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Thermodynamic Study on the Extraction of Cobalt Complex with 8-Quinolinol into 1,1,2,2-Tetrachloroethane

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The extraction behavior of cobalt(II) into 1,1,2,2-tetrachloroethane (TCE) with 8-quinolinol (HQ) from an aqueous solution in the presence of various inorganic anions (X^-) such as perchlorate, nitrate, and chloride ions was studied themodynamically. The extraction equation can be written as

$$2Co^{2+}+6HQ_{(o)}+X^- \rightleftarrows Co_2Q_3(HQ)_3{}^+{}_{(o)}+X^-_{(o)}+3H^+$$

The ion-pair of the binuclear complex (complex ion-pair) dissociates to a complex cation and an inorganic anion in the organic phase. The extraction constant increases in proportion to the radius of the counter anion. Changes in the enthalpy and entropy are negative for the overall extraction of cobalt with 8-quinolinol. These thermodynamic parameters were compared with those of zinc and cadmium. The temperature effect on the extraction behavior of cobalt with 8-quinolinol was also investigated in a chloroform system for comparison.

In recent years a number of studies have been carried out concerning the various factors affecting the solvent extraction of a metal chelate. However, only a few thermodynamic studies have been carried out.[1-5] Nakayama[6,7] studied the effect of temperature on the extraction of 8-quinolinol itself and copper, zinc and cadmium chelate of 8-quinolinol into TCE. Yamada et al.[8] clarified the mechanism of a synergistic solvent extraction of metal diphenylcarbazonate using thermodynamic data. It is thought that thermodynamic data provide valuable information regarding extraction mechanisms.

The extraction behavior of cobalt with 8-quinolinol into chloroform has been studied by several investigators.[9-13] It was reported that the species extracted into chloroform is the self-adduct, such as $CoQ_2(HQ)_2$[9,10] or CoQ_2HQ.[11,12] While Sekido et al.[13] found that an ion-pair complex containing a large anion, such as perchlorate, $Co_2Q_3(HQ)_3X$, is extracted below pH 5.1.

In this study, the temperature effects on the extraction behavior of cobalt with 8-quinolinol were investigated in both TCE and chloroform systems.

Experimental

Reagents. 8-Quinolinol was recrystallized twice from ethanol. Cobalt chloride ($CoCl_2\cdot 6H_2O$) was used to prepare a stock solution of cobalt. A ^{60}Co solution (1 mCi) was obtained from the Japan Radio-isotope Association. Sodium Salts of perchlorate, nitrate and chloride as well as other chemicals were all of analytical grade.

Apparatus. Extraction was carried out in a cylindrical glass tube with a magnetic stirrer in a Yamato BH-71 water bath regulated at a temperature of ±0.05 °C. The cobalt concentration in the aqueous phase was determined by a Rigaku Denki energy dispersive X-ray fluorescence spectrometer Ultra-trace system according to a previously reported method.[14] In the case of $[Co]_{init.}=10^{-8}$ M ($[Co]_{init.}$ is the initial concentration of cobalt in the aqueous phase, 1M=1 mol dm^{-3}), the concentration of cobalt was determined by measuring the γ-radio-activity of aliquots of both phases with a Packard Auto-Gamma 5100 single-channel pulse-height analyzer. For pH measurements, a Philips PW 9422 pH meter was used.

Extraction Procedure. A 30 ml portion of a buffered cobalt solution was stirred with a 10 ml portion of the 8-quinolinol solution of organic solvent standing in a constant-temperature bath for 30 min (a time period required to attain equilibrium). The initial aqueous solution was adjusted to the desired pH with a small amount of an acetic acid-acetate buffer solution, and to an ionic strength of 0.1 with sodium perchlorate, sodium nitrate or sodium chloride.

After stirring, the pH of the aqueous phase measured in situ was taken as the equilibrium pH. After phase separation, the concentration of cobalt in the aqueous phase was determined by an X-ray fluorescence spectrometer after concentrating cobalt as a diethyldithiocarbamate (DDTC) complex on a Millipore filter. Measurements were carried out by using a Mo anode and a Ge secondary target under excitation conditions of 35 kV-30 mA. The data-accumulation time was usually 100 s and the Co$K\alpha$ line intensity was used throughout the analytical calculations. The equilibrium concentration of cobalt in the organic phase was calculated from the aqueous equilibrium concentration and the initial concentration. The volume of the aqueous phases was corrected for temperature with values of the water density in the Smithsonian tables. The volumes of the organic phases were corrected for temperature using an experimentally determined density function. The density of TCE at any desired temperature employed could be obtained using the formula $1.597-1.562\times10^{-3}(t-20)$, where t is the temperature in degrees centigrade.

Results and Discussion

Extraction of Cobalt into TCE with 8-Quinolinol in the Presence of Various Inorganic Anions. All investigations were carried out below pH 6.0, because the species containing no anion, $Co_2Q_4(HQ)_2$, may be extracted in higher pH ranges.[13]

Plots of log$D$ vs. pH at 25 °C in the presence of perchlorate, nitrate and chloride ions are shown in Fig. 1. The slopes of 1.5 indicate that the ratios Co : Q^- are 2 : 3, since the predominant species of cobalt in the aqueous phase is considered to be Co^{2+}. The order of the distribution ratios is $ClO_4^- > NO_3^- > Cl^-$. In Figs. 2—4 the relationship between log$D$ vs. log[HQ]$_o$ at various temperatures is shown for perchlorate, nitrate and chloride ions, respectively. In a perchlorate system, the slopes are 3 up to 70 °C. In a nitrate system, the slopes are 3 up to 55 °C. At 70 °C the slope is nearly down to 2. In a chloride system, the slopes change from 3 to nearly 2 above 55 °C. These facts suggest that the extracted species is 1 : 3 chelate at room temperatures and 1 : 2 chelate at sufficiently high temperatures for the nitrate and chloride systems. The effects of the concentration of the inorganic anions (ClO_4^-, NO_3^-, and Cl^-) on the distribution of cobalt in TCE were examined. Here, the ionic strength of the aqueous phase was adjusted to 0.1 with sodium sulfate. All of the plots of log$D$ vs. log[X^-] indicate a slope of nearly 0.5. This suggests that the ratios Co : X^- are 2 : 1.

From the slope analysis stated above, the extracted species is considered to be $Co_2Q_3(HQ)_3X$. In addition, the plots of log$D$ vs. log[Co]$_{aq}$ are constant in the cobalt concentration range from 10^{-6} M to 10^{-4} M. This is generally accepted as being evidence for the existence of a mononuclear complex in the organic phase. However, our analysis of the results suggests

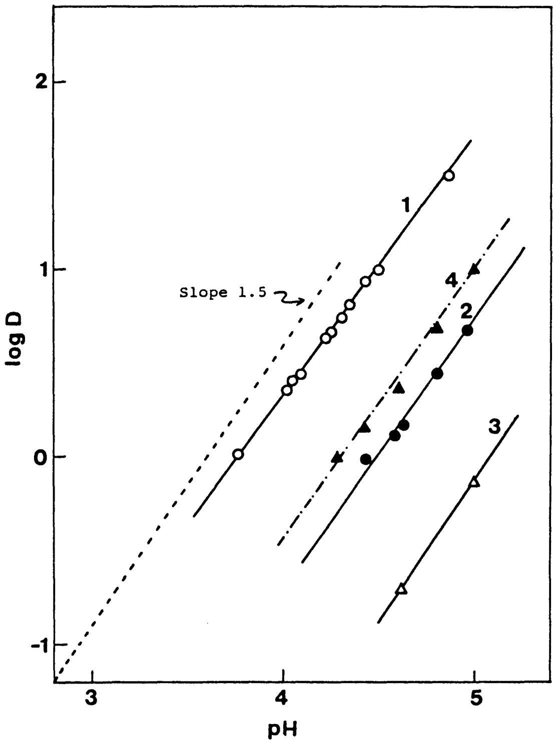

Fig. 1. Effect of pH on the distribution ratio of cobalt between TCE and water in the presence of various inorganic anions at 25 °C.
[Co]$_{init.}$=5 ppm, 0.09 M salts+0.01 M(AcOH-AcONa buffer), [HQ]$_o$=10^{-2}M 1; $NaClO_4$, 2; $NaNO_3$, 3; NaCl, [HQ]$_o$=2.1×10^{-2} M 4; NaCl.

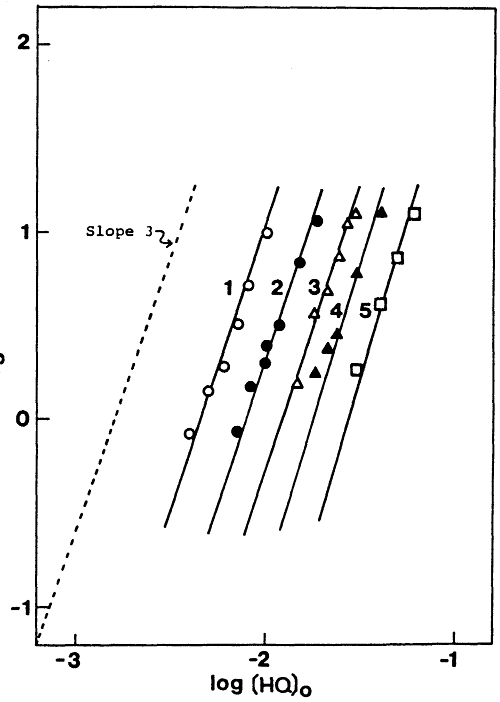

Fig. 2. Effect of 8-quinolinol concentration on the distribution ratio of cobalt between TCE and water in the presence of perchlorate.
pH 4.05, 1; 10 °C 2; 25 °C 3; 40 °C 4; 50 °C 5; 70 °C.

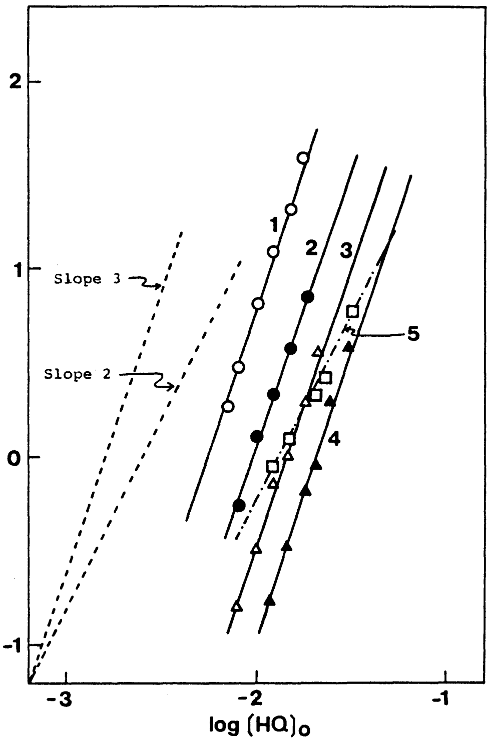

Fig. 3. Effect of 8-quinolinol concentration on the distribution ratio of cobalt between TCE and water in the presence of nitrate.
pH 4.6, 1; 10 °C 2; 25 °C 3; 40 °C 4; 55 °C 5; 70 °C.

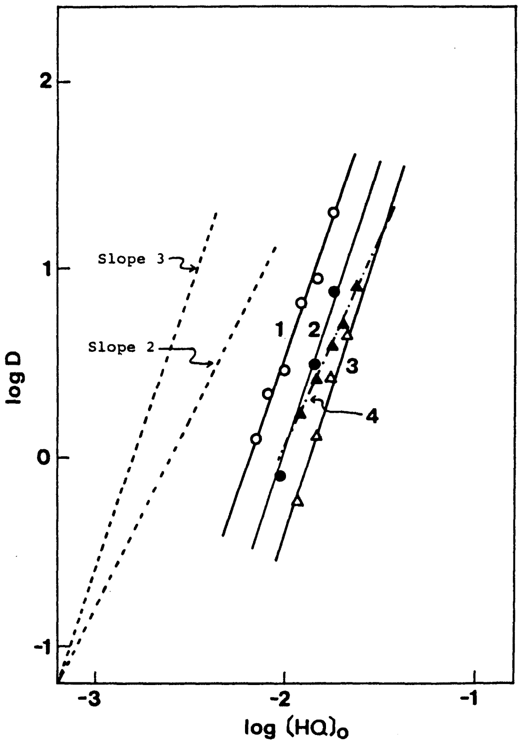

Fig. 4. Effect of 8-quinolinol concentration on the distribution ratio of cobalt between TCE and water in the presence of chloride.
pH 5.0, 1; 10 °C 2; 25 °C 3; 40 °C 4; 55 °C.

that the binuclear complex of cobalt dissociates in TCE in a way similar to the case of cadmium and zinc, as previously stated.[6,7]

Therefore, the extraction equation can be given as

$$2Co^{2+}+6HQ_{(o)}+X^- \rightleftharpoons Co_2Q_3(HQ)^+_{3(o)}+X^-_{(o)}+3H^+. \quad (1)$$

where o refers to the species in the organic phase. The extraction constant is

$$K_{ex} = \frac{[Co_2Q_3(HQ)_3{}^+]_o\,[X^-]_o\,[H^+]^3}{[Co^{2+}]^2\,[HQ]_o^6\,[X^-]} \,. \quad (2)$$

To maintain electrical neutrality in the organic phase, $[Co_2Q_3(HQ)_3{}^+]_o = [X^-]_o$, Eq. 2 can be transformed into

$$K_{ex} = \frac{[Co_2Q_3(HQ)_3{}^+]_o^2\,[H^+]^3}{[Co^{2+}]^2\,[HQ]_o^6\,[X^-]} \,. \quad (3)$$

The distribution ratio, D, can be given as

$$D = 2K_{ex}^{1/2}[HQ]_o^3[H^+]^{-3/2}[X^-]^{1/2}. \quad (4)$$

This equation means that plots of $\log D$ vs. $\log[HQ]_o$ show a slope of 3; plots of $\log D$ vs. pH show a slope of 1.5; and plots of $\log D$ vs. $\log[X^-]$ show a slope of 0.5. Thus, the assumption that the ion-pair of the binuclear complex would dissociate in the organic phase agrees well with the experimental results. It is, therefore, apparent that the extraction mechanism of cobalt with 8-quinolinol into TCE is similar to those of cadmium and zinc. The dissociation of an ion-associated complex in an organic solvent whose dielectric constant is relatively large, such as nitrobenzene (34.8), has already reported. However, the dielectric constant of TCE is 8.2 (at 20 °C). In order to certify the dissociation of the binuclear complex in TCE, the conductivities of the extract of zinc into TCE were measured. The results of conductivity measurements support the assumption that the ion-pair of the binuclear complex dissociates into a complex cation and an inorganic anion in TCE.[15] It has already been reported that many compounds, for example triarylmethyl chloride, dissociate in chlorinated ethanes such as 1,2-dichloroethane and TCE whose dielectric constants are not very large.[16,17]

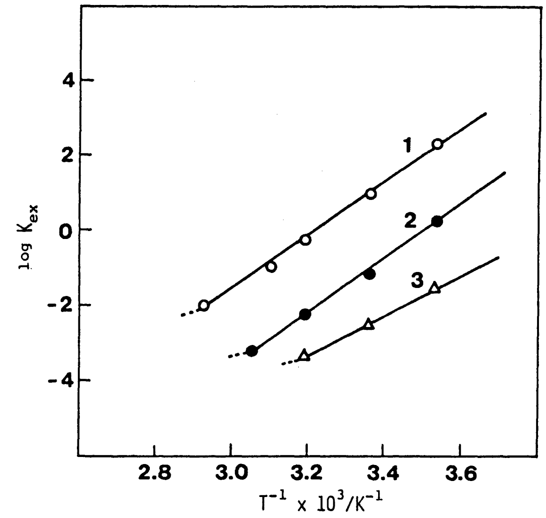

Fig. 5. Temperature effect on the extraction constants of cobalt between TCE and water.
1; $NaClO_4$ system, 2; $NaNO_3$ system, 3; NaCl system.

Plots of $\log K_{ex}$ vs. $1/T$ in the presence of perchlorate, nitrate and chloride are shown in Fig. 5. The distribution ratios decrease remarkably with an increase in the temperature for each anion. This trend is more remarkable for a larger anion, such as perchlorate. The slopes of $\log K_{ex}$ vs. $1/T$ plots become gentle for smaller anions, such as chloride. Changes in the slope of $\log K_{ex}$ vs. $1/T$ suggest that the extracted species in high-temperature ranges are different from those in low-temperature ranges. This is supported by the fact that the slopes of plots of $\log D$ vs. $\log[HQ]_o$ become smaller than 3 at high temperatures, especially for the smaller anions as stated above. At high temperatures, the extraction of anhydrous chelate CoQ_2 may occur in a manner similar to zinc extraction with 2-methyl-8-quinolinol.[15] In a perchlorate system, the extractable ion-associated compound is formed even at high temperatures because the ionic redius of perchlorate is fairly large.

The value of the enthalpy change, ΔH, was calculated from the slope. The value of the entropy change, ΔS was calculated from the corresponding ΔH and K_{ex}

values. The results are listed in Table 1. The data show that the extraction of the complex ion-pair is an exothermic reaction. Extraction in the perchlorate system is mainly enthalpy controlled, resulting in a positive $\log K_{ex}$ value. In nitrate and chloride systems, negative enthalpy changes are canceled by large negative entropy changes, resulting in negative $\log K_{ex}$ values. In a nitrate system, the contribution of the entropy is larger than that in a perchlorate system. Plots of ΔG and ΔH of ion-pair extraction of cobalt vs. ΔG and ΔH of hydration of perchlorate, nitrate and chloride ions are shown in Fig. 6. These indicate that the dehydration of perchlorate, nitrate and chloride ions plays an important role in ion-pair extraction. These thermodynamic parameters were compared with those of zinc and cadmium, since the extraction mechanism of cobalt is similar to those of zinc and cadmium. The ΔH values of the extraction of cobalt, zinc and cadmium are listed in Table 2.[7)] In perchlorate and nitrate systems, the larger the size of metal ion, the more exothermic is the ion-pair extraction (Co^{2+} 0.72 Å, Zn^{2+} 0.74 Å, Cd^{2+} 0.97 Å[19)]). In a chloride system, ΔH values for all metal ions are almost the same.

Extraction of Cobalt into Chloroform with 8-Quinolinol in the Presence of Perchlorate Ion. The extraction behavior of cobalt with 8-quinolinol into chloroform was studied at various temperatures for a comparison with that in the TCE system. The concentration ratio of perchlorate to metal ion in chloroform was 0.5. Plots of $\log D(1+D)$ vs. pH are shown in Fig. 7. Here, the slopes are 3. The distribution decreases with a rise in temperature, which is similar to the case of TCE. Plots of $\log D(1+D)$ vs. $\log [HQ]_o$ are straight lines with slopes of 6. Plots of log D vs. $\log [Co]_{aq}$ give a straight line with a slope of 1 in the vicinity of $[Co]_{init.}=10^{-4}$—10^{-5} M. These results suggest that the extracted binuclear complex of cobalt would almost associate in chloroform, unlike the case in the TCE system. This is probably attributable to the fact that the dielectric constant of chloroform (4.9) is lower than that of TCE. Nevertheless, the dissociation of a com-

Table 1. Thermodynamic Values for Extraction of Co(II) with 8-Quinolinol into TCE in the Presence of Various Anions at 25 °C

System	$\log K_{ex}$	ΔG kJ mol^{-1}	ΔH kJ mol^{-1}	ΔS J K^{-1} mol^{-1}
$NaClO_4$	0.98	−5.59	−137	−441
$NaNO_3$	−1.22	6.96	−135	−476
NaCl	−2.50	14.3	−101	−387

Table 2. ΔH(kJ mol^{-1}) Values for Extraction of Cobalt, Zinc, and Cadmium Chelates with 8-Quinolinol into TCE

System	Co	Zn[7)]	Cd[7)]
$NaClO_4$	−137	−153	−169
$NaNO_3$	−135	−151	—
NaCl	−101	−95.4	−108

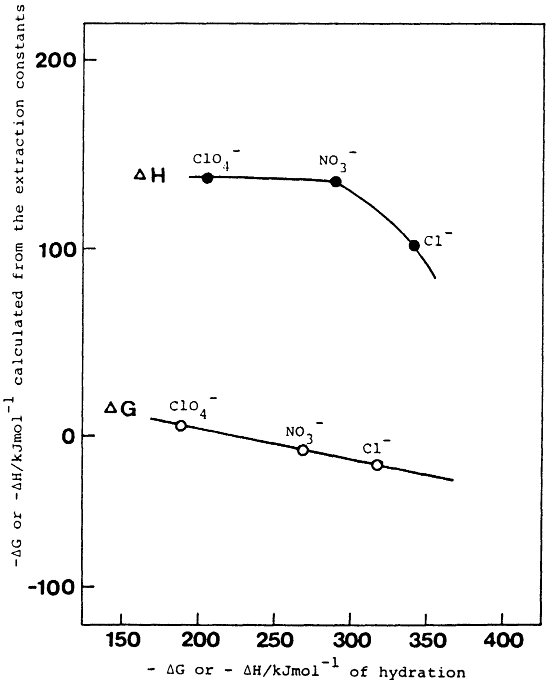

Fig. 6. Relationship between thermodynamic parameters for extraction of cobalt chelates with 8-quinolinol into TCE in the presence of various inorganic anions and hydration energies of those anions.

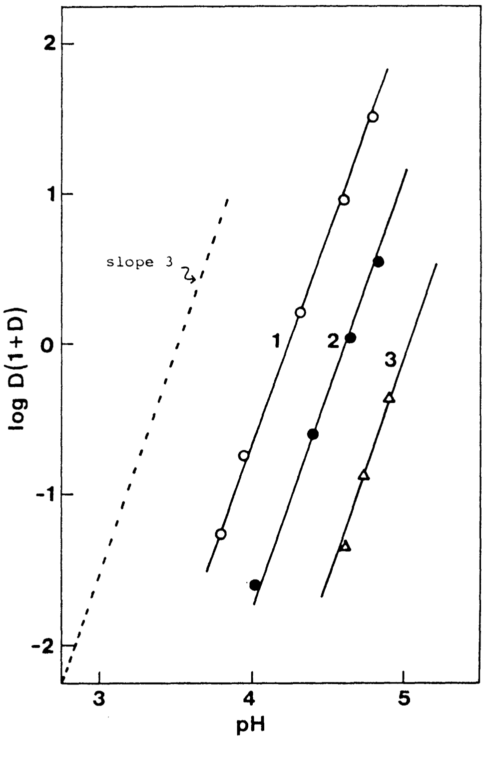

Fig. 7. Effect of pH on the distribution ratio of cobalt between chloroform and water in the presence of perchlorate.
1; 10°C 2; 25°C 3; 40°C.

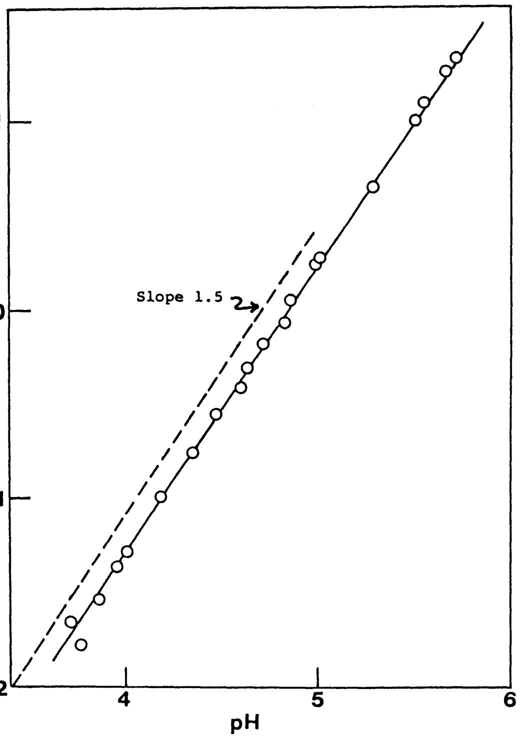

Fig. 8. Effect of pH on the distribution ratio of cobalt between chloroform and water in the presence of perchlorate ion in the case of low $[\mathrm{Co}]_{\mathrm{init.}}$. $[\mathrm{Co}]_{\mathrm{init.}}=10^{-8}$ M, $[\mathrm{HQ}]_{\mathrm{o}}=10^{-2}$ M, 0.09 M $\mathrm{NaClO_4}$ +0.01 M AcOH-AcONa buffer, temp=20 °C.

plex ion-pair is expected, even in a chloroform system when $[\mathrm{Co}]_{\mathrm{init.}}$ is sufficiently low. Figure 8 shows the plots of $\log D$ vs. pH in the case of $[\mathrm{Co}]_{\mathrm{init.}}=10^{-8}$ M. This experiment was conducted by using $^{60}\mathrm{Co}$ as a cobalt tracer. The slope of 1.5 indicates that cobalt is extracted into chloroform by a similar mechanism occurring in the TCE system. Sekido et al. suggested that cobalt is extracted into chloroform as a monomeric complex of 8-quinolinol when $[\mathrm{Co}]_{\mathrm{init.}}$ is lower than 10^{-6} M from the fact that the log D values are independent of $[\mathrm{Co}]_{\mathrm{init.}}$ in this concentration range.[13] Our result, however, demonstrates that the dissociation of the complex ion-pair is more likely than the extraction of the monomeric complex.

When $[\mathrm{Co}]_{\mathrm{init.}}$ is more than 10^{-5} M, the extraction equation can be written as

$$2\mathrm{Co}^{2+}+6\mathrm{HQ}_{(\mathrm{o})}+\mathrm{ClO_4}^{-} \rightleftharpoons \mathrm{Co_2Q_3(HQ)_3(ClO_4^{-})}_{(\mathrm{o})}+3\mathrm{H}^{+}. \tag{5}$$

The extraction constant is given by

$$K_{\mathrm{ex}} = \frac{[\mathrm{Co_2Q_3(HQ)_3(ClO_4^{-})}]_{\mathrm{o}}\,[\mathrm{H}^{+}]^{3}}{[\mathrm{Co}^{2+}]^{2}\,[\mathrm{HQ}]_{\mathrm{o}}^{6}\,[\mathrm{ClO_4}^{-}]}\,. \tag{6}$$

The distribution ratio, D, is represented by

$$D=2K_{\mathrm{ex}}[\mathrm{Co}^{2+}][\mathrm{HQ}]_{\mathrm{o}}^{6}[\mathrm{H}^{+}]^{-3}[\mathrm{ClO_4}^{-}]. \tag{7}$$

Since $[\mathrm{Co}^{2+}]=[\mathrm{Co}]_{\mathrm{init.}}/(1+D)$, Eq. 7 can be transformed to

$$D(1+D)=2K_{\mathrm{ex}}[\mathrm{Co}]_{\mathrm{init.}}[\mathrm{HQ}]_{\mathrm{o}}^{6}[\mathrm{H}^{+}]^{-3}[\mathrm{ClO_4}^{-}]. \tag{8}$$

The $\log K_{\mathrm{ex}}$ values are 4.04, 2.85, and 1.61 at 10, 25, and 40 °C, respectively. The $\log K_{\mathrm{ex}}$ value at 25 °C agrees with the value given by Sekido et al.[13] (2.60). Thermodynamic data at 25 °C are $\Delta G=-16.3$ kJ mol^{-1}, $\Delta H=-137$ kJ mol^{-1} and $\Delta S=-405$ J K^{-1} mol^{-1}. The values of enthalpy and entropy changes for chloroform are negative, similar to those for ion-pair extraction.

Comparing the extraction mechanism of cobalt 8-quinolinol complex into TCE with that into chloroform, the extracted binuclear complex of cobalt almost dissociates in TCE, while it almost associates in chloroform. Accordingly, it is considered that the difference in the thermodynamic parameters between TCE and chloroform systems would depend on the difference in the thermodynamic parameters of the distribution of 8-quinolinol and its cobalt complex and of the dissociation of the extracted binuclear cobalt complex in TCE. The values of $\log K_{\mathrm{DR}}$, ΔH, and ΔS for the distribution of 8-quinolinol are 2.64, −5.02 kJ mol^{-1}, and 33.5 J K^{-1} mol^{-1} for TCE[6] and 2.63, −9.02 kJ mol^{-1}, and 20.0 J K^{-1} mol^{-1} for chloroform,[4] respectively. The difference in the ΔH values for the distribution constant between TCE and chloroform is small. Moreover, the difference in ΔH values for the distribution of binuclear cobalt complex between TCE and chloroform systems may be small because the distribution species of cobalt for TCE is similar to that for chloroform.[15] Then, since the ΔH values for the extraction constant have almost the same values for both solvents, the ΔH value for the dissociation of an extracted binuclear cobalt complex in TCE would not be so large.

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