

Effect of Ammonium Salts on the Solvent Extraction of Some Transition Metals with Liquid Cation Exchangers

By

Junji SHIBATA*, Sanji NISHIMURA* and Shigeru MUKAI**

(Received December 27, 1975)

Abstract

The extractions of some transition metal ions from an ammoniacal solution with di-(2-ethyl hexyl) phosphoric acid*** and Versatic Acid 911 diluted in benzene were investigated in order to clarify the effect of ammonia on the solvent extraction. As regards the result, the extraction of these metals with D2EHPA was not affected by ammonia, while the extraction with Versatic Acid 911 was considerably affected. These results were discussed by the average ligand number of metal ammine complexes. Theoretical consideration on the solvent extraction in the presence of ammonia was performed to predict the extent of interference on the solvent extraction by the formation of metal ammine complexes in the aqueous phase. The results of this consideration were in good accordance with the experimental results of copper and zinc extraction, and were in near coincidence with the experimental results of nickel and cobalt extraction. However, there was no coincidence between the results of the theoretical consideration and the experimental results of cadmium extraction.

1. Introduction

The separation and purification of metals by liquid-liquid solvent extraction has been reported by several researchers. In their papers, extraction mechanism, extraction characteristics and applications of practical operation have been reported in detail.^{1,2)} Using organic solvents to extract inorganic compounds has been employed in the field of analytical chemistry and treatment of nuclear fuel. Recently, this practice was extended to the separation and purification of common metal ions owing to the improvement of the extraction technique and the development of cheaper solvents, such as carboxylic acid.

Recently, solvent extraction has been used to extract metal ions from the

* Department of Chemical Engineering, Kansai University

** Department of Mineral Science and Technology, Kyoto University

*** Abbreviated as D2EHPA henceforth.

leached solutions of ores, and the separation of such pairs of metal ions as nickel and cobalt, zinc and manganese, zirconium and hafnium etc. comes into question. As the chemical properties of nickel and cobalt are quite similar, the separation of these metal ions is difficult. Ritcey³⁾ tried to separate copper, nickel and cobalt with LIX-63. Ashbrook⁴⁾ applied the solvent extraction to the separation of nickel and cobalt from the ammoniacal solution containing copper, nickel and cobalt with D2EHPA.

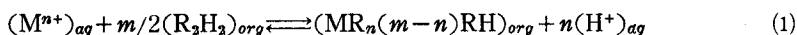
However, only a few studies⁽⁵⁻⁷⁾ have been reported and there is much left to be investigated concerning the effect of ammonia on the solvent extraction.

It is well known that many transitional elements such as copper, nickel, cobalt, zinc and cadmium combine with free ammonia in the aqueous solution to form strong complexes, known as metal ammine complexes. Therefore, under the condition of the formation of metal ammine complexes, the concentration of free metal ions in the aqueous solution decreases, and extraction % of these metal ions becomes low. Therefore, the effect of ammonia on the extraction is an extremely important problem in the solvent extraction of metal ions.

In the present paper, the extraction of these transitional metals from sodium nitrate and ammonium nitrate solutions with D2EHPA and Versatic Acid 911 was investigated. Also, a theoretical consideration on the solvent extraction in the presence of ammonia was performed to predict the extent of interference on the extraction by the formation of metal ammine complexes in the aqueous phase.

2. Extraction Equilibria

Assuming that the extraction of H₂O and hydrolysis of metal ion can be neglected, and that the extracted species in the organic phase is not polymerized, the extraction equilibrium of metals in Mⁿ⁺-RH system may be represented generally by



where Mⁿ⁺ is an n-valent metal ion, R₂H₂ is the dimeric carboxylic acid or dialkyl phosphoric acid and m is the total number of acid molecules involved in the extracted species. The equilibrium constant for the above equation is expressed as

$$K = [MR_n(m-n)RH]_{org} [H^+]_{aq}^n / [M^{n+}]_{aq} [R_2H_2]_{org}^{m/2} \quad (2)$$

where [] is the molarity of each species and the subscripts org and aq refer to the organic and aqueous phases, respectively. The distribution coefficient of the metal ion between the two phases is defined as

$$D = [M]_{org} / [M^{n+}]_{aq} = [MR_n(m-n)RH]_{org} / [M^{n+}]_{aq} \quad (3)$$

Substituting equation (2) into equation (3), the following equation can be obtained.

$$D = K [R_2H_2]_{org}^{m/2} / [H^+]_{aq}^n \quad (4)$$

Assuming that the concentration of R_2H_2 , $[R_2H_2]_{org}$, is considerably greater than the concentration of the metal ion and therefore can be regarded as constant, $K[R_2H_2]_{org}^{m/2}$ also becomes constant. When the constant part of equation (4) is replaced with K_e , equation (4) can be written as

$$D = K_e / [H^+]_{aq}^n \quad (5)$$

Taking logarithms of equation (4),

$$\log D = \log K + n\text{pH} + m/2 \log [R_2H_2]_{org} \quad (6)$$

Partially differentiating equation (6) with respect to pH under the condition where $[R_2H_2]_{org}$ may be regarded as constant,

$$[\partial \log D / \partial \text{pH}]_{[R_2H_2]_{org}} = n \quad (7)$$

As is obvious from equation (7), the value of n is determined from the slope of a log D-pH plot. If the pH of 50 % extraction, that is, $\log D = 0$, is represented by $\text{pH}_{0.5}$, equation (6) becomes as

$$\log K + m/2 \log [R_2H_2]_{org} = -n\text{pH}_{0.5} \quad (8)$$

In the same manner, equation (5) becomes as

$$\log K_e = -n\text{pH}_{0.5} \quad (9)$$

In the presence of the metal ion and the ammonium ion (HL^+) in the aqueous phase with sufficient pH to produce the free ammonia (L), the metal ammine complexes ML^{n+} , ML_2^{n+} , ML_3^{n+} , ML_i^{n+} , ML_7^{n+} will form. Dissociation of the ammonium ion and formation of the metal ammine complexes is as follows.



The dissociation constant K_L of the ammonium ion and the over-all formation constant K_i of metal ammine complex ML_i^{n+} are represented as equations (12) and (13), respectively.

$$K_L = [H^+][L] / [HL^+] \quad (12)$$

$$K_i = k_1 k_2 k_3 \dots k_i = [ML_i^{n+}] / [M^{n+}][L]^i \quad (13)$$

Assuming that free metal ions decrease because of the formation of metal ammine complexes thereby lowering the extraction of metal, and that metal ammine complexes are not extracted in the organic phase, the distribution coefficient in the presence of ammonia is given as

$$D' = [M]_{org} / \sum_{i=0}^I [ML_i^{n+}]_{aq} \quad (14)$$

Substituting equations (3), (5), (12) and (13) into equation (14), the following equation is obtained.

$$D' = K_e / \sum_{i=0}^I K_i K_L^i [H^+]^{n-i} [HL^+]^i \quad (15)$$

Introducing the average ligand number of the ammonia ligand combined with one of the metal ions, i_{av} , and assuming that there is only one metal ammine complex with the ligand number of i_{av} , equation (14) can be written as

$$D'_{av} = K_e / K_{i_{av}} K_L^{i_{av}} [H^+]^{n-i_{av}} [HL^+]^{i_{av}} \quad (16)$$

Converting equation (16) into logarithmic form, equation (16) becomes

$$\log D'_{av} = \log K_e - \log K_{i_{av}} K_L^{i_{av}} + (n - i_{av})\text{pH} - \log [HL^+]^{i_{av}} \quad (17)$$

Partially differentiating equation (17) with respect to pH under the condition where $[HL^+]$ is regarded as constant.

$$[\partial \log D'_{av} / \partial \text{pH}] [HL^+] = n - i_{av} \quad (18)$$

As is obvious from equation (18), when pH is markedly raised to form metal ammine complexes in the aqueous phase, the value of i_{av} increases and as a result, equation (18) changes from positive to negative. It will be known, therefore, that a graph of $\log D$ against pH has a shape like a paraboloid, and that the maximum extraction occurs at the pH where the relation of $[\partial \log D'_{av} / \partial \text{pH}] = 0$, that is, when $n = i_{av}$. The slope at any point of a $\log D$ -pH graph may be determined by equation (18).

It is possible to predict the extent of hindrance to the extraction by the formation of metal ammine complexes using equation (15), where the values of K_L and K_i are available in literature, and the other values are obtained experimentally.

3. Experimental

3.1. Reagents

3.1.1. Aqueous solution

The aqueous solution was composed of metal sulphates of 0.005 mol/l and sodium nitrate or ammonium nitrate of 1.00 and 3.00 mol/l. Metal sulphates, sodium nitrate and ammonium nitrate were of an analytical reagent grade. De-ionized water was used throughout the work.

3.1.2. Organic solution

The organic phase was a binary solution of D2EHPA and benzene, or Versatic Acid 911 and benzene. The D2EHPA and Versatic Acid 911 used in this work were supplied by the Kao Soap Company Limited and the Shell Chemical Company, respectively. The D2EHPA was purified in the usual way^{8,9)}, and the purity

after this purification was 98.9%. Versatic Acid 911 was used without further purification. D2EHPA and Versatic Acid 911 were both known to be dimeric in non-polar solvent^{10,11}, and the structure and properties of these acids are shown in Tables 1 and 2, respectively.

3.2. Procedure

An amount of 15 ml of the aqueous solution and the same amount of organic solution were poured together into a 50 ml glass-stoppered conical flask. Aqueous NaOH solution was added in order to adjust the pH of the aqueous solution. The flask was then installed in a shaking device (Iwaki KM shaker) and shaken for 25 minutes at 25°C. After equilibrium, the aqueous and organic phases were separated by centrifuging at 2500 rpm for 15 minutes. Then, the flask was immersed in a water bath maintained at 25°C. The metal ion content and pH value of this equilibrium aqueous phase were measured. The metal ion content was determined by titration with sodium diaminoethanetetraacetate (EDTA) solution¹². The indicators were PAN for copper, Cu-PAN for nickel and cobalt, and XO for zinc and cadmium. Partially, the metal ion content was determined by atomic absorption spectrometry. Visible absorption spectra and infrared absorption spectra of the extracted species were obtained, using the Hitachi 124 spectrophotometer and the Shimadzu IR 400

Table 1 Structure and properties of D2EHPA

Structural formula	$(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_2\text{O})_2\text{P}(=\text{O})(\text{OH})$
Acid value (mg KOH/g)	178.9
Purity (%)	98.9
Specific gravity (g/cm ³ at 25°C)	0.964
Viscosity (c. s. at 25°C)	26.7

Table 2 Structure and properties of Versatic Acid 911

Structural formula	$\begin{array}{c} \text{R}_1 \\ \\ \text{R}_2\text{---C---COOH} \\ \\ \text{CH}_3 \end{array} \quad (\text{R}_1, \text{R}_2 = \text{C}_3\text{---C}_4)$
Acid value (mg KOH/g)	326.2
Purity (%)	99.0
Specific gravity (g/cm ³ at 25°C)	0.922
Viscosity (c. s. at 25°C)	31.74
Solubility (g/l pH=4.0)	0.10

spectrophotometer, respectively.

4. Results and discussion

4.1. Distribution equilibria with D2EHPA

The extraction of Cu, Ni and Co from 1.00 mol/l sodium nitrate or ammonium nitrate solution with D2EHPA is shown in Fig. 1. The extraction of Zn and Cd under the same condition is shown in Fig. 2. As is obvious from Figs. 1 and 2, a log D -pH graph in the 1.00 mol/l NH_4NO_3 system shifts to a higher pH than that in the 1.00 mol/l NaNO_3 system. The difference is 0.155, 0.203, 0.151 pH unit for Cu, Ni and Co, 0.070, 0.150 pH unit for Zn and Cd respectively. But the slope of a log D -pH graph for each metal is nearly equal and parallel straight lines are obtained. The data for the extraction from 1.00 mol/l NaNO_3 system are summarized in Table 3. In Table 3, n and $\text{pH}_{0.5}$ are determined by the least squares method. The distribution constant of the ammonium ion, K_L and the over-all formation constants of the metal ammine complexes, $K_f^{13,14}$ are shown in Table 4. Substituting the values of n , K_e , K_L and K_f shown in Tables 3 and 4 into equation (15), the values of log D at any pH can be determined.

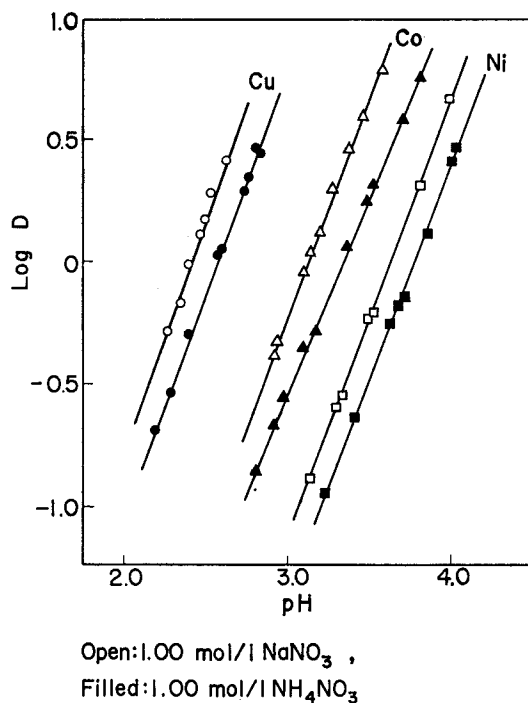


Fig. 1 Extraction of Cu, Ni and Co with 0.85 mol/l D2EHPA from an aqueous phase of 1.00 mol/l NaNO_3 or NH_4NO_3 .

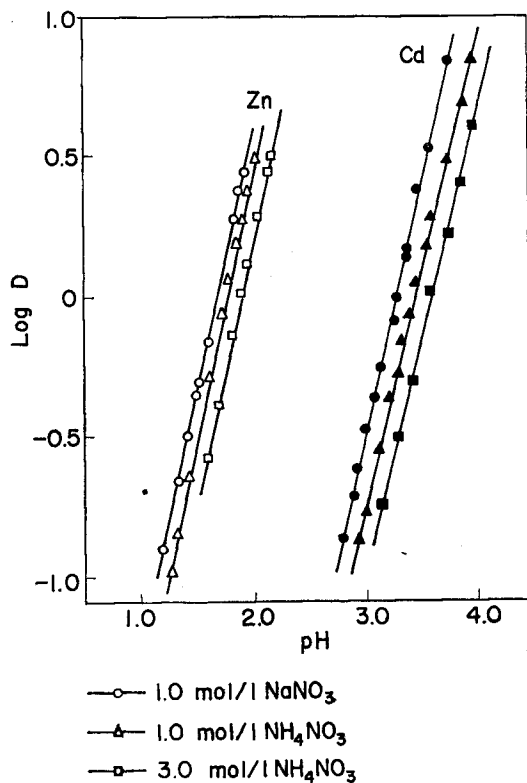


Fig. 2 Extraction of Zn and Cd with 0.2 mol/l D2EHPA from an aqueous phase of NaNO₃ or NH₄NO₃.

Table 3 Values of n , $\text{pH}_{0.5}$ and K_e on the extraction from 1.00 mol/l NaNO₃ solution

	Cu	Ni	Co	Zn	Cd
n	1.952	1.803	1.864	1.969	1.744
$\text{pH}_{0.5}$	2.418	3.621	3.129	1.705	3.298
K_e	1.909×10^{-5}	2.958×10^{-7}	1.472×10^{-6}	4.394×10^{-4}	1.771×10^{-6}

Table 4 Over-all formation constants of metal ammine complexes

	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$	$\log K_5$	$\log K_6$
Cu	4.14	7.62	10.50	12.61	—	—
Ni	2.77	4.99	6.70	7.86	8.59	8.60
Co	2.08	3.67	4.96	5.42	5.57	4.91
Zn	2.27	4.61	7.01	9.06	—	—
Cd	2.60	4.65	6.04	6.92	6.60	4.90

$\text{p}K_L$ in 1.00 M NH₄NO₃ at 25°C, $\text{p}K_L = -\log K_L = 9.37$

The theoretical distribution coefficient from equation (15) agrees completely with the experimental results in the 1.00 mol/l NaNO_3 system, which clarifies that the extraction of these metal ions with D2EHPA is not affected by ammonia. It is apparent that over the pH ranges considered, the terms of $i \geq 1$ in the denominator of equation (15) are extremely small compared with the term of $i=0$, and that over these pH ranges, metal ammine complexes of the five metals are not produced. The shift in log D -pH graphs to the higher pH is not due to the formation of metal ammine complexes, but only to the different salt effects between sodium nitrate and ammonium nitrate. Though the values of n for each metal in Table 3 are a little smaller than the theoretical value of 2, it is because D2EHPA dissolves in the aqueous phase to form the complexes between metal ions and D2EHPA¹⁵⁾, which reduce the average charge of metal ion in the aqueous phase.

4.2. Distribution equilibria with Versatic Acid 911

The extraction of Cu, Ni and Co from 1.00 mol/l sodium nitrate or ammonium nitrate solutions with Versatic Acid 911 is shown in Fig. 3. The extraction of Zn and Cd under the same conditions is shown in Fig. 4. Since Versatic Acid 911 is a somewhat weaker organic acid than D2EHPA, consequently the metal ions are extracted at a higher pH. From the results shown in Figs. 3 and 4, it is recognized that the extraction of these metals in the 1.00 mol/l NH_4NO_3 system is considerably hindered, and the effect of ammonia is remarkable. Especially, as pH in the aqueous phase is raised and the concentration of free ammonia is increased, the effect of ammonia on the extraction becomes notable.

Also, the log D -pH graph has a shape like a paraboloid since the maximum extraction occurs at a certain pH. Calculated by the least squares method, Table 5 summarizes the results from the 1.00 mol/l NaNO_3 system shown in Figs. 3 and 4. In Table 5, the value of α added to $\text{pH}_{0.5}$ is the correction factor caused from the difference of the salt effect between sodium nitrate and ammonium nitrate, where α may be regarded as the shift on log D -pH graphs obtained in the D2EHPA system. $K_{e(\alpha p)}$ is an appropriate value of K_e for the 1.00 mol/l NH_4NO_3 system, determined by taking account of the difference of the salt effect. Substitution of the values in Table 5 into equation (13) yields the theoretical distribution coefficient shown by the dotted line in Figs. 3 and 4. It is recognized from Figs. 3 and 4 that the theoretical values for copper, nickel and zinc are in fairly good accordance with the experimental results, while the theoretical values for cobalt and cadmium slightly differ from the experimental results.

Ashbrook⁷⁾ and Haffenden⁵⁾ have mentioned that the difference of cobalt between both values at a higher pH is attributed to the extraction of metal ammine complexes in the organic phase or the oxidation of cobalt (II) in the

aqueous phase. However, the formation constant of the cobalt (III) ammine complexes is greater than that of cobalt (II), and if there are cobalt (III) ions in the aqueous phase, the distribution coefficient must be smaller at a higher pH. In this study, it was found that there were no metal ammine species in the organic phase, based on the measurement of the infrared absorption spectra. As is stated after, therefore, it may be suggested that the dimeric species exist at a higher pH and, that the formation of the dimeric species takes part in the difference at the higher pH.

The theoretical treatment was developed according to the assumption that the extracted species contain only monomer. However, taking the existence of dimer as the extracted species into account, the extraction equilibrium is represented as,



Equilibrium constant K_2 and distribution coefficient D_2 are given as follows.

$$K_2 = [(MR_n(m-n)RH)_{2,org}]^{1/2} [H^+]_{aq}^n / [M^{n+}]_{aq} [R_2H_2]_{org}^{m/2} \quad (20)$$

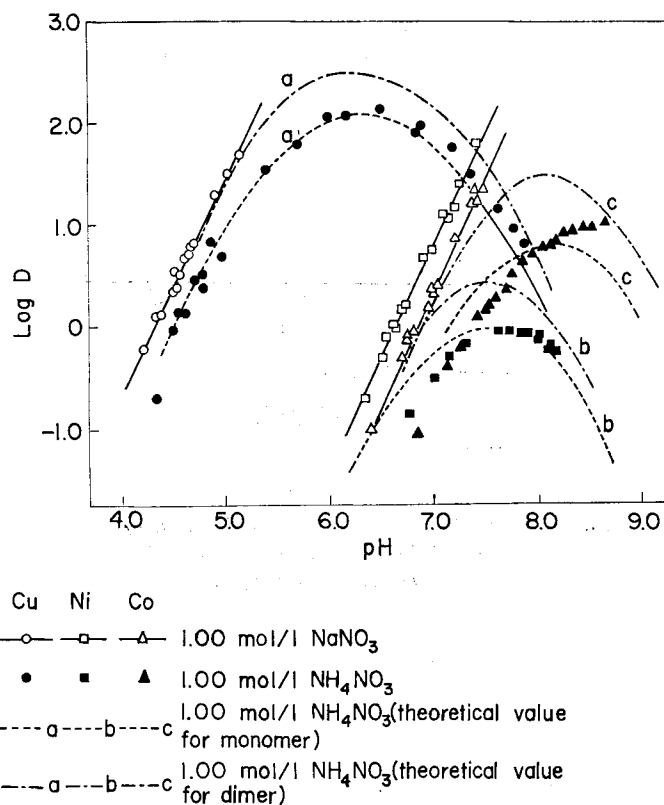


Fig. 3 Extraction of Cu, Ni and Co with 0.2 mol/l Versatic Acid 911 from an aqueous phase of 1.00 mol/l NaNO₃ or NH₄NO₃.

$$D_2 = [M]_{org} / [M^{n+}]_{aq} = 2[(MR_n(m-n)RH)_2]_{org} / [M^{n+}]_{aq} \quad (21)$$

From equations (20) and (21)

$$D_2 = K_2 [M]_{org}^{1/2} / [H^+]_{aq}^n \quad (22)$$

Applying $pH_{0.5}$ to equation (22) and taking logarithms,

$$\log K_2 = -npH_{0.5} - 1/2 \log([M]_{total}/2) \quad (23)$$

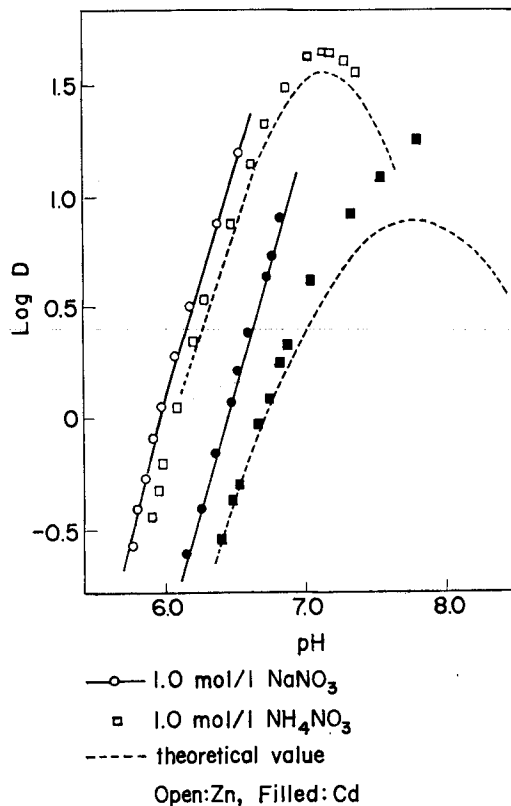


Fig. 4 Extraction of Zn and Cd with 0.2 mol/l Versatic Acid 911 from an aqueous phase of 1.00 mol/l NaNO₃ or NH₄NO₃.

Table 5 Values of n and $pH_{0.5}$ in NaNO₃ solution, and the appropriate K_e values in the presence of 1.00 mol/l NH₄NO₃

	Cu	Ni	Co	Zn	Cd
n	2.126	2.188	2.156	2.451	2.271
$pH_{0.5}$	4.311	6.594	6.815	5.990	6.440
$pH_{0.5+\alpha}$	4.466	6.745	7.019	6.060	6.585
$K_e(\text{ap.})$	3.199×10^{-10}	1.764×10^{-15}	7.364×10^{-18}	1.403×10^{-15}	1.111×10^{-15}

In the presence of ammonia in the aqueous phase, the distribution coefficient is expressed as,

$$D_2 = [M]_{org} / \sum_{i=0}^I [ML_i^{2+}]_{aq} \quad (24)$$

Substituting equations (12), (13) and (21) into equation (24) gives

$$D_2 = K_2 [M]_{org}^{1/2} / \sum_{i=0}^I K_i K_L^i [HL^+]^i [H^+]^{n-i} \quad (25)$$

From the definition of the distribution coefficient,

$$D_2 = [M]_{org} / ([M]_{total} - [M]_{org}) \quad (26)$$

Equating equation (25) to equation (26) and substituting known values and an arbitrary pH, a quadratic equation about $[M]_{org}$ can be obtained, from which $[M]_{org}$ at any pH is determined. Thus, the distribution coefficient D'_2 in the presence of the dimeric species may be found from equation (25). The theoretical

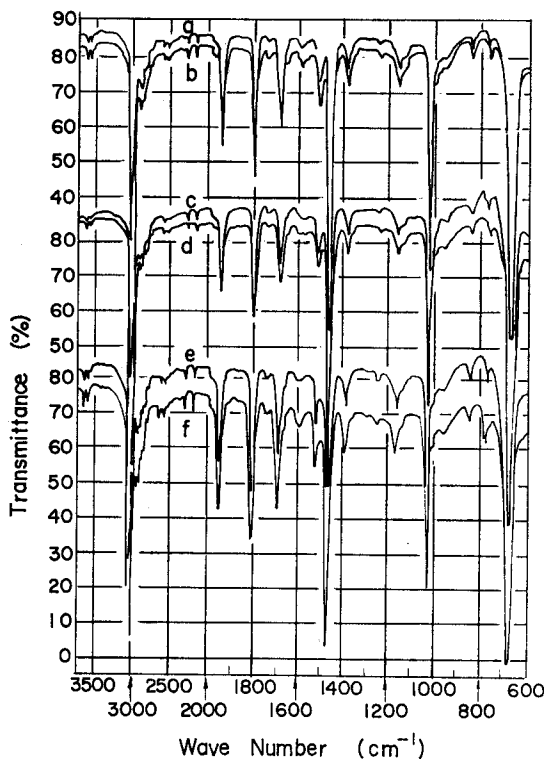


Fig. 5 Infrared spectra of extracts with 0.2 mol/l Versatic Acid 911.

- (a) Cu (II) from 1.00 M NaNO₃, pH 8.07
- (b) Cu (II) from 1.00 M NH₄NO₃, pH 8.11
- (c) Co (II) from 1.00 M NaNO₃, pH 7.89
- (d) Co (II) from 1.00 M NH₄NO₃, pH 8.08
- (e) Ni (II) from 1.00 M NaNO₃, pH 7.94
- (f) Ni (II) from 1.00 M NH₄NO₃, pH 8.15

values of D'_2 , which are shown by the dot and dash line in Fig. 3, are wholly greater than the experimental results, and at the higher pH, the values of D'_2 for copper, nickel and cobalt have a tendency to gradually approach the experimental results.

Development of the theoretical treatment taking the product of dimer into account seems to explain why the theoretical value shown in Fig. 3 does not agree with the experimental results at the higher pH. This is also recognized from the measurement of the visible absorption spectra of the extracted species. The visible absorption spectrum of the copper extract at an equilibrium pH of 8.18 has the absorption peaks at 375 and 690 nm. This peak of 375 nm is indicative of copper carboxylate dimers, which has been reported by Fletcher¹⁵ and Tanaka^{16,17}.

In the development of this theory, it is assumed that the metal ammine complexes in the aqueous phase are not extracted with Versatic Acid 911. Then, the infrared spectra of the extracted species of copper, nickel and cobalt were measured in order to confirm whether metal ammine complexes existed in the organic phase. These are shown in Fig. 5. The infrared spectra of the extracted species in the extraction from NaNO_3 and NH_4NO_3 coincide completely, from which it is confirmed that metal ammine complexes did not exist in the organic phase. It is reported that the presence of metal ammine complexes in the organic phase, results in absorption bands at approximately 1628 and 3414 cm^{-1} for copper⁽¹⁸⁾, and 820 , 1325 , 1600 , 3170 and 3240 cm^{-1} for cobalt¹⁹.

The extracted species of cadmium with carboxylic acid is shown to be monomer, $\text{CdR}_2\text{4RH}^{20}$. Therefore, the difference between the experimental results

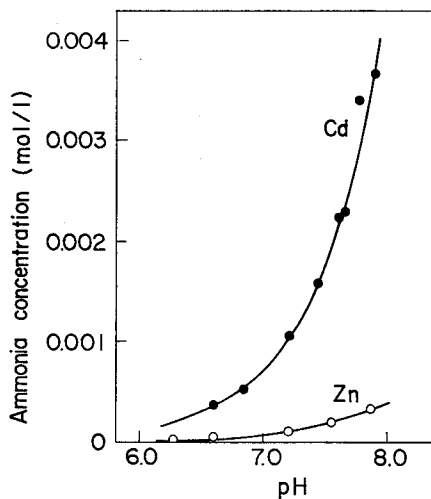


Fig. 6 Total ammonia concentration in the organic phase measured by the indophenol method.

and the theoretical values of cadmium in Fig. 4, is not attributed to the formation of dimer as in the case of cobalt. Then, in order to examine the concentration of ammonia in the organic phase, the equilibrium organic phase of zinc and cadmium was stripped with dilute nitric acid solution and this strip solution was measured by the indophenol method²¹. The results obtained are shown in Fig. 6. The amount of ammonia in the equilibrium organic phase of cadmium extraction is small at the lower pH, where cadmium ammine complexes are difficult to form; while it increases remarkably at the higher pH, where cadmium ammine complexes are easy to produce.

This has a correlation with the fact that the experimental results gradually diverge from the theoretical values according to the increase of pH. Thus, the difference between the experimental results and the theoretical values may be ascribed to the extractability of cadmium ammine complexes. On the other hand, the amount of ammonia in the equilibrium organic phase of zinc extraction is small and scarcely changes with the increase of pH. Thus, zinc ammine complexes are difficult to be extracted in the organic phase.

4.3. Consideration from average ligand number of metal ammine complexes

The average ligand number at any pH was calculated and the consideration of the experimental results from this average ligand number was tried. The average ligand number is computed as follows.

Mole fraction of ammonia, α , is given by equation (27), using the dissociation constant of the ammonium ion, K_L , and the hydrogen ion concentration, $[H^+]$.

$$\alpha = \frac{[NH_3]}{[NH_3] + [NH_4^+]} = \frac{K_L}{K_L + [H^+]} \tag{27}$$

Then, the mole fractions of free metal ion and metal ammine complexes ML^{n+} , ML_2^{n+} , ML_I^{n+} are represented respectively by,

$$\begin{aligned} \beta_0 &= [M^{n+}]/C_M = 1 / \sum_{i=0}^I K_i (\alpha C_L)^i \\ \beta_1 &= [ML^{n+}]/C_M = K_1 (\alpha C_L) / \sum_{i=0}^I K_i (\alpha C_L)^i \\ \beta_2 &= [ML_2^{n+}]/C_M = K_2 (\alpha C_L)^2 / \sum_{i=0}^I K_i (\alpha C_L)^i \\ &\vdots \qquad \qquad \qquad \vdots \qquad \qquad \qquad \vdots \\ \beta_I &= [ML_I^{n+}]/C_M = K_I (\alpha C_L)^I / \sum_{i=0}^I K_i (\alpha C_L)^i \\ \beta_0 + \beta_1 + \beta_2 + \dots + \beta_I &= 1 \end{aligned} \tag{28}$$

where K_i is the over-all formation constant, C_L is the total ammonia concentration and C_M is the total metal ion concentration. As the total ammonia concentration is so much greater than the metal ion concentration in this study, it can be regarded as constant. The average ligand number is defined as,

$$i_{av} = (\alpha C_L - [L]) / C_M$$

$$= \frac{[ML^{n+}] + 2[ML_2^{n+}] + \dots + I[ML_I^{n+}]}{[M^{n+}] + [ML^{n+}] + [ML_2^{n+}] + \dots + [ML_I^{n+}]}$$
(29)

The next equation about the average ligand number is obtained by using equations (28) and (29).

$$i_{av} = \beta_1 + 2\beta_2 + 3\beta_3 + \dots + I\beta_I$$
(30)

The average ligand number at any pH can be determined from equations (27), (28) and (30). These calculated values are shown in Fig. 7 for copper, nickel and cobalt, in Fig. 8 for zinc and in Fig. 9 for cadmium, respectively.

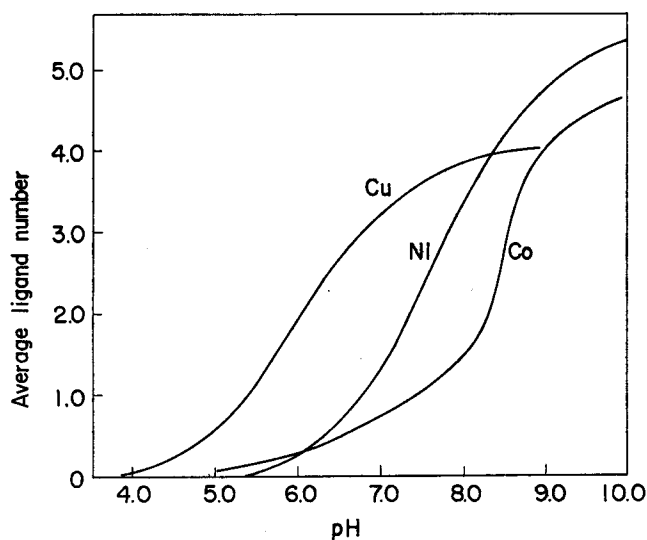


Fig. 7 Relationship between pH and the average ligand number of ML_1^{n+} .

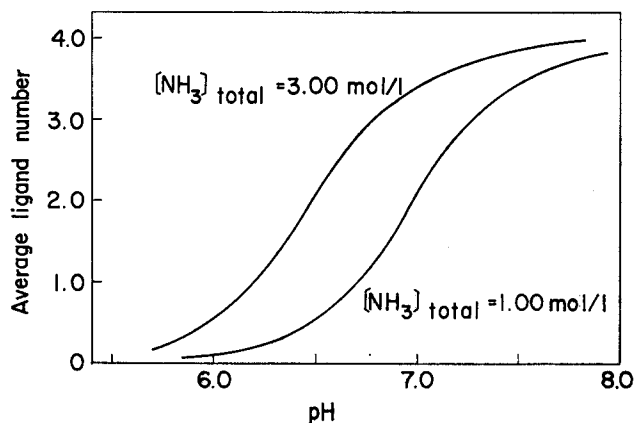


Fig. 8 Relationship between pH and the average ligand number of ZnL_1^{n+} .

It is obvious from these figures that the metal ammine complexes of these five metals exist at the pH above 4 and are not formed at the pH region which these metals are extracted with D2EHPA. On the other hand, the conspicuous formation of metal ammine complexes is recognized in the pH region of the extraction with Versatic Acid 911. If the concentration of total ammonia increases, then the formation of metal ammine complexes occurs from the lower pH and results in an i_{av} -pH curve shift to the acidic range.

Clarifying the relationship between the average ligand number and pH is useful for investigating not only the formation of metal ammine complexes, but also the pH value with the maximum distribution coefficient. According to equation (18), this pH is given as the pH where the average ligand number becomes equal to the value of n . Thus, the pH giving the maximum distribution coefficient in the metal-Versatic Acid 911 system is shown in Table 6, compared with the pH obtained from Figs. 3 and 4. Both pH values agree closely. In the case of the cobalt or cadmium-Versatic Acid 911 system, the extraction of these metals is not in accord with this theory, consequently, these metals are not mentioned.

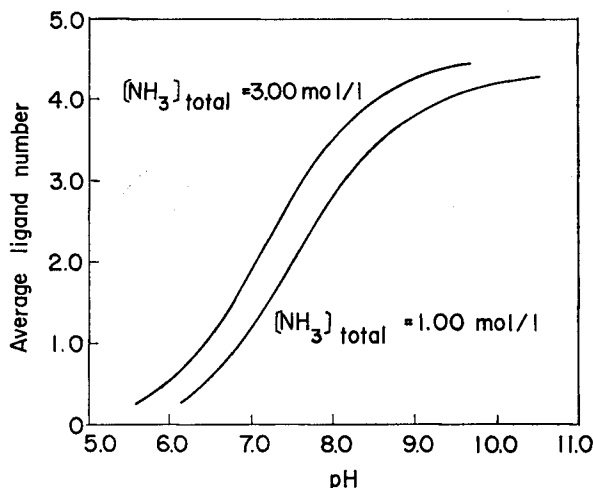


Fig. 9 Relationship between pH and the average ligand number of CdL_1^{2+} .

Table 6 Comparison of the pH values with maximum distribution coefficient on 1.00 mol/l NH_4NO_3 system

Metals	Cu	Ni	Zn
Extraction study	6.35	7.50	7.13
Average ligand number	6.16	7.38	7.08

As mentioned above, the average ligand number is determined only by the kinds of metal and ligand, and pH. It is clear, therefore, that a log D -pH curve keeps the same parabolic shape and only moves parallel up and down, even if the concentrations of extractant and metal are changed.

4.4. Extraction equilibria when the concentration of extractant and total ammonia are increased

When the concentration of the extractant and total ammonia was increased, the extraction was examined and the results were investigated from the average ligand number. The extraction of copper, nickel and cobalt from 1.00 mol/l NaNO_3 solution with 2.0 mol/l Versatic Acid 911, and the theoretical curves obtained from equation (18) are shown in Fig. 10. The theoretical curves for the 0.2 mol/l Versatic Acid 911 system are also represented in this figure in the interest of comparison. As the extractability increases with the increase of extractant concentration, the distribution coefficient at any pH is raised. Namely, log D -pH curve moves parallel up with the increase of extractant concentration, where the pH with maximum distribution coefficient is kept constant. These pH values were 6.35, 7.50 and 8.10

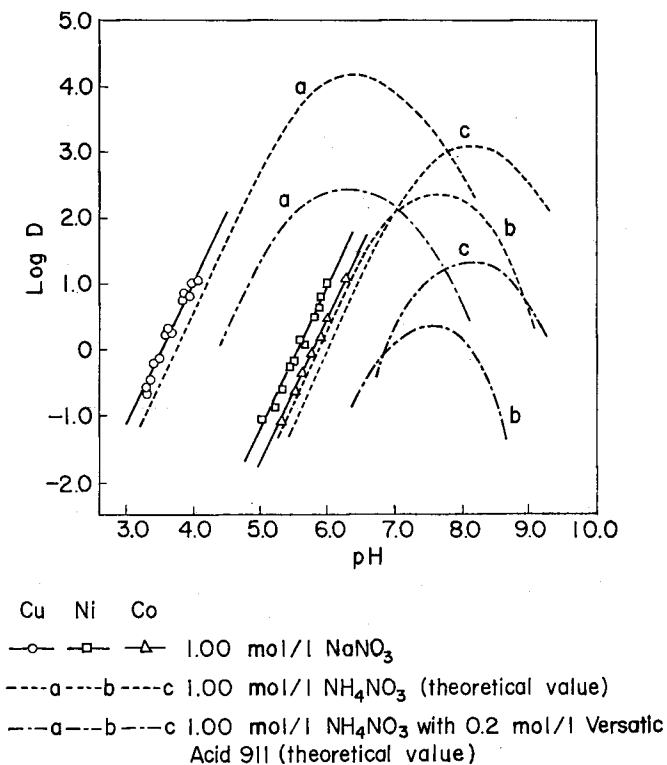


Fig. 10 Extraction of Cu, Ni and Co with 2.0 mol/l Versatic Acid 911.

for copper, nickel and cobalt respectively regardless of the concentration of the extractant.

The extraction of zinc and cadmium from 1.00 and 3.00 mol/l NH_4NO_3 solutions with 0.2 mol/l Versatic Acid 911 was shown in Fig. 11. It is recognized that the effect of ammonia on the extraction of zinc begins to occur at the lower pH with the increase of the total ammonia concentration, and the effect is more remarkable on 3.00 mol/l NH_4NO_3 solution than 1.00 mol/l. The pH with the maximum distribution coefficient moves to such lower pH as might be expected from the average ligand number. Both extractions of zinc from 1.00 and 3.00 mol/l NH_4NO_3 solutions are in approximate accordance with the theoretical values. However, the extraction of cadmium differs from the theoretical values. With the higher concentration of total ammonia the difference between both values becomes greater. This may be attributed to the extractability of cadmium ammine complexes as mentioned before.

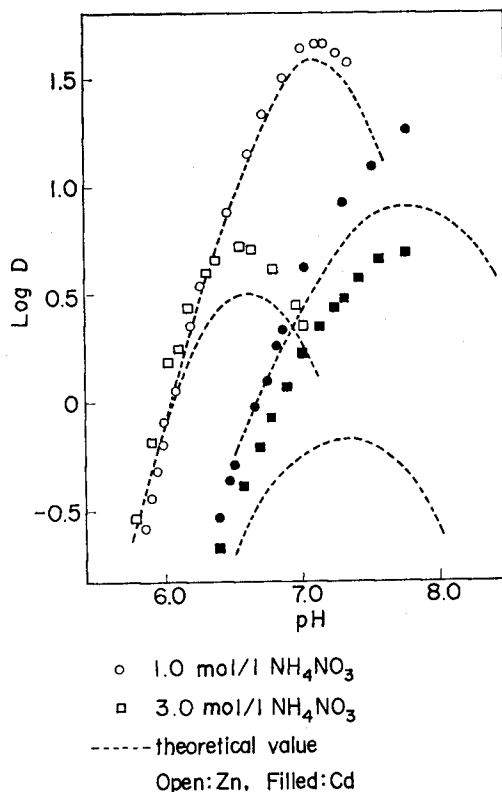


Fig. 11 Extraction of Zn and Cd with 0.2 mol/l Versatic Acid 911 from 1.00 or 3.00 mol/l NH_4NO_3 solution.

5. Conclusion

In this paper, the extraction of some transitional metal ions from sodium nitrate and ammonium nitrate with D2EHPA and Versatic Acid 911 was investigated in order to clarify the effect of ammonia on the extraction of these metal ions. Theoretical treatment on the solvent extraction in the presence of ammonia was developed to predict the extent of hindrance to the extraction by the formation of metal ammine complexes in the aqueous phase. Then, the average ligand number of metal ammine complexes at any pH was calculated, from which the experimental results were considered. The results obtained can be summarized as follows.

1) The extraction of these metal ions with D2EHPA is not affected by ammonia, but only by the difference of the salt effect between sodium nitrate and ammonium nitrate.

2) The extraction with Versatic Acid 911 is considerably hindered, and the effect of ammonia in the aqueous phase is remarkable.

3) The experimental distribution coefficients of copper and zinc are in fairly good accordance with the theoretical values derived from the assumption of nonextractability of metal ammine complexes. The values for the extraction of nickel and cobalt nearly agree, while the values for cadmium extraction do not agree, which is ascribed to the extractability of cadmium ammine complexes.

4) Clarifying the relationship between the average ligand number and pH is useful for investigating not only the formation of metal ammine complexes, but also the pH value with the maximum distribution coefficient. From the consideration by the average ligand number, metal ammine complexes are not formed at the pH region where these five metals are extracted with D2EHPA, while the remarkable formation of metal ammine complexes is recognized at the pH region of the extraction with Versatic Acid 911. The pH values giving a maximum distribution coefficient from the average ligand number agree closely with the pH values obtained from the experimental results.

5) Though the separation of such metals as nickel and cobalt, and zinc and cadmium is very difficult, it may become easy by selecting a suitable pH and ammonia concentration in the ammonium nitrate-Versatic Acid 911 system.

References

- 1) G. M. Ritcey : Can. Min. J., **90** (1969), June 73
- 2) M. J. Zakarias and M. J. Cahalan : Trans. Inst. Min. Metall., **75** (1966), C 245
- 3) G. M. Ritcey and B. H. Lucas:Can. Min. Metall. Bull., **65** (1972), May 46
- 4) A. W. Ashbrook and G. M. Ritcey:Trans. Inst. Min. Metall., **78**(1969), C 57

- 5) W. J. Haffenden and G. J. Lawson: *Advances in Extractive Metallurgy*, Inst. Min. Metall., (1968), 678
- 6) D. S. Flett and D. W. West: *J. Inorg. Nucl. Chem.*, **29**(1967), 1365
- 7) A. W. Ashbrook: *J. Inorg. Nucl. Chem.*, **34**(1972), 1721
- 8) D. F. Peppard, J. R. Rerraro and G. W. Manson: *J. Inorg. Nucl. Chem.*, **7**(1958), 231
- 9) M. Asano, Y. Okajima and T. Nishi: *Tech. Repts. Eng. Res. Inst. Kyoto Univ.*, (1963), 117
- 10) C. A. Blake et al. : *Ind. Engng. Chem.*, **50**(1958), 1763
- 11) A. W. Fletcher and D. S. Flett: *J. Appl. Chem.*, **14**(1964), 250
- 12) K. Ueno: *Kireito Tekiteihou*, Nankodo, Tokyo, (1960)
- 13) A. Ringbom : *Complexation in Analytical Chemistry*(translated by N. Tanaka and H. Sugi), Sangyotoshyo, Tokyo, (1965), 275
- 14) J. Bjerrum: *Metal Ammine Formation in Aqueous Solution*, P. Haase and son, Copenhagen, (1957), 296
- 15) M. L. Brisk and W. J. McManamey : *J. Appl. Chem.*, **19**(1969), 103
- 16) M. Tanaka and N. Nakasuka : *Solvent Extraction Chemistry*, North Holland, Amsterdam, (1967), 2591
- 17) M. Tanaka and N. Nakasuka : *J. Inorg. Nucl. Chem.*, **31**(1969), 2591
- 18) K. Nakamoto: *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley, New York, (1963), 143
- 19) K. Nakamoto : *Advances in Chemistry Series*, American Chemical Society Publication, No 62, (1967), 396
- 20) T. Saito, T. Tanabe, S. Nishimura and Y. Kondo : *J. Min. Metall. Inst. Japan*, **88** (1972), 215
- 21) JIS K0102, (1971), 40