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Calculation of Mutual Diffusion Coefficients near the Critical Region from the Peng–Robinson Equation of State

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We observed that the mutual diffusion coefficients of benzene in supercritical carbon dioxide exhibited a maximum at pressures above the critical pressure of the mixture, and a strong concentration dependence near the critical point. These surprising experimental results can be explained by replacing the concentration gradient of diffusion with a chemical potential gradient as suggested from irreversible thermodynamics. Then, it can be understood that diffusion coefficients have a maximum value at the critical point of a mixture. The Peng–Robinson equation of state was used to illustrate these relationships.

Introduction

In a previous paper [Nishiumi et al., 1996], we observed that the mutual diffusion coefficients of organic compounds in supercritical carbon dioxide exhibited a maximum above the binary critical pressure at a constant temperature. Previous researchers also have reported anomalies in the diffusion coefficient near the binary critical point [Dythe and Hafskjold, 1995; Semenov and Berezhnoi, 1981; Tsekhanskaya, 1971; Umezawa and Nagashima, 1992]. In this paper, we report on diffusion coefficients estimated from the Peng–Robinson equation of state and show the qualitative behavior near a binary critical point.

Taylor Method

Mutual diffusion coefficients of acetone [Nishiumi et al., 1996] in supercritical carbon dioxide were measured by the Taylor dispersion method [Taylor, 1953], which has been widely used for the determination of diffusion. In the Taylor dispersion method, the average concentration C at distance z at a given time t after pulse input of a solute in a laminarly flowing solvent is given by the equation

$$C = \frac{1}{2}\left(\frac{M}{\pi R_0^2}\right)\left(\frac{1}{\sqrt{\pi kt}}\right)\exp\left(-\frac{(z-\bar{u}t)^2}{4kt}\right) \qquad (1)$$

where k is an apparent diffusion coefficient, R_0 is the inner radius of a tube, and $\bar{u}$ is the average flow velocity. Taylor derived the relation between the apparent diffusion coefficient k and the mutual diffusion coefficient D_{12} as follows:

$$D_{12} = \frac{(R_0\bar{u})^2}{48k} \qquad (2)$$

We estimated an apparent diffusion coefficient k by fitting eq 1 to experimental data. When we fitted k into eq 2, a mutual diffusion coefficient D_{12} was obtained. Generally, diffusion coefficients estimated from the

Taylor dispersion method are considered to be in infinitely dilute solutions. However, we found even a small change in the solute composition had a strong effect on the diffusion coefficients obtained near the critical point. Therefore, we distinguish D^0_{12} from D_{12} in eq 2.

Experimental Apparatus

Liquid carbon dioxide was fed into a diffusion tube at a constant volumetric flow rate with a compressor [Nishiumi et al., 1996]. The diffusion tube was held at constant temperature (± 0.1 K) with a water jacket. The diffusion tube (10.28 ± 0.01 m length, 1.07 ± 0.01 mm i.d.) was oriented in a horizontal position to minimize buoyancy, gravity, and Coriolis effects. A small amount of solute was introduced into the system just before the diffusion tube with a six-way valve. Radial diffusion in the laminar fluid flow was recorded at the tube outlet with a UV detector.

Experimental Results

The effects of the injected volume of benzene on diffusion coefficients of benzene in supercritical carbon dioxide at 313.15 K is shown in Figure 1. At low solute concentrations, such as 0.7-μL injected volume, mutual diffusion coefficients decreased monotonically with pressure. When the injected volume was increased to 5.7 or 13.1 μL, diffusion coefficients exhibited a maximum and decreased near the critical pressure of carbon dioxide (7.38 MPa) or was almost the same as that of a mixture, although it is not clear whether it reaches zero at the critical point. Although the solute composition is very small, Figure 1 shows that diffusion coefficients are much affected by composition difference near the critical point.

Mutual Diffusion Coefficients in an Infinitely Dilute Solution D^0_{12}

Mutual diffusion coefficients in an infinitely dilute solution D^0_{12} could be correlated with the Schmidt number ratio [Funazukuri et al., 1993]. The Schmidt number is defined as

$$Sc = \eta_2/\rho_2 D^0_{12} \qquad (3)$$

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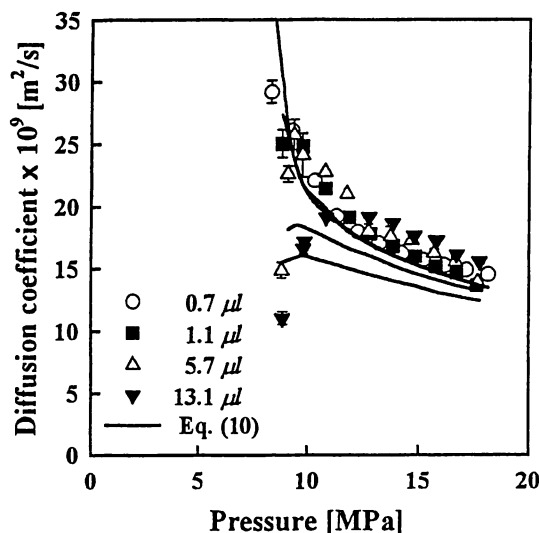
Figure 1. Effect of the injected volume on the diffusion coefficient of benzene in supercritical carbon dioxide at 313.15 K.

vhere ρ_2 and η_2 are the density and the viscosity of a solvent, respectively. The Schmidt number can be expressed as the product of a correction factor at high pressures Sc^+, and at atmospheric pressure Sc^*

$$Sc = Sc^+ Sc^* \qquad (4)$$

For Sc^+, the following equation holds:

$$Sc^+ = \frac{5}{6}\left(\frac{\sigma_1 + \sigma_2}{2\sigma_2}\right)^2 \left(\frac{2M_1}{M_1 + M_2}\right)^{1/2} \qquad (5)$$

σ and M are the effective hard-sphere diameter and the molecular weight of components 1 and 2, respectively. σ_1 and σ_2 were set equal to 0.535 and 0.394 nm, which are the Lennard-Jones diameters replacing of the effective hard-sphere diameters, respectively [Reid et al., 1987]. For Sc^*,

$$\ln(Sc^* - 1) = \sum_{i=0}^{5} a_i(v_0/v) \qquad (6)$$

where v is the molar volume and v_0 is the closed-packed hard-sphere volume of the solvent. The coefficients a_i were determined by fitting experimental data on diffusion coefficients at atmospheric pressure.

The viscosity of the supercritical fluid used in the Schmidt number was calculated by the equation of Chung et al. [1988]. At high pressures, D^0_{12} can be calculated using the above correlation and the density of a solvent at the given conditions.

Anomalies in the Mutual Diffusion Coefficients at the Critical Point

On the basis of the results from irreversible thermodynamics, we assumed that the binary diffusion coefficient was proportional to a chemical potential gradient. The modified equation for the binary diffusion coefficient based on the work of Darken [1948] was expressed as

$$D_{12} = QL_0 \qquad (7)$$

where Q and L_0 are the thermodynamic factor and the kinetic factor defined as

$$Q = (x_1/RT)(\partial \mu_1/\partial x_1)_{P,T} \qquad (8)$$

and

$$L_0 = x_1 D^0_{21} + x_2 D^0_{12} \qquad (9)$$

where x is the composition, μ is the chemical potential, and D^0 is the diffusion coefficient in the infinitely dilute solution. The value of Q is unity for an ideal gas mixture or an ideal solution. We used the following equation instead of eq 7 because the experiments were carried out at low concentrations:

$$D_{12} = D^0_{12}Q \qquad (10)$$

where D^0_{12} was estimated from the Schmidt number in eq 6. The following relation, well-known for vapor—liquid equilibrium, is satisfied at the critical point of a mixture:

$$(\partial \mu_1/\partial x_1)_{P,T} = 0 \qquad (11)$$

Considering eq 11, the mutual diffusion coefficients should approach zero at the critical point.

Equation of State

Since the chemical potential and its derivative play an important role in diffusion, an equation of state can be used to reveal the diffusion behavior. In this work, we applied the Peng—Robinson equation of state [Peng and Robinson, 1976] to calculate the chemical potential gradient. The Peng—Robinson equation of state is given by

$$P = \frac{RT}{v - b} - \frac{a(T)}{v(v + b) + b(v - b)} \qquad (12)$$

a and b for the pure component are given as

$$a = 0.45724(R^2 T_c^2/P_c)\alpha \qquad (13)$$

$$b = 0.07780(RT_c/P_c) \qquad (14)$$

where

$$\alpha^{1/2} = 1 + m(1 - T_r^{1/2}) \qquad (15)$$

$$m = 0.37464 + 1.54226\omega - 0.26992\omega^2 \qquad (16)$$

For mixtures, the following mixing rules were used:

$$a = \sum\sum x_i x_j (1 - \delta_{ij})(a_i a_j)^{1/2} \qquad (17)$$

$$b = \sum x_i b_i \qquad (18)$$

The δ_{ij} in eq 17 was determined to be 0.07 by fitting experimental vapor—liquid equilibrium data [Mukesh, 1982]. However, it should be noted that the value δ_{ij} estimated from vapor—liquid equilibrium data is not usually applicable near the critical point because cubic equations of state do not, in general, fit the pure-component critical point.

Using the Peng—Robinson equation of state, the value of Q was calculated at fixed P, T, and x_1. At pressures in this work, the Peng—Robinson equation of state gives only one root for density calculation. The effect of the
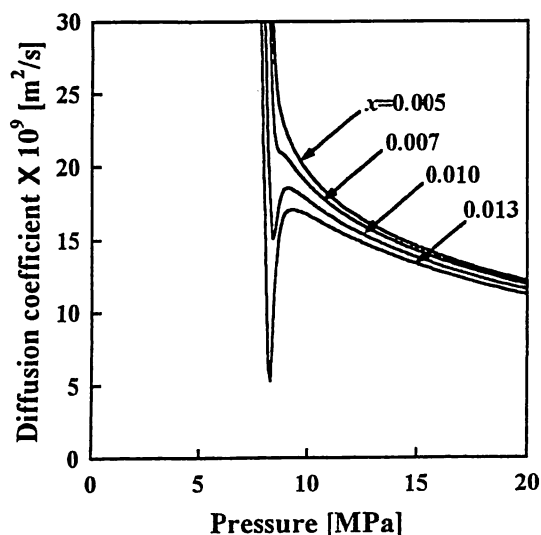
Figure 2. Effect of the solute mole fraction on the diffusion coefficient calculated with the Peng–Robinson equation of state at 313.15 K ($\delta_{ij} = 0.07$).
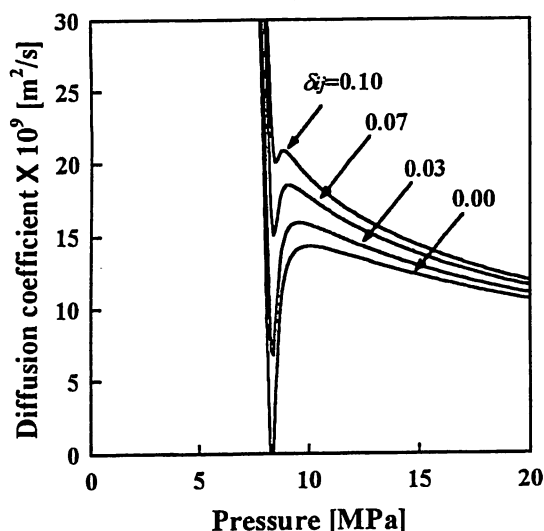

Figure 3. Effect of the binary interaction parameter δ_{ij} on diffusion coefficients calculated with the Peng–Robinson equation of state at 313.15 K (solute composition $x_1 = 0.01$).

solute composition on calculated diffusion coefficients from the equation of state for $\delta_{ij} = 0.07$ is shown in Figure 2. Diffusion coefficients decreased monotonically at solute compositions less than 0.005. Unusual sigmoidal behavior occurred at higher mole fractions according to the results calculated. The behavior of the maximum point is consistent qualitatively with the experimental values, although minimum points could not be observed because the signal from the detector became unstable as the critical point was approached. Therefore, we concluded that the chemical potential gradient model was preferable to the composition gradient model in Fick's law. The effect of binary interaction δ_{ij} for $x_1 = 0.01$ on calculated diffusion coefficients is shown in Figure 3. Considering the value of $1 - \delta_{ij}$ is a measure of attraction force, diffusion coefficients decrease with attraction between a solute molecule and a solvent.

Mutual Diffusion Coefficient D_{12} Taking into Consideration Composition Dependence

Since the solute is dispersed radially in the solvent, it is very difficult to define the precise solute composi-
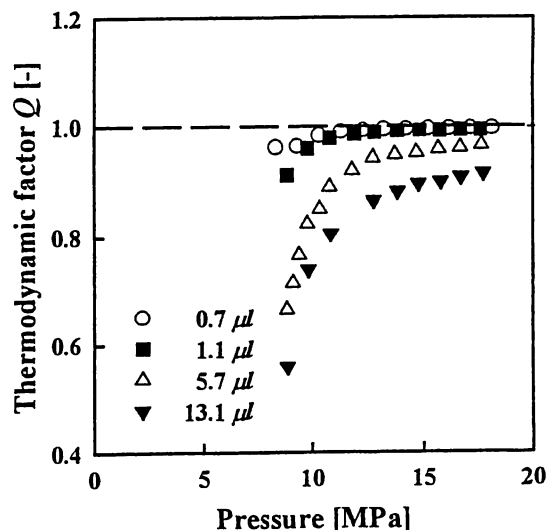
Figure 4. Calculated results of the thermodynamic factor Q from the characteristic composition.

tion. In this work, we used a characteristic composition based on a tube volume containing 68% of the solute volume, which was between reflection points of an error function signal. This value should be closely related to the average composition of a solute. From the characteristic composition, it was possible to estimate the thermodynamic factor Q, as shown in Figure 4. At small injection volumes, the solution behaves like an ideal solution. Mutual diffusion coefficients of benzene by eq 10 are shown in Figure 1. The calculated results show a similar trend of composition dependence as the experimental results, although the maximum point is not so clear. We found it difficult to obtain the optimum binary interaction parameter δ_{ij} in the vicinity of the binary critical point because δ_{ij} has a strong effect on the diffusion behavior in this region. Cussler [1980] suggested that eq 7 does not correctly describe diffusion near the critical point. However, we have showed that an equation of state is useful to explain some of the behavior of mutual diffusion coefficients in the critical region. More complicated expressions should be considered such as those of Liu [Liu and Ruckenstein, 1997].

Conclusions

Our experimental results showed that, at the binary critical point, diffusion coefficients exhibited a maximum and a strong concentration dependence of a solute near the critical point. The Peng–Robinson equation could predict the strong concentration dependence of diffusion coefficients near the critical point.

Nomenclature

a, b, m = Peng–Robinson constants
a_i = coefficient in eq 5
C = concentration, mol m^{-3}
D = mutual diffusion coefficient, m^2 s^{-1}
k = apparent diffusion coefficient, m^2 s^{-1}
L = length of the diffusion tube, m
L_0 = kinetic factor = $x_1 D^0{}_{21} + x_2 D^0{}_{12}$, m^2 s^{-1}
M = molecular weight, kg
P = pressure, Pa
Q = thermodynamic factor = $(x_1/RT)(\partial\mu_1/\partial x_1)_{P,T}$
R = gas constant, J K^{-1} mol^{-1}
R_0 = radius of the tube, m
Sc = Schmidt number = $\mu_2/P_2 D^0{}_{12}$

t = time, s

T = temperature, K

$\bar{u}$ = mean velocity, m s^{-1}

V = volume, m^3 mol^{-1}

x = composition

z = distance from injection point, m

Greek Letters

α = Peng–Robinson parameter

δ_{ij} = binary interaction parameter

η = viscosity, Pa s

μ = chemical potential

ρ = density, mol m^{-3}

σ = effective hard-sphere diameter, m

ν = molar volume, m^3 mol^{-1}

ν_0 = closed-packed hard-sphere volume, m^3 mol^{-1}

ω = acentric factor

Superscripts

0 = infinite dilution

+ = reduced value

* = atmospheric pressure

Subscripts

1 = solute (benzene)

2 = solvent (carbon dioxide)

c = critical value

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