Solvent Extraction Studies of Holmium with Acidic Extractants

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Abstract

Liquid–liquid extraction studies of holmium with 2-ethylhexyl phosphoric acid mono-2-ethylhexyl ester, naphthenic, and Versatic 10 acids have been carried out. The nature of the extracted species and the extraction equilibrium constants of these systems have been determined from aqueous nitrate solution. The extraction mechanism and complexation models have been proposed.

Key Words: Solvent extraction; Holmium; Versatic 10, Naphthenic acid

INTRODUCTION

Because of the importance of lanthanide metals in their fluorescent, magnetic, optical, catalytic, phosphor, and laser properties, the achievement of high purity of these elements has stimulated great interest. Major advances have been made toward the preparation of high purity rare earth oxides. The extraction behavior of lanthanides has drawn attention since clean and effective separation of these elements from each other is a difficult task. Most high purity lanthanide salts have been achieved by ion-exchange and solvent extraction methods. However, the separation of these elements by the ion-exchange technique is tedious and time consuming. Recently, solvent extraction has emerged as a powerful tool for the industrial-scale separation of lanthanides (1–3).

An interesting aspect of solvent extraction of lanthanide elements is to achieve a better separation factor for consecutive elements. A number of new extractants have been synthesized (4) for this purpose, but very few are useful for the industrial-scale separation of lanthanides. Among the

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extractants, carboxylic acids have proved efficient. However, detailed studies of the extraction mechanism and the complexation of lanthanide elements with carboxylic acids are lacking. Very few investigations have been made on these aspects (5). This paper describes solvent extraction studies of holmium with carboxylic acids in detail.

EXPERIMENTAL

Reagents

The commercial carboxylic acid extractants, 2-ethylhexyl phosphoric acid mono-2-ethylhexyl ester (EHPNA) (Daihachi Chemical Industry Co. Ltd., Japan), naphthenic, and Versatic 10 acids (Shell Chemicals), were used. The appropriate concentrations of carboxylic acid extractants were prepared in benzene. The carboxylic acid concentration in the organic phase was determined volumetrically with potassium hydroxide in ethyl alcohol by using the indicator phenolphthalein. The organic solutions were prepared by diluting a desired amount of extractant with benzene. Rare earch metal ion solutions were prepared by dissolving an appropriate quantity of rare earth trioxide in nitric acid. After evaporating any excess acid, the solution was diluted to 250 mL with distilled water. The solutions were standardized complexometrically (6) at pH 5.0 with xylenol orange as the indicator. All other chemicals used were analytical grade.

Apparatus

A digital pH meter, type 120 (ELICO, India), with glass and calomel electrodes.

Procedure

The experiments were carried out by equilibrating equal volumes of aqueous and organic phases. The aqueous solution contained the desired concentration of metal ion and 1 M sodium nitrate. The two phases were shaken for 10 min. After separation of the two phases, the holmium concentration in the aqueous phase was determined volumetrically with EDTA. The concentration of holmium in the organic phase was determined with EDTA after stripping with an appropriate concentration of nitric acid.

pH Determination

The pH of the aqueous phase was roughly adjusted to the desired value by addition of dilute solutions of nitric acid and sodium hydroxide. pH was measured precisely in the aqueous solution with a glass electrode-pH meter after equilibration of the two phases.

RESULTS AND DISCUSSION

Extraction Equilibrium

It is assumed that the trivalent metal ions (M^{3+}) are extracted as a n-meric complex with carboxylic acid [composition $(MA_3 \cdot mHA)_{n,o}$] into the organic phase. The extraction equilibrium can be written as

$$nM^{3+} + n\left(\frac{3+m}{2}\right)(HA)_{2,o} \rightleftharpoons (MA_3 \cdot mHA)_{n,o} + 3nH^+ \qquad (1)$$
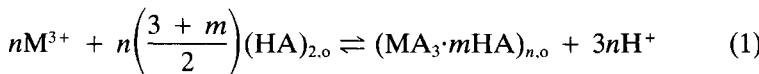
The extraction equilibrium constant, K_{ex}, can be represented by

$$K_{ex} = [(MA_3 \cdot mHA)_n]_o [H^+]^{3n} [M^{3+}]^{-n} [(HA)_2]_o^{-n[(3+m)/2]} \qquad (2)$$

The total metal ion concentration, C_{M_0}, extracted into the organic phase, can be expressed as

$$C_{M_0} = n[(MA_3 \cdot mHA)_n]_o$$

$$= nK_{ex}[M^{3+}]^n [(HA)_2]_o^{n[(3+m)/2]} [H^+]^{-3n} \qquad (3)$$

Taking the logarithm of both sides of Eq. (3):

$$\log C_{M_0} = \log (nK_{ex}[(HA)_2]_o^{n[(3+m)/2]}) + n \log ([M^{3+}]/[H^+]^3) \qquad (4)$$

Extraction of Holmium with Carboxylic Acids

The effective extraction of holmium with EHPNA, naphthenic, and Versatic 10 acids occurs for a pH of the aqueous phase ranging from 2 to 3.5, 3.5 to 5.5, and 4.5 to 6.0, respectively. At a pH higher than 3.5, 5.5, and 6.0 for EHPNA, naphthenic, and Versatic 10 acids, respectively, the extraction exceeds 98%. It was observed that there is no clear-cut separation of phases at higher pH values. The results of holmium extraction with 0.005, 0.3, and 0.3 M for EHPNA, naphthenic, and Versatic 10 acids are given in Fig. 1. The plots of log D values of holmium as a function of aqueous pH for EHPNA, naphthenic, and Versatic 10 acids are linear with slopes of almost 3.

The dependence of holmium extraction of the initial metal ion concentration in the aqueous phase and at constant concentrations of EHPNA, naphthenic, and Versatic 10 acids in the organic phase is given in Fig. 2. It follows that the extraction of holmium with EHPNA, naphthenic, and Versatic 10 acids does not depend on the initial metal ion concentration
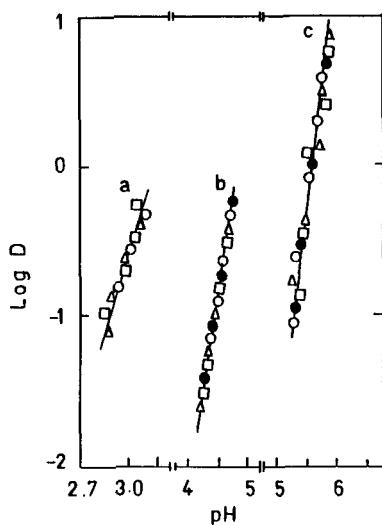
FIG. 1. (a) Log D as a function of pH, Ho(III) = ($\square$) 3 × 10^{-3} M, ($\triangle$) 2 × 10^{-3} M, and ($\bigcirc$) 10^{-3} M; EHPNA = 5 × 10^{-3} M. (b) Log D as a function of pH, Ho(III) = ($\bullet$) 3 × 10^{-3} M, ($\bigcirc$) 2 × 10^{-3} M, ($\triangle$) 10^{-3} M and ($\square$) 5 × 10^{-4} M; naphthenic acid = 0.3 M. (c) Log D as a function of pH, Ho(III) = ($\bullet$) 4 × 10^{-3} M, ($\bigcirc$) 2 × 10^{-3} M, ($\triangle$) 10^{-3} M and ($\square$) 5 × 10^{-4} M; Versatic 10 = 0.3 M.
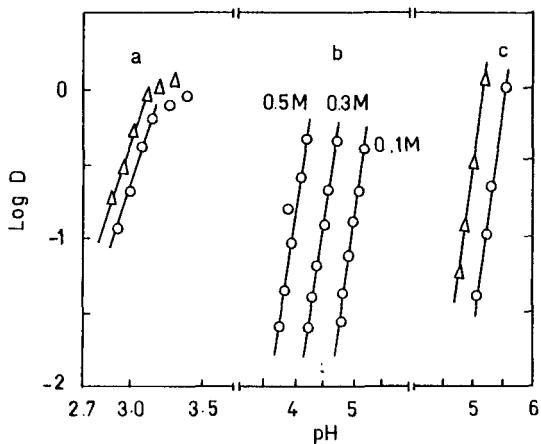
FIG. 2. (a) Plots of log D vs pH, Ho(III) = 2 × 10^{-3} M; EHPNA = ($\triangle$) 7.5 × 10^{-3} M and ($\bigcirc$) 5 × 10^{-3} M. (b) Plots of log D vs pH, Ho(III) = 2 × 10^{-3} M; naphthenic acid = 0.5 M, 0.3 M, and 0.1 M. (c) Plots of log D vs pH, Ho(III) = 2 × 10^{-3} M; Versatic 10 = ($\triangle$) 0.5 M and ($\bigcirc$) 0.3 M.
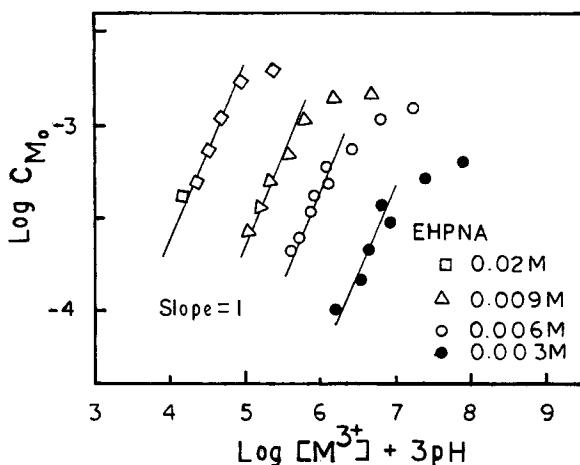
FIG. 3. Plots of log C_{M_0} as a function of log [M^{3+}] + 3pH for holmium.

in the aqueous phase. This fact indicates that the mononuclear holmium complex is extracted in the organic phase. This was confirmed from the plots of log C_{M_0} vs log [M^{3+}] + 3pH presented in Figs. 3–5.

Figures 3–5 show that plots of log C_{M_0} as a function of log [M^{3+}] + 3pH based on Eq. (4) for holmium extraction with acidic extractants. All of the plotted points at constant concentrations of EHPNA, naphthenic, and Versatic 10 acids in Figs. 3–5 lie on straight lines, the slopes of which give the degree of polymerization of holmium complexes of EHPNA, naphthenic, and Versatic 10 acids in the organic phase. As is evident from these
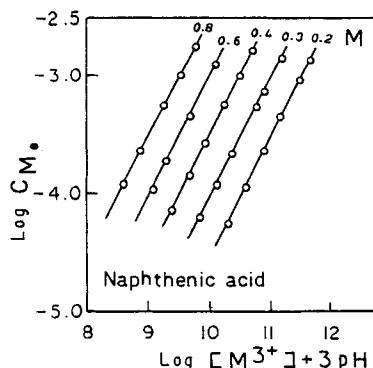
FIG. 4. Log C_{M_0} vs log [M^{3+}] + 3pH for holmium.
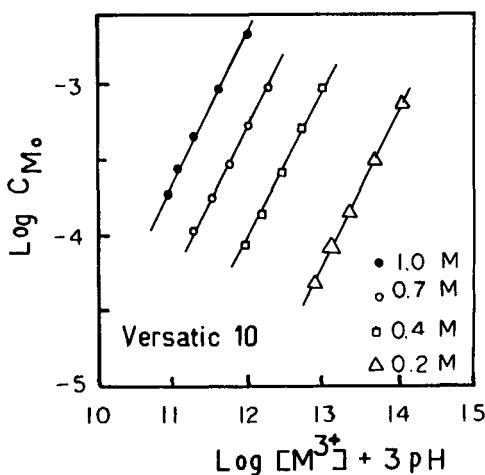
FIG. 5. Log C_{M_0} vs log $[M^{3+}]$ + 3pH for holmium.

figures, straight lines of slope 1 were observed for all systems. This indicates that $n = 1$, that is, holmium is extracted as a monomeric species $HoA_3 \cdot mHA$ in the extraction systems with EHPNA, naphthenic, and Versatic 10 acids. When $n = 1$, Eq. (4) can be written as

$$\log [M^{3+}] + 3pH = -\frac{(3 + m)}{2} \log [(HA)_2]_0 + \log (C_{M_0}/K_{ex}) \quad (5)$$

For EHPNA, naphthenic, and Versatic 10 acid systems, the values of the intercepts of the straight lines in Figs. 3–5 at a constant value of C_{M_0} were plotted against $-\log [(HA)_2]_0$ based on Eq. (5), as shown in Fig. 6. The slope of the good linear relationship 4.0 ($m = 5$) was observed for EHPNA, naphthenic, and Versatic 10 acid systems as expected from Eq. (5).

From the above experimental results, it was confirmed that the value of m is 5. Therefore, the extracted complex was found to be $MA_3 \cdot 5HA$ for EHPNA, naphthenic, and Versatic 10 acid systems. The stoichiometry for the extraction equilibrium reaction of holmium is as follows for these systems:

$$Ho^{3+} + 4(HA)_{2,o} \rightleftharpoons HoA_3 \cdot 5HA_o + 3H^+ \quad (6)$$

The extraction equilibrium constant values observed were log $K_{ex} = 2.73$, -11.0, and -14.04 for the EHPNA, naphthenic, and Versatic 10 acid systems, respectively. The log K_{ex} values of holmium with these acids were
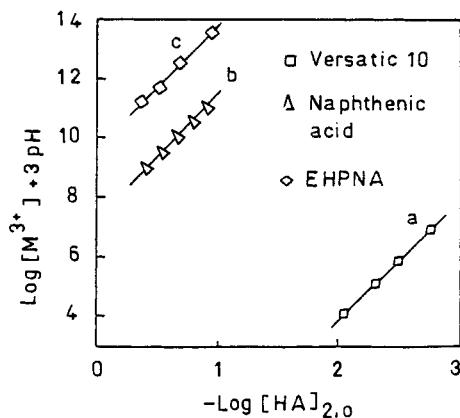
FIG. 6. (a) Plots of log $[M^{3+}]$ + 3pH vs $-\log [HA]_{2,0}$ for the holmium–EHPNA system. (b) Plots of log $[M^{3+}]$ + 3pH vs $-\log [HA]_{2,0}$ for the holmium–naphthenic acid system. (c) Plots of log $[M^{3+}]$ + 3pH vs $-\log [HA]_{2,0}$ for the holmium–Versatic 10 acid system.

observed in the following decreasing order: EHPNA > naphthenic acid > Versatic 10 acid.

The log K_{ex} values of lanthanide elements for these systems increase from lanthanum to lutetium (7). However, EHPNA has proved to be an efficient extractant because of its higher separation factors for consecutive elements. Although heavy rare earths were selectively extracted with these extractants, the extraction sequence of yttrium with respect to rare earths varies depending on the extractant, i.e., EHPNA, Dy < Y < Lu; naphthenic acid, Pr < Y < Gd[(2)]; Versatic acid, Dy < Y < Lu (Fig. 7).
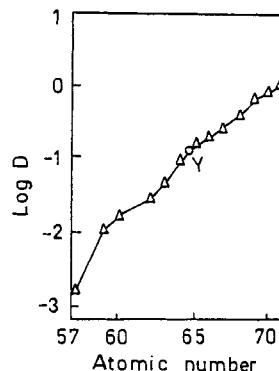
FIG. 7. Plots of log D vs atomic number of rare earths. Versatic 10 = 0.4 M, pH 5.25 ± 0.05, M(III) = 2 × 10^{-3} M.

The Extraction Mechanism and Complexation Model

The extraction of lanthanide ions into an organic phase containing carboxylic acid as an extractant is given in its simplest form by

$$M^{3+} \cdot aH_2O + \frac{3}{2}(HA)_2 \cdot iH_2O_o \rightleftharpoons$$

$$MA_3 \cdot bH_2O + 3H^+ + \left(a + \frac{3}{2}i - b\right)H_2O \quad (7)$$
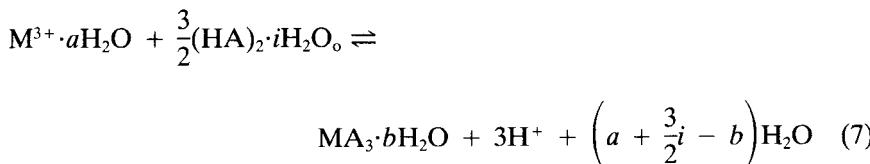
where a, i, and b indicate the hydrated water molecules attached to the metal ion, carboxylic acid, and metal ion complex, respectively. This shows that the hydrated water molecules may play an important role during the complexation process. However, as a result of dimer formation of the extractant in the organic phase, the extraction mechanism, which depends on the extractant and metal ion concentrations, is rather more complex. Thus, in an active pH range and at low metal ion loading, the extraction is considered to occur as follows:

$$M^{3+} \cdot aH_2O + \frac{(3 + m)}{2}(HA)_{2,o} \cdot iH_2O \rightleftharpoons$$

$$MA_3 \cdot mHA \cdot SH_2O + 3H^+ + \left(a + \frac{(3 + m)}{2}i - S\right)H_2O \quad (8)$$
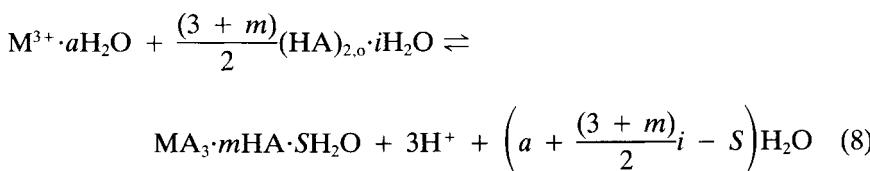
where S indicates the water molecules hydrated to the metal ion complex. Although the monomeric complexes of rare earth elements have been extracted into the organic phase with these carboxylic acids, the degree of solvation of lanthanide ions with carboxylic acid does depend on pH and the concentrations of acidic extractant and metal ion. The proposed models of the extraction mechanism and complexation of lanthanide ions with these carboxylic acids are based on taking the metal ion and ligand concentrations into account, and the pK_a values of the carboxylic acids (Figs. 8 and 9).

The coordinated water molecules of lanthanide ions and complexation with carboxylic acids are major parameters in the behavior of the extraction of lanthanides. It has been observed that the m value varies from 0 to 5 for EHPNA, naphthenic, and Versatic 10 acids depending on the experimental conditions (8). However, the m value observed for D$_2$EHPA was 0 to 3. Although the coordination number of lanthanide elements lies between six and nine, the saturation of coordination sites of lanthanide elements with a strong acidic extractant with fewer molecules in comparison

Organic $(HA)_2 \cdot i\,H_2O \rightleftharpoons HA \cdot \frac{i}{2}H_2O + MA_3 \cdot b\,H_2O \rightleftharpoons MA_3 \cdot m\,HA \cdot s\,H_2O$

phase $(a + (\frac{3+m}{2})i - s)H_2O$

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Aqueous $(HA)_2 \cdot i\,H_2O \rightleftharpoons HA \cdot \frac{i}{2}H_2O$

$(H^+ + A^-) \cdot \frac{i}{2}H_2O + M^{3+} \cdot a\,H_2O \rightleftharpoons MA_3 \cdot b\,H_2O + 3H^+$

phase $(a + \frac{3}{2}i - b)H_2O$
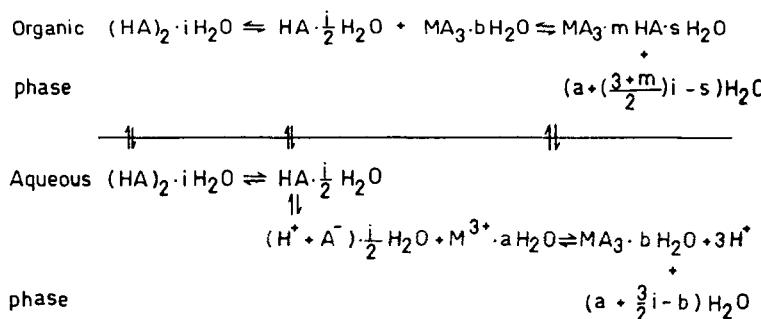
FIG. 8. The extraction mechanism of lanthanide elements with chelating extractant during the adduct complexation.

with that of weak acidic extractants depends on the basic strength and number of coordinating oxygen atoms available for coordination.

The pK_a values measured by means of pH titration for the D_2EHPA, EHPNA, naphthenic, and Versatic 10 acids are 1.72, 3.2, 5.3, and 5.9, respectively. The complexation of a metal ion with a chelating extractant depends on the pH, the extractant concentration, and the salt concentration used in the acidic range in the system. The acid strength of these acids can be arranged in the following decreasing order based on dissociation constants: D_2EHPA > EHPNA > naphthenic acid > Versatic 10.

The hard base characteristic of the anions of these acids follows the above trend. Adduct complex formation depends on the hard base characteristic of the solvating agent and the hard acid characteristic and coordination number of the metal ion.

During the adduct complex formation process for the same experimental conditions, the number of molecules of chelating extractant required is

D₂EHPA   PC-88A(EHPNA)

Versatic 10 or Naphthenic acid
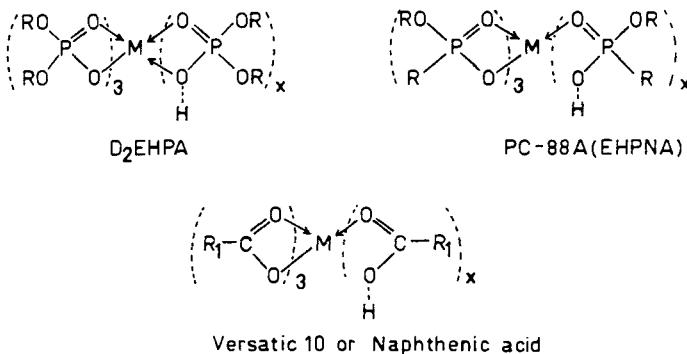
FIG. 9. The complexation between lanthanide ions and carboxylic acids.

dependent on the hard base characteristics of the oxygen atoms in the carboxylic acid group and the competition for the oxygen atoms of water molecules from the inner coordination sphere of the metal ion. It can be inferred that the two oxygen atoms in D_2EHPA from the carboxylic acid group are more basic in nature because they replace the coordination bond formed by the water oxygen atom (9). Therefore, with the smaller number of D_2EHPA molecules, it is possible to replace water molecules from the inner coordination sphere of the metal ion during adduct complex formation. In the case of EHPNA, naphthenic, and Versatic 10 acids, the oxygen atoms are less basic in nature in comparison with D_2EHPA. It may not be strong enough to compete with the oxygen from water in the coordination sphere of the metal ion during the adduct complex formation process, depending on the electronegative charge on the oxygen atom. The interactions in the coordination sphere will be stronger for the smaller ion and the higher the dipole moment of the donor extractant group. Therefore, additional molecules of chelating extractant are required to saturate the coordination sites (Fig. 9). Thus, the coordination sites of the lanthanide ions may be saturated by the acidic extractant due to the variation of the number of molecules, m, as per their acidic strength in the species, $MA_3 \cdot mHA$, for strong and weak acids.

The chelating extractants coordinating through oxygen are effective extractants for the hard acid metal ion. The lanthanide elements are in the hard acid class. Their hard acid characteristics increase from lanthanum to lutetium, and yttrium is in the heavy rare earths category. The anions of D_2EHPA, EHPNA, naphthenic, and Versatic 10 acids act as bases. The hard base characteristics of D_2EHPA, EHPNA, naphthenic, and Versatic 10 anions can be arranged in decreasing order according to their acid strength: D_2EHPA > EHPNA > naphthenic acid > Versatic 10.

The hard acids (lanthanides) and hard bases (the above anions) complexation increases from lanthanum to lutetium for these acids in the order given above.

The extraction equilibrium constants for metal chelate can be defined by the "hard and soft acids and bases" (HSAB) rule. To express the strength and hard–soft factors of chelating ligand and metal ion in terms of scale is very important. Since the concept of HSAB was introduced by Pearson (10), the selection of chelating ligands for solvent extraction studies of metals has become an easy task. However, as far as solvent extraction studies are concerned, little information based on the HSAB rule has been reported. The relation among the equilibrium constant, strength factor, and soft factor is given by Eq. (9) for metal ion and ligand:

$$\log K = S_M S_A + \sigma_M \sigma_A \tag{9}$$

where K is an equilibrium constant for the formation of a complex MA, and the subscripts M and A denote Lewis acid and base, respectively. However, S and σ represent the strength and soft factors of Lewis acid and base. By using the above equation, the extraction constant (K_{ex}) for a metal chelate can be explained quantitatively, and the softness of a chelating agent can be evaluated.

The extraction of equilibrium of metal ion (M^{3+}) with a chelating agent (HA) can be expressed as follows:

$$M^{3+} + (3 + m)(HA)_o \rightleftharpoons MA_3 \cdot mHA + 3H^+ \tag{10}$$

The extraction equilibrium constant for a particular extraction system is defined as the equilibrium constant for Reaction (10). The distribution coefficients $(K_{dm}$ for a metal ion complex and K_{dr} for a chelating ligand) can be expressed by

$$\log K_{dm} = (3 + m) \log K_{dr} \tag{11}$$

Equation (12) can be obtained

$$\log \beta = \log K_{ex} + (3 + m)pK_a \tag{12}$$

where β is the stability constant for $MA_3 \cdot mHA$ in the aqueous phase and pK_a is the acid dissociation exponent of HA. The value of the right-hand side of Eq. (12) is applied to Eq. (9) and $\beta = K$ is assumed. Therefore, Eq. (12) becomes

$$\log K_{ex} + (3 + m)pK_a = S_M S_A + \sigma_M \sigma_A \tag{13}$$

Here, the S_A scale is defined on the basis of the electrostatic affinity of a metal ion toward a chelating anion or molecule. The formation of an extractable chelate $MA_3 \cdot mHA$ proceeds according to

$$M(H_2O)_a^{3+} + (3 + m)HA \cdot iH_2O \rightleftharpoons$$

$$MA_3 \cdot mHA \cdot SH_2O + (a + (3 + m)i - S)H_2O \tag{14}$$
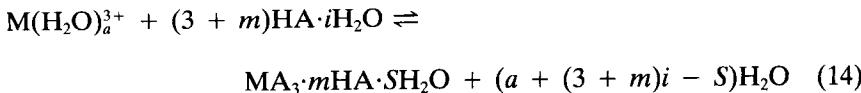
In the case of the carboxylic acid extraction system, the forward reaction accompanies dehydration of an aqueous metal ion, and the resulting M^{3+} forms a metal chelation and adduct complex with HA. The dehydration process is the inverse process of hydration of a metal ion. In this process, the hydration entropy, $\Delta S°$, plays an important role when the electrostatic bonding ability of aH_2O molecules toward a metal ion equals that of $(3 + m)HA$. The driving force of the forward reaction of Eq. (14) is attributable to an entropy change caused by an increase in the number of molecules

and a decrease in the charge of the reactants. The S_M and σ_M scales are defined by the following equations (11):

$$S_M = -\frac{2\Delta S°}{2.30R} \qquad (15)$$

$$\sigma_M = \frac{\Delta H°}{2.30RT} \qquad (16)$$

The strength parameter (S_A of the ligand) is closely related to pK_a, which may mainly be affected by the electrostatic force. Equation (13) indicates that S_A and σ_A are effective parameters for expressing the strength and softness of a chelating ligand. The results obtained by this calculation method will be useful for selecting a ligand for the mutual separation of metal ions. Equation (17) can be obtained from Eq. (13):

$$\log D = S_M S_A + \sigma_M \sigma_A + (3 + m)(\log [HA]_o - pK_a) + 3pH \qquad (17)$$

Here, S_M and σ_M are constant for holmium for these carboxylic acid systems. $[HA]_o$ and pH can be maintained constant under the same experimental conditions, and thus D values depend on the S_A, σ_A, and pK_a values of carboxylic acids. However, D values of holmium with different chelating extractants of the same pK_a at the same experimental conditions depend on the parameters S_A and σ_A.

Acknowledgment

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