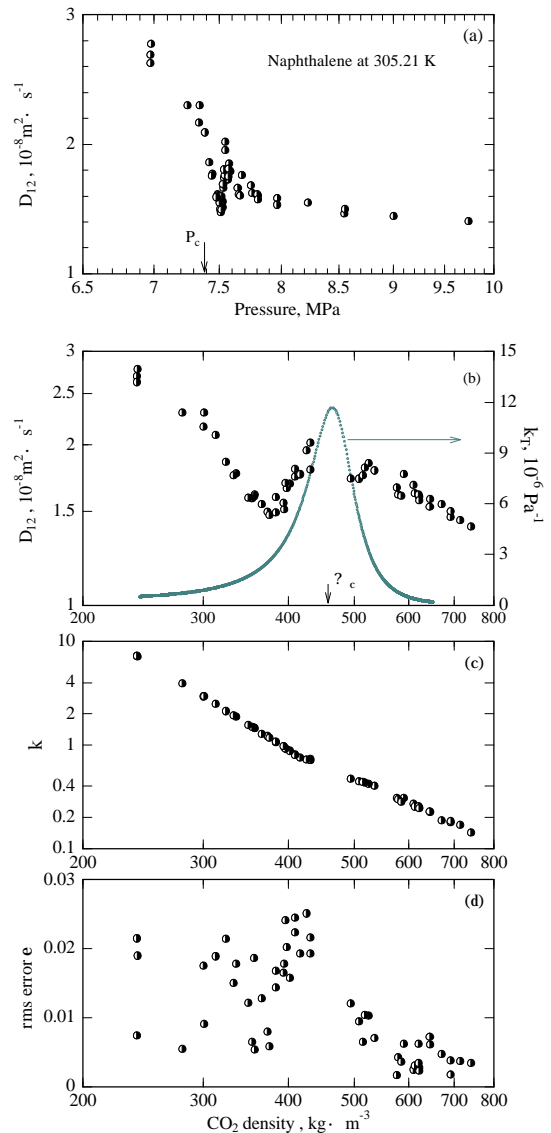


Figure 2. (a) D_{12} vs. pressure, and effects of CO_2 density on (b) D_{12} , (c) k and (d) root-mean-square fitting error for naphthalene.

are involved in the system. The parameter determination was carried out by the curve fitting method, which was found to be more accurate than the moment method which has been often employed. Figure 2 shows (a) D_{12} vs. CO_2 pressure, and effects of CO_2 density on (b) D_{12} , (c) k and (d) root-mean-square fitting error for naphthalene measured at 305.21 K with a polymer coated capillary column. As similarly observed for benzene by the Taylor dispersion, D_{12} values show the sharp decrease at about 7.5 MPa.

The density showing the D_{12} minimum value is almost consistent with that for benzene at the same temperature. Although the fitting errors at the density showing the D_{12} anomalous decrease increased and deviated, those for naphthalene were mainly less than 0.02, which indicates the good fitting of the response curve calculated to that measured. While this reason

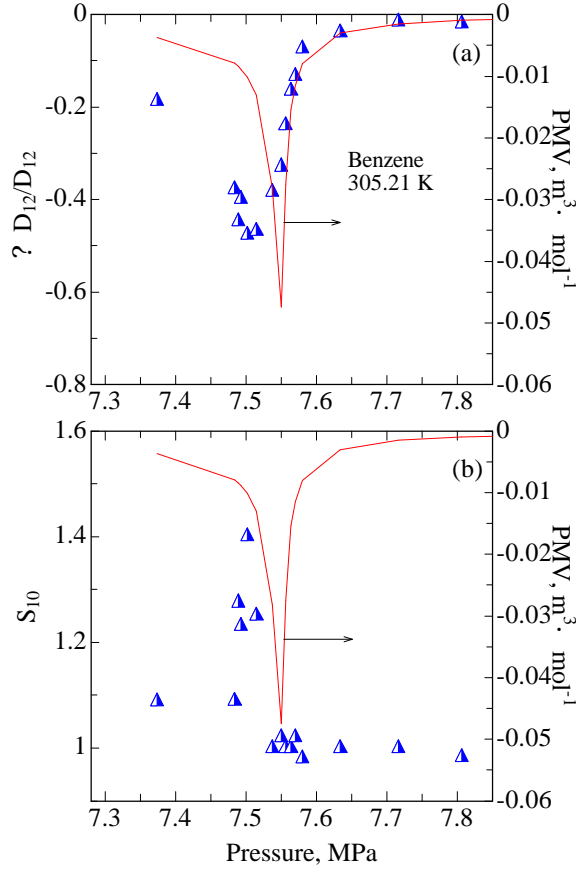


Figure 3. (a) $\Delta D_{12}/D_{12}$ and (b) S_{10} vs. pressure, together with PMV.

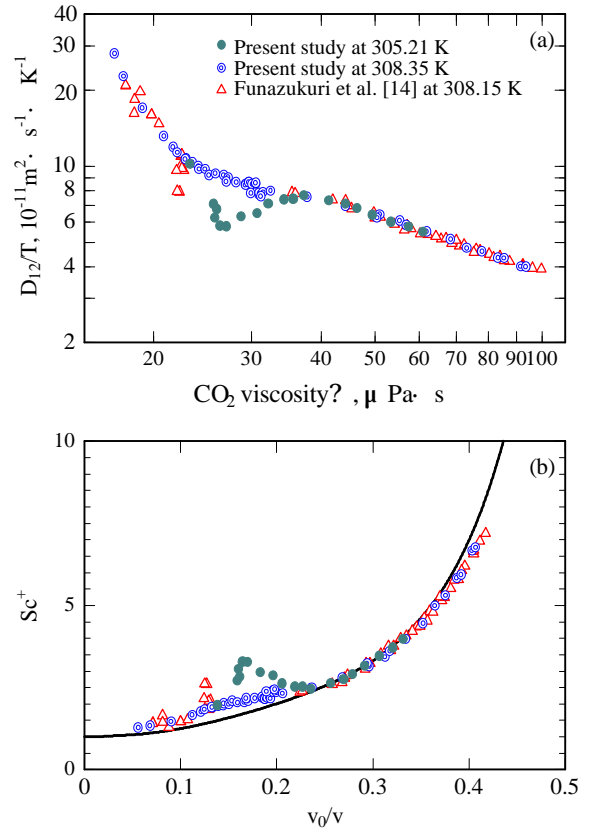


Figure 4. Validity of correlations: (a) viscosity correlation, and (b) the Schmidt number for benzene.

is not clarified, the response curve becomes sharp due to the chromatographic effect. Although the slight deviation of k values from the straight line in logarithmic plot of k vs. CO_2 density, the density does not agree with that showing the D_{12} anomalous decrease.

Figure 3 shows the pressure dependences for benzene at 305.21 K on (a) normalized anomalous decrease $\Delta D_{12}/D_{12}$ and (b) S_{10} , defined as the ratio of the latter half peak width to the frontal value at 10% peak height, which indicates the peak distortion. If S_{10} is unity, the peak is symmetrical and the tailing is not observed. The pressures showing the anomalous decrease are consistent with those showing S_{10} values higher than unity, and not with those showing large negative values of solute partial molar volume PMV. The $\Delta D_{12}/D_{12}$ values show a similar behavior to those of PMV, but the $\Delta D_{12}/D_{12}$ values are slightly shifted toward lower pressure by 0.05 MPa. Note that PMV values were estimated by the Peng-Robinson equation of state with the van der Waals mixing rule and $k_{ij} = 0.077$ [16].

Figure 4 plots (a) D_{12}/T vs. CO_2 viscosity and (b) the Schmidt number correlation for benzene in the present study and literature values [14]. It is found that the data showing anomalous decrease are deviated from those predicted from both correlations. The data for naphthalene, not shown in figure, also show the same tendency as that for benzene.

Conclusions

Binary diffusion coefficients were measured in the near critical region of carbon

dioxide for benzene by the Taylor dispersion method and for naphthalene by the tracer response technique with a polymer coated capillary column at 305.21 K and 308.35 K over the pressure range from 7 to 26 MPa. For both solutes the anomalous decreases of binary diffusion coefficients were observed, but the values did not tend to become zero as the pressure reached the critical pressure. The pressure showing the maximum D_{12} decrease was fully consistent with that showing the maximum S_{10} value, and not with that at minimum PMV value. This suggests that the anomalous decrease results from the peak distortion by the transient measurements such as the Taylor dispersion and the tracer response method. The cause of the peak distortion is not still clarified, and the further studies are required. The data deviated from two correlations in terms of the viscosity and the Schmidt number indicate the data showing anomalous decrease.

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