Bull. Chem. Soc. Jpn., 55, 90—94 (1982)

The Extraction of Bivalent Transition Metals from Aqueous Chloride Solutions by Long-chain Alkyl Quaternary Ammonium Carboxylates

Taichi SATO* and Masahiro YAMAMOTO

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

(Received January 13, 1981)

The extraction of bivalent manganese, cobalt, nickel, and copper from aqueous chloride solutions by long-chain alkyl quaternary ammonium carboxylates, prepared by combination of trioctylmethylammonium chloride ($R_3R'NCl$) and carboxylic (octanoic, decanoic, and lauric) acids ($R''COOH$) in benzene, has been investigated under different conditions. The organic phases are examined by spectrophotometry and infrared spectral measurement. The mechanism of the extraction is discussed on the basis of the results obtained. The extraction efficiency follows the order $Cu > Co \simeq Ni > Mn$, and the extraction process is expressed as $M^{2+}(aq) + 2Cl^-(aq) + 3R_3R'NR''COO(org) \rightleftarrows (R_3R'N)[M(R''COO)_3](org) + 2R_3R'NCl(org)$, in which $M = Mn$, Co, Ni, and Cu. The extracted species of bivalent manganese, cobalt, nickel, and copper exist as the complex $(R_3R'N)[M(R''COO)_3]$ in an octahedral arrangement.

The extraction of metals from acid solutions by high molecular weight amines has been reported by a number of investigators, but there are few observations on the extraction of metals from aqueous solution in the vicinity of neutral range. Although carboxylic acids are a possible group of reagents to extract the metals in the vicinity of neutral range,[1)] their extraction efficiencies depend remarkably on the pH of the aqueous phase. Accordingly the mixed ionic solvent system consisting of long-chain alkyl quaternary ammonium carboxylates is considered of effective for such extraction. This system has been mainly applied to the extraction of magnesium,[2—4)] but observations on the extraction of other metals are limited. We have been studying the extraction systems with long-chain alkyl quaternary ammonium compounds,[5)] and the present study extends the work to the extraction of bivalent manganese, cobalt, nickel, and copper from aqueous chloride solutions by alkyl quaternary ammonium carboxylates.

Experimental

Reagent. The alkyl quaternary ammonium carboxylates were prepared by mixing calculated amounts (equal volumes of solutions in 0.5 mol dm^{-3} each) of trioctylmethylammonium chloride (General Mills, $R_3R'NCl$, Aliquat-336) and carboxylic acids (octanoic, decanoic, and lauric acids represented as $C_nH_{2n+1}COOH$ with $n=7$, 9, and 11, respectively or $R''COOH$), and treated with an excess amount of sodium hydroxide, and then washed thoroughly with distilled water to remove sodium and chloride ions. The resulting materials ($R_3R'NR''COO \cdot 5H_2O$) which exhibit the properties illustrated in Table 1 are diluted with benzene. The aqueous solution of nickel (II) chloride was prepared by dissolving nickel chloride hydrate ($NiCl_2 \cdot 6H_2O$) in water and its pH value was adjusted by adding perchloric acid. The aqueous solutions of other bivalent metals were similarly prepared by dissolving their salts ($MnCl_2 \cdot 4H_2O$, $CoCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$) in water. The used reagents were of analytical grade.

Extraction and Analytical Procedures. The procedure for obtaining distribution coefficient (the ratio of the equilibrium concentration of metal in the organic phase to that in the aqueous phase), E°_{a}, was described previously:[6)] equal volumes (15 cm^{-3}) of the organic and aqueous phases were shaken for 10 min, and then the metal in the organic phase was stripped with 1 mol dm^{-3} hydrochloric acid. All experiments were carried out at 20 °C except the examination on temperature-dependence of distribution coefficient. The concentration of nickel was determined by edta titration using Cu–PAN (1-(2-pyridylazo)-2-naphthol) as an indicator.[7)] Following indicators were used for the determination of other metals by edta titration: BT (Eriochrome Black T) for manganese;[8)] XO (Xylenol Orange) for cobalt;[9)] PAN for copper.[10)] The concentration of chloride in the organic phase was determined by Volhard's method, and the water content of the organic phase by Karl-Fischer titration. The complexes freed from benzene were prepared by drying the metal saturated organic phase *in vacuo* at 50 °C.

Spectrophotometry and Infrared Spectral Measurement. The absorption spectra were obtained on a Shimadzu Model QV-50 spectrophotometer, using matched 1.00 cm fused silica cells, and the infrared spectra on a JASCO Model IRA-1 grating infrared spectrophotometer for measurement at 4000—650 cm^{-1}, and Model IR-F for measurement at 700—200 cm^{-1}, using a capillary film between thallium halide or polyethylene plates.

Results and Discussion

Extraction Isotherm. When nickel(II) is extracted with trioctylmethylammonium laurate from aqueous nickel chloride solution of 1 g dm^{-3} at varying pH values, the distribution coefficient steeply rises with increasing pH in the range of pH 2—3, and then becomes almost constant at pH$>\approx 3$, as shown in Fig. 1. The lowering in the distribution coefficient at low pH arises from the decrease of the available extractant, caused by the extraction of acid from aqueous solution. This interpretation is supported by the fact that hydrochloric acid is extracted by quaternary compound according to the reaction:

$$H^+(a) + Cl^-(a) + R_3R'NR''COO(o) \rightleftharpoons R_3R'NCl(o) + R''COOH(o), \qquad (1)$$

in which (a) and (o) mean aqueous and organic phases, respectively. In order to elucidate further the reaction between a benzene solution of quaternary compound and aqueous hydrochloric acid solution, the variation of $[Cl]_{org}$ with $[HCl]_{initial\,aq}$ was examined by the extraction of aqueous solutions containing hydrochloric acid in the absence of nickel chloride with 0.2 mol dm^{-3} quaternary ammonium laurate. The chloride concentration in the organic phase revealed a constant

TABLE 1. PROPERTIES OF TRIOCTYLMETHYLAMMONIUM CARBOXYLATE

Property		Trioctylmethylammonium carboxylate			Aliquat-336
		Octanoate	Decanoate	Laurate	
Molecular weight a)		607	660	679	442
Appearance at room temperature		Viscous liquid	Viscous liquid	Viscous liquid	Viscous liquid
Colour		Yellowish brown	Light brown	Light yellow	Yellowish brown
Specific gravity at 20 °C		0.884	0.885	0.894	0.884
Refractive index at 20 °C		1.4594	1.4593	1.4592	1.4733
Viscosity at 20 °C, cp		1585	1590	1636	2550
Solubility b) in	Benzene	>100	>100	>100	>100
	Kerosene	>100	>100	>100	<2
	Cyclohexane	>100	>100	>100	>100
	2-Propanol	>100	>100	>100	>100
	Carbon tetrachloride	>100	>100	>100	>100
	Water	<1	<1	<1	<1

a) Apparent molecular weight determined by using benzene on a Hitachi Model 115 isothermal molecular weight apparatus. b) Solubility in grams per solvent in 100 g.

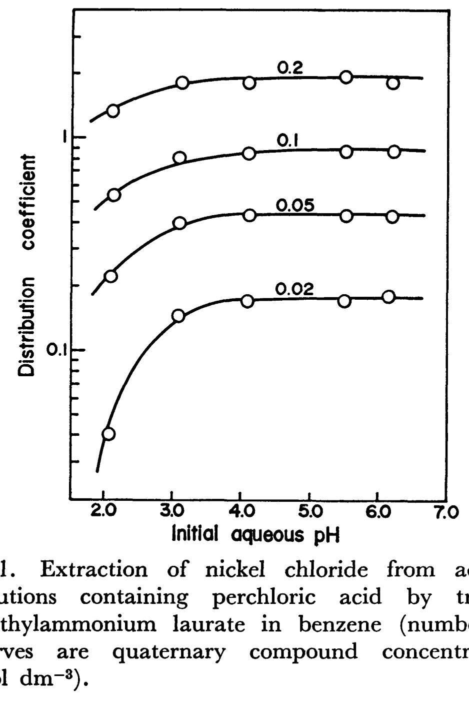

Fig. 1. Extraction of nickel chloride from aqueous solutions containing perchloric acid by trioctylmethylammonium laurate in benzene (numbers on curves are quaternary compound concentrations, mol dm^{-3}).

value of 0.02 mol dm^{-3} at the aqueous hydrochloric acid concentration above 0.02 mol dm^{-3} (Fig. 2). Additionally, the infrared spectra of the organic phase showed the formation of carboxylate supporting the reaction in Eq. 1. In addition, as the similar results are obtained in the extraction of perchloric acid with the quaternary compound, the reaction analogous to Eq. 1 holds in the extraction of perchloric acid, as well. Accordingly the quaternary compound is favorably utilized to extract metals from nearly neutral aqueous solutions at pH 5—8, since its compound is easily decomposed by acid.

In the extraction of aqueous solution containing nickel chloride at a constant pH of 5.5 with 0.01 mol dm^{-3} quaternary compound, the molar ratios of $[R_3R'NR''COO]_{org}$ and $[Cl]_{org}$ to $[Ni]_{org}$ plotted as a function of $[Ni]_{initial\ aq}$ approach the limiting values of 3 and 2, respectively, indicating the composition of the organic phase in the molar ratio of nickel/chlorine/quaternary compound = 1:2:3. However, when the initial aqueous nickel concentration increases above 10 g dm^{-3}, the latter molar ratio becomes over 2, because the hydrochloric acid arising from the hydrolysis of nickel chloride in the aqueous phase is extracted into the organic solution. This stoichiometry corresponds to the result obtained by the continuous variation method. In the extraction at a constant $[Cl]_{aq}$ of 0.1 mol dm^{-3}, the variation of $[Ni]_{org}$ as a function of the molar fraction of $[Ni]_{initial\ aq}/([Ni]_{initial\ aq}+[R_3R'NR''COO]_{org})$ at a fixed concentration of 0.1 mol dm^{-3} gives a maximum at the molar ratio of $[Ni]_{initial\ aq}$ to $[R_3R'NR''COO]_{org}$ of 1:3. Accordingly the extraction of nickel chloride from aqueous solutions by trioctylmethylammonium compound is expressed by the equilibrium equation:

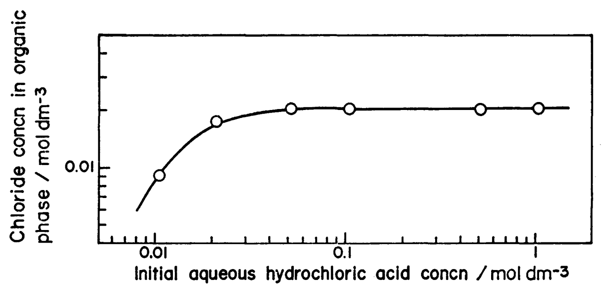

Fig. 2. Variation of the chloride concentration in the organic phase with initial aqueous hydrochloric acid concentration for the extraction of hydrochloric acid by 0.02 mol dm^{-3} trioctylmethylammonium laurate in benzene.

$$Ni^{2+}(a) + 2Cl^-(a) + 3R_3R'NR''COO(o) \rightleftharpoons (R_3R'N)[Ni(R''COO)_3](o) + 2R_3R'NCl(o). \quad (2)$$

This is also supported by the dependence of distribution coefficient on the concentrations of extractant and aqueous chloride. Equation 2 leads to the relationship:

$$K = [(R_3R'N)[Ni(R''COO)_3]]_{org}[R_3R'NCl]^2_{org}/[Ni^{2+}]_{aq}[Cl^-]^2_{aq}[R_3R'NR''COO]^3_{org}, \quad (3)$$

in which K is the equilibrium constant. If we assume that $E^0_a=[Ni]_{org}/[Ni]_{aq}$, $[Cl^-]_{aq}=2[Ni]_{aq}$, and $[R_3R'NCl]_{org}=2[Ni]_{org}$, the following relation is derived:

$$K = E^0_a[R_3R'NCl]^2_{org}/[Cl^-]^2_{aq}[R_3R'NR''COO]^3_{org} \quad (4)$$

$$= E^{0\,3}_a/[R_3R'NR''COO]^3_{org}. \quad (5)$$

Thus Eqs. 4 and 5 should be satisfied by

$$\log\{E^0_a[R_3R'NCl]^2_{org}/[R_3R'NR''COO]^3_{org}\} = \log K + 2\log[Cl^-]_{aq} \quad (6)$$

and

$$\log E^\circ_a = (1/3)\log K + \log[R_3R'NR''COO]_{org}. \quad (7)$$

In the extraction of nickel chloride from aqueous solutions containing perchloric acid, the log-log plots of E^0_a *vs.* the free quaternary compound concentration, $[R_3R'NR''COO]_{org}$, give straight lines with the slopes of 1.0 and 1.1 for the initial aqueous acidities of 0 and 0.01 mol dm^{-3}, respectively, suggesting a first-power dependence of the distribution coefficient on the solvent concentration. For the extraction of nickel chloride from aqueous solutions containing lithium chloride, the distribution coefficient rises with increasing the initial aqueous lithium chloride concentration (Table 2). However, when the extraction of aqueous lithium chloride solutions in the absence of nickel chloride is examined as in the case of acid extraction (Fig. 2), the increase of $[Cl]_{org}$ is slight with increasing the aqueous lithium chloride concentration (Table 2). Therefore, in the extraction of nickel chloride from aqueous solutions containing lithium chloride, the increase of the distribution coefficient with the initial aqueous lithium chloride concentration is attributed to the salting-out effect of lithium chloride. In this extraction, the log-log plots of $E^0_a[R_3R'NCl]^2_{org}/[R_3R'NR''COO]^3_{org}$ *vs.* $[Cl^-]_{aq}$ suggest a second-power dependence of the distribution coefficient on the aqueous chloride concentration.

The result for the extraction of bivalent manganese, cobalt, and copper from aqueous solutions containing their chlorides at 1 g dm^{-3} with trioctylmethylammonium laurate in the absence of perchloric acid are shown in Table 3, compared with that for nickel (II). Although the extraction efficiency is in the order Cu>Co≃Ni>Mn, the log-log plots of E^0_a *vs.* $[R_3R'NR''COO]_{org}$ for bivalent manganese, cobalt, and copper give straight lines with the slope of approximately unity, suggesting that their equilibria are indicated by the expression similar to Eq. 2 in the extraction of nickel(II). These facts are also supported by the variation in the stoichiometric composition of their organic phases as a function of the initial aqueous metal concentrations, and, in addition, by the continuous variation method for the metal concentrations in their organic phases. Hence it is presumed that the extraction of bivalent transition metals from aqueous chloride solutions by quaternary compound proceeds in the following expression:

$$M^{2+}(a) + 2Cl^-(a) + 3R_3R'NR''COO(o) \rightleftharpoons (R_3R'N)[M(R''COO)_3](o) + 2R_3R'NCl(o), \quad (8)$$

where M=Mn, Co, Ni, and Cu.

Temperature Effect. The extraction of aqueous solution (pH 5.5) containing nickel chloride at 1 g dm^{-3} with 0.02 mol dm^{-3} trioctylmethylammonium laurate at the temperature 10—50 °C gives the result that the distribution coefficient is little influenced by varying the temperature. When the similar experiments were carried out for the extraction of bivalent manganese, cobalt, and copper, the effect of temperature on the distribution coefficients was small (Fig. 3). From the thermodynamic values (the change in free energy, enthalpy, and entropy) for Eq. 8 estimated together with the equilibrium constants at 20 °C (Table 4), the order Cu>Co≃Ni>Mn corresponds to the increase in the free energy change and/or the decrease in the equilibrium constant, although the individual change in enthalpy or entropy does not indicate a reciprocal relation with the extraction efficiency. The equilibrium constants calculated by Eq. 7 agree with those indicated in Table 4. Especially the order of the extraction efficiency depends presumably on the variation in the equilibrium constants with different metal ions.

Infrared and Absorption Spectra. The infrared

TABLE 2. EXTRACTION OF AQUEOUS SOLUTIONS CONTAINING LITHIUM CHLORIDE IN THE ABSENCE OR THE PRESENCE OF NICKEL CHLORIDE AT 1 g dm^{-3} WITH TRIOCTYLMETHYLAMMONIUM LAURATE IN BENZENE

Initial aq [LiCl]/mol dm^{-3}	$[Cl]_{org}\times10^3$/mol dm^{-3} a)	E^0_a
0.01	0.657	0.178
0.02	0.750	0.269
0.05	0.938	0.385
0.1	1.31	0.495
0.2	1.78	0.645
0.5	3.10	1.03
1.0	4.40	1.36

a) The extraction in the absence of nickel chloride.

TABLE 3. EXTRACTION OF BIVALENT MANGANESE, COBALT, NICKEL, AND COPPER FROM AQUEOUS SOLUTIONS CONTAINING THEIR CHLORIDES AT 1 g dm^{-3} WITH TRIOCTYLMETHYLAMMONIUM LAURATE IN BENZENE

$[R_3R'NR''COO]$ / mol dm^{-3}	Distribution coefficient, E^0_a			
	Mn	Co	Ni	Cu
0.01	0.0575	0.0912	0.0908	0.579
0.02	0.140	0.204	0.175	1.92
0.05	0.325	0.450	0.451	12.4
0.1	0.637	0.941	0.938	42.3
0.2	1.24	1.93	1.99	118

TABLE 4. THERMODYNAMIC VALUES[a)] ESTIMATED FROM THE TEMPERATURE-DEPENDENCE OF DISTRIBUTION COEFFICIENTS FOR BIVALENT TRANSITION METALS, COMPARED WITH THE EQUILIBRIUM CONSTANTS

Metal	ΔG / kJ mol^{-1}	ΔH / kJ mol^{-1}	ΔS / J K^{-1} mol^{-1}	K b)
Mn	−15.65	−5.06	36.11	6.2×10^2
Co	−18.62	14.48	113.0	2.1×10^3
Ni	−17.66	0	60.25	1.4×10^3
Cu	−43.85	−25.10	64.02	6.6×10^7

a) ΔG, ΔH, and ΔS represent the changes in free energy, enthalpy and entropy, respectively. b) K denotes the equilibrium constant at 20 °C for Eq. 8.

TABLE 5. INFRARED SPECTRAL DATA FOR THE ORGANIC EXTRACTS FROM AQUEOUS SOLUTIONS CONTAINING CHLORIDES OF MANGNESE, COBALT, NICKEL, AND CCPPER WITH 0.01 mol dm^{-3} TRIOCTYLMETHYLAMMONIUM LAURATE IN BENZENE

Frequency/cm^{-1}							Probable assignment
$R_3R'NCl$	$R_3R'NR''COO$	Organic extract					
		Mn(II)	Co(II)	Ni(II)		Cu(II)	
		10[b]	10	1	20	1	
3420 (mb)[a]	3320 (mb)	3380 (mb)	3380 (mb)	3370 (mb)	3400 (mb)	3360 (mb)	OH stretching
2920 (s)	2920 (s)	2920 (s)	2920 (s)	2920 (s)	2920 (s)	2920 (s)	CH stretching
2860 (ms)	2860 (ms)	2860 (ms)	2860 (ms)	2860 (ms)	2860 (ms)	2860 (ms)	
		2600 (sh)	2600 (sh)		2600 (sh)	2600 (sh)	OH stretching
		1720 (sh)	1720 (sh)		1720 (w)	1720 (w)	CO stretching
1625 (wb)	1650 (sh)	1640 (w)	1640 (sh)	1640 ((sh)	1640 (sh)	1640 (sh)	OH bending
	1560 (m)	1560 (m)	1560 (m)	1560 (m)	1560 (m)	1560 (m)	CO stretching
1465 (m)	1465 (m)	1465 (m)	1465 (m)	1465 (m)	1465 (m)	1465 (m)	CH_3 degenerate bending CH_2 scissoring
					1425 (m)	1410 (m)	CO stretching OH bending
1375 (m)	1380 (m)	1380 (m)	1380 (m)	1380 (m)	1380 (m)	1380 (m)	CO stretching CH_3 sym. bending and/or
					1180 (w)		CO stretching OH bending
725 (w)	725 (w)	725 (w)	725 (w)	725 (w)	725 (w)	725 (w)	CH_2 rocking

a) s=Strong, ms=medium strong, m=medium, w=weak, b=broad, sh=shoulder. b) This represents initial aqueous metal chloride concentration, g dm^{-3}.

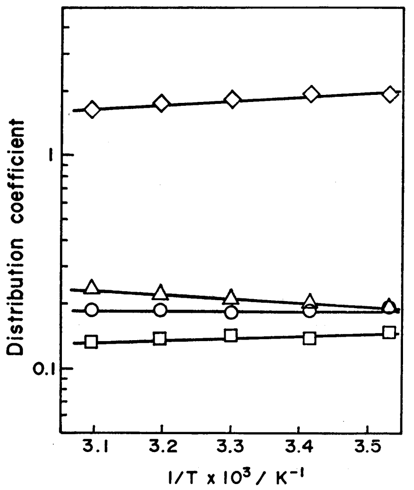

Fig. 3. Temperature-dependence of distribution coefficient for the extraction of bivalent transition metals from aqueous solutions containing their chlorides at 1 g dm^{-3} by 0.02 mol dm^{-3} trioctylmethylammonium laurate in benzene (□, △, ○, and ◇ represent the extractions of manganese, cobalt, nickel, and copper, respectively).

spectra of the organic extracts from the extraction of aqueous nickel chloride solutions at trioctylmethylammonium laurate were compared with that of the quaternary ammonium compound. The frequencies and possible band assignments are given in Table 5. In the infrared spectrum of carboxylic acid, the C–O stretching bands appear at 1710 and 1400—1200 cm^{-1}.[11] However, the quaternary compound shows the similar bands at 1560 and 1380 cm^{-1}, indicating that the extractant exists in the organic phase as a carboxylate,[12] $R_3R'NR''COO \cdot 5H_2O$. As for the infrared spectra of the organic nickel(II) extracts, the C–O stretching modes appear at the same frequencies as those of the quaternary compound. However, the relative intensity relation between the absorption band at 1465 cm^{-1} (the CH_3 degenerate bending and CH_2 scissoring) and the band at 1380 cm^{-1} (the C–O stretching vibration superposed on the CH_3 symmetrical bending absorption) becomes converse in comparison with that for the quaternary compound, in which the former band is slightly stronger than the latter one. For the nickel(II) complex, the latter band is more intense than the former one because the carboxylate group is coordinated to nickel ion as a bidentate ligand.[12,13] At higher loading, the C–O stretching bands appear at 1720, 1425, and 1180 cm^{-1}; this is ascribed to the presence of carboxylic acid formed by the combination of a part of extractant with the hydrochloric acid which results from the hydrolysis of nickel chloride in the aqueous phase at high concentrations. Further, the absorption due to the Ni–Cl vibration is not observed in far-infrared region, indicating that the chloride ion in the organic phase is not coordinated to nickel ion. Similar infrared results are also observed for the extraction of aqueous solutions containing chlorides of manganese, cobalt, and copper (Table 5).

In addition, the absorption spectra of the organic solutions from the extraction of manganese, cobalt, nickel, and copper chlorides with the quaternary compound are illustrated in Fig. 4. The spectrum of the organic nickel(II) species reveals the characteristic feature of a six-coordinated complex ion,[14] showing absorption bands at 25000, 14700, 13300, and 8300 cm^{-1} which are ascribed to three spin-allowed transitions from the ground state $^3A_{2g}(F)$ to the states

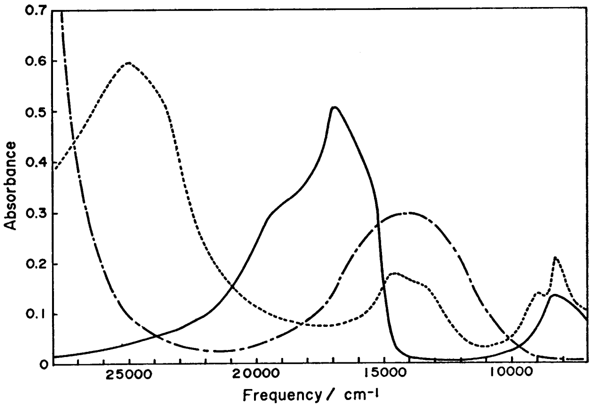

Fig. 4. Absorption spectra of the organic solutions from the extraction of aqueous solution containing chlorides of cobalt, nickel and copper at 100, 100, and 20 g dm^{-3}, respectively, with 0.05 mol dm^{-3} trioctylmethylammonium laurate in benzene (continuous, broken and chain lines represent the organic solutions of cobalt, nickel, and copper, respectively).

$^3T_{1g}(P)$, $^3T_{1g}(F)$, and $^3T_{2g}(F)$, respectively. The ligand field parameters for the complex $(R_3R'N)[Ni(R''COO)_3]$ are calculated by using the matrix elements determined by Tanabe and Sugano:[15] $B = 950\ cm^{-1}$ and $10\,D_q = 8550\ cm^{-1}$. The difference between the calculated value of $10\,D_q$ and the observed one (8300 cm^{-1}) may be attributed to the assignment of the absorption at 8300 cm^{-1} to the transition to $^3T_{2g}(F)$, although two absorptions appear at 8200 and 8300 cm^{-1}. This is because the state $^2T_{2g}(F)$ should be split into two states ^3E and $^3A_1$, if the symmetry of the complex is lowered from O_h to D_3.[16] Further the factor β is estimated to be 0.88, implying relative low covalent bond character in the nickel(II) complex. The spectrum of the organic cobalt(II) species exhibits the typical absorption of a six-coordinated complex at 19230, 16950, and 8260 cm^{-1}, transitions from $^4T_{1g}(F)$ to $^4T_{1g}(P)$, $^4A_{2g}(F)$, and $^3T_{2g}(F)$, respectively. Accordingly the calculated value of $10\,D_q$ (9500 cm^{-1}) in the cobalt(II) complex is close to the value of $10\,D_q$ (9300 cm^{-1}) in the aqua ion $[Co(H_2O)_6]^{2+}$.[14] For the organic extract of copper(II) complex, the value of $10\,D_q = 13990\ cm^{-1}$ resembles that in the hexaaquacopper(II) species. In contrast, the organic manganese(II) extract reveals a strong charge-transfer absorption at 34000—20000 cm^{-1}, covering the weak absorption due to the spin-forbidden transitions.

Therefore, the extracted species of bivalent manganese, cobalt, nickel, and copper exist as the octahedral complex $(R_3R'N)[M(R''COO)_3]$.

Effect of Carboxylic Acid. In the extraction of solution (at pH 5.5) containing nickel chloride at 1 g dm^{-3} by quaternary ammonium compounds with octanoic, decanoic, and lauric acids, the plots of the distribution coefficient *vs.* the free quaternary compound concentration gave a straight line with the slope of nearly unity for respective carboxylates (Fig. 5). From this the effect of the different kinds of carboxylic acid on the extraction efficiency is not remarkable, although their efficiencies increase in the order of octanoic, decanoic, and lauric acids. Thus the extraction mechanism of nickel by quaternary compounds is supposed to be almost the same for each carboxylate (Eq. 2). Similar results are obtained for the extraction of bivalent manganese, cobalt, and copper by quaternary compound, as well.

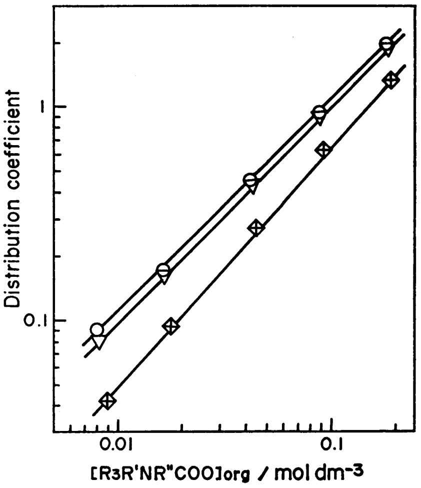

Fig. 5. Log-log plots of distribution coefficient *vs.* free alkylammonium carboxylate concentration for the extraction of aqueous solution containing nickel chloride by quaternary compounds (⊕, ▽, and ○ represent quaternary compounds with octanoic, decanoic, and lauric acids).

References

1) E. G. Miller, *Talanta*, **21**, 685 (1974).

2) J. C. Davis and R. R. Grinstead, *J. Phys. Chem.*, **74**, 147 (1970).

3) C. Hanson and S. L. N. Murthy, "Proc. Int. Solvent Extraction Conf., Lyon, 1974," ed by Soc. Chem. Ind., London (1974), Vol. 1, p. 779.

4) C. Hanson, M. A. Hughes, and S. L. N. Murthy, *J. Inorg. Nucl. Chem.*, **37**, 191 (1975).

5) *E.g.*, T. Sato and H. Watanabe, *Anal. Chim. Acta*, **49**, 463 (1970); T. Sato, *J. Inorg. Nucl. Chem.*, **34**, 3835 (1972); T. Sato, S. Kotani, and M. L. Good, *ibid.*, *Chem.*, **35**, 2547 (1973); **36**, 451 (1974); T. Sato, H. Watanabe, and S. Kikuchi, *J. Appl. Chem. Biotechnol.*, **25**, 63 (1975); T. Sato, H. Watanabe, S. Kotani, and M. L. Good, *Anal. Chim. Acta*, **84**, 397 (1976).

6) T. Sato, *J. Inorg. Nucl. Chem.*, **24**, 1265 (1962).

7) H. Flaschka and H. Abdine, *Chemist-Analyst*, **45**, 58 (1956).

8) H. Flaschka, *Chemist-Analyst*, **42**, 56 (1953).

9) J. Kinnunen and B. Wennerstrand, *Chemist-Analyst*, **46**, 92 (1957).

10) K. L. Cheng and R. H. Bray, *Anal. Chem.*, **27**, 782 (1955); K. L. Cheng, *Anal. Chem.*, **30**, 243 (1958).

11) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley, New York (1958), p. 161.

12) K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds," 3rd ed, Wiley-Interscience, New York (1978), p. 230.

13) S. D. Robinson and M. F. Uttley, *J. Chem. Soc.*, 1912 (1973).

14) *E.g.*, N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3977 (1959).

15) Y. Tanabe and S. Sugano, *J. Phys. Soc. Jpn.*, **9**, 753, 766 (1954).

16) T. S. Piper and R. L. Carlin, *J. Chem. Phys.*, **35**, 1809 (1960).