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The Extraction of Divalent Manganese, Cobalt, Copper, Zinc, and Cadmium from Hydrochloric Acid Solutions by Tri-*n*-octylamine

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Abstract

The distribution of divalent manganese, cobalt, copper, zinc, and cadmium between hydrochloric acid solutions and solutions of tri-*n*-octylamine (TOA, R_3N) in benzene has been investigated under different conditions. It is found that the extraction of these divalent metals by TOA proceeds as $MCl_2(aq) + 2R_3NHCl(org) \rightleftharpoons (R_3NH)_2MCl_4(org)$. The electronic, electron spin resonance, and infrared spectral results indicate that all the complexes formed in the organic phases are in a tetrahedral arrangement. Further, the stability constants of the aqueous chloro complexes of divalent manganese, cobalt, copper, and zinc are determined on the basis of the equilibrium equation.

INTRODUCTION

The extraction by long-chain aliphatic amines has been used to extract various metal ions from aqueous solutions (*1*). In the previous papers we have also reported the extraction of cobalt(II) (*2–4*), copper(II) (*5, 6*), zinc(II) (*6*), zirconium(IV) (*7*), vanadium(IV) (*8*), and uranium(VI) (*9–11*) from hydrochloric acid solutions by tri-*n*-octylamine (TOA, R_3N). In connection with them, this paper extends the work to obtain further information on the extraction behavior of divalent manganese, cobalt, copper, zinc, and cadmium from hydrochloric acid solutions by TOA.

EXPERIMENTAL

Chemicals

TOA (Koei Chemical Co., Ltd., Osaka), used as an extractant without purification, was of high purity. Aqueous solutions of divalent manganese, cobalt, copper, zinc, and cadmium were prepared by dissolving their chlorides ($MnCl_2 \cdot 4H_2O$, $CoCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $ZnCl_2$, and $CdCl_2 \cdot 2.5H_2O$) in hydrochloric acid and lithium chloride solutions. Other chemicals were of analytical reagent grade.

Procedures

The distribution coefficients were obtained by the procedures described previously (*2–8*). Preliminary experiments showed that equilibration between two phases for the extraction of each metal was complete in 10 min. All metals in the organic phase were stripped with 0.1 *M* hydrochloric acid except cadmium which was stripped with 1 *M* nitric acid. The concentration of metals was determined by EDTA titration using BT (Eriochrome Black T) for manganese (*12*); XO (Xylenol Orange) for cobalt (*13*), copper (*13*), and zinc (*14*); and Cu-PAN (1,2-pyridylazo-2-naphthol) for cadmium (*15*) as indicators. For the complexes prepared by drying the loaded organic phase in vacuo, the electronic, infrared (IR), and electron spin resonance (ESR) spectral measurements were carried out as described previously (*8, 16, 17*). ESR parameter was calculated by spectral simulation using a FACOM 230-45S computer (*16, 17*). The determination of the stability constants of the aqueous complexes formed in this extraction system was made on the same computer.

RESULTS AND DISCUSSION

Extraction Isotherms

The extractions of divalent manganese, cobalt, copper, zinc, and cadmium with solutions of TOA in benzene from aqueous hydrochloric acid solutions at an initial metal concentration of 1 g/L, each at 20°C, gave the representative results illustrated in Fig. 1. This shows that the shapes of the extraction isotherms resemble one another, but the order of extraction

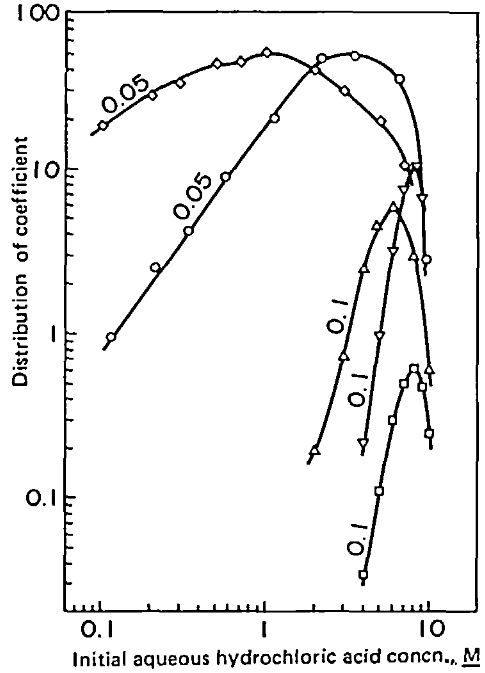

FIG. 1. Extraction of divalent manganese (□), cobalt (▽), copper (△), zinc (○), and cadmium (◇) from hydrochloric acid solutions at initial metal concentration of 1 g/L by TOA in benzene. (Numerals on curves are TOA concentrations, *M*.)

efficiency is as follows: below 1 *M* HCl, Cd > Zn >> Cu, Co, Mn; at 4 *M* HCl, Zn > Cd > Cu > Co > Mn; at 7 *M* HCl, Zn > Cd > Co > Cu > Mn. On the other hand, when the hydrochloric acid in the aqueous phase is replaced by lithium chloride, no decrease in the distribution coefficient occurs at higher chloride concentration, suggesting that the chloride ion takes part in the metal extraction. In Fig. 1 the distribution coefficient for manganese, cobalt, and copper varied remarkably with the aqueous hydrochloric acid concentration. Because the log-log plot of the distribution coefficient vs the activity of the chloride ion in the aqueous phase should have a tangent which reflects the average charge of the metal species in the aqueous phase, a tangent to the curve obtained should not be more than two. In the extraction of manganese, cobalt, and copper with TOA, a plot of log D vs log a_{HCl}, in which a_{HCl} refers to the mean activity of hydrochloric acid in aqueous phase, gives extraction isotherms with a tangent of ≤ 2. From this it is seen that up to 8, 8, and 6 *M* HCl for manganese, cobalt, and copper, respectively, the steep rise in the distribution coefficient with increasing hydrochloric acid concentration is mainly ascribed to the remarkable increase in the activity of chloride in the aqueous phase.

In the extraction of divalent metals from hydrochloric acid solutions by TOA, we postulate an equilibrium equation similar to the extraction of other metals (*7, 11*), i.e.

$$MCl_2(a) + mR_3NHCl(o) \rightleftharpoons (R_3NH)_mMCl_{2+m}(o) \tag{1}$$

where (a) and (o) refer to aqueous and organic phases, respectively.

Assuming $m = 2$ for the extraction of divalent metals by TOA, log-log plots of the distribution coefficient vs $\gamma(C_A - 2C_M)$ at constant hydrochloric acid give straight lines with slopes of ~2, in which γ is the activity coefficient of TOA (*4*), and C_A and C_M are the initial TOA concentration and metal concentration in the organic phase after equilibrium. This result suggests that the following expression is applicable to the extraction by TOA:

$$MCl_2(o) + 2R_3NHCl(o) \rightleftharpoons (R_3NH)_2MCl_4(o) \tag{2}$$

in which M = Mn, Co, Cu, Zn, and Cd. This is also supported by the results for loading tests to the organic phases in the extraction of divalent metals with 0.1 *M* TOA in benzene from hydrochloric acid solutions at constant concentration. The observed molar ratios of [M]/[Cl]/[R_3NH] in the organic phases attain to the stoichiometric composition $(R_3NH)_2MCl_4$ with increasing aqueous metal concentrations (Table 1).

Determination of Stability Constant of Aqueous Chloro Complexes

As these extraction systems are expressed by Eq. (2), the following relationship apply:

$$K = \frac{[(R_3NH)_2MCl_4]_{(o)}}{\beta_2[M^{2+}]_{(a)}[Cl^-]^2_{(a)}[R_3NHCl]^2_{(o)}} \tag{3}$$

and

$$D = \frac{K\beta_2[Cl^-]^2_{(a)}[R_3NHCl]^2_{(o)}}{1 + \sum_{j=1}^{n} \beta_j[Cl^-]^j_{(a)}} \tag{4}$$

TABLE 1
Molar Ratios of $[M]/[Cl]/[R_3NH]$ for the Organic Phases from the Extraction of Divalent Manganese, Cobalt, Copper, Zinc, and Cadmium from Aqueous Solutions with 0.1 *M* TOA in Benzene at 20°C[a]

	Molar ratio		
Metal	[M]	[Cl]	$[R_3NH]$
Mn	1.0	4.0	2.1
Co	1.0	4.3	2.0
Cu	1.0	3.8	1.9
Zn	1.0	3.8	2.0
Cd	1.0	4.1	2.0

[a] Aqueous solutions contain the chlorides of divalent metals at initial concentrations of 200, 200, 200, 100, and 100 g/L in hydrochloric acid of 8, 8, 6, 3, and 3 *M*, respectively.

in which K is the equilibrium constant and β_j is the overall stability constant, viz., $[MCl_j^{(2-j)+}]_{(a)}/[M^{2+}]_{(a)}[Cl^-]^j_{(a)}$. In Eq. (4), $[R_3NHCl]_{(o)}$ may be replaced by $[R_3NHCl]_{\text{initial(o)}} - 2M[M]_{(o)}$, and $[Cl^-]_{(a)}$ by $(Cl^-]_{\text{initial(a)}} - 2[M]_{(o)}$, where the subscripts "initial(a) and (a) and (o)" denote the initial and equilibrated concentrations of aqueous or organic phase, respectively. The value of $[R_3NHCl]_{(o)}$ is the activity of R_3NHCl obtained with the aid of the activity coefficient (*6*). If Eq. (4) is considered as a function containing five parameters and two variables, the parameters may be determined by applying a trial-and-error method of least square analysis (*6, 18, 19*).

For the extractions of zinc(II) and copper(II), the distribution equilibria are analyzed using Eq. (4) because the distribution data used for deducing the parameters β_j of the aqueous species formed in the systems are obtained at low aqueous acidity as reported previously (*6*). However, since the data at higher aqueous acidity apply to the extraction of manganese(II) and cobalt(II) (Table 2), the distribution coefficient may be affected by hydrochloric acid extracted into the organic phase (*1*). Accordingly, the available TOA concentration is determined beforehand as the initial $[R_3NHCl]$ on the basis of the extraction data for hydrochloric acid by TOA. In addition, considering the increase in the mean activity and salting-out

TABLE 2
Distribution Data for Divalent Metals for Calculation of β_j

Mn^a		Co^b		Cu^c		Zn^d	
Initial aq [HCl], *M*	*D*	Initial aq [HCl], *M*	*D*	Initial aq [HCl], *M*	*D*	Initial aq [HCl], *M*	*D*
3	0.008	3	0.0421	0.1	0.00447	0.01	0.053
	0.006		0.0440	0.15	0.00319	0.03	0.112
3.5	0.0190	3.5	0.104	0.2	0.00700	0.05	0.200
	0.0199	4	0.217	0.25	0.00842	0.07	0.325
4	0.0430		0.228	0.3	0.00934	0.1	0.40
	0.0446	4.5	0.470	0.35	0.00873	0.2	0.945
4.5	0.0954		0.570	0.4	0.0113	0.3	1.56
5	0.132	5	0.977	0.5	0.0102	0.5	6.07
	0.164	5.5	1.49				
5.5	0.134	6	3.13				
6	0.400		3.16				
	0.425	6.5	5.37				
		7	7.33				

[a] Initial aq [Mn] = 0.008 *M* and initial $[R_3NHCl]$ = 0.130 *M*.
[b] Initial aq [Co] = 0.008 *M* and initial $[R_3NHCl]$ = 0.08 *M*.
[c] Initial aq [Cu] = 0.008 *M* and initial $[R_3NHCl]$ = 0.05 *M*.
[d] Initial aq [Zn] = 0.0072 *M* and initial $[R_3NHCl]$ = 0.03 *M*.

effect of hydrochloric acid, the experimental corrected term $[Cl]^r_{(a)}$ is introduced into Eq. (4); i.e.,

$$D = \frac{K\beta_2[Cl^-]^{2+r}_{(a)}[R_3NHCl]^3_{(o)}}{1 + \sum_{j=1}^{n} \beta_j[Cl^-]^j_{(a)}} \qquad (5)$$

The resulting stability constants are illustrated in Table 3, and some representative simulation curves are indicated in Fig. 2, using the parameter $r = 8$ for manganese(II) and cobalt(II). From this it is found that the simulation curves are in good agreement with the experimental ones, although the cases of copper(II) and zinc(II) are obtained as $r = 0$ in Eq. (5). The values of β_j agree with those from previous work (*6, 18, 19*), indicating that the present method is reliable. Accordingly, the distribution of the different chloro complexes of divalent metals in aqueous solutions are calculated utilizing the values of the β_j as functions of the initial aqueous chloride concentration (Figs. 3 and 4).

TABLE 3
Stability Constants of the Chloro Complexes of Divalent Metals in the Aqueous Phase

Metal	β_1	β_2	β_3	β_4	K
Mn	0.575	0.299	0.130	0.0425	0.043
Co	0.392	0.169	0.080	0.0091	0.24
Cu	11.6	3.15	1.02	0.51	1.6×10^3
Zn	5.35	2.76	1.07	0.27	1.8×10^6

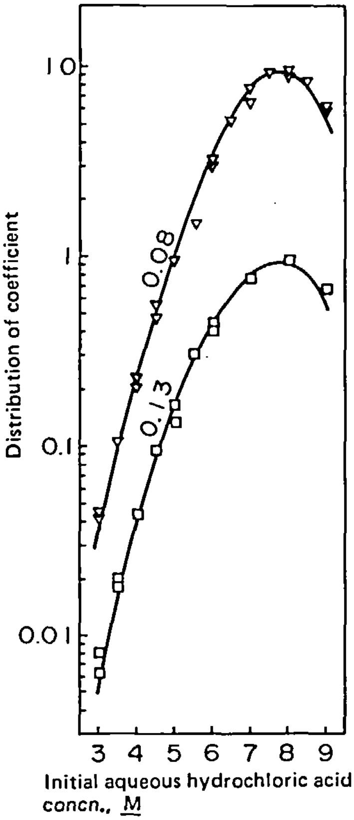

FIG. 2. Simulation curves for the extraction of divalent manganese (□) and cobalt (▽) from hydrochloric acid solutions with TOAHCl in benzene at 20°C. (Numerals on curves are TOAHCl concentrations, *M*; continuous lines denote the calculated extraction curves; □, ▽, observed values.)

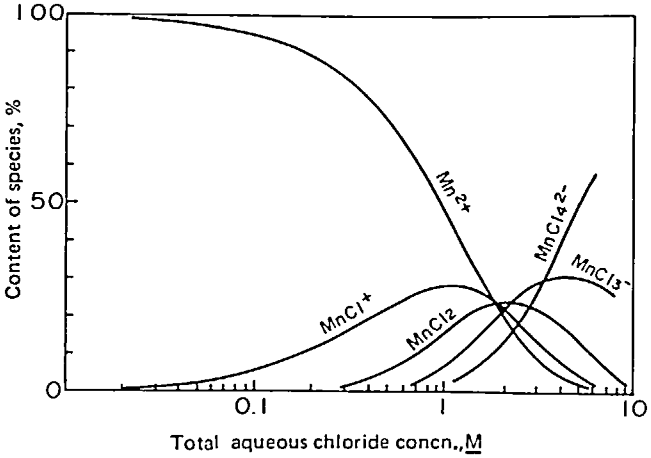

FIG. 3. Distribution of manganese(II) species in aqueous chloride solutions at 0.008 *M* Mn(II).

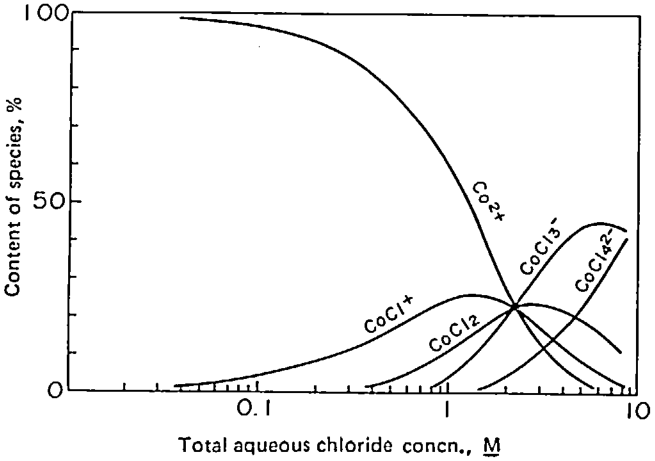

FIG. 4. Distribution of cobaltous species in aqueous chloride solutions at 0.008 *M* Co(II).

Electronic, ESR, and IR Spectra

The characteristic absorptions due to manganese ion in an octahedral environment appear in the spectra of aqueous solutions of manganese chloride in hydrochloric acid, although the bands at 24,800 and 28,100 cm^{-1} are assigned to the transitions $^6A_{1g}$ $(S) \rightarrow {}^4E_{1g}$, $^4A_{1g}(G)$ and $^6A_{1g}(S) \rightarrow {}^4T_{2g}(D)$, respectively. The spectra of organic extracts are different from those of aqueous manganese chloride solutions nearly identical with four coordinated species $(Et_4N)_2MnCl_4$ (*20*). By assuming the manganese species in the organic phase as shown in Table 4, it is considered that the coordination number of manganese decreases from six to four during extraction with TOA.

According to Lindenbaum et al. (*21*), the formation in small amounts of an octahedral manganese species in the organic phase is not excluded because of its weak intensity in comparison with that of the tetrahedral species. This possibility is not always supported by ESR result: the ESR spectrum of the organic extract from the extraction of aqueous solution containing manganese chloride at an initial concentration of 1 g/L in 8 *M* hydrochloric acid with 0.1 *M* TOA in benzene at 20°C reveals resonance with six hyperfine lines (Fig. 5). It is apparent that only one manganese complex exists in the organic phase. For this complex the hyperfine splitting constant and the *g*-value are calculated to be 61×10^{-4} cm^{-1} and 1.996, respectively. The value of the hyperfine splitting constant is ~30% lower than that of the

TABLE 4
Electronic Spectra of the Organic Extracts from the Extraction of Divalent Manganese, Cobalt, and Copper from Hydrochloric Acid Solutions by TOA in Benzene at 20°C

Metal	Frequency (cm^{-1})	Probable assignment
Mn	31,750	$^6A_1(S) \rightarrow {}^4T_1(P)$
	27,780	$^6A_1(S) \rightarrow {}^4E(D)$
	27,030	$^6A_1(S) \rightarrow {}^4T_2(D)$
	23,150	$^6A_1(S) \rightarrow {}^4E, {}^4A_1(G)$
	22,420	$^6A_1(S) \rightarrow {}^4T_2(G)$
	21,930	$^6A_1(S) \rightarrow {}^4T_1(G)$
Co	14,700	$^4A_2(F) \rightarrow {}^4T_1(P)$
	6,300	$^4A_2(F) \rightarrow {}^4T_1(F)$
Cu	24,390	Charge transfer
	10,500	$^2B_2(D) \rightarrow {}^2A_1(D)$
	9,100	$^2B_2(D) \rightarrow {}^2B_1(D)$

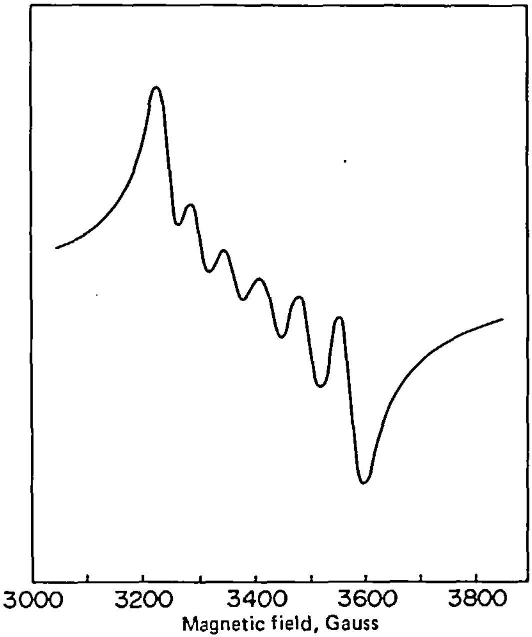

FIG. 5. ESR spectrum of the organic extract from the extraction of aqueous solution containing manganese chloride at an initial concentration of 1 g/L in 8 *M* hydrochloric acid with 0.1 *M* TOA in benzene at 20°C.

octahedral species $Mn(H_2O)_6^{2+}$, indicating that this stereochemistry is tetrahedral (*22*).

The electronic spectra of aqueous chloride solutions of cobalt and copper exhibit the absorptions ascribed to the transitions due to the tetra- and/or octahedral species, and the bands arising from the tetrahedral species appear at higher hydrochloric acid concentrations and increase in intensity with increasing concentration. For the spectra of organic extracts, the absorptions are assigned to the transitions for copper(II) ion in D_{2d} symmetry and for cobalt(II) ion in T_d symmetry (Table 3).

In the electronic spectra of tetrachlorocopper(II) complexes, the empirical correlation between the angle Cl-Cu-Cl and the *d*-*d* transition has been derived by Harlow et al. (*23*) and Lamontte-Brasseur (*24*). According to them, the transition energy appears to be a smooth function of the distortion. On the basis of their results, the angle of Cl-Cu-Cl is estimated to be 130°, suggesting that the species $(R_3NH)_2CuCl_4$ is distorted more than the species $(R_3R'N)_2CuCl_4$ formed in the extraction by tricaprylmethylammonium chloride (Aliquat-336, $R_3R'NCl$), which has an angle of 126°. This may be

TABLE 5

IR Spectral Data for the Organic Extracts from the Extraction of Divalent Manganese, Cobalt, Copper, Zinc, and Cadmium from Aqueous Solutions with 0.1 *M* TOA in Benzene at 20°C[a]

Frequency (cm^{-1})[b]						
$R_3NHCl \cdot H_2O$	Mn	Co	Cu	Zn	Cd	Probable assignment
3360(wb)	3425(wb)	3420(wb)	3460(wb)	3440(wb)	3440(wb)	OH stretching
2940(s)	2940(s)	2940(s)	2940(s)	2940(s)	2940(s)	CH stretching
2880(ms)	2850(ms)	2850(ms)	2850(ms)	2850(ms)	2850(ms)	(sym and asym)
2350(w)	2800(mb)	2900(mb)	2800(mb)	2900(mb)	2900(mb)	NH^+ stretching
1625(vw)	1620(vw)	1620(vw)	1620(vw)	1620(vw)	1620(vw)	OH bending
						CH_3 degenerate bending
1465(m)	1465(m)	1465(m)	1465(m)	1465(m)	1465(m)	CH_2 scissoring
1380(w)	1380(w)	1380(w)	1380(w)	1380(w)	1380(w)	CH_3 sym bending
715(w)	730(w)	739(w)	730(w)	730(w)	730(w)	CH_2 rocking
	284(w)	297(w)	277(w)	295(w)	250(w)	M-Cl stretching

[a] Aqueous solutions contain the chlorides of divalent metals at intial concentrations of 200, 200, 200, 100, and 100 g/L in hydrochloric acid of 8, 8, 6, 3, and 3 *M*, respectively.

[b] s = strong, ms = medium strong, m = medium, w = weak, vw = very weak, b = broad.

interpreted as the difference in the nature of the extractant: The bond A^+-Cl^- of TOA hydrochloride has much more covalency than of Aliquat-336, in which A refers to R_3NH and $R_3R'N$.

IR spectral results for the organic extracts prepared by drying the organic phases saturated with divalent manganese, cobalt, copper, zinc, and cadmium are given in Table 5 together with their probable assignment. Since the M-Cl stretching vibration of the four-coordinated tetrahedral species MCl_4^{2-} occurs in the region 300-250 cm^{-1} (25), it is expected that the species formed in Eq. (2), $(R_3NH)_2MCl_4$, possesses a tetrahedral structure.

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