

Remarkable Enhancement Effect of 2,2,2-Trifluoroethanol on the Solubility of Tris(pentane-2,4-dionato)chromium(III) in Supercritical Carbon Dioxide by Outer-Sphere Complexation through Hydrogen Bonding

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The solubility of tris(pentane-2,4-dionato)chromium(III) ($Cr(acac)_3$) in supercritical carbon dioxide ($SC\text{-}CO_2$) with and without modifiers was investigated by UV–vis spectrophotometry. The influence of some polar and nonpolar modifiers, such as methanol, ethanol, 2,2,2-trifluoroethanol (TFE), acetone, chloroform, and benzene, was studied by changing the temperature, pressure, and concentration of the modifiers. Alcohols, particularly TFE, demonstrated a large solubility enhancement of $Cr(acac)_3$ among these modifiers. In contrast, acetone having a relatively larger polarity gave a lower enhancement effect than chloroform and benzene. The measurement of the IR absorption spectra of TFE in the presence of $Cr(acac)_3$ in $SC\text{-}CO_2$ suggested that a drastic solubility enhancement of $Cr(acac)_3$ upon the addition of TFE could be ascribed to the formation of the stable $Cr(acac)_3$–TFE complex through hydrogen bonding. The association constants of $Cr(acac)_3$ with TFE in $SC\text{-}CO_2$ could be determined from the relationship of the solubility enhancement against the TFE concentration.

Supercritical fluids have attracted much attention as alterable reaction media to organic solvents, and have been widely used in various fields, such as analytical, organic, biological, and industrial chemistries.[1–3] They allow us to change the physical properties, such as the density, dielectric constant, diffusion coefficient, and refractive index, of the solvent media with relatively small changes in the pressure and temperature. Among the supercritical fluids, a supercritical carbon dioxide fluid ($SC\text{-}CO_2$) has been widely used as analytical media for extraction and chromatography, because it is non-toxic, cheap, and environmentally acceptable, and has a relatively mild critical point ($T_c = 304.1$ K, $P_c = 7.38$ MPa).

The supercritical fluid extraction (SFE) of metal complexes from solid and aqueous media into $SC\text{-}CO_2$ has become a feasible alternative separation method to solvent extraction.[4–10] Previously, we also reported on the SFE of gallium(III) and palladium(II) with 2-methyl-8-quinolinol derivatives.[11–15] However, the solubility of a solute in $SC\text{-}CO_2$ is generally much lower than that in conventional organic solvents. Therefore, modifiers, such as methanol and acetonitrile, have been employed for increasing the solubility of metal chelates in $SC\text{-}CO_2$.[16,17] Some authors have investigated the solubilities of metal chelates in $SC\text{-}CO_2$ modified with organic solvents.[18,19] However, there have been few studies on the interaction between the metal chelate and the modifier in $SC\text{-}CO_2$.[20] Therefore, an understanding about it is still not enough, regardless of the fundamental significance for SFE.

Recently, a synergistic effect of tributyl phosphate (TBP) on SFE of tris(β-diketonato)lanthanoid(III) has been reported.[21,22] It has been explained by the formation of an adduct between the coordinately unsaturated tris(β-diketonato)lanthanoid(III) and TBP in the $SC\text{-}CO_2$ phase. On the other hand, one of the present authors demonstrated a novel synergistic extraction system for coordinately saturated chelates with chlorinated phenols as the synergist in a liquid–liquid system.[23–27] This synergism can be explained by the formation of outer-sphere complexes through hydrogen bonding between metal chelates and chlorinated phenols in the organic phase. Such an interaction between metal chelate and the hydrogen-bond donor is expected to be applicable to improving of the low solubility of the metal chelate in $SC\text{-}CO_2$.

β-Diketone is one of the most popular organic chelating agents. Tris(pentane-2,4-dionato)chromium(III) ($Cr(acac)_3$) is selected as a sample, since it is coordinately saturated, stable, and a substitution-inert complex. In the synergistic extraction system, the formation of outer-sphere complexes through hydrogen bonding between $Cr(acac)_3$ and chlorinated phenols has already been reported.[28] 2,2,2-Trifluoroethanol (TFE) is selected as a modifier of a hydrogen-bond donor, since its structure is similar to those of methanol and ethanol used as modifiers.

In this study, we investigated the effect of various organic modifiers on the solubility of $Cr(acac)_3$ in $SC\text{-}CO_2$ by UV–vis spectrophotometry. The FT-IR absorption spectra of TFE in the both absence and presence of $Cr(acac)_3$ in $SC\text{-}CO_2$ were measured to reveal a hydrogen bonding between $Cr(acac)_3$ and TFE in $SC\text{-}CO_2$. The association constants of $Cr(acac)_3$ with TFE in $SC\text{-}CO_2$ at various pressures and temperatures were also determined by a solubility-equilibrium analysis.

Experimental

Reagents. $Cr(acac)_3$ was purchased from Dojindo Lab. (Kumamoto, Japan) and recrystallized from a benzene and hexane mixture. TFE (>95%, DAIKIN), methanol, ethanol, acetone,

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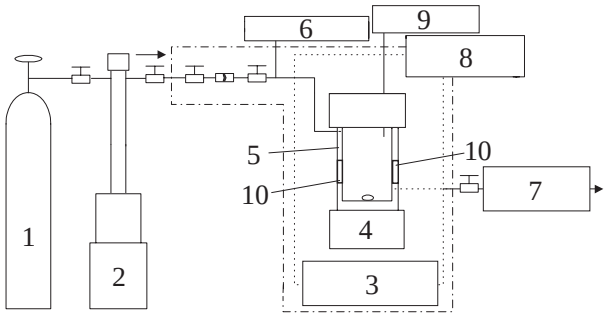

Fig. 1. Schematic drawing of the apparatus for measuring the solubility of $Cr(acac)_3$ in supercritical CO_2. 1; Liquid CO_2 cylinder, 2; syringe pump, 3; UV–vis spectrophotometer, 4; magnetic stirrer, 5; stainless optical cell, 6; pressure gauge, 7; back pressure regulator, 8; thermostated parts with a water circular, 9; digital temperature indicator, and 10; sapphire windows.

chloroform, and benzene (HPLC grade, Wako) were used as obtained. Liquid CO_2 (99.99%, Nippon Sanso) and carbon tetrachloride (HPLC grade, Wako) were also used.

Solubility Measurement. The apparatus for measuring the solubility of $Cr(acac)_3$ in SC-CO_2 is illustrated in Fig. 1. A stainless-steel cell (Jasco) of 2.35 cm^3 inner volume and 11 mm path length, with a pair of sapphire windows (10 mm in diameter and 6 mm thick), was installed in a UV–vis spectrophotometer (Jasco, V-550). The temperature of the cell was controlled at 318–338 K using a water jacket with a thermostated water circulator and monitored with a digital temperature indicator (Fenwal). A large excess of $Cr(acac)_3$ (about 100 mg) and a known amount of modifier were placed into the cell; then, CO_2 compressed to 10.1–22.3 MPa by a syringe pump was introduced into the cell, and stirred with a magnetic stirrer for 60 min. After standing for 5 min, the absorption spectrum of $Cr(acac)_3$ dissolved in SC-CO_2 was measured. The absorbance was confirmed to be constant after prolonged stirring.

Molar Absorptivity Measurement. The molar absorptivities of $Cr(acac)_3$ in SC-CO_2 with and without 0.26 mol dm^{-3} TFE at 20.3 MPa and 318 K were measured in the same manner as described above, except for the addition of a small, but known, amount of $Cr(acac)_3$. An aliquot of acetone solution of $Cr(acac)_3$ was pipetted into the cell and heated to remove the acetone from the cell by evaporation. It was ascertained that all $Cr(acac)_3$ put into the cell was completely dissolved. The SC-CO_2 phase containing from 9.1×10^{-4} to 8.0×10^{-3} mol dm^{-3} of $Cr(acac)_3$ was finally obtained.

The molar absorptivities of $Cr(acac)_3$ in various organic solvents were also measured with a Jasco 560 spectrophotometer at 298 K.

IR Spectrum Measurement. The IR spectra of 0.020 mol dm^{-3} TFE and 0.040 mol dm^{-3} methanol in carbon tetrachloride in the presence or absence of 0.020–0.040 mol dm^{-3} $Cr(acac)_3$ were measured by a Fourier-transform IR spectrophotometer (Shimadzu, FTIR-8200A) at 298 K. A demountable cell with calcium fluoride windows was used, and the path length was adjusted to 1 mm.

The IR spectra of 0.100 mol dm^{-3} TFE in SC-CO_2 in the presence or absence of excess solid $Cr(acac)_3$ in the cell were also measured with a FT/IR-620 (Jasco). The inner volume and path length of the optical cell were 2.0 cm^3 and 5 mm, respectively.

Table 1. Molar Absorptivities of $Cr(acac)_3$ at 562 nm in Several Media

Solvent	ε/dm^3 mol^{-1} cm^{-1}
Supercritical CO_2[a)]	66 ± 1
Supercritical CO_2 containing 0.26 mol dm^{-3} TFE[a)]	65 ± 1
TFE[b)]	69.2 ± 1.4
Chloroform[b)]	69.1 ± 0.3
Benzene[b)]	70.7 ± 0.3

a) 318 K and 20.3 MPa. b) 273 K and 0.1 MPa.

The windows of the optical cell were made of ZnS. The temperature of the cell and the pressure of SC-CO_2 were kept constant at 318 K and 17 MPa, respectively. The IR spectra were measured at 4 cm^{-1} wavenumber resolution.

Results and Discussion

Determination of Molar Absorptivity of $Cr(acac)_3$ in SC-CO_2. Absorption spectra for the d–d transition of $Cr(acac)_3$ were measured in various organic solvents and modified and non-modified SC-CO_2 with 0.26 mol dm^{-3} TFE. The absorption band with a maximum absorbance at 562 nm, which is assigned to the $^4T_{2g} \leftarrow {}^4A_{2g}$ transition,[29] hardly shifted in all media. The molar absorptivites (ε_{562}) of $Cr(acac)_3$ at 562 nm in SC-CO_2 with and without 0.26 mol dm^{-3} TFE at 318 K and 20.3 MPa were determined, and are listed in Table 1 along with those in various organic solvents. These values are very close among all media. Therefore, the ε_{562} value obtained in non-modified SC-CO_2, 66 ± 1 dm^3 mol^{-1} cm^{-1}, was used to calculate the solubility of $Cr(acac)_3$ in SC-CO_2 containing different amounts of TFE and other modifiers.

Solubility in Pure SC-CO_2. The solubility, S_0 (g dm^{-3}), of $Cr(acac)_3$ in pure SC-CO_2 was measured at the various temperatures and pressures. Figure 2 shows national logarithmic plots of S_0 against the density of SC-CO_2, ρ (g dm^{-3}). The ρ value at a given temperature and pressure was calculated using the freeware EOS-SCx ver. 0.2,[30] which is a calculation program for the density and thermodynamic properties of water, methanol, and carbon dioxide by the equations-of-state. The plot at a constant temperature increases almost linearly, and the line is shifted upward with an increase in the temperature. The experimental solubility data of a metal complex was generally correlated using the empirical model proposed by Chrastil:[31]

$$\ln S_0 = k \ln \rho + a/T + b, \quad (1)$$

where k is the solvation number of the solute, $a = \Delta H/R$ (where ΔH is the sum of the enthalpies of vaporization and solvation), and b is a constant. According to Eq. 1, the values of k, a, and b were calculated by the least-squares method on plots of $\ln S_0$ in Fig. 2 as a function of $\ln \rho$ and $1/T$. The calculated values were $k = 4.3 \pm 0.2$, $a = (-4.1 \pm 0.4) \times 10^3$ K, and $b = -16 \pm 1$. The value of ΔH was calculated as -34 kJ mol^{-1} from the value of a. The solvation number obtained lay within 3–7, reviewed by Smart and co-workers for β-diketonatometals.[32] The calculated lines depicted using these parameters well represented the observed solubility data at all temperatures (see: Fig. 2).

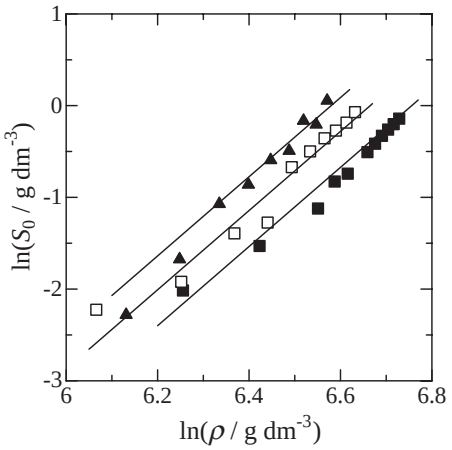

Fig. 2. Solubility isomers for Cr(acac)$_3$ in pure supercritical CO$_2$ at 318 K (●), 328 K (□), and 338 K (■). Lines represent correlation by Eq. 1.

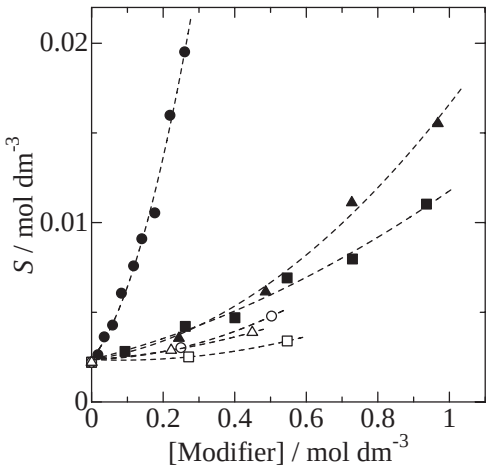

Fig. 3. Dependency of the solubility of Cr(acac)$_3$ in supercritical CO$_2$ on the concentration of modifier at 318 K and 20.3 MPa. TFE (●), methanol (▲), ethanol (■), chloroform (○), benzene (△), and acetone (□).

Solubility of Cr(acac)$_3$ in SC-CO$_2$ Containing Organic Modifiers. Figure 3 shows plots of the solubility, S (g dm^{-3}), in the modified SC-CO$_2$ against the concentration of the modifier at 318 K and 20.3 MPa. Methanol, ethanol, TFE, acetone, chloroform, and benzene were used as modifiers. The relative permittivities (ε_r) among these modifiers become larger in the following order: benzene ($\varepsilon_r = 2.28$) < chloroform (4.81) < acetone (20.7) < ethanol (24.6) < TFE (26.5) < methanol (32.7). The solubility increased with the increase in the concentration of the modifier. Alcohols, particularly TFE, demonstrated the largest solubility enhancement of Cr(acac)$_3$ among the modifiers used; TFE drastically improved the solubility of Cr(acac)$_3$ in SC-CO$_2$ much more than methanol, which has often been used as a modifier. In contrast, acetone, having a large polarity ($\varepsilon_r = 20.7$), gave a lower enhancement effect than chloroform and benzene, implying that the polarity of a modifier hardly contributed to the solubility enhancement in this system. In other words, most of the enhancement effect should be ascribed to the solute–solute interaction between Cr(acac)$_3$ and the modifier molecules. Similar results were also observed under different conditions of the temperature and pressure. The detailed study about TFE which showed a remarkable solubility enhancement effect was subsequently carried out.

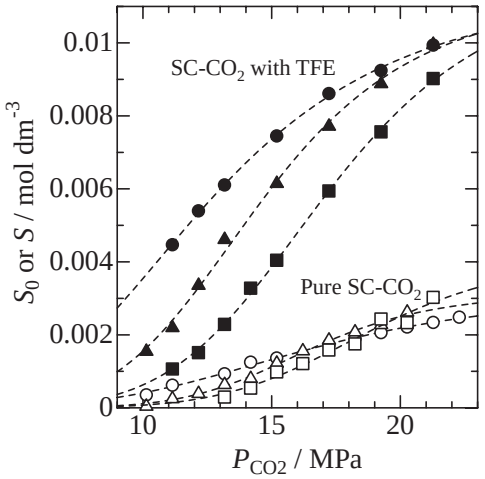

Fig. 4. Solubility dependency of Cr(acac)$_3$ in supercritical CO$_2$ with and without 0.14 mol dm^{-3} TFE on the pressure of CO$_2$. 318 K (○, ●), 328 K (△, ▲), and 338 K (□, ■).

Figure 4 shows the pressure dependency of the solubility of Cr(acac)$_3$ in SC-CO$_2$ in the absence and presence of 0.14 mol dm^{-3} TFE at various temperatures. The solubility enhancement factor (S/S_0) at a constant pressure became larger in the following order: 338 K < 328 K < 318 K. This suggested that the interaction between Cr(acac)$_3$ and TFE became weaker because of the increase in temperature.

IR Spectroscopy. In order to reveal the interaction between Cr(acac)$_3$ and the modifier in SC-CO$_2$, the IR absorption spectra of TFE and methanol in carbon tetrachloride and SC-CO$_2$ were measured. As shown in Fig. 5A, the sharp absorption bands at 3620 and 3645 cm^{-1} observed in carbon tetrachloride were assigned to the O–H stretching vibration of free TFE and methanol, respectively.[33] Upon the addition of Cr(acac)$_3$, these sharp bands decreased and new broad bands appeared in a lower wavenumber region for both alcohol systems. These spectral changes are ascribed to the hydrogen bonding formation between Cr(acac)$_3$ and those alcohols.[33] The decrease in the absorbance and the shift of the wavenumber of the O–H stretching vibration for TFE were larger than those for methanol, implying that TFE forms stronger hydrogen bonding than methanol.[34] This is ascribed to the difference in the proton-donating property of those alcohols. TFE with a strong electron-withdrawing group of trifluoromethyl is a much stronger proton-donor than methanol (TFE, pK_a 12.4; methanol, pK_a 15.3).[35] Figure 5B shows the IR absorption spectra of TFE in the absence or presence of Cr(acac)$_3$ in SC-CO$_2$. The absorption spectra from 3780 to 3540 cm^{-1} could not be measured due to the strong absorption of CO$_2$. The IR spectrum of TFE in the absence of Cr(acac)$_3$ had no absorption band around 3450 cm^{-1}. On the other hand, a broad band around 3450 cm^{-1} was observed in the SC-CO$_2$ system containing both TEF and Cr(acac)$_3$. This broad band was not observed in the SC-CO$_2$ system containing only Cr(acac)$_3$ (spectrum not shown). These results gave a clear evidence of

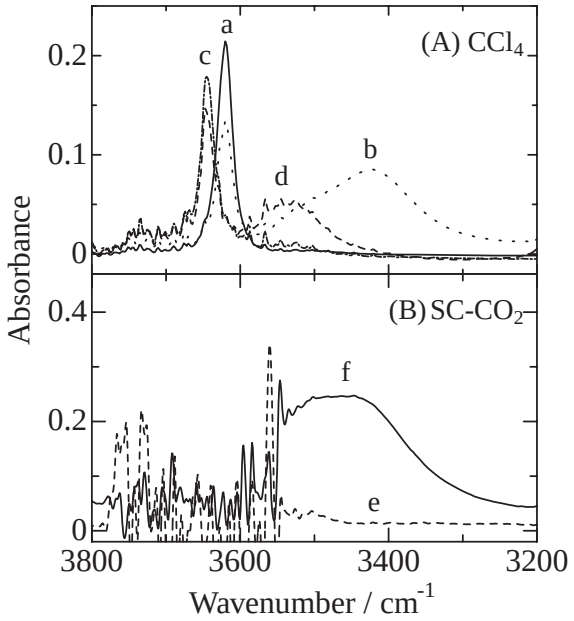

Fig. 5. FT-IR absorption spectra of TFE and methanol in the absence and presence of $Cr(acac)_3$ in carbon tetrachloride (A) and supercritical CO_2 (B). a; 0.020 mol dm^{-3} TFE, b; 0.020 mol dm^{-3} TFE + 0.020 mol dm^{-3} $Cr(acac)_3$, c; 0.040 mol dm^{-3} methanol, d; 0.040 mol dm^{-3} methanol + 0.040 mol dm^{-3} $Cr(acac)_3$, e; 0.100 mol dm^{-3} TFE, and f; 0.100 mol dm^{-3} TFE + excess solid $Cr(acac)_3$. CCl_4 system: optical length; 1 mm, temperature; 298 K, pressure; 0.1 MPa. Supercritical CO_2 system: optical length; 5 mm, temperature; 318 K, pressure; 17 MPa.

the hydrogen-bond formation between TFE and $Cr(acac)_3$ in SC-CO_2. Previously, we revealed that the stronger hydrogen-bond between β-diketonatometal complexes and phenols was formed in aprotic solvents, such as heptane and carbon tetrachloride, than in protogenic solvents, such as chloroform.[26] Because of a nonpolar and aprotic solvent of SC-CO_2, $Cr(acac)_3$ forms hydrogen bonds with alcohol molecules in SC-CO_2 to cause an increase in the solubility. Therefore, a drastic solubility enhancement of $Cr(acac)_3$ in SC-CO_2 upon the addition of TFE is ascribed to the formation of a stable association complex of $Cr(acac)_3$ with TFE through hydrogen bonding.

Determination of Association Constants between $Cr(acac)_3$ and Alcohols. When $Cr(acac)_3$ associates with alcohols (ROH) as the modifier in SC-CO_2, the apparent solubility of $Cr(acac)_3$ in the presence of ROH can be expressed as

$$S = [Cr(acac)_3] + \Sigma[Cr(acac)_3 \cdot n\mathrm{ROH}] = [Cr(acac)_3](1 + \Sigma\beta_n[\mathrm{ROH}]^n), \quad (2)$$

where β_n is the association constant in SC-CO_2 corresponding to the following equilibrium:

$$Cr(acac)_3 + n\mathrm{ROH} \rightleftharpoons Cr(acac)_3 \cdot n\mathrm{ROH}, \quad (3)$$

$$\beta_n = \frac{[Cr(acac)_3 \cdot n\mathrm{ROH}]}{[Cr(acac)_3][\mathrm{ROH}]^n}. \quad (4)$$

The concentration of free $Cr(acac)_3$ should always be constant,

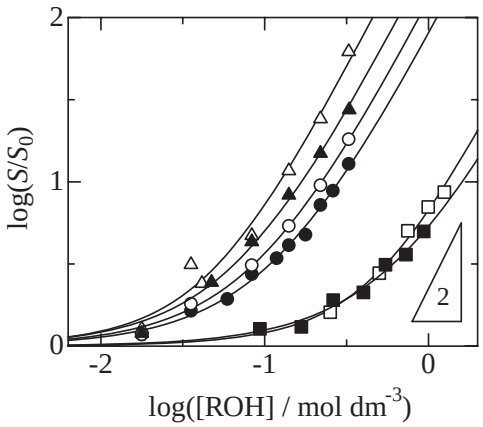

Fig. 6. Enhancement of the solubility ratio of $Cr(acac)_3$ as a function of the concentration of TFE, methanol and ethanol in supercritical CO_2 for several pressures. TFE: 10.1 MPa (△), 12.2 MPa (▲), 15.2 MPa (○), 20.3 MPa (●); methanol: 20.3 MPa (□); ethanol: 20.3 MPa (■).

because an excess of $Cr(acac)_3$ exists in the cell. Therefore, the following equation can be derived:

$$S/S_0 = 1 + \Sigma\beta_n[\mathrm{ROH}]^n. \quad (5)$$

A term of S/S_0 shows the solubility enhancement of $Cr(acac)_3$ upon the addition of ROH, and is directly related to the association constant in SC-CO_2 by Eq. 5.

Figure 6 shows plots of $\log(S/S_0)$ vs log[ROH] at 318 K. The slope of the plots became larger than 1 at higher ROH concentrations. This suggests that $Cr(acac)_3$ forms two types of outer-sphere complexes, i.e., $Cr(acac)_3 \cdot$ROH and $Cr(acac)_3 \cdot 2$ROH, with TFE, methanol, or ethanol in SC-CO_2. Probably, the hydrogen bond between $Cr(acac)_3$ and ROH is formed through the coordinated oxygen atoms on an open octahedral face perpendicular to the C_3 axis of $Cr(acac)_3$. Because $Cr(acac)_3$ has two open octahedral faces,[36] two molecules of the alcohol occupy either of the two faces, respectively. Each β_n value was calculated by a non-linear least-squares method based on Eq. 5 for the plots of $\log(S/S_0)$ vs log[ROH], and listed in Table 2. The values of β_1 and β_2 for TFE are higher than those for methanol and ethanol, because the acidity of hydroxyl hydrogen atom for TFE is higher than that for methanol, as described above. As the pressure is lower, the values of the association constants become higher. Because the density of CO_2 decreases as the pressure becomes lower, the mole fraction of TFE increases. Therefore, $Cr(acac)_3$ tends to associate with TFE molecules in SC-CO_2 at lower pressure.

Figure 7 shows plots of $\log(S/S_0)$ vs log[ROH] at constant CO_2 density (696 g dm^{-3}) and various temperatures. The solubility enhancement became larger at a lower temperature. This result seems to be reasonable because hydrogen bonding is generally an exothermic reaction. These plots were also analyzed using Eq. 5, and the β_n values were obtained as listed in Table 2.

Conclusion

In this study, we found that TFE drastically improved the solubility of $Cr(acac)_3$ in SC-CO_2 much more than methanol and ethanol, which have generally been used as a modifier.

Table 2. Association Constants of Cr(acac)$_3$ with Alcohols (ROH) in Supercritical CO$_2$

ROH	P_{CO2}/MPa	ρ/g dm^{-3}	T/K	log β_1 [a)]	log β_2 [a)]
TFE	10.1	512	318	1.29 ± 0.20	2.64 ± 0.09
	12.1	664	318	1.30 ± 0.09	2.31 ± 0.06
	13.1	696	318	1.13 ± 0.06	2.20 ± 0.04
	15.2	747	318	1.19 ± 0.06	2.05 ± 0.05
	20.3	816	318	1.11 ± 0.05	1.82 ± 0.05
	16.6	696	328	1.05 ± 0.04	2.00 ± 0.03
	20.3	696	338	0.98 ± 0.07	1.78 ± 0.06
MeOH	20.3	816	318	0.22 ± 0.16	0.61 ± 0.05
EtOH	20.3	816	318	0.36 ± 0.08	0.31 ± 0.15

a) $\beta_n = [\mathrm{Cr(acac)_3 \cdot }n\mathrm{ROH}]/([\mathrm{Cr(acac)_3}][\mathrm{ROH}]^n)$.

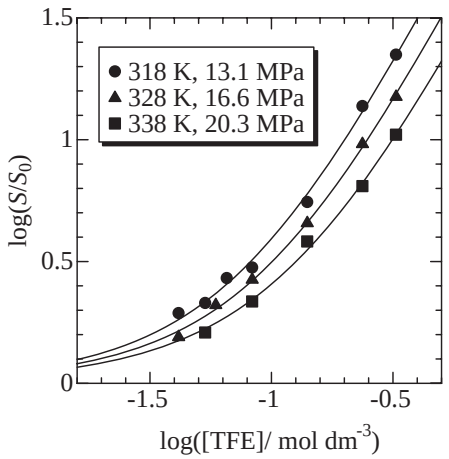

Fig. 7. Enhancement of the solubility ratio of Cr(acac)$_3$ as a function of the concentration of TFE in supercritical CO$_2$ at constant density (696 g dm^{-3}) and various temperatures.

In the present system, the solubility enhancement upon the addition of a modifier should be mainly ascribed to the solute–solute interaction between Cr(acac)$_3$ and the modifier molecules in SC-CO$_2$ and the effect of the polar modification of the SC-CO$_2$ phase was small. From IR measurements, the remarkable solubility enhancement effect of TFE can be ascribed to the formation of an association complexes of Cr(acac)$_3$ with TFE through hydrogen bonding in SC-CO$_2$. The hydrogen-bond of Cr(acac)$_3$ with TFE results in a further lowering of the polarity of Cr(acac)$_3$, because the basic site of Cr(acac)$_3$, i.e., three coordinating oxygen atoms on an open octahedral face, is blocked with TFE. The compositions of the association complexes formed in SC-CO$_2$ were ascertained to be Cr(acac)$_3$·TFE and Cr(acac)$_3$·2TFE based on a solubility equilibrium analysis, and the association constants of these complexes in SC-CO$_2$ at various pressures and temperatures were also determined. The modifier effect observed in the present study is promising to overcome the disadvantage of the lower solubility of a solute in SC-CO$_2$. Moreover, this method can be expected to provide a great enhancement for SFE of various organic compounds and metal chelates from solid and aqueous media, or to affect the retention behavior of metal chelates in supercritical fluid chromatography.

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