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Diffusion Coefficients of Naphthalene and Dimethylnaphthalene in Supercritical Carbon Dioxide

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ABSTRACT

A new experimental apparatus based on a pseudo-steady state solid dissolution method has been designed to measure the diffusion coefficients of supercritical carbon dioxide(1)-naphthalene(2) and supercritical carbon dioxide(1)-dimethylnaphthalene isomers(2) systems. The diffusion coefficients were measured at 308.2 K. In order to establish the validity of this method and the performance of the apparatus, the experimental results of the diffusion coefficients of naphthalene in supercritical carbon dioxide were compared with the literature data measured by other methods. The decrease of diffusion coefficient of naphthalene was observed near the critical point of carbon dioxide. The diffusion coefficients of 2,6-dimethylnaphthalene (2,6-DMN) and 2,7-dimethylnaphthalene (2,7-DMN) show almost the same values. The diffusion coefficients of these isomers are about 10% lower than those of naphthalene.

INTRODUCTION

Supercritical fluid extraction has been given much attention recently as one of the new separation technologies in the chemical industry. One of useful physical properties needed for the design of supercritical extractors and separators is the diffusion coefficients of high-boiling compounds under the supercritical conditions. However, measurements of the diffusion coefficients have been limited and thermodynamic analysis of diffusion behavior has not been fully advanced. In previous works, the solubilities of dimethylnaphthalene isomers in

supercritical carbon dioxide were measured [1] and the adsorption separation of the isomeric dimethylnaphthalene mixture of 2,6-DMN and 2,7-DMN extracted in supercritical carbon dioxide was studied by using various zeolites [2, 3]. The possibility for the adsorption separation of the isomeric mixture under the supercritical condition was investigated in the previous study. The transport properties such as diffusion coefficient are necessary for discussion on the separation mechanism at the supercritical condition. However, the diffusion coefficient data in the supercritical region are limited.

Recently, Liong et al. [4] have reviewed the diffusion in supercritical fluids. Iomtev and Tsekhanskaya [5] have used unsteady-state method to measure the diffusion coefficients of naphthalene in supercritical carbon dioxide and ethylene. Debenedetti and Reid [6] measured the diffusion coefficients of benzoic acid and 2-naphthol in supercritical carbon dioxide. Knaff and Schlünder [7] measured the diffusion coefficients for naphthalene and caffeine in supercritical carbon dioxide by using a pseudo-steady state solid dissolution technique. Lamb et al. [8] measured the diffusion coefficients of naphthalene in supercritical carbon dioxide and ethylene by using the NMR fixed field gradient spin-echo Bessel function analysis technique. Funazukuri et al. [9, 10] were used the Taylor-Aris method to measure the diffusion coefficients of unsaturated fatty acid methyl esters and organic compounds in supercritical carbon dioxide. The Taylor-Aris method was used in many other literature to measure the diffusion coefficients in supercritical fluids. Nishiumi et al. [11] measured the diffusion coefficients of acetone in supercritical carbon dioxide by the Taylor-Aris method. They show the diffusion coefficients

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sharply decrease near the critical point of carbon dioxide. The abnormality of diffusion coefficients of naphthalene in supercritical carbon dioxide near the critical point were also reported by Tsekhanskaya [12]. Liong et al. [4] obserbed the diffusion coefficient was essentially zero in the vicinity of the binary critical point.

In this work, the diffusion coefficients of $CO_2(1)$-naphthalene(2), $CO_2(1)$-2,6-DMN(2) and $CO_2(1)$-2,7-DMN(2) systems were measured by using a pseudo-steady state solid dissolution technique proposed by Knaff and Schlünder [7] and the experimental diffusion data were correlated by using the Schmidt number correlation proposed by Funazukuri et al. [13].

EXPERIMENTAL

Theoretical

A schematic of a capillary in a diffusion cell is shown in Figure 1. The diffusion coefficients of naphthalene and dimethylnaphthalene isomers (component 2) in supercritical carbon dioxide (component 1) can be obtained from both mass transfer and mass balance considerations. The mass transfer equation for component 2 is given by eq.(1), assuming that the solute concentrations at the capillary entrance and at the solid solute interface are zero and saturated solubility, respectively, and that the concentration profile is linear along the axis of diffusion [7].

$$N_2 = \frac{n_g D_{21} A_p y_2}{h}$$

where N_2 is the transfer rate of the component 2, n_g is the molar gas density, D_{21} is the diffusion coefficient, A_p is the interfacial area, y_2 is the saturated solubility and h is the distance from capillary entrance to the surface of the solid solute.

It is also assumed that the rate of solute removed from the capillary entrance is larger than the rate of the solute transported there by the diffusion process. Therefore the mass balance for the diffusing solute in the capillary is

$$N_2 = \frac{A_p \rho_2}{M_2} \frac{dh}{dt}$$

where ρ_2 is the packed mass density and M_2 is the molar mass. By combining eqs. (1) and (2) and integrating, the expression for diffusion coefficient is given by eq.(3).

$$D_{21} = \frac{\rho_2 \left(h_e^2 - h_b^2\right)}{2 M_2 n_g y_2 \Delta t}$$

where h_b and h_e are the distances at the beginning and the end of the experiment and Δt is the elapsed time. h_b was measured by using a micrometer. h_e was calculated from ρ_2 and the weights of capillary at the beginning and the end of the experiments, because the packed mass density changed during depressurization after the experiment. Further, n_g and y_2 for the $CO_2(1)$-naphthalene(2) system were given by the data of Tsekhanskaya et al. [14]. y_2 for the $CO_2(1)$-dimethylnaphthalene isomer(2) systems were cited from the data of Iwai et al. [1] and n_g

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for these systems were replaced by the molar density of pure carbon dioxide calculated by the equation from Angus et al. [15]. Although the density data for these mixtures are not available, the values of density for pure carbon dioxide are considered to be little different from these mixtures in the high pressure region.

Materials

Reagent-grade naphthalene (more than 99.0mol% supplied by Nacalai Tesque, Inc.) and reagent-grade 2,6-DMN (more than 99.0mol% supplied by Wako Pure Chem. Ind., Ltd.) and 2,7- DMN (more than 98.0mol% supplied by Wako Pure Chem. Ind., Ltd.) were used. High-purity carbon dioxide (more than 99.9 %, Sumitomo Seika Co.) was used as received.

Apparatus

A flow-type apparatus was used in this study and a pseudo-steady state solid dissolution method was adopted to measure the diffusion coefficients in supercritical carbon dioxide. The apparatus is shown schematically in Figure 2. From a gas cylinder (1), carbon dioxide was supplied and liquefied through a cooling unit (5). The liquefied carbon dioxide was send to a preheater (10) by a high-pressure liquid chromatography pump (6). When carbon dioxide passed through the preheater, it became a supercritical fluid. The diffusion cell (11) was made of SUS316, and its inner diameter and length were 30 mm and 200 mm, respectively. Twelve or four capillaries which partially filled with the solid solute were attached in the diffusion cell, as

shown in Figure 2. The depths of capillaries were about 10 mm and the inner diameters were about 0.9, 1.0, 1.1, 1.2 mm, respectively. The preheater and diffusion cell were immersed into a water bath (14) at an experimental temperature which was controlled within ± 0.2 K. Valve V6 was closed, and valves V4, V5 were opened to introduce supercritical carbon dioxide into the diffusion cell. When supercritical carbon dioxide passed through the diffusion cell, the solid solute dissolved and diffused into supercritical carbon dioxide. The pressure was measured by a precision Bourdon gauge (8), of which the accuracy was ± 0.15 % and the fluctuation of pressure was about ± 0.05 MPa. The supercritical carbon dioxide containing solute was decompressed through an expansion valve, V8.

RESULTS AND DISCUSSION

The diffusion coefficient measurements were carried out under several elapsed times and flow rates at given pressures as shown in Figures 3 and 4. As illustrated in Figure 3, the diffusion coefficients obtained are independent of elapsed times by the time to be longer than 20 h. The experimental results of diffusion coefficient are independent of flow rates, as shown in Figure 4. Although it is difficult to control the flow rate for long time, the fluctuation of flow rate was very small as compare with the flow rate range shown in Figure 4.The diffusion coefficients were determined as an average value obtained from the all capillaries and the maximum deviation from average value was 16 %. The reproducibilities of diffusion coefficients were within 5 % in the high pressure range above 8.70 MPa and about 8 % in the low pressure range below 8.70

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MPa.

The experimental diffusion coefficients of naphthalene and dimethylnaphthalene isomers in supercritical carbon dioxide at 308.2 K are listed in Table 1 and illustrated in Figures 5 and 6. The diffusion coefficients of naphthalene obtained in this study are in good agreement with the literature data [8] in the high pressure range. The diffusion coefficients of naphthalene near the critical point decrease as shown in Figures 5 and 6. The same phenomena was reported by Nishiumi et al. [11] and Tsekhanskaya [12]. The diffusion coefficients of 2,6-DMN and 2,7-DMN show almost the same value. The diffusion coefficients of dimethylnaphthalene isomers are about 10% lower than those of naphthalene.

CORRELATION

The Schmidt number correlation proposed by Funazukuri et al. [13] was used to calculate the diffusion coefficients. The Schmidt number correlation is given by

$$\ln\left(Sc^+ - 1\right) = \sum_{i=0}^{5} a_i \left(\frac{v_0}{v}\right)^i$$

where v is the molar volume, v_0 is the closed-packed hard sphere volume of solvent and a_i is the coefficient determined by Funazukuri et al. [13].

$$Sc^+ = Sc / Sc^*$$

where $Sc^*=5/6$ for self-diffusion. For binary diffusion, the following equation can be used.

$$Sc^* = \frac{5}{6}\left(\frac{\sigma_1 + \sigma_2}{2\sigma_1}\right)^2 \left(\frac{2m_2}{m_1 + m_2}\right)^{1/2}$$

where σ and m are the effective hard-sphere diameter and the molecular weight, respectively. The effective hard-sphere diameter of solvent(1) was calculated by

$$v_0 = N_{AV}\sigma_1^3 / \sqrt{2} \tag{7}$$

where N_{AV} is Avogadro number and v_0 was calculated from the equation proposed by Funazukuri et al. [17]. The effective hard-sphere diameter of solute(2) was calculated by

$$\sigma_1 / \sigma_2 = \sigma_{vw,1} / \sigma_{vw,2} \tag{8}$$

where σ_{vw} is the van der Waals diameter estimated by the method of Bondi [18]. The parameters of Schmidt number correlation are listed in Table 2 and 3. The density and viscosity of supercritical fluids which are necessary to convert the Schmidt number into diffusion coefficient are replaced by those of pure carbon dioxide calculated by the equation of Angus et al. [15] and Chung et al. [19], respectively.

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The correlation results by the Schmidt number correlation show good agreement with the experimental data except for the near critical region, as shown in Figures 5 and 6.

CONCLUSION

A pseudo-steady state solid dissolution method was adopted to measure the diffusion coefficients of naphthalene and dimethylnaphthalene isomers in supercritical carbon dioxide at 308.2 K. The decrease of diffusion coefficient of naphthalene are observed near the critical point. The diffusion coefficients of dimethylnaphthalene isomers are almost the same values. The Schmidt number correlation show good agreement with the experimental data except for the near critical region.

ACKNOWLEDGMENTS

LIST OF SYMBOLS

A_p	= interfacial area of capillaries	$[m^2]$
a_i	= coefficient in Eq.(4) determined by Funazukuri et al.	[-]
D	= diffusion coefficient	$[m^2\ s^{-1}]$

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h	= distance from capillary entrance to surface of solid solute	[m]
M	= molar mass	[kg mol^{-1}]
m	= molecular weight	[-]
N	= transfer rate	[mol s^{-1}]
N_{AV}	= Avogadro number	[mol^{-1}]
n	= molar density	[mol m^{-3}]
P	= pressure	[Pa]
Sc	= Schmidt number	[-]
T	= absolute temperature	[K]
t	= time	[s]
v	= molar volume	[m^3 mol^{-1}]
v_0	= closed-packed hard sphere volume of solvent	[m^3 mol^{-1}]
y	= solubility (mole fraction)	[-]

Greek letters

σ	= effective hard-sphere diameter	[m]
σ_{vw}	= van der Waals diameter	[m]
ρ	= packed mass density	[kg m^{-3}]

Superscripts

+	= reduced value
*	= atmospheric pressure

Subscripts

b	= beginning of experiment
e	= end of experiment
g	= supercritical gas mixture
1	= solvent (supercritical carbon dioxide)
2	= solute (naphthalene or dimethylnaphthalene isomers)

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Table 1. Diffusion coefficients of naphthalene, 2,6-dimethylnaphthalene and 2,7-dimethylnaphthalene(2) in supercritical carbon dioxide(1) at 308.2 K

Component	P [MPa]	n_1 [mol cm^{-3}] [a]	n_g [mol cm^{-3}] [b]	y_2 [-]	$D_{21} \times 10^8$ [m^2 s^{-1}]
Naphthalene	7.21	0.00544	0.00519	0.00045 [b]	3.83
	7.50	0.00623	0.00577	0.00060 [b]	3.32
	7.70	0.00703	0.00651	0.00083 [b]	3.23
	7.86	0.00803	0.00763	0.00127 [b]	2.91
	7.92	0.00858	0.00919	0.00210 [b]	2.40
	7.99	0.00944	0.01116	0.00354 [b]	2.04
	8.02	0.00989	0.01178	0.00409 [b]	1.86
	8.03	0.01004	0.01200	0.00430 [b]	1.59
	8.12	0.01142	0.01380	0.00626 [b]	1.28
	8.14	0.01167	0.01394	0.00644 [b]	1.22
	8.18	0.01211	0.01420	0.00676 [b]	1.31
	8.21	0.01239	0.01435	0.00696 [b]	1.42
	8.70	0.01448	0.01518	0.00810 [b]	1.53 [e]
	11.8	0.01735	0.01763	0.0121 [b]	1.13
	15.2	0.01859	0.01890	0.0146 [b]	1.06 [e]
2,6-dimethyl-naphthalene	9.10	0.01519		0.00195 [c]	1.18 [e]
	14.6	0.01841		0.00306 [c]	0.96 [e]
	19.5	0.01959		0.00383 [d]	0.82 [e]
2,7-dimethyl-naphthalene	10.7	0.01672		0.00351 [c]	1.11 [e]
	15.0	0.01852		0.00472 [c]	0.94 [e]
	20.0	0.01968		0.00529 [c]	0.87 [e]

[a] Angus et al. [15]. [c] Iwai et al. [1]. [e] Four capillaries were used.

[b] Tsekhanskaya et al. [14]. [d] Kurnik et al. [16].

Table 2. Values of constants a_i in Eq.(4) [a]

i	a_i
0	-4.92519817×10^0
1	5.45529385×10^1
2	-2.45231443×10^2
3	6.07893924×10^2
4	-7.08884016×10^2
5	3.29611433×10^2

[a] Funazukuri et al. [13].

Table 3. Parameters of Schmidt number correlation

Component	v_0 [cm^3 mol^{-1}]	σ_{vw} [nm]
Carbon dioxide	19.7 [a]	0.397 [b]
Naphthalene		0.617 [b]
Dimethylnaphthalene		0.673 [b]

[a] Funazukuri et al. [17].

[b] Bondi [18].

Figure 1. Capillary in diffusion cell.

Figure 2. Experimental apparatus and capillaries attached in diffusion cell. (1. Gas Cylinder,
2. Dryer, 3. Filter, 4. Pressure Gauge, 5. Cooling Unit, 6. Feed Pump, 7. Stopper,
8. Precision Pressure Gauge, 9. Safety Valve, 10. Pre-heater, 11. Diffusion Cell,
12. Trap, 13. Gas Meter, 14. Water Bath, V1, 3-7. Stop Valve, V2. Back Pressure
Regulator, V8. Expansion Valve)

Figure 3. Relationship between diffusion coefficient of naphthalene in supercritical carbon
dioxide and elapsed time. (   ) 11.8 MPa; vertical lines represent fluctuations in
experimental results.

Figure 4. Relationship between diffusion coefficient of naphthalene in supercritical carbon
dioxide and flow rate of carbon dioxide. (   ) 15.2 MPa; (   ) 11.8 MPa; (   ) 8.70 MPa;
(   ) 7.70 MPa; (   ) 7.21 MPa; vertical lines represent fluctuations in experimental
results.

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Figure 5. Diffusion coefficients of naphthalene, 2,6-dimethylnaphthalene and 2,7-dimethyl-naphthalene in supercritical carbon dioxide at 308.2 K as function of pressure. Experimental: (   ) Lamb et al. [8]; (   ) Knaff and Schlünder. [7]; (   ) This work, naphthalene; (   ) This work, 2,6-dimethylnaphthalene; (   ) This work, 2,7-dimethylnaphthalene. Correlation: (   ) ⸺naphthalene; (   ) dimethylnaphthalene.

Figure 6. Diffusion coefficients of naphthalene, 2,6-dimethylnaphthalene and 2,7-dimethyl-naphthalene in supercritical carbon dioxide at 308.2 K as function of molar density. Experimental: (   ) Lamb et al. [8]; (   ) Knaff and Schlünder. [7]; (   ) This work, naphthalene; (   ) This work, 2,6-dimethylnaphthalene; (   ) This work, 2,7-dimethylnaphthalene. Correlation: (   ) ⸺naphthalene; (   ) dimethylnaphthalene.

$CO_2(1)$ n_g

h

A_p

y_2 0

ρ_2

M_2

Solid Solute(2)