Diffusion Near the Critical Point

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ABSTRACT

Measuring mutual diffusion coefficients of benzene in supercritical carbon dioxide using the Taylor dispersion method, we observed an astonishing phenomenon that diffusion coefficients approached zero near the critical point of a mixture. We can explain the phenomenon based on the assumption that mutual diffusion coefficients are governed by a term of gradient of chemical potential, because a mutual diffusion coefficient becomes essentially zero at the critical point of a mixture. The assumption provides a method to estimate diffusion coefficients form an equation of state. The calculated results are consistent with the critical behavior of approaching zero. Defining characteristic composition from experimental data, application of a BWR equation of state revealed the qualitative composition dependence of diffusion coefficients of benzene in supercritical carbon dioxide.

1. INTRODUCTION

Previously, we measured mutual diffusion coefficients of acetone [1] and benzene [2] in supercritical carbon dioxide with light absorption detector based on the Taylor dispersion method [3]. As a result, we observed that diffusion coefficients approached zero at the binary critical point. Calculation of chemical potential from generalized BWR equation of state showed qualitatively composition dependence of benzene on diffusion coefficient.

2. EXPERIMENTAL

2.1 Data Treatment

According to Taylor, average concentration C at distance z when time t passed after pulse input in a laminar flow is given by a following equation

$$C = \frac{1}{2}\left(\frac{M}{\pi R_0^{\,2}}\right)\left(\frac{1}{\sqrt{\pi k t}}\right)\exp\left(-\frac{(z-ut)}{4kt}\right) \tag{1}$$

where k denotes an apparent diffusion coefficient, R_0 an inner radius of a tube, u an average flow velocity. Taylor derived the relation between the apparent diffuison coefficient k and mutual diffusion coefficient D_{12}, Eq. (2)

$$D_{12} = \frac{R_0^{\,2} u^2}{48k} \tag{2}$$

We estimated an apparent diffusion coefficient k by fitting our experimental data to Eq .(1). Substituting k into Eq. (2), a mutual diffusion coefficient D_{12} is obtained.

2.2 Apparatus

Figure 1 is a schematic experimental apparatus. Carbon dioxide in a cylinder was liquified by a cool pump. Liquified carbon dioxide was supplied at constant volumetric rate by a compressor and introduced into a diffusion tube. Circulating warm water through an outer tube keeps the constant temperature of an inner diffusion tube. Longitudinal temperature was kept within 0.1K. In this work, we used a straight diffusion tube because of no effects of gravity, centrifugal force and buoyancy. A solute was injected through a six-port valve into supercritical carbon dioxide. Concentration of benzene was determined from absorption spectra at 269.5 nm, 265.0 nm and 252.0 nm for 13.1μl, 5.7μl and the other two injection volumes, 0.7, 1.1μl, respectively. Pressure was regulated by a back pressure valve. Length of diffusion tube is 10.20.1m long, and 0.880.017 mm inner diameter. The response signal was recorded by an absorption detector. Figure 2 is a typical distribution curve of benzene. Radial diffusion in a laminar flow causes an error function curve.

3. EXPERIMENTAL RESULTS

Diffusion coefficients of benzene in supercritical carbon dioxide at 313.15K were shown in Fig. 3 and listed in Table.1. We can understand that injected volume of benzene has strong effect on diffusion coefficients. In the case of injected volumes 0.7 or 1.1μl, diffusion coefficients are decreasing with pressure as usual. But when injected volume is 5.7 or 13.1μl, we could recognize that they have maximum points and seemed to approach zero near the critical pressure of a mixture. The results seem to have strong composition dependence on diffusion coefficients near the critical point, as the similar results in our previous work for acetone in supercritical carbon dioxide [1].

Figure 4 shows the effects of temperature on diffusion coefficients of benzene in supercritical carbon dioxide at 304.15, 313.15, 323.15K. Above about 13MPa, the diffusion coefficients increase with temperature at the same pressure. At lower pressures than about 13MPa, we observed maximum points at 313.15 and 323.15K, although we could not find a maximum point at 304.15K at the critical point.

Cussler [4] proposed a theory about the critical anomalies of mutual diffusion coefficients. However, we found it difficult to apply a light absorption method in the vicinity of a binary critical point, due to no light transparency or high density fluctuations. Sengers and coworkers [5] reported that the Taylor dispersion method could not be applied to measure of diffusion coefficients near the critical point. Absolute average deviations (*AAD*) are estimated by Eq. (3) in the area between two inflection points of a recorded curve.

$$AAD[\%] = \frac{100}{n}\sum^{n}\left|\frac{\left(D_{exp} - D_{cal}\right)}{D_{exp}}\right| \tag{3}$$

where n is the number of data. Deviation *AAD* becomes greater in the vicinity of the critical pressure of a mixture or in the case of biggest injected volume, 13.1mℓ.

4. ESTIMATION OF DIFFUSION COEFFICIENTS

4.1 Diffusion Coefficient D^0 in Infinite Dilution

We assumed that the binary diffusion coefficient may be proportional to a chemical potential gradient. The modified equation of the binary diffusion coefficient based on the work of Darken [6] follows as

$$D_{12} = \left(x_1 D^0{}_{21} + x_2 D^0{}_{12}\right) \cdot Q \tag{4}$$

where Q is the thermodynamic factor defined as

$$Q = x_1 / RT\left(\partial\mu_1 / \partial x_1\right) = x_2 / RT\left(\partial\mu_2 / \partial x_2\right) \tag{5}$$

where x_i composition, μ_i chemical potential of a species i. We used Eq. (6) in stead of Eq. (4) under assumption of infinite dilution,

$$D_{12} = D^0{}_{12} \cdot Q \tag{6}$$

It means that a gradient of chemical potential provide an extended driving force instead of a gradient of concentration. At the critical point, the following equations are satisfied

$$\left(\partial\mu_1 / \partial x_1\right)_{P,T} = \left(\partial\mu_2 / \partial x_2\right)_{P,T} = 0 \tag{7}$$

Accordingly, it reveals that a mutual diffusion coefficient is essentially zero at the critical point. Hayduk and Cheng [7] investigated the effect of solvent viscosity on the infinite dilution diffusion coefficient and proposed that,

$$D^0{}_{12} = a\eta_2^{\,b} \tag{8}$$

where the constants a and b are particular. In this work, a, b were determined by fitting experimental data in the case of 0.7μl injected volume. The viscosity of the solvent was calculated by the equation of Chung et al. [8]. $D^0{}_{12}$ is proportional to $\eta_2^{-0.96}$ in this correlation, .

4.2 Equation of State

We applied a BWR equation of state to calculate the gradient of chemical potential with composition. The BWR equation of state with generalized fifteen coefficients [9] is expressed as follows,

$$
\begin{aligned}
P = {} & \rho RT \\
& + \left(B_0 RT - A_0 - \frac{C_0}{T^2} + \frac{D_0}{T^3} - \frac{E_0}{T^4} \right) \rho^2 \\
& + \left(bRT - a - \frac{d}{T} - \frac{e}{T^4} - \frac{f}{T^{23}} \right) \rho^3 \\
& + \alpha \left(a + \frac{d}{T} + \frac{e}{T^4} + \frac{f}{T^{23}} \right) \rho^6 \\
& + \left(\frac{c}{T^2} - \frac{g}{T^8} - \frac{h}{T^{17}} \right) \rho^3 \left(1 + \gamma \rho^2 \right) exp\left(-\gamma \rho^2 \right)
\end{aligned}
\tag{9}
$$

Fifteen coefficients are functions of T_c, ρ_c and. These parameters are functions of mole fraction, for example, for C_0 in Eq. (9). where

$$C_{0ij} = \left(0.356306 + 1.70871 \omega_{ij} \right) RT_{0ij} V_{cij} \tag{11}$$

$$T_{cij} = m_{ij} \sqrt{T_{ci} T_{cj}} \tag{12}$$

where m_{ij} is binary interaction parameters. In this work, m_{ij} is assumed 1.0 in order to show qualitative critical behavior.

4.3 Characteristic Composition

It is very difficult to know composition of benzene in supercritical carbon dioxide. In this work, we define characteristic composition based on a tube volume containing 68 % of a solute volume, which lies between reflection points of an error function signal, which seems to be strongly related to average composition of a solute. We can estimate mole fraction by knowing fluid density under the pressure of a system. Figure 5 shows that characteristic composition obtained from the experimental data decreases as pressure increases above 10 MPa.

4.4 Composition Dependence of Mutual Diffusion Coefficients

Using the characteristic compositions from experimental data, mutual diffuison coefficients of benzene were calculated based on Eq. (6), as shown in Fig. 3. The calculated results explain the similar trend of composition dependence as experimental results, however a maximum point is not so clear.

5. CONCLUSION

We obtained striking experimental results that diffusion coefficients of benzene in supercritical carbon dioxide seem to approach zero near the binary critical pressure. To explain the critical behavior, we introduced a thermodynamic factor Q, which contains chemical potential term. The calculated results are consistent with the critical behavior of approaching zero. Taking into consideration of concentration effects from experimental data, application of a BWR equation of state revealed the qualitative composition dependence of diffusion coefficients of benzene in supercritical carbon dioxide.

LIST OF SYMBOLS

A_0, B_0, C_0, D_0, E_0, a, b, c, d, e, f, g, h, a, g		
	coefficients in BWR equation of state in Eq. (9)	[-]
C	concentration	[mol m^3]
D	mutual diffusion coefficient	[m^2 s^{-1}]
k	apparent diffusion coefficient	[m^2 s^{-1}]
L	length of diffusion tube	[m]

m_{ij}	binary interaction parameter	[-]
M	mass of material	[kg]
n	number of data	[-]
P	pressure	[Pa]
Q	thermodynamic factor	[-]
R	gas constant	[l atm K^{-1} mol^{-1}]
R_0	radius of tube	[m]
t	time	[s]
T	temperature	[K]
$\bar{u}$	mean velocity	[m s^{-1}]
V_c	critical volume	[m^3 mol^{-1}]
x	composition	[-]
z	distance from injection point	[m]

Greeks

m	chemical potential	[-]
r	density	[mol m^{-3}]
w	acentric factor	[-]
h	viscosity	[Pa s]

Superscript

infinite dilution

Subscripts

1	solute (benzene)
2	solvent (carbon dioxide)

c	critical property
cal	calculated values
exp	experimental values

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Table.1. Diffusion coefficients of benzene in supercritical carbon dioxide at 313.15 K

Pressure [MPa]	D X 10^{-9} [m^2/s]	*AAD* []
8.53	16.78	1.497
9.07	15.78	0.290
9.56	15.38	0.188
10.10	14.29	0.115
10.59	13.99	0.135
11.03	13.37	0.245
11.47	12.16	0.309
12.65	11.07	0.265
13.63	10.73	0.240
14.42	10.34	0.268
15.69	9.94	0.280
16.28	9.61	0.348
17.65	9.13	0.465
18.34	8.85	0.381

Pressure [MPa]	D X 10^{-9} [m^2/s]	*AAD* []
8.58	17.15	0.549
9.07	18.08	0.637
9.51	18.05	0.069
10.15	15.30	0.089
10.49	14.16	0.107
10.89	13.90	0.193
11.67	12.58	0.183
12.06	12.67	0.092
13.68	10.97	0.262
14.42	10.54	0.237
15.69	10.02	0.166
16.67	9.67	0.280
17.75	9.29	0.293
18.53	8.90	0.251

Pressure [MPa]	D X 10^{-9} [m^2/s]	*AAD* []
8.48	8.290	2.300
9.02	11.92	0.823
9.56	13.98	0.626
10.10	14.98	0.486
10.49	14.58	0.407
10.98	14.27	0.505
11.57	13.19	0.367
12.50	12.19	0.402
13.73	12.21	0.222
14.91	10.70	0.182
15.691	10.03	0.313
16.67	9.45	0.241
17.75	9.45	0.241
18.83	9.18	0.282

Pressure [MPa]	D X 10^{-9} [m^2/s]	*AAD* []
8.58	5.26	4.245
9.02	7.23	2.606
9.41	9.28	2.358
9.95	10.63	2.325
10.44	11.16	2.577
11.08	12.00	1.996
11.82	11.56	2.027
12.70	11.94	1.897
13.63	11.72	1.942
14.66	11.43	1.917
15.54	11.40	1.666
16.52	11.06	1.508
17.75	9.41	1.639
18.55	9.718	1.658

FIGURE CAPTIONS

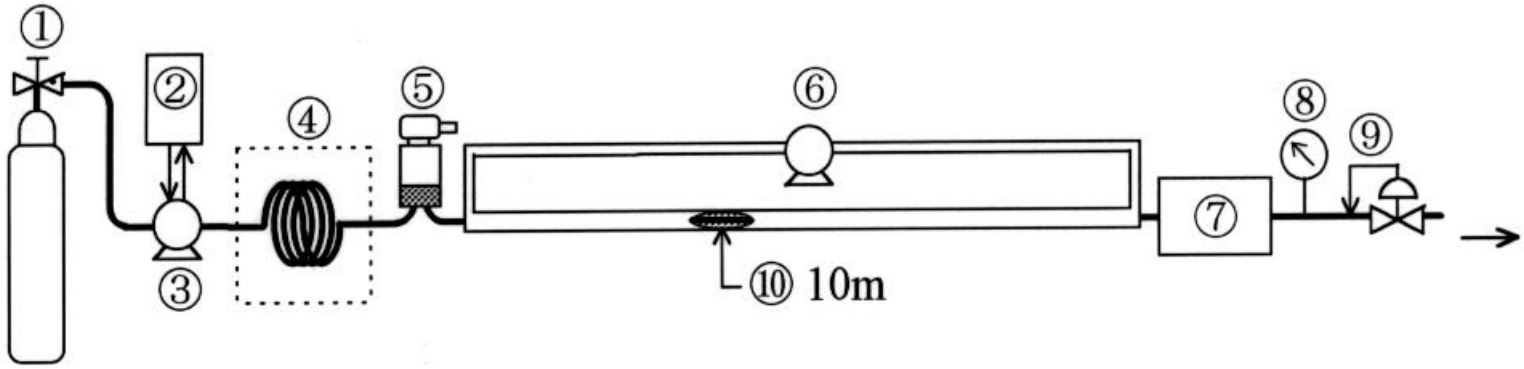
Fig. 1 Experimental apparatus for the detecting of benzene concentration in supercritical carbon dioxideCO_2 cylinder Cooler Compressor Air thermostatInjection valve Water thermostat Absorption detector Pressure gauge Back pressure valve Diffusion tube

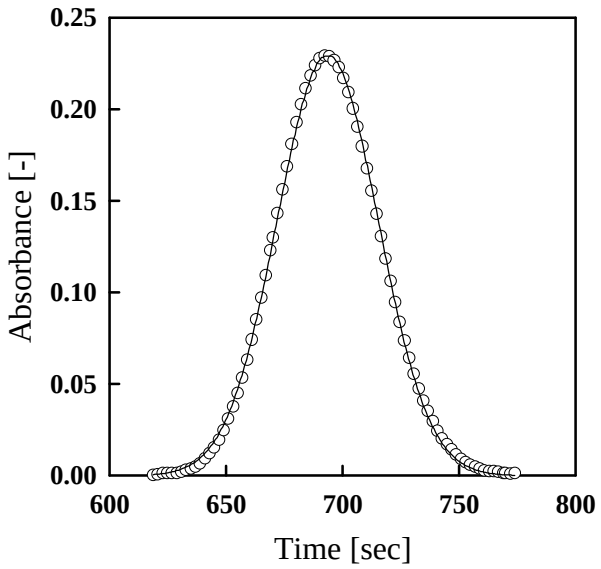
Fig. 2. Typical absorbance distribution of benzene in supercritical carbon dioxide (11.3MPa, 313.15K, 0.7㎖)

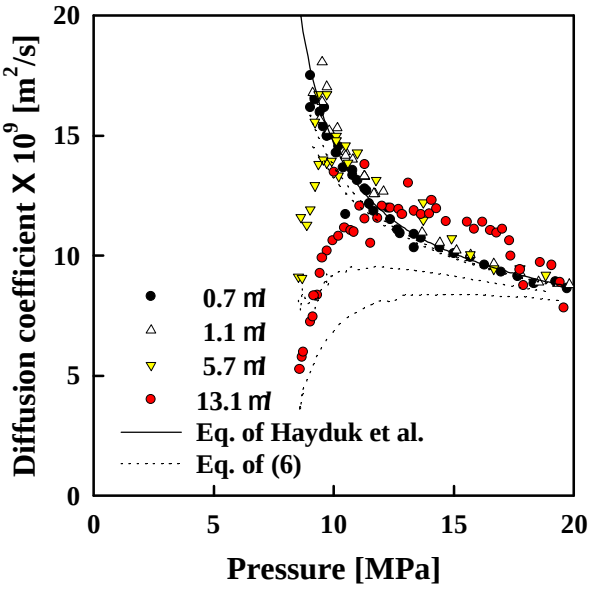
Fig. 3. Effect of diffusion coefficients of benzene in supercritical carbon dioxide at 313.15K

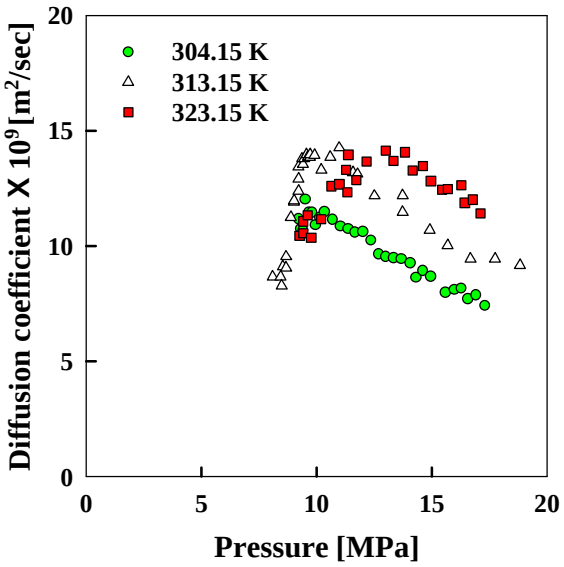
Fig. 4. Effect of temperature on diffusion coefficient of benzene in supercritical carbon dioxide (5.7㎖)

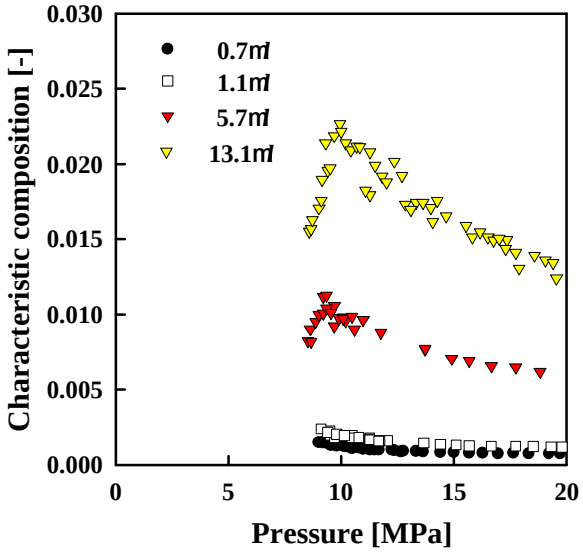
Fig.5 Effect of pressure on characteristic composition


①
②
③
④
⑤
⑥
⑦
⑧
⑨
⑩ 10m


0.25
0.20
0.15
0.10
0.05
0.00
Absorbance [-]
600
650
700
750
800
Time [sec]


Diffusion coefficient X 10^9 [m^2/s]
Pressure [MPa]
0
5
10
15
20
0.7 ml
1.1 ml
5.7 ml
13.1 ml
Eq. of Hayduk et al.
Eq. of (6)


304.15 K
313.15 K
323.15 K
Diffusion coefficient X 10^9 [m^2/sec]
Pressure [MPa]
0
5
10
15
20
0
5
10
15
20


0.030
0.025
0.020
0.015
0.010
0.005
0.000
Characteristic composition [-]
0.7ml
1.1ml
5.7ml
13.1ml
0
5
10
15
20
Pressure [MPa]