Studies on the Extraction Equilibria of Cu, Ni, Co and Mn with Versatic Acid 911*

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The distribution of Cu, Ni, Co and Mn between an aqueous solution of constant ionic strength and Versatic Acid 911 diluted with benzene was investigated. Only one extracted species of Cu was revealed to have a dimeric structure of the composition $(\text{CuR}_2 \cdot \text{RH})_2$, while both monomer and dimer were found in the extraction of Ni, Co and Mn. The curve-fitting method was employed to determine these species, from which the composition of the extracted species was found to be $\text{NiR}_2 \cdot 4\text{RH}$ and $(\text{NiR}_2 \cdot 2\text{RH})_2$, $\text{CoR}_2 \cdot 4\text{RH}$ and $(\text{CoR}_2 \cdot 2\text{RH})_2$, and $\text{MnR}_2 \cdot 4\text{RH}$ and $(\text{MnR}_2 \cdot 2\text{RH})_2$, respectively. The apparent equilibrium constants of the above species and those between monomer and dimer were also determined. The curve-fitting method was proved to be a precise method for determining the equilibrium constants and extracted species.

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I. Introduction

The application of solvent extraction extends over to many fields including analytical chemistry, atomic energy industry, and metallurgy of non-ferrous and rare metals.

There are acidic organophosphorus esters and carboxylic acids in the extractants belonging to liquid cation exchangers. Among them, Versatic Acid and naphthenic acid which can be obtained in large quantities and economically as a byproduct of petroleum industry are being used to clarify the extraction mechanism^{(1)~(11)} and utilized in some commercial plants^{(12)~(14)}.

Many studies on the solvent extraction of metals with carboxylic acids have been carried out and the carboxylic acids used are those of 7~15 carbons^{(15)~(27)}. Metal ions of interest are mainly copper, nickel and cobalt, and the extraction of ferrous, zinc, cadmium, lead, aluminium, magnesium, calcium ions, etc. have been also investigated. Fletcher *et al.* have been studied the extraction equilibria of copper, nickel and cobalt with naphthenic acid to determine $(\text{CuR}_2 \cdot \text{RH})_2$, $(\text{NiR}_2 \cdot 2\text{RH})_2$ and $(\text{CoR}_2 \cdot 2\text{RH})_2$ as a extracted species, respectively, where RH is carboxylic acid. Tanaka

et al.⁽³⁾⁽²⁸⁾⁽²⁹⁾ reported $(\text{CuR}_2 \cdot \text{RH})_2$ as the extracted species of copper and the existence of monomeric and dimeric species as the extracted species of nickel and cobalt in a series of the extraction studies using capric acid. Haffenden and Lawson⁽²⁾ have adopted the overall formation to describe the extracted species of copper with pivalic acid and concluded $\text{Cu}_{1.9}\text{R}_{1.38}(\text{RH})_{2.1}$ as the overall composition.

It is of fundamentally importance in the studies of solvent extraction to determine the composition of the extracted species and the extraction constants. This is essential to the application to industrial processes as well as the elucidation of the extraction mechanism. Although many studies on the extraction of metal ions with carboxylic acids have been reported, there is much yet to be investigated concerning the extraction equilibria of copper, nickel, cobalt and manganese with Versatic Acid 911.

In the present paper, the extraction equilibria of some metal ions with Versatic Acid 911 were investigated in order to clarify the extraction characteristics of those metals, and determine the composition of the extracted species and the apparent equilibrium constant.

II. Extraction Equilibrium

Some methods to analyze the composition of

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the extracted species on the basis of the distribution experiment have been attempted^{(1)(2)(28)~(31)}. In the presence of only one species in the organic phase, the composition is easily determined. When the species of different compositions more than two are formed in the organic phase, however, the extraction equilibria are complicated and the determination of the compositions is difficult.

In general, the extraction equilibrium of a divalent metal ion with carboxylic acids may be represented by

where M^{2+} is a divalent metal ion, R_2H_2 is the dimeric carboxylic acid, x is the degree of polymerization and m is the total number of acid molecules involved in the species. The equilibrium constant for the above equation is expressed as

$$K_{x,m} = \frac{[(MR_2 \cdot mRH)_{x,org}][H^+]^{2x}}{[M^{2+}]^x [R_2H_2]_{org}^{x(1+m/2)}}, \quad (2)$$

where $[]$ is the molarity of each species and the subscript *org* refers to the organic phase. Assuming that the extracted species from monomer to X -mer take part in the metal extraction and the number of carboxylic acid solvating to the species changes from 0 to M , the distribution coefficient of the metal ion between the two phases is represented by

$$D = C_{MO}/C_{MW} = \sum_{x=1}^X \sum_{m=0}^M x[(MR_2 \cdot mRH)_{x,org}]/C_{MW}, \quad (3)$$

where C_{MO} and C_{MW} refer to total metal ion concentrations in the organic and aqueous phases, respectively. Substitution of eq. (2) into eq. (3) gives the next equation:

$$C_{MO} = \sum_{x=1}^X \sum_{m=0}^M xK_{x,m}C_{MW}^x [R_2H_2]_{org}^{x(1+m/2)} / [H^+]^{2x} \beta_M^x. \quad (4)$$

From eqs. (3) and (4)

$$D = \sum_{x=1}^X \sum_{m=0}^M xK_{x,m}C_{MW}^{x-1} [R_2H_2]_{org}^{x(1+m/2)} / [H^+]^{2x} \beta_M^x. \quad (5)$$

In eqs. (4) and (5), β_M is the coefficient to take into account the formation of metal complexes in the aqueous phase as shown in eq. (6):

$$C_{MW} = \beta_M [M^{2+}]. \quad (6)$$

Equations (4) and (5) are the most accurate expressions that show the extraction equilibrium of divalent metal ions, but it is difficult to use these equations to analyze the experimental data without simplification. Then, assuming that there exists only the species, $(MR_2 \cdot mRH)_x$ in the organic phase, eq. (4) is simplified as

$$C_{MO} = xK_{x,m}C_{MW}^x [R_2H_2]_{org}^{x(1+m/2)} / [H^+]^{2x} \beta_M^x. \quad (7)$$

Taking logarithms of eq. (7),

$$\log C_{MO} = x(\log C_{MW} + 2 \text{pH} - \log \beta_M) + \log xK_{x,m} + x(1+m/2) \log [R_2H_2]_{org}. \quad (8)$$

According to eq. (8), the plot of $(\log C_{MW} + 2\text{pH} - \log \beta_M)$ vs $\log C_{MO}$ at a constant $[R_2H_2]_{org}$ should give the degree of polymerization, x , of the extracted species. The plot of $\{\log C_{MO} - x(\log C_{MW} + 2\text{pH} - \log \beta_M)\}$ vs $\log [R_2H_2]_{org}$ gives the total number of carboxylic acid molecules involved in the extracted species and the equilibrium constant K_{xm} is determined from the intercept of the above plot at $\log [R_2H_2]_{org} = 0$.

When monomeric and polymeric species more than two coexist in the organic phase, however, it is difficult to determine the composition of the extracted species. Since the concentration of carboxylic acid is much larger than the metal concentration in this study, it is sufficient to take the species up to the dimer into account. Now, if the monomeric and dimeric species are represented by $MR_2 \cdot mRH$ and $(MR_2 \cdot nRH)_2$ respectively, the next equation is obtained from eq. (5):

$$D = K_{1m}[R_2H_2]_{org}^{1+m/2} / [H^+]^2 \beta_M + 2K_{2n}C_{MW}[R_2H_2]_{org}^{2(1+n/2)} / [H^+]^4 \beta_M^2, \quad (9)$$

$$D[H^+]^2 \beta_M = K_{1m}[R_2H_2]_{org}^{1+m/2} (1 + 2K_{2n}K_{1m}^{-1} [R_2H_2]_{org}^{1+n-m/2} C_{MW} [H^+]^{-2} \beta_M^{-1}). \quad (10)$$

In eq. (10), under the condition of constant $[R_2H_2]_{org}$ the plot of $(\log D - 2pH + \log \beta_M)$ vs $(\log C_{MW} + 2pH - \log \beta_M)$ gives the curve which begins with zero slope and approaches the straight line of unit slope. At the part with zero slope, a main extracted species is monomeric $MR_2 \cdot mRH$ and at the part with unit slope a dimeric species exists predominantly. Then, the number of carboxylic acid molecules solvating to the extracted species, m and n and the equilibrium constants, K_{1m} and K_{2n} can be determined using a curve-fitting method⁽³²⁾⁽³³⁾.

Suppose that a number of experimental points (a, f) are measured over a certain range of the variable a , where f is related to a by

$$f(a) = k_0 + k_1 a, \quad (11)$$

k_0 and k_1 being unknown constants to be determined.

$$x = \log a, \quad y = \log f. \quad (12)$$

Representing a and f as eq. (12), and normalizing by using the auxiliary variable v gives the next equation:

$$X = x + p_1 = \log v, \quad Y = y + p_2 = \log (1 + v). \quad (13)$$

From eqs. (11)~(13),

$$p_1 = \log k_1 - \log k_0, \quad p_2 = -\log k_0. \quad (14)$$

In this study $k_0 = K_{1m}[R_2H_2]_{org}^{1+m/2}$ and $k_1 = 2K_{2n}[R_2H_2]_{org}^{2+n}$ are valid from eq.(10). Therefore, the difference on the y axis, $-p_2$, gives $\{\log K_{1m} + (1+m/2) \log [R_2H_2]_{org}\}$ and the difference on the x axis, $-p_1$, gives $-\{\log 2K_{2n} - \log K_{1m} + (1+n-m/2) \log [R_2H_2]_{org}\}$. When these values over the various extractant concentrations are plotted against $\log [R_2H_2]_{org}$, the slopes give $(1+m/2)$ and $-(1+n-m/2)$ respectively. Equilibrium constants K_{1m} and K_{2n} may be determined from the intercept at $\log [R_2H_2]_{org} = 0$.

III. Experimental

1. Reagents

The aqueous solution was composed of metal nitrates of 0.005 and 0.01 mol/dm³. Moreover, the aqueous solution contained sodium nitrate

to keep an ionic strength constant of 0.1. The organic solution was a binary solution of Versatic Acid 911 and benzene. Versatic Acid 911 was supplied by the Shell Chemical Company and used as received. Versatic Acid 911 is known to be dimeric in non-polar solvent⁽³⁴⁾, and the structure and properties are shown elsewhere⁽⁷⁾⁽⁹⁾⁽¹⁰⁾⁽²⁴⁾. The concentration of Versatic Acid 911 is from 0.1 to 2.0 mol RH/dm³, which is large enough to ignore the decrease in free acid with formation of the extracted species.

2. Procedure

Equal volumes of the aqueous and organic solutions (15 cm³ each) were poured together into a 50 cm³ centrifuge tube. Aqueous NaOH solution was added in order to adjust pH of the aqueous solution. The tube was then installed in a shaking device (Iwaki KM shaker) and shaken for 25 min at 25°C. After attaining a state of equilibrium, the aqueous and organic phases were separated by centrifuging at 2500 rpm for 15 min. Then, the tube was immersed in a water bath maintained at 25°C. The metal ion content and pH of this aqueous solution were measured. The metal ion content was determined by titration with disodium ethylenediaminetetraacetate (EDTA) solution⁽³⁵⁾.

IV. Results and Discussion

1. Extraction equilibrium of copper

The extraction of copper from the copper nitrate solution of constant concentration 0.005 mol/dm³ was carried out with 0.5~2.0 mol/dm³ Versatic Acid 911. The results are shown in Fig. 1. The extraction of copper occurs at a lower pH with increasing extractant concentration. In Fig. 2 $\log C_{MO}$ vs $(\log C_{MW} + 2pH)$ is plotted under the constant extractant concentration. As the formation of metal complexes in the aqueous phase is regarded as being negligibly small under the experimental conditions, β_M is considered to be unity. As shown in Fig. 2, each plot falls on a straight line and the slope is nearly equal to 2 regardless of the extractant concentration. Therefore,

Fig. 1 Extraction of copper with Versatic Acid 911. $C_M=0.005 \text{ mol/dm}^3$, Ionic strength=0.1

Fig. 2 Determination of degree of polymerization in the extraction of copper with Versatic Acid 911. $C_M=0.005 \text{ mol/dm}^3$, Ionic strength=0.1

the extracted species of copper appears to be dimeric. $(\log C_{M0} - 2 \log C_{MW} - 4 \text{ pH})$ vs $\log [R_2H_2]_{\text{org}}$ is plotted in Fig. 3. The plots give the straight line of slope 3, from which the value of m is obtained to be unity. Then, the composition of the extracted species should be given by $(CuR_2 \cdot RH)_2$. The equilibrium constant of copper extraction is determined to be $K_{2,1} = 2.00 \times 10^{-13}$ from Fig. 3.

From the above consideration the extraction equilibrium of copper with Versatic Acid 911 is represented by

Fig. 3 Determination of number of Versatic Acid 911 involved in the extracted species of copper. $[RH]=0.5 \sim 2.0 \text{ mol/dm}^3$, $C_M=0.005 \text{ mol/dm}^3$, Ionic strength=0.1

2. Extraction equilibrium of nickel

The extraction of nickel from the aqueous solution of constant concentration 0.005 mol/dm^3 was carried out using $0.2 \sim 1.0 \text{ mol/dm}^3$ Versatic Acid 911 and the results are shown in Fig. 4. The extraction of nickel increases and the extraction curve shifts to the lower pH side with increase in the extractant concentra-

Fig. 4 Extraction of nickel with Versatic Acid 911. $C_M=0.005 \text{ mol/dm}^3$, Ionic strength=0.1

Fig. 5 Determination of degree of polymerization in the extraction of nickel with Versatic Acid 911. $C_M = 0.005 \sim 0.01$ mol/dm³, Ionic strength = 0.1. Solid lines are theoretical values calculated by using the constants determined in the present study.

tion. The degree of the association of the extracted species is determined from the relationship of $\log C_{MO}$ vs $(\log C_{MW} + 2 \text{ pH})$ under the constant extractant concentration. These plots, which are shown in Fig. 5, indicate that the monomeric and dimeric species are responsible for the extraction of nickel. When the metal concentration in the organic phase is below 2.5×10^{-4} mol/dm³, the monomer can exist predominantly and above this concentration the dimer will become the main species. As mentioned above, when the species of more than two different compositions are formed in the organic phase, the determination of the extracted species requires the application of the curve-fitting method. Figure 6 is obtained by plotting $(\log D - 2 \text{ pH})$ against $(\log C_{MW} + 2 \text{ pH})$ under the constant extractant concentration. The curve fitting method using normalized curves $Y = \log(1 + v)$, $X = \log v$, is applied to the plots in Fig. 6. The dotted lines in Fig. 6 are the asymptotes of the normalized curves. The values of the co-ordinate of this intersection are plotted against $\log [R_2H_2]_{org}$ in Fig. 7. Thus two different straight lines are obtained

Fig. 6 Application of curve fitting method for determination of extracted species of nickel. Solid lines are theoretical values.

Fig. 7 Determination of number of Versatic Acid 911 involved in the extracted species of nickel and the equilibrium constant of nickel extraction.

where $m=4$ and $n=2$. Then, the extracted species of nickel are given by $NiR_2 \cdot 4RH$ and $(NiR_2 \cdot 2RH)_2$. Equilibrium constants K_{14} , K_{22} are determined from the intercepts at $\log [R_2H_2]_{org} = 0$ in Fig. 7.

From the above consideration, the extraction equilibrium of nickel is expressed as

The equilibrium between monomer and dimer is represented by

As the composition of the extracted species and the equilibrium constants have been determined, the theoretical distribution coefficient can be calculated from eq. (9). Equation (9) may be written as

$$D = K_{14}([\text{R}_2\text{H}_2]_{\text{org}}^3/[\text{H}^+]^2) \\ \times (1 + 2K_{22}[\text{R}_2\text{H}_2]_{\text{org}} C_{\text{MW}}/K_{14}[\text{H}^+]^2). \quad (19)$$

The theoretical values calculated from eq. (19) are represented by solid lines in Figs. 5 and 6. The theoretical values are in good agreement with the experimental values. This suggests that the curve-fitting method would be appropriate for a precise determination of the equilibrium constants and extracted species.

3. Extraction equilibrium of cobalt

The extraction of cobalt from 0.005 mol/dm³ cobalt nitrate solution was carried out with 0.1~1.0 mol/dm³ Versatic Acid 911. The results are shown in Fig. 8 in terms of extraction % vs equilibrium pH. Cobalt is quantitatively extracted at pHs above 5.5 and the extractability

Fig. 8 Extraction of cobalt with Versatic Acid 911. $C_M = 0.005 \text{ mol/dm}^3$, Ionic strength = 0.1

increases with the extractant concentration. The existence of monomer and dimer was also recognized in the extraction of cobalt. Therefore, these extracted species should be determined using a curve-fitting method. Using the same procedure as the determination of extraction equilibrium of nickel, the extraction equilibrium of cobalt is expressed as follows:

4. Extraction equilibrium of manganese

The result of the extraction of manganese from 0.005 mol/dm³ aqueous solution using 0.5~1.5 mol/dm³ Versatic Acid 911 are shown in Fig. 9 in terms of extraction % vs equilibrium pH. The use of a curve-fitting method should be again taken, because of the fact that the monomeric and dimeric species are responsible for the extraction of manganese. The compositions of the extracted species and the equilibrium constants are determined as follows:

In the studies to determine the extracted species, the concentration of the extractant much larger than that of metal ions is generally used in order to neglect the decrease of the free extractant. In this study the extraction of manganese was carried out under the condition where the metal ion concentration was so high that the decrease of the free extractant could not be ignored. The concentrations of

Fig. 9 Extraction of manganese with Versatic Acid 911. $C_M=0.005 \text{ mol/dm}^3$, Ionic strength=0.1

Versatic Acid 911 and the metal ion were 0.1 and 0.024 mol/dm^3 , respectively, and the other conditions were the same as the previous conditions. Under these conditions, the decrease of the free extractant cannot be neglected. Then, assuming that the extraction proceeds according to eq. (24), the next equation is obtained from eq. (24):

$$\log D = \log C_{MW} + 4 \text{ pH} + 4 \log [R_2H_2]_{\text{org}} + \log 2K_{22}, \quad (26)$$

where $[R_2H_2]_{\text{org}}$ should be calculated according to the next equation.

$$[R_2H_2]_{\text{org}} = 0.1 \times 0.5 - 2C_{MO}. \quad (27)$$

Equation (26) shows that the plot of $\log D$ vs $(\log C_{MW} + 4 \text{ pH} + 4 \log [R_2H_2]_{\text{org}})$ gives a straight line with unit slope if the extracted species is a dimer, that is, the extraction follows eq. (24). The results are shown in Fig. 10. When the metal concentration in the organic phase is below $8.2 \times 10^{-3} \text{ mol/dm}^3$, the relationship of the straight line with unit slope holds, but above this value the plots deviate from the straight line. It is considered, therefore, that more polymeric species is formed with increasing metal concentration in the organic phase.

V. Conclusions

The distribution of Cu, Ni, Co and Mn between an aqueous solution of constant ionic

Fig. 10 Relationship between $\log D$ and $(\log C_{MW} + 4 \log [R_2H_2]_{\text{org}} + 4 \text{ pH})$ in the extraction of manganese with Versatic Acid 911. $[RH]=0.1 \text{ mol/dm}^3$, $C_M=0.024 \text{ mol/dm}^3$, Ionic strength=1.0

strength and Versatic Acid 911 diluted in benzene was studied. It was demonstrated that only one extracted species of copper has a dimeric structure of the composition $(CuR_2 \cdot RH)_2$, while both monomer and dimer were found in the extraction of nickel, cobalt and manganese. The compositions of the extracted species were $NiR_2 \cdot 4RH$ and $(NiR_2 \cdot 2RH)_2$, $CoR_2 \cdot 4RH$ and $(CoR_2 \cdot 2RH)_2$, and $MnR_2 \cdot 4RH$ and $(MnR_2 \cdot 2RH)_2$, respectively. The extraction equilibrium constant of each metal was also determined using a curve-fitting method. The theoretical distribution coefficients calculated from the equilibrium constants in this study were compared with the experimental values. Both values coincide quite well, which proves that the curve-fitting method used is a method for precise determination of the equilibrium constants and extracted species.

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