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<https://hdl.handle.net/2324/12523>

出版情報 : Journal of Chemical Engineering of Japan. 38 (11), pp.865-869, 2005-11-20. 化学工学
会

バージョン :

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Diffusion Coefficients of Cetyl Alcohol in Supercritical Carbon Dioxide

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Keywords: Experiment, Molecular Simulation, Diffusion Coefficient, Supercritical Carbon Dioxide

The diffusion coefficients of cetyl alcohol in supercritical carbon dioxide were measured by the pseudo steady state solid dissolution method at 308.2 K. The Schmidt number correlation was applied to correlate with the experimental diffusion coefficients. Further, molecular dynamics simulation was performed to calculate the diffusion coefficients by an all atom model of solute. The correlated results by the Schmidt number correlation show good agreement with the experimental results. The calculated results by molecular dynamics simulation give fair estimation to the experimental data without adjustable parameters.

Introduction

The supercritical fluid extraction has been given much attention recently as one of the new separation technologies in the chemical industry. It is very useful if natural products can be separated and purified with high selectivity. One of the important physical properties necessary for designing a supercritical extractor, a separator and a reactor is a diffusion coefficient in the supercritical fluids. The diffusion data of natural products in supercritical gas are essentially important in the process design of the supercritical fluid extraction. However, the measurement of diffusion coefficients under the supercritical condition is difficult so that the diffusion coefficient data in the supercritical region are quite limited. The Taylor dispersion method (Taylor, 1953; Aris, 1956) has been the most useful technique to measure the diffusion coefficients in supercritical fluids (Swaid and Schneider, 1979; Liong *et al.*, 1991; Suárez *et al.*, 1998). The modified Taylor dispersion method (Funazukuri *et al.*, 2002) and the chromatographic impulse response method (Funazukuri *et al.*, 2000; Kong *et al.*, 2004) were developed to measure diffusion coefficients. These methods were reviewed by Funazukuri *et al.* (2004). In previous works (Higashi *et al.*, 1998a, 1999), the authors applied a pseudo steady state solid dissolution method (Knaff and Schlünder,

1987) to measure the diffusion coefficients of aromatic compounds in supercritical carbon dioxide. In this work, the diffusion coefficients of cetyl alcohol in supercritical carbon dioxide, which is one of the natural products, were measured by the pseudo steady state solid dissolution method. The solubility data are necessary to determine the diffusion coefficients by this method. The available solubility data of cetyl alcohol were already reported by Iwai *et al.* (1991). Thus, cetyl alcohol was selected as a solute in the present study. The diffusion coefficients were correlated by the Schmidt number correlation (Funazukuri *et al.*, 2004).

On the other hand, the molecular simulation may be also feasible and helpful to obtain the thermodynamic properties for mixtures under high pressure. The authors applied a molecular dynamics simulation to calculate the diffusion coefficients of aromatic compounds in supercritical carbon dioxide (Iwai *et al.*, 1997; Higashi *et al.*, 1998b). In this work, the diffusion coefficients of cetyl alcohol in supercritical carbon dioxide were simulated by the molecular dynamics simulation.

1. Experimental

1.1 Materials

Cetyl alcohol of reagent grade (approximately 99 mol% supplied by Sigma-Aldrich Co.) was used as received without further purification. High-purity carbon dioxide, with the minimum purity of 99.999%, was supplied by Sumitomo Seika Chemicals Co., Ltd.

Received on March 14, 2005. Correspondence concerning this article should be addressed to H. Higashi (E-mail address: higashi@t.kanagawa-u.ac.jp).

1.2 Apparatus and procedure

The pseudo steady state solid dissolution method (Knaff *et al.*, 1987) was adopted to measure the diffusion coefficients of cetyl alcohol in supercritical carbon dioxide. The experimental apparatus and details of the procedure were reported previously (Higashi *et al.*, 1998a, 1999). The diffusion coefficients can be obtained by the following equation.

$$D_{21} = \frac{\rho_2 (h_c^2 - h_b^2)}{2m_2 C y_2^{\text{sat}} \Delta t} \quad (1)$$

where ρ_2 and m_2 are the packed mass density and the molar mass of solid solute, respectively. h_b and h_c are the distances from the entrance of capillary to the surface of the solid solute at the beginning and the end of the experiment and Δt is the elapsed time. C and y_2^{sat} are the molar density and saturated solubility for the system. h_b , h_c and ρ_2 were determined by using a micrometer with the scale of 10^{-3} mm and an electric balance with the scale of 10^{-5} mg. The molar densities of the mixture were replaced by the molar densities of pure carbon dioxide calculated by the equation of Angus *et al.* (1976). The saturated solubilities for cetyl alcohol in supercritical carbon dioxide were cited from the data of Iwai *et al.* (1991).

2. Correlation

The Schmidt number correlation proposed by Funazukuri *et al.* (2004) was used to calculate the diffusion coefficients. The diffusion coefficient at the infinite dilution condition is represented by the following equation by definition of the Schmidt number.

$$D_{21} = \frac{1}{Sc} \left(\frac{\mu_1}{\rho_1} \right) \quad (2)$$

The density and viscosity of the solvent are given by those of pure carbon dioxide calculated by the equation of Angus *et al.* (1976) and Chung *et al.* (1988), respectively.

The Schmidt number correlation is given by

$$Sc = Sc^+ \cdot Sc^* \quad (3)$$

Sc^+ is associated with the molar volume of the solvent by the following equation.

$$\ln(Sc^+ - 1) = \sum_{i=0}^5 a_i \left(\frac{v_0}{v} \right)^i \quad (4)$$

where v is the molar volume of the solvent, v_0 is the closed-packed hard sphere volume of the solvent, and

Table 1 Parameters for Schmidt number correlation

Component	v_0 [$\text{m}^3 \text{mol}^{-1}$]	d_{vdw} [nm]
Carbon dioxide	19.7×10^{-6} *	0.397**
Cetyl alcohol		0.822**

*calculated by the method of Funazukuri *et al.* (1992) at 308.2 K

**calculated by the method of Bondi (1964)

a_i is the coefficient ($a_0 = 0.284093$, $a_1 = 2.55177$, $a_2 = -2.26978$, $a_3 = 0.756249$, $a_4 = -0.08903$) determined by Funazukuri *et al.* (2004).

The closed-packed hard sphere volume of the solvent was calculated from the polynomial function of temperature proposed by Funazukuri *et al.* (1992).

$$v_0 = \frac{1}{1.384} \sum_{i=0}^4 b_i T^i \quad (5)$$

where $b_0 = 4.452 \times 10^{-5}$, $b_1 = -1.152 \times 10^{-7}$, $b_2 = 2.749 \times 10^{-10}$, $b_3 = -3.073 \times 10^{-13}$, $b_4 = 1.290 \times 10^{-16}$.

In Eq. (3), $Sc^* = 5/6$ for self-diffusion. For binary diffusion, the following equation can be used.

$$Sc^* = \frac{5}{6} \left(\frac{d_1 + d_2}{2d_1} \right)^2 \left(\frac{2M_2}{M_1 + M_2} \right)^{1/2} \quad (6)$$

where d and M are the effective hard-sphere diameter and the molecular weight, respectively.

The ratio of effective hard-sphere diameters of solvent (1) to solute (2) was assumed by

$$\frac{d_1}{d_2} = \frac{d_{\text{vdw},1}}{d_{\text{vdw},2}} \quad (7)$$

where d_{vdw} is the van der Waals diameter estimated by the method of Bondi (1964). The parameters of the Schmidt number correlation are listed in **Table 1**.

3. Simulation

3.1 Models and potential functions

Carbon dioxide was treated as a Lennard-Jones molecule (single site model) and cetyl alcohol was treated as a flexible model of all atoms (all atom model). The Lennard-Jones (12-6) potential function was used for all sites in the simulation,

$$\phi(r_{ij}) = 4\varepsilon_{ij} \left\{ \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right\} \quad (8)$$

Table 2 Potential parameters

Site	σ [nm]	ϵ/k [K]
Carbon dioxide*	0.372	236.1
Cetyl alcohol**		
C	0.343	52.9
H	0.257	22.2
O	0.312	30.2

*Iwai *et al.* (1997)**universal force field (Rappe *et al.*, 1992)

where ϕ is the intermolecular potential, ϵ is the energy parameter, σ is the size parameter, r is the distance, and i and j denote the particles i and j , respectively.

The potential parameters for the single site model of carbon dioxide were referred from the model proposed by Iwai *et al.* (1997). These parameters were determined by the PVT behavior of pure carbon dioxide. The parameters for the all atom model of the solute were adopted from the universal force field (Rappe *et al.*, 1992) in the Cerius² software (Accelrys Software Inc.). The charge of the solute molecules was unconsidered and the conformation of the solute molecule was optimized by minimizing the energy. All the parameters used in the present study are listed in **Table 2**. The arithmetic and geometric combining rules were used respectively to calculate the size and energy parameters between unlike molecules.

3.2 Simulation conditions and analysis

An NVT ensemble MD simulation was applied to calculate the diffusion coefficients of carbon dioxide and cetyl alcohol in supercritical carbon dioxide. The time step of the calculations was set to 1 fs. The system consisted of 300 carbon dioxide molecules and one cetyl alcohol molecule. The simulation steps were 1.0×10^4 for equilibrium and were 1.0×10^6 for production. The cut-off length was set to the half-cell. The calculated diffusion coefficients are considered as the infinite dilution diffusion coefficients of the cetyl alcohol in supercritical carbon dioxide. The diffusion coefficients for carbon dioxide, D_{11} , and cetyl alcohol, D_{21} , were calculated by the mean square displacement (MSD) of the center of mass for the molecules,

$$D_{11} = \lim_{t \rightarrow \infty} \frac{1}{6t} \langle [\mathbf{r}_1(t) - \mathbf{r}_1(0)]^2 \rangle \quad (9)$$

$$D_{21} = \lim_{t \rightarrow \infty} \frac{1}{6t} \langle [\mathbf{r}_2(t) - \mathbf{r}_2(0)]^2 \rangle \quad (10)$$

where \mathbf{r} is the position of a particle and t is time. The diffusion coefficients were determined by the slope of MSD from 2 to 10 ps.

Table 3 Experimental results for diffusion coefficients of cetyl alcohol in supercritical carbon dioxide at 308.2 K

P [MPa]	$C \times 10^6$ [mol m ⁻³]*	y_2^{sat} [—]**	$D_{21} \times 10^8$ [m ² s ⁻¹]
10.6	0.01687	0.00101	0.807
12.8	0.01780	0.00164	0.701
15.8	0.01877	0.00209	0.637
18.7	0.01944	0.00270	0.618

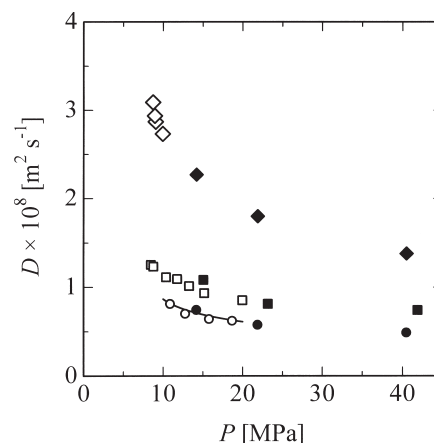
*calculated by equation of state of Angus *et al.* (1976)**Iwai *et al.* (1991)

Fig. 1 Diffusion coefficients of carbon dioxide and cetyl alcohol in supercritical carbon dioxide as a function of pressure at 308.2 K. Experimental: (\diamond) carbon dioxide, O'hern and Martin (1955); (\square) naphthalene, Higashi *et al.* (1999); (\circ) cetyl alcohol, this work; Schmidt number correlation: (—) cetyl alcohol; MD calculations: (\blacklozenge) carbon dioxide, (\blacksquare) naphthalene, Higashi *et al.* (2005); (\bullet) cetyl alcohol, this work

4. Results and Discussion

The experimental results did not depend on the flow rate of carbon dioxide. The diffusion coefficients were determined from an arithmetic average of several measurements and the maximum deviation from the average value was within 10%. The reproducibilities were within 5%. The experimental results for diffusion coefficients of cetyl alcohol in supercritical carbon dioxide at 308.2 K were listed in **Table 3** and illustrated in **Figure 1**. The diffusion coefficients smoothly decrease as pressure increases, because the density of carbon dioxide increases as pressure increases. Fulton *et al.* (1991) reported that alcohol does not aggregate in supercritical carbon dioxide at dilute conditions. In the present work, the experimental results for diffusion coefficients of cetyl alcohol are about one third of those of carbon dioxide and are about 30% smaller than the results of naphthalene measured by

the same apparatus (Higashi *et al.*, 1999), because the size of the cetyl alcohol molecule is larger than that of the naphthalene molecule. The diameter of cetyl alcohol used for the Schmidt number correlation is about 1.3 times larger than that of naphthalene and the molecular weight of cetyl alcohol is about 1.9 times larger than that of naphthalene.

The correlated results by the Schmidt number correlation show good agreement with the experimental results as shown in Figure 1. The availability of the Schmidt number correlation was proved for the chain molecule.

The simulated results of diffusion coefficients of carbon dioxide and cetyl alcohol are shown in Figure 1. The simulated results for carbon dioxide smoothly admit to the experimental results. The simulated results for cetyl alcohol by the all atom model are fair estimations to the experimental data without adjustable parameters. The simulated results for naphthalene by the all atom model (Higashi *et al.*, 2005) were also fair estimation to the experimental results.

The molecular shapes of naphthalene and cetyl alcohol are very different from each other. Naphthalene is a flat molecule and cetyl alcohol is a chain molecule. However, the diffusion coefficients of both molecules are well represented by the Schmidt number correlation and by the molecular simulation with the all atom model. The molecular shapes would be reflected by these models.

Conclusions

The diffusion coefficients of cetyl alcohol in supercritical carbon dioxide were measured by a pseudo steady state solid dissolution method. The experimental results were correlated by the Schmidt number correlation. Further, the molecular dynamics simulation was performed to calculate the diffusion coefficients. The Schmidt number correlation is available to correlate the diffusion coefficients of chain molecules, such as cetyl alcohol. The diffusion coefficients of cetyl alcohol in supercritical carbon dioxide by molecular dynamics simulations represent reasonable results against the experimental data without adjustable parameters for a binary system.

Nomenclature

C	= molar density	[mol m ⁻³]
D	= diffusion coefficient	[m ² s ⁻¹]
d	= diameter of a molecule	[m]
h	= distances from the entrance of a capillary to the surface of solid solute	[m]
M	= molecular weight	[—]
m	= molar mass	[kg mol ⁻¹]
P	= pressure	[Pa]
r	= distance between molecules	[m]
\mathbf{r}	= position of a particle	[m]
t	= time	[s]
y	= solubility (mole fraction)	[—]

Δt	= elapsed time	[s]
ε	= energy parameter	[J]
ρ	= packed mass density	[kg m ⁻³]
σ	= size parameter	[m]
ϕ	= potential	[J]

<Subscript>

b	= beginning of the experiment
e	= end of the experiment
i, j	= molecules i and j
sat	= saturated
vdw	= van der Waals
1	= carbon dioxide
2	= cetyl alcohol

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