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Adsorption Studies of Divalent Metal Ions with Extraction Resin Containing 1-Hexyl-4-ethyloctyl Isopropylphosphonic Acid

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ABSTRACT

Equilibrium distributions of cobalt(II), nickel(II), zinc(II), cadmium(II), and copper(II) have been studied in the adsorption with extraction resin containing 1-hexyl-4-ethyloctyl isopropylphosphonic acid (HEOPPA) as an extractant from chloride medium. The distribution coefficients are determined as a function of pH. The data are analyzed both graphically and numerically. The extraction of the metal ions can be explained assuming the formation of metal complexes in the resin phase with a general composition $ML_2(HL)_q$. The adsorbed species of the metal ions

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are proposed to be ML_2 and the equilibrium constants are calculated. The efficiency of the resin in the separation of the metal ions is provided according to the separation factors values. The separation of Zn from Ni, Cd, Cu, Co, and Co from Ni, Cd, Cu with the resin is determined to be available. Furthermore, Freundlich's isothermal adsorption equations and thermodynamic quantities, i.e., ΔG, ΔH, and ΔS are determined.

Key Words: Adsorption; Divalent metal ions; Extraction resin; 1-Hexyl-4-ethyloctyl isopropylphosphonic acid.

INTRODUCTION

Solvent extraction and ion exchange technologies have been extensively applied to the recovery and separation of metal ions. Many reagents are used as extractants, among which organophosphorus acids have attracted much attention.[1,2] 1-Hexyl-4-ethyloctyl isopropyl phosphonic acid (HEOPPA) is a new extractant developed by Shanghai Institute of Organic Chemistry (Shangai, 20032, P.R. China). Lu et al.[3] determined some basic constants of HEOPPA, such as solubility, dissociation constants, dimerization constants, and distribution constants between water and *n*-heptane by a potentiometric two-phase titration. HEOPPA has higher extraction capacity and lower pH_{50} value compared with bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex272), and a higher selectivity compared with di-(2-ethylhexyl)-phosphoric acid (D2EHPA) or 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH/EHP) when used to extract rare earth elements.[4]

Extraction resins (previously called Levextrel resins) and extractant-impregnated resins have attracted special attention because of their great potential for highly selective separation and concentration of metal ions from aqueous solutions.[5–7] During the last 20 years, there has been a lot of research about resins containing organophosphorus acids, such as HEH/EHP, Cyanex272, and di-(2-ethylhexyl) thiophosphoric acid (DEHTPA).[8–11] Yoshizuka et al.[12] studied the distribution equilibria in the adsorption of Co^{2+} and Ni^{2+} on extraction resins containing Cyanex272 from aqueous ammonium nitrate and sulfuric solutions. Cortina et al.[13] investigated the distribution of Zn^{2+}, Cu^{2+}, and Cd^{2+} with extraction resins containing Cyanex272 from nitric and hydrochloric acids and calculated the equilibrium constants. Akita et al.[14] determined the separation factors of Zn/Cu and Co/Ni by the sorption with a macromolecular resin containing D2EHPA and HEH/EHP as 55.2 and 6.73, respectively.

A few years ago, our research group began to study the adsorption of metal ions with extraction resins. Luo[15] studied the adsorption of Zn^{2+}, Co^{2+}, and

Ni^{2+} with extraction resin containing Cyanex302 from sulfuric solutions and compared the results of different metal ions. Wang et al.[16,17] investigated the adsorption and separation of heavy rare earth (III) with extraction resin containing Cyanex272 and HEOPPA, respectively. Satisfactory results with high purity and yield of rare earth oxides have been obtained with the resins.

In the present work, the adsorption of Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, and Cu^{2+} from chloride medium with extraction resin containing HEOPPA has been investigated. The extracted species are proposed and the equilibrium constants of the adsorbed species are calculated. The efficiency of the resin in the separation of the metal ions is provided. Freundlich's isothermal adsorption equations and thermodynamic quantities are also determined.

EXPERIMENTAL

Reagents

HEOPPA with a purity greater than 99% was supplied by Shanghai Institute of Organic Chemistry. Extraction resin containing HEOPPA, obtained from Beijing Institute of Chemical Engineering and Metallurgy, Ministry of Nuclear Industry, size 0.07 to 0.15 mm, was used. The resin was prepared by adding the extractant to a mixture of styrene and divinylbenzene copolymers.[18] It was washed with 3 mol/L HCl and water to eliminate inorganic impurities and monomeric material.

Stock solutions of MCl_2 (M = cobalt, nickel, zinc, cadmium, copper) were prepared with AR chemicals. The concentrations of M^{2+} were determined either by EDTA titration or by spectrophotometer. All other reagents used were of analytical reagent grade.

Apparatus

A pHS-3C digital pH meter made by Shanghai Rex Instruments Factory was used for pH measurements. A UV-VIS-NIR recording spectrophotometer, model UV-365, made by Shimadzu Company was used for absorption measurements.

Methods

The adsorption of metal ions was carried out in batch experiments at 303 ± 1 K. Samples of resin containing HEOPPA and 5 ml aqueous solution

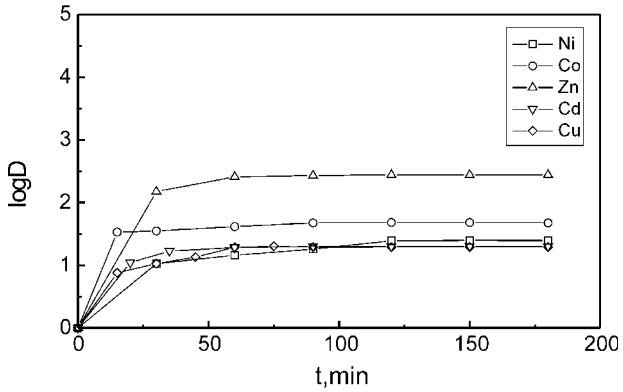

Figure 1. Effect of time on the adsorption of M^{2+} with extraction resin containing HEOPPA. Extraction resin = 0.05 g, $[M^{2+}]$ = 35.0 μg/mL, [(Na,H)Cl] = 0.20 mol/L.

were placed in special glass-stoppered tubes and shaken to achieve equilibrium. To determine the time to reach equilibrium, the distribution coefficients of M^{2+} were determined as a function of time at constant pH values, concentration of M^{2+} and mass of resin. As seen in Fig. 1, 2 h was enough time to reach equilibrium for all the metal ions. After phase separation with a high-speed centrifuge, the concentration of M^{2+} in the aqueous phase was analyzed. The amount of metal ions adsorbed by the resin was determined by the difference. The distribution ratio of metal ions was obtained as described[13]:

$$D = \frac{V}{m} \cdot \frac{C_0 - C}{C} \tag{1}$$

where C_0 and C denote the initial total concentration and the equilibrium concentration of metal ions in aqueous phase, respectively; m stands for the mass of dry resin; and V represents the volume of the aqueous phase.

RESULTS AND DISCUSSION

Stoichiometry of Sorption of Divalent Metals with Extraction Resin Containing HEOPPA

Metal distribution data from aqueous solutions of 0.2 mol/L (Na, H) Cl with extraction resin containing HEOPPA are plotted as log D vs. pH in Fig. 2. The distribution functions are straight lines with a slope of about 2, which

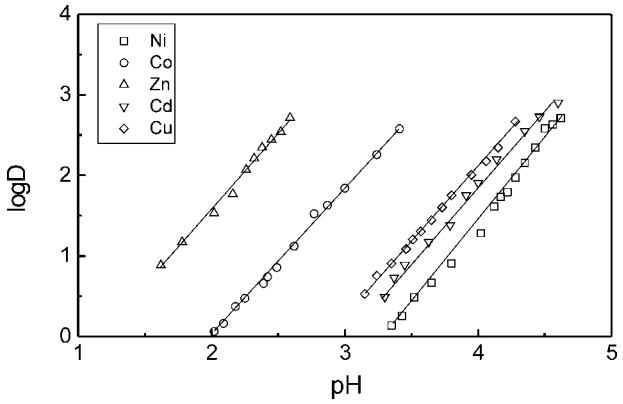

Figure 2. Effect of equilibrium pH on the adsorption of M^{2+} with extraction resin containing HEOPPA. Extraction resin = 0.05 g, $[M^{2+}] = 35.0\ \mu g/mL$, [(Na,H)Cl] = 0.20 mol/L.

indicates that 2 protons are released in the adsorption reaction of metal ions by the resin phase.

Accordingly, the extraction of these metal ions with the resin can be described with the following general reaction[13]:

$$M^{2+} + (2 + q - t)HL_{(r)} + tCl^- \leftrightarrow MCl_tL_{2-t}(HL)_{q(r)} + (2 - t)H^+ \quad (2)$$

where r denotes the resin phase; q and t denote unknown coefficients.

Assuming that Cl^- ions are not co-extracted by the resin phase, Eq. (2) can be expressed as:

$$M^{2+} + (2 + q)HL_{(r)} \leftrightarrow ML_2(HL)_{q(r)} + 2H^+ \quad (3)$$

The equilibrium constant of the extraction process can be defined as:

$$K = \frac{\alpha_{ML_2(HL)_{q(r)}}\alpha_{H^+}^2}{\alpha_{M^{2+}}\alpha_{HL_{(r)}}^{2+q}} = \frac{[ML_2(HL)_q]_{(r)}[H^+]^2}{[M^{2+}][HL]_{(r)}^{2+q}} \cdot \frac{\gamma_{ML_2(HL)_{q(r)}}\gamma_{H^+}^2}{\gamma_{M^{2+}}\gamma_{HL_{(r)}}^{2+q}} \quad (4)$$

where α and γ denote the activity and the activity coefficients of species in the aqueous and the resin phase, respectively.

Rearranging Eq. (4), the following expression can be obtained:

$$K = K_{ex} \cdot \Gamma \quad (5)$$

where K_{ex} is the stoichiometric equilibrium constant for the extraction, i.e.,

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the observed concentration equilibrium constant, which can be expressed as the following:

$$K_{ex} = \frac{[ML_2(HL)_q]_{(r)}[H^+]^2}{[M^{2+}][HL]_{(r)}^{2+q}} \tag{6}$$

Γ is the term containing all the activity coefficients. As a preliminary hypothesis, the term Γ can be expected to remain constant as long as the ionic strength in the aqueous phase is constant and the variations in the resin phase concentrations are small.

To relate the distribution of the metal ions with their composition in the resin phase, the formation of the simplest species may be assumed. Hence, if only one species of the type $ML_2(HL)_{q(r)}$ is formed, the distribution ratio for M^{2+} becomes:

$$D = K_{ex}[HL]_{(r)}^{2+q}[H^+]^{-2}$$

$$\log D - 2pH = (2+q)\log[HL]_{(r)} + \log K_{ex} \tag{7}$$

where $[HL]_{(r)}$ can be calculated according to $[HL]_{(r)} = [HL]_{(r),0} - (2+q)[M^{2+}]_{(r)}$; $[HL]_{(r),0}$ denotes the initial HEOPPA content in the sorbent.

Figure 3 shows the effects of resin amounts on the amounts (Q) of M^{2+} adsorbed with extraction resin containing HEOPPA when the concentration of

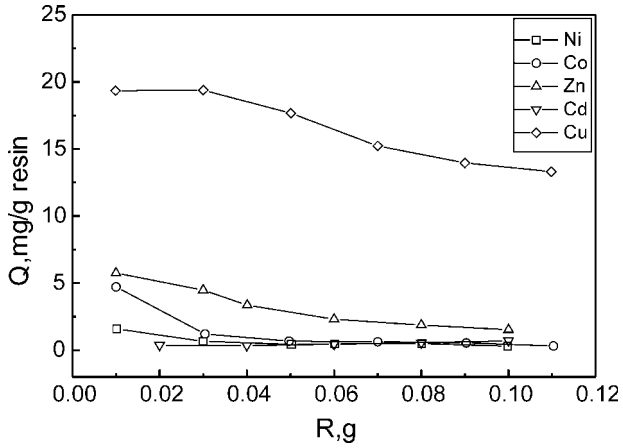

Figure 3. Effect of resin amount on the adsorption of M^{2+} with extraction resin containing HEOPPA. $[M^{2+}] = 35.0\,\mu g/mL$, $[(Na,H)Cl] = 0.20\,mol/L$.

M^{2+}, acidity in aqueous phase, and ionic strength are constant. The Q values decrease firstly and then remain constant with an increase of the mass of extraction resin (R). The total loading capacity of the resin for the extractant is determined to be 47.29% by titrating with standard NaOH after marination in ethanol for 12 hours. The total amount of M^{2+} adsorbed up to resin saturation is determined to be 39.3 mg Co^{2+}/g·resin, 38.2 mg Ni^{2+}/g·resin, 41.3 mg Zn^{2+}/g·resin, 72.2 mg Cd^{2+}/g·resin, and 41.5 mg Cu^{2+}/g·resin, respectively.[16,17] The molar ratio of HEOPPA and M^{2+} can be calculated to be about 2 for the metal ions. Accordingly, the sorption reactions of M^{2+} from chloride medium with extraction resin containing HEOPPA can be described as:

$$M^{2+} + 2HL_{(r)} \leftrightarrow ML_{2(r)} + 2H^{+}$$

Equation (7) can thus be rewritten as:

$$\log D - 2pH = 2\log [HL]_{(r)} + \log K_{ex} \quad (8)$$

According to Eq. (8), K_{ex}, the equilibrium constants for the species formed can be calculated as shown in Table 1.

Evaluation of the Separation Factors of Divalent Metals with Extraction Resin Containing HEOPPA

The separation of different transition metal ions from the same solution has always been of interest. A useful indication as to whether this can be achieved is given by the separation factors (β). In metal extraction, for practical purposes, the separation factors are defined from pH_{50} (pH at which 50% of the metal is extracted). The separation factors of Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, and Cu^{2+} have been expressed in terms of ΔpH_{50} from experimental curves of metal extraction percentage (*%E*) as a function of pH. The extraction

Table 1. Values of K_{ex} for the adsorption of M(II) with extraction resin containing HEOPPA.

M(II)	Co	Ni	Zn	Cd	Cu
$\log K_{ex}$	-2.21 ± 0.08	-4.82 ± 0.13	-0.68 ± 0.05	-4.35 ± 0.08	-4.10 ± 0.10

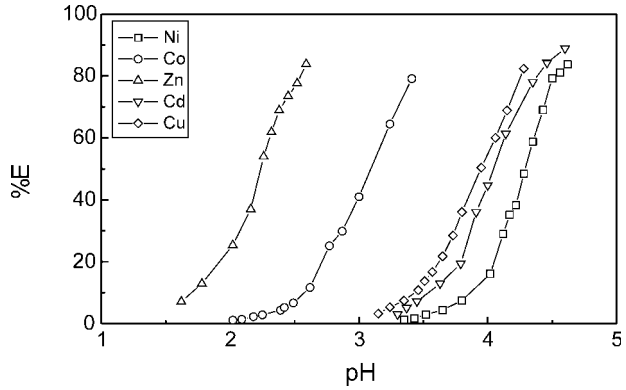

Figure 4. Effect of equilibrium pH on the extraction percentage (*%E*) of M^{2+} with extraction resin containing HEOPPA. Extraction resin = 0.05 g, $[M^{2+}]$ = 35.0 μg/mL, [(Na,H)Cl] = 0.20 mol/L.

percentage and β are defined as:

$$\%E = \frac{c_0 - c}{c_0} \times 100 \tag{9}$$

$$\log \beta = 2\,\Delta pH_{50} \tag{10}$$

where C_0 and C are as mentioned previously.

Figure 4 shows the extraction percentage, *%E*, as a function of the equilibrium pH. The values of pH_{50} and ΔpH_{50} for the extraction of M^{2+} with the resin containing HEOPPA are calculated as given in Table 2.

The separation factors data in Table 2 indicate that it is possible to separate Zn from Ni, Cd, Cu, Co and Co from Ni, Cd, and Cu using extraction resin containing HEOPPA. As is well known, it has been of interest to separate

Table 2. pH_{50}, ΔpH_{50}, and log β values of M(II) adsorbed by extraction resin containing HEOPPA.

	Co	Ni	Zn	Cd	Cu		
pH_{50}	3.09	4.28	2.23	4.07	3.95		
	Zn/Ni	Zn/Cd	Zn/Cu	Zn/Co	Co/Ni	Co/Cd	Co/Cu
ΔpH_{50}	2.05	1.84	1.72	0.86	1.19	0.98	0.86
log β	4.10	3.68	3.44	1.72	2.38	1.96	1.72

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divalent metal ions from each other all along. The adsorption with extraction resin containing HEOPPA may provide an effective method to separate certain divalent metal ions according to the separation factors.

Effect of the Initial Concentration of Metal Ions on the Adsorption

The effect of the concentration of M^{2+} on the sorption by the resin phase is given in Fig. 5. Freundlich's isothermal adsorption equation, [19] can be written as:

$$\log Q = \frac{1}{n} \cdot \log C + \log K \tag{11}$$

where K and $\frac{1}{n}$ stand for Freundlich's constants. $\log K$ and $\frac{1}{n}$ for M^{2+} are determined according to the slope and intercept values in Fig. 5 and Eq. (11) can thus be rewritten as:

For Co^{2+} : $\log Q = 1.04 \ \log C + 3.40$;

For Zn^{2+} : $\log Q = 0.87 \ \log C + 3.60$;

For Cu^{2+} : $\log Q = 0.66 \ \log C + 3.68$

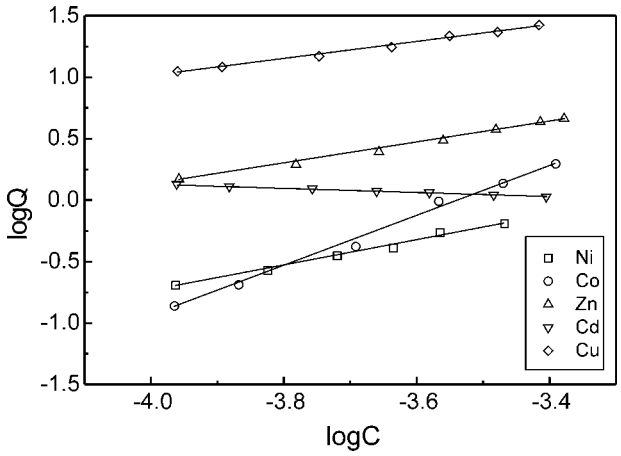

Figure 5. Effect of M^{2+} concentration on the adsorption of M^{2+} with extraction resin containing HEOPPA. Extraction resin = 0.05 g, [(Na,H)Cl] = 0.20 mol/L.

For Ni^{2+} : $\log Q = 2.06\ \log C + 7.29$;

For Cd^{2+} : $\log Q = 0.18\ \log C - 0.59$;

Effect of the Experimental Temperature on the Adsorption

The amounts (Q) of M^{2+} adsorbed with extraction resin containing HEOPPA were studied at different temperatures (20°C ~ 50°C) at fixed concentrations of M^{2+}, amounts of extraction resin, ion strength, and acidities in the aqueous phase. The log D vs. $(1/T)$ plots are shown in Fig. 6. The change of enthalpy of the reactions, ΔH, can be determined according to the following equation:

$$\Delta \log D/\Delta(1/T) = -\Delta H/2.303R$$

ΔG and ΔS of the system at 30°C can thus be calculated too.

$$\Delta G = -RT\ln K_{ex}$$

$$\Delta G = \Delta H - T\Delta S \Rightarrow \Delta S = \frac{\Delta H - \Delta G}{T}$$

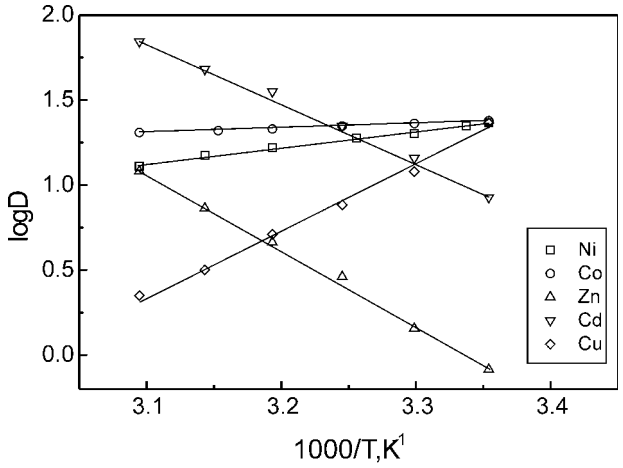

Figure 6. Effect of experimental temperature on the adsorption of M^{2+} with extraction resin containing HEOPPA. Extraction resin = 0.05 g, $[M^{2+}]$ = 35.0 μg/mL, [(Na,H)Cl] = 0.20 mol/L.

Table 3. Thermodynamic parameters for the adsorption of M(II) with extraction resin containing HEOPPA.

M(II)	Co	Ni	Zn	Cd	Cu
ΔH (kJ mol^{-1})	−5.20	−18.00	86.04	67.12	−73.79
ΔG (kJ mol^{-1})	12.82	27.98	3.95	25.26	23.81
ΔS (J K^{-1} mol^{-1})	−59.44	−151.67	270.79	138.08	−321.95

The values of ΔH, ΔG, and ΔS are given in Table 3, showing that the adsorption processes of Co^{2+}, Ni^{2+}, and Cu^{2+} with extraction resin containing HEOPPA are exothermic reactions. The processes of Zn^{2+} and Cd^{2+} endothermic ones.

CONCLUSION

The adsorption of cobalt(II), nickel(II), zinc(II), cadmium(II), and copper(II) with extraction resin containing HEOPPA has been discussed. The stoichiometry of sorption of metal ions is proposed and equilibrium constants of the sorbed species are given. The extracted species are determined as ML_2 for all the metal ions. The efficiency of the resin in the separation of the five metal ions is provided according to the separation factors. It is possible to separate Zn from Ni, Cd, Cu, Co and Co from Ni, Cd, Cu with the resin, which provides an effective method to separate certain divalent metal ions. Freundlich's isothermal adsorption equations have been obtained. Thermodynamic quantities, i.e., ΔG, ΔS, and ΔH are also calculated for the system. The adsorption processes of Co^{2+}, Ni^{2+}, and Cu^{2+} are exothermic reactions; whereas, those of Zn^{2+} and Cd^{2+} are endothermic ones.

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