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Solubility determination of organometallic complexes in supercritical carbon dioxide by chromatographic impulse response method

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Abstract

The solubilities of organometallic complexes in supercritical CO_2 were determined from retention factors measured by the chromatographic impulse response (CIR) method, in which a solute was pulse-injected into a supercritical CO_2 flowing in a polymer coated open capillary column, and the response curve, i.e. time change of solute concentration, was monitored at the exit of the column. The retention factor and binary diffusion coefficient were simultaneously obtained as two parameters so that the fitting error between response curves of solute species measured and calculated was minimized. The validities of the method and the apparatus employed in this study were verified by determining the solubilities of naphthalene, which have extensively been reported in the literature. Then, the solubilities of organometallic complexes such as ferrocene and cobalt (III) acetylacetonate in supercritical CO_2 were determined. The data determined in this study were in good agreement with the literature data. The solubilities were also correlated with the Chrastil equation including the three adjustable parameters.

Keywords: Solubility, Chromatography, Supercritical carbon dioxide, Organometallic complex, Naphthalene, Diffusion coefficient

1. Introduction

Supercritical (sc) processes are increasingly of an importance in a variety of applications as green chemistry processing [1]. A feasibility study and design of sc process require the data of solubilities of the interesting compounds in the sc fluids. Although there is a lot of literature reporting solubility measurements in sc fluids [2-4], they are still limited. Moreover, the development of a new experimental approach with more accuracy, less time consuming and the use of fewer sample amount is also required.

The solubility measurements of solid compounds in sc CO_2 have been made by various methods, which can be classified into the static and dynamic ways. In the static methods the apparatus is simple, and accurate data can be obtained. However, it takes a long time to achieve the saturation condition and it is not easy for low solubility compounds.

On the other hand, in the dynamic methods the saturation condition is achieved relatively fast even in the case of low solubility. However, the method needs a fully saturated flow in the system, and sometimes it has experimental difficulties in valve clogging and sampling of saturated sc mixture. The method for trapping and quantifying the solute from the sc phase also becomes less accurate at lower pressures or higher temperatures where the solubility is low [4]. In addition, the method is not only relatively time consuming but also generally necessary to provide sufficient amounts of pure solute to keep an equilibrium state.

The chromatographic method also makes it possible to obtain the solubilities of solid solutes in sc fluids using chromatographic retention measurements. Since the retention factor is correlated with the solubility under each condition [5-9], the solubility can be determined from the correlation between solubility and retention factor measured chromatographically. Moreover, this method is attractive because a small amount of sample is sufficient, and the effect of impurity contained in the sample is possibly excluded due to the chromatographic separation. Thus, measurements of peak retention times in chromatograms are experimentally

simple and much easier than direct solubility measurements, once the correlation between solubility and retention factor is established using a couple of solubility data measured separately.

So far, packed adsorption columns were mostly employed in the chromatographic measurements of solubilities in sc CO_2 [5-9]. Since retention factor is sensitively dependent on pressure, large pressure drop between the inlet and outlet of the column is not favorable, in particular, near critical pressure. Moreover, the retention factor may be affected by not only stationary phase but also pore structure of particles. The packed column also has many uncertainties with respect to packing configuration, adsorption behavior, dispersion in packed column, etc.

Instead of an adsorption packed column, the use of a polymer coated open capillary column can be more suitable for measuring the retention data due to the following two advantages at least. First, the pressure drop along the column must be two orders of magnitude smaller than that in packed column. Second, capillary columns have fewer active sites, which may affect the retention factor, and mass transfer of the intended species can be more accurately described with a mathematical model. However, the study on solubility determination using a coated open column in the chromatographic method is limited [10].

So far, the authors have developed the chromatographic method with a polymer coated capillary column, namely the chromatographic impulse response (CIR) method [11,12], which is a useful tool for simultaneously measuring both retention factors and diffusion coefficients of various compounds in sc CO_2 [13,14]. The chromatographic peak, i.e. time change of the solute concentration in the column, can be fully reproduced by the CIR model having two physical properties of retention factor and diffusion coefficient. Recently, the authors have reported both retention factors and diffusion coefficients of organometallic complexes such as

ferrocene, and 1,1'-dimethylferrocene [15], and palladium(II) acetylacetonate ($Pd(acac)_2$) and cobalt(III) acetylacetonate ($Co(acac)_3$) [16] in sc CO_2 using the CIR method.

Despite the great potential of organometallic complexes for a variety of applications in organic synthesis, removal of toxic metal compounds, and processing of advanced functional materials as catalysts or precursors, the available solubility data of the organometallic complex in sc CO_2 [17-20] are obviously fewer than those of other compounds in sc CO_2. Furthermore, the solubilities of metal complexes in sc CO_2 calculated by existing correlations are difficult to obtain since the other physical properties of the metal complexes, less available in the literature, are required for the calculations. Thus, the objectives in the present study are (1) to determine the solubilities of naphthalene in sc CO_2 by the CIR method to confirm the validity the experimental apparatus and procedure, (2) to accumulate new experimental data for ferrocene and $Co(acac)_3$, and (3) to correlate the data.

2. Theory

2.1 Parameter estimation

When a solute is pulse injected into a fully developed laminar flow in a polymer coated cylindrical column, the average concentration $c_a(t)$ on the cross section of the column is described as follows [11,12]:

$$c_a(t) = \left(\frac{m}{\pi R^2}\right)\frac{1}{(1+k)\sqrt{4\pi at}}\exp\left\{-\frac{(L-Ut)^2}{4at}\right\} \tag{1}$$

where

$$a = \frac{D_{12}}{1+k} + \frac{1+6k+11k^2}{1+k}\frac{R^2U^2}{48D_{12}} \tag{2}$$

$$U = \frac{u_0}{1+k} \tag{3}$$

where t is the time, m the injected amount of solute, R the radius of the column, L the distance between the injection point and detection point, k the retention factor, and D_{12} the infinite dilution binary diffusion coefficient of the solute in the fluid, and U and u_0 are the average velocities of the solute and the fluid, respectively. Note that on the inner wall of the coated column, it is assumed that the distribution constant between fluid and stationary phase is independent of solute concentration and the solute instantaneously reaches equilibrium between the fluid phase and the stationary phase.

When u_0 is measured experimentally, the k and D_{12} can be simultaneously determined by the curve fitting with minimizing the root-mean-square (rms) fitting error ε, defined by Eq. (4), for the measured $c_{\mathrm{exp}}(t)$ and calculated $c_{\mathrm{a}}(t)$ curves.

$$\varepsilon = \sqrt{\int_{t_1}^{t_2} \left(c_{\mathrm{exp}}(t) - c_{\mathrm{a}}(t) \right)^2 dt \Big/ \int_{t_1}^{t_2} \left(c_{\mathrm{exp}}(t) \right)^2 dt} \tag{4}$$

where t_1 and t_2 correspond to the times at the front and latter 10% peak heights, respectively, of the measured response curve.

2.2 Determination of solubility

The solubility y can be expressed with retention factor k and solvent density ρ in Eq (5) [10].

$$y = C \frac{1}{\rho k} \tag{5}$$

where

$$C = A \exp\left(\frac{B}{T} \right) \tag{6}$$

where C is a constant to be determined experimentally at each temperature, inherently depends on the chromatographic column, system temperature and the solute, and A and B are constants. If at least one reliable solubility value is available at the temperature and pressure where k value has been obtained, C can be determined using Eq. (5). Once C is known, the solubility isotherm at various pressures can be determined from the k values measured chromatographically.

3. Experimental

3.1 Experimental apparatus and procedure

A schematic diagram of the experimental apparatus is shown in Fig. 1. An open capillary column (UACW-15W-1.0F, the Frontier Laboratories Ltd., Japan, R = 0.265 mm, L = 16.293 m, and R_{coil} = 0.155 m) was employed. It is chemically bonded on column inner surface with poly(ethylene glycol) 20M (PEG20M, polymer thickness of 1 μm) as the stationary phase, and CO_2 was used as a fluid phase in our chromatographic retention measurements by the CIR method. Pure CO_2 from a cylinder at room temperature was fed by a syringe pump (260D, ISCO) through a filter to a preheating column, an injector (Model 7520, equipped with a 0.5 or 1.0 μL rotor, Rheodyne), and the coated column, which were immersed in a constant temperature water bath (T-105, Thomas Kagaku Co., Ltd., Japan). The temperature was maintained at the prescribed value within ± 0.01 K. The pressure of the system was regulated within 5 kPa by the syringe pump and a back pressure regulator (Model SCF-Bpg/M with modification, JASCO, Japan). A packed column was installed upstream at the regulator to stabilize the pressure of the system.

Once the system had reached the desired temperature and pressure and had been stabilized, the CO_2 was started to flow at a constant flow mode by the pump. After the prescribed temperature, pressure and flow rate had become constant, the system was held

under the same condition at least more 2 h prior to a solute injection. In this study, only a single pulse of each solute dissolved in sc CO_2 or hexane was loaded through the injector into the column for each retention measurement. The chromatographic peaks, as time change of the solute concentration in sc CO_2, in terms of absorbance, were monitored with a high-pressure detector (multi-UV-Vis detector MD 1510, JASCO, Japan) by scanning at wavelengths from 195 to 550 nm with increments of 1 nm and time interval of 1.6 s. The flow rate of the fluid was measured with a soap bubble flow meter.

3.2 Experimental conditions

Naphthalene (99%) and ferrocene (98%) were obtained from Aldrich, and used without further purification. CO_2 with purity higher than 99.95% was purchased from Air Gases Tokai Ltd., Japan.

The chromatographic retention measurements were carried out in sc CO_2 for naphthalene at 308.15 K and pressures from 7.00 to 40.00 MPa, and for ferrocene at 333.15 K and from 10.00 to 30.00 MPa by the CIR method. Each solute was injected to the column as a solution of 0.5 or 1.0 μL for naphthalene predissolved in sc CO_2 or in hexane and for ferrocene dissolved in hexane (4.17×10^{-3} g/mL). Note that when the naphthalene predissolved in sc CO_2 was injected, the injector with our slight modification was used.

At least two measurements were carried out at a given temperature and pressure. Note that all values listed in Tables 2, 4 and 5 are the average values for the double or triplicate measurements under each condition. The wavelengths of 275 and 260 nm were employed for naphthalene and ferrocene, respectively. The pressure drop between the column inlet and outlet was as low as less than 5 kPa.

4. Semiempirical correlation

To correlate the experimental solubility data in sc CO_2, many models have been proposed. Most of approaches are density based correlations. Chrastil [21] developed a semiempirical solubility correlation, given by:

$$\ln y = a_0 + \frac{a_1}{T} + a_2 \ln \rho \tag{7}$$

where units of the solubility y, the sc CO_2 density ρ and the system temperature T are mole fraction, kg/m^3 and K, respectively, and a_0, a_1 and a_2 are constants as adjustable fitting parameters. The parameters in the semiempirical equation were optimally fitted in this study by minimizing the objective function of average-absolute-relative-deviation (AARD) defined as

$$\mathrm{AARD}(\%) = \frac{100}{N}\sum_{i=1}^{N}\left|1 - \frac{y_{\mathrm{cal}}}{y_{\mathrm{exp}}}\right| \tag{8}$$

where N is the number of experimental data points, y_{cal} and y_{exp} correspond to the calculated and measured solubilities by the equation and experimental, respectively.

5. Results and discussion

5.1 Naphthalene

The effects of the injected amount of naphthalene on (a) absorbance of the peak top of a response curve, (b) k and D_{12}, (c) $u_0 \times$ (peak area), and (d) rms fitting error ε in CO_2 at 308.15 K and 13.30 MPa (ρ = 790.67 kg/m^3) are shown in Fig. 2. Various amounts of naphthalene dissolved in hexane (4.17×10^{-5}, 4.17×10^{-4}, 4.17×10^{-3} and 4.17×10^{-2} g/mL) were injected (1 μL) into the column. Correspondingly the injected amounts of naphthalene were 3.3×10^{-4}, 3.3×10^{-3}, 3.3×10^{-2} and 3.3×10^{-1} μmol, respectively. The injected amounts may depend on both of the accuracy of the solution concentration and the injector volume. From Eq (1), the value of $u_0 \times$ (peak area) is proportional to the injected amount of m. In fact, as shown in Fig. 2 (c),

the values of u_0 × (peak area) are proportional to the injected amounts over the range examined in this study. As mentioned in part of Theory, the k values are independent of the injected amounts as shown in Fig. 2 (b), as well as rms values and diffusion coefficients. The average k value is 0.0818 for naphthalene in CO_2 at 308.15 K and 13.30 MPa. Since the values of $DeSc^{1/2}$ and ε are lower than 8 and 1%, respectively [12], diffusion coefficient (D_{12}=1.230×10^{-8} m^2/s) is also determined accurately.

The validities of the method and experimental apparatus were preliminary confirmed by measuring the solubility of naphthalene in sc CO_2, because the solubilities were well studied in the literature [22-28]. McHugh and Paulaitis [23], Iwai et al.[24] and Goodarznia and Esmaeilzadeh [28] measured the solubilities to validate their experimental equipments and procedures for naphthalene in sc CO_2. These data at 308.15 K and 13.3 MPa are presented in Table 1, together with the k value measured in this study. The constant C in Eq. (5) can be then determined and given in the Table 1.

The k values for naphthalene measured in this study at 308.15 K and different CO_2 densities ranging from 220 to 972 kg/m^3, corresponding to 7.0 to 40.0 MPa by the CIR method are plotted in Fig. 3, together with the values of ε and u_0 × (peak area). In general, the ε values are increasing as approaching the critical point [11]. However, in this study all ε values are lower than 1%, which indicates that the chromatographic peaks are well reproduced by the CIR model in Eqs (1) to (3) and the measured k values are considered to be reliable [12]. All values of u_0 × (peak area) are lower than 1.5×10^{-1} AU m, and the value at 790.67 kg/m^3 (308.15 K and 13.30 MPa) is 8.8×10^{-3} AU m, corresponding to an injected amount less than 3.0×10^{-3} μ mol as read out from the line in the Fig. 2 (c).

Over an entire range of CO_2 density in logarithmic plots of k vs. CO_2 density, the k values show a straight line. Using the C value shown in Table 1, the y values of naphthalene in sc CO_2 at 308.15 K were determined from the k values using Eq. (5). All values $DeSc^{1/2}$,

D_{12}, k and y are listed in Table 2, together with the CO_2 densities. When the value of $DeSc^{1/2}$ is lower than 9.5 for a large k in the CIR method, the effect of the secondary flow due to column coiling on the D_{12} value in terms of the second moment is within an accuracy of 1% [29]. Note that the uncertainties in the k and y values were less than 2.5% for all solutes measured in this study. The uncertainty in D_{12} values were also estimated to be less than 2.5 % except at pressures lower than 8.1 MPa, corresponding to $DeSc^{1/2} > 9.5$ listed in Table 2. For the data with $DeSc^{1/2} > 9.5$, the D_{12} values may be affected somewhat by the secondary flow and less accurate than those with $DeSc^{1/2} < 9.5$. However, the k values can be considered to be hardly affected by the secondary flow even at high $DeSc^{1/2}$ values [29].

Fig. 4 compares the y values to those in the literature. It can be seen that the present results are satisfactorily in agreement with those of measurements reported by various investigators such as Tsekhanskaya et al. [22], McHugh and Paulaitis [23], Iwai et al. [24], Reverchon et al. [25], Stassi et al. [26], Sauceau et al. [27] and Goodarznia and Esmaeilzadeh [28]. The experimental data at 308.15 K obtained in this study are also well correlated with Eq. (7) with an AARD of 4.4% for 35 data points, together with the determined parameters of a_0 to a_2 which are listed in Table 3. Thus, the solubilities can be accurately determined by the chromatographic measurements, even only one solubility datum is used, as shown in Table 1.

5.2 $Co(acac)_3$ and ferrocene

Using the same procedure as for naphthalene, the solubilities for $Co(acac)_3$ in sc CO_2 at 313.15 and 333.15 K were obtained from the k values reported in our recent study [16]. Similarly, those for ferrocene in sc CO_2 were also determined at 308.15, 313.15, and 323.15 K from the k values reported in our previous study [15], together with those measured at 333.15 K in this study, where 2.3×10^{-2} μ mol (1.0 μL at a concentration of 4.21×10^{-3} g/mL) was injected for each run. These results for $Co(acac)_3$ and ferrocene are presented in Tables 4

and 5, and in Figs 5 and 6, respectively. The literature data [8,20] are also shown in Figs 5 and 6. Note that the constant *C* in Eq. (5) for ferrocene at each temperature was determined using the solubility data reported by the direct measurement by Cowey et al. [8], and the data shown in Fig. 6 were obtained from the chromatographic retention data reported in their study [8].

It is seen that the isotherm solubility data obtained from the chromatographic measurements with a coated column in this study are substantially consistent with those determined from the chromatographic method with a packed column [8] and the UV-vis spectroscopic technique [20]. The highest solubilities for both organometallic complexes are observed both from Figs 5 and 6 at the highest temperatures and pressures studied. It can be also observed that the solubilities of ferrocene are larger than those of $Co(acac)_3$ in sc CO_2. As shown in Figs 5 (b) and 6(b), the solubility data for $Co(acac)_3$ and ferrocene reported in this study are well correlated with Eq. (7) with AARD values of 3.6% and 3.7%, respectively, which are also listed in Table 3. The data for ferrocene determined at higher CO_2 densities in this study deviate from those of Cowey et al. [8]. The reason is not clarified, and the further study is needed.

6. Conclusions

The chromatographic method with a polymer coated capillary column using curve fitting is a powerful tool for determining the solubilities of solid compounds in supercritical fluids. In this study over a wide pressure range up to 40.0 MPa the solubilities of naphthalene at 308.15 K, ferrocene at 308.15 to 333.15 K and cobalt (III) acetylacetonate at 313.15 and 333.15 K in supercritical CO_2 were determined by the method. The results validate the method. In addition, it was observed that the solubilities of ferrocene were larger than those of cobalt (III) acetylacetonate in supercritical CO_2. The determined solubility data of

naphthalene, ferrocene and cobalt (III) acetylacetonate in supercritical CO_2 were correlated with the Chrastil semiempirical correlation with 4.4%, 3.6% and 3.7%, respectively.

List of symbols

AARD	average absolute relative deviation
a_0, a_1, a_2	coefficients in Eq. (7)
C	constant given by Eq. (5)
$c_a(t)$	average concentration given by Eq. (1)
$c_{exp}(t)$	concentration measured experimentally
D_{12}	binary diffusion coefficient
De	Dean number
k	retention factor
L	distance between injection point and detection point
m	injected amount of solute
P	pressure
R	radius of diffusion column
Sc	Schmidt number
T	temperature
t	time
U	average velocity of solute
u_0	average velocity of fluid
ε	fitting error defined by Eq. (4)
η	viscosity
ρ	density

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Table 1

Solubility data y reported in the literature, retention factor k measured and the constant C determined in this study for naphthalene in sc CO_2 at 308.15 K and 13.3 MPa.

Literature			ρ(kg/m^3)	Present study	
Reference	$10^2\,y$	Average $10^2\,y$		k	C
McHugh and Paulaitis [23]	1.410				
Iwai et al. [24]	1.410	1.406	790.67	0.0818	0.909
Goodarznia and Esmaeilzadeh [28]	1.398				

Table 2

Retention factors k and solubility data y for naphthalene in sc CO_2 at 308.15 K, together with D_{12} and $DeSc^{1/2}$ values.

P(MPa)	ρ(kg/m^3)	k	$10^2\,y$	$10^8\,D_{12}$ (m^2/s)	$DeSc^{1/2}$
7.00	220.08	8.225	0.050	3.865	14.5
7.40	259.77	4.384	0.080	3.322	12.0
7.52	275.71	3.601	0.092	3.101	12.9
7.60	288.44	2.907	0.108	2.947	12.0
7.70	307.69	2.311	0.128	2.836	10.0
7.80	331.50	1.716	0.160	2.599	10.3
7.90	367.10	1.161	0.213	2.403	8.1
8.02	433.28	0.648	0.324	2.164	11.7
8.10	491.42	0.413	0.448	2.048	9.6
8.15	521.76	0.331	0.527	1.898	6.9
8.20	542.80	0.297	0.564	1.870	7.2
8.25	560.19	0.265	0.611	1.813	4.1
8.30	574.64	0.245	0.645	1.779	5.3
8.35	585.75	0.228	0.679	1.740	6.1
8.40	595.70	0.210	0.725	1.724	6.7
8.45	604.40	0.196	0.767	1.716	7.0
8.50	612.12	0.194	0.764	1.676	6.4
8.52	614.98	0.194	0.762	1.713	8.3
8.55	619.06	0.182	0.806	1.663	7.4
8.60	625.37	0.175	0.830	1.646	6.6
8.70	636.50	0.171	0.835	1.671	7.9
8.80	646.10	0.163	0.863	1.650	7.4
9.00	662.13	0.151	0.908	1.617	6.8
9.99	712.21	0.123	1.035	1.440	6.7
10.00	712.59	0.124	1.031	1.473	6.7

11.00	743.95	0.099	1.236	1.386	5.2
12.00	767.07	0.092	1.293	1.354	6.4
13.30	790.67	0.082	1.395	1.230	6.3
14.00	801.41	0.080	1.411	1.254	5.8
15.00	814.90	0.075	1.497	1.174	6.4
20.00	865.72	0.062	1.697	1.079	7.0
25.00	901.23	0.054	1.854	1.013	7.1
30.00	929.11	0.049	1.995	0.931	6.7
35.00	952.29	0.046	2.058	0.888	6.5
40.00	972.26	0.043	2.160	0.822	5.5

Table 3
Determined a_0, a_1 and a_2 values in Eq. (7).

Solute	N [a]	a_0	a_1	a_2	AARD(%)
Naphthalene	35	-12.5185	-2600	2.5014	4.3
$Co(acac)_3$	15	-22.7436	-5120.00	4.2769	3.6
Ferrocene	67	-15.4136	-2755.51	2.6876	3.7

[a] Number of data.

Table 4

Retention factors k and solubility data y for $Co(acac)_3$ in sc CO_2 at 313.15 and 333.15 K.

313.15 K			
P (MPa)	ρ(kg/m^3)	k [a]	$10^5\,y$ [b]
9.7	602.58	1.069	0.830
10.0	628.61	0.857	0.993
11.0	683.52	0.543	1.441
13.0	743.04	0.344	2.092
18.0	819.51	0.195	3.347
20.0	839.81	0.176	3.618
25.0	879.49	0.140	4.343
30.0	909.89	0.122	4.818
40.0	956.07	0.102	5.484

333.15 K			
P (MPa)	ρ(kg/m^3)	k [a]	$10^5\,y$ [b]
15.0	604.09	0.662	2.304
18.0	687.25	0.326	4.112
20.0	723.68	0.246	5.175
25.0	786.55	0.163	7.185
30.0	829.71	0.129	8.607
40.0	890.14	0.097	10.669

[a] From Kong et al. [16].
[b] Determined in this study.

Table 5

Retention factors k and solubility data y for ferrocene in sc CO_2 at 308.15 to 333.15 K.

308.15 K			
P (MPa)	ρ(kg/m^3)	k [a]	$10^3\,y$ [b]
8.02	433.28	0.786	0.338
8.23	553.73	0.314	0.662
8.52	614.98	0.217	0.863
8.52	614.98	0.218	0.859
8.72	638.53	0.187	0.962

11.02	744.47	0.103	1.495
15.02	815.32	0.078	1.821
17.02	838.29	0.066	2.097
20.02	865.89	0.058	2.279
22.02	881.29	0.057	2.279
25.02	901.35	0.053	2.412
30.02	929.21	0.047	2.637
30.02	929.21	0.047	2.650
35.02	952.38	0.042	2.890
40.18	972.93	0.039	3.038

313.15 K			
P (MPa)	ρ(kg/m^3)	k [a]	$10^3\ y$ [b]
8.02	280.19	4.362	0.098
8.52	358.08	1.618	0.207
8.72	406.53	0.972	0.304
9.02	490.71	0.468	0.522
9.22	535.98	0.344	0.651
9.22	535.98	0.344	0.652
9.22	535.98	0.351	0.638
9.22	535.98	0.346	0.647
9.51	581.27	0.252	0.819
9.52	582.52	0.256	0.804
9.52	582.52	0.250	0.823
9.52	582.52	0.261	0.789
9.52	582.52	0.252	0.819
10.02	630.11	0.189	1.006
11.02	684.34	0.140	1.253
11.02	684.34	0.139	1.260
11.02	684.34	0.139	1.257
11.02	684.34	0.139	1.262
11.02	684.34	0.140	1.256
12.02	718.34	0.115	1.457
15.02	780.55	0.081	1.894
20.02	840.00	0.065	2.198
25.03	879.69	0.056	2.434
30.03	910.05	0.051	2.596
35.08	935.18	0.046	2.790

35.08	935.18	0.046	2.814
40.06	956.31	0.041	3.077

323.15 K			
P (MPa)	ρ(kg/m^3)	k [a]	$10^3\ y$ [b]
10.02	386.70	0.949	0.371
10.02	386.70	0.957	0.367
11.02	504.72	0.366	0.737
11.02	504.72	0.358	0.754
12.02	585.97	0.201	1.154
13.02	636.96	0.155	1.380
13.02	636.96	0.156	1.369
13.02	636.96	0.157	1.364
13.02	636.96	0.156	1.367
15.02	700.24	0.105	1.854
16.02	722.50	0.087	2.155
20.02	784.54	0.068	2.538
25.02	834.36	0.055	2.961
30.03	870.62	0.049	3.189
35.02	899.34	0.044	3.468
40.34	924.82	0.037	3.986

333.15 K					
P (MPa)	ρ(kg/m^3)	k [b]	$10^3\ y$ [b]	$10^8\ D_{12}$ (m^2/s) [b]	$DeSc^{1/2}$ [b]
10.00	289.95	2.198	0.227	2.965	9.9
11.00	357.79	1.016	0.398	2.530	8.1
12.00	434.43	0.507	0.657	2.329	9.1
13.00	505.35	0.296	0.968	2.055	7.2
14.00	561.37	0.203	1.271	2.040	15.4
15.00	604.09	0.153	1.569	1.692	5.4
20.00	723.68	0.086	2.332	1.360	5.3
25.00	786.55	0.064	2.892	1.168	5.8
30.00	829.71	0.053	3.276	1.093	5.2

[a] From Kong et al. [15].
[b] Determined in this study.

Figure captions

Fig. 1. Schematic diagram of the apparatus. (1) CO_2 cylinder; (2) filter; (3) ISCO syringe pump; (4) water bath; (5) preheating column; (6) Heise pressure gauge; (7) injector; (8) diffusion column; (9) packed column; (10) computer; (11) UV-Vis multi-detector; (12) back pressure regulator; (13) soap bubble flow meter.

Fig. 2. Effects of the injected amount of naphthalene on (a) absorbance of the peak top of a response curve, (b) k and D_{12}, (c) $u_0 \times$ (peak area), and (d) ε in sc CO_2 at 308.15 K and 13.30 MPa in this study.

Fig. 3. Plots of (a) k and (b) ε and $u_0 \times$ (peak area) vs. CO_2 density ρ for naphthalene in sc CO_2 measured at 308.15 K in this study.

Fig. 4. Comparison of solubility data for naphthalene in sc CO_2 at 308.15 K: ◑, this work; ○, Tsekhanskaya et al. [22]; □, McHugh and Paulaitis [23]; ▽, Iwai et al. [24]; ◎, Reverchon et al. [25]; ◬, Stassi et al. [26]; ⊡, Sauceau et al. [27]; ▽, Goodarznia and Esmaeilzadeh [28].

Fig. 5. Plots of (a) y vs. CO_2 pressure P and (b) y vs. CO_2 density ρ for $Co(acac)_3$ in sc CO_2: this work at 313.15 K (◑) and 333.15 K (▲), and Haruki et al. [20] at 313.15 K (○) and 333.15 K (△).

Fig. 6. Plots of (a) y vs. CO_2 pressure P, (b) y and (c) ε vs. CO_2 density ρ for ferrocene in sc CO_2: this work at 308.15 K (◨), 313.15 K (◑), 323.15 K (▼) and 333.15 K(▲), and Cowey et al. [8] at 313.15 K (○), 323.15 K (▽) and 333.15 K(△).

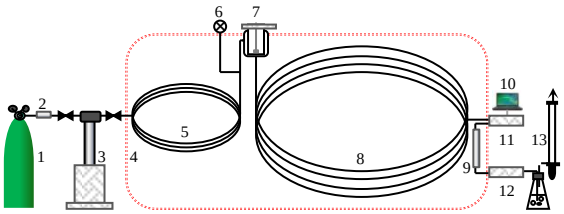

Fig. 1

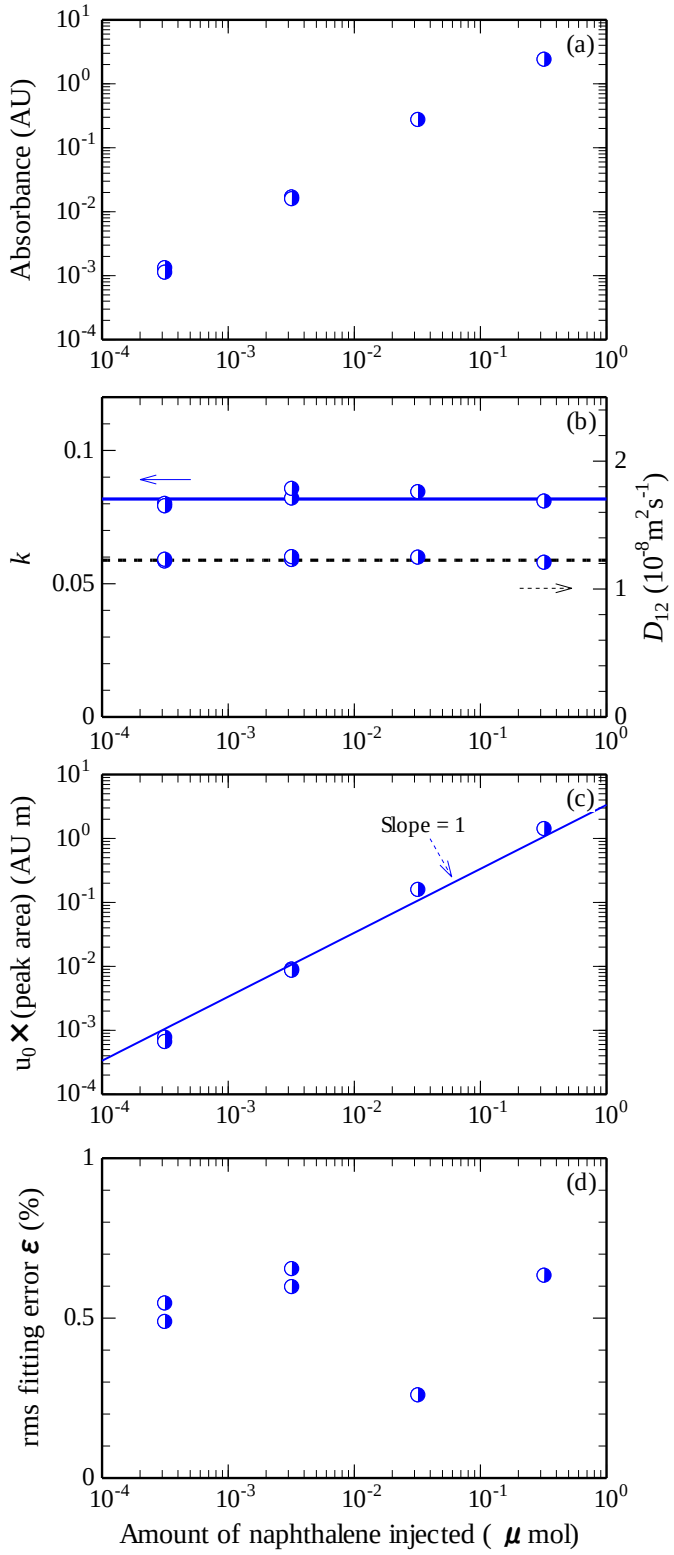
(a)
Absorbance (AU)
(b)
k
D_{12} (10^{-8}m^{2}s^{-1})
(c)
Slope = 1
u_0 × (peak area) (AU m)
(d)
rms fitting error ε (%)
Amount of naphthalene injected (μ mol)

Fig. 2

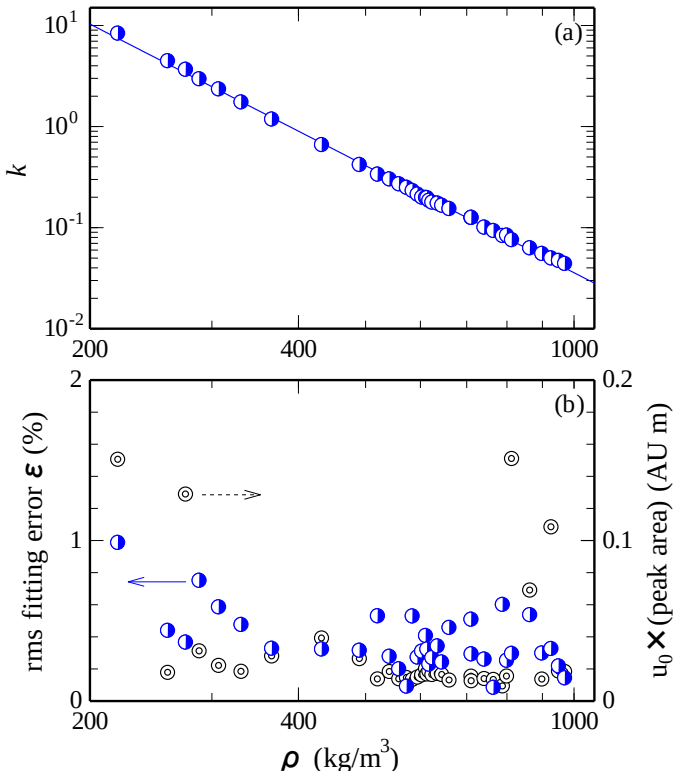
(a)
k
10^1
10^0
10^-1
10^-2
200
400
1000
(b)
rms fitting error ε (%)
u0 × (peak area) (AU m)
2
1
0
0.2
0.1
0
ρ (kg/m3)

Fig. 3

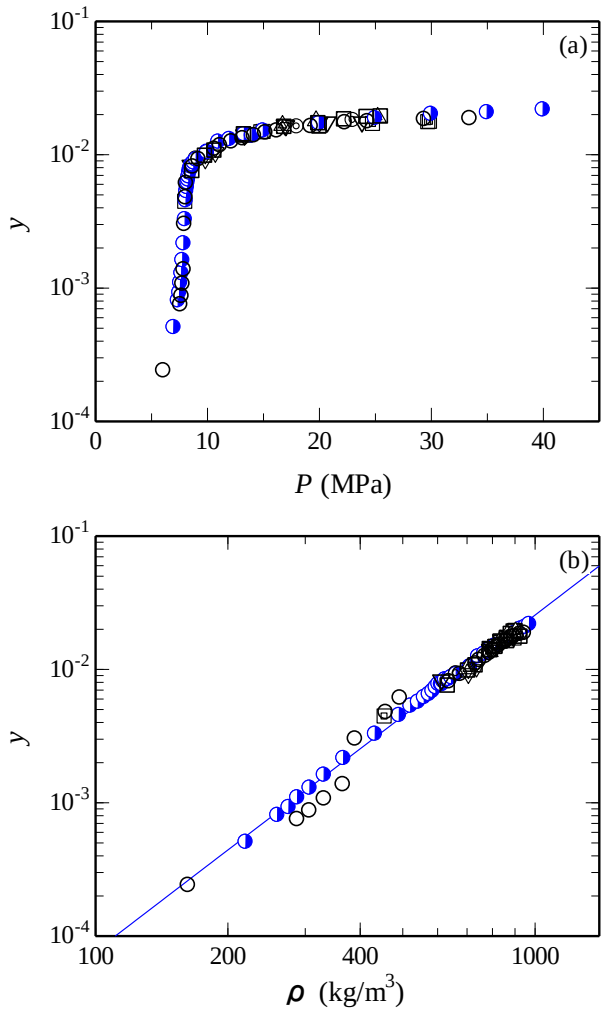

Fig. 4

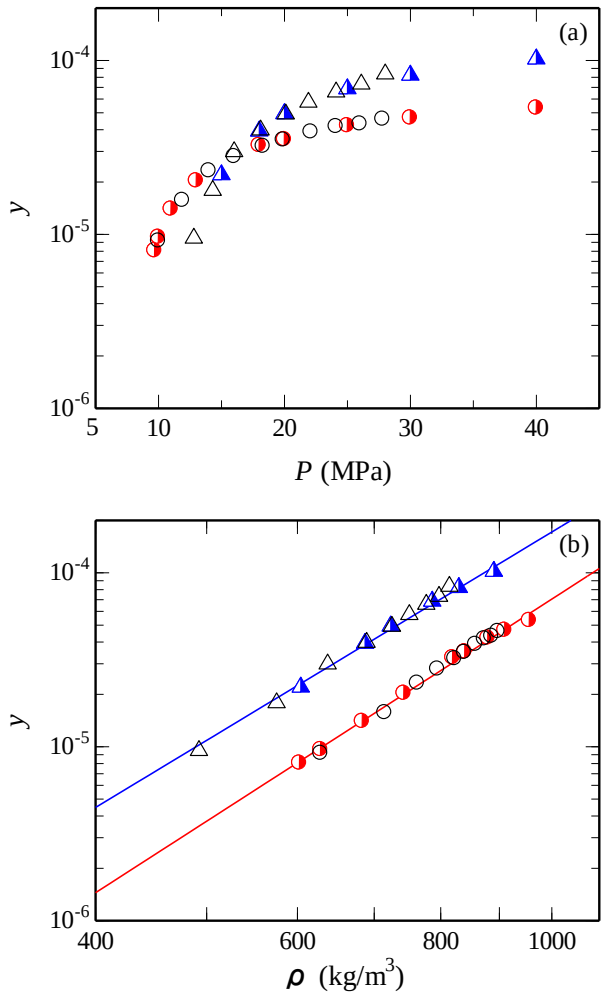
(a)
10^{-4}
10^{-5}
10^{-6}
y
5
10
20
30
40
P (MPa)
(b)
10^{-4}
10^{-5}
10^{-6}
y
400
600
800
1000
ρ (kg/m^3)

Fig. 5

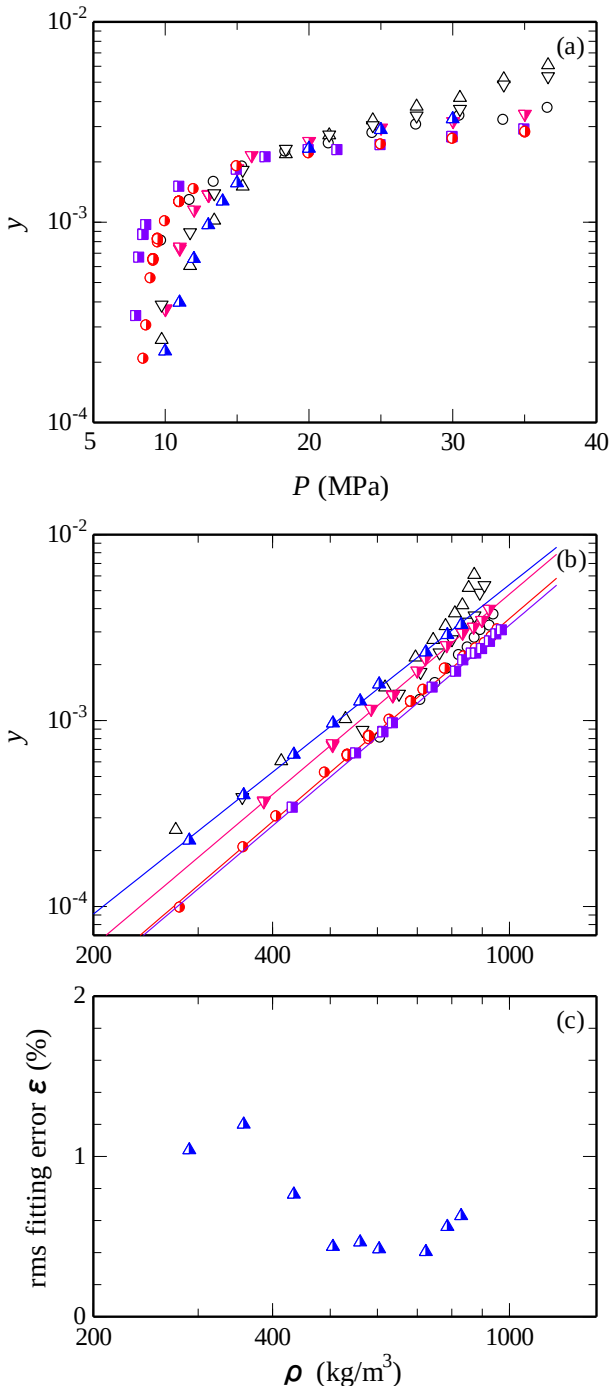

Fig. 6