TEMPERATURE EFFECTS ON THE SOLVENT EXTRACTION OF METAL CHELATES (II) ZINC AND CADMIUM CHELATES OF 8-QUINOLINOL

By

Eiichiro NAKAYAMA

Instrumental Analysis Research Center, Faculty of Science, Kyoto University, Kyoto

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ABSTRACT

The distribution behavior of zinc chelate of 8-quinolinol has been investigated concerning three different types of organic solvents over the temperature range of 20° to 90°C. It has been proved that the degree of temperature effect on the distribution ratio of zinc largely depends on the extraction mechanism. In the TCE (1,1,2,2,-tetrachloroethane) extraction system a new type of extraction mechanism has been found out and an interesting effect of temperature has been observed. Further cadmium has been similarly examined in TCE for the comparison with zinc.

1. Introduction

In the previous paper by the author[1] it has been shown that the thermodynamic properties of the distribution equiliburium of 8-quinolinol is vrey similar to that of its copper chelate in several organic solvents, and that the transfer of both reagent and chelate from the aqueous phase to the organic phase is accompanied by a small negative enthalpy change. The aim of the present work is to investigate the zinc chelate of 8-quinolinol in the same way and to clarify the distribution mechanism.

In earlier work, Schweitzer et al.[2] suggested that the composition of the extracted zinc chelate of 8-quinolinol is different depending on the solvent used in the extraction. Recently it was discovered that when zinc was extracted with 8-quinolinol into chloroform, it formed a binuclear complex with a large anion such as perchlorate in the aqueous phase by Oki[3] and Sekido and others[4],[5]. In this study the temperature effect on the distribution behavior of the zinc chelate of 8-quinolinol between water and several organic solvents have been examined with respect to the extraction mechanism. The organic solvents used were TCE (1,1,2,2,-tetrachloroethane), p-xylene and 1-octanol similarly as in the previous study[1].

Cadmium Chelate of 8-quinolinol was similarly examined in TEC for the comparison with zinc, since TCE had been found to have interesting properties as an extracting solvent.

2. Experimental

Reagent and Apparatus; All of the chemicals and apparatus used were essentially the same as previously described with the exception that ^{65}Zn was supplied by

the Japan Radio-isotope Association.

Procedure;　The extraction procedure was also essentially the same as previously described.　The concentration of cadmium was determined with an atomic absorption spectrometer as copper was in the previous paper.　However the concentration of zinc was determined by measuring the γ-radio-activity of aliquots of both phases with a single-channel pulse-hight analyser (Osaka Denpa Model LA-3T).

3.　Results and Discussion

3-1　Extraction of zinc chelate of 8-quinolinol into TCE in the presence of various inorganic anions.

It was anticipated that the distribution ratio of zinc would depend on the total concentration of zinc when its concentration was sufficiently high as has been observed in chloroform[3] because TCE is very similar to chloroform in structure.　In order to avoid complicating effects of temperature on the equilibrium that is the origin of this phenomenon, the total concentration of zinc was kept less than 10^{-6}M. And under this experimental condition, it was found that the distribution ratio of zinc is almost independent of the concentration of zinc as is later described.

It had been also expected that the zinc chelate would precipitate in TCE under the same conditions as it precipitates in chloroform.　After through the investigations using γ-activities of ^{65}Zn as zinc tracer, it was found that in the high pH range the concentration of zinc in both the phases decreased after extraction pro-
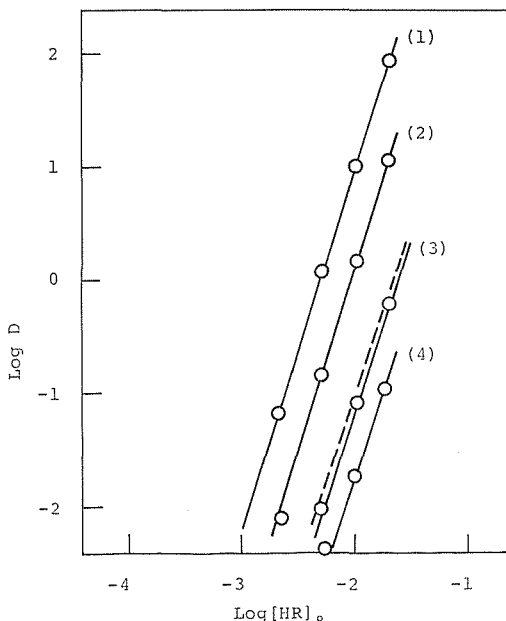

Fig. 1.　Effect of the 8-Quinolinol Concentration on the Distribution Ratio of Zinc
between TCE and Water in the Presence of Various Inorganic Anions
pH 5.0, $[Zn]_T = 10^{-6}$ M, 0.09N salts+0.01M (AcOH-AcONa buffer)
(1) NaClO$_4$ (2) NaNO$_3$ (3) NaCl (---AcOH-AcONa) (4) Na$_2$SO$_4$

cedure due to the precipitation of chelate on the glass walls or at the phase inter-face, on the other hand little decreased in the low pH ranges below pH 5.5.   There-fore all the extraction experiments thereafter were performed at pH 5.0 or below.

Four types of plots were analyzed to decide the composition of zinc chelate under various conditions; logD versus log $[HR]_0$, logD versus pH, logD versus log $[X^-]$ and logD versus log $[Zn]_T$ at constant values of all the other factors respec-tively.   Here D is the distribution ratio of zinc, $[HR]_0$ the concentration of 8-qui-nolinol in the organic phase, $[X^-]$ the concentration of inorganic anions in the aque-ous phase and $[Zn]_T$ the total concentration of zinc, respectively.

In Fig. 1 values of logD at pH 5.0 for several inorganic anions are plotted against the log $[HR]_0$.   The broken line curve shows the results with an acetic acid-acetate buffer solution used to adjust the pH of the aqueous phase to 5.0.   It seems that three 8-quinolinol (or 8-quinolinolate, R^-) molecules combine with one zinc molecule in these extraction system, since all the curves make slopes of 3.   The order of the distribution ratio is perchlorate>nitrate>chloride>sulphate, the larger the anion, the more readily the zinc chelate is extracted.

Figs. 2~5 show the relationship between logD and log $[HR]_0$ at various temper-atures for each anion.   For the perchlorate system as shown in Fig. 2 the curves make slopes of exactly 3 at each temperature.   And for the nitrate system in Fig. 3, the curves also make slopes of 3 up to fairly high temperatures.   But it is observed at 80°C the slope becomes slightly less than 3, the decrease of the slope with rise in the temperature is more for the chloride system as shown in Fig. 4.   At 80°C, the slope of the curve is nearly down to 2.   Moreover the extreme tendency is ob-served for the sulphate system in Fig. 5.   In this system, the slopes of the curves
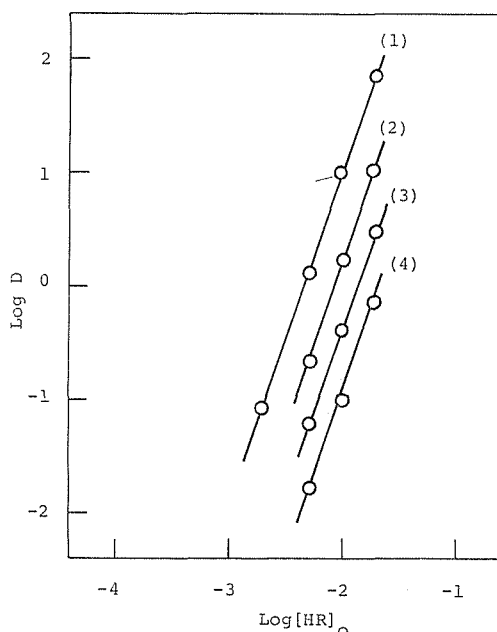

Fig. 2.   Effect of the 8-Quinolinol Concentration on the Distribution Ratio of Zinc
between TCE and Water in the Presence of Perchlorate
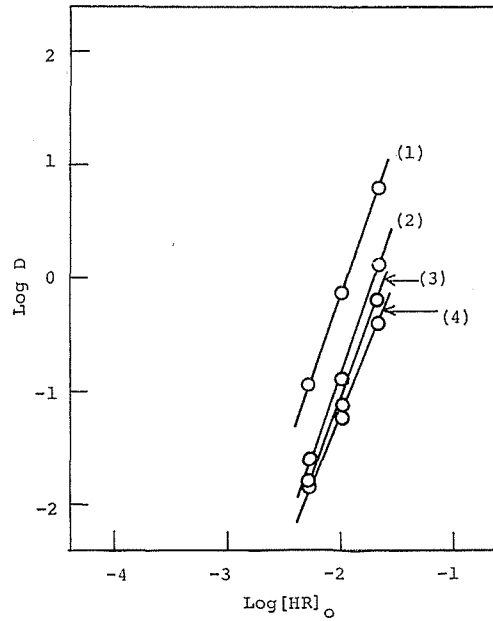pH 5.0, (1) 20°C (2) 40°C (3) 60°C (4) 80°C

Fig. 3. Effect of the 8-Quinolinol Concentration on the Distribution Ratio of Zinc
between TCE and Water in the Presence of Nitrate
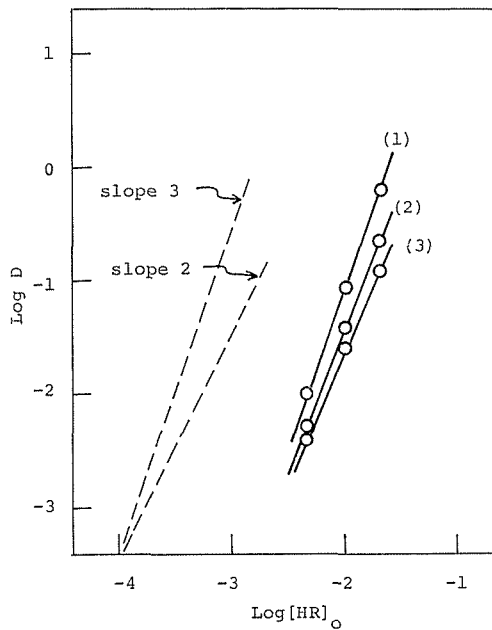pH 5.0, (1) 20 °C (2) 40 °C (3) 60 °C (4) 80 °C

Fig. 4. Effect of the 8-Quinolinol Concentration on the Distribution Ratio of Zinc
between TCE and Water in the Presence of Chloride
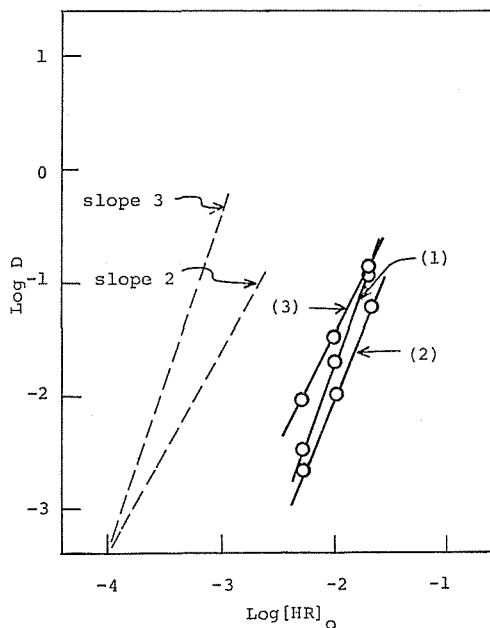pH 5.0, (1) 20 °C (2) 40 °C (3) 80 °C

Fig. 5.   Effect of the 8-Quinolinol Concentration on the Distribution ratio of Zinc
between TCE and Water in the Presence of Sulphate
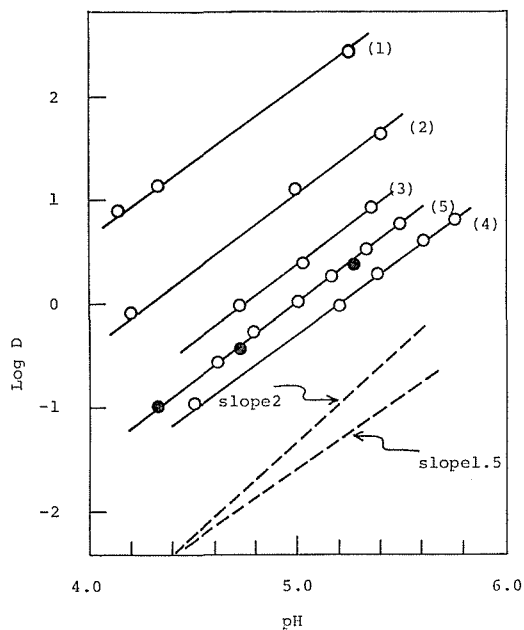pH 5.0, (1) 20°C (2) 40°C (3) 80°C

Fig. 6.   Effect of pH on the Distribution Ratio of Zinc between TCE and Water
(1)~(4); $NaClO_4$ system, $[HR]_0 = 2 \times 10^{-2}$ M (1) 20°C (2) 40°C (3) 60°C (4)
80°C   (5) $NaClO_4$ system, $[HR]_0 = 5 \times 10^{-3}$ M, 25°C   (●) NaCl system, $[HR]_0$
$= 2 \times 10^{-2}$ M, 20°C

drop from 3 to nearly 2 above 40°C.   It is considered that two 8-quinolinol mo-
lecules combine with one zinc molecule in the chelate when the curves show slopes
of 2.   Therefore two types of chelates are extracted into the organic phase in these
extraction systems and a chelate whose composition is ZnR_2 is predominant zinc
species in the organic phase at high temperatures for the chloride and sulphate
systems.

The curves in Fig. 6 show the relationship between logD and pH at various
temperatures.   Scweitzer[2] and Freiser and others[6] reported that this curve makes
a slope of 2 in the case of chloroform.   However, in the case of TCE the curves
have slopes of 1.5 for the perchlorate system in the temperature range of 20 to 80°C,
curves (1)~(4) also hold for a different concentration of 8-quinolinol, curve (5)
and for the chloride system at 20°C shown by black points.   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-quinolinolate and one and hlaf molecules of hydrogen ions apparently combine
with one zinc molecule.

In Fig. 7 values of logD are plotted against log [X⁻].   In the perchlorate and
nitrate systems, the slopes of curves (1) and (2) are equally 0.5 at pH 5.0.   This
phenomenon is not accidentally so at pH 5.0, but holds at a different pH.   It
seems that half a molecule of anion apparently attaches itself to one zinc molecule
in these systems.

The curves in Fig. 8 show the relationship between logD and log $[Zn]_T$ in the
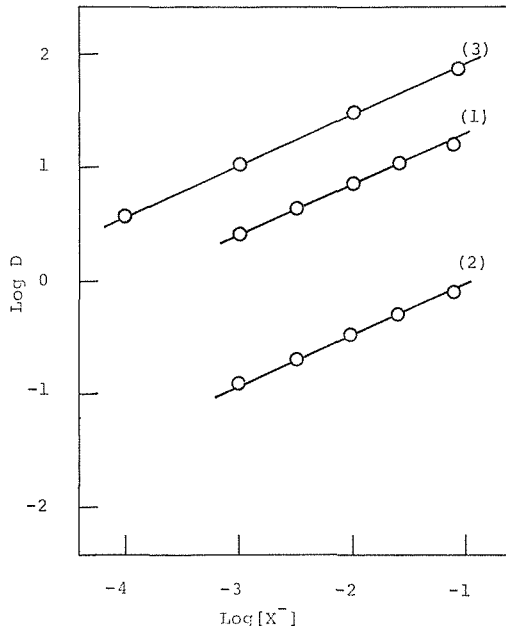

Fig. 7.   Effect of the Concentration of Inorganic Anions on the Distribution Ratio
of Zinc between TCE and Water
(1) $NaClO_4$ system, $[HR]_0 = 10^{-2}$ M, pH 5.0, 20 °C
(2) $NaNO_3$ system, $[HR]_0 = 10^{-2}$ M, pH 5.0, 20 °C
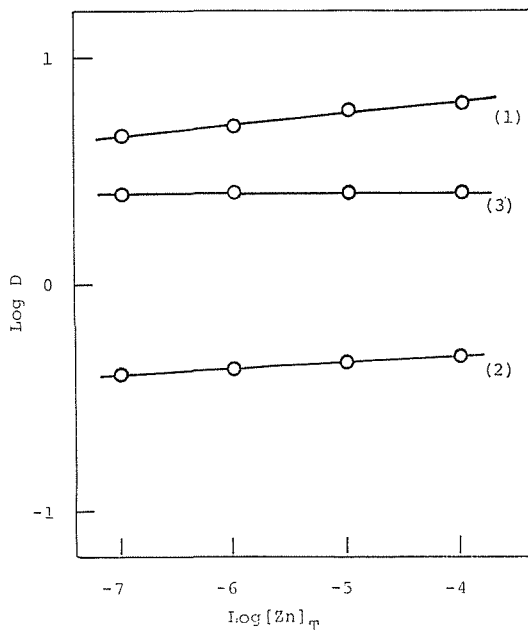(3) $NaClO_4$ system, $[HR]_0 = 10^{-1}$ M, pH 3.8, 20 °C

Fig. 8.   Effect of the Metal Concentration on the Distribution Ratio of Zinc between
TCE and Water
(1) $NaClO_4$ system, pH 4.0, $[HR]_0 = 2 \times 10^{-2}$ M
(2)   NaCl system, pH 4.8, $[HR]_0 = 2 \times 10^{-2}$ M
(3)   Pyridine adduct system, pH 6.0, $[HR]_0 = 10^{-3}$ M, $[Py]_0 = 2 \times 10^{-1}$ M

perchlorate and chloride systems.   The curves make slopes of nearly 0, but the logD values increase only slightly as the concentration of zinc increases as shown by curves (1) and (2).   The fact that logD value 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[3].   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 $ZnR_3H_{3/2}X_{1/2}$ from above results,

$$Zn_2R_6H_3X_{(0)} \rightleftharpoons ZnR_3H_2^+{}_{(0)} + ZnR_3HX^-{}_{(0)}$$

where subscript O indicates the species existing in the organic phase.
      Then if the binuclear complex would almost dissociate in the organic phase as follows,

$$Zn_2R_6H_3X_{(0)} \rightleftharpoons Zn_2R_6H_3^+{}_{(0)} + X^-{}_{(0)} \tag{1}$$
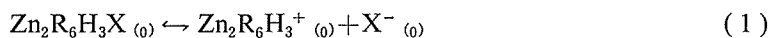
the distribution ratio of zinc between organic and aqueous phases is given by following equation when the solution is acidic, because the simple zinc ion is the predominant zinc species in the aqueous phase.

$$D = \frac{2[Zn_2R_6H_3^+]_0}{[Zn^{2+}]} \tag{2}$$

The extraction equation can be written as follows,

$$2Zn^{2+}+6HR_{(o)}+X^- \leftrightharpoons Zn_2R_6H_3^+{}_{(o)}+X^-{}_{(o)}+3H^+ \tag{3}$$
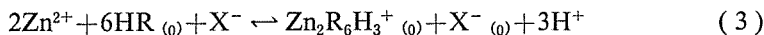
and the extraction constant K_{ex} is given as follows.

$$K_{ex}=\frac{[Zn_2R_6H_3^+]_0[X^-]_0[H^+]^3}{[Zn^{2+}]^2]HR]_0^6[X^-]} \tag{4}$$

The concentration of cation and anion in the organic phase must be equal to each other taking into account the electrical neutrality, $[Zn_2R_6H_3^+]_0=[X^-]_0$ therefore equation (4) can be written as follows.

$$K_{ex}=\frac{[Zn_2R_6H_3^+]^2[H^+]^3}{[Zn^{2+}]^2[HR]_0^6[X^-]} \tag{5}$$

Introducing equation (5) into equation (2) following expression is derived.

$$D=2K_{ex}^{1/2}[HR]_0^3[H^+]^{-3/2}[X^-]^{1/2} \tag{6}$$

or,

$$\log D=\frac{1}{2}\log K_{ex}+\log 2+3\log[HR]_0+\frac{3}{2}pH+\frac{1}{2}\log[X^-] \tag{6'}$$

This equation means that a plot of $\log D$ against $\log [HR]_0$ gives a slope of 3, a plot of $\log D$ against pH gives a slope of 1.5 and a plot of $\log D$ against $\log[X^-]$ gives a slope of 0.5. Thus the assumption that the binuclear complex would dissociate in the organic phase as shown in equation (1) agrees well with the experimental results. However it is considered that only a small amount of associated binuclear complex exists in the organic phase because $\log D$ values increase slightly as the concentration of zinc increases. If only one species would exist in the organic phase $\log D$ values were completely independent of concentration of zinc as observed in the pyridine adduct system, curve (3) in Fig. 8. In this system only one species ZnR_2Py (Py=pyridine) exists in the organic phase as is later described.

In Fig. 9 values of $\log D$ at pH 5.0 are plotted against the reciprocal of temperature for the four anions. The larger the size of anion, the steeper is the slope of $\log D$ versus $1/T$. The curve for the perchlorate system is linear up to about 70°C, for the nitrate system the curve is linear up to about 60°C and the curves in the chloride and sulphate systems are linear only up to about 40°C. The slope of $\log D$ versus $1/T$ decreases rapidly at low temperature and only mildly in the high temperature range, but in the sulphate system $\log D$ decreases slowly at low temperature and even increases as the temperature rises above 60°C.

The results agree well with the fact that the dissociation of an ionic associated compound increases greatly in a highly polar solvent with a rise in temperature but does not increase in a low polar solvent. It is considered that the dissociation of zinc chelate in the aqueous phase increases remarkably as the temperature rises on the other hand the disosciation is less in the organic phase, since the dielectric constants of water and TCE are 80 and 8.2 (at 20°C) respectively. Consequently $\log D$ values decrease considerably as the temperature rises, especially in the presence of perchlorate which forms an extractable ion-associated compound.

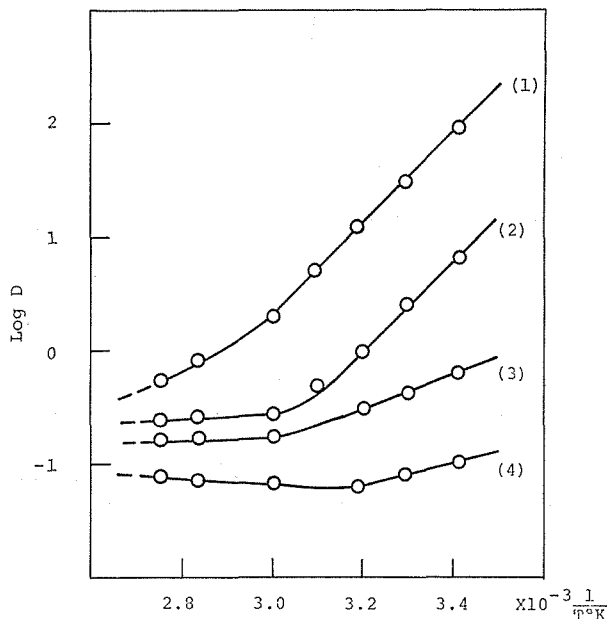The change of the slope of $\log D$ vs. $1/T$ at high temperature range can be ex-

Fig. 9. Temperature Effect on the Distribution Ratio of Zinc betweem TCE and Water
pH 5.0, $[HR]_0 = 2 \times 10^{-2}$ M
(1) NaClO$_4$ system, (2) NaNO$_3$ system, (3) NaCl system, (4) Na$_2$SO$_4$ system

plained as follows.

In these extraction systems a small amount of anhydrous chelate ZnR$_2$ is usually extracted besides the binuclear complex. And the extraction of this chelate may be not so hardly affected by the temperature as the binuclear complex does because its composition is similar to copper chelate CuR$_2$. Therefore logD values become independent of the temperature when the concentration of the binuclear complex decreases at high temperature and ZnR$_2$ becomes the predominant species in the organic phase.

When pyridine is introduced into these systems as an adduct-forming agent, the distribution equilibrium becomes independent of the inorganic anions in the aqueous phase and the effect of temperature becomes negligibly small. Therefore logD in the pyridine adduct system changes little when the temperature rises from 20 to 60°C. In the case of chloroform mixed with pyridine, the distribution ratio D in the acidic range can be expressed by the following equation,

$$\log D = \log K'_{ex} + 2\log[HR]_0 + 2pH + \log[Py]_0 \qquad (7)$$

where $[Py]_0$ is the concentration of pyridine in the organic phase and $K'_{ex} = K'_c K_a^2 P'_c P_r^{-2} K_{ad}$ (K'_c is the aqueous formation constant of ZnR$_2$, K_{ad} is the organic adduct formation constant, P'_c is the partition coefficient of ZnR$_2$ and the other symbols are the same as described above. This same relation also holds in the case of TCE mixed with pyridine.

3–2   Extraction of the zinc chelate of 8-quinolinol into 1-octanol and p-xylene;

According to the report of Schweitzer et al.[2], if an alcohol is used as an extract-

ing solvent, the zinc chelate of 8-quinolinol is extracted as a solvent-adduct compound with two attached molecules of alcohol, ZnR_2S_2 (S is an alcohol). In the case of 1-butanol, the distribution ratio D in the acidic range where Zn^{2+} is predominant zinc species in the aqueous phase was can be expressed.

$$logD=logK''_{ex}+2log[HR]_0+2pH \qquad\qquad (8)$$

where $K''_{ex}=K''_cK^2_aP''_cP^{-2}_r$ (K''_c and P''_c in the expression are practically the same as K'_c and P'_c since the concentration of the solvent does not appear in the equation.) It is also confirmed that this same relation holds in the case of 1-octanol.

In Fig. 10 values of logD at pH 5.0 are plotted against the reciprical of temperature in the 1-octanol extraction. In this system, logD decreases slightly as the temperature rises. As well, no appreciable difference is observed in the distribution ratio when sodium chloride is substituted for sodium perchlorate to adjust the ionic strength in the aqueous solution to 0.1.

In the *p*-xylene extraction system, the precipitation of zinc chelate occurs even in the low pH range. Therefore a detail investigation about temperature effects was ommited for this system. Fig. 11 shows that the total γ-activities of ^{65}Zn in both the aqueous and organic phases suddenly decrease above pH 4.5 after 10 min. of shaking. Fig. 12 also shows that the total γ-activities disappear in both phases after a short shaking time. These phenomena indicate that hydrated zinc chelate $ZnR_2 \cdot 2H_2O$ may precipitate and deposit at the interface of both the phases.

This surface adsorption has been observed in the solid-liquid separation after liquid-liquid extraction in which biphenyl is used as a molten solvent at 80°C. Fig. 13 shows the apparent distribution ratio as a function of pH in the biphenyl extraction system. Although zinc is fairly well extracted into the organic phase in the neutral
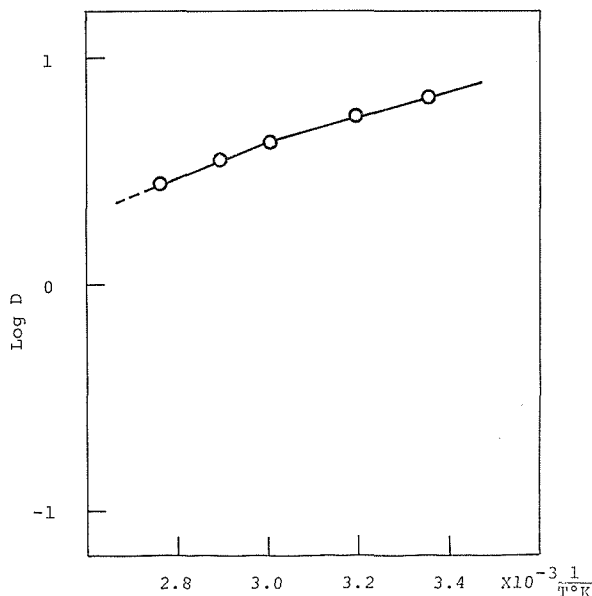

Fig. 10. Temperature Effect on the Distribution Ratio of Zinc between 1-Octanol and Water
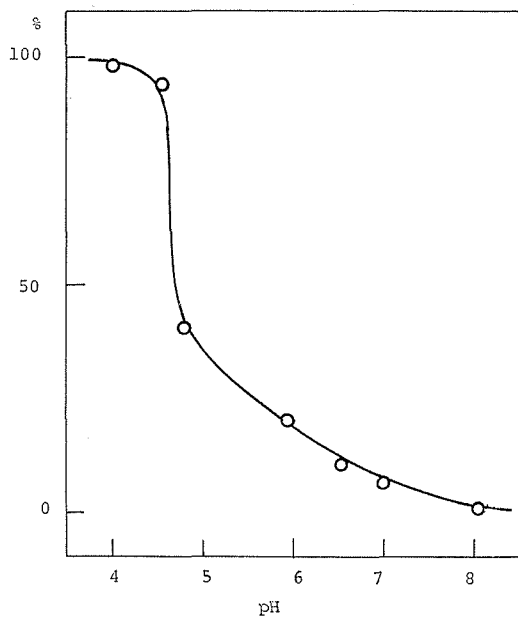pH 5.0, $[HR]_0=2 \times 10^{-2}$ M

Fig. 11.   Relationship between Total Concentration of Zinc in the Both Phases and
pH in the p-Xylene Extraction System
$[HR]_0 = 10^{-1}$ M, $[Zn]_T = 10^{-5}$ M, 28 °C, shaking time; 10 min., ionic strength;
0.1
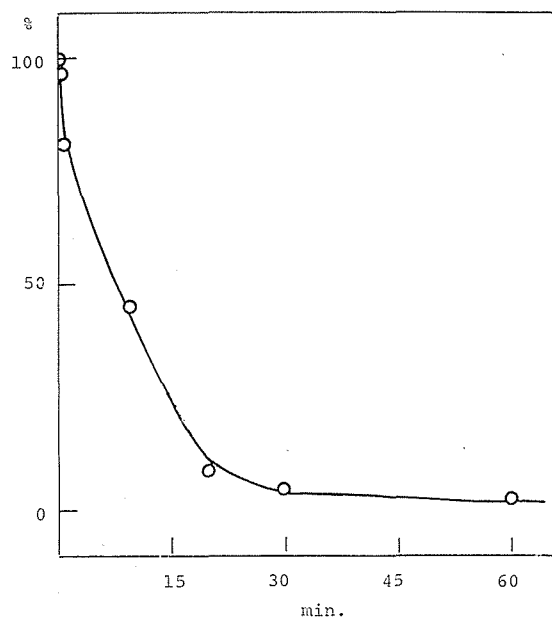

Fig. 12.   Relationship between Total Concentration of Zinc in the Both Phases and
the Shaking Time in the p-Xylene Extraction System
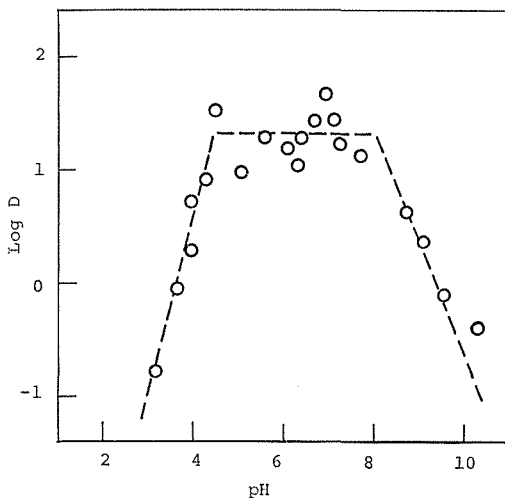pH 5.0, $[HR]_0 = 10^{-1}$ M, $[Zn]_T = 10^{-5}$ M, 28 °C, ionic strength; 0.1

Fig. 13. Relationship between Distribution Ratio of Zinc and pH in the Biphenyl
Extraction System
$[HR]_0 = 10^{-1}$ M, $[Zn]_T = 10^{-5}$ M, 80°C ionic strength; 0.1

pH range, the logD values are not reproducible and widely scattered. Since the phases are separated in this method after the organic phase is solidified, the precipitated chelate is adsorbed at the surface of the organic phase resulting in extremely high distribution in the organic phase. The γ-activities is extremely high at the surface and very low at the inside. Since p-xylene and biphenyl have little adduct-forming ability and their dielectric constants are very low, being 2.3 (at 20°C) and 2.5 (at 75°C) respectively, a solvent-adduct or an ion-associated compound cannot be formed in the organic phase and hence zinc is not extracted quantitatively into these solvents.

3-3 Extraction of cadmium chelate of 8-quinolinol into TCE in the presence of some inorganic anions.

The extraction behavior of cadmium chelate in TCE extraction system is very similar to that of zinc chelate. The binuclear complex also dissociates in the organic phase as follows,

$$Cd_2R_6H_3X_{(0)} \rightleftharpoons Cd_2R_6H_3^+{}_{(0)} + X^-{}_{(0)}$$
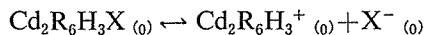
because the curves in Figs. 14, 15 and 16 give the same slopes as the case of zinc; the plot of logD against log $[HR]_0$ gives the slope of 3, the plot of logD against pH gives the slope of 1.5 and the plot of logD against log $[X]^-$ gives the slope of 0.5.

In Fig. 17, values of logD at pH 5.0 are plotted for perchlorate and chloride systems against the reciprocal of temperature. Different from the case of zinc cheleate the curves are linear up to fairly high temperatures even for the chloride system. It is thought that cadmium forms a more extractable ion-associated compound than zinc, on the other hand the aqueous formation constant of cadmium chelate of 8-quinolinol is lower than that of zinc because the ionic radius of cadmium is larger than zinc.
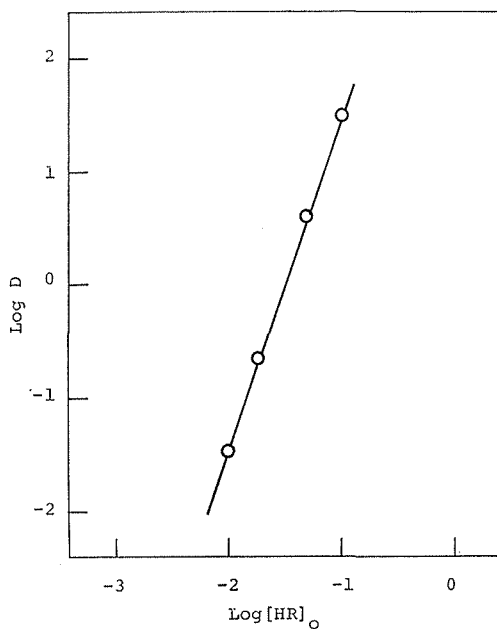
Fig. 14.   Effect of the 8-Quinolinol Concentration on the Distribution Ratio of
Cadmium between TCE and Water in the Presence of Perchlorate
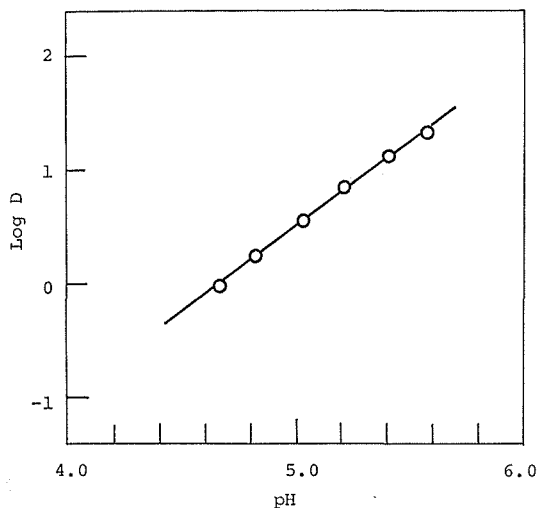pH 5.0, $[Cd]_T = 5 \times 10^{-6}$ M, 20 °C

Fig. 15.   Effect of the pH on the Distribution Ratio of Cadmium between TCE and
Water in the Presence of Perchlorate
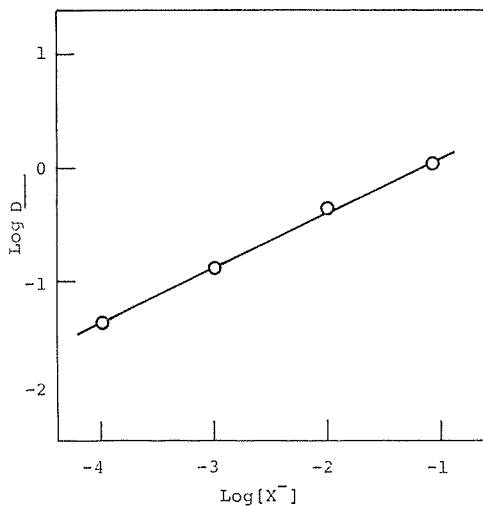$[HR]_0 = 5 \times 10^{-2}$ M, $[Cd]_T = 5 \times 10^{-6}$ M, 20 °C

Fig. 16. Effect of the Perchlorate Concentration on the Distribution Ratio of Cadmium
         between TCE and Water
             pH 5.0, $[HR]_0 = 5 \times 10^{-2}$ M, $[Cd]_T = 5 \times 10^{-6}$ M, 20°C
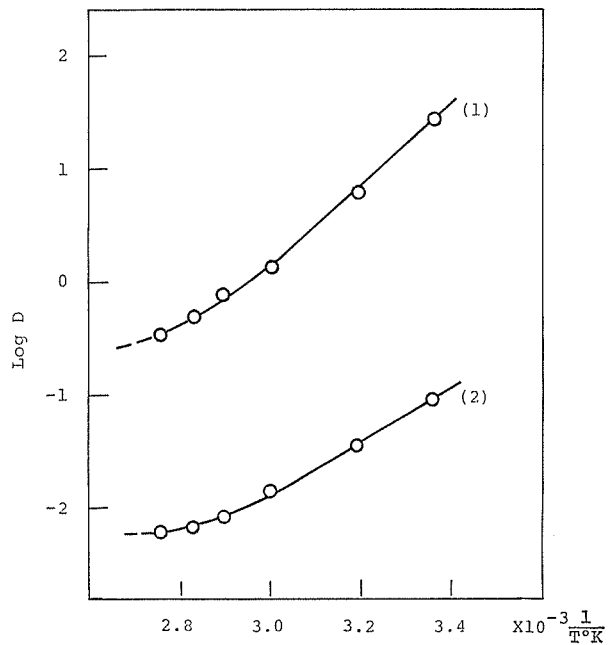

Fig. 17. Temperature Effect on the Distribution Ratio of Cadmium between TCE
         and Water
             pH 5.0, $[HR]_0 = 10^{-1}$ M, (1) $NaClO_4$ system, (2) NaCl system

Table 1. ΔH Values for Extraction Constants of Zinc and Cadmium Chelates of
8-Quinolinol ΔH kcal/mole

Solvents	Systems	Constants*	Zinc	Cadmium
TCE	$NaClO_4$	K_{ex}	−36.6	−40.4
	$NaNO_3$	”	−36.0	——
	NaCl	”	−22.8	−25.8
	Na_2SO_4	”	−11.0	——
	py adduct	K'_{ex}	0	——
1-octanol	——	K''_{ex}	− 2.5	——

* see equation (6), (7) and (8)

The thermodynamic data calculated by the slopes in the low temperature range
in the various extraction systems are summarized in Table 1.

In the series of the ion-associated complexes of zinc and cadmium, the order
of their ΔH values correlates with their extractability. Thus, the larger the size
of inorganic anion or metal ion, the larger is the absolute values of ΔH.

Although a direct comparison of measured distribution data for different
extraction systems may be meaningless because the included equilibrium constants
are quite different from each other, the ΔH values for adduct systems are lower
than that for extraction systems of ion-associated complexes.

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