Enhanced Extraction of Tris(pentane-2,4-dionato)cobalt(III) in Supercritical Carbon Dioxide/Water Systems by Association with Fluorinated Phenols

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The distribution behavior of tris(pentane-2,4-dionato)cobalt(III) [Co(acac)3] between supercritical carbon dioxide (SC-CO2) and water was investigated in the absence and presence of fluorine- and trifluoromethyl-substituted phenols (PhOH). The distribution of Co(acac)3 into SC-CO2 was enhanced by adding fluorine- and trifluoromethyl-substituted PhOH because of the formation of Co(acac)3·PhOH association complexes via hydrogen bonding. The Co(acac)3·PhOH association constant in the biphasic SC-CO2/water system was determined from the relationship between the distribution enhancement and the PhOH concentration in the supercritical medium. Lower association constants were obtained in the biphasic SC-CO2/water system compared with those in the single-phase SC-CO2 system, and this was ascribed to hydrogen bonding inhibition by H2O molecules dissolved in SC-CO2. Finally, the thermodynamic parameters and the number of CO2 molecules released upon the association of Co(acac)3 and 3,5-bis(trifluoromethyl)phenol were calculated by using data on the formation constant as a function of pressure and temperature.

1. Introduction

Supercritical carbon dioxide (SC-CO2) extraction has been applied industrially in the extraction of some organic compounds such as caffeine, nicotine, and cholesterol [1]. Many studies have dealt with the SC-CO2 extraction of metal ions with chelating agents from both solid and liquid matrixes [2-4]. However, the SC-CO2 extraction of metal ions with chelating agents typically suffers from low solubility of the chelate complexes in the supercritical medium compared with conventional organic solvent extraction, which decisively hinders its industrial application. With the aim to increase the solubility of the metal complexes in SC-CO2, a number of approaches have been investigated. In particular, the addition of a modifier (e.g., methanol, ethanol, and acetone) represents an effective method [5-9].

We recently reported a significant solubility enhancement of coordinatively saturated chelates of chromium(III) and cobalt(III) in SC-CO2 upon the addition of fluorine-containing alcohols and phenols (PhOH) as modifiers [10-12]. This solubility enhancement effect was ascribed to the formation of association complexes with the metal complexes via hydrogen bonding in SC-CO2, as revealed by Fourier transform infrared spectroscopy (FT-IR). In addition, the effects of the structure and the physical properties of the fluorine-containing PhOH on the formation of the association complex were elucidated. This modifier effect of fluorine-containing alcohols and PhOH thus resulted in a very useful method to
overcome the low solubility of metal complexes in SC-CO₂. The distribution enhancement of coordinatively saturated chelates with halogen-containing PhOH as hydrogen donors has been extensively reported in liquid–liquid extraction systems [13-20]. Thus, we anticipate that the association between coordinatively saturated chelates and PhOH via hydrogen bonding can be applied to enhance the distribution of coordinately saturated chelates from the aqueous phase to SC-CO₂ during liquid–liquid extraction.

In this study, we investigate the effects of several fluorine- and trifluoromethyl-substituted PhOH on the distribution enhancement of the coordinately saturated chelate tris(pentane-2,4-dionato)cobalt(III) [Co(acac)₃] in the biphasic SC-CO₂/water system. The association between Co(acac)₃ and PhOH in SC-CO₂ while varying pressure and temperature is also described in detail at equilibrium conditions. The equilibrium constants obtained for the biphasic SC-CO₂/water system are compared with those of the single-phase SC-CO₂ system.

2. Experimental

2.1 Reagents

Co(acac)₃ (>95%, Aldrich) was recrystallized from toluene and hexane and subsequently vacuum dried at 373 K for 3 h. 3,5-Bis(trifluoromethyl)phenol (BTMP; >96%, Tokyo Chemical Industry CO., Ltd.), 2-(trifluoromethyl)phenol (2-TFMP; >95%, Tokyo Chemical Industry CO., Ltd.), 3-(trifluoromethyl)phenol (3-TFMP; >98%, Tokyo Chemical Industry CO., Ltd.), 4-(trifluoromethyl)phenol (4-TFMP; 97%, Aldrich), 3,5-difluorophenol (3,5-DFP; >97%, Tokyo Chemical Industry CO., Ltd.), and 2,3,4,5,6-pentafluorophenol (PFP; 99%, Aldrich) were used as received. Liquid CO₂ (99.99%) was purchased from Taiyo Nissan Co. Ltd. Double-distilled water was further purified using a Milli-Q system (Millipore). The rest of the chemicals used were of analytical reagent grade and used without further purification.

2.2 Apparatus

The apparatus for measuring the distribution ratio of Co(acac)₃ in the SC-CO₂/water system is shown schematically in Figure 1. The system contained a syringe pump (Model 100DX, Isco), a pump controller (Series D, Isco), a stainless-steel optical cell (Jasco), two UV–Vis spectrophotometers (USB2000, Ocean Optics), a stainless-steel mixing cell (cylinder, 10 cm³ inner volume), and an arc lamp light source (Apex Source Arc 150W XE OF, Newport). The stainless-steel optical cell (inner volume 3.08 cm³; path length: 0.98 cm) contained two pairs of sapphire windows (diameter: 10 mm; thick: 6 mm), and a water jacket. The temperature of the cell was controlled by using a water jacket provided with a thermostated water circulator and monitored with a digital temperature indicator (Fenwal). The mixing cell was placed in a thermostated water bath. The pressure inside the cell was monitored using a digital pressure gauge (TDC-CSE, Toyo Sokki).

2.3 SC-CO₂/water distribution measurements

A known quantity of PhOH was introduced into the mixing cell after which compressed CO₂ (10–22 MPa) was added by the syringe pump and stirred with a magnetic stirrer for 1 h. An aqueous solution (1.54 cm³) containing 8.0 × 10⁻⁴ mol dm⁻³ of Co(acac)₃ was introduced into the optical cell. The temperature of the optical cell was varied from 318 to 338 K. The SC-CO₂–PhOH mixture was introduced into the optical cell by opening the valve located between the mixing cell and the optical cell. After pressure stabilization in
the optical cell, the valve was closed. The solutions in the optical cell were stirred with a magnetic stirrer for 3 h and subsequently settled for 10 min. The absorption spectra of the Co(acac)$_3$ in both the SC-CO$_2$ and the aqueous phases were measured by the UV–Vis spectrophotometers. The initial PhOH concentration in the SC-CO$_2$ phase was calculated by dividing the amount of PhOH by the sum of the volume of the mixing cell and one-half of the volume of the optical cell. The pH and ionic strength in the aqueous phase were maintained at 2.4 and 0.1 mol dm$^{-3}$, respectively, by using (H$^+$, Na$^+$)ClO$_4$.

The distribution constants of the PhOH between the SC-CO$_2$ and the water phases were also measured in the absence of Co(acac)$_3$ in a similar way.

### 3. Results and Discussion

#### 3.1 Effect of the PhOH structure on the distribution enhancement of Co(acac)$_3$ into SC-CO$_2$

The effect of the PhOH structure on the distribution of Co(acac)$_3$ in the SC-CO$_2$/water system was investigated by using six types of PhOH. The acid dissociation constants at 298 K ($K_a$) and the distribution constants between SC-CO$_2$ and water at 318 K and 20 MPa ($K_{D,PhOH}$) for the PhOHs used are listed in Table 1 [19, 21, 22]. Figures 2a and b show the absorption spectra of Co(acac)$_3$ at various BTMP concentrations in both the SC-CO$_2$ and aqueous phases, respectively. The absorption band (maximum absorbance at ca. 596 nm, which was assigned to the $^1T_{1g} \leftarrow ^1A_{1g}$ transition [23]) did not shift in the presence of PhOH. The

<table>
<thead>
<tr>
<th>PhOH</th>
<th>$K_a$</th>
<th>$K_{D,PhOH}$</th>
</tr>
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<tbody>
<tr>
<td>3,5-DFP</td>
<td>8.66$^a$</td>
<td>$-$0.04</td>
</tr>
<tr>
<td>PFP</td>
<td>5.53$^a$</td>
<td>0.33</td>
</tr>
<tr>
<td>2-TFMP</td>
<td>8.25$^b$</td>
<td>0.55</td>
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<tr>
<td>3-TFMP</td>
<td>8.95$^b$</td>
<td>0.62</td>
</tr>
<tr>
<td>4-TFMP</td>
<td>8.68$^b$</td>
<td>0.53</td>
</tr>
<tr>
<td>BTMP</td>
<td>7.65$^c$</td>
<td>1.87</td>
</tr>
</tbody>
</table>

a) Ref. 21, b) Ref. 22, c) Ref. 19

![Schematic drawing of the apparatus used to measure the distribution of Co(acac)$_3$ between SC-CO$_2$ and water.](image)
absorbance of Co(acac)$_3$ in SC-CO$_2$ increased with the BTMP concentration at the expense of its absorbance in the aqueous phase, thereby clearly revealing a distribution enhancement of Co(acac)$_3$ into SC-CO$_2$ by BTMP by the formation of the association complex Co(acac)$_3$·BTMP via hydrogen bonding. Similar distribution enhancements were observed for all of the PhOHs used.

When Co(acac)$_3$ associates with PhOH in SC-CO$_2$, the apparent distribution ratio of the Co(acac)$_3$ in the presence of PhOH can be expressed as

$$D = \frac{[\text{Co(acac)}_3]_{CO_2} + \sum [\text{CoL}_n \cdot n\text{PhOH}]_{CO_2}}{[\text{Co(acac)}_3]_{aq}}$$

where $D$ and $D_0$ are the distribution ratio of Co(acac)$_3$ in the presence and absence of PhOH, respectively. The subscripts CO$_2$ and aq refer to the SC-CO$_2$ and aqueous phases, respectively, while $\beta_n$ is the formation constant of the association complex in the SC-CO$_2$ phase as represented by the following equilibria:

$$\text{Co(acac)}_3 \cdot CO_2 + n\text{PhOH} \leftrightarrow \text{CoL}_n \cdot n\text{PhOH} \cdot CO_2$$

$$\beta_n = \frac{[\text{Co(acac)}_3 \cdot n\text{PhOH}]_{CO_2}}{[\text{Co(acac)}_3]_{CO_2} \cdot [\text{PhOH}]_{CO_2}^n}$$

Figure 3 shows log-log plots of the relative increase in the distribution ratio ($D/D_0$) of Co(acac)$_3$ as a function of the PhOH concentration in the SC-CO$_2$ phase for the different PhOHs under study. The corresponding PhOH concentrations in the SC-CO$_2$ phase were calculated using the $K_{D,PhOH}$ values listed in Table 1. The plots in Figure 3 were used to calculate the formation constants ($\beta_n$) by applying a nonlinear least-squares method (Equation 1). The slope values were lower than one in the experimental concentration region for all the PhOHs under study. Figure 4 shows the relationship between $\beta_n$ and $K_a$ for the corresponding PhOHs. For PhOHs with no fluorine or trifluoromethyl group at the ortho position, the $\beta_n$ logarithmic values decreased linearly with $pK_a$. This contrasts with the plots corresponding to ortho fluorine- or trifluoromethyl-substituted PFP and 2-TFMP, which were below this straight line. This result may be produced by two factors. One is the steric hindrance of the fluorine or trifluoromethyl groups at the ortho position. The other is a weakening of the hydrogen-bond donor ability for these phenols due to intramolecular hydrogen bonding between the hydroxyl group and the fluorine or trifluoromethyl substituent in the ortho position. It has been reported that in nonpolar solvents, intermolecular hydrogen bonding occurs in phenols bearing fluorine or trifluoromethyl substituents in the ortho position [24, 25].

The formation constants obtained in the biphasic SC-CO$_2$/water system were compared with those obtained previously in the single-phase SC-CO$_2$ system [12]. Figure 5 shows the dependence of the $\beta_n$ logarithmic values for Co(acac)$_3$·BTMP in both the single-phase and biphasic systems on the pressure ($P$) at 318 K. The $\beta_n$ values in the biphasic system were lower than those in the single-phase system. Similar results were obtained at different temperatures (328 K and 338 K). Figure 6 shows the logarithmic values...
Figure 2. Absorption spectra of Co(acac)$_3$ at various BTMP concentrations in the SC-CO$_2$ and aqueous phases at 20 MPa and 318 K. The initial Co(acac)$_3$ concentration in the aqueous phase was $8.0 \times 10^{-4}$ mol dm$^{-3}$.

Figure 3. Enhancement of the distribution ratio of Co(acac)$_3$ as a function of the PhOH concentration in SC-CO$_2$ at 20 MPa and 318 K.

Figure 4. Relationship between the formation constant ($\beta_1$) and the acid dissociation constant ($K_a$) for the PhOH herein studied.

Figure 5. Dependency of the formation constant ($\beta_1$) for Co(acac)$_3$·BTMP on the CO$_2$ pressure at 318 K.
of $\beta_1$ for Co(acac)$_3$·PhOH in the single-phase SC-CO$_2$ system versus the biphasic SC-CO$_2$/water system. A good linear relationship (correlation coefficient $|r| = 0.995$) was found as follows:

$$\log \beta_1 \text{(biphase)} = 1.07 \log \beta_1 \text{(single-phase)} - 0.33. \quad (4)$$

This reveals that the Co(acac)$_3$–PhOH interaction is similar in both the single-phase SC-CO$_2$ and the biphasic SC-CO$_2$/water systems. As shown by the intercept (-0.33), the $\beta_1$ values were somewhat lower in the biphasic SC-CO$_2$/water system compared with the single-phase SC-CO$_2$ system. Since the solubility of H$_2$O in SC-CO$_2$ is about 0.1 mol dm$^{-3}$ under the present experimental conditions [26], the dissolved H$_2$O may prevent PhOH from associating with Co(acac)$_3$ via hydrogen bonding in the biphasic SC-CO$_2$/water system. This can account for the lower $\beta_1$ values obtained for the biphasic SC-CO$_2$/water system.

### 3.2 Influence of the pressure and the temperature on the distribution ratio of Co(acac)$_3$ in the presence of BTMP

The influence of pressure and temperature on the distribution enhancement of Co(acac)$_3$ into SC-CO$_2$ by the generation of a Co(acac)$_3$·BTMP association complex via hydrogen bonding was studied in detail at equilibrium conditions. Thus, an analysis of the distribution of Co(acac)$_3$ in the absence and presence of BTMP was conducted at various pressures and temperatures.

First, the distribution ratio ($D_0$) of Co(acac)$_3$ between SC-CO$_2$ and water was investigated while varying pressure and temperature in the absence of BTMP. The dependence of the solubility of Co(acac)$_3$ in SC-CO$_2$ ($S_{CO2}$) on the CO$_2$ molarity can be analyzed using the empirical model proposed by Chrastil [27]:

$$\ln S_{CO2} = k \ln [CO2] - \Delta H_{vap,CO2}/RT + g_{s,CO2}, \quad (5)$$

where $k$ is the number of CO$_2$ molecules required to form the solvato-complex Co(acac)$_3$(CO$_2$)$_k$ in SC-CO$_2$, $\Delta H_{vap,CO2}$ is the sum of the vaporization and solvation enthalpies, and $g_{s,CO2}$ is the constant of the entropy.
term. On the other hand, the solubility of Co(acac)$_3$ in the aqueous solution ($S_{aq}$) can be defined using the enthalpy ($\Delta H_{s,aq}$) and the constant of the entropy term ($q_{s,aq}$) for the dissolution as follows:

$$\ln S_{aq} = \frac{\Delta H_{s,aq}}{RT} + q_{s,aq}. \quad (6)$$

$D_0$ can be expressed as the ratio of $S_{CO2}$ and $S_{aq}$ as follows:

$$D_0 = \frac{S_{CO2}}{S_{aq}}. \quad (7)$$

By neglecting the solubility change of Co(acac)$_3$ in the aqueous phase while increasing the SC-CO$_2$ pressure, the following equation can be derived from Equations (5), (6), and (7):

$$\ln D_0 = k\ln [CO2] - \frac{\Delta H_d}{RT} + q_d, \quad (8)$$

where $\Delta H_d = \Delta H_{s,CO2} - \Delta H_{s,aq}$ and $q_d = q_{s,CO2} - q_{s,aq}$. Therefore, the number of CO$_2$ molecules required to form the solvato-complex ($k$), the solvation enthalpy ($\Delta H_d$), and the constant of the entropy term ($q_d$) can be obtained from the dependence of $D_0$ on the molarity of CO$_2$ and the temperature (Figure 7). The molarity of CO$_2$ was calculated for each temperature and pressure using the freeware EOS-SCx ver. 0.2 [28], a program for determining the density and thermodynamic properties of water, methanol, and carbon dioxide using the equations of state. The $k$, $\Delta H_d$, and $q_d$ values were calculated according to Equation (8) using the least-squares method for the $\ln D_0$ vs. $\ln [CO2]$ and $1/T$ plots. These values were found to be $k = 5.44 \pm 0.13$, $\Delta H_d = 50.9 \pm 1.9$ kJ mol$^{-1}$, and $q_d = 2.28 \pm 0.65$. The $k$ value of the biphasic SC-CO$_2$/water system was close to that previously obtained in the single-phase SC-CO$_2$ system (5.44 ± 0.13 vs. 5.87 ± 0.11 [12]). This suggests that the solvato-complex formed in SC-CO$_2$ is virtually identical in both systems. Notably, the lines depicted using these parameters were in good agreement with the observed distribution data at all the temperatures under study (Figure 7). The distribution ratio of BTMP between SC-CO$_2$ and water ($D_{0,BTMP}$) was also investigated while varying pressure and temperature. Figure 8 shows the natural logarithmic plots of $D_{0,BTMP}$ as a function of the molarity of CO$_2$ at various temperatures. The number of CO$_2$ molecules
required to form the solvato-complex \( \text{BTMP}(\text{CO}_2)_l \) in the SC-CO\(_2\) phase \((l)\), the enthalpy \((\Delta H_{d,\text{BTMP}})\) and the constant of the entropy term \((q_{d,\text{BTMP}})\) for BTMP were calculated according to Equation (8) by replacing \(D_0\) and \(k\) by \(D_{0,\text{BTMP}}\) and \(l\), respectively, using the least-squares method for the ln \(D_{0,\text{BTMP}}\) vs. ln \([\text{CO}_2]\) and 1/\(T\) plots. The values for BTMP were found to be \(l = 4.02 \pm 0.09\), \(\Delta H_{d,\text{BTMP}} = 21.5 \pm 1.2 \text{ kJ mol}^{-1}\), and \(q_{d,\text{BTMP}} = -1.59 \pm 0.43\).

The distribution enhancement of \(\text{Co(acac)}_3\) between SC-CO\(_2\) and water upon the addition of BTMP was measured while varying pressure and temperature. The \(\beta_i\) values were then obtained from the log \((D/D_0)\) vs. log \([\text{BTMP}]_{\text{CO}_2}\) plots. Figure 9 shows the natural logarithmic plots for the obtained \(\beta_i\) values as a function of the \(\text{CO}_2\) molarity at various temperatures. The ln \(\beta_i\) values decreased linearly with ln \([\text{CO}_2]\) at constant temperature. This result implies that the \(\text{CO}_2\) molecules participated in the association reaction between \(\text{Co(acac)}_3\) and BTMP.

The equilibrium equation (2) was then redefined by considering the presence of solvato-complexes as follows:

\[
\begin{align*}
\text{Co(acac)}_3(\text{CO}_2)_k + \text{BTMP}(\text{CO}_2)_l & \rightleftharpoons \text{Co(acac)}_3 \cdot \text{BTMP}(\text{CO}_2)_m + (k + l - m)\text{CO}_2, \\
\end{align*}
\]

where \(m\) is the number of \(\text{CO}_2\) molecules required to form the solvato-complex \(\text{Co(acac)}_3 \cdot \text{BTMP}(\text{CO}_2)_m\). The formation constant after consideration of the presence of solvato-complexes, \(\beta_i'\), is then defined as follows:

\[
\beta_i' = \frac{[\text{Co(acac)}_3 \cdot \text{BTMP}(\text{CO}_2)_m] [\text{CO}_2]^{l(l-m)}}{[\text{Co(acac)}_3(\text{CO}_2)_k] [\text{BTMP}(\text{CO}_2)_l]},
\]

(10)

Therefore, \(\beta_i\) is represented using \(\beta_i'\) and \([\text{CO}_2]\) as

\[
\ln \beta_i = \ln \beta_i' - (k + l - m) \ln [\text{CO}_2].
\]

(11)

By including the thermodynamic parameters represented by the enthalpy change \((\Delta H_d)\) and the entropy term \((q_a)\) for \(\beta_i'\), the following equation can be obtained:

\[
\ln \beta_i = -(k + l - m) \ln [\text{CO}_2] - \Delta H_d/RT + q_a.
\]

(12)

The \(k + l - m\), \(\Delta H_d\), and \(q_a\) values were calculated according to Equation (9) using the least-squares method for the \(\ln \beta_i\) vs. ln \([\text{CO}_2]\) and 1/\(T\) plots. These values were found to be \(4.66 \pm 0.11\), \(-43.4 \pm 1.4 \text{ kJ mol}^{-1}\), and \(3.66 \pm 0.51\), respectively. The \(m\) value for \(\text{Co(acac)}_3 \cdot \text{BTMP}(\text{CO}_2)_m\) was determined \((4.80 \pm 0.19)\) from the previously obtained \(k\) and \(l\) values \((5.44 \pm 0.13\) and \(4.02 \pm 0.09\), respectively). The \(m\) value obtained in the biphasic SC-CO\(_2\)/water system was somewhat lower than the one obtained previously in the single-phase SC-CO\(_2\) system \((5.62 \pm 0.17\) [12]). The positive value for \(k + l - m\) indicates that \(\text{CO}_2\) molecules are released upon association of \(\text{Co(acac)}_3\) with BTMP in the SC-CO\(_2\) phase, thereby resulting in a lower formation constant at higher \(\text{CO}_2\) pressures. The large negative \(\Delta H_d\) value suggests the formation of a strongly hydrogen-bonded complex, and this result seems reasonable because hydrogen bonding is generally an exothermic reaction.
4. Conclusion

The effects of several fluorine- and trifluoromethyl-substituted PhOHs on the distribution ratio of Co(acac)$_3$ between SC-CO$_2$ and water were investigated using UV–Vis spectrophotometry. A large distribution enhancement of Co(acac)$_3$ was achieved by adding PhOH because of the formation of Co(acac)$_3$:PhOH association complexes via hydrogen bonding in the SC-CO$_2$ phase. The $\beta_1$ values for Co(acac)$_3$:PhOH were determined from the relationship between the distribution enhancement and the PhOH concentration in the SC-CO$_2$ phase. The $\beta_1$ values were somewhat lower in the biphasic SC-CO$_2$/water system compared with SC-CO$_2$ because of the inhibition of hydrogen bonding by the H$_2$O molecules dissolved in SC-CO$_2$. The thermodynamic parameters and the numbers of CO$_2$ molecules released upon association of Co(acac)$_3$ and BTMP in the biphasic SC-CO$_2$/water system were close to those obtained in the single-phase SC-CO$_2$ system. The results obtained in this study revealed that the association between coordinatively saturated chelates and PhOH via hydrogen bonding is useful to enhance the distribution of chelates from the aqueous to the SC-CO$_2$ phases. These results provide valuable information to improve the extraction properties of SC-CO$_2$ for metal chelates showing relatively low extractability characteristics.

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