Solubility Measurement of Noble-Metal-Chelates in Supercritical CO_2

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Solubility of noble metal (Pt, Pd Ag) chelates, which were used in material synthesis, to supercritical CO_2 was evaluated using flow type apparatus at 313 K and from 9.6 to 29.4 MPa. Noble metal chelates having CO_2-philic ligands, such as cyclooctadiene and fluoroacetylacetonato showed much higher solubility to acetylacetonato chelates. The molar fraction solubility of (1, 5-Cyclooctadiene) dimethyl platinum (II) was in order of 10^{-4} and that of (1, 5-Cyclooctadiene) (hexafluoroacetylacetonato) silver (I) was in order of 10^{-3}. The solubility of Pt acetylacetonate and Pd acetylacetonate were observed in the order of 10^{-5}. Correlations of the experimental data using solution model with density dependent solubility parameter were performed.

INTRODUCTION

Supercritical CO_2 ($scCO_2$) has excellent properties as a solvent for impregnation of guest compounds into matrix, because of its low viscosity and high diffusivity. Preparation of composite materials by impregnation using $scCO_2$ have been focused as dry, simple and energy-saving process for nanocomposite materials.

Noble-metal-dispersed composites have been attracted as catalyst, electronic or optical materials. Preparation of such composite using noble-metal chelates soluble to $scCO_2$ has been developed [1-5]. Solubility of those chelates in $scCO_2$ is necessary to the design of the material processing, but details were not yet reported. In this work, with relation to our research on preparation of polymer-metal composite, solubility of some noble metal chelates [1-4] in $scCO_2$ was measured. Experimental data of acetylacetonato chelates were correlated with a solution model proposed by Guigard et. al [6].

EXPERIMENTAL

Noble-metal chelates measured in this work were shown in **Table 1**. All chemicals were purchased from Aldrich and used without further purification. Since these chelates were humidity senstive, handling of these reagents were performed under inert (N_2) atmoshere. Ag(I)(COD)(hfa) was treated under shaded contitions. Flow type extraction apparatus (**Fig. 1**) was used for the measurements. Samples (0.2-1g) were mixed with grass beads (0.5mm) and

Table 1 Noble-metal complexes used in this work

Reagents	Abbreviation	Purity	Supplier
Platinum (II) acetylacetonate	$Pt(II)(acac)_2$	99.99%	Aldrich
(1,5-Cyclooctadiene)-dimethyl platinum(II)	$Pt(II)(COD)(Me)_2$	98%	Aldrich
Palladium(II) acetylacetonate	$Pd(II)(acac)_2$	98%	Aldrich
(1,5-Cyclooctadiene)(hexafluoro-acetylacetonato)silver(I)	Ag(I)(COD)(hfa)	99%	Aldrich

sealed in the extraction column(f) and connetcted to the flow line. The column(f) was left for 1 hour after introduction of $scCO_2$ for saturation and then $scCO_2$ was flown through the system. The amount of the extracted reagent was measured using both weighing and UV-VIS absortionmetory after dissoluving the extractant to tetrahydroflane. Removable dry solute receiver was designed for weighing. The flow rate of $scCO_2$ and sampling interval was determined carefully for each samples to make the extraction equibrium. It was ragned from 0.1-1 dm^3min^{-1}. The solubility of the regent was determined from the extracted amount of the solute and the amount of CO_2 measured by flow meter(k).

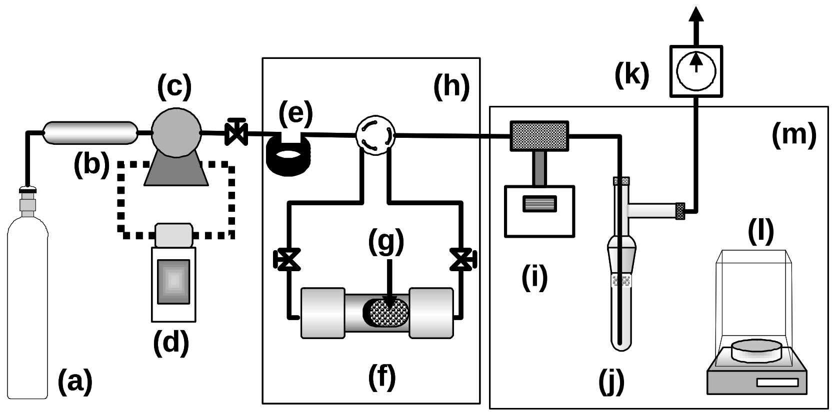

Fig. 1 Schematic apparatus for this work. (a) CO_2 cylinder, (b)Dehydration column, (c)CO_2 pump, (d) Cooling bath, (e) Preheat coil, (f) Extraction column, (g)Sample with glass beads, (h) Constant temperature air bath (i) Backpressure regulator, (j) Removable solute receiver, (k) Integrating flow meter, (l) Microbalance (m) Glove box for inner gas.

RESULTS AND DISCUSSION

Table 2 summerized the experimental mole fraction solubilities (y_2) of the chelates to $scCO_2$ at 313 K. The solubilities of the chelates increased with increasing the pressure.

The solubility of Pt(II)$(acac)_2$ and Pd(II) $(acac)_2$ were ranged in the order of $10^{-5.}$ These values were close to the solubility of other acetylacetonato chelates of divalent and trivalent

Table 2 Experimental mole fraction solubilities in $scCO_2$

Sample	T / K	P / MPa	Y_2 x 10^5
Pt(II)$(acac)_2$	313.2	9.8	1.35
		14.7	2.52
		19.6	3.00
		24.5	3.20
		29.4	3.59
Pd(II)$(acac)_2$	313.2	9.8	0.71
		19.6	2.25
		29.4	3.26
Pt(II)(COD)$(Me)_2$	313.2	9.8	10.8
		19.6	86.9
		29.4	117
Ag(I)(COD)(hfa)	313.2	9.8	75.7
		19.6	1360
		29.4	1330

metal, such as Cu(II), Cr(III), [7] and Co(III), Mn(III), Zn(II) [8].repored in previous studies. Pt(II)(COD)(Me)$_2$ and Ag(I)(COD)(hfa), having CO_2-philic ligands, showed much higher solubilities than acetylacetonato chelates, as expected. **Fig. 2** shows relationship between scCO_2 density and y_2 with the data of Cu(II) acetylacetonate (Cu(II)(acac)$_2$) and Cr(III) acetylacetonate (Cr(III)(acac)$_3$) by Lagalante, et. al [7].

The solublility of Pt(II)(acac)$_2$ and Pd(II)(acac)$_2$ were correlated with a solution model proposed by Guigard et. al [6]. The model includes the solubility parameter that depends on density of scCO_2. The solubility (y_2) of the solute is given by following equation:

$$y_2 = \exp\left[\frac{-\Delta H_{fus}^{m}}{RT_m}\left(\frac{T_m}{T}-1\right)-\frac{v_2^L\phi_1{}^2}{RT}\left(\delta_2-\delta_1\right)^2\right] \quad (1)$$

where solubility parameter of solute, δ_2, is given as follows:

$$\delta_2 = a + b\rho_{scf}^{c} \quad (2)$$

where a, b and c are empirical peremeters, and they were generally optimized with the experimental data. Thus, the values of ΔH_{fus}^{m}, T_m and V_2^L are required for the correlation. In this study, the V_2^L was estimated by group contribution method by Fedors [9]. The ΔH_{fus}^{m} was evaluated by an assumption of a linear relation of the molecular weight for acetylacetonate

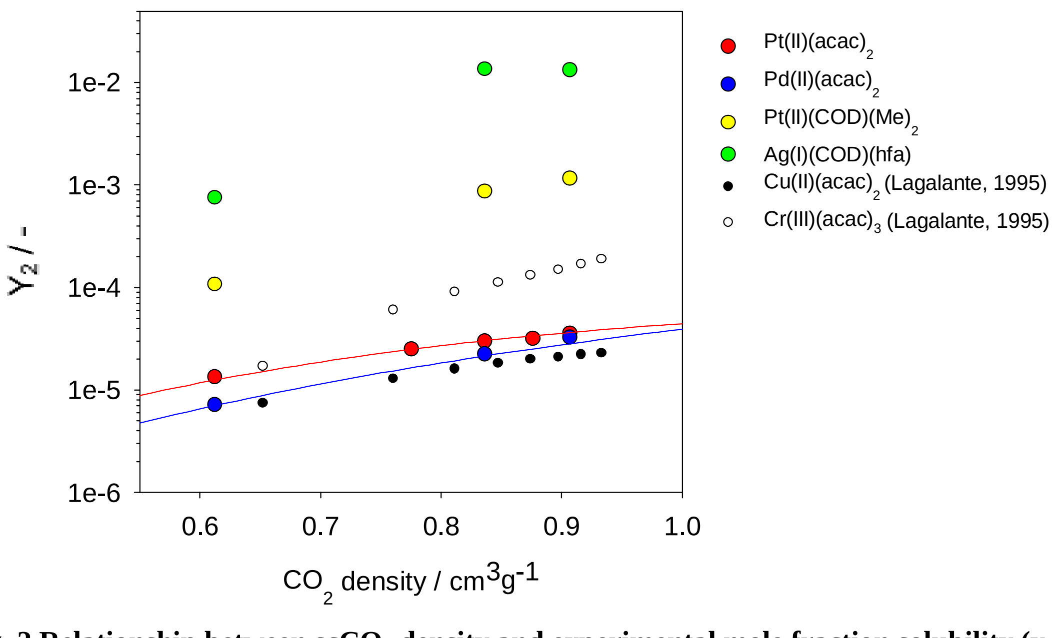

Fig. 2 Relationship between scCO_2 density and experimental mole fraction solubility (y_2) with the data of Cu(II) (acac)$_2$ and Cr(III) (acac)$_2$ in ref [7]. Solid lines show the correlation results of Pt(II)(acac)$_2$ and Pd(II)(acac)$_2$ according to ref [6]. V_2^L is estimated to be 204.2 cm^3/mol for both of the chelates. ΔH_{fus}^{m} and T_m were assumed to be 21240 J/ mol and 522 K for Pt(II)(acac)$_2$, and to be 32000 J/ mol and 512 K for Pd(II)(acac)$_2$, respectively. The fitting parameters a, b, and c were calculated to 13.959, 12.874 and 1.2701 for Pt(II)(acac)$_2$ and 13.406, 12.401 and 1.2318 for Pd(II)(acac)$_2$, respectively.

chelates [7, 10]. The value of T_m for Pt(II)(acac)$_2$ reported at 522 K [11] was used, and that of Pd(II)(acac)$_2$ was determined by thermal measurement. The parameters a, b and c were optimized to minimize the errors between calculated and experimental y_2 values. The calculation results were shown in **Fig.2** with solid lines. The experimental data were well correlated with the solution model. However, the validity of the parameters should be reconsidered. Thermal measurement to estimate these parameters of the solute are under investigation.

CONCLUSIONS

Solubility of noble-metal chelates used in material synthesis to scCO_2 was measured at 313 K and from 9.6 to 29.4 MPa using flow-type apparatus. The mole fraction solubility (y_2)of Pt(II)(acac)$_2$ and Pd(II)(acac)$_2$ was determined to be the order of 10^{-5}, which is similar to the other acetylacetonato chelates of divalent and trivalent metal. The y_2 of Pt(COD)(Me)$_2$ and of Ag(COD)(Hfa) was observed to be very high, which is in order of 10^{-4} and 10^{-3}, respectively.

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NOMENCLATURE

a, b, c	: parameters for the power fit (eq. 2)	
ΔH_{fus}^{m}	: enthalpy of fusion of fusion	(J*mol^{-1})
R	: Gas constant	(8.314 J mo^{l-1} K^{-1})
T	: Temperature	(K)
T_m	: Melting point of solute	(K)
V_2^L	: Molar volume of solute	(cm^3/mol)
y_2	: Solubility of solute	(mol fraction)
δ_1	: Solubility Parameters of scCO_2	(MPa$^{1/2}$)
δ_2	: Solubility Parameters of solute	(MPa$^{1/2}$)
Φ_1	: Ideal volume fraction of scCO_2	
ρ_{scf}^{c}	: density of scCO_2	(g cm^{-3})

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