Effects of Temperature on the Solvent Extraction of Zinc and Cadmium Complexes with 8-Quinolinol and 2-Methyl-8-quinolinol into 1,1,2,2-Tetrachloroethane, 1-Octanol, and *p*-Xylene

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The effects of temperature on the extraction of zinc(II) and cadmium(II) complexes with 8-quinolinol (HQ) and 2-methyl-8-quinolinol (HR) into three different types of organic solvents whose boiling points are relatively high were studied. 1) In the case of 1,1,2,2-tetrachloroethane (TCE), the extraction equilibrium can be written as follows (except for that of zinc with 2-methyl-8-quinolinol):

$$2M^{2+} + 6HQ_{(o)} + X^- \rightleftarrows M_2Q_3(HQ)_3{}^+{}_{(o)} + X^-{}_{(o)} + 3H^+,$$

where X^- refers to various inorganic anions. An ion-pair of the binuclear complex (complex ion pair) dissociates into a complex cation and an inorganic anion in the organic phase. The distribution ratios decrease remarkably with an increase in temperature. 2) In the 1-octanol (S) extraction system, zinc and cadmium are extracted as solvent-adducts, such as $MQ_2 \cdot S_2$. The distribution ratios are almost constant with a change in temperature. 3) In the *p*-xylene extraction system, a hydrated metal complex, $MQ_2 \cdot 2H_2O$, may precipitate and be deposited at the interface of both phases, except for the extraction of zinc with 2-methyl-8-quinolinol. 4) The zinc complexes of 2-methyl-8-quinolinol are extracted into TCE and *p*-xylene as anhydrous complexes, such as MR_2. The distribution ratios increase with an increase in temperature. Moreover, zinc can be separated from cadmium at high temperatures using 2-methyl-8-quinolinol and TCE.

Numerous studies have been conducted regarding the various factors affecting the solvent extraction of metal chelate. A few thermodynamic studies have been carried out. In these studies, however, measurements were conducted in the low-temperature region, below 50 °C, since volatile organic solvents, such as chloroform and benzene, were used.[1–5] As previously reported,[6–8] we studied the temperature effects on the extraction of 8-quinolinol, itself, and its divalent metal chelates into several organic solvents whose boiling points are relatively high over the temperature range 10 to 90 °C.

In this study the effects of temperature on the extraction behavior of zinc and cadmium with 8-quinolinol and 2-methyl-8-quinolinol between water and three different organic solvents were investigated with regard to the extraction mechanism. The organic solvents used were 1,1,2,2-tetrachloroethane, 1-octanol, and *p*-xylene, which were chosen as homologues of chloroform, 1-butanol, and benzene, respectively. The results for 2-methyl-8-quinolinol were compared with those for 8-quinolinol. Moreover, in order to corroborate the dissociation of the binuclear complex in TCE, the conductivities of the extract into TCE were measured.

Experimental

Reagents. Commercially available 8-quinolinol was purified by recrystallization from ethanol after steam distillation. A ^{65}Zn solution (1 mCi) was obtained from the Japan Radioisotope Association. Sodium salts of perchlorate, nitrate and chloride and other chemicals were all of analytical grade.

Apparatus. Extraction was carried out in a cylindrical glass tube with a magnetic stirrer in a water bath. The temperature was controlled by a thermoregulator to ±0.1 °C. A JASCO Ubest-30 spectrophotometer was used for the determination of 2-methyl-8-quinolinol. The concentration of zinc was determined by measuring the γ-radioactivity of aliquots of both aqueous and organic phases with a Packard Auto-Gamma 5100 single-channel pulse-height analyzer. Cadmium in both the phases was determined by a Nippon Jarrel Ash 8200 atomic absorption spectrophotometer equipped with a Nippon Jarrel Ash FLA 100 graphite furnace atomizer. For pH measurements, a Hitachi-Horiba M-5 pH meter equipped with a glass-calomel electrode pair for high-temperature work was used.

The conductivity measurements were carried out at 25.00±0.01 °C with a Yokogawa Hewlett Packard bridge, Type BV-Z-13B and a Yanagimoto conductivity cell, Type C.

Procedures. Partition of 2-Methyl-8-quinolinol: Equal (25 ml) volumes of the TCE solution containing a known concentration of 2-methyl-8-quinolinol and an aqueous solution pre-saturated with TCE were shaken in a constant-temperature bath for 3 h. The aqueous phase was adjusted to pH 8 with a borate buffer solution, and to an ionic strength of 0.1 with sodium perchlorate. After equilibration, the phases were immediately separated and cooled to room temperature. An aliquot of the aqueous phase was extracted into chloroform, while an aliquot of the organic phase was dissolved into chloroform. Then, the concentrations of 2-methyl-8-quinolinol were determined by measuring its UV absorbance at 312 nm.

Extraction Procedure: A 30 ml portion of a buffered zinc or cadmium solution was stirred with a 10 ml portion of 8-

quinolinol or 2-methyl-8-quinolinol solution of organic solvents standing in a constant-temperature bath for 30 min, which was found to be adequate for the attainment of distribution equilibrium. The pH of the initial aqueous solution was adjusted to the desired value with a small amount of an acetic acid–acetate buffer solution. Also, the ionic strength of the aqueous solution was adjusted to 0.1 with sodium salts.

The pH value of the aqueous phase, measured in situ after stirring, was taken as the equilibrium pH value. After phase separation, the concentration of zinc was determined by measuring the γ-radioactivity of aliquots of both phases with a single-channel pulse-height analyzer. In the case of cadmium, the concentration of cadmium in the aqueos phase was immediately determined with an atomic absorption spectrophotometer; the organic phase was analyzed after back extracting into a nitric acid solution. In each case, the volume of the aqueous phase was corrected for temperature with the values of the water density given in the Smithsonian tables; the volumes of the organic phases were corrected for temperature with experimentally determined density functions. Thus, the density at any temperature employed could be calculated using the following formulae: $1.597-1.562\times10^{-3}(t-20)$ for 1,1,2,2-tetrachloroethane, $0.8610-8.783\times10^{-4}(t-20)$ for *p*-xylene, and $0.8256-7.415\times10^{-4}(t-20)$ for 1-octanol, where temperature is in degrees centigrade.

All the extraction experiments were carried out below pH 5.5, since metal ions could be adsorbed on the wall of a glass container or the interface of both phases at higher pH.

Results and Discussion

Extraction of Zinc and Cadmium Complexes of 8-Quinolinol into TCE in the Presence of Several Inorganic Anions. The extraction of the zinc 8-quinolinol complex has been reported by several investigators.[9–14] A number of different species thought to have been extracted into the chloroform have been proposed: for example, $ZnQ_2HQ\cdot H_2O$,[9] $ZnQ_2(HQ)_2$,[10,11] and $ZnQ_2HQ\cdot S$,[12] where S represents the organic solvent. Furthermore, Oki et al.[13] and Sekido et al.,[14,15] have reported that an ionic association complex having the composition $Zn_2Q_3(HQ)_3{}^+ClO_4{}^-$ is extracted into chloroform from a zinc solution containing perchlorate ion.

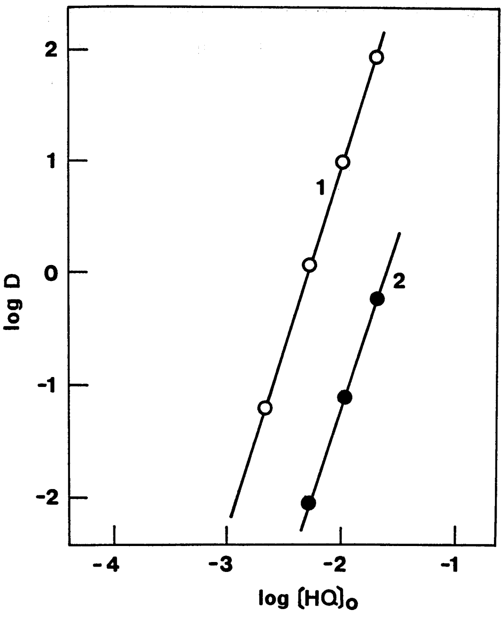

Fig. 1. Effects of 8-quinolinol concentration on the distribution ratio of zinc between TCE and water in the presence of perchlorate and chloride at 20 °C. $[Zn]_T=10^{-6}$ M, 0.09 M salts+0.01 M (AcOH-AcONa buffer) pH 5.0, 1; $NaClO_4$, 2; NaCl.

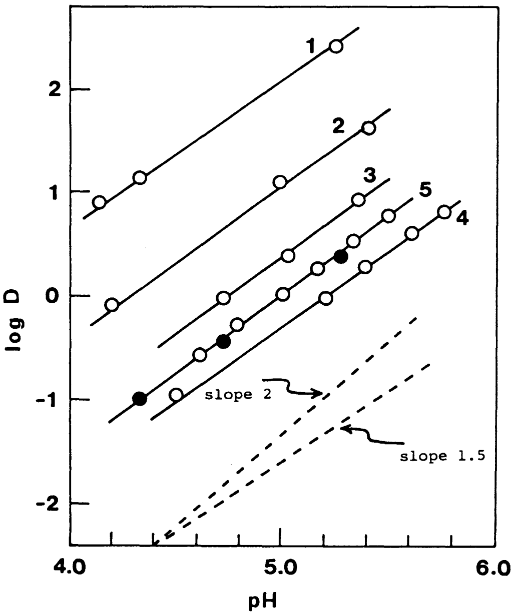

Fig. 2. Effects of pH on the distribution ratio of zinc between TCE and water.
1—5; $NaClO_4$ system, $[HQ]_o=2\times10^{-2}$ M, 1; 20 °C, 2; 40 °C, 3; 60 °C, 4; 80 °C, 5; $[HQ]_o=5\times10^{-3}$ M, 25 °C, ●; NaCl system, $[HQ]_o=2\times10^{-2}$ M, 20 °C.

Four types of plots were analyzed in order to determine the composition of zinc chelate under various conditions: $\log D$ vs. $\log[HQ]_o$, $\log D$ vs. pH, $\log D$ vs. $\log[X^-]$, and $\log D$ vs. $\log[Zn]_T$ at constant conditions for all the other factors, respectively. Herer, D is the distribution ratio of zinc; $[HQ]_o$, the concentration of 8-quinolinol in the organic phase; $[X^-]$, the concentration of inorganic anions in the aqueous phase; and $[Zn]_T$, the total concentration of zinc, respectively. Plots of $\log D$ vs. $\log[HQ]_o$ at 20 °C in the presence of perchlorate and chloride ions are shown in Fig. 1. It seems that three 8-quinolinol molecules combine with one zinc ion in these extraction systems, since all curves have solpes of 3. The curves in Fig. 2 show the relationship between $\log D$ and the pH at various temperatures. The curves have slopes of 1.5 for the perchlorate system in the temperature range 20 to 80 °C and for the chloride system at 20 °C, as indicated by solid circles. In these systems it is supposed that one and a half hydrogen ions dissociate from three molecules of 8-quinolinol to form a chelate in the aqueous phase. In other words, three molecules of 8-

quinolinol and one and half molecules of hydrogen ions apparently combine with one zinc ion. In Fig. 3 values of log D are plotted against log$[X^-]$. In the perchlorate and chloride systems, the slopes of curves (1) and (2) both equal 0.5 at pH 5.0. This phenomenon is not accidental at pH 5.0, but also holds at different pH. It seems that half a molecule of anion apparently attaches itself to one zinc molecule in these systems. The curves in Fig. 4 show the relationship between log D and log$[Zn]_T$ in the perchlorate and chloride systems. The curves have slopes of nearly 0, though log D values increase only slightly as the concentration of zinc increases. The fact that log D is independent of the concentration of zinc has been considered to indicate that a mononuclear complex is the predominant zinc species in the organic phase.[13] However, if a mononuclear complex were the predominant species, unusual ionic dissociation of the binuclear complex in the organic phase must be assumed as follows, since the apparent composition of this complex is $ZnQ_3H_{3/2}X_{1/2}$ from above results:

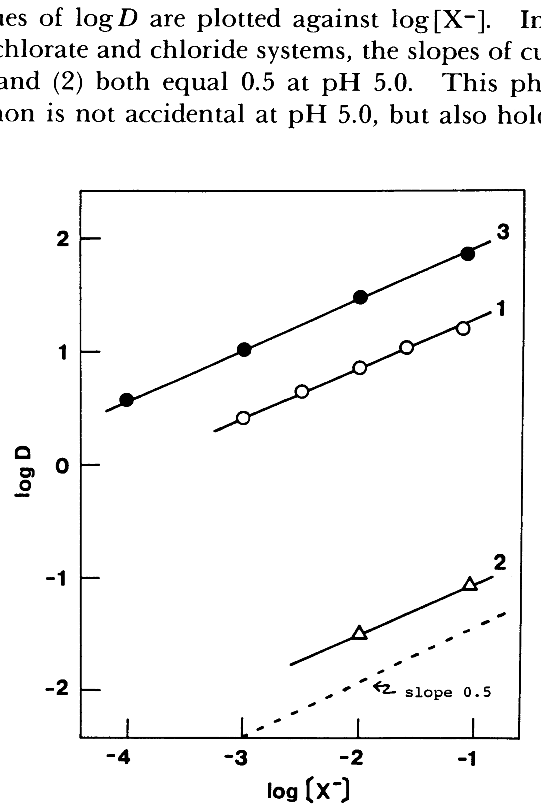

Fig. 3. Effects of concentration of inorganic anions on the distribution ratio of zinc between TCE and water at 20 °C.
$[HQ]_o=10^{-2}$ M, pH 5.0, 1; NaClO$_4$ system, 2; NaCl system, 3; $[HQ]_o=10^{-1}$ M, pH 3.8, NaClO$_4$ system.

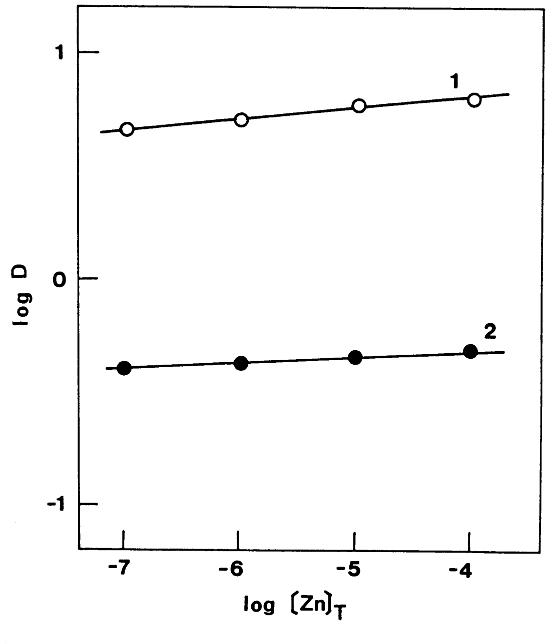

Fig. 4. Effects of metal concentration on the distribution ratio of zinc between TCE and water at 20 °C.
$[HQ]_o=2\times10^{-2}$ M, 1; NaClO$_4$ system, pH 4.0, 2; NaCl system, pH 4.8.

$$Zn_2Q_6H_3X_{(o)} \rightleftarrows ZnQ_3H_2{}^+{}_{(o)} + ZnQ_3HX^-{}_{(o)}, \tag{1}$$

where subscript o refers to the species in the organic phase.

Then, if the binuclear complex almost dissociates in the organic phase,

$$Zn_2Q_6H_3X_{(o)} \rightleftarrows Zn_2Q_6H_3{}^+{}_{(o)} + X^-{}_{(o)}, \tag{2}$$

the distribution ratio of zinc between the organic and aqueous phases in the acidic media would be given by following equation, since the simple zinc ion is the predominant zinc species in the aqueous phase:

$$D = \frac{2[Zn_2Q_6H_3{}^+]_o}{[Zn^{2+}]} \tag{3}$$

The extraction equation can be written as

$$2Zn^{2+} + 6HQ_{(o)} + X^- \rightleftarrows Zn_2Q_3(HQ)_3{}^+{}_{(o)} + X^-{}_{(o)} + 3H^+. \tag{4}$$

The extraction constant is

$$K_{ex} = \frac{[Zn_2Q_3(HQ)_3{}^+]_o[X^-]_o[H^+]^3}{[Zn^{2+}]^2[HQ]_o{}^6[X^-]} \tag{5}$$

In order to keep the electrical neutrality in the organic phase, $[Zn_2Q_3(HQ)_3{}^+]_o=[X^-]_o$, Eq. 5 can be transformed into

$$K_{ex} = \frac{[Zn_2Q_3(HQ)_3{}^+]_o{}^2[H^+]^3}{[Zn^{2+}]^2[HQ]_o{}^6[X^-]} \tag{6}$$

The distribution ratio, D can be given as

$$D = 2K_{ex}{}^{1/2}[HQ]_o{}^3[H^+]^{-3/2}[X^-]^{1/2}. \tag{7}$$

This equation means that plots of log D vs. log$[HQ]_o$ show a slope of 3, plots of log D vs. pH a slope of 1.5 and plots of log D vs. log$[X^-]$ 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.

The dissociation of ion-associated complexes in an organic solvent with a dielectric constant that is relatively high, such as nitrobenzene (34.8), has already been reported. However, the dielectric constant of

TCE is 8.2 (at 20 °C). In order to corroborate the dissociation of the binuclear complex in TCE, the conductivities (Λ) of the extract into TCE in the presence of perchlorate or chloride were measured at 25 °C. The zinc concentration was varied from 10^{-5} to 10^{-3} M (1 M=1 mol dm^{-3}). Plots of Λ vs. $\sqrt{C}$ of zinc chelate of 8-quinolinol extracted into TCE are shown in Fig. 5. The limiting equivalent conductivities (Λ_0) can be calculated from the equation as follows:

$$\Lambda_0 = \frac{0.820|Z_i|}{\eta r_s}, \tag{8}$$

where η is the viscosity of the organic solvent and r_s is the Stokes radius. η of TCE at 25 °C is 1.60. The ionic radii of perchlorate and chloride are 2.4 Å[16] and 1.67 Å.[17] The ionic radius of the complex cation, $Zn_2Q_6H_3^+$, was estimated to be 8.7 Å by assuming it is 1.5-times larger than that of the simple chelate, ZnQ_2 (5.8 Å).[18] The dissociation constants were calculated to be 5.04×10^{-6} and 2.67×10^{-6}, respectively, from the degrees of dissociation ($\alpha=\Lambda/\Lambda_0$). Therefore, at a zinc concentration of 10^{-6} M, where the extraction experiment was carried out, it is considered that 98 and 77% of the ion pair of the binuclear zinc complexes could dissociate in TCE when in the presence of perchlorate and chloride, respectively. The results of conductivity measurements endorse the assumption that the ion pair of the binuclear complex dissociates into a complex cation and an inorganic anion in TCE.

The extraction behavior of cadmium chelate of 8-quinolinol into TCE is similar to that of the zinc chelate. The binuclear complex also dissociates in the organic phase as

$$2Cd^{2+}+6HQ_{(o)}+X^- \rightleftarrows Cd_2Q_3(HQ)_3{}^+{}_{(o)}+X^-{}_{(o)}+3H^+. \tag{9}$$

The slopes of the plots of $\log D$ vs. $\log[HQ]_o$, $\log D$ vs. pH and $\log D$ vs. $\log[X^-]$ are 3, 1.5, and 0.5, respectively.

Plots of $\log D$ vs. $1/T$ for zinc and cadmium in the presence of perchlorate and chloride ions are shown in Fig. 6. The distribution ratios decrease remarkably with an increase in temperature for both zinc and cadmium. The curves for cadmium are linear up to fairly high temperatures, even for the chloride system, when compared to that of zinc. The changes of the slope of $\log D$ vs. $1/T$ suggest that the extracted species at high-temperature ranges are different from those at low-temperature ranges. This is supported by the fact that the slopes of the plots of $\log D$ vs. $\log[HQ]_o$ in the zinc extraction system become smaller than 3 at high temperatures, especially for smaller anions, such as chloride and sulfate.[7] At high temperatures, the extraction of anhydrous chelate ZnQ_2 may occur in a manner similar to the 2-methyl-8-quinolinol system (as stated below). In the case of cadmium, a stable ion-associated compound is formed even in the chloride system at high temperatures because the ionic radius of the complex cation for cadmium is larger than that for zinc.

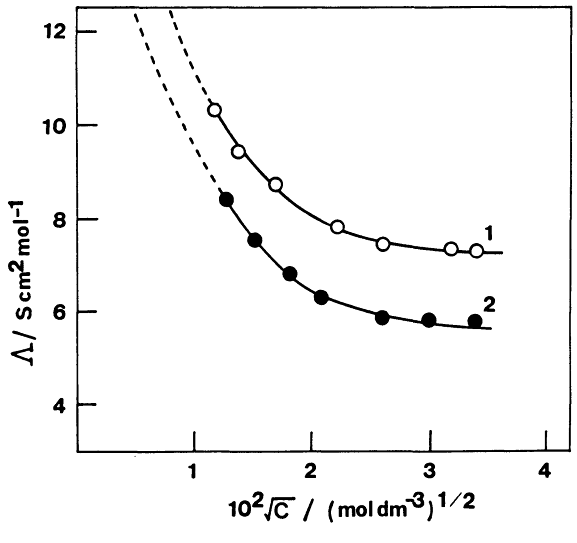

Fig. 5. Λ vs. $\sqrt{C}$ plots of zinc chelate of 8-quinolinol extracted into TCE at 25 °C.
1; NaClO$_4$ system, 2; NaCl system.

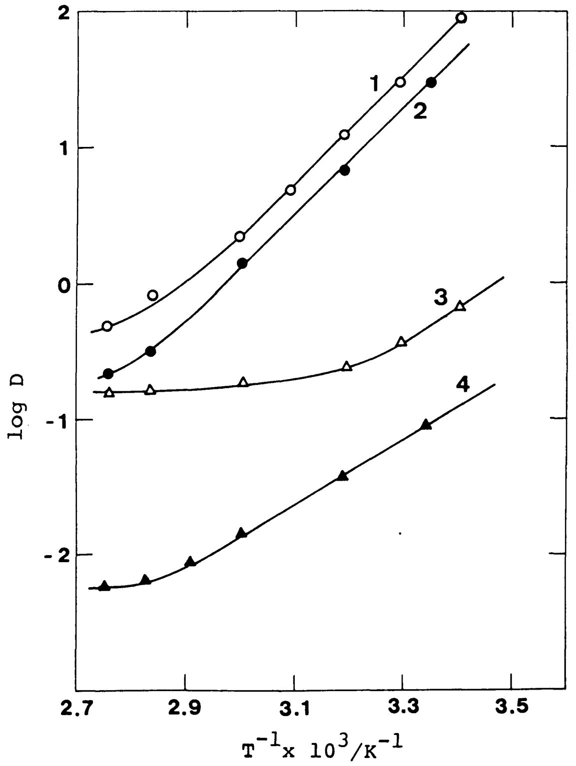

Fig. 6. Effects of temperature on the distribution ratio of zinc and cadmium with 8-quinolinol between TCE and water.
pH 5.0, 1; Zn, NaClO$_4$ system, $[HQ]_o=2\times10^{-2}$ M, 2; Cd, NaClO$_4$ system, $[HQ]_o=10^{-1}$ M, 3; Zn, NaCl system, $[HQ]_o=2\times10^{-2}$ M, 4; Cd, NaCl system, $[HQ]_o=10^{-1}$ M.

Extraction of Zinc and Cadmium with 2-Methyl-8-quinolinol into TCE in the Presence of Several Inorganic Anions. Since the chemical nature of 2-methyl-8-quinolinol is similar to that of 8-quinolinol, a large difference in the extraction behaviors of metal ions between both the ligands is not observed in most cases. In some cases, however, the structures of complexes with 2-methyl-8-quinolinol are quite different from those with 8-quinolinol, probably due to a steric hindrance effect of the methyl group, although this is debatable.[19]

The extraction of zinc and cadmium with 2-methyl-8-quinolinol into TCE in the presence of perchlorate and chloride ions was studied at various temperatures for a comparison with that with 8-quinolinol.

Plots of $\log D$ vs. variables such as pH, the concentrations of 2-methyl-8-quinolinol and concentrations of inorganic anions were obtained in order to determine the stoichiometry of the extracted species. The slopes of $\log D$ vs. pH, $\log D$ vs. $\log[\mathrm{HR}]_o$ and $\log D$ vs. $\log[\mathrm{X}^-]$ are 1.5, 3, and 0.5, respectively. Additionally, plots of $\log D$ vs. $\log[\mathrm{Cd}]_T$ are constant in the cadmium concentration range 10^{-6} M to 10^{-4} M. Therefore, the extraction behavior of the cadmium chelate of 2-methyl-8-quinolinol into TCE is similar to those of zinc and cadmium chelates of 8-quinolinol into TCE.

Hence, the extraction equation can be given as

$$2\mathrm{Cd}^{2+} + 6\mathrm{HR}_{(o)} + \mathrm{X}^- \rightleftarrows \mathrm{Cd}_2\mathrm{R}_3(\mathrm{HR})_3{}^+{}_{(o)} + \mathrm{X}^-{}_{(o)} + 3\mathrm{H}^+. \quad (10)$$

The extraction behavior of zinc-2-methyl-8-quinolinol chelate into TCE is unlike the case of cadmium. The slopes of $\log D$ vs. pH are 2 at each temperature. The plots of $\log D$ vs. $\log[\mathrm{HR}]_o$ at a constant pH are linear with a slope of 2. The distribution ration of zinc are uneffected by the kind of inorganic anion involved. Thus, it can be concluded that only a single species, the simple 1 : 2 chelate, ZnR_2, is present in TCE. The overall raction can be represented by

$$\mathrm{Zn}^{2+} + 2\mathrm{HR} \rightleftarrows \mathrm{ZnR}_2 + 2\mathrm{H}^+. \quad (11)$$

In Fig. 7, the values of $\log D$ at pH 5.5 are plotted against the reciprocal of temperature for zinc and cadmium. In the case of cadmium, the distribution ratios decrease remarkably with an increase in temperature for perchlorate and chloride. The trend is similar to those of zinc and cadmium chelates of 8-quinolinol into TCE. However, in the case of zinc, the distribution ratios increase with an increase in temperature. The opposite effect is noted in the cases of cadmium and zinc with 8-quinolinol. These results indicate that the difference in distribution ratios of zinc and cadmium can be enhanced at high temperatures. Hence, solvent extraction with 2-methyl-8-quinolinol at high temperatures can be applied to the separation of zinc and cadmium in aqueous samples.

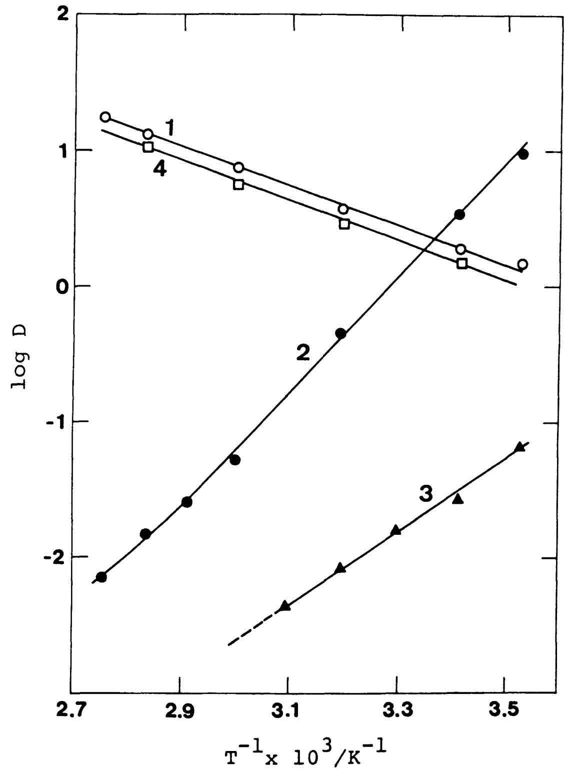

Fig. 7. Effects of temperature on the distribution ratio of zinc and cadmium with 2-methyl-8-quinolinol between TCE (or *p*-xylene) and water. pH 5.5, solvent=TCE, 1; Zn , $[\mathrm{HR}]_o = 5\times10^{-2}$ M, 2; Cd, $\mathrm{NaClO_4}$ system, $[\mathrm{HR}]_o = 10^{-1}$ M, 3; Cd, NaCl system 4; solvent=*p*-xylene, Zn, $[\mathrm{HR}]_o = 2\times10^{-1}$ M.

The principal difference between 8-quinolinol and 2-methyl-8-quinolinol in the extraction of zinc into TCE is that the former forms a self-adduct complex whereas the latter forms a simple 1 : 2 complex. In the case of cadmium, both the ligands form self-adduct complexes, probably because the ionic radius of cadmium (0.97 Å) is larger than that of zinc (0.74 Å).

Extraction of Zinc and Cadmium with 8-Quinolinol and 2-Methyl-8-quinolinol into *p*-Xylene. In the 8-quinolinol extraction system, the precipitation of zinc and cadmium chelates occur even in the low-pH range. Therefore, a detailed investigation concerning the temperature effects was omitted. The total γ-activities of $^{65}\mathrm{Zn}$ in both the aqueous and organic phases suddenly decrease above pH 4.5 after 10 min of shaking. At pH 5.0, about 20% of zinc disappears after 1 min of shaking, and almost all zinc in both phases disappears after 20 min of shaking. These phenomena indicate that the hydrated chelate $\mathrm{ZnQ_2 \cdot 2H_2O}$ may precipitate and be deposited at the interface of both phases.

In the 2-methyl-8-quinolinol extraction system, no zinc in either phase disappears. This indicates that the 2-position methyl group not only interrupts the formation of a self-adduct complex of zinc, but also makes the dehydration of the zinc chelate easy. The extraction of zinc with 2-methyl-8-quinolinol into *p*-

xylene was evaluated by a slope analysis. The results showed that the zinc chelate of 2-methyl-8-quinolinol is extracted into *p*-xylene as a simple 1:2 complex, ZnQ_2, similar to the case of the extraction of the zinc chelate of 2-methyl-8-quinolinol into TCE. The distribution ratios increase with an increase in temperature, as shown in Fig. 7. Similar effects are noted in zinc extraction with 2-methyl-8-quinolinol into TCE.

Extraction of Zinc and Cadmium with 8-Quinolinol or 2-Methyl-8-quinolinol into 1-Octanol. According to the report of Schweitzer et al.,[1)] when 1-butanol is used as an extracting solvent, the zinc chelate of 8-quinolinol is extracted as a solvent-adduct compound, $ZnQ_2 \cdot S_2$ (S is an alcohol molecule). In the case of a 1-octanol extraction system, the extraction mechanism of zinc and cadmium with 8-quinolinol or 2-methyl-8-quinolinol is similar to the case of 1-butanol. The slopes of $\log D$ vs. $\log[\mathrm{HQ}($ or $\mathrm{HR})]_o$ exhibit a linear range with a slope of 2. Additionally, the plots of $\log D$ vs. $\log[\mathrm{S}]_o$, when 1-octanol is dissolved in hexane, give a straight line of slope 2. These results suggest that the extracted species in octanol is a solvent-adduct compound, $MQ_2 \cdot S_2$ or $MR_2 \cdot S_2$. Temperature effects on the distribution ratios of zinc and cadmium with 8-quinolinol and 2-methyl-8-quinolinol are shown in Fig. 8. The distribution ratios are almost constant with a change in temperature.

Thermodynamic Parameters. The thermodynamic parameters for the distribution of 8-quinolinol[6)] and 2-methyl-8-quinolinol between organic solvents and water are listed in Table 1. The values of $\log K_{\mathrm{DR}}$ (K_{DR} is the distribution constant of reagent) for TCE, which have not been reported, are of a similar order to those for chloroform.[20,21)] In all cases the ΔH values are negative and the ΔS values are positive. Hence, the fact that 8-quinolinol and 2-methyl-8-quinolinol are more soluble in organic solvents such as TCE, *p*-xylene, and 1-octanol than in water is due to the favorable contributions of both enthalpy and entropy. All the values of ΔH for the distribution processes of 8-quinolinol and 2-methyl-8-quinolinol are smaller than the values of the hydrogen-bond energy (10 to 25

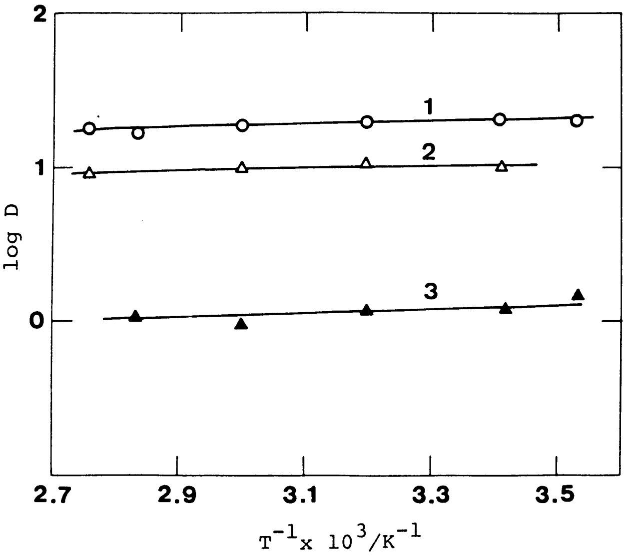

Fig. 8. Effects of temperature on the distribution ratio of zinc and cadmium between 1-octanol and water.
1; Zn, 8-quinolinol, $[\mathrm{HQ}]_o=10^{-2}$ M, 2; Zn, 2-methyl-8-quinolinol, $[\mathrm{HR}]_o=5\times10^{-2}$ M, 3; Cd, 2-methyl-8-quinolinol, $[\mathrm{HR}]_o=5\times10^{-2}$ M.

Table 1. Thermodynamic Values for the Distribution of 8-Quinolinol and 2-Methyl-8-quinolinol between Organic Solvents and Water at 20 °C

Ligand	Solvent	$\log K_{\mathrm{DR}}$	ΔG kJ mol^{-1}	ΔH kJ mol^{-1}	ΔS J K^{-1} mol^{-1}
8-Quinolinol	TCE	2.64	−14.8	−5.02	33.5
	p-Xylene	2.09	−11.7	−4.18	25.5
	1-Octanol	1.94	−10.9	−3.35	25.9
2-Methyl-8-quinolinol	TCE	3.15	−17.7	−9.10	29.4

Table 2. Thermodynamic Values for Extraction of Zn(II) with 8-Quinolinol and 2-Methyl-8-quinolinol into TCE, *p*-Xylene, and 1-Octanol at 20 °C

Ligand	Solvent	Species	$\log K_{\mathrm{ex}}$	ΔG kJ mol^{-1}	ΔH kJ mol^{-1}	ΔS J K^{-1} mol^{-1}
8-Quinolinol	TCE	$Zn_2Q_3(HQ)_3^+ClO_4^-$	−0.66	3.70	−153	−535
	TCE	$Zn_2Q_3(HQ)_3^+Cl^-$	−4.70	26.4	−95.4	−416
	p-Xylene	Precipitated	—	—	—	—
	1-Octanol	$ZnQ_2 \cdot S_2$	—	—	≃0	—
2-Methyl-8-quinolinol	TCE	ZnR_2	−8.10	45.4	33.5	−40.6
	p-Xylene	ZnR_2	−9.42	52.8	33.5	−65.9
	1-Octanol	$ZnR_2 \cdot S_2$	—	—	≃0	—

Table 3. Thermodynamic Values for Extraction of Cd(II) with 8-Quinolinol and 2-Methyl-8-quinolinol into TCE, *p*-Xylene, and 1-Octanol at 20 °C

Ligand	Solvent	Species	$\log K_{ex}$	ΔG	ΔH	ΔS
				kJ mol^{-1}	kJ mol^{-1}	J K^{-1} mol^{-1}
8-Quinolinol	TCE	$Cd_2Q_3(HQ)_3^+ClO_4^-$	−5.57	31.2	−169	−683
	TCE	$Cd_2Q_3(HQ)_3^+Cl^-$	−10.33	58.0	−108	−567
	p-Xylene	Precipitated	—	—	—	—
	1-Octanol	$CdQ_2\cdot S_2$	—	—	≃0	—
2-Methyl-8-quinolinol	TCE	$Cd_2R_3(HR)_3^+ClO_4^-$	−8.92	50.0	−163	−727
	TCE	$Cd_2R_3(HR)_3^+Cl^-$	−13.27	74.4	−106	−616
	p-Xylene	precipitated	—	—	—	—
	1-Octanol	$CdR_2\cdot S_2$	—	—	≃0	—

kJ mol^{-1}).

The thermodynamic parameters for the extraction of zinc and cadmium with 8-quinolinol and 2-methyl-8-quinolinol into TCE, *p*-xylene, and 1-octanol are summarized in Tables 2 and 3.

In a series of the ion-associated complexes of zinc and cadmium, the values of ΔH are largely negative, which shows that the extraction of the complex ion pair is an exothermic reaction. The order of their ΔH values correlates with their extractability. Thus, the larger is the size of an inorganic anion or metal ion, the larger is the absolute values of ΔH. The values ΔS are also largely negative and proportional to those of ΔH in the ion-associated complex series of metals and inorganic anions. This is generally the trend observed in the thermodynamics of ion-pair extraction, indicating that the exothermic property is partly compensated with the term of ΔS. The values of ΔH for the extraction of cadmium with 2-methyl-8-quinolinol are similar to those of cadmium with 8-quinolinol in the presence of perchlorate and chloride. The extraction mechanism of cadmium with 2-methyl-8-quinolinol is similar to that of cadmium with 8-quinolinol.

The extraction of zinc with 2-methyl-8-quinolinol into TCE and *p*-xylene is an endothermic reaction, unlike the extraction of zinc with 8-quinolinol into TCE. It has been reported that this behavior is characteristic of chelating reactions in which the water molecules of the inner-coordination sphere of the metal ion are displaced by the chelating reagent.[22] The extraction constant (K_{ex}) of zinc with 2-methyl-8-quinolinol into TCE and *p*-xylene is a composite of the chelate formation constant, β_2, and its distribution constant, K_{DC}, as well as of the reagent acid-dissociation constant, K_a, and its distribution constant, K_{DR}: $K_{ex}=\beta_2 K_{DC} K_a^2/K_{DR}^2$. β_2 and K_a are independent of the organic solvent. Therefore, the difference in the extraction constant between TCE and *p*-xylene can be related to the difference in the product, $K_{DC}K_{DR}^{-2}$. The values of ΔH for extraction constants are both 33.5 kJ mol^{-1} for TCE and *p*-xylene. It is conceivable that the difference in the ΔH values for the distribution coefficients of 2-methyl-8-quinolinol between TCE and *p*-xylene would be small, since the difference in the ΔH values for those of 8-quinolinol between both the solvents is also small (Table 1). Therefore, it is considered that the value of ΔH for the distribution constant of the zinc chelate with 2-methyl-8-quinolinol into TCE is almost the same as that into *p*-xylene. This means that the distribution of ZnR_2 into the organic phase is controlled by its own dehydration. The minute difference in the ΔG values between the TCE and *p*-xylene system is attributed to the ΔS term, probably due to the solvent-adduct ability of TCE with zinc chelates. The ΔH values for solvent-adduct systems are quite small, being close to zero.

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