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Enhancement Effect of Pentafluorophenol on the Liquid-Liquid Partition of Tris(acetylacetonato) Complexes of Chromium(III) and Cobalt(III)

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The partition coefficient of tris(acetylacetonato)-chromium(III) and -cobalt(III) ($M(acac)_3$) between heptane and aqueous solutions was remarkably enhanced by the presence of pentafluorophenol (PFP). This effect was ascribed to the formation of the hydrogen-bonded association complexes, $M(acac)_3 \cdot PFP$ and $M(acac)_3 \cdot 2PFP$, in the organic phase, and the association constants were determined.

The liquid-liquid partition of neutral metal complexes is an important process governing the extractability in the solvent extraction of metal ions. A series of our studies on the partition coefficient have demonstrated that it is primarily governed by the formation energy of a cavity of suitable size to accommodate the solute in both phases.1-4) But in the case of metal acetylacetonates (2,4-pentanedionates), even coordinatively saturated complexes such as tris(acetylacetonato)-chromium(III) ($Cr(acac)_3$) and -cobalt(III) ($Co(acac)_3$), the partition coefficient is much lower than that calculated from the cavity formation energy.4) It may be due to the specific interaction such as hydrogen bonding between the metal complexes and water molecules in the aqueous phase. Thus the partition coefficient is considered to be strongly influenced by the specific solute-solvent interaction, but there have been no reliable information on the role of hydrogen bonding in the partition of metal complexes.

In this report, the effect of pentafluorophenol (PFP) as a strong proton donor on the partition of $Cr(acac)_3$ and $Co(acac)_3$ is studied in detail to manifest the importance of the hydrogen-bond interaction with the proton donor in the partition of the metal complexes.

$Cr(acac)_3$ and $Co(acac)_3$ were obtained from Dojin Chemical Co.,

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recrystallized from hexane, and dried in vacuo. PFP (Aldrich, more than 99% purity) was used as obtained. Heptane was purified by the usual manner. Water was doubly distilled. Other reagents were of guaranteed reagent grade and used without further purification.

The partition coefficient of the complexes between heptane and 0.10 M (1 M = 1 mol dm^{-3}) sodium perchlorate solutions was determined in the presence or absence of PFP as follows: An aqueous solution containing 3.3×10^{-5}- 2.9×10^{-4}M $Cr(acac)_3$ or $Co(acac)_3$ was mechanically shaken with pure heptane or a heptane solution containing 1.0×10^{-3}- 5.0×10^{-1}M PFP for 5 - 60 min at 298 K. The absorbance of the the aqueous phase before ($A_{i,aq}$) and after (A_{aq}) shaking was measured at 331 nm for $Cr(acac)_3$ and 325 nm for $Co(acac)_3$, where PFP did not interfere with the absorption of the complexes. The partition coefficient of the complexes was calculated as $(A_{i,aq}- A_{aq})V_{aq}A_{aq}{}^{-1}V_{org}{}^{-1}$, where V_{aq} and V_{org} denote the volumes of aqueous and organic phases, respectively. The proton concentration of the aqueous phase was adjusted to 10^{-2}- 10^{-3}M with perchloric acid so that the dissociation of PFP, of which the acid-dissociation constant is $10^{-5.2}$,5) could be neglected. The partition coefficient of PFP was also determined by the similar batch technique measuring the absorbance of the organic phase at 263 nm before and after shaking in the absence of the complexes.

All the partition equilibria were established within 5-min shaking. The partition coefficients of the complexes (P_0) in the absence of PFP were obtained by more than 12 measurements with the different concentration of the complexes in the range of 3.4×10^{-5}- 3.7×10^{-4}M in the organic phase: $P_0 = 0.370\pm0.018$ for $Cr(acac)_3$ and 0.0945 ± 0.0051 for $Co(acac)_3$. They are in good agreement with the literature values, 0.351 of $Cr(acac)_3$ and 0.105 of $Co(acac)_3$.6) The partition coefficient of PFP (P_{PFP}) was obtained as 0.455 ± 0.030 by 12 measurements at the PFP concentration of 2.9×10^{-3}- 3.1×10^{-2}M in the organic phase.

The apparent partition coefficients of the complexes (P') in the presence of PFP are shown in Fig. 1 as the plots of $\log(P'/P_0)$ vs. $\log([PFP]_{org}/M)$. Here $[PFP]_{org}$ denotes the equilibrium concentration of PFP in the organic phase and is given by P_{PFP} and the initial concentration of PFP in the organic phase (C_{PFP}): $[PFP]_{org} = C_{PFP}(V_{aq}V_{org}{}^{-1}P_{PFP}{}^{-1} + 1)^{-1}$. The partition coefficients of the complexes are remarkably enhanced with increase in the PFP concentration. Especially, the partition coefficient of $Co(acac)_3$ rises about 330-fold by the presence of 0.038 M PFP in the organic phase. The enhancement of the partition coefficient of $Cr(acac)_3$ with PFP is a little smaller than that of $Co(acac)_3$.

This novel enhancement effect of PFP can be ascribed to the specific interaction between the metal acetylacetonates and PFP in the organic

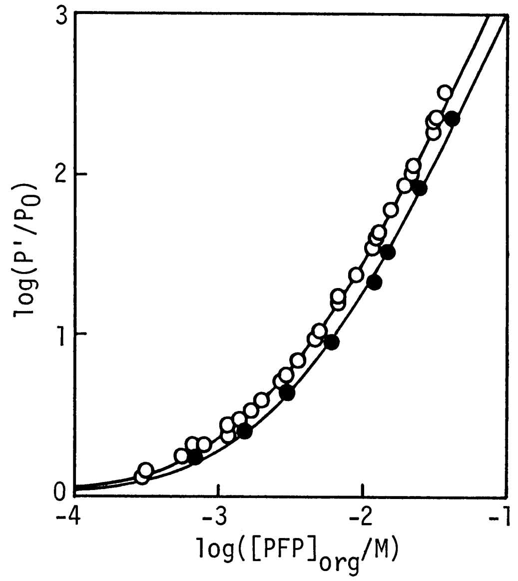

Fig. 1. Enhancement of the partition coefficient of $Cr(acac)_3$(●) and $Co(acac)_3$(○) as a function of the equilibrium concentration of PFP in the organic phase. The solid lines are the regression curves based on Eq. 3.

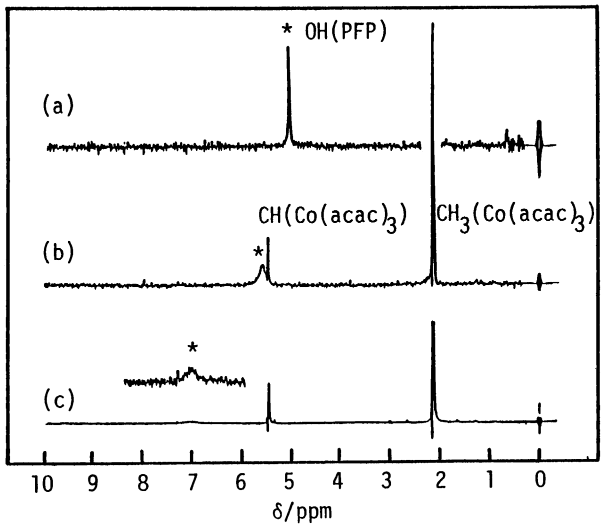

Fig. 2. ^{1}H-NMR spectra of 0.10 M PFP in CCl_4 in the presence of $Co(acac)_3$ measured with Varian EM-390 spectrometer (90 MHz) at 308 K. $Co(acac)_3$ concentration: a, 0 M; b, 0.010 M; c, 0.050 M.

phase. The spectroscopic research was carried out in order to identify the nature of the interaction. The absorption band at 560 - 590 nm of the complexes in heptane, assigned to the d-d transition,7) was not change by the presence of 0.05 M PFP. This result clearly denied a possibility of the direct coordination of PFP to the inner sphere of the complexes. Figure 2 shows the ^{1}H-NMR spectra of PFP in carbon tetrachloride in the presence of $Co(acac)_3$. The signal of hydroxyl proton of PFP shifts to the lower magnetic field with increase in the $Co(acac)_3$ concentration. This paramagnetic shift can be explained by the hydrogen bonding.8) Therefore, it was concluded that the enhancement of the partition coefficient of the complexes results from the association of the complexes with PFP in the organic phase by hydrogen bonding of the hydroxyl hydrogen atom of PFP to the outer sphere (probably ligand oxygen atoms) of the complexes.

In order to obtain more detailed information on the complex-PFP interaction, the association constant was determined by the partition-equilibrium analysis. When one molecule of the metal acetylacetonate ($M(acac)_3$) and i (i = 1 - n) molecules of PFP form the association complex ($M(acac)_3 \cdot iPFP$) in the organic phase, the apparent partition coefficient of $M(acac)_3$, P', in the presence of PFP can be expressed using the intrinsic partition coefficient of $M(acac)_3$, P_0, in the absence of PFP:

$$P' = \frac{[M(acac)_3]_{org} + \sum_{i=1}^{n} [M(acac)_3 \cdot iPFP]_{org}}{[M(acac)_3]_{aq}} = P_0 (1 + \sum_{i=1}^{n} \beta_{ass,i} [PFP]_{org}^{\ i}), \quad (1)$$

where $\beta_{ass,i}$ is the association constant in the organic phase corresponding to the following equilibrium:

$$M(acac)_{3,org} + i\ PFP_{org} \rightleftharpoons M(acac)_3 \cdot iPFP_{org}. \quad (2)$$

Therefore, the following equation can be derived:

$$P'/P_0 = 1 + \sum_{i=1}^{n} \beta_{ass,i} [PFP]_{org}^{\ i}. \quad (3)$$

This equation indicates that the slope of the plot of $\log(P'/P_0)$ vs. $\log([PFP]_{org}/M)$ equals the mean number of PFP molecule associating with one molecule of $M(acac)_3$. The slopes of the plots in Fig. 1 are close to 2 for both the complexes at the higher concentration region of PFP, and reveal the formation of 1:1 and 1:2 association complexes of $M(acac)_3$ with PFP. From the plots in Fig. 1, the association constants, $\beta_{ass,1}$ and $\beta_{ass,2}$, were computed by the nonlinear least-squares method (SALS program, University of Tokyo) based on Eq. 3, and very large values were obtained: $\log(\beta_{ass,1}/M^{-1}) = 2.90$ and $\log(\beta_{ass,2}/M^{-2}) = 4.98$ for $Cr(acac)_3$, and $\log(\beta_{ass,1}/M^{-1}) = 3.04$ and $\log(\beta_{ass,2}/M^{-2}) = 5.23$ for $Co(acac)_3$.

In conclusion, PFP was found to exert the remarkable enhancement effect on the partition of $Cr(acac)_3$ and $Co(acac)_3$, and this effect was ascribed to the formation of the highly stable association complexes of the metal acetylacetonates with PFP in the organic phase by hydrogen bonding. Such association is expected to occur for other metal complexes, and PFP will give much enhancement to the extraction of various metal chelates.

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