Infinite dilution partial molar volumes of platinum(II) 2,4-pentanedionate in supercritical carbon dioxide

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Infinite dilution partial molar volumes of platinum(II) 2,4-pentanedionate in supercritical carbon dioxide

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Abstract

The effects of temperature and density on retention of platinum(II) 2,4-pentanedionate in supercritical fluid chromatography were ~~are~~ investigated at temperatures of 308.15 to 343.15 K and pressure range from 8 to 40 MPa by the chromatographic impulse response method with curve fitting. The retention factors were ~~are~~ utilized to derive the infinite dilution partial molar volumes of platinum(II) 2,4-pentanedionate in supercritical carbon dioxide. The determined partial molar volumes were ~~are~~ small and positive ~~and close to zero~~ at high pressures but exhibited ~~exhibits~~ very large and negative values in the highly compressible near critical region of carbon dioxide.

Keywords: Partial molar volume; Supercritical fluid chromatography; Retention factor; Platinum(II) 2,4-pentanedionate; Supercritical carbon dioxide; Chromatographic impulse response method.

1. Introduction

A supercritical fluid is an adjustable solvent at a temperature and pressure above its critical point, which can easily diffuse through materials like a dense gas, dissolve solutes like a liquid and has many advantages such as good selectivity, facile, fast, low surface tension, simple post supercritical treatments. Now, the applications of supercritical fluids have expanded dramatically over a wide range of fields from foods to pharmaceuticals, from biological applications and pollution abatement to new materials manufacture. Supercritical fluid chromatography (SFC) [1,2] has often been employed to determine thermodynamic properties of a solute at infinite dilution in the supercritical fluid, which are essential for the newly proposed supercritical process designs, computerized optimization and scale up. The partial molar volume, which is a macroscopic thermodynamic property for supercritical fluid mixture, is of importance to investigate the pressure and temperature dependence of fugacity coefficient and consequently solubility. The partial molar volume could be also employed to characterize the clustering of supercritical fluid molecules around solute molecules or to examine whether the distribution of the supercritical fluid molecules is relatively homogeneous on the microscopic scale. In addition, the study of the partial molar volumes at the limit of infinite dilution appears to be of particular interest, which can provide insight into the nature of solute and solvent interactions since the solute and solute interactions disappear at the infinite dilution condition. Thus, the partial molar volumes of a solute in supercritical fluid are important in both theoretical and practical aspects. The partial molar volume measurements can be classified into the direct and indirect ways [2,3]. Direct method is based on density or volume determinations with great precision between the solution and the pure solvent, which in general results in large uncertainties and therefore requires special care especially in the near critical point or at high dilution. On the other hand, indirect method is based on measuring solute retention with density at a constant temperature by SFC. In this respect the determination is easier, but requires accurate measurements for the retention factors over a wide range of density, since the partial molar volume is derived from the slope of retention factor versus density. So far, many studies have reported on the measurements for infinite dilution partial molar volumes of various solutes in supercritical carbon dioxide by SFC with a packed column [4-9] or a polymer coated open tubular capillary column [3,10-20]. And some researchers [21-26] have obtained the partial molar volumes in supercritical carbon dioxide by using the direct methods based on density or volume measurements. van Wasen and Schneider [4] have ~~has~~ pointed out that the direct method was difficult to determine partial molar volumes at infinite dilution conditions.

Platinum(II) 2,4-pentanedionate ($Pt(acac)_2$) is an important metal complex, which is being extensively employed in the impregnation, deposition of platinum and as catalysts and precursors in preparation of advanced functional materials in the supercritical fluid processing [27-30]. To the authors' knowledge, no information on the partial molar volumes of $Pt(acac)_2$ in supercritical carbon dioxide has yet been available. The purpose of this work is to measure the partial molar volumes of $Pt(acac)_2$ at infinite dilution in supercritical carbon dioxide. First, the chromatographic retention factors of $Pt(acac)_2$ were measured at infinite dilution in supercritical carbon dioxide by the chromatographic impulse response (CIR) ~~CIR~~ method with curve fitting [2,31-33], which is SFC with a poly(ethylene glycol) coated open tubular capillary column. The chromatographic retention measurements were performed at temperatures of 308.15 to 343.15 K and pressures of 7.99 - 40.0 MPa in this study. Then, the infinite dilution partial molar volumes of $Pt(acac)_2$ in supercritical carbon dioxide were obtained from the retention data and carbon dioxide density correlation.

2. Theoretical background

2.1 Measurements of retention factor

A solute component is pulse-injected into a fluid which is fully developed laminar flow in a polymer coated capillary column in the CIR method, the chromatographic response is governed by a system of coupled partial differential equations, and the average concentration $c(t)$ is described as follows [2,31-33]:

$$c(t)=\left(\frac{m}{\pi R^2}\right)\frac{1}{(1+k)\sqrt{4\pi at}}\exp\left\{-\frac{\left(L-\frac{u_0}{1+k}t\right)^2}{4at}\right\} \tag{1}$$

where t is the time, m the injected amount of solute, R the radius of the column, k the retention factor, defined as the ratio of a solute amount in the polymer phase to that in the fluid phase, and a the effective diffusivity, L the distance between the injection point and detection point, and u_0 the average velocity of the fluid flowing in the column. Note that it is assumed the solute instantly reaches equilibrium between the stationary phase and the mobile phase.

Generally, k is easily determined by measuring peak retention times using the basic chromatographic equation (Eq. (2)) or employing the first and the second temporal moments [31].

$$k=\frac{t}{t_0}-1 \tag{2}$$

where t and t_0 are ~~is~~ the retention times of the solute and the carrier solvent, respectively. ~~t_0 the time of an inert particle.~~ In this study, the k values were determined by the curve fitting technique [31] with minimizing the root-mean-square (rms) fitting error ε, defined by Eq. (3), for the measured $c_{\mathrm{exp}}(t)$ and predicted $c(t)$ curves.

$$\varepsilon=\sqrt{\int_{t_1}^{t_2}\left(c_{\mathrm{exp}}(t)-c(t)\right)^2dt\bigg/\int_{t_1}^{t_2}\left(c_{\mathrm{exp}}(t)\right)^2dt} \tag{3}$$

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

2.2 Determination of partial molar volume

The infinite dilution partial molar volume can be derived from k using Eq. (4) [9].

$$\bar{v}_{1,\mathrm{m}}^{\infty}=R_gT\beta_{\mathrm{T}}\left\{1+\left(\frac{\partial\ln k}{\partial\ln\rho}\right)_{\mathrm{T}}\right\}+\bar{v}_{1,\mathrm{s}}^{\infty} \tag{4}$$

where $\bar{v}_{1,\mathrm{m}}^{\infty}$ and $\bar{v}_{1,\mathrm{s}}^{\infty}$ are the infinite dilution partial molar volumes of solute for mobile phase and stationary phase, respectively, and R_g the gas constant, β_T the isothermal compressibility, and ρ the density of fluid. Although the value of $\bar{v}_{1,\mathrm{s}}^{\infty}$ was assumed to be zero at near critical point [3], it cannot be negligible in the region far from the critical point. Consequently, when the value of $\bar{v}_{1,\mathrm{s}}^{\infty}$ is not available directly in the literature, it can be used the molar volume of the solute. ~~When the value of $\bar{v}_{1,\mathrm{s}}^{\infty}$ is not usable in literature or difficult to estimate, the $\bar{v}_{1,\mathrm{m}}^{\infty}$ is usually obtained by assuming $\bar{v}_{1,\mathrm{s}}^{\infty}$ to be zero. This assumption may be valid in the near critical region since $\bar{v}_{1,\mathrm{m}}^{\infty}$ is usually much larger than $\bar{v}_{1,\mathrm{s}}^{\infty}$ in the region.~~

3. Experimental

3.1 Experimental apparatus and procedure

The schematic diagram of the apparatus for the chromatographic retention measurements is shown in Fig.1. The apparatus is composed of a syringe pump (260D, ISCO, USA), a water bath (T-105, Thomas Kagaku Co., Ltd., Japan), an injector (Model 7520, 0.5 μL rotor, Rheodyne), a coated open tubular capillary column (UACW-15W-1.0F, Frontier Laboratories Ltd. Japan), a detector (Model MD-1510, JASCO, Japan), a back pressure regulator (Model SCF-Bpg/M with modification, JASCO, Japan) and a flow meter. The experimental procedure was described as below, which is almost the same as the recent study [34,35~~33~~]. As a chromatographic column, the polymer coated open capillary column (polyethylene glycol thickness of 1 μm, the column radius of 0.251 mm, length of 15.28 m, and coil radius of 0.163 m) was used. The polymer chemically bonded on the column inner surface was utilized as the stationary phase and carbon dioxide was used as the mobile phase. The retention factors can be obtained using the stationary phase and the mobile phase. The chromatographic column was placed ~~put~~ horizontally in the water bath, which can maintain ~~control~~

the temperature within ± 0.01 K. The pressure of the system was controlled by the pump, a packed column and the back pressure regulator, which can regulate ~~control~~ the pressure within ± 0.005 MPa. When the system temperature, pressure and flow rate became constant, the flowing system was held under the same conditions for at least a further 2 h. Then, only a single pulse of Pt(acac)$_2$ predissolved in organic solvents (ethanol and dichloromethane) or in supercritical carbon dioxide was loaded through an injector into the fluid flowing for each retention measurement. The chromatographic curves were measured by a UV-Vis multi-detector by scanning at wavelengths from 195 to 400 nm and the flow rate of carbon dioxide was measured with a soap bubble flow meter after reduction to atmospheric pressure.

3.2 Experimental conditions

Pt(acac)$_2$ (99%, Pt($C_5H_7O_2$)$_2$, molecular weight (MW) of 393.3) was obtained from Aldrich, dichloromethane (99.5%) and ethanol (99.5%) were purchased from Wako Japan. These reagents were employed ~~directly~~ without further purification. Carbon dioxide with purity higher than 99.95 % was used from Air Gases Tokai Ltd., Japan.

The chromatographic retention measurements were carried out in supercritical carbon dioxide for Pt(acac)$_2$ at 308.15, 313.15, 323.15, 333.15, 343.15 K and pressures from 7.99 to 40.00 MPa by the CIR method with curve fitting.

The effects of the wavelengths on measured k values have been examined from 195 to 400 nm. It was observed that the measured k values are independent of ~~all~~ wavelengths studied. In this work the wavelength of 240 nm was used. Note that the curve fitting method was employed in determining ~~all~~ k values, and all ε values obtained in this study are lower than 1% which indicates good fit [31]. In addition, the effects of carbon dioxide velocities u_0 on the k have ~~has~~ also demonstrated that the measured k values do not depend on u_0 at constant temperature and pressure even at high carbon dioxide velocity of around 0.04 m/s. This fact indicates that the component of Pt(acac)$_2$ instantly reaches equilibrium between the stationary phase and the mobile phase.

4. Results and discussion

4.1. Effects of dissolving solvents

In the retention measurements in supercritical carbon dioxide, the solute can be predissolved in liquid solvents or in supercritical conditions before an injection. Note that the injector with our slight modification was employed just as shown in Fig. 1, when Pt(acac)$_2$ was predissolved in supercritical CO$_2$. Fig. 2 illustrates the typical chromatographic response peaks measured and calculated of Pt(acac)$_2$ in supercritical carbon dioxide at 240 nm, 313.15 K and 11.00 MPa for the cases of Pt(acac)$_2$ predissolved (a) in dichloromethane, (b) in ethanol and (c) in supercritical carbon dioxide, together with the corresponding UV data measured by the detector, and (d) the effects of the dissolving solvents of (dichloromethane, ethanol and supercritical carbon dioxide) on the measured k values. As shown in Fig. 2 (a), the injected dichloromethane solution of Pt(acac)$_2$ was chromatographically separated into dichloromethane and Pt(acac)$_2$ respectively due to different retention factors, which can be seen from its UV data. The similar behavior was observed from Fig. 2(b) when ethanol solution of Pt(acac)$_2$ was injected. On the other hand, when the Pt(acac)$_2$ dissolved in supercritical carbon dioxide was injected, as shown in Fig. 2(c), as expected, there was only the peak of Pt(acac)$_2$ obtained. In addition, excellent agreements were seen between the experimentally measured and theoretically calculated curves for Pt(acac)$_2$ using the CIR curve fitting technique for all three cases. Fig. 2 (d) shows the effects of the dissolving solvents such as dichloromethane (Fig. 2(a)), ethanol (Fig. 2(b)) and supercritical carbon dioxide (Fig. 2(c)) on the measured k values. It was found that the measured k values are independent of the dissolving solvents. Note that in this study the dichloromethane solution of Pt(acac)$_2$ was mainly used in the retention measurements.

4.2. Effects of injected amounts

The effects of the injected amounts *m* of $Pt(acac)_2$ on measured *k* values in supercritical carbon dioxide at 313.15 K and 11.00 MPa are shown in Fig. 3. Six difference solutions of $Pt(acac)_2$ in dichloromethane over the wide range of the solute concentrations (4×10^{-5}, 4×10^{-4}, 2×10^{-3}, 4×10^{-3}, 9×10^{-3} and 2×10^{-2} g/mL) were used. Correspondingly the injected amounts of $Pt(acac)_2$ were 5.09×10^{-5}, 5.09×10^{-4}, 2.54×10^{-3}, 5.09×10^{-3}, 1.14×10^{-2} and 2.54×10^{-2} μmol, respectively. All *k* values measured are nearly constant for the injected amounts from 5.09×10^{-5} to 2.54×10^{-2} μmol examined in this study, as seen from Fig. 3. This indicates that there is no effects of the injected amounts of $Pt(acac)_2$ on the measured *k* values. In this study all measurements were carried out with 2×10^{-3} g/mL dichloromethane solution of $Pt(acac)_2$.

4.3. Retention factors

The effect of carbon dioxide densities on *k* values for $Pt(acac)_2$ measured by the CIR method with curve fitting in supercritical carbon dioxide at 308.15, 313.15, 323.15, 333.15, 343.15 K and 7.99 to 40.00 MPa is shown in Fig. 4. In this study the *k* values were the average values for those ~~the values~~ measured at least three times under each condition. The *k* data simply decrease with increasing densities, decrease with increasing temperatures. Note that the *k* can be related by the solubility [34~~32~~]. At a given temperature, the decrease in *k* with increase density is reflected on the solubility increases. It was found from the logarithmic plot of the *k* versus the carbon dioxide density ρ that the ln *k* is a monotonically decreasing with increasing ln ρ and is well correlated by using Eq.(5). Note that the measured *k* data are not a physical property, but are in good agreement with the data reported in previous study [35~~33~~].

$$\ln k = c_1 + c_2 \ln\rho + c_3(\ln\rho)^2 + c_4(\ln\rho)^3 + c_5 T \qquad (5)$$

Where ρ is in kg m^{-3}, c_1, c_2, c_3, c_4 and c_5 are constants, T is in K. The parameters of c_1 to c_5 were determined simultaneously by fitting to the experimental retention factors. The objective function of average absolute relative deviation (AARD) employed in the correlation is as follows:

$$\mathrm{AARD}(\%)=\frac{1}{N}\sum_{i=1}^{N}\left|1-\frac{k_{\mathrm{corr}}}{k}\right|\times 100 \tag{6}$$

Where N is the number of experimental data points, k_{corr} and k correspond to the correlated and measured retention factors by the equation and experimental, respectively. The optimized parameters in Eq.(5) are shown in Table 1, together with the AARD(%).

4.4. Partial molar volumes

Since the value of $\bar{v}_{1,\mathrm{s}}^{\infty}$ in Eq (4) for Pt(acac)$_2$ was ~~is~~ not available directly ~~usable~~ in the literature, the authors used the density value of 2.336 g/cm^3 for solid Pt(acac)$_2$ [36] to obtain the solute molar volume of 1.684×10^{-4} m^3/mol as an approximate value for $\bar{v}_{1,\mathrm{s}}^{\infty}$. Then, the partial molar volumes, $\bar{v}_{1,\mathrm{m}}^{\infty}$, of Pt(acac)$_2$ in supercritical carbon dioxide was obtained from Eqs (4) and (5) ~~by assuming $\bar{v}_{1,\mathrm{s}}^{\infty}$ to be zero~~. The determined $\bar{v}_{1,\mathrm{m}}^{\infty}$ results in supercritical carbon dioxide at 308.15, 313.15, 323.15, 333.15, 343.15 K and 7.99 to 40.00 MPa are listed in Table 2. Fig. 5 shows the $\bar{v}_{1,\mathrm{m}}^{\infty}$ values obtained in this study for Pt(acac)$_2$ in supercritical carbon dioxide as a function of pressure, and comparison of the reported $\bar{v}_{1,\mathrm{m}}^{\infty}$ data at 313.2 K between this work and the previous studies [15,16,19,20]. As shown in Fig. 5 (a), the partial molar volumes ~~values~~ of Pt(acac)$_2$ are small and positive ~~show small and close to zero~~ when the pressures increases up to 20 MPa away from the critical pressure, but become very large and negative with decreasing pressure, especially near 8.8 MPa at 313.15 K and 8.0 MPa at 308.15 K. The tendencies are quite similar to those for ubiquinone CoQ10 [14], unsaturated fatty acids [15,16], α-tocopherol and β-carotene [17], long-chain triglycerides [18], myristoleic acid and its methyl ester [19] and γ-linolenic acid and its esters [20]. The result of large negative partial molar volumes of a solute physically indicates that clustering of solvent molecules around a solute was caused by a strongly attractive interaction between the solvent and the solute [21]. This phenomenon can be explained both in terms of local density enhancement due to solvent molecules around solutes and the divergence of density fluctuations near the critical region [8]. In addition, it can be seen from Fig. 5 (b) and (c) that the absolute magnitude of the partial molar volumes of Pt(acac)$_2$ with MW of 393.3 have similar values to those of unsaturated fatty acids such as α-linolenic acid [15] with MW of 278.4, γ-linolenic acid [20] with MW of 278.4 and linoleic acid [16] with MW of 280.4, but higher than those of myristoleic acid with MW of 226.4 [19] and lower than those of arachidonic acid with MW of 304.5 [16] at the pressures lower than 10.25 MPa. The comparison results reveal that the absolute magnitude of the partial molar volumes of Pt(acac)$_2$ with lower polarizability show relatively smaller values in the supercritical carbon dioxide although Pt(acac)$_2$ has relatively higher molecular weight of 393.3.

5. Conclusions

The chromatographic impulse response method with curve fitting was utilized to measure the infinite dilution partial molar volumes of platinum(II) 2,4-pentanedionate at temperatures of 308.15, 313.15, 323.15, 333.15, 343.15 K and pressures of 7.99 - 40.00 MPa in supercritical carbon dioxide. The results of the partial molar volumes were small and positive ~~minus and close to zero at high pressures but exhibited very large and negative values near the highly compressible critical region.~~ with the pressures increasing up to 20 MPa away from the critical pressure, but became very large and negative with decreasing pressure, especially near 8.8 MPa at 313.15 K and 8.0 MPa at 308.15 K.

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Table 1

Correlated results using Eq. (5).

T(K)	N	c_1 (-)	c_2 (-)	c_3 (-)	c_4 (-)	c_5 (-)	AARD (%)
308.15	22	58.570	-16.145	1.6963	-0.09057	-	2.1
313.15	28	107.137	-39.391	5.3916	-0.2860	-	1.8
323.15	18	59.290	-15.038	1.2673	-0.05452	-	2.0
333.15	21	73.604	-22.108	2.4104	-0.1160	-	1.8
343.15	14	107.393	-38.329	4.9679	-0.2493	-	0.9
Common	103	74.160	-19.982	2.2284	-0.1144	-0.02135	2.4

Table 2

Partial molar volumes of $Pt(acac)_2$ at infinite dilution in supercritical carbon dioxide.

308.15 K			
P (MPa)	ρ(kg/m^3)	β_T (1/MPa)	$\bar{v}_{1,m}^{\infty}$ (10^{-3} m^3/mol)
7.99	412.4	1.5832	-18.446
8.00	419.1	1.6312	-18.990
8.05	455.6	1.6290	-18.862
8.10	490.8	1.3378	-15.404
8.20	542.8	0.7233	-8.220
8.30	574.1	0.4406	-4.933
8.50	612.1	0.2387	-2.592
9.00	662.1	0.1086	-1.088
10.00	712.8	0.0526	-0.441
10.50	729.8	0.0422	-0.320
11.00	743.9	0.0353	-0.240
12.00	767.1	0.0267	-0.141
15.00	815.1	0.0157	-0.014
16.00	827.2	0.0139	0.008
18.00	848.0	0.0112	0.038
20.00	865.7	0.0095	0.058
25.00	901.2	0.0069	0.088
29.00	924.0	0.0057	0.102
30.00	929.1	0.0054	0.105
35.00	952.3	0.0045	0.116
38.00	964.6	0.0041	0.121
40.00	972.3	0.0038	0.124

313.15 K			
P (MPa)	ρ(kg/m^3)	β_T (1/MPa)	$\bar{v}_{1,m}^{\infty}$ (10^{-3} m^3/mol)
8.75	414.8	0.6762	-7.908
8.80	429.1	0.6732	-7.853
8.85	443.6	0.6547	-7.618
9.00	485.5	0.5423	-6.249
9.10	510.4	0.4568	-5.226
9.20	532.0	0.3764	-4.270
9.50	580.0	0.2197	-2.417
9.70	602.6	0.1665	-1.789
10.00	628.6	0.1201	-1.243
10.50	660.2	0.0807	-0.780

11.00	683.5	0.0604	-0.541
12.00	717.8	0.0401	-0.303
12.50	731.2	0.0344	-0.236
14.00	763.3	0.0241	-0.115
15.05	781.0	0.0200	-0.067
15.50	787.8	0.0186	-0.051
16.00	794.9	0.0173	-0.035
17.30	811.5	0.0146	-0.004
17.50	813.8	0.0143	0.000
18.00	819.5	0.0135	0.009
19.50	835.0	0.0116	0.031
20.00	839.8	0.0111	0.037
25.00	879.5	0.0078	0.077
29.00	904.3	0.0063	0.094
30.00	909.9	0.0060	0.097
35.00	934.8	0.0049	0.110
38.00	947.9	0.0044	0.116
40.00	956.1	0.0041	0.119

323.15 K

P (MPa)	ρ(kg/m^3)	β_T (1/MPa)	$\bar{v}_{1,m}^{\infty}$ (10^{-3} m^3/mol)
10.30	420.9	0.2941	-3.453
10.50	445.6	0.2742	-3.196
10.70	469.5	0.2482	-2.868
11.00	502.6	0.2069	-2.355
11.50	548.8	0.1479	-1.630
12.00	584.7	0.1082	-1.145
13.00	636.1	0.0661	-0.634
14.00	672.2	0.0462	-0.392
15.00	699.8	0.0351	-0.258
16.00	722.1	0.0282	-0.174
18.00	757.1	0.0201	-0.075
20.00	784.3	0.0156	-0.021
25.00	834.2	0.0099	0.047
29.00	863.9	0.0077	0.074
30.00	870.4	0.0073	0.079
35.00	899.2	0.0058	0.097
38.00	914.1	0.0052	0.105
40.00	923.3	0.0048	0.109

333.15 K			
P (MPa)	ρ(kg/m^3)	β_T (1/MPa)	$\bar{v}_{1,m}^{\infty}$ (10^{-3} m^3/mol)
11.80	419.0	0.1846	-2.176
12.00	434.4	0.1760	-2.061
12.50	471.5	0.1513	-1.739
13.00	505.4	0.1263	-1.419
13.50	535.3	0.1044	-1.141
14.00	561.4	0.0867	-0.918
15.00	604.1	0.0620	-0.607
16.00	637.5	0.0468	-0.417
17.00	664.6	0.0371	-0.295
18.00	687.2	0.0304	-0.212
20.00	723.7	0.0221	-0.108
22.00	752.4	0.0172	-0.047
24.00	776.1	0.0140	-0.007
25.00	786.6	0.0128	0.008
26.00	796.3	0.0118	0.020
28.00	814.0	0.0102	0.040
29.00	822.1	0.0096	0.049
30.00	829.7	0.0090	0.056
35.00	862.9	0.0069	0.082
38.00	879.8	0.0061	0.092
40.00	890.1	0.0056	0.098

343.15 K			
P (MPa)	ρ(kg/m^3)	β_T (1/MPa)	$\bar{v}_{1,m}^{\infty}$ (10^{-3} m^3/mol)
13.07	405.7	0.1385	-1.648
13.55	432.4	0.1269	-1.488
14.06	459.8	0.1137	-1.310
14.56	485.1	0.1008	-1.139
15.06	508.6	0.0888	-0.981
16.00	547.8	0.0699	-0.734
17.00	582.8	0.0549	-0.540
18.00	612.2	0.0442	-0.402
20.00	659.1	0.0308	-0.228
22.00	695.1	0.0231	-0.129
25.00	736.9	0.0165	-0.044
29.00	779.1	0.0118	0.016
30.00	788.0	0.0110	0.027
35.00	826.1	0.0082	0.063

Figure Captions

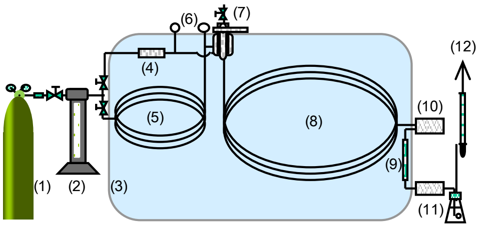
Fig. 1. Schematic diagram of the apparatus. (1) CO_2; (2) ISCO syringe pump; (3) water bath; (4) sample packed column; (5) preheating column; (6) Heise pressure gauge; (7) injector; (8) coated capillary column; (9) packed column; (10) UV-Vis multi-detector; (11) back pressure regulator; (12) soap bubble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

Fig. 2. Typical chromatographic peaks measured (dash line) and calculated (solid line) for $Pt(acac)_2$ in supercritical carbon dioxide at 240 nm, 313.15 K and 11.00 MPa for the cases of $Pt(acac)_2$ predissolved (a) in dichloromethane, (b) in ethanol and (c) in supercritical carbon dioxide before injection, together with the corresponding UV data measured by the detector, and (d) the effects of the dissolving solvents of (dichloromethane, ethanol and supercritical carbon dioxide) on the measured k values.

Fig. 3 Effects of the injected amount m of $Pt(acac)_2$ on the k values measured in supercritical carbon dioxide at 240 nm, 313.15 K and 11.00 MPa.

Fig. 4. Plot of $\ln k$ vs. $\ln [\rho(\mathrm{kg/m^3})]$ for $Pt(acac)_2$ in supercritical carbon dioxide at 308.15, 313.15, 323.15, 333.15 and 343.15 K (the lines are ~~is~~ predicted by Eq. (5)).

Fig. 5. Plots of (a) the $\bar{v}_{1,\mathrm{m}}^{\infty}$ experimental data measured in this study for $Pt(acac)_2$ at 308.15, 313.15, 323.15, 333.15 and 343.15 K in supercritical carbon dioxide, ~~and (b)~~ comparison of the present $\bar{v}_{1,\mathrm{m}}^{\infty}$ data with the literature data [15,16,19,20] reported at 313.2 K and (b) at 7 - 40 MPa, and its enlarged view (c) at 9 - 12 MPa.



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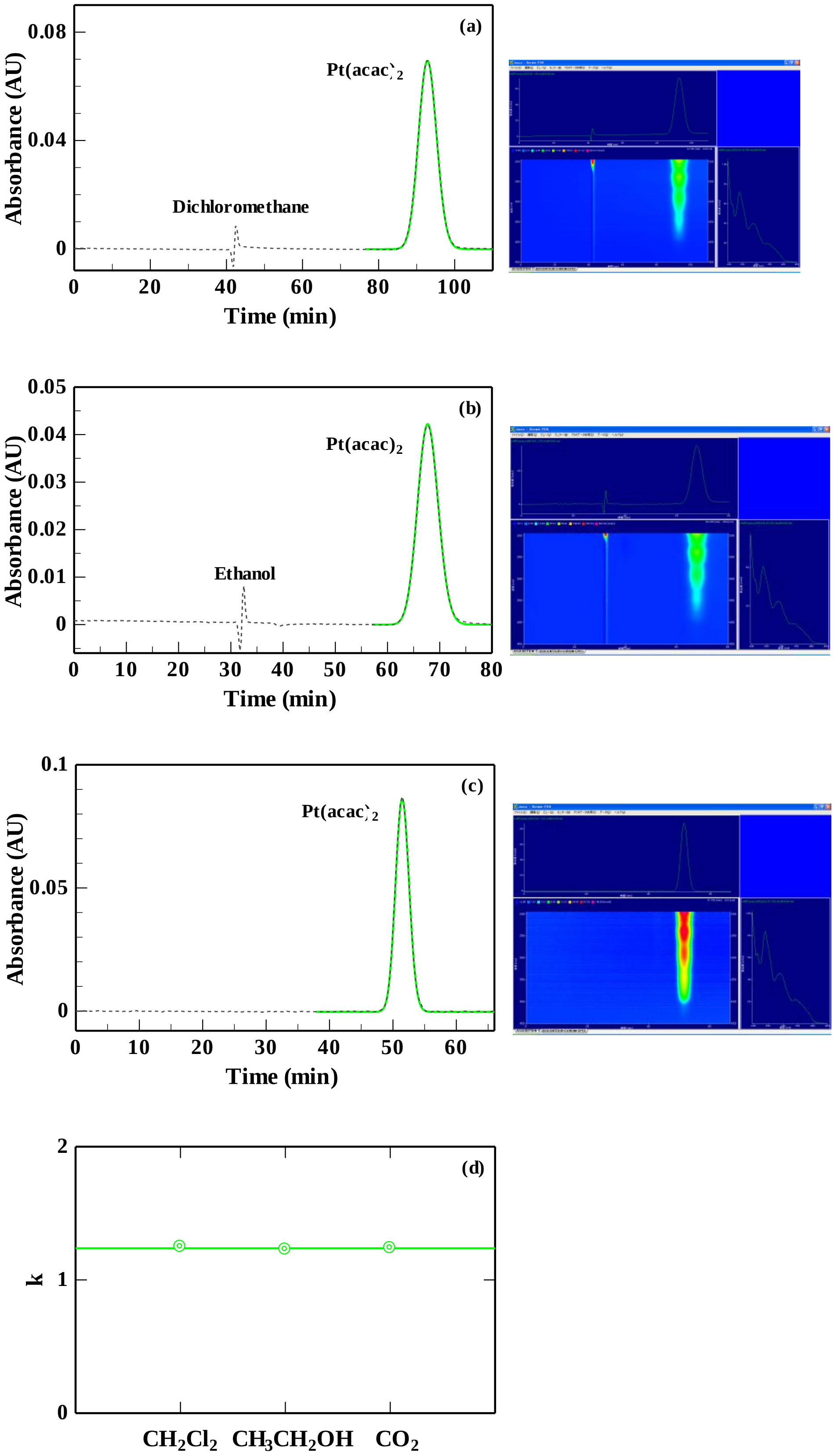

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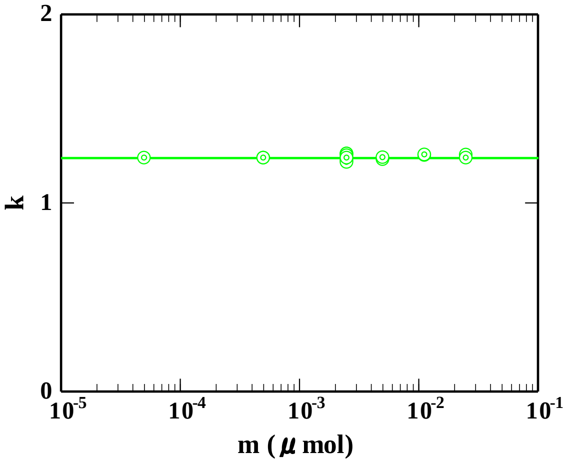
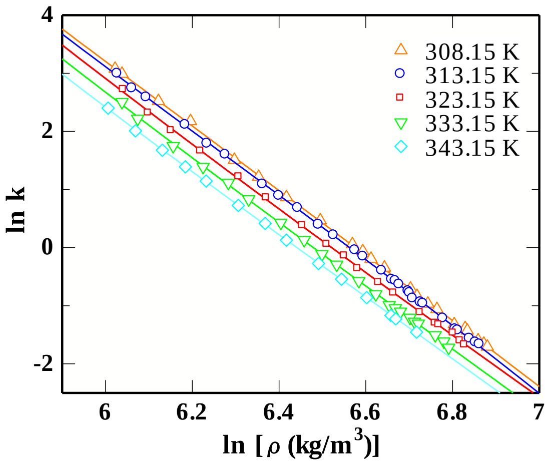


Fig. 3 Effects of the injected amount *m* of Pt(acac)$_2$ on the *k* values measured in supercritical carbon dioxide at 240 nm, 313.15 K and 11.00 MPa.



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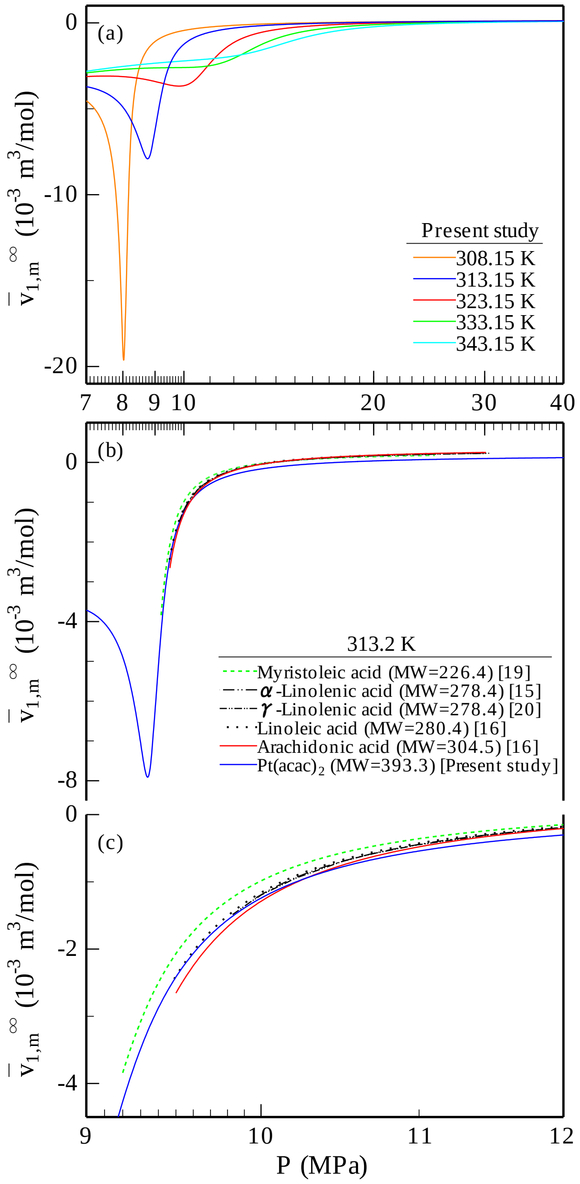

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