ADVANCES IN INORGANIC CHEMISTRY AND RADIOCHEMISTRY, VOL. 29

SOLVENT EXTRACTION OF METAL CARBOXYLATES

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I. Introduction

Carboxylic acids are conveniently utilized in the extraction of a number of metal ions. The dissolution of metal soaps in trichlorobenzene was first noticed by Biffen and Snell (*12*). The first example of the liquid–liquid extraction involving a metal carboxylate appears to be the extraction of scandium with benzoic acid prior to the colorimetric determination (*54*).

In the early 1950s there were proposed several procedures involving carboxylic acids for separation of metals such as copper and beryllium (*9, 87, 140, 149*). After these analytical applications of the carboxylate extraction system, Hök-Bernström published a series of papers dealing with the quantitative analysis of the extraction equilibria involving metal carboxylates (*48–50*). Since then the extraction of metal carboxylates has been extensively studied and the subject has been reviewed from time to time by the following authors: Fletcher and Flett (*23*), Flett and Jaycock (*26*), Ashbrook (*8*), Miller (*85*), Rice (*118*), and Brzózka and Rózycki (*14*). Martinov has elaborated a data compilation of the extraction of metals with organic acids including carboxylic acids (*78b*).

The carboxylate extraction system has been recognized as more advantageous than the chelate extraction system, since one can deal with more concentrated metal solutions in the former than in the latter. Thus the application of the carboxylate extraction to hydrometallurgy has been attempted, and in this connection extensive studies have been carried out in the Soviet Union and the United Kingdom.

There have been a number of physicochemical studies on the organic solutions of metal soaps and the critical solution temperature has been determined for a metal soap–organic solvent pair: below this temperature we observe no appreciable dissolution of the metal soap, while above this particular temperature, dissolution becomes appreciable. According to these studies, metal soaps are in the form of micelles composed of several formula units of metal carboxylate, and the composition of the solute species was said to be indefinite (*78a, 94*).

With nonchelating agents such as carboxylates, the coordination–saturation is not expected to occur at the same time as the charge neutralization, which would be the case with some chelating agents. Thus, in order to satisfy the coordination number of a metal ion in a carboxylate, it is necessary either to add neutral ligands such as carboxylic acids or to form polymerized species, in which metal ions share apices or edges with each other. The polymerization of metal carboxylates is characterized either by the liberation of free carboxylic acid or by the formation of hydroxo or oxo bridges.

Though the extraction of metals with carboxylic acids is sometimes very complicated, we have in effect extracted species of definite composition when we study the system as a function of the concentration of free carboxylic acid.

The formation of a dimerized extracted species was first reported for the extraction of copper(II) with propanoic acid (*40, 41*). Later, nickel and cobalt were found to be extracted as dimers (*22*), and a mixed copper(II) carboxylate dimer involving acetate and decanoate was reported (*147*). More recently, attention has been drawn to the extraction of heteropolynuclear metal carboxylates (*90, 91*).

In these complicated extraction systems containing the polymeric and/or hydroxo species, one would expect the solvent used as a diluent to exert a considerable effect on the extraction equilibrium. In the extraction of gallium(III) with decanoic acid it has been found that the less polar the solvent, the more polymerized the extracted species (*150*). More recently, the solvent effect on the extraction (*156*) and dimerization (*151, 153*) of copper(II) decanoate has been interpreted according to regular solution theory (*141, 142*).

II. Partition of a Carboxylic Acid between the Aqueous and Organic Phases

In the solvent extraction of metal ions with carboxylic acids, it is indispensable to have information about the partition of the carboxylic acid between the aqueous and organic phases. The carboxylic acid is known to dimerize in nonsolvating solvents.

The partition of a carboxylic acid HA into an organic solvent is written as

$$(\mathrm{HA})_w \rightleftharpoons (\mathrm{HA})_o$$

where the subscripts refer to the water (w) or organic (o) phase. The partition constant is defined as

$$K_{\mathrm{D,HA}} = [\mathrm{HA}]_o[\mathrm{HA}]_w^{-1}. \tag{1}$$

The dimerization of HA in the organic phase is given by the following:

$$2(\mathrm{HA})_o \rightleftharpoons (\mathrm{HA})_{2,o}$$

with $(\mathrm{HA})_{2,o}$ denoting the dimeric acid in the organic phase, and the dimerization constant defined as

$$K_2 = [(\mathrm{HA})_2]_o[\mathrm{HA}]_o^{-2}. \tag{2}$$

In the solvent extraction of metal ions with carboxylic acids, these equilibria should be considered along with the dissociation of HA in the aqueous phase:

$$\mathrm{HA} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^+} + \mathrm{A^-}, \qquad K_a = [\mathrm{H_3O^+}][\mathrm{A^-}][\mathrm{HA}]^{-1}. \tag{3}$$

In Table I, the partition and dimerization constants of some carboxylic acids are given.

Values of K_D are higher for polar solvents such as 4-methyl-2-pentanone and octanol than for nonpolar solvents such as benzene and hexane. On the contrary, K_2 values are higher in nonpolar solvents than in polar solvents. These facts result from the extensive solvation of carboxylic acids in polar or coordinating solvents. Thus for a carboxylic acid (*18, 19, 67*)

$$\log K_2 = -2 \log K_D + \text{constant}. \tag{4}$$

TABLE I

PARTITION AND DIMERIZATION CONSTANTS OF CARBOXYLIC ACIDS AT 25°C[a]

Acid		Solvent					
		Toluene	Benzene	Chloroform	1,2-DCE[b]	NB[c]	IPE[d]
Propanoic:	$\log K_D$	−1.47	−1.36	−0.96	−0.99	−0.86	−0.09
	$\log K_2$	2.39	2.21	1.94	1.53	0.97	−0.30
Butanoic:	$\log K_D$	0.68[e]	−0.79	−0.27[f]	−0.39	−0.34	0.48
	$\log K_2$	1.98[e]	2.28	1.69[f]	1.45	0.95	−0.37
Pentanoic:	$\log K_D$	−0.20[f]	−0.16	0.19[f]	0.23	0.23	1.05
	$\log K_2$	2.30[f]	2.36	1.82[f]	1.35	1.01	−0.20
Hexanoic:	$\log K_D$	0.56[f]	0.31	1.05[f]	0.82	0.77	1.48
	$\log K_2$	2.13[f]	2.45	1.40[f]	1.19	0.96	−0.19
Octanoic:	$\log K_D$		1.67[g]	2.17[g]			
	$\log K_2$		2.51[g]	2.46[g]			
Decanoic:	$\log K_D$		2.41[h]				
	$\log K_2$		2.80[h]				
Benzoic:	$\log K_D$	0.06[i]	0.14[i]		0.59[i]		
	$\log K_2$	2.48[i]	2.46[i]		1.56[i]		

[a] Data from reference *67*.
[b] 1,2-Dichloroethane.
[c] Nitrobenzene.
[d] Isopropyl ether.
[e] Ref. *65*.
[f] Ref. *134*.
[g] Ref. *128*.
[h] Ref. *144*.
[i] Ref. *29*.

The more extensive the solvation of monomeric acid, the less extensive the dimerization. The extensive solvation favors the partition of an acid and a higher partition constant results.

Values of $\log K_D$ increase with increasing carbon number in carboxylic acids. The increment of $\log K_D$ for an added methylene group is mainly due to the volume contribution of the methylene group to the partition, and thus it varies little from solvent to solvent, i.e., $\Delta \log K_D/CH_2 = 0.56 - 0.64$ (*21, 31, 141*). The different $\Delta \log K_D/CH_2$ values for different solvents are ascribable to the different solute–solvent interactions, and have been discussed elsewhere in more detail (*31*).

In the partition of an acid between the aqueous and organic phases, hydration of the acid inevitably occurs. In addition to the monohydrates of monomer and dimer, the dimer dihydrate (*29*) and trihydrate (*30*) have been found in some organic solvents. Högfeldt has also proposed the trihydrate of dimeric trichloroacetic acid and the monohydrate of tetrameric acetic acid in some solvents (*47, 71*).

The dimerization constants of carboxylic acids determined by the partition method are usually lower than the values obtained by IR spectroscopy, cryoscopy, or dielectric measurements (*100*). The correction for hydration gives dimerization constants expected from values in dry solvents by spectroscopic or dielectric measurements (*29, 30*).

III. Solvent Extraction of Metal Ions with Carboxylic Acids

A. EQUILIBRIUM TREATMENT

As stated earlier the polymeric species are often involved in the extraction of metal carboxylates. Therefore, the extraction equilibrium is sometimes more complicated than in the chelate extraction system. As is evident from the following treatment, it is advantageous and often indispensable to study the total metal concentration in the organic phase [Eq. (8)] instead of the conventionally utilized distribution ratio of the metal [Eq. (7)].

When a j-merized metal carboxylate of the composition $M_jA_aH_h$ $(nj = a - h)$ is responsible for the extraction of a metal ion M^{n+} with a carboxylic acid HA, the extraction equilibrium is written as:

$$jM^{n+} + \tfrac{a}{2}(HA)_{2,o} \rightleftharpoons (M_jA_aH_h)_o + njH^+ \tag{5}$$

with

$$K_{ex(jah)} = \frac{[M_jA_aH_h]_o[H^+]^{nj}}{[M^{n+}]^j[(HA)_2]_o^{a/2}}. \tag{6}$$

The distribution ratio (D) of the metal between the organic and aqueous phases is given by

$$\begin{aligned} D = \frac{C_{M,o}}{C_{M,w}} &= \sum_j \sum_a j[M_jA_aH_h]_o/[M^{n+}]\alpha_M \\ &= \sum_j \sum_a (jK_{ex(jah)}[M^{n+}]^{(j-1)}\alpha_M^{-1}[(HA)_2]_o^{a/2}[H^+]^{-nj}), \end{aligned} \tag{7}$$

where $C_{M,o}$, $C_{M,w}$, and α_M are the total concentrations of the metal in the organic and aqueous phases, and the side-reaction coefficient taking into account the complexation of the metal in the aqueous phase (*119*), respectively. On the other hand, the total concentration of the metal in the organic phase is written as

$$C_{\mathrm{M,o}} = \sum_j \sum_a j[\mathrm{M}_j\mathrm{A}_a\mathrm{H}_h]_{\mathrm{o}} = \sum_j \sum_a (jK_{\mathrm{ex}(jah)}[\mathrm{M}^{n+}]^j[(\mathrm{HA})_2]_{\mathrm{o}}^{a/2}[\mathrm{H}^+]^{-nj}). \quad (8)$$

When only $M_jA_aH_h$ is responsible for the extraction, Eqs. (9) and (10) are derived from Eqs. (7) and (8), respectively:

$$\log D = (j-1)\log[\mathrm{M}^{n+}] + \tfrac{a}{2}\log[(\mathrm{HA})_2]_{\mathrm{o}} - nj\log[\mathrm{H}^+] - \log\alpha_{\mathrm{M}} + \log j + \log K_{\mathrm{ex}(jah)}, \quad (9)$$

and

$$\log C_{\mathrm{M,o}} = j(\log[\mathrm{M}^{n+}] - n\log[\mathrm{H}^+]) + \tfrac{a}{2}\log[(\mathrm{HA})_2]_{\mathrm{o}} + \log j + \log K_{\mathrm{ex}(jah)}. \quad (10)$$

According to Eq. (9), the conventional plot of $\log D$ against $-\log[H^+]$ at a constant $[(HA)_2]_o$ should yield a straight line with a slope of n only when j and α_M are equal to unity. For the polymeric extracted species, the distribution ratio, D, depends not only on $[H^+]$ and $[(HA)_2]_o$ but also on the metal ion concentration. Therefore, the plot according to Eq. (9) yields a curve (Fig. 1). As shown in Fig. 1, the plot falls on the straight

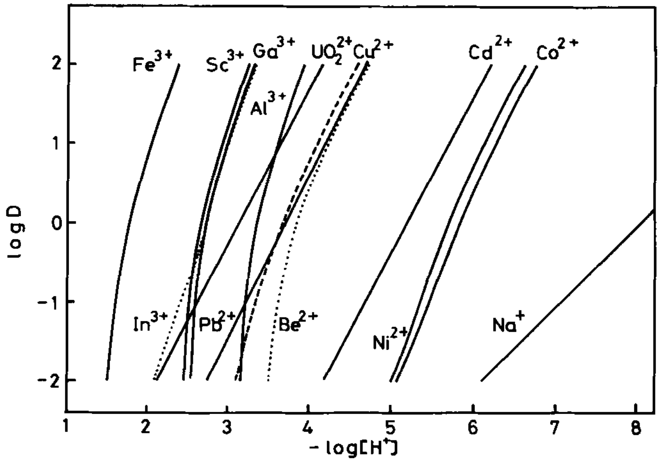

FIG. 1. Plot of $\log D$ vs. $-\log[H^+]$ for the extraction of metal ions with decanoic acid in benzene. Solid lines are calculated by Eq. (9) with the results taken from refs. *63, 89, 91, 92, 143–146, 154–156*, at the total metal concentration $C_M = 5 \times 10^{-3}$ mol dm^{-3}, and the total concentration of decanoic acid $C_{HA} = 1.0$ mol dm^{-3}.

line with a slope of n for relatively high values of D ($D > 10$). In such cases, we may conclude quite erroneously a monomeric species like MA_n even for a polymeric extracted species $(MA_n)_j$.

According to Eq. (10), on the other hand, the plot of $\log C_{M,o}$ against $(\log[M^{n+}] - n\log[H^+])$ at a constant carboxylic acid concentration should yield a straight line with a slope of j, the degree of polymerization. If two or more species with different degrees of polymerization are responsible for the extraction, as in the case of indium, cobalt, and nickel (*145, 143, 144*), this plot gives rise to a curve (Fig. 2). By analysis of this curve we see the variation in the degree of polymerization of the extracted species (*143–145*). It may be noted that in most cases free carboxylic acid is liberated in the polymerization of the metal carboxylate. Thus the higher the carboxylic acid concentration and the lower the metal concentration in the organic phase, the lower will be the degree of polymerization of the extracted carboxylate.

The plot according to Eq. (10) is of general use in studies not only on the carboxylate extraction system but also on the chelate extraction system. For instance, vanadium (V) 8-quinolinolate was found to be extracted as an oxo-bridged dimeric form (*158*), whose structure was later established by X-ray crystallography (*157*).

Equation (10) yields directly the following relation:

$$\log C_{M,o} - j(\log[M^{n+}] - n\log[H^+]) = \frac{a}{2}\log[(HA)_2]_o + \log j + \log K_{ex(jah)}. \quad (11)$$

The left-hand side of Eq. (11) can be plotted against $\log[(HA)_2]_o$ under conditions where only one j-merized carboxylate is responsible for the

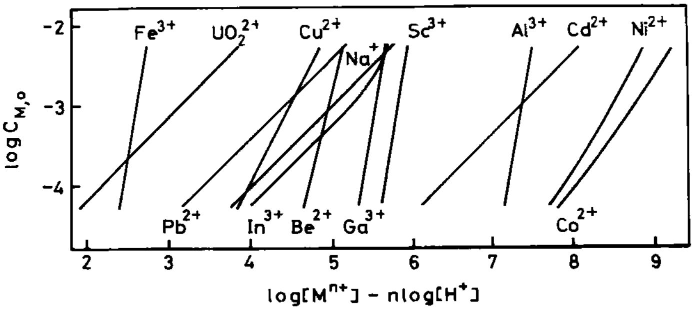

FIG. 2. Plot of $\log C_{M,o}$ vs. $(\log[M^{n+}] - n\log[H^+])$ for the extraction of metal ions with decanoic acid in benzene. Solid lines are calculated by Eq. (10) with the results taken from the same references as in Fig. 1 under the same conditions as in Fig. 1.

extraction. The plot gives rise to a straight line with a slope of $a/2$, thus permitting the determination of the number of carboxylate residues involved in the extracted species. From the intercept of the plot, we find the extraction constant $\log K_{\mathrm{ex}(jah)}$. When two or more species involving a different number of carboxylate residue are responsible for the extraction, the plot of the left-hand side of Eq. (11) vs. $\log[(\mathrm{HA})_2]_o$ gives rise to a curve. In this case, according to the curve-fitting method, in which the plot is compared with a family of normalized curves, the total number of carboxylate residues involved in the extracted species and the corresponding extraction constants can be determined (*89, 92, 155*).

When the coordination number of the metal ion in the extracted species is not satisfied with carboxylate and carboxylic acid, the water determination should be made on the extracted species. If a hydrated extracted species is involved in the extraction, the following equilibrium is relevant to the extraction:

$$j\mathrm{M}^{n+} + \tfrac{a}{2}(\mathrm{HA})_{2,o} + w\mathrm{H_2O} \rightleftharpoons [\mathrm{M}_j\mathrm{A}_a\mathrm{H}_h(\mathrm{H_2O})_w]_o + nj\mathrm{H}^+ \tag{12}$$

with

$$K_{\mathrm{ex}(jahw)} = [\mathrm{M}_j\mathrm{A}_a\mathrm{H}_h(\mathrm{H_2O})_w]_o[\mathrm{H}^+]^{nj}[\mathrm{M}^{n+}]^{-j}[(\mathrm{HA})_2]_o^{-a/2}.$$

When the charge on the metal ion is completely neutralized with carboxylate, h is zero or positive and $a \geqq nj$. However in some cases we find a negative h. In these cases, the water determination is indispensable in finding the correct composition of the extracted species. If we find h water molecules for $\mathrm{M}_j\mathrm{A}_a\mathrm{H}_{-h}$, the extracted species should be written as $\mathrm{M}_j\mathrm{A}_a(\mathrm{OH})_h$ with the following extraction equilibrium:

$$j\mathrm{M}^{n+} + \tfrac{a}{2}(\mathrm{HA})_{2,o} + h\mathrm{H_2O} \rightleftharpoons [\mathrm{M}_j\mathrm{A}_a(\mathrm{OH})_h]_o + nj\mathrm{H}^+ \tag{13}$$

with

$$K_{\mathrm{ex}(ja-h)} = [\mathrm{M}_j\mathrm{A}_a(\mathrm{OH})_h]_o[\mathrm{H}^+]^{nj}[\mathrm{M}^{n+}]^{-j}[(\mathrm{HA})_2]_o^{-a/2}.$$

If, on the other hand, the number of water molecules found for $\mathrm{M}_j\mathrm{A}_a\mathrm{H}_{-h}$ is $h/2$, then $h/2$ oxo group(s) should be involved in the extracted species instead of h hydroxo group(s). In that case, following equilibrium becomes relevant to the extraction:

$$j\mathrm{M}^{n+} + \tfrac{a}{2}(\mathrm{HA})_{2,o} + \tfrac{h}{2}\mathrm{H_2O} \rightleftharpoons (\mathrm{M}_j\mathrm{A}_a\mathrm{O}_{h/2})_o + nj\mathrm{H}^+ \tag{14}$$

with

$$K_{\mathrm{ex}(ja-h/2)} = [\mathrm{M}_j\mathrm{A}_a\mathrm{O}_{h/2}]_o[\mathrm{H}^+]^{nj}[\mathrm{M}^{n+}]^{-j}[(\mathrm{HA})_2]_o^{-a/2}.$$

B. EXTRACTION OF METAL IONS

The composition and extraction constant of various metal carboxylates are tabulated in Table II.

1. *Alkali Metals*

Alkali metal salts are generally used in order to keep constant the ionic strength of the aqueous phase. Therefore, even in the extraction of a metal ion other than alkali metal ions with carboxylic acids, we should also consider the extraction of alkali metal ions either as a simple carboxylate or a mixed-metal carboxylate.

In the extraction of alkali metal ions with C_7–C_9 aliphatic carboxylic acids, Mikhailichenko and Rozen found the following order of extractability: $K^+ > Cs^+ > Na^+ > Li^+$ (*83, 120*).

For the extraction of sodium ions with decanoic acid in benzene, Nakasuka *et al.* (*91*) proposed the following extraction equilibria:

$$Na^+ + 2(HA)_{2,o} \rightleftharpoons [NaA(HA)_3]_o + H^+$$

$$Na^+ + 3(HA)_{2,o} \rightleftharpoons [NaA(HA)_5]_o + H^+$$

$$Na^+ + 4(HA)_{2,o} \rightleftharpoons [NaA(HA)_7]_o + H^+$$

TABLE II

EXTRACTION OF METAL IONS WITH CARBOXYLIC ACIDS

Organic Phase[a]	Extracted Species, log K_{ex}	Reference
	Alkali metals	
Nona/decane	$NaA(HA)_4(H_2O)_w$	*55, 56*
Nona/isooctanol	$NaA(H_2O)_w$, −9.69	*59*
Deca/benzene	$NaA(HA)_3$, −8.28; $NaA(HA)_5$, −7.22; $NaA(HA)_7$, −7.64	*91*
Vers/*n*-octane	$NaA(HA)_2$; $NaA(HA)_3$	*79*
	Alkaline earth metals	
Deca/benzene	Be_4A_6O, −22.6	*63*
Naph/kerosene	BeA_2, −8.37	*5*
Naph/kerosene	MgA_2, −13.90	*5*
C_7–C_9 mix/octane	$MgA_2(HA)_4$, −12.16	*81*
Naph/kerosene	CaA_2, −12.63	*5*
C_7–C_9 mix/octane	$CaA_2(HA)_4$, −11.13	*81*
(Penta, Hexa, Octa, Deca)/octane	$SrA_2(HA)_4(H_2O)_4$, −10.68, −10.57, −10.46, −10.38	*82*
Vers/*n*-octane	$SrA_2(HA)_2$; $SrA_2(HA)_3$	*79*
Naph/kerosene	SrA_2, −11.28	*5*
C_7–C_9 mix/octane	$SrA_2(HA)_4$, −10.42	*81*

(*continued*)

TABLE II (*continued*)

Organic Phase[a]	Extracted Species, log K_{ex}	Reference
Naph/kerosene	BaA_2, −9.77	*5*
C_7–C_9 mix/octane	$BaA_2(HA)_4$, −9.64	*81*
	Al, Ga, In, and Tl	
Deca/benzene	$Al_6A_{12}(OH)_6$, −46.1	*146, 155*
Deca/benzene	$Ga_6A_{18}(H_2O)_6$, −34.3; $Ga_6A_{12}(OH)_6$, −35.8; $Ga_jA_aH_h$ $(j < 6)$	*155*
Deca/toluene	$Ga_6A_{18}(H_2O)_w$ $(w > 6)$, −33.21; $Ga_jA_aH_h$ $(j < 6)$	*150*
Deca/CB	Ga_3A_9, −19.14	*150*
Deca/1,2-DCE	GaA_3, −9.42; Ga_3A_9, −18.9	*150*
Deca/1-octanol	$GaA_2(OH)$, −9.54; $Ga_2A_4(OH)_2$, −14.92; Ga_2A_6, −15.26	*150*
Hexa/$CHCl_3$	$InA_3(HA)_3$	*125*
Deca/benzene	$InA_3(HA)_3$, −7.34; $In_3A_9(HA)_3$, −18.6; $In_6A_{12}(OH)_6$, −36.1	*145*
Hexa/MIBK	$TlA(HA)_2$	*130*
Hexa/benzene, $CHCl_3$	$TlA(HA)_3$	*130*
Hexa/NB	$TlA(HA)_4$	*130*
	Pb	
Deca/benzene	$PbA_2(HA)_2$, −7.12; $PbA_2(HA)_4$, −6.80	*92*
Vers 9/benzene	$PbA_2(HA)_2$	*115*
	Sc, Y, and Lanthanides	
Buta/*i*-butanol	ScA_3, −8.53	*36*
Hexa, α-BrHexa/$CHCl_3$	$ScA_3(HA)_3$	*138*
Deca/benzene	Sc_6A_{18}, −32.8	*154*
α,α′-DAC/heptane	$LnA_3(HA)_3$: La, −13.90; Ce, −13.61; Pr, −13.16; Nd, −12.85; Sm, −12.17; Eu, −12.28; Gd, −12.96; Dy, −12.81; Ho, −12.66; Tm, −13.26; Yb, −13.16; Lu, −13.13	*20*
Hexa/heptane	$LnA_3(HA)_3$	*20*
Hexa, α-BrHexa/$CHCl_3$	$LaA_3(HA)_3$	*138*
Vers/benzene	CeA_4	*117*
$Me_2(OH)$Hexa/$CHCl_3$	$NdA_3(HA)_5$; $Nd_2A_6(HA)_h$; Nd_2A_6; $(NdA_3)_j$ $(j > 2)$	*86*
Naph/n-octane	$Nd_2A_6(HA)_6(H_2O)_w$ $(w = 5–6)$	*84*
St/kerosene	EuA_3, −7.58	*75*
Hexa/MIBK	TmA_3HA	*129*
Hexa/$CHCl_3$	$TmA_3(HA)_5$	*129*
	Actinides	
Deca/benzene	$ThA_4(HA)_4$	*64*
Salicylic/MIBK	$Th(HA)_4 \cdot H_2A$ (H_2A, salicylic acid)	*49*
Methoxybenzoic/MIBK	ThA_4	*49*
Hexa/$CHCl_3$	$UO_2A_2(HA)_2$	*135*
Deca/benzene	$UO_2A_2(HA)_2(H_2O)_2$, −5.66; $UO_2A_2(HA)_4(H_2O)_2$, −5.83	*89*

TABLE II (*continued*)

Organic Phase[a]	Extracted Species, log K_{ex}	Reference
Deca/benzene	$UO_2A_2(HA)_2$	*64*
Vers 9/benzene	UO_2A_2HA	*116*
Salicylic/MIBK	$UO_2(HA)_2$; $UO_2(HA)_2 \cdot H_2A$	*48*
Methoxybenzoic/MIBK	UO_2A_2	*48*
Deca/benzene	$AmA_3(HA)_5$	*64*
	Mn, V, and Fe	
Deca/benzene	$Mn_2A_4(HA)_4$	*11*
Naph/decane	$MnA_2(HA)_2$, −10.94	*39*
Deca/benzene	$(VO)_2A_4$, −13.7	*93*
Octa/(decane, benzene, NB + CCl_4, CCl_4, TCB, *i*-amOAc, $(i\text{-}Pr)_2CO$, *i*-amOH[b])	$Fe_3A_9(H_2O)_3$, −14.54, −14.63, −14.77, −15.00, −15.47, −18.74, −19.17,	*58, 61*
Deca/benzene	Fe_3A_9, −9.9	*143*
	Co and Ni	
(Hexa, Octa, Deca)/heptane	$CoA_2(HA)_2$, −11.88, −11.44, −11.26; $CoA(OH)(HA)_2 \cdot H_2O$	*70*
Octa/heptane	$CoA_2(HA)_4$, −12.04; $Co_2A_4(HA)_4$, −20.32	*53*
Octa/decane	$Co_2A_4(HA)_4(H_2O)_w$	*37*
Octa/octanol	CoA_2	*127*
Deca/benzene	$CoA_2(HA)_4$, −11.2, −11.21[c]; $Co_2A_4(HA)_4$, −19.7, −19.28[c]	*143*
Naph/benzene	$Co_2A_4(HA)_4$	*22*
Octa/heptane	$Ni_2A_4(HA)_4$, −19.13	*53*
Octa/decane	$Ni_2A_4(HA)_4(H_2O)_w$	*37*
Deca/benzene	$NiA_2(HA)_4$, −11.34, −11.27[c]; $Ni_2A_4(HA)_4$, −19.15, −19.17[c]	*144*
Naph/benzene	$Ni_2A_4(HA)_4$	*22*
	Cu	
Propa/$CHCl_3$	Cu_2A_4	*40*
Propa/$CHCl_3$	$Cu_2A_4(HA)_2$	*41*
(Buta, Penta, Hexa, Hepta, Octa, Nona, Deca)/benzene	$Cu_2A_4(HA)_2$, −11.50, −11.56, −11.48, −11.58, −11.65, −11.56, −11.58	*66*
Octa/heptane	$Cu_2A_4(HA)_2$, −12.57	*53*
Deca/CCl_4	$Cu_2A_4(HA)_2$, −10.97	*10*
Deca/benzene	$Cu_2A_4(HA)_2$	*147*
Deca/(*n*-Hexn, cy-Hexn, CCl_4, toluene, benzene, CB, 1,2-DCE)	$Cu_2A_4(HA)_2$, −11.88, −11.67, −11.61, −11.57, −11.36, −11.30, −11.10	*156*

(*continued*)

TABLE II (*continued*)

Organic Phase[a]	Extracted Species, log K_{ex}				Reference
			Cu		
Deca/alcohols	CuA_2	CuA_2HA	Cu_2A_4	$Cu_2A_4(HA)_2$	
1-Octanol	−8.41	−8.65	−13.36	−13.77	*152*
1-Heptanol	−8.26		−13.48	−13.72	*151*
1-Hexanol	−8.25		−13.73	−13.77	*151*
1-Pentanol	−8.13		−14.00	−14.03	*151*
Cyclohexanol	−8.34		−14.45	−14.19	*151*
Deca/ketones	CuA_2	CuA_2HA	Cu_2A_4	$Cu_2A_4(HA)_2$	*153*
2-Octanone	−9.74	−9.33	−13.88	−14.22	
5-Methyl-2-Hexanone	−9.70	−9.50	−14.18	−14.44	
MIBK	−9.65	−9.47	−14.34	−14.58	
2-Hexanone	−9.54	−9.40	−14.35	−14.43	
2-Pentanone	−9.36	−9.39	−14.74	−14.74	
3-Pentanone	−9.29	−9.37	−14.70	−14.50	
Pal/benzene	$Cu_2A_4(HA)_2$, −12.0				*42*
St/benzene	$Cu_2A_4(HA)_2$				*13*
α-BrSt/benzene	$CuA_2(HA)_2$				*13*
Piva/toluene	$Cu_2A_4(HA)_2$, −13.2; monomer				*43*
Vers 10/*n*-hexn	$Cu_2A_4(HA)_2$, −12.96				*52*
cy-PA/benzene	$CuA_2(HA)_2$				*121*
cy-Hexa/benzene	$CuA_2(HA)_4$; $Cu_2A_4(HA)_4$				*15*
Naph/benzene	$Cu_2A_4(HA)_2$				*22*
	Zn, Cd, and Hg				
Hexa/CCl_4	ZnA_2; $ZnA_2(HA)_4$				*88*
Vers 9/benzene	$ZnA_2(HA)_2$				*114*
Vers 10/benzene	$ZnA_2(HA)_4$, −10.82; Zn_2A_4, −19.29				*124*
Naph/PE	$ZnA_2HA \cdot H_2O$, −10.72				*132*
Naph/PE	$CdA_2(HA)_2$, −9.29				*132*
Hexa/$CHCl_3$	$HgA_2(HA)_2$				*133*
Naph/PE	$Hg_2A_4(HA)_4$, 0.76				*132*

[a] Propa, Propanoic acid; Buta, butanoic acid; Penta, pentanoic acid; Hexa, hexanoic acid; Hepta, heptanoic acid; Octa, octanoic acid; Nona, nonanoic acid; Deca, decanoic acid; Pal, palmitic acid; St, stearic acid; Piva, trimethylacetic acid; Vers, Versatic acid; α-BrHexa, α-bromohexanoic acid; α-BrSt, α-bromostearic acid; $Me_2(OH)$Hexa, 2,5-dimethyl-2-hydroxyhexanoic acid; α,α′-DAC, α,α′-dialkylcarboxylic acid; Naph, naphthenic acid; cy-PA, cyclopentylacetic acid; cy-Hexa, cyclohexanecarboxylic acid; C_7–C_9 mix, C_7–C_9 mixture; CB, chlorobenzene; cy-Hexn, cyclohexane; 1,2-DCE, 1,2-dichloroethane; $(i\text{-Pr})_2CO$, diisopropyl ketone; *i*-amOAc, isoamyl acetate; *i*-amOH, isoamyl alcohol; MIBK, 4-methyl-2-pentanone; NB, nitrobenzene; *n*-Hexn, *n*-hexane; PE, petroleum ether; TCB, 1,2,4-trichlorobenzene.

[b] Depolymerized.

[c] Values from ref. *90*.

2. *Alkaline Earth Metals*

According to Mikhailichenko and co-workers (*81*), the extraction constant decreases with increasing hydration of the extracted species: $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$. They (*82*) have also found the extracted species $SrA_2(HA)_4(H_2O)_4$ in octane. The coordination number of 10 for strontium is quite unlikely. The increase in the length of the carbon chain causes only a slight increase of the extraction constant.

Alekperov *et al.* (*5*) suggested the polymerization of Sr(II) naphthenate in kerosene from the fact that the extraction curve (log *D* vs. pH) was shifted to the lower pH region with increasing initial concentration of strontium.

Kodama *et al.* (*63*) found that Eq. (14) was relevant to the extraction of beryllium(II) with decanoic acid in benzene. The Karl–Fischer titration revealed one water per four Be, and these authors proposed the following extraction equilibrium:

$$4Be^{2+} + 3(HA)_{2,o} + H_2O \rightleftharpoons (Be_4A_6O)_o + 8H^+$$

Beryllium is unique among the metal ions so far studied in that it is extracted as a tetrameric carboxylate, whose structure was thought to be similar to the tetrameric beryllium acetate. In the latter, four beryllium atoms are bridged by one oxo and six acetates (*148*).

3. *Aluminum, Gallium, Indium, and Thallium*

These metal ions are known to form up to hexameric decanoate in noncoordinating solvents such as toluene and benzene (*145, 146, 150, 155*). In the indium extraction, the three species, i.e., monomer, trimer, and hexamer, all having a definite composition, are in equilibrium with each other in the organic phase (*145*):

$$In^{3+} + 3(HA)_{2,o} \rightleftharpoons [InA_3(HA)_3]_o + 3H^+$$

$$3In^{3+} + 6(HA)_{2,o} \rightleftharpoons [In_3A_9(HA)_3]_o + 9H^+$$

$$6In^{3+} + 6(HA)_{2,o} + 6H_2O \rightleftharpoons [In_6A_{12}(OH)_6]_o + 18H^+$$

Schweitzer and Anderson (*125*), working at a very low metal concentration, found the monomeric indium species $InA_3(HA)_3$ in the extraction with hexanoic acid in chloroform. This composition is in accord with that found in the decanoate extraction (*145*).

Because of its strong hydrolytic tendency, the extraction behavior of Tl(III) has not been studied, while Tl(I) was reported to be extracted as monomers of different composition in different organic solvents (*130*).

4. *Germanium, Tin, and Lead*

Andrianov and Poladyan (*7*) extracted germanium with octanoic acid in the presence of iron(III).

Mikami and Takei (*80*) extracted tripropyltin(IV) with acetic, monochloroacetic, dichloroacetic, and formic acids in carbon tetrachloride. The partition constant of the extracted species, Pr_3SnA (Pr = propyl; $A = CH_3COO^-$, CH_2ClCOO^-, and $CHCl_2COO^-$), increased with increasing chlorine substitution of acetic acid.

Two extracted species, $PbA_2(HA)_2$ and $PbA_2(HA)_4$, have been found in the extraction of lead with decanoic acid in benzene (*92*).

5. *Scandium, Yttrium, and Lanthanides*

A series of investigations (*32–35, 101*) on the extraction of these elements with carboxylic acids has been carried out by workers in the Soviet Union. Miller and associates (*86*) extracted lanthanides with 2,5-dimethyl-2-hydroxyhexanoic acid in chloroform. The heavy lanthanides after samarium were not extracted. In the extraction of neodymium the extracted species such as $NdA_3(HA)_5$ and $Nd_2A_6(HA)_h$ were found together with small amounts of Nd_2A_6 and still smaller amounts of further aggregates $(NdA_3)_j$ (*86*).

Danilov and co-workers (*20*) studied the extraction of lanthanides with α,α'-dialkylcarboxylic and hexanoic acids in *n*-heptane. The extracted species is invariably $LnA_3(HA)_3$. As is obvious from Table II, the "gadolinium break" is observed in the extraction constants.

The hexameric scandium decanoate extracted in benzene is different from the hexameric Al(III), Ga(III), and In(III) decanoates in that the former is neither hydrated nor hydrolyzed (*154*). Galkina and Strel'tsova (*36*), in the butanoic acid/*iso*-butanol system, attempted to separate Sc from rare earths and the other metals. They proposed the monomeric Sc(III) butanoate, ScA_3, as the extracted species. In this extraction system, the polymerization of scandium butanoate in the organic phase seems to be prevented by solvation with *iso*-butanol. In the study of the synergistic effect of various amines on the extraction of lanthanum and scandium with hexanoic and α-bromohexanoic acids in chloroform, Sukhan *et al.* (*138*) proposed $LaA_3(HA)_3$ and $ScA_3(HA)_3$ as the extracted species.

6. *Actinides*

The extractability of 20 different metal ions with a series of aliphatic carboxylic acids (from pentanoic to decanoic acids) in chloroform was examined by Pietsch and Sinic (*99*). In this work, the maximum extractability of thorium was obtained with hexanoic acid and that of uranium with nonanoic acid. Pietsch (*97*) also described the extraction of thorium with hexanoic acid in chloroform together with lead and iron. The extraction of thorium butanoate by chloroform is useful for the separation of thorium from the following metals: Ca, Mg, Ba, Pb, Zn, Cd, Be, Ni, and Co (*98*).

Hök-Bernström carried out the extraction of UO_2^{2+} with salicylic(H_2A) and methoxybenzoic(HA) acids in 4-methyl-2-pentanone. She proposed the extracted species $UO_2(HA)_2$ and $UO_2(HA)_2 \cdot H_2A$ for salicylic acid and UO_2A_2 for methoxybenzoic acid (*48*). In a subsequent study (*49*) on the extraction of thorium (IV) with salicylic, methoxybenzoic, and cinnamic acids in 4-methyl-2-pentanone, thorium was extracted as $Th(HA)_4 \cdot H_2A$ by salicylic acid and ThA_4 by methoxybenzoic acid. Koehly *et al.* (*64*) found that, in decanoic acid–benzene systems, americium(III), thorium(IV), and uranium(VI) were extracted as $AmA_3(HA)_5$, $ThA_4(HA)_4$, and $UO_2A_2(HA)_2$, respectively. According to a study on the extraction of uranium(VI) with decanoic acid in benzene, uranium was extracted as $UO_2A_2(HA)_2(H_2O)_2$ and $UO_2A_2(HA)_4(H_2O)_2$ (*89*). Later, Sukhan and co-workers (*135*) showed that $UO_2A_2(HA)_2$ was responsible for the extraction of uranium (VI) with hexanoic acid in chloroform.

7. *Transition Metals*

Kyrš tried to separate Zr from Nb by the extraction with aliphatic carboxylic acids (from C_7 to C_9) in benzene (*72*), and proposed $Zr(OH)_3A$ (*73*), which does not appear to be extractable.

Nakasuka *et al.* (*93*) found the dimeric species $(VO)_2A_4$ in the extraction of vanadium(IV) with decanoic acid in benzene.

In the extraction of Mn(II) from ammonium chloride solution with decanoic acid benzene, Bartecki *et al.* (*11*) reported that the prevailing species in the organic phase was a dimeric complex, $Mn_2A_4(HA)_4$, in addition to a small amount of tri- and tetramers. The monomeric extracted species $MnA_2(HA)_2$, found in decane (*39*), seems unlikely.

a. Iron. Trimeric iron(III) decanoate Fe_3A_9 was found in the extraction of iron with decanoic acid in benzene (*143*). A composition such as $Fe_3(OH)_hA_{9-h}$ or Fe_3A_9O cannot be excluded. In the extraction of iron (III) by octanoic acid in decane, Khol'kin *et al.* (*57*) described a hydrated trimer, $Fe_3A_9(H_2O)_3$, as an extracted species.

Monomeric(*17, 24*) and dimeric(*159*) iron(III) carboxylates are not realistic in nonpolar solvents.

b. Cobalt and Nickel. These two metal ions behave very similarly in the extraction with carboxylic acids. A monomer $MA_2(HA)_4$ and a dimer $M_2A_4(HA)_4$ are in equilibrium in nonpolar solvents, while in coordinating solvents such as octanol, a monomer, MA_2, prevails (see Table II). The monomeric extracted species $CoA_2(HA)_2$ and $CoA(OH)(HA)_2 \cdot H_2O$ (*70*) seem unlikely.

c. Copper. Copper(II) is extracted as a dimer $Cu_2A_4(HA)_2$ in nonpolar solvents (*10, 22, 41–43, 51–53, 66, 147, 156*). The stability of the dimer is so high that no appreciable amount of monomer can be detected in most nonpolar solvents. However, with some sterically crowded carboxylic acids such as trimethylacetic acid (*43*), α-bromostearic acid (*13*), cyclohexanecarboxylic acid (*15*), and cyclopentylacetic acid (*121*), a monomeric species is found together with the dimer. Because of the extensive solvation by alcohols and ketones, monomeric and dimeric species are in equilibrium in these solvents (*151, 153*).

The extraction of copper(II) by various aliphatic carboxylic acids (from butanoic to decanoic acids) in benzene is written as

$$2Cu^{2+} + 3(HA)_{2,o} \xrightleftharpoons{K_{ex(262)}} [Cu_2A_4(HA)_2]_o + 4H^+ \tag{15}$$

The extraction constant is formulated as

$$\log K_{ex(262)} = \beta_{26} K_{D,Cu_2A_4(HA)_2} K_{D,(HA)_2}{}^{-3}, \tag{16}$$

where β_{26} denotes the overall formation constant of $Cu_2A_4(HA)_2$ in the aqueous phase, i.e.,

$$\beta_{26} = [Cu_2A_4(HA)_2][H^+]^4[Cu^{2+}]^{-2}[(HA)_2]^{-3},$$

and $K_{D,Cu_2A_4(HA)_2}$ and $K_{D,(HA)_2}$ denote the partition constants of the dimeric copper decanoate and the dimeric carboxylic acid. Kojima *et al.* (*66*) found that the extraction constants for $Cu_2A_4(HA)_2$ fell in the region from −11.5 to −11.6, irrespective of the number of carbon atoms in the carboxylic acid (see Table II).

From the additive nature of the molar cohesive energy and molar volume of the ligand in a complex, it has been shown that the log(partition constant) of a complex MA_n is approximately n times that of the ligand HA (*141*) [cf. Eqs. (17) and (18)]. Then from Eq. (16) we see that $K_{ex(262)} \simeq \beta_{26}$. Since pK_a is almost the same for these aliphatic carboxylic acids, one may realize that β_{26} and hence $\log K_{ex(262)}$ should not differ much for aliphatic carboxylic acids with different numbers of carbon atoms. A finer picture of the subject will be drawn below in Eq. (21).

The extraction constant was found to remain constant also for the extraction of cobalt (*70*) and strontium (*82*) by different carboxylic acids.

Inoue *et al.* (*51*) studied the extraction kinetics of copper(II) versatate and the interfacial adsorption equilibrium of Versatic 10.

In the extraction of copper(II) with decanoic acid in 1-octanol, Yamada *et al.* (*152*) noted that the monomeric and dimeric Cu(II) decanoates were responsible for the extraction:

$$Cu^{2+} + 2(HA)_o \rightleftharpoons (CuA_2)_o + 2H^+$$

$$Cu^{2+} + 3(HA)_o \rightleftharpoons (CuA_2HA)_o + 2H^+$$

$$2Cu^{2+} + 4(HA)_o \rightleftharpoons (Cu_2A_4)_o + 4H^+$$

$$2Cu^{2+} + 6(HA)_o \rightleftharpoons [Cu_2A_4(HA)_2]_o + 4H^+$$

Further in the extraction of copper(II) decanoates by various alcohols (*151*) and ketones (*153*), Yamada *et al.* revealed that the monomeric Cu(II) decanoate was extracted together with the dimeric ones. We will come back to this subject later.

Bold and Băluşescu (*13*) found the monomeric copper(II) α-bromostearate $CuA_2(HA)_2$ in the extraction of Cu(II) with α-bromostearic acid in benzene. The bromine in the α-position was said to prevent sterically the formation of dimeric copper(II) species. α-Bromocarboxylic acid, being stronger than the nonsubstituted homologues, is anticipated to form a less stable copper carboxylate dimer.

The selective extraction of copper(II) with phenylacetic acid and its derivatives has been described by Adam and co-workers (*2–4*).

d. Zinc, Cadmium, and Mercury. Zinc(II) is extracted as monomers involving different numbers of free carboxylic acid units [$ZnA_2(HA)_h$, with $h = 0, 1, 2, 4$] in different nonpolar solvents (*88, 114, 124, 132*). In the presence of sodium, a mixed-metal complex $ZnNaA_3(HA)_5$ is extracted with decanoic acid in benzene (*91*). Also, in the extraction of cadmium, $CdNaA_3(HA)_5$ and $CdNaA_3(HA)_7$ were found in addition to $CdA_2(HA)_4$.

In the naphthenic acid (mixture of cyclopentylalkylcarboxylic acids)–petroleum ether systems, Singh *et al.* (*132*) found the extracted species of Zn(II), Cd(II), and Hg(II) to be $ZnA_2HA{\cdot}H_2O$, $CdA_2(HA)_2$, and $Hg_2A_4(HA)_4$, respectively, and the extraction constant to decrease in the order Hg > Cd > Zn. They also extracted $HgA_2(HA)_2$ with hexanoic acid in chloroform (*133*).

C. COEXTRACTION

Ruthenium(III) butanoate and naphthenate are well extracted when copper (*149*) or iron (*76*) is present but not at all in their absence. For Cr(III), Nb(V), Sr(II), Ce(III), and Y(III) naphthenates, the higher extractability was observed in the presence of iron (*60, 76*). Alekperov and Makov (*6*) noted that the coextraction of Ru with Fe(III), Co(II), and Cu(II) naphthenates increased in the order Cu < Co < Fe.

In the decanoic acid–benzene system, Nakasuka *et al.* (*91*) found the coextraction of sodium ion with zinc(II) and cadmium(II) as the following mixed-metal decanoates: $ZnNaA_3(HA)_5$ and $CdNaA_3(HA)_a$ ($a = 5, 7$). Lead was also reported to be extracted with sodium ion [as $Na_2PbA_4(HA)_8$] (*95*), as was cobalt (*131*).

Pyatnitskii and associates (*104*) found the coextraction of iron(III) in the extraction of copper(II) from tartaric acid solutions with hexanoic acid in chloroform containing pyridine. The coextraction was claimed to be due to the formation of an ion associate $Cu(Py)_xAFeT$ (Py, pyridine; T, tartarate; and A, hexanoate).

Nakasuka *et al.* (*90*) found the following extraction equilibrium for the extraction of cobalt by decanoic acid in benzene in the presence of nickel:

$$Co^{2+} + Ni^{2+} + 4(HA)_{2,o} \xrightleftharpoons{K_{ex(mix)}} [CoNiA_4(HA)_4]_o + 4H^+$$

with $\log K_{ex(mix)} = -19.1$.

Since the coextraction is not unusual, particularly in the extraction of polymerized metal carboxylates, much attention should be paid to the formation of mixed-metal carboxylates in the separation of metal ions.

D. SYNERGISTIC EXTRACTION OF METAL CARBOXYLATES

A number of investigations on the synergistic effect of a second extractant, such as amines and oximes, on the extraction of metal carboxylates have been carried out. The utilized synergists include 8-hydroxyquinoline-2-aldoxime for Zr(IV) and Hf(IV) (*122, 123*), various amines (*25*), Lix 63 (*27*) and nonylphenol (*28*) for Cu(II), dialkylphosphoric acids for Hf(IV) (*44*), rhodamine B for Be(II) (*102*), trioctylphosphine oxide for U(VI) (*69, 77*), *p*-alkylphenol for Cs(I) (*1*), collidine for Zr(IV) and Sc(III) (*62*), and nonchelating oximes for Ni(II) and Co(II) (*103*). Mareva *et al.* (*77*) have successfully utilized a salicylic acid–trioctylphosphine oxide mixture for the separation of uranium from rare earths, thorium, zirconium, and iron.

Studies on the stoichiometry of mixed-ligand carboxylate complexes involved in synergistic extraction systems include $Sn(Ox)_2A_2$ (HA, trichloroacetic acid; HOx, 8-quinolinol) by Petrukhin *et al.* (*96*); ZnA_2Q and ZnA_2Q_2 (HA, butanoic, pentanoic, and hexanoic acids; Q, quinoline) in carbon tetrachloride by Moriya and Sekine (*88*); $CoX_2A_2H_2$ (HA, Versatic 911; HX, Kelex 100) in kerosene by Lakshmanan and Lawson (*74*); VOA_2B_3 (HA, trichloroacetic acid; B, neutral oxygen and nitrogen donors) by Rao and Sarma (*113*); $UO_2ClO_4A(TOPO)_2$ (HA, benzoic acid; TOPO, trioctylphosphine oxide) in carbon tetrachloride by Konstantinova (*68*); and $UO_2A_2B_2$ (HA, hexanoic acid; B, pyridine, 2-aminopyridine, benzylamine or 1,10-phenanthroline) in chloroform by Sukhan and co-workers (*135*).

Pyatnitskii and associates have extensively studied the synergistic extraction of metal ions with various carboxylic acids(HA) and amines(B) in chloroform. According to their results, iron(II) is extracted as FeA_2B_2 (*112*); iron(III) as FeA_3B_b ($b = 1, 2, 3$) (*109, 110, 139*); cobalt(II) and nickel(II) as MA_2B_b ($b = 2, 3$) (*106, 107, 109, 136, 137*); copper(II) as CuA_2B_b ($b = 1, 2$) (*105, 107, 108, 111, 136*).

Hirose and co-workers extracted copper(II) (*45*) and zinc(II) (*46*) with decanoic acid in benzene in the presence of pyridine(B). They found the following equilibria.

For copper:

$$Cu^{2+} + \tfrac{5}{2}(HA)_{2,o} + B_w \xrightleftharpoons{K_{ex(1531)}} [CuA_2(HA)_3B]_o + 2H^+$$

$$Cu^{2+} + 2(HA)_{2,o} + 2B_w \xrightleftharpoons{K_{ex(1422)}} [CuA_2(HA)_2B_2]_o + 2H^+$$

$$2Cu^{2+} + \tfrac{5}{2}(HA)_{2,o} + B_w \xrightleftharpoons{K_{ex(2511)}} [Cu_2A_4(HA)B]_o + 4H^+$$

with the extraction constants $\log K_{ex(1531)} = -4.31$, $\log K_{ex(1422)} = -0.61$, and $\log K_{ex(2511)} = -7.88$.

For zinc:

$$Zn^{2+} + \tfrac{5}{2}(HA)_{2,o} + B_w \xrightleftharpoons{K_{ex(1531)}} [ZnA_2(HA)_3B]_o + 2H^+$$

$$Zn^{2+} + \tfrac{3}{2}(HA)_{2,o} + B_w \xrightleftharpoons{K_{ex(1311)}} [ZnA_2(HA)B]_o + 2H^+$$

with the extraction constants $\log K_{ex(1531)} = -6.09$ and $\log K_{ex(1311)} = -7.02$.

The synergistic effect of pyridine is larger for zinc than for copper. This will stem from the high stability of dimeric copper carboxylate in the organic phase.

E. Solvent Effect on the Extraction of Metal Carboxylates

Plaksin *et al.* (*101*) found that $pH_{1/2}$ values for the extraction of lanthanides with aliphatic carboxylic acids (C_7–C_9) decreased in the order heptanol > decanol > isoamyl acetate > *m*-xylene > dichlorodiethyl ether > carbon tetrachloride > kerosene.

Schweitzer and associates investigated the extraction of metal hexanoates and found $TlA(HA)_3$ in benzene and chloroform, $TlA(HA)_2$ in 4-methyl-2-pentanone, and $TlA(HA)_4$ in nitrobenzene (*130*); $TmA_3(HA)_5$ in chloroform and TmA_3HA in 4-methyl-2-pentanone (*129*); and ZnA_2HA in all studied solvents (*126*). This latter composition seems unlikely since the normal coordination number of zinc is 4 or 6.

In the extraction systems with octanoic acid, Gindin *et al.* (*38*) revealed that the formation of dimeric cobalt(II) and nickel(II) octanoates tended to decrease with increasing dielectric constant of the organic solvent: decane > benzene > α-chloronaphthalene > chloroform > nitrobenzene > 3-methyl-1-butanol. Because 3-methyl-1-butanol is a solvating solvent, no dimerization of Co(II) and Ni(II) octanoates was observed in this solvent.

Brzózka and Rózycki (*16*) stated that $pH_{1/2}$ for copper(II) cyclohexanecarboxylate and the concentration of the monomeric copper(II) species in the organic phase increased in the order carbon tetrachloride < benzene < 3-methyl-1-butanol. Yamada *et al.* found that the less polar the solvent, the more polymerized is the extracted species of gallium(III) decanoate (*150*) (see Table II).

In most inert solvents the extraction equilibrium of copper(II) is given by Eq. (15), with the extraction constant formulated as Eq. (16).

The molar volume and the solubility parameter of the dimeric copper decanoate are given (*141*) as

$$V_{Cu_2A_4(HA)_2} = 3 \times 0.9 V_{(HA)_2}, \tag{17}$$

$$\delta_{Cu_2A_4(HA)_2} = 1/0.9^{1/2} \delta_{(HA)_2}. \tag{18}$$

The partition constant of a solute B in terms of molar concentration is given by

$$\log K_{D,B} = 0.43 V_B (\delta_w - \delta_o)(\delta_w + \delta_o' - 2\delta_B)/RT, \tag{19}$$

where

$$\delta_o' = \delta_o + \frac{RT}{\delta_w - \delta_o}\left(\frac{1}{V_o} - \frac{1}{V_w}\right), \tag{20}$$

and V_B, V_o, V_w, δ_B, δ_o, and δ_w denote the molar volumes and the solubility parameters for the solute B, the organic solvent, and water, respectively. Combining Eqs. (16)–(20), we obtain

$$\log K_{ex(262)} = \frac{-0.13\, V_{(HA)_2}(\delta_w - \delta_o)(\delta_w + \delta'_o - 1.03\delta_{(HA)_2})}{RT} + \log \beta_{26} \quad (21)$$

As predicted from Eq. (21), $\log K_{ex(262)}$ is indeed linearly related with $(\delta_w - \delta_o)(\delta_w + \delta_o' - 1.03\delta_{(HA)_2})$ with the theoretical slope of $-0.13\, V_{(HA)_2}/RT$. Equation (21) describes the solvent effect on the copper decanoate extraction very nicely (*156*).

The influence of solvent on the extraction of copper(II) with decanoic acid in some alcohols (*151*) and ketones (*153*) was studied by Yamada and associates who found that in these solvents both the monomeric and dimeric Cu(II) decanoates were responsible for the extraction. In this case the dimerization of copper carboxylate was formulated as in Eq. (22):

$$2CuA_2 \overset{K_{dim}}{\rightleftharpoons} Cu_2A_4 \quad (22)$$

This is an important factor in the solvent extraction. Yamada *et al.* attempted to understand the solvent effect on the above reaction in the following manner.

According to the regular solution theory, the dimerization constant of copper(II) decanoate, K_{dim}, described above can be written as follows (*142, 151*):

$$\log K_{dim} - \log V_0 = 0.43 n V_o(\delta_o - \delta')^2/RT + \log K^{\circ}_{dim} - 3.$$

Here δ' refers to the solubility parameter of copper(II) decanoate; K°_{dim} denotes the dimerization constant of Cu(II) decanoate in an ideal solution; and n represents the number of solvent molecules set free in the dimerization of Cu(II) decanoate, that is, $nV_o = 2V_{CuA_2} - V_{Cu_2A4}$, where V_{CuA_2} and $V_{Cu_2A_4}$ indicate the molar volume of the *solvated* monomeric and dimeric Cu(II) decanoates. CuA_2 and Cu_2A_4 are assumed to have the same solubility parameter (*141*), and δ' was found to be 24.1 ($J^{1/2}$ $cm^{-3/2}$) (*151*). The plot of ($\log K_{dim} - \log V_o$) against $0.43\, V_o(\delta_o - \delta')^2/RT$ was remarkably linear (*151, 153*). From this plot the values of n and $\log K^{\circ}_{dim}$ were found to be 4.5 and 3.14 for alcohols, and 2.8 and 3.19 for ketones by the least-squares method. From these results they concluded that, because of extensive solvation, the monomeric copper(II) decanoate is more stabilized in alcohols than in ketones.

IV. Concluding Remarks

Despite a considerable effort during the last two decades, relatively slow progress has been made in physicochemical aspects of the metal carboxylate extraction. The stoichiometry proposed for the extracted species still appears quite unlikely in some cases.

In the extraction of metal ions with carboxylic acids, it is not unusual to find polymerized species with carboxylates, hydroxo, and/or oxo groups acting as bridging ligands. In this connection, one is strongly recommended to utilize, instead of the conventional log D plot, the plot of logarithmic total metal concentration in the organic phase against $(\log[M^{n+}] - n \log[H^+])$ in order to find the correct composition of the extracted species.

The formation of heteropolynuclear carboxylates is a common phenomenon, which must be taken into account particularly in the separation of metal ions.

It is encouraging to see that regular solution theory has been utilized with success in understanding the effect of solvent and extractant on the metal carboxylate extraction.

To conclude, it may be said at present that problems of fundamental importance still await careful study from different points of view.

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