Extraction of Bivalent Manganese, Cobalt, Copper, Zinc, and Cadmium from Hydrochloric Acid Solutions by Long-chain Alkyl Quaternary Ammonium Chloride in Various Organic Solvents

Taichi SATO,* Takato NAKAMURA, and Teruo FUJIMATSU

Department of Applied Chemistry, Faculty of Engineering, Shizuoka University, Johoku, Hamamatsu 432

(Received January 20, 1981)

The extraction of bivalent manganese, cobalt, copper, zinc and cadmium from hydrochloric acid solutions by tricaprylmethylammonium chloride (Aliquat-336) has been examined using various diluents such as benzene, chlorobenzene, *o*-dichlorobenzene, toluene, *o*-xylene, *m*-xylene, nitrobenzene, carbon tetrachloride, chloroform, and 1,2-dichloroethane. It was found that by assuming a regular solution, the distribution coefficient and the enthalpy change associated with metal extraction can be expressed in terms of the solubility parameters of Aliquat-336, diluent and the complex formed in the organic phase and their molar volumes. An empirical relation holds between distribution coefficient and the viscosity of diluent.

The influence of diluent on solvent extraction of metal has been studied by a number of researchers who attempted to correlate the distribution of metal between organic and aqueous phases with the physicochemical properties of organic solvent such as dielectric constant,[1,2] dipole moment,[1] and solubility parameter.[3-8] Nevertheless the role of diluent in the extraction process of metal has not been elucidated satisfactorily.

In the extraction of cadmium(II), zinc(II), lead(II), and copper(II) from 2 mol dm^{-3} hydrochloric acid solutions by octadecylbenzyldimethylammonium chloride in various diluents, Leszko and Zaborska[8] suggested that the relationship between the distribution coefficient and the solubility parameter of diluent derived by Vdovenko *et al.*[5] is applicable not to the extraction of lead(II) and copper(II) but to the extraction of cadmium(II) and zinc(II). Studies have been carried out on the extraction of zirconium(IV),[9] vanadium(IV),[10] and uranium(VI)[11] from hydrochloric acid solutions by tricaprylmethylammonium chloride (Aliquat-336, $R_3R'NCl$; $R=C_8—C_{10}$). In the present work, the extraction of bivalent manganese, cobalt, copper, zinc, and cadmium by Aliquat-336 in various organic solvent has been studied in order to examine the correlation between the distribution coefficient and physicochemical properties of diluent.

Experimental

Reagent. Aliquat-336 (General Mills) purified by washing several times with aqueous sodium chloride solution and hexane[9] was diluted in benzene, chlorobenzene, *o*-dichlorobenzene, toluene, *o*-xylene, *m*-xylene, nitrobenzene, carbon tetrachloride, chloroform, and 1,2-dichloroethane. The concentration of Aliquat-336 in organic solvents was determined by Volhard's method with nitrobenzene. Aqueous solutions of bivalent manganese, cobalt, copper, zinc, and cadmium were prepared by dissolving their chlorides ($MnCl_2\cdot4H_2O$, $CoCl_2\cdot6H_2O$, $CuCl_2\cdot2H_2O$, $ZnCl_2$, and $CdCl_2\cdot2.5H_2O$) in hydrochloric acid. The chemicals used were of analytical reagent grade.

Extraction and Analytical Procedures. Equal volumes (15 ml) of organic and aqueous phases, placed in 50 ml stoppered conical flasks, were shaken for 10 min (preliminary experiments showed that equilibration was complete in 10 min) in a water-bath maintained at the required temperature. The initial concentration of metal chloride in aqueous phase was 0.01 mol dm^{-3}. After equilibrium, the mixture was centrifuged and separated and then the aliquots of both phases were pipetted to determine the distribution coefficient (the ratio of the equilibrium concentration of metal in the organic phase to that in the aqueous phase, D). Manganese, cobalt, copper, and zinc in the organic phase were stripped with 0.1 mol dm^{-3} HCl, and cadmium in the organic phase with 1 mol dm^{-3} HNO_3. The concentration of metal in the aqueous solutions was determined by edta titration using the following indicator: XO (Xylenol Orange) for cobalt,[12] copper,[12] and zinc;[13] BT (Eriochrome Black T) for manganese;[14] Cu–PAN (PAN=1-(2-Pyridylazo)-2-naphthol) for cadmium.[15]

Results and Discussion

Extraction Isotherm. When bivalent manganese, cobalt, copper, zinc, and cadmium are extracted into benzene solution of Aliquat-336 from aqueous solutions of their chlorides at 0.01 mol dm^{-3} containing hydrochloric acid of varying acidity at 20 °C, the extraction efficiency is in the order Cd>Zn>Cu>Co>Mn for [HCl]<5 mol dm^{-3} and Cd>Zn>Co>Cu>Mn for [HCl]>5 mol dm^{-3} (Fig. 1). The distribution coefficient rises with increasing aqueous acidity to a maximum occurring at initial hydrochloric acid concentration of 8, 8, 5, 2, and 1 mol dm^{-3} for manganese, cobalt, copper, zinc, and cadmium, respectively, and then falling again. The shape of the extraction curves is not much influenced by the kind of diluent (Table 1). Thus the extractions are expressed by a reaction similar to that for zirconium(IV),[9] vanadium(IV),[10] and uranium(VI),[11]

$$MCl_4^{2-}(a) + 2R_3R'NCl(o) \rightleftharpoons (R_3R'N)_2MCl_4(o) + 2Cl^-(a), \quad (1)$$

where M=Mn, Co, Cu, Zn, and Cd, (a) and (o) denote aqueous and organic phases, respectively. This is supported by the results for the dependency of distribution coefficient on the extractant concentration and variation of metal concentration in the organic phase as a function of initial aqueous metal concentration at a constant acidity.

The extraction efficiency of Aliquat-336 for bivalent metal depends on the nature of the diluent and is in the following order: for manganese(II) 1,2-$C_2H_4Cl_2$>

Table 1. The distribution coefficient of bivalent manganese, cobalt, copper, zinc, and cadmium in the extraction from hydrochloric acid solutions by Aliquat-336 in various diluents

Metal	$[HCl]_{aq}$ / mol dm^{-3}	Distribution coefficient[a)] C_6H_6	$C_6H_5CH_3$	o-$C_6H_4(CH_3)_2$	m-$C_6H_4(CH_3)_2$	C_6H_5Cl
Mn	3	0.050	0.025	0.025	0.033	0.059
	5	0.011	0.059	0.040	0.070	0.17
	7	0.22	0.17	0.13	0.14	0.40
	8	0.25	0.23	0.15	0.17	0·43
Co	3	0.060	0.020	0.068	0.045	0.24
	5	0.68	0.51	0.51	0.58	2.70
	7	5.84	2.49	2.45	2.79	8.80
	8	6.22	2.67	3.00	3.36	8.37
Cu	2	0.18	0.13	0.12	0.097	0.42
	3	0.57	0.43	0.39	0.33	1.12
	5	1.12	0.913	0.908	0.824	2.10
	8	0.492	0.38	0.37	0.35	0.862
Zn	0.05	4.36	3.99	—[b)]	3.14	8.55
	0.1	9.27	8.79	—	7.28	18.3
	0.5	130	110	—	75	290
	1	400	290	—	160	480
Cd	0.02	87	55.7	—	49.4	97
	0.1	300	210	—	190	290
	1	280	310	—	270	260
	8	6.70	4.62	—	4.82	7.77

Metal	$[HCl]_{aq}$ / mol dm^{-3}	Distribution coefficient[a)] o-$C_6H_4Cl_2$	$C_6H_5NO_2$	$CHCl_3$	CCl_4	1,2-$C_2H_4Cl_2$
Mn	3	0.072	0.710	0.017	0.047	0.14
	5	0.26	0.15	0.040	0.10	1.01
	7	0.61	0.33	0.11	0.19	2.10
	8	0.68	0.36	0.15	0.24	1.39
Co	3	0.44	0.47	0.023	0.090	0.827
	5	4.14	3.67	0.16	0.39	7.02
	7	12.4	6.93	1.19	2.17	10.4
	8	15.9	4.91	1.58	2.63	7.32
Cu	2	0.614	0.49	0.052	0.072	0.57
	3	1.55	1.41	0.064	0.025	1.95
	5	3.17	2.45	0.21	0.765	6.03
	8	1.15	0.750	0.29	0.28	1.35
Zn	0.05	10.4	11.7	0.25	2.54	12.7
	0.1	27.2	25.8	0.36	4.75	36.6
	0.5	310	240	1.90	83	210
	1	600	500	3.46	210	600
Cd	0.02	120	95	0.49	14.8	76
	0.1	310	250	0.925	49.5	250
	1	210	310	1.64	130	200
	8	10.0	6.69	0.756	3.59	10.4

a) The concentration of Aliquat-336 is 0.05 mol dm^{-3} for manganese, cobalt, and zinc, 0.025 mol dm^{-3} for copper and 0.03 mol dm^{-3} for cadmium. b) No datum.

o-$C_6H_4Cl_2$ > $C_6H_5NO_2$ > C_6H_5Cl > C_6H_6 > CCl_4 > m-$C_6H_4(CH_3)_2$ > $C_6H_5CH_3$ > o-$C_6H_4(CH_3)_2$ > $CHCl_3$ from 3 mol dm^{-3} HCl; for cobalt(II) 1,2-$C_2H_4Cl_2$ > $C_6H_5NO_2$ > o-$C_6H_4Cl_2$ > C_6H_5Cl > CCl_4 > o-$C_6H_4(CH_3)_2$ > C_6H_6 > m-$C_6H_4(CH_3)_2$ > $CHCl_3$ > $C_6H_5CH_3$ from 3 mol dm^{-3} HCl; for copper(II) o-$C_6H_4Cl_2$ > 1,2-$C_2H_4Cl_2$ > $C_6H_5NO_2$ > C_6H_5Cl > C_6H_6 > $C_6H_5CH_3$ > o-$C_6H_4(CH_3)_2$ > m-$C_6H_4(CH_3)_2$ > CCl_4 > $CHCl_3$ from 2 mol dm^{-3} HCl; for zinc(II) 1,2-$C_2H_4Cl_2$ > $C_6H_5NO_2$ > o-$C_6H_4Cl_2$ > C_6H_5Cl > C_6H_6 > $C_6H_5CH_3$ > m-$C_6H_4(CH_3)_2$ > CCl_4 > $CHCl_3$ from 0.05 mol dm^{-3} HCl and for cadmium(II) o-$C_6H_4Cl_2$ > C_6H_5Cl > $C_6H_5NO_2$ > C_6H_6 > 1,2-$C_2H_4Cl_2$ > $C_6H_5CH_3$ > m-$C_6H_4(CH_3)_2$ > CCl_4 > $CHCl_3$ from 0.02 mol dm^{-3} HCl. We see that the extraction efficiency of Aliquat-336 in aromatic solvent with electron-accepting radical such as Cl or NO_2 is higher than that with electron-donating one like CH_3, and that chloroform reveals a very poor extraction because of a hydrogen bond-

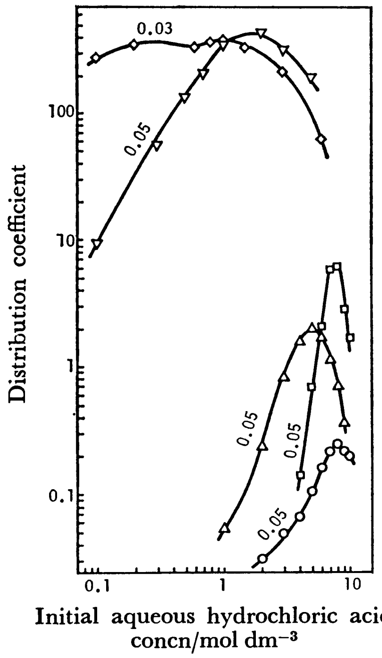

Fig. 1. Extraction of bivalent manganese, cobalt, copper, zinc, and cadmium from hydrochloric acid solutions by Aliquat-336 in benzene (numerals on curves are Aliquat-336 concentrations, mol dm^{-3}; ○ Mn, □ Co, △ Cu, ▽ Zn, ◇ Cd).

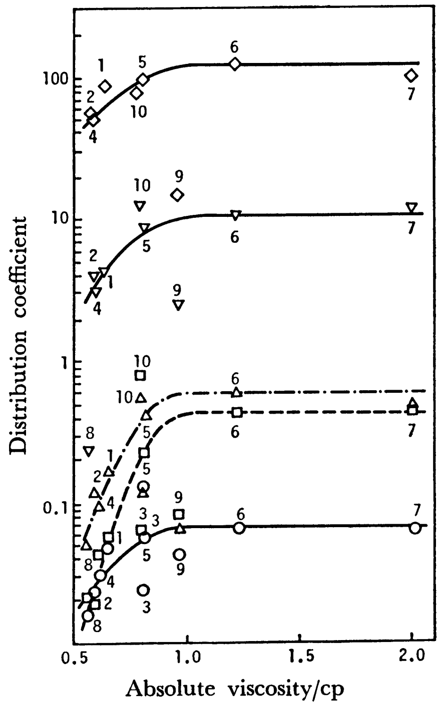

Fig. 2. Dependence of the distribution coefficient on absolute viscosity of diluent (○, □, △, ▽, and, represent the extractions of Mn(II) from 3 mol dm^{-3} HCl soln, Co(II) from 3 mol dm^{-3} HCl soln., Cu(II) from 2 mol dm^{-3} HCl soln, Zn(II) from 0.05 mol dm^{-3} HCl soln, and Cd(II) from 0.02 mol dm^{-3} HCl soln., respectively): 1) benzene, 2) toluene, 3) *o*-xylene, 4) *m*-xylene, 5) chlorobenzene, 6) *o*-dichlorobenzene, 7) nitrobenzene, 8) chloroform, 9) carbon tetrachloride, 10) 1,2-dichloroethane.

ing to extractant. However, no simple relation exists between the distribution coefficient and the dipole moment and dielectric constant of diluent which represent the polarities of molecule and solution, respectively.

Dependence of Distribution Coefficient on Viscosity. The variation of the distribution coefficient for bivalent manganese, cobalt, copper, zinc, and cadmium plotted as a function of the absolute viscosity of diluent, η_d, is given in Fig. 2. The value of η_d are as follows: 0.65, 0.59, 0.81, 0.61, 0.82, 1.23, 2.01, 0.56, 0.97, and 0.80 cp for benzene, toluene, *o*-xylene, *m*-xylene, chlorobenzene, *o*-dichlorobenzene, nitrobenzene, chloroform, carbon tetrachloride, and 1,2-dichloroethane. The distribution coefficients for manganese, cobalt, copper, zinc, and cadmium are indicated by means of the data for the extraction at 3, 3, 2, 0.05, and 0.02 mol dm^{-3}, respectively, in the lowest hydrochloric acid concentrations shown in Table 1. Since the reaction[15)]

$$R_3R'NCl(o) + H^+(a) + Cl^-(a) \rightleftharpoons R_3R'NCl \cdot HCl(o) \quad (2)$$

takes place at higher aqueous acidity, the data at low acidity are used to avoid the reduction on the distribution of metal resulting from the competition between reactions (1) and (2).

The distribution coefficient increases with increase in the viscosity of diluent at $\eta_d \leq 1$ cp, but little change occurs at $\eta_d \leq 1$ cp (Fig. 2). In all the extraction systems studied, the distribution coefficient becomes constant as the viscosity of diluent approaches that of water. An empirical correlation is found between the distribution coefficient and the viscosity of diluent in the range $\eta_d \leq 1$ cp:

$$\log D/D_o = A(\eta_d - 1)^2, \quad (3)$$

where D_o denotes the distribution coefficient for *o*-dichlorobenzene, and A the slope obtained when log D/D_o is plotted against $(\eta_d \leq 1)^2$. Values of the slope calculated by the method of least squares are −2.59, −7.04, −4.93, −2.94, and −2.03 for manganese, cobalt, copper, zinc, and cadmium, respectively.

Effect of Solubility Parameter. From the Hildebrand-Scatchard equation[16)] for the excess free energy of a regular solution, formula was worked out by Vdovenko *et al.*[15)] for the distribution coefficient in terms of the solubility parameter:

$$\log D = (2/2.3RT)(V_c\delta_c - nV_e\delta_e)\delta_d + \{(nV_e - V_c)/2.3\}(\delta_d^2/RT - 1/V_d) + \text{const}, \quad (4)$$

where V and δ denote molar volume and solubility parameter, respectively, subscripts c, e, and d being the complex formed in the organic phase, extractant and diluent, respectively. Assuming that the composition in aqueous phase and the concentration of extractant in various diluents are constant, and the molar volumes of diluents do not differ from each other, the following relation is derived:

$$\{1/(\delta_d - \delta_s)\} \log (D/D_o) = \{(nV_e - V_c)/2.3RT\}(\delta_d + \delta_s) + 2(V_c\delta_c - nV_e\delta_e)/2.3RT, \quad (5)$$

where the subscript s refers to the diluent chosen as standard

Table 2. Temperature dependence of distribution coefficient for the extraction of bivalent manganese, cobalt, copper, zinc, and cadmium from hydrochloric acid solution[a)] by Aliquat-336[b)] in various diluents

Metal	Diluent	Distribution coefficient				Change in enthalpy
		10 °C[c)]	20 °C[c)]	30 °C[c)]	40 °C[c)]	kJ mol^{-1}
Mn	C_6H_6	0.0497	0.0498	0.0499	0.0500	0.17
	$C_6H_5CH_3$	0.023	0.025	0.033	0.038	12
	o-$C_6H_4(CH_3)_2$	0.023	0.025	0.034	0.034	9.9
	m-$C_6H_4(CH_3)_2$	0.028	0.033	0.035	0.039	8.3
	C_6H_5Cl	0.044	0.059	0.077	0.10	20
	o-$C_6H_4Cl_2$	0.084	0.072	0.098	0.11	6.3
	$C_6H_5NO_2$	0.037	0.071	0.12	0.17	36
	$CHCl_3$	0.007	0.017	0.034	0.055	50
	CCl_4	0.03	0.047	0.066	0.071	23
	1,2-$C_2H_4Cl_2$	0.15	0.14	0.13	0.13	−3.4
Co	C_6H_6	0.045	0.060	0.090	0.12	24
	$C_6H_5CH_3$	0.015	0.020	0.040	0.070	37
	o-$C_6H_4(CH_3)_2$	0.054	0.068	0.075	0.091	9.3
	m-$C_6H_4(CH_3)_2$	0.035	0.045	0.085	0.090	20
	C_6H_5Cl	0.21	0.24	0.28	0.37	10
	o-$C_6H_4Cl_2$	0.31	0.44	0.60	0.73	23
	$C_6H_5NO_2$	0.60	0.47	0.48	0.57	−1.2
	$CHCl_3$	0.050	0.023	0.015	0.007	−48
	CCl_4	0.080	0.090	0.10	0.13	12
	1,2-$C_2H_4Cl_2$	0.85	0.83	0.77	0.75	−3.0
Cu	C_6H_6	0.13	0.18	0.27	0.22	28
	$C_6H_5CH_3$	0.091	0.13	0.17	0.17	27
	o-$C_6H_4(CH_3)_2$	0.085	0.21	0.15	0.18	23
	m-$C_6H_4(CH_3)_2$	0.069	0.097	0.14	0.14	25
	C_6H_5Cl	0.35	0.42	0.49	0.50	19
	o-$C_6H_5Cl_2$	0.54	0.61	0.72	0.84	17
	$C_6H_5NO_2$	0.55	0.49	0.44	0.40	−12
	$CHCl_3$	0.054	0.052	0.054	0.053	1.9
	CCl_4	0.068	0.072	0.11	0.14	22
	1,2-$C_2H_4Cl_2$	0.85	0.57	0.49	0.32	−3.3
Zn	C_6H_6	4.59	4.36	4.49	4.05	−3.4
	$C_6H_5CH_3$	4.03	3.99	3.76	3.75	−2.2
	m-$C_6H_4(CH_3)_2$	2.80	3.14	3.36	3.49	7.4
	C_6H_5Cl	9.55	8.55	7.83	7.78	−7.1
	o-$C_6H_4Cl_2$	15.3	14.4	13.3	13.2	−4.4
	$C_6H_5NO_2$	18.1	11.7	7.80	5.20	−26
	$CHCl_3$	0.20	0.25	0.29	0.33	8.9
	CCl_4	2.69	2.54	2.26	2.12	−5.6
	1,2-$C_2H_4Cl_2$	16.3	12.7	8.71	5.83	−29
Cd	C_6H_6	100	87	61	46	−21
	$C_6H_5CH_3$	78	55	42.1	29.8	−26
	m-$C_6H_4(CH_3)_2$	68	49	40	31	−20
	C_6H_5Cl	130	97	71	63	−19
	o-$C_6H_4Cl_2$	150	140	140	130	−8.5
	$C_6H_5NO_2$	100	95	62	43	−24
	$CHCl_3$	0.52	0.45	0.48	0.47	−3.7
	CCl_4	23.3	14.8	11.4	8.53	−26
	1,2-$C_2H_4Cl_2$	150	76	41.9	26.1	−47

a) The concentration of hydrochloric acid is 3 mol dm^{-3} for manganese and cobalt, 2 mol dm^{-3} for copper, 0.05 mol dm^{-3} for zinc, and 0.02 mol dm^{-3} for cadmium. b) The concentration of Aliquat-336 is 0.05 mol dm^{-3} for manganese, cobalt, and zinc, 0.025 mol dm^{-3} for copper, and 0.03 mol dm^{-3} for cadmium. c) Temperature of extraction.

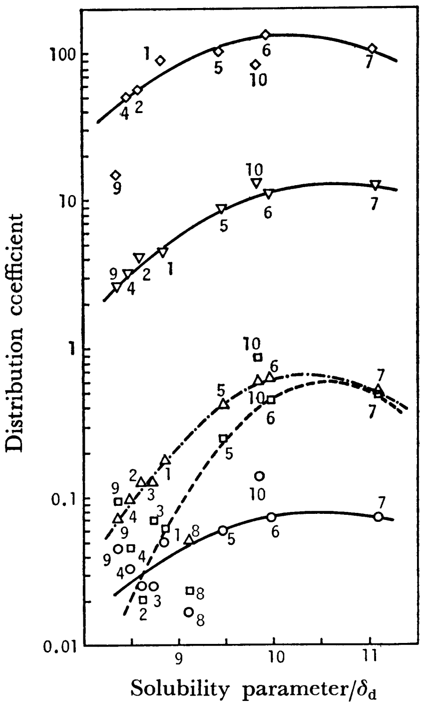

Fig. 3. Dependence of the distribution coefficient on the solubility parameter of diluent (○, □, △, ▽, and ◇ represent the extractions of Mn(II) from 3 mol dm^{-3} HCl soln, Co(II) from 3 mol dm^{-3} HCl soln, Cu(II) from 2 mol dm^{-3} HCl soln, Zn(II) from 0.05 mol dm^{-3} HCl soln, and Cd(II) from 0.02 mol dm^{-3} HCl soln, respectively): 1) benzene, 2) toluene, 3) *o*-xylene, 4) *m*-xylene, 5) chlorobenzene, 6) *o*-dichlorobenzene, 7) nitrobenzene, 8) chloroform, 9) carbon tetrachloride, 10) 1,2-dichloroethane.

In Fig. 3 showing the plots of log D *vs.* δ_d, the curves for manganese, cobalt, copper, zinc, and cadmium are obtained from the values of $(nV_e - V_e)/2.3RT$ as −0.165, −0.510, −0.370, −2.00, and −0.210, respectively, and $2(V_c\delta_c - nV_e\delta_e)/2.3RT$ as 3.45, 10.7, 7.64, 4.22, and 4.27, respectively, which are estimated by Eq. 5 using nitrobenzene as standard. In this case, the values of δ_d are as follows: 9.1, 8.9, 9.0, 8.8, 9.6, 10.0, 10.9, 9.3, 8.7, and 9.9 for benzene, toluene, *o*-xylene, *m*-xylene, chlorobenzene, *o*-dichlorobenzene, nitrobenzene, chloroform, carbon tetrachloride, and 1,2-dichloroethane, respectively. The parabolic dependence of distribution coefficients on the solubility parameter is obtained, suggesting that Eq. 4 gives a good estimate for the value of distribution coefficients in the extraction of these bivalent metals from hydrochloric acid solutions by Aliquat-336. However, since the large deviation from the parabola is observed in the extraction with chloroform, it seems that the negative deviation arises from the non-random interaction due to hydrogen bonding between chloroform and Aliquat-336.

Temperature Effect. The equilibrium constant in reaction (1) and the distribution coefficient are given by

$$K = [(R_3R'N)_2MCl_4][Cl^-]^2/[MCl_4^{2-}][R_3R'NCl]^2 \tag{6}$$

and

$$D = [(R_3R'N)_2MCl_4]/[M^{2+}](1+\Sigma\beta_i[Cl^-]^i), \tag{7}$$

where β_i refers to the overall stability constant in the reaction

$$M^{2+}(a) + iCl^-(a) \rightleftharpoons MCl_i^{(2-i)+}(a). \tag{8}$$

From Eqs. 6 and 7 the following relationship is obtained:

$$K = D(1+\Sigma\beta_i[Cl^-]^i)/\beta_4[Cl^-]^2[R_3R'NCl]^2. \tag{9}$$

By assuming that the values of overall stability constant β_4 and the term $(1+\Sigma\beta_i[Cl^-]^i)$ do not change significantly in the temperature range studied, the change in enthalpy, ΔH, associated with the reaction(1) can be estimated by means of the Van't Hoff equation. The distribution coefficients for bivalent manganese, cobalt, copper, zinc, and cadmium from aqueous hydrochloric acid solutions with solutions of Aliquat-336 in various diluents, measured in the temperature range 10—40 °C, are summarised in Table 2 in comparison with the values of ΔH.

The extraction process of bivalent metals is considered by a Born-Harber type of cycle. The change in enthalpy observed is the sum of five terms which represent enthalpies for dehydration of the species MCl_4^{2-} $(-\Delta H_1)$, for desolvation of $R_3R'NCl$ $(-\Delta H_2)$, for the reaction of MCl_4^{2-} with $R_3R'NCl$ (ΔH_3), for hydration of Cl^- (ΔH_4) and for dissolution of the complex $(R_3R'N)_2MCl_4$ into organic phase (ΔH_5). The magnitude and sign of the change in enthalpy observed depend on the contribution from enthalpies in these processes. The ΔH_1 and ΔH_4 values are correlated with the composition of aqueous acidity, since the water activity decreases with increase in hydrochloric acid concentration, while the ΔH_3 value is independent of the kind of diluent. If the concentration of hydrochloric acid in the aqueous phase remains constant, the change in enthalpy observed is expressed by

$$\Delta H = -2\Delta H_2 + \Delta H_5 + \text{const.} \tag{10}$$

Partial molar enthalpies for dissolution of Aliquat-336 and the complex $(R_3R'N)_2MCl_4$ into organic solvent given by $V_e\phi_d^2(\delta_d-\delta_e)^2$ and $V_c\phi'^2_d(\delta_d-\delta_c)^2$, from regular solution theory,[17] give the equation

$$\Delta H = -2V_e\phi_d^2(\delta_d-\delta_e)^2 + V_c\phi'd^2(\delta_d-\delta_c)^2 + \text{const}, \tag{11}$$

where ϕ_d and ϕ'_d refer to the volume fraction of diluent. This provides the equation

$$\Delta H = (V_c\phi'^2_d - 2V_e\phi_d^2)\delta_d^2 + 2(2V_e\phi_d^2\delta_e - V_c\phi'^2_d\delta_c)\delta_d + \text{const.} \tag{12}$$

We see that when ΔH is plotted against δ_d, its shape depends on the magnitude of the term $(V_c\phi'^2_d - 2V_e\phi_d^2)$. For $V_c\phi'^2_d < 2V_e\phi_d^2$ or $V_c\phi'^2_d > 2V_e\phi_d^2$, the plot should give a parabola with a maximum or minimum at $\delta_d = (V_c\phi'^2_d\delta_c - 2V_e\phi_d^2\delta_e)/(V_c\phi'^2_d - 2V_e\phi_d^2)$. In contrast, a linear relationship is expected for $V_c\phi'^2_d = 2V_e\phi_d^2$. The value of $(V_c\phi'^2_d - 2V_e\phi_d^2)$ is determined by means of

$$(\Delta H - \Delta H_s)/(\delta_d - \delta_s) = (V_c\phi'^2_d - 2V_e\phi_d^2)(\delta_d+\delta_s) + 2(2V_e\phi_d^2\delta_e - V_c\phi'^2_d\delta_c). \tag{13}$$

The $(V_c\phi'^2_d - 2V_e\phi_d^2)$ and $2(2V_e\phi_d^2\delta_e - V_c\phi'^2_d\delta_c)$ are the slope and intercept of the line, respectively, when

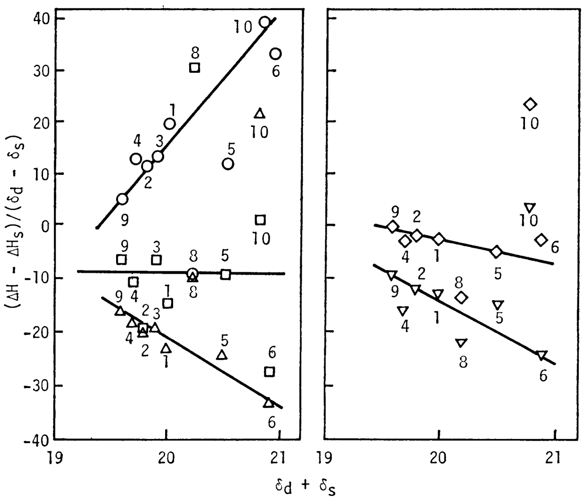

Fig. 4. Correlation between $(\Delta H-\Delta H_s)/(\delta_d-\delta_s)$ and $\delta_d+\delta_s$ for the correlation of bivalent manganese, cobalt, copper, zinc, and cadmium from hydrochloric acid solutions by Aliquat-336 in various diluents (○ Mn, □ Co, △ Cu, ▽ Zn, ◇ Cd): 1) benzene, 2) toluene, 3) *o*-xylene, 4) *m*-xylene, 5) chlorobenzene, 6) *o*-dichlorobenzene, 7) nitrobenzene, 8) chloroform, 9) carbon tetrachloride, 10) 1,2-dichloroethane.

$(\Delta H-\Delta H_s)/(\delta_d-\delta_s)$ is plotted as a function of $(\delta_d+\delta_s)$. The plots for manganese, cobalt, copper, zinc and cadmium show the linear relationship in Fig. 4, although the points for chloroform and 1,2-dichloroethane deviate from the lines in all the cases studied. The values of $(V_c\phi'^2_d-2V_e\phi_d^2)$ obtained indicate that $V_c\phi'^2_d>2V_e\phi_d^2$ is satisfied for manganese (as 6.2), $V_c\phi'^2_d=2V_e\phi_d^2$ for cobalt (as zero), and $V_c\phi'^2_d<2V_e\phi_d^2$ for copper, zinc and cadmium (as −3.1, −2.7, and −3.2, respectively). The plots of ΔH against δ_d confirm that Eq. 12 holds in the enthalpy change for various diluents. This suggests that the change in enthalpy for the extraction of bivalent manganese, cobalt, copper, zinc, and cadmium by Aliquat-336 in various diluents depends on the solubility parameter of diluent, the molar volume of the complex formed in the organic phase and Aliquat-336, and the volume fraction of diluent.

Conclusion

A parabolic dependency of the distribution coefficient on the solubility parameter of diluent is observed in the extraction by Aliquat-336 in organic solvents except chloroform and 1,2-dichloroethane, indicating that Eq. 4 derived from the regular solution theory is satisfied. The enthalpy change associated with metal extraction is also explained by assuming a regular solution. It is concluded that in the extraction of bivalent manganese, cobalt, copper, zinc, and cadmium from hydrochloric acid solutions by Aliquat-336 in various organic solvents, the distribution coefficient depends on the solubility of the complex formed in the organic diluent and the solubility parameter being an important factor for evaluation the distribution coefficient.

Distribution coefficients increase with increase in the viscosity of diluent in the range $\eta_d\leq 1$ cp, and an empirical relation is obtained between the distribution coefficient and the viscosity of diluent. It is found that in the extraction by Aliquat-336 in aromatic solvents, the distribution coefficient in the diluents with electron-accepting radical is higher than that with an electron-donating one.

The authors wish to thank Messrs. Wataru Sangawa, Tadashi Fujishita, and Akihiro Takahashi for their assistance in experiments.

References

1) T. Sato, *J. Inorg. Nucl. Chem.*, **27**, 1399 (1965); **30**, 1065 (1968).
2) O. V. Singh and S. N. Tandon, *J. Inorg. Nucl. Chem.*, **36**, 439 (1974).
3) W. Smulek and S. Siekierski, *J. Inorg. Nucl. Chem.*, **24**, 1651 (1962).
4) S. Siekierski and R. Olszer, *J. Inorg. Nucl. Chem.*, **25**, 1351 (1963).
5) V. M. Vdovenko, T. V. Kovaleva, and M. A. Ryazanov, *Radiokhimiya*, **7**, 133 (1965).
6) H. A. Mottola and H. Freiser, *Talanta*, **13**, 55 (1966).
7) H. M. H. Irving and R. H. Al-Jarrah, *Anal. Chim. Acta*, **63**, 79 (1973).
8) M. Leszko and W. Zaborska, *Rocz. Chim.*, **51**, 1961 (1977).
9) T. Sato and H. Watanabe, *Anal. Chim. Acta*, **49**, 463 (1970).
10) T. Sato, S. Ikoma, and T. Nakamura, *J. Inorg. Nucl. Chem.*, **39**, 395 (1977).
11) T. Sato, *J. Inorg. Nucl. Chem.*, **34**, 3835 (1972).
12) J. Kinnunen and B. Wennerstrand, *Chem. Anal.*, **46**, 92 (1957).
13) J. Körble and R. Pribil, *Chem. Anal.*, **45**, 102 (1956).
14) H. Flaschka, *Mikrochim. Acta*, **39**, 38 (1952).
15) T. Sato, H. Watanabe, and S. Kikuchi, *J. Appl. Chem. Biotechnol.*, **25**, 63 (1975).
16) G. Scatchard, *Chem. Rev.*, **8**, 321 (1931).
17) A. F. M. Barton, *Chem. Rev.*, **75**, 731 (1975).