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Biçak Niyazi[a]; Sungur Şana[b]; Tan Nükhet[b]; Gaz Mustafa[a]
[a] Department of Chemistry, Istanbul Technical University, Istanbul, Turkey [b] Faculty of Engineering, Kadir Has University, Istanbul, Turkey

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SEPARATION SCIENCE AND TECHNOLOGY, 37(10), 2353–2368 (2002)

CHELATE EXTRACTION OF TRANSITION METAL IONS BY ETHYLENE DIAMINE DIACETIC ACID WITH *N*-SUBSTITUTED OCTADECYL GROUPS

Biçak Niyazi,[1,*] Sungur Şana,[2] Tan Nükhet,[2] and Gazi Mustafa[1]

[1]Department of Chemistry, Istanbul Technical University, 80626 Maslak, Istanbul, Turkey
[2]Faculty of Engineering, Kadir Has University, Selimpasa, Istanbul, Turkey

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ABSTRACT

An organic-soluble chelating agent, *N*,*N*′-di-*n*-octadecyl ethylenediamine-*N*,*N*′-diacetic acid (DOED) has been synthesized in two steps by (i) condensation of dibromoethane with 1-amino octadecane (octadecylamine) and (ii) subsequent reaction with sodium chloro acetate in alcohol–water mixture. The chelating agent in 2-ethylhexanol-cyclohexanol (1:1) solutions shows extremely high chelating ability for Ni(II), Co(II), Cu(II), Fe(III), Cr(III), and Cd(II) ions in neutral aqueous solutions. Extractions take place by the formation of (1:1) ligand-to-metal complexes, and extraction coefficients are in the range 0.74–0.99. The ligand can be regenerated almost quantitatively by washing its complexes with 1 *M* HCl and 0.2 *M* NaOH solutions successively.

*Corresponding author. E-mail: bicak@itu.edu.tr

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In each extraction step, the organic solution exhibits a clear-cut phase separation and does not need salting out. The chelating agent can be regenerated and recycled more than 24 times, without losing its extracting ability, due to nonhydrolyzability of linkages in its structure. Experiments indicate that in high metal concentrations (more than 1 *M*), the solvent mixture itself is able to extract appreciable amounts of metal ions (33–53%). The solubility in organic solvents, induced by long aliphatic chains, seems to be general and the method presented offers possibility of large scale chelate extraction of metal ions of relatively low concentrations.

Key Words: Chelate extraction of metal ions; Ethylenediamine diacetic acids; Metal extraction

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INTRODUCTION

The chelate extraction process, in which metal ions are extracted as their complexes, is one of the most important method of separation. In chelate extraction, the organic solvent containing the chelating agent is treated with metal ion solutions at neutral pHs. There appears excellent books dealing with basic principles and developments in extraction (1). Numerous reports have been published for chelate extraction of metal ions. A well known example is the extraction of dithizone Pb(II) and Zn(II) complexes with chloroform or carbontetrachloride (2). Extraction of the uncharged red bis-dimethyl glyoxime complex of Ni(II) with chloroform, provides a means of separation from Cu(II), Fe(III), and Co(II) (3). Most of these studies have focused on the analytical level of applications.

In addition, there are many interesting reports aimed at large scale applications in literature. Extraction using tributyl phosphate for uranyl ions (4) and extractions based on fatty acid salts of some metal ions (5) can be considered as industrial processes. Recently, some calix[4]arenes, with crown-6 moieties, have been demonstrated to be useful in the separation of heavy metal ions from smaller cations (6). In most of the successful chelate extractions, the general idea is to enhance the solubility of ligand in organic solvents by the incorporation of long alkyl chains (7,8). For instance, some organic soluble dialkyl sulfoxides have been used for the extraction of metal ions including uranium and thorium (9).

Increasing demands, especially for environmental cleaning-up, necessitates the designing of new efficient chelating agents.

Besides the economical factors, the basic requirements of an organic ligand, for an industrial level of chelate extraction, can be summarized as follows:

i) Strong chelating ability which provides operating in wide pH-ranges.

ii) Chemical stability and regenerability which allows recycling of the chelating agent.
iii) High solubility in organic solvents which are immiscible with water.

The first requirement is already being established by many low molecular weight organic ligands. The second and third requirements seem to be essential for large scale chelate extractions.

The chemical stability means nonhydrolyzability in drastic acid–base treatments that, it is important in the regeneration steps in the processes. The ligands with hydrolyzable groups or linkages are not suitable for industrial levels of treatments even if they have high chelating abilities.

Solubility in organic solvents is of great importance in chelate extraction. It is expected that if metal ions are effectively surrounded by hydrophobic ligands, which are able to bring charge neutralization, distribution will strongly favor in dissolving organic solvents without much regard for the nature of the solvent itself. If the chelation proceeds via true coordination, the ligands must carry anionic groups in order to neutralize the positive charge of the metal ion. This type of neutral complex refers to as inner complex or inner sphere complex. Neutral complex formation enhances the hydrophobicity and solubility in organic solvents. In the light of the above considerations, this study targeted to synthesize an excellent chelating agent for efficient extraction of metal ions. For this purpose, *N*,*N*′-di-*n*-octadecyl ethylenediamine-*N*,*N*′-diacetic acid (DOED) was synthesized by the condensation of chloroacetic acid with *N*,*N*′ dioctadecyl ethylenediamine. This compound has been designed so as to have the following advantages: (i) high chelating ability as in the case of many iminoacetic ligands, (ii) solubility in organic solvents in free and complexed forms, and (iii) chemical stability against acid and base hydrolysis even in harsh conditions. In other words, high chelating ability and remarkable organic solubility properties have been incorporated into the structure of the ligand. As far as we know, there appear no reports in literature, dealing with the use of organic soluble imino acetic acid ligands as chelating agent for metal ion extractions. The structure of the ligand has been confirmed by elementary microanalysis and ^{1}H-NMR. Its chelating ability in liquid–liquid extraction of some transition metal ions [Cu(II), Ni(II), Co(II), Fe(III), Cr(III), Cd(II)] has been investigated at various pH and concentrations.

EXPERIMENTAL

Materials

2-Ethylhexanol (E-Merck, Darmstadt, Germany) was distilled before use. All the other chemicals (octadecyl amine (Fluka, Buchs, Switzerland),

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chloracetic acid (E-Merck), dibromoethane (Aldrich, Milwaukee, WI, USA), and cyclohexanol (Fluka) were analytical grade. They were used without any further purification. Nuclear magnetic resonance (NMR) spectra were taken by Brucker 250 MHz.

Synthesis of *N*,*N*′ Dioctadecylethylenediamine

In a 250 mL flask, equipped with a reflux condenser, octadecylamine (40.4 g, 0.15 m) and dibromoethane (6.5 mL, 0.075 m) 60 mL ethanol and 30 g anhydrous K_2CO_3 (as HBr trapping agent) were placed and heated to 80°C for 16 hr with stirring. Upon cooling to room temperature, a voluminous precipitate was observed. At that time, the solution of 4.2 g (75.0 mmol) KOH in 20 mL ethanol was added to the mixture. The reaction was continued for another 72 hr. Another 4.2 g (75.0 mmol) KOH solution was added to the mixture after 24 and 48 hr, respectively. At the end of the reaction, the hot mixture was filtered and washed with hot alcohol (20 mL). The filtrate was dried with anhydrous Na_2SO_4. One-third of the solution was evaporated and maintained at room temperature, while crystalline precipitate (*N*,*N*′ dioctadecyl ethylenediamine) was filtered and dried under vacuo at room temperature for 48 hr. The crude product was recrystallized from ethanol. The yield was 32.8 g. (77.5%) Mp: 90°C.

Elementary analysis: (Calc. for $C_{38}H_{80}N_2$) (found) C: 76.5% (77.1), H: 14.1% (14.7), N: 4.96% (4.6)

^{1}H-NMR spectra (DMSO-d_6 solvent, TMS as internal standard), δ: 4.75 ppm (board s, 2H, –NH–, D_2O exch.), 2.5–3.8 ppm (m, 8H, $-CH_2-N-$), 0.9–1.4 ppm (broad d, 70H, alkyl protons).

Synthesis of *N*,*N*′-di-*n*-Octadecyl Ethylenediamine-*N*,*N*′-Diacetic Acid

Chloroacetic acid weighing 9.45 g (0.1 mol) was dissolved in 6 mL of water in a beaker which was placed in an ice-bath. While stirring, a solution of 5.3 g (0.05 mol) Na_2CO_3 in 15 mL of water was added dropwise to the solution. The solution was stirred until foaming subsided (for about 45 min). This solution was slowly added to the solution of 22.6 g (0.04 mol) *N*,*N*′ dioctadecyl ethylene diamine in 75 mL of ethanol in a 250 mL flask equipped with a reflux condenser. The mixture was stirred for 72 hr at room temperature and heated to 70°C for 6 hr. After cooling, the mixture was poured into 500 mL of water. The precipitate was filtered by suction and washed with excess of water. The crude product was recrystallized from ethanol (200 mL). Vacuum dried (42 hr) sample was 24.2 g (88.8%) based on the amine component Mp: 130°C. The product is soluble in

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cyclohexanol, 2-ethylhexanol, pyridine, hot ethanol, and insoluble in water, dimethyl sulfoxide, $CHCl_3$, and CCl_4.

Elementary analysis: (Calc. for $C_{42}H_{84}N_2O_4$) (found) C: 74.1% (74.8), H: 12.35% (13.0), N: 4.1% (4.0).

^{1}H-NMR spectra (DMSO-d_6 solvent, TMS as internal standard), d: 6.5 ppm (board s, 2H, —COOH—, D_2O exch.), 2.5–4.0 ppm (m, 12H, —CH_2—N—), 0.9–1.4 ppm (broad d, 70H, alkyl protons).

Chelate Extractions of Metal Ions

N,*N*′-di-*n*-octadecyl ethylenediamine-*N*,*N*′-diacetic acid (10.2 g, 15.0 mmol) was dissolved in 2-ethylhexanol-cylohexanol (1:1) mixture and diluted to 150 mL. The solution was divided into 25 mL portions. Extraction experiments were carried out by using these samples. Each portion was transferred into separatory funnels and shaken with 25 mL of 0.2 *M* NaOH solution to neutralize carboxyl groups of the chelating agent. Then, it was washed with water (25 mL). No salt was added to hasten phase separation. Phase separation was rapid enough in each case. The solutions were separately interacted with one of the aqueous solutions (25 mL) of metal salts Ni(II), Co(II), Cu(II), Fe(III), Cr(III), Cd(II). Chloride salts of the metals were used except Cd (II). The cadmium salt was $Cd(CH_3COO)_2{\cdot}2H_2O$. After 2 min of vigorous shaking, the metal ion concentration of aqueous phases were analyzed by AAS or colorimetric methods. From the difference between the initial and final concentrations of the aqueous solutions, extracted amounts were calculated (Table 1).

pH-Dependent Metal Extractions

To examine the effect of pH of the aqueous phase, the same experiments were repeated with metal ion solutions prepared in buffer solutions ($HCl + NH_4Cl$ pH: 2.02, NaOH + citric acid pH: 3.04, pH: 4.03, and pH: 6.02) (which were prepared by using 0.1 mol L^{-1} concentrations of each component). Concentrations of the residual metal ions were pictured as a function of pH as shown in Fig. 1.

Regeneration of the Chelating Agent

In order to regenerate the ligand from its metal complex, the aqueous layer was drained off and organic layer was shaken with 25 mL of 1 *M* HCl solution. An immediate decolorization of the organic phase took place and the acid layer became colored with characteristic color of the metal chloride [except for Cd(II)].

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Table 1. Chelate Extraction Characteristics of the Ligand for Various Metal Ions (in Nonbuffered Aqueous Solutions)

Metal Ion	Color	Initial Concentration ($mol\,L^{-1}$)	Final Concentration ($mol\,L^{-1}$)	Extracted Metal[a]	K ($L\,mol^{-1}$)	K_D	G	Recovered Metal by Acid (%)[b]
Ni(II)	Green	0.10	0.0163	0.835	3.15×10^2	5.13	0.84	99.8
Cu(II)	Blue	0.10	0.0060	0.936	2.61×10^3	15.7	0.94	99.6
Co(II)	Pink	0.10	0.0122	0.875	5.2×10^2	7.20	0.88	99.7
Cr(III)	Dark green	0.10	0.0170	0.827	3.04×10^2	4.88	0.83	99.6
Fe(III)	Yellow	0.10	0.0092	0.905	1.07×10^3	9.87	0.91	99.7
Cd(II)	Colorless	0.10	0.0260	0.720	1.09×10^2	2.85	0.74	97.3

[a] Extracted metal in mol metal/mol ligand.
[b] On the basis of analysis of acidic stripping solution.

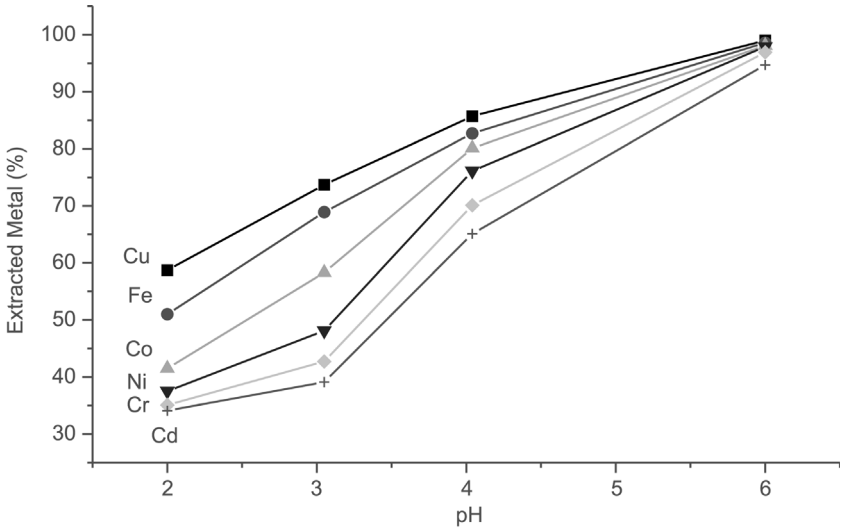

Figure 1. Percentage extraction of various metal ions (with $0.1\,\text{mol}\,\text{L}^{-1}$ initial concentrations) vs. pH.

Five milliliters of the acid phase was separated and transferred into a 25 mL volumetric flask through a filter paper. By analysis of the sample, decomplexed metal contents were calculated and listed in Table 1. Acid treatment rendered the ligand free of metal ion almost quantitatively. On washing with 0.2 *M* NaOH solution, the chelating agent gets regenerated and ready for next uses.

Recycling of the Ligand

The recycling ability of the ligand was examined by successive extraction and acid–base treatments using 0.1 *M* $NiCl_2$ solution. This process was repeated 24 times. After the final step, extracted nickel was found to be the same with that of the initial step.

Determination of the Protonation Constants of the Ligand

In a separate experiment, 25 mL of the ligand solution was washed with 0.2 *M* NaOH solution and with 50 mL of distilled water. Fresh water (25 mL) was charged to the separating funnel. The mixture was titrated potentiometrically with 0.25 *M* HCl solution. In each addition (0.5 mL), the pH electrode of the pH-

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meter was dipped into the aqueous phase and pH values were measured soon after each addition of the titer. Variation of the pH, as a function of mL of the HCl solution added, was pictured (Fig. 2). From the titration curve, protonation constants of dicarboxylate form of the ligand were estimated simply by the method of half-neutralization points.

Logarithmic values of the protonation constants were found to be $\log \beta_1 = 11.6$, $\log \beta_2 = 8.7$, $\log \beta_3 = 5.1$, and $\log \beta_4 = 1.4$. Apparently, these values correspond to stepwise conversions of ($L^{2-}\cdot 2Na^+$), ($HL^-\cdot Na^+$), ($H_3L^+\cdot Cl^-$), ($H_4L^+\cdot 2Cl^-$) species, respectively.

RESULTS AND DISCUSSION

In the present study, an organic-soluble ligand, DOED was synthesized by two step condensation reactions according to the following reaction sequences (Sch. 1).

Elementary analysis and ^{1}H-NMR spectra of the product establish the proposed structure. By examining various organic solvents and solvent mixtures, it was found that 2-ethylhexanol–cyclohexanol (1:1) mixture is a suitable solvent and provides a good solubility for the ligand and clear-cut phase separation with water.

Apparently, the organic solubility has been induced by the long aliphatic tails constituting two octadecyl groups. Like all the imino acetic acid ligands, metal chelating ability of the tetradentate ligand is expected to be reminiscent of ethylenediamine tetraacetic acid (EDTA) which is a well-known complexing agent. In other words, in designing the ligand, the organic solubility and strong

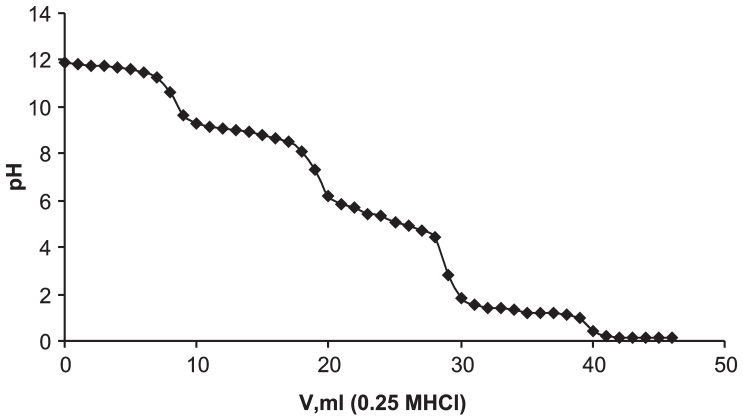

Figure 2. pH–titration curve of the ligand (0.1 mol L^{-1}) in 25 mL of the solvent mixture.

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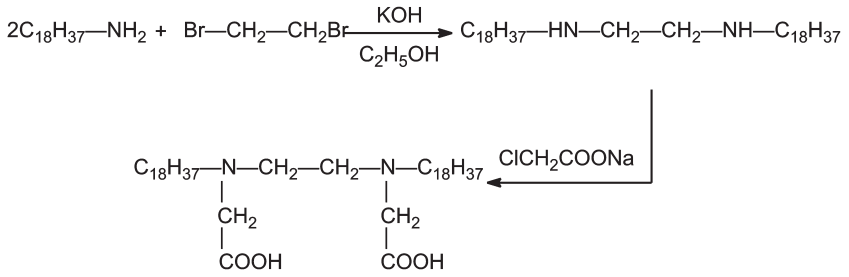

Scheme 1.

complexing ability have been combined. Not having any hydrolyzable linkage, the ligand is suitable for regeneration by acid–base treatments, which is important for use in continuous extracting systems.

Metal Extractions

In the metal extraction experiments, 0.1 *M* solution of the ligand, in the sodium form, was mixed and shaken with aqueous metal ion solutions (0.1 *M*).

Extracted metal ion contents were followed by analysis of the residual metal contents of the aqueous solutions.

For this purpose, first, 0.1 *M* of the ligand solutions were shaken with 0.2 *M* NaOH solutions. After discharging the aqueous phase, it was contacted with metal ion solutions. The metal extractions could be followed visually by an intense color developed in the organic phase with a simultaneous disapparance of the color of the aqueous phase. This observation implies that the ligand is very efficient in liquid–liquid extraction of metal ions. Around the neutral pHs', the extraction coefficient, *G*, rises as high as 0.98 values (Table 1).

The chelate extraction equilibrium can be written in terms of the overall equilibrium constant *K* (herein L and M denote ligand and metal ion).

$$[L^{2-}]_{org} + [M^{n+}]_{aq} + (n-2)[X]_{aq} \overset{K}{\rightleftharpoons} [LMX^{n-2}]_{org}.$$

When the oxidation state $n = 2$, the equation simply reduces to,

$$[L^{2-}]_{org} + [M^{2+}]_{aq} \overset{K}{\rightleftharpoons} [LM]_{org}.$$

In nonbuffered conditions, the proton concentration can be neglected and the overall complex formation in the extraction can be written as,

$$K = \frac{[LM]_{org}}{[L^{2-}]_{org}[M^{n+}]_{aq}}.$$

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Since the initial concentrations of metal ions and ligand are known, by determining the residual metal ion concentration, the equilibrium constant K can be obtained. The K values obtained by this way are reasonably high for various metal ions as shown in Table 1.

Since this equilibrium relates to the protonation constant of the deprotonated ligand, the protonation constants were calculated, based on half-neutralization points, from the potentiometric titration curve in Fig. 2.

The data collected were $\log \beta_1 = 11.6$, $\log \beta_2 = 8.7$, $\log \beta_3 = 5.1$, and $\log \beta_4 = 1.4$. These results reveal that the ligand is highly susceptible to protonation. It is obvious that complexation of metal ions can be performed best with the ligand in deprotonated form. Because of the steric factors, a second ligand could not come close to the metal ion already complexed. In other words, a possibility of metal complex formation by more than one ligand can be eliminated. Except for Cr(III) and Fe(III), the other metal ion complexes formed are to be neutral. In the case of Cr(III) and Fe(III), the relevant complexes should accompany one small ion (chloride) to establish the charge neutralization in the ligand/metal (1:1) complexes. This has been evidenced by chloride analysis of the aqua solution after extraction of Cr(III). This analysis gave $2.24\,\text{mol}\,\text{L}^{-1}$ of chloride concentration. Since each chromium is assumed to accompany one chlorine atom after 83% of Cr(III) extraction (Table1), decrease in chloride concentration must be $0.083\,\text{mol}\,\text{L}^{-1}$. Difference from the initial chloride ($0.3\,\text{mol}\,\text{L}^{-1}$) concentration is $2.17\,\text{mol}\,\text{L}^{-1}$ which is somewhat different from the experimental value, $2.24\,\text{mol}\,\text{L}^{-1}$, most probably due to partial exchange of chloride in organic phase by hydroxyl ions in water. On the basis of these considerations, metal complexation can be depicted simply as shown in Sch. 2.

On the basis of the same extraction results, the distribution coefficients, K_D of the extractions can be found similarly. The distribution coefficient:

$$K_D = \frac{[ML]_{org}}{[M]_{aq}}$$

.

Overall extraction coefficient:

$$G = \frac{[LM]_{org} V_{org}}{[LM]_{aq} V_{org} + [M^{2+}]_{aq} V_{aq}}.$$

Since the volumes of the aqueous and organic phases are equal to each other, the extraction coefficient will reduce to:

$$G = \frac{ML_{org}}{ML_{org} + M_{aq}} = \frac{K_D}{1 + K_D}.$$

Both K_D and G values are reasonably high, which implies successful extraction of the metal ions studied (Table 1).

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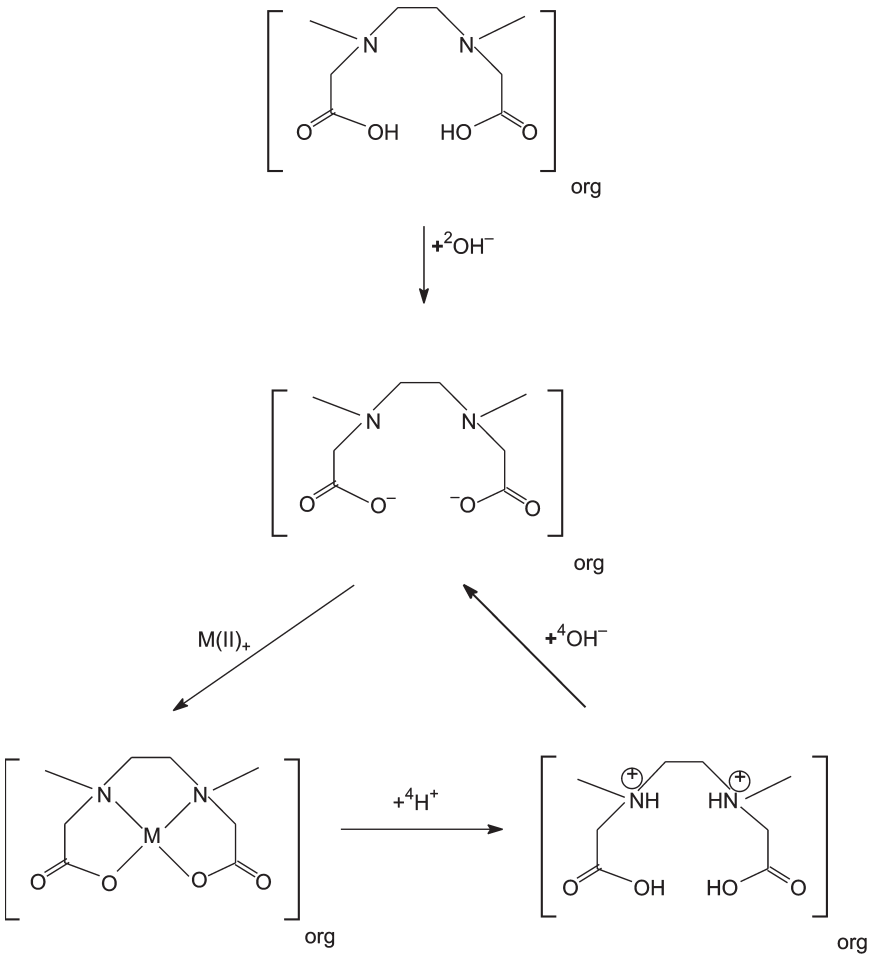

Scheme 2.

Here, during the extraction, hydrophilicity is being changed. At the beginning, sodium salt of carboxyl groups induces some hydrophilicity, which provides an interaction facility with the metal ions in water. Whereas when the ligand coordinates with the metal ions, an inner-sphere neutral complex will form. Since uncharged metal complexes are generally hydrophobic in nature, these tend to dissolve in organic phase rather than in water. Of course, long aliphatic chains play the main role in solubility of the ligand in free, ionic, or complexed states in the 2-ethylhexanol–cyclohexanol mixture. These solvents

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are suitable for practical application view point due to their nonvolatility around room temperature.

Although K values in Table 1 are low when compared with the stability constants of EDTA complexes (10^{16}–10^{18}), these are enough to provide good extractions.

Recovery of the Metal Ions and Recyling of the Ligand

After removal of the aqueous solutions in the extraction experiments, metal ions extracted into the organic phase can be recovered simply by shaking with 1 *M* HCl solutions in a separatory funnel. An immediate decolorization of the organic phase is followed by the developing of a deep color in aqueous phase. Metal analyses of the acid solutions indicate that metal contents of the organic phase can be washed out quantitatively by acid treatment in the first contact. The extracted metal ions are almost equal to those found in acidic stripping solutions (Table 1).

After decomplexation by acid treatment, the imino groups of the ligand turn into iminium groups. The acid solution containing metal ion is transferred to a beaker and the organic phase is shaken by 0.2 *M* NaOH solution.

By this way, the imino groups of the ligand become free and the carboxyl groups become ionized. In this form, the ligand in the organic phase has been regenerated and ready for use in the next cycles.

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Effect of pH

To examine the effect of pH of aqueous solution, metal ion extractions were repeated with buffered metal solutions. Concentrations of the residual metal ions–pH plots yield characteristic s-shaped curves (Fig. 1) for each metal ion. The middle points of the s-curves lie in the pH range 2.7–3.2 and differ somewhat from one metal ion to another, which imply the possibility of selective extraction of some binary mixtures. However, no sharp distinction is possible for the mixtures with three or more components. Of course, selectivity can be attained by using appropriate masking agents. In this study, this aspect was not dealt with. Decomplexation by acid treatment depends on free acid concentration in the aqueous phase, and the following overall decomplexation equilibrium takes place:

$$[\mathrm{LM}]_{\mathrm{org}} + 4[\mathrm{H}^+]_{\mathrm{aq}} \overset{K'}{\rightleftarrows} [\mathrm{LH}_4^{2+}]_{\mathrm{org}} + [\mathrm{M}^{n+}]_{\mathrm{aq}},$$

$$K' = \frac{[\mathrm{LH}_4^{2+}]_{\mathrm{org}}[\mathrm{M}^{n+}]_{\mathrm{aq}}}{[\mathrm{LM}]_{\mathrm{org}}[\mathrm{H}^+]_{\mathrm{aq}}^4}.$$

Decomplexation (instability) constants K', for various metal ions, can be obtained from pH-dependent extraction curves in Fig. 1.

Here, K' values have been estimated simply based on K and β_4 values as follows.

By multiplying both sides of the above equations by K we get,

$$KK' = \frac{[LH_4^{2+}]_{org}}{[L^{2-}]_{org}[H^+]_{aq}^4}.$$

By definition, the right-hand side should be equal to β_4 (protonation constant of the ligand). Then, $K' = \beta_4/K = 10^{1.4}/K = 25.1/K$. Decomplexation constants obtained by this way (Table 2) indicate that the equilibrium is greatly in favor of extraction of the metal ions, in the presence of deprotonated ligand.

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Effect of Metal Ion Concentrations

To examine the effect of concentration, extraction experiments were repeated with the aqueous solutions (25 mL) containing various amounts of metal ions (0.01, 0.05, 0.1, 1.5, and 2 *M*). Extracted amounts were obtained similarly. Ratios of extracted metal ion concentrations to the initial ligand concentration (0.1 *M*) is expected to have a maximum value of unity. Since metal extraction is believed to proceed via formation of L/M (1:1) complexes, the maximum value of $[LM]/[L^{2-}]_0$ should be equal to unity, where the denominator term refers to initial ligand concentration in the organic phase.

Surprisingly, in high metal concentrations, this ratio lies above the maximal value 1 (Table 2). In other words, extracted amounts exceed the theoretical metal binding capacity of the ligand at high metal ion concentrations. This phenomenon must be because of extracting the ability of the organic solvent mixture itself. To prove this, assumption, extractions were repeated under the same conditions without using the ligand. In the case of 1.5 and 2.0 *M* concentrations, the organic solvent mixture becomes distinctly colored upon shaking with the solutions. It is clearly inferred from Table 3 that reasonable amounts of metal ions are being extracted from concentrated metal ion solutions by the organic solvent mixture. Hence, over extractions at high metal concentrations arise from the contribution of the solvent mixture in the extractions.

CONCLUSION

The ligand DOED is a versatile chelating agent for extraction of transition metal ions. Its ionic forms and metal complexes are soluble in cyclohexanol-2-

Table 2. Effect of Metal Ion Concentrations on the Extraction

Metal Ion	Initial Conc. (M)	Final Conc. (M)	G (%)	$[LM]/[L^{2-}]_0$	K'[a]
Cu (II)	0.02	2.4×10^{-4}	98.6	0.197	1.16×10^{-2}
	0.05	2.5×10^{-3}	99.5	0.475	
	0.1	0.06	94.0	0.40	
	1.5	0.375	75.0	11.25	
	2	0.7	65.0	13.0	
Ni (II)	0.02	0.0003	98.5	0.197	7.96×10^{-2}
	0.05	0.0077	84.6	0.423	
	0.1	0.0163	83.7	0.837	
	1.5	0.5158	65.6	9.84	
	2	0.8929	55.3	11.07	
Co (II)	0.02	0.0004	98.0	0.196	4.82×10^{-2}
	0.05	0.0049	90.2	0.451	
	0.1	0.0122	87.8	0.878	
	1.5	0.4501	70.0	10.5	
	2	0.7342	63.3	12.66	
Fe (III)	0.02	0.0002	99	0.198	2.34×10^{-2}
	0.05	0.0029	94.2	0.471	
	0.1	0.0092	90.8	0.908	
	1.5	0.4054	73.0	10.95	
	2	0.7604	62.0	12.4	
Cr (III)	0.02	0.0006	97.0	0.194	8.25×10^{-2}
	0.05	0.009	82.0	0.41	
	0.1	0.017	83.0	0.83	
	1.5	0.5555	63.0	9.45	
	2	0.9615	52.0	10.40	
Cd (II)	0.02	0.001	95.0	0.19	2.3×10^{-1}
	0.05	0.011	78.0	0.39	
	0.1	0.026	74.0	0.74	
	1.5	0.5999	60.0	9.001	
	2	1.0205	49.0	9.80	

[a] K' values are based on the measurements for 0.1 M metal concentrations.

ethylhexanol mixtures (1:1). By using the deprotonated form of the ligand, it is possible to extract metal ions in relatively low concentrations as low as 0.02 M.

The metal ions extracted can be recovered simply by washing with acid and base. Due to nonhydrolyzability of the linkages involved and ease of phase

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Table 3. Extraction of Metal Ions by the Solvent Mixture Without Ligand

Metal Ion	Initial Conc. (*M*)	Final Conc. (*M*)	*G* (%)
Cu (II)	0.1	0.1	0.08 <
	1.5	1.02	32
	2	1.2	40
Ni (II)	0.1	0.1	0
	1.5	0.87	42
	2	1	50
Co (II)	0.1	0.1	0
	1.5	0.94	37
	2	1.14	43
Fe (III)	0.1	0.1	0.01
	1.5	0.99	34
	2	1.14	43
Cr (III)	0.1	0.1	0
	1.5	0.83	45
	2	0.91	55
Cd (II)	0.1	0.1	0
	1.5	0.48	68
	2	0.89	56

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separation, the ligand can be recycled many times (more than 24 times), and the method presented seems to be very attractive for application in continuous extraction systems.

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