Solubilities of Palladium(II) β -Diketonates (β -Diketonate = Acetylacetonate, Trifluoroacetylacetonate, Thenoyltrifluoroacetonate) in Supercritical Carbon Dioxide

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The solubilities of palladium(II) β -diketonates (PdL_2 , L = acetylacetonate (acac), trifluoroacetylacetonate (tfa), and thenoyltrifluoroacetonate (tta)) in supercritical carbon dioxide (SC- CO_2) from 318 – 338 K and 8 – 25 MPa were investigated by UV-vis spectrophotometer equipped with a high-pressure optical cell. The molar absorptivities for $\text{Pd}(\text{acac})_2$, $\text{Pd}(\text{tfa})_2$, and $\text{Pd}(\text{tta})_2$ in SC- CO_2 were estimated as $1.14 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 324 nm, $8.16 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ at 336.5 nm, and $2.70 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 322.5 nm, respectively. Solubilities in SC- CO_2 increase in order of $\text{Pd}(\text{tta})_2 < \text{Pd}(\text{acac})_2 < \text{Pd}(\text{tfa})_2$, i.e., $6.5 \times 10^{-6} < 5.2 \times 10^{-5} < 1.3 \times 10^{-4} \text{ M}$ at 318 K and 11.5 MPa. The experimental solubilities were correlated using the equation proposed by Chrastil and the thermodynamic parameters for each PdL_2 were estimated.

1. Introduction

In recent years, supercritical carbon dioxide (SC- CO_2) extraction has attracted attention as an alternative for conventional solvent extraction using organic solvents from viewpoint of environmental load reduction [1,2]. Carbon dioxide (CO_2) is not toxic and corrosive, is chemically inert, is inexpensive and easily available, and has relatively mild critical point (critical temperature: 31.3°C, critical pressure: 7.4 MPa). SC- CO_2 is a medium capable of continuously changing physical properties such as density and diffusion coefficient by adjusting pressure and temperature. These characteristics give many advantages in extraction and separation of substances. SC- CO_2 extraction is particularly developed in the food industry because of its high safety as a solvent [3], and the extraction of caffeine from coffee beans has been put to practical use early [4,5]. Furthermore, SC- CO_2 extraction of high value-added essences contained in natural products such as perfumes, dyes, spices, and medical products is also performed [6-9]. However, studies on recovering metal elements from various media by SC- CO_2 extraction have been conducted [10-16]. However, there is almost no practical application of SC- CO_2 extraction of metal elements.

Palladium is one of the essential elements in industrial production, because it is commonly used in industry for a variety of purposes, such as in electronic devices and automobile exhaust gas purification catalysts. Therefore, the separation and recovery of palladium from various media is of great importance. β -Diketones are one of most popular chelating agents used to recover palladium. They are often used as extractants in the study of SC- CO_2 extraction of metals [17-21]. The extractability and solubility of metal chelates in SC- CO_2 are greatly affected by the substituents of chelating agents. It has been reported that fluorine substitution in a chelating agent could greatly enhance the extractability and

solubility of its metal complexes in SC-CO₂ [22-25]. However, there are not many studies that have examined in detail the effect of the substituent of the chelating agent on the solubility of its metal complexes in SC-CO₂. It is important to accumulate basic research data to expand the application of supercritical carbon dioxide extraction to metal ions in the future.

In this paper, we investigate the solubilities of Pd(II) β -diketonates (PdL₂, L = acetylacetonate (acac), trifluoroacetylacetonate (tfa), and thenoyltrifluoroacetonate (tta)) in SC-CO₂ by UV-vis spectrophotometer equipped with a high-pressure optical cell. Furthermore, thermodynamic parameters for the solubility of PdL₂ in SC-CO₂ were estimated using the model equation proposed by Chrastil [26].

2. Experimental

2.1 Reagents

Pd(acac)₂ was purchased from Tokyo Chemical Industry Co., Ltd. and used as received. Pd(tfa)₂ and Pd(tta)₂ were synthesized according to the methods in the literature [27,28]. Liquid CO₂ (99.99%) was purchased from Taiyo Nissan Co., Ltd.

2.2 Solubility apparatus

The apparatus for measuring the solubility of PdL₂ in SC-CO₂ were almost the same as those reported previously [29]. The apparatus consists of a high-pressure syringe pump (Model 100DX; Isco), a pump controller (Series D; Isco), a high-pressure optical cell (Jasco), a UV-vis spectrophotometer (Blue-Wave UVNb-200; StellarNet), and a deuterium lamp light source (Shimadzu). The high-pressure optical cell was built from 316 stainless-steel and is fitted with sapphire windows (10 mm in diameter and 6 mm thick). The path length and inner volume of the cell are 0.98 cm and 2.71 cm³, respectively. The temperature of the cell is controlled within ± 0.2 K using a water jacket with a thermostated water circulator and is monitored with a digital temperature indicator (Fenwal).

2.3 Solubility Measurements

Excessive amounts of PdL₂ (about 100 mg) were placed into the cell controlled thermostatically. After sealing the cell, CO₂ compressed by the high-pressure syringe pump was introduced into the cell, and stirred with a magnetic stirrer for 60 min. After standing for 5 min, the UV-vis absorption spectrum of PdL₂ dissolved in SC-CO₂ was measured. The absorbance was confirmed to be constant even when the stirring and standing time were extended. CO₂ pressure and temperature were changed in the ranges from 8 – 25 MPa and 318 – 338 K, respectively.

2.4 Molar absorptivity measurements

All calibration standards were prepared as follows. PdL₂ methanol solution containing a known amount of each PdL₂ was added into the high-pressure optical cell by micropipette. The methanol in the cell was evaporated and removed by heating. After dissolving in SC-CO₂, UV-vis absorption spectra of PdL₂ in SC-CO₂ were measured. Each standard was measured in triplicate. The molar absorptivity of each PdL₂ in SC-CO₂ was determined from the relationship between absorbance and the concentration based

Table 1. Molar absorptivity of PdL₂ at absorbance maximum wavelength in supercritical CO₂ at 318 K.

PdL ₂	$\epsilon / 10^4 \text{ M}^{-1} \text{ cm}^{-1}$	$\lambda_{\text{max}} / \text{nm}$
Pd(acac) ₂ ^a	1.14 ± 0.02	324
Pd(tfa) ₂ ^a	0.816 ± 0.017	337
Pd(tta) ₂ ^b	2.70 ± 0.04	323

a) 15 MPa, b) 25 MPa

on Lambert-Beer law. Temperature was kept at 318 K. CO₂ pressures for Pd(acac)₂ and Pd(tfa)₂ were set to 15 MPa. CO₂ pressure for Pd(tta)₂ was set to 25 MPa, because solubility of Pd(tta)₂ in SC-CO₂ was relatively low.

3. Results and Discussion

3.1 Solubility of PdL₂ in SC-CO₂

To determine the solubility of PdL₂ in SC-CO₂, the molar absorptivities for each PdL₂ were determined. The absorbance of PdL₂ increased linearly with an increase in its concentration in SC-CO₂. The molar absorptivities (ϵ) for each PdL₂ at the maximum wavelength in SC-CO₂ were determined based on the Lambert-Beer law and are listed in Table 1. The absorption spectra of PdL₂ hardly changed by changing temperature and pressure. The ϵ values of Pd(acac)₂ in SC-CO₂ were confirmed to be hardly changed in the ranges from 10 – 20 MPa and 318 – 338 K (within $\pm 3\%$). Therefore, the ϵ values obtained were used for the calculation of the solubility of PdL₂ in SC-CO₂ under all conditions.

The solubility, C (M), of PdL₂ in SC-CO₂ was measured at the various temperatures and pressures. Figures 1(a) – 1(c) show the natural logarithmic plots of C against the CO₂ molarity, $[\text{CO}_2]$ (M), in the temperature range from 318 to 338 K for Pd(acac)₂, Pd(tfa)₂ and Pd(tta)₂, respectively. The CO₂ molarity at a given temperature and pressure was calculated using the freeware EOS-SCx ver. 0.2, which is the calculation program for density and thermodynamic properties of water, methanol, and carbon dioxide by the equations-of-state [30]. The solubility increased with an increase in the CO₂ molarity, i.e. the CO₂ density, at a constant temperature and in the temperature at a constant CO₂ molarity for all PdL₂. However, there were large solubility differences among PdL₂. Figure 2 shows the dependency of the solubility on the CO₂ molarity at 318K. Solubilities in SC-CO₂ increase in order of Pd(tta)₂ < Pd(acac)₂ < Pd(tfa)₂, i.e., $6.5 \times 10^{-6} < 5.2 \times 10^{-5} < 1.3 \times 10^{-4}$ M at 318 K and 11.5 MPa. Pd(tfa)₂ having a trifluoromethyl group was the highest solubility in SC-CO₂. This agrees with previous studies showing that fluorinated compounds have higher solubilities in SC-CO₂. On the other hand, the solubility of Pd(tta)₂ in SC-CO₂ was the lowest despite having a trifluoromethyl group. The relatively bulky 2-thienyl group of Pd(tta)₂ may hinder

Figure 1. Natural logarithmic plots of the solubility against the CO₂ molarity in the temperature range from 318 to 338 K. (a) Pd(acac)₂, (b) Pd(tfa)₂, (c) Pd(tta)₂. Mesh planes represent correlation by equation 1.

dissolution in SC-CO₂. However, further researches will be needed to clarify the effect of the 2-thienyl group on the solubility in SC-CO₂.

3.2. Correlation of Experimental Solubility Data

The dependence of the solubility of PdL₂ in SC-CO₂ on the CO₂ molarity were correlated using the empirical model proposed by Chrastil [26]:

$$\ln C = k \ln [\text{CO}_2] - \Delta H/RT + q, \quad (1)$$

where k is the number of CO₂ molecules required to form the solvato-complex PdL₂(CO₂) _{k} in SC-CO₂, ΔH is the sum of the vaporization and solvation enthalpies, and q is the constant of the entropy term. By performing a multiple regression on C as a function of $[\text{CO}_2]$ and $1/T$, the values of k , ΔH , and q are obtained. These values are listed in Table 2. The k value for Pd(acac)₂ was 7.1 ± 0.2 . This was close to the k value (6.6 ± 0.1) for Pd(acac)₂ reported previously [31]. The k values of Pd(tfa)₂ and Pd(tta)₂ were 5.2 ± 0.2 . It has been reported that the k value of fluorinated complexes is lower than that of alkylated complexes [25,32]. The result obtained in this study is same tendency with that reported previously. Pd(tfa)₂ having the highest solubility and Pd(tta)₂ having the lowest solubility had the same k value. This result suggests that the k value i.e., the number of CO₂ molecules associated with PdL₂ does not play an important

role in determining the solubility of PdL₂ in SC-CO₂. The ΔH values increase in order of Pd(tta)₂ ($35.0 \pm 3.6 \text{ kJ mol}^{-1}$) < Pd(acac)₂ ($51.4 \pm 7.0 \text{ kJ mol}^{-1}$) < Pd(tfa)₂ ($83.2 \pm 4.4 \text{ kJ mol}^{-1}$), which is the same tendency of solubility. Furthermore, the q values, which are the constant of the entropy term, also increase with the same tendency. It is suggested that the enthalpy change and entropy term play an important role in the solubility of PdL₂ in SC-CO₂. However, further studies by using other metallic elements and different ligands are needed to discuss in detail the effects of enthalpy change and entropy term on the solubility of metal complexes in SC-CO₂.

4. Conclusion

The solubilities of Pd(acac)₂, Pd(tfa)₂, and Pd(tta)₂ in SC-CO₂ were measured by UV-vis spectrophotometer from 318 – 338 K and 8 – 25 MPa. The dependence of the solubility of PdL₂ in SC-CO₂ on the CO₂ molarity could be correlated using the empirical model proposed by Chrastil. Solubilities in

Figure 2. Dependences of the solubility on the CO₂ molarity in supercritical CO₂ at 318 K.

Table 2. Coefficients and enthalpies for the solubility of PdL₂ in supercritical CO₂ calculated using Chrastil model.

PdL ₂	k	$\Delta H / \text{kJ mol}^{-1}$	q
Pd(acac) ₂	7.1 ± 0.2	51.4 ± 7.0	-9.2 ± 2.5
Pd(tfa) ₂	5.2 ± 0.2	83.2 ± 4.4	8.8 ± 1.6
Pd(tta) ₂	5.2 ± 0.2	35.0 ± 3.6	-12.8 ± 1.2

Numbers after $\pm$ denote standard errors.

SC-CO₂ increase in order of Pd(tta)₂ < Pd(acac)₂ < Pd(tfa)₂. It is suggested that the enthalpy change, ΔH , plays a more important role than the number of CO₂ molecules associated with PdL₂ in determining the PdL₂ solubility in SC-CO₂. The results on the effect of pressure and temperature on the solubility obtained in this study provide useful information for applying SC-CO₂ extraction to metal complexes.

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