Extraction of Cu, Ni and Co with Sodium Salt of Di-2-ethylhexylphosphoric Acid

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The extraction of some metal ions with the sodium salt of di-2-ethylhexylphosphoric acid (D2EHPA) is investigated in order to clarify the extraction characteristics and mechanism. The sodium salt of D2EHPA extracts metal ions primarily by the exchange reaction of sodium ion to the metal ion and the extractability depends on the initial concentration of the extractant and metal ions or these factors and the initial pH. The conversion of D2EHPA into the salt form enables one to obtain the high and constant extractability from an acidic solution regardless of the initial pH over a wide pH range.

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I. Introduction

Recently, solvent extraction has been used to extract and separate metal ions from the leached solution by hydrometallurgical treatment of ores and some other materials^{(1)–(6)}. The application of solvent extraction extends over to many fields including analytical chemistry, atomic energy industry, and extractive metallurgy of non-ferrous and rare metals. The extraction mechanism, the extraction characteristics and applications to a practical operation have been reported in detail in the papers represented^{(7)–(15)}.

The extractability with acidic extractants, such as D2EHPA and carboxylic acid, highly depends on the pH in aqueous solution and decreases with the progress of extraction process because the pH decreases as the extraction proceeds. Then, alkali has to be added into the aqueous phase in order to neutralize the liberated proton. However, when the acidic extractant previously converted into the salt form, such as sodium salt or other metal salts, is used, the extraction process is an exchange reaction of metal ions between the aqueous and organic phases and does not give rise to the lowering of pH in the aqueous phase. This process will proceed without the addition of alkali.

In this paper, the extraction of some metal

ions with salt form extractant was investigated in order to clarify the extraction characteristics and mechanism.

II. Exchange Extraction Equilibrium

The application of exchange extraction can raise significantly the selectivity in a separation process⁽¹⁶⁾. The salt form extractant denoted $M_I R_m$ may be exchanged with metal ions in an aqueous phase, M_{II}^{n+} , according to the following equation,

where the organic phases are indicated by bars. All of the metal ions are not extracted with salt form extractant, but only more extractable metal ions than the metal ion M_I^{m+} constituting salt form extractant may be extracted. It is determined by the extraction order found experimentally on various metal ions whether the exchange extraction occurs to a metal ion of interest or not. The extraction order of metal ions with D2EHPA is as follows:

The exchange equilibrium constant of eq. (1) is expressed as,

$$K_{ex} = [M_I^{m+}]^n [\overline{M_{II} R_n}]^m / [M_{II}^{n+}]^m [\overline{M_I R_m}]^n. \quad (2)$$

The extraction equilibria of metal ions M_I^{m+} and M_{II}^{n+} with acidic extractant and the equilibrium constants are represented, respectively, by

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and

When eq. (1) is in equilibrium, eqs. (3) and (4) are set up simultaneously. Consequently, the next relationship is valid between eqs. (2), (3) and (4).

$$K_{ex} = (K_{II})^m / (K_I)^n. \quad (5)$$

The requirement to promote the exchange extraction sufficiently is that $(K_{II})^m$ is much larger than $(K_I)^n$. If the charge of a metal ion, M_1^{m+} , is equal to that of a metal ion, M_{II}^{n+} , eq. (5) is written as,

$$K_{ex} = K_{II} / K_I, \quad (6)$$

which is equal to the separation factor for both metal ions.

The exchange extraction of divalent metals with the sodium salt extractant utilized mainly in this study is represented as

When the phase ratio of organic to aqueous, V_O/V_A , is equal to unity, the mass balance with respect to the initial concentration of sodium salt extractant is written as

$$[\overline{NaR}]_i = [\overline{NaR}]_e + [Na^+]_e, \quad (8)$$

where the subscripts i and e denote initial and equilibrium states, respectively. Dividing both sides of eq. (8) by the initial metal concentration, $[M^{2+}]_i$, the following equation is obtained:

$$\frac{[\overline{NaR}]_i}{[M^{2+}]_i} = \frac{[\overline{NaR}]_e}{[M^{2+}]_i} + \frac{[Na^+]_e}{[M^{2+}]_i}. \quad (9)$$

Assuming the complete exchange between sodium ions and metal ions, the equation $2[\overline{MR_2}]_e = [Na^+]_e$ is valid. The equilibrium concentration of sodium salt extractant, $[\overline{NaR}]_e$, in eq. (9) may be approximately regarded as zero under the condition where the exchange extraction proceeds sufficiently. Then, eq. (9) is simplified as

$$E = \frac{[\overline{MR_2}]_e}{[M^{2+}]_i} = 1/2 \cdot \frac{[\overline{NaR}]_i}{[M^{2+}]_i}, \quad (10)$$

where E is the extractability of a metal ion and depends upon the ratio of the initial concentration of sodium salt extractant to that of metal ions.

In the above consideration the complete exchange, in which the initial pH is nearly equivalent to the equilibrium pH after extraction, is assumed. When the initial pH is extremely low, however, the extraction of protons or the stripping of sodium ions in the organic phase as well as the exchange extraction of eq. (7) will occur, as shown in the following equation.

Equation (11) enables one to extract metal ions from a more acidic solution with sodium salt extractant. When metal ions are extracted from an acidic solution with sodium salt extractant, decrease of the sodium salt extractant is shown by $([H^+]_i - [H^+]_e)$, where $[H^+]_i$ and $[H^+]_e$ are the initial and equilibrium concentration of hydrogen ions, respectively. Therefore, the extractability E in the extraction from an acidic solution is expressed as

$$E = \frac{[\overline{NaR}]_i - ([H^+]_i - [H^+]_e)}{2[M^{2+}]_i}. \quad (12)$$

Since $[H^+]_i$ is much larger than $[H^+]_e$ under the above experimental conditions, the extractability from the acidic solution of separate metal ions depends on the initial concentration of sodium salt extractant and a metal ion, and the initial pH irrespective of the kind of a metal ion.

III. Experimental

The aqueous solution was prepared by dissolving metal nitrate of an analytical reagent grade into distilled water. The concentrations of the metal ion were 0.1 and 0.25 kmol/m³. The organic solution was prepared by the following procedure. First of all, D2EHPA was diluted to one liter by kerosene and 5 vol% tri-n-butyl phosphate (TBP). Then, this solution was neutralized by various portions of 10 kmol/m³ NaOH solution, which gave the various compositions of D2EHPA and the sodium salt as shown in Table 1. TBP

Table 1 Composition of extractant.

No.	D2EHPA (kmol/m ³)	D2EHPA-Na salt (kmol/m ³)
1	0.033	0.467
2	0.125	0.375
3	0.212	0.288
4	0.284	0.236
5	0.414	0.086

was added in order to prevent the third phase formation and to increase the solubility of sodium salt extractant in kerosene. D2EHPA used in this work was supplied by the Union Carbide Corporation and used without further purification.

Equal volumes of the aqueous and organic solutions (15 cm³ each) were poured together into a 50 cm³ centrifuge tube. The tube was then installed in a shaking device and shaken for 1.5 ks (25 min) at 298 K (25°C). After having attained a state of equilibrium, the aqueous and organic phases were separated by centrifuging at 41.7 s⁻¹ (2500 rpm) for 900 s (15 min). Then, the tube was immersed in a water bath maintained at 298 K. The metal ion concentrations and pH values in this aqueous phase were measured. The metal ion contents were determined by atomic absorption spectrometry.

IV. Results and Discussion

The extraction of copper with D2EHPA and

its sodium salt was carried out. Results obtained are summarized in Table 2. On the extraction with D2EHPA the equilibrium pH is always lower than the initial pH, and the high extraction percentage is not obtained over the initial pH range 3–4. This is sufficiently estimated from the fact that the extraction with D2EHPA is the exchange reaction between the proton in the organic phase and the metal ion in the aqueous phase. On the other hand, when the sodium salt of D2EHPA is used, equilibrium pH and extraction are kept nearly constant irrespective of the initial pH over pH 2–4. The high extraction over 85% is obtained in this case.

The extraction of copper, nickel and cobalt from the more acidic separate solutions is shown in terms of extraction percentage vs initial pH in Figs. 1 and 2. The control of the pH was carried out with dilute nitric acid. In the case of 0.25 kmol/m³ metal nitrate solution the extraction becomes largest and constant at the pH over 2, and in 0.1 kmol/m³ metal nitrate solution the largest and constant extraction is obtained at the pH over 0.6. As expected from eq. (11), the sodium salt of D2EHPA extracts metal ions from the more acidic solution of the pH below 1, and then the amount of sodium ions released from the organic phase is larger than that of the extracted metal ion. Extraction seems to be determined by the initial concentration of the sodium salt extractant and a metal ion or these factors and the initial pH regardless of

Table 2 Extraction of copper with D2EHPA and the sodium salt.

Extractant	Aqueous pH		Extraction (%)	Organic Cu(II) concn. (kmol/m ³)	Exchanged Na (kmol/m ³)
	Initial	Equilibrium			
D2EHPA	2.7	1.4	7.79	0.0195	
	3.9	1.4	7.79	0.0195	
	4.1	1.6	11.69	0.0292	
	4.1	2.0	29.89	0.0473	
D2EHPA-Na	0.8	3.2	64.35	0.1609	0.4673
	1.0	3.6	74.27	0.1857	0.4465
	2.0	3.8	84.26	0.2101	0.3917
	2.7	3.9	85.14	0.2129	0.3836
	3.6	4.0	85.71	0.2143	0.3836
	4.0	4.0	86.27	0.2157	

D2EHPA: 0.500 kmol/m³, D2EHPA-Na salt: 0.467 kmol/m³, Initial copper ion concentration: 0.25 kmol/m³

Fig. 1 Extraction of metals with D2EHPA-Na salt from nitrate solution.

Fig. 2 Extraction of metals with D2EHPA-Na salt from nitrate solution.

the kind of metal ions. The relationship between equilibrium pH and extraction is shown in Fig. 3. Positions of these extraction curves are similar to those of D2EHPA.

Fig. 3 Relationship between extraction and equilibrium pH on extraction of metals with D2EHPA-Na salt.

Extractant: D2EHPA-Na 0.5 kmol/m³
 Metal: ○ Cu(NO₃)₂ 0.10 kmol/m³
 ◐ Co(NO₃)₂ 0.10 kmol/m³
 ● Ni(NO₃)₂ 0.10 kmol/m³

Fig. 4 Relationship between extraction and initial concentration of D2EHPA-Na salt.

Equation (10) should be valid under the conditions of complete exchange extraction. In Fig. 4 extraction of each metal ion is plotted against the initial concentration of the sodium salt of D2EHPA. Extraction increases in proportion to an increase in the concentration of sodium salt extractant, and it is determined by the initial concentration of sodium salt extractant and a metal ion.

The exchange equilibrium constant K_{ex} is represented by the ratio between the extraction equilibrium constants of the two metal ions with D2EHPA. The apparent extraction equilibrium constants of sodium, copper, cobalt and nickel with D2EHPA, and the apparent exchange equilibrium constants with the sodium salt of D2EHPA are expressed in Table 3. The extraction equilibrium constant of sodium has a value reported by Kojima *et al.*⁽¹⁷⁾ and the other constants were determined in this study. K_{ex} was calculated from the ratio of the two equilibrium constants and K'_{ex} was obtained experimentally. The experimental constants of copper and cobalt are in fairly good accordance with the calculated constants, which confirms eq. (5).

The extraction from the mixed solution of

Table 3 Apparent equilibrium constants and exchange equilibrium constants.

	Na	Cu	Co	Ni
K	$10^{-4.26}$	$10^{-3.46}$	$10^{-4.86}$	$10^{-5.27}$
K_{ex}	—	$10^{5.06}$	$10^{3.66}$	$10^{3.25}$
K'_{ex}	—	$10^{5.03}$	$10^{3.54}$	$10^{4.54}$

Fig. 5 Extraction of metals with D2EHPA-Na salt from mixed metal nitrates solution.

Fig. 6 Extraction of metals with D2EHPA-Na salt from mixed metal nitrates solution.

Extractant: D2EHPA-Na salt + D2EHPA = 0.5 kmol/m³

Metal: ○ Cu²⁺ 6.25 kg/m³
 ● Co²⁺ 6.00 kg/m³
 ● Ni²⁺ 5.75 kg/m³

copper, nickel and cobalt with the sodium salt of D2EHPA was examined. Aqueous feed solutions were composed of 0.25 or 0.1 kmol/m³ of three metal nitrates with 2.40 or 2.95 initial pH. Results obtained are shown in Figs. 5 and 6 in terms of extraction percentage vs initial concentration of sodium salt extractant. The extraction of copper, which is most extractable or most exchangeable to sodium ion, occurs preferentially and the amount of extracted copper increases with an increase in the sodium salt extractant. On the other hand, the extraction of nickel and cobalt is kept considerably low regardless of the concentration of sodium salt extractant and proceeds markedly after the complete extraction of copper.

Distribution of metal ions was measured varying the volume ratio of the organic phase to the aqueous phase (V_O/V_A). The results are shown in Table 4. When the value of V_O/V_A is large, the separation factor is small, but the extraction of copper progressively increases with the decrease in V_O/V_A values, that is, the relative decrease of the sodium salt extractant. Similarly the extraction from the mixed solution of nickel and cobalt with sodium salt extractant is shown in Table 5. The change in V_O/V_A from 2/1 to 1/5 results in the enhancement of the separation factor from 0.99 to 6.24.

Table 4 Extraction with D2EHPA-Na salt from mixed metal nitrate solutions.

V_o/V_A	Eq. pH	Organic metal concn. (kg/m ³)			Separation factor	
		Cu	Ni	Co	D_{Cu}/D_{Ni}	D_{Cu}/D_{Co}
2/1	5.75	3.03	2.70	2.83	2.07	1.92
1/1	4.82	6.05	2.20	4.10	48.8	14.0
1/2	4.18	11.15	0.52	1.40	174	62.6
1/3	3.89	12.15	0.30	0.38	104	85.2
1/5	3.75	12.50	0.15	0.15	127	133

Aqueous solution: Cu 6.25 kg/m³, Ni 5.75 kg/m³, Co 6.00 kg/m³, pH 3.00
Organic solution: 0.5 kmol/m³ D2EHPA-Na salt

Table 5 Extraction with D2EHPA-Na salt from mixed metal nitrate solutions.

V_o/V_A	Eq. pH	Organic metal concn. (kg/m ³)		Separation factor
		Co	Ni	D_{Co}/D_{Ni}
2/1	5.38	5.68	5.38	0.99
1/1	5.07	9.35	4.00	4.19
1/2	4.99	10.90	2.60	5.65
1/3	4.95	11.70	2.40	5.87
1/5	4.91	11.50	2.00	6.24

Aqueous solution: Co 15.10 kg/m³, Ni 14.30 kg/m³, pH 3.80
Organic solution: 0.5 kmol/m³ D2EHPA-Na salt

It should be emphasized, therefore, that the concentration of the sodium salt of D2EHPA must be equivalent to that of the objective metal ions in the aqueous feed solution.

V. Conclusions

It was demonstrated that the sodium salt of D2EHPA extracts metal ions primarily by the exchange reaction of sodium ion to the metal ion, and the extractability depends on the initial concentration of sodium salt extractant and a metal ion or these factors and the

initial pH. The conversion of D2EHPA into salt form enables one to obtain the high and constant extractability from an acidic solution regardless of the initial pH over a wide pH range. The exchange equilibrium constant with salt form extractant is represented by the ratio between extraction equilibrium constants of the two metal ions with D2EHPA itself; one of metal ions exists in the salt form extractant and the other is in the aqueous solution. In the extraction from the solution containing various metal ions, if the sodium salt of D2EHPA equivalent to the concentration of the metal ion desired to extract is utilized, the separation factor will be enhanced.

REFERENCES

- (1) M. J. Zakarias: Trans. Inst. Metall., **75** (1966), C245.
- (2) C. Hanson: Chem. Eng., (1968) Aug. 26, 76.
- (3) D. S. Flett: Trans. Inst. Metall., **83** (1974), C30.
- (4) H. Reinhardt: Chem. Ind., (1975) March 1, 210.
- (5) G. M. Ritcey: CIM Bulletin, (1975) June, 85.
- (6) D. S. Flett: Chem. Ind., (1977) Sept. 3, 706.
- (7) C. Hanson: Intern. Symp. Solvent Extn. Metall. Processes, 1972, Antwerp, (1972), p. 5.
- (8) D. S. Flett and M. J. Jaycock: *Ion Exchange and Solvent Extraction* Vol. 3, Marcel Dekker Inc., New York, (1973), p. 1.
- (9) T. Sato and M. Ueda: Proc. Intern. Sol. Extn. Conf., 1974, Lyon, Vol. 1, (1974), p. 871.
- (10) G. M. Ritcey, A. W. Ashbrook and B. H. Lucas: CIM Bulletin, (1975) Feb., 105.
- (11) J. Shibata and S. Nishimura: J. Japan Inst. Metals, **39** (1975), 206 (in Japanese).
- (12) S. Mukai, J. Shibata and S. Nishimura: J. Japan Inst. Metals, **39** (1975), 976 (in Japanese).
- (13) J. Shibata, S. Nishimura and S. Mukai: Mem. Fac. Eng., Kyoto Univ., **38** (1976), 55.
- (14) J. Shibata and S. Nishimura: Trans. JIM, **18** (1977), 794.
- (15) J. Shibata and S. Nishimura: Trans. JIM, **20** (1979), 111.
- (16) A. J. Van der Zeeuw: Hydrometallurgy, **2** (1977), 275.
- (17) I. Kojima, J. Fukuta and M. Tanaka: J. Inorg. Nucl. Chem., **31** (1969), 1815.