Selective Separation of In(III), Ga(III), and Zn(II) from Dilute Solution Using Solvent-Impregnated Resin Containing Di(2-ethylhexyl) Phosphoric Acid

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ABSTRACT: The aim of this work was to study the separation of In(III), Ga(III), and Zn(II) from sulfate solution using solvent-impregnated resin containing di(2-ethylhexyl) phosphoric acid. The influence of pH on the extraction of each metal was determined. Extraction isotherms were then studied at selected pH. Results showed that In(III) can be first extracted from aqueous solutions at pH 2 using the resin, then Ga(III) and Zn(II) coextracted at pH 3, and the separation can be carried out by using different concentra-

tions of eluents. Loaded resins can be regenerated, and the metals can be recovered selectively. Two fixed-bed columns arranged in series were successfully used for the separation and recovery of these three metal ions from multi-component solution. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 253–259, 2006

Key words: solvent-impregnated resin; separation; In(III); Ga(III); Zn(II); D2EHPA

INTRODUCTION

It is now widely accepted that the use of polymeric resins in metal recovery offers many advantages over the use of the liquid-liquid extraction technique. The most important advantages are the simplicity of equipment and operation and the possibility of using the polymeric adsorbent for many extraction cycles without losses in the metal extraction capacity. Unfortunately, the preparation of polymer ion exchangers, with chelating groups connected to the polymer matrix by chemical bonds, is usually very complex and is time and money consuming. Therefore, the concept of solvent-impregnated resins (SIR) was developed; it is a very simple and in many cases the only way to prepare ion-exchange resins containing reactive groups with special properties, which cannot be immobilized by chemical bonding. This concept includes the incorporation of the solvent-extraction reagent (ligand) by a physical impregnation technique into the polymer.¹

Since the mid of 1970s, SIR have acquired great importance as a technique with interesting features for the recovery and chromatographic separation of metal ions because they bridge the gap between two separation techniques of solvent extraction and ion exchange. They combine not only the advantages of solid ion exchange for processing highly diluted solutions with specific properties of extractants, but also a high distribution ratio and selectivity characteristic of the extractants dissolved in a liquid organic phase with simplicity of equipment and operation characteristic of solid ion exchange technology. Consequently, the resins are very much suitable for recovering or scavenging a specified metal ion with high selectivity, for which conventional solvent extraction is unfavorable. It is much easier to use than solvent extraction systems and less expensive than chelating resins. The ease of SIR preparation, the selectivity characteristics of extractants in the SIR, and the wide choice of reagents (extractants) of desired selectivity are advantages of the impregnated polymers with respect to those with the covalent bound ligand groups. Furthermore, the extraction characteristics of the resin can be evaluated from previous data on the solvent extraction.²⁻⁵

In recent years, the demands for In and Ga have increased because of their use as semiconductor materials such as InP or GaAs. However, In and Ga are not mined for themselves, as they appear very widely dispersed on the earth's surface. The two metals show similar chemical behavior, and one significant source for them is Zn refinery residue as minor components.^{6–7} Because of the strategic importance of the elements, any efforts for the mutual separation and recovery of the metals are completely justified. Liquid–liquid extraction has been applied to the practical

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separation and recovery of In and Ga from the residue.⁸⁻¹³ However, the main drawback of solvent extraction process is related to the loss of extractant, resulting from its partial dissolving in the aqueous phase, which may cause environmental hazards and economic limitations. Ion exchange technology can be considered as an alternative method. However, it has some drawbacks: slow adsorption and desorption rates, poor selectivity, and requirement of concentrated solution of electrolytes for recovery. Furthermore, the development of highly selective chelating ion-exchange resins entails a very tedious and timeconsuming search for highly selective functional groups.¹⁴ Therefore, there is a growing interest in the development of new methods for the separation and recovery of In and Ga.

In the past few years, the application of SIR in metal extraction separation processes has focused on hydrometallurgical and analytical applications, in most of the case related to rare metals field applications.^{15–18} However, to our knowledge, few types of SIR were used in separation and recovery of In and Ga. The purpose of this study is to investigate the different adsorption and elution behaviors of In, Ga, and Zn from sulfate solution with SIR containing di(2-ethyl-hexyl) phosphoric acid (D2EHPA) and to separate them from each other.

EXPERIMENTAL

Materials

The extractant D2EHPA was purchased from the Chemical Reagent Factory of Beijing, People's Republic of China. The chemical structure of this extractant is as follows:



where R is

The polymer adsorbent HZ-803 was obtained from Shanghai Huazhen Polymers Co., People's Republic of China. The properties of polymer adsorbent HZ-803 is summarized in Table I. In, Ga, and all other chemicals used were of analytical grade and purchased from Shanghai Chemical Reagent Company, People's Republic of China.

TABLE IProperties of Polymer Adsorbent HZ-803

Properties	HZ-803
Chemical structure	Styrene DVB
Moisture content/%	60.5
Surface area/m ² /g	575
Average pore diameter/nm	6
Total porosity/cm ³ pore/cm ¹ -R	0.97
Specific gravity	1.10

Preparation of the SIR

The SIR was prepared according to the dry impregnation method.¹⁹ Ten gram of dry resin (HZ-803) was added to 25 mL of D2EHPA/*n*-ethanol solution. The mixture was stirred for 48 h at 25°C to ensure the impregnation of extractant into the pores of HZ-803 resin. Then, solid HZ-803 resin was dried at 40°C to remove ethanol. To ensure complete elimination of solvent, the weight of solid was measured periodically until the weight reaches a constant value.

Determination of the amount of impregnated D2EHPA

The extractant investigated in this study is acid type. Therefore, the amount of impregnated extractant was evaluated after washing a known amount of resin with ethanol, which completely eluted the extractant, and the content of extractant was determined by NaOH titration. A calibration curve of extractant titration with NaOH was established to determine the amount of extractant.¹⁹

Analyzes of metal ions in solution

The concentration of In(III) or Ga(III) in single-component solution was determined spectrophotometrically with GBC UV–vis 916 spectrophotometer (Australia).^{20–21} The concentration of Zn(II) in single-metal solution was determined by titration with EDTA in high concentration and by GBC UV–vis 916 spectrophotometer in low concentration.²⁰ The concentrations of In(III), Ga(III), and Zn(II) in multi-component were analyzed by using Thermo Jarrell Ash ICP-IRIS Advantage 1000 (USA).

Batch test of In(iii), Ga(iii), and Zn(ii) adsorption

In the case of solid/liquid extraction, experiments were performed using solutions at a concentration of 200 mg/L of metals. The ionic strength was adjusted with sodium sulfate (0.1 mol/L). The liquid/solid ratio was maintained at 0.2 L/g, dry weight. In the case of extraction isotherms, the initial metal concentration was varied, and the contact time was fixed. The solu-





Figure 1 (a) Effect of pH on the extraction efficiency of In (III), Ga(III), and Zn(II) on D2EHPA SIR. Aqueous phase: 0.2 g/L of metal in 0.1 mol/L Na₂SO₄. Liquid/solid ratio: 0.2 L/g. (b) Effect of pH on their distribution coefficients In(III), Ga(III), and Zn(II) on D2EHPA SIR. Aqueous phase: 0.2 g/L of metal in 0.1 mol/L Na₂SO₄. Liquid/solid ratio: 0.2 L/g.

tion was mixed and shaken in a stoppered glass flask submerged in a thermostatted water bath. On the basis of the preliminary experiments (data are not shown), the equilibrium time in the adsorption of In(III), Ga(III), and Zn(II) was maintained at 2.5, 2.0, and 1.5 h, respectively. The amount of metals adsorbed per gram of the dry resin, expressed as q, was calculated as the change of metal concentrations before and after equilibration divided by the weight of the dry resin used. The distribution coefficient of metal, D, defined as the ratio of metal concentration in the resin phase (mol/g) and the aqueous phase (mol/mL) is represented by eq. (1).²²

$$D = Q/C_e \tag{1}$$

where C_e denotes the equilibrium concentration of metal in the aqueous solution.



Figure 2 SP for the separation of In(III), Ga(III), and Zn(II). Influence of pH. Aqueous phase: 0.2 g/L of metal in 0.1 mol/L Na₂SO₄. Liquid/solid ratio: 0.2 L/g.

Column test for adsorbing and stripping metals

For continuous extraction, SIRs were packed in columns (i.d. 10 mm). A total of 3.0 g of resin was introduced (packing depth: 90 mm). The columns were fed by upflow using a peristaltic pump: the flow rate was 30 mL/h. Preliminary experiments were performed using single-component solution at a concentration of 200 mg/L of metals in 0.1 mol/L sodium sulfate and pH controlled at the optimum pH for selective separation established in previous experiments. The columns were preconditioned at the optimum pH, flowing through the columns sodium sulfate solution (0.1 mol/L) at the selected pH. In the case of column systems, before the elution step, the column was rinsed with 20 mL of a 0.1 mol/L sodium sulfate solution. HCl solutions were used for the recovery of metals from loaded resins. Finally, extraction was performed in ternary solutions (200 mg/L of metals in 0.1 mol/L sodium sulfate) using a pair of columns filled with the SIR (5 g), the solutions being controlled to



Figure 3 Effect of temperature on the distribution coefficients with D2EHPA SIR. Aqueous phase: 0.2 g/L of metal in 0.1 mol/L Na₂SO₄. Liquid/solid ratio: 0.2 L/g.



Figure 4 Extraction Isotherms [In(III), Ga(III)] using D2EHPA SIR. In(III): pH 2; Ga(III): pH 3.

selected pH values. The residual metal concentration in the aqueous phase was determined by ICP. The amount of metal extracted was obtained by mass balance.

All the experiments were carried out at room temperature (298 K) except for the study of temperature effect on capacity.

RESULTS AND DISCUSSION

Study of In(iii), Ga(iii), and Zn(ii) extraction from single-component solutions using D2EHPA SIR

Effect of pH

Figure 1 shows the effect of pH on the extraction efficiency of In(III), Ga(III), Zn(II) (Fig. 1(a)), and on their distribution coefficients (Fig. 1(b)) from sulfate solution using this SIR. The relative separation of the curves gives a first possible approach for the selective separation of metal ions. In ion extraction was shifted to more acid pH solutions, while Ga and Zn were shifted to less acid solutions: the separation of In from the other two metals with this resin will be possible by controlling the pH.

It is interesting to observe that, for each system, with the pH range investigated, the distribution coefficients (*D*) reached values as high as 10^3 – 10^4 mL/g, depending on the metal. The distribution of the metal between the liquid and the solid phases was strongly displaced toward the transfer to the resin.

It appears from Figure 1(b) that the logarithm of the distribution coefficient may be described as a linear function of the pH for the metals. The slope of these curves may be used to determine the number of protons that have been exchanged with the metal during sorption. Considering the general exchange reactions between the metal ions in solution and the resin:

$$M^{n+} + (n+q) HL_R = (ML_n (HL)_q)_R + nH^+$$
 (2)

where M^{n+} denotes metal ions, and HL_R denotes D2EHPA SIR.

The apparent stability constant is written as

$$K = \frac{[ML_n(HL)_q]_R[H^+]^n}{[M^{n+1}][HL]_R^{n+q}}$$
(3)

$$K = D \frac{[\mathrm{H}^+]^n}{[\mathrm{HL}]_R^{n+q}} \tag{4}$$

Equation (3) is only valid with only one metal-extractant complex. Under these conditions, it is possible to transform eq. (3) into

$$\log D = \log K + (n+q)\log[HL]_{\mathbb{R}} + n \,\mathrm{pH} \qquad (5)$$

$$\log D = \log K' + n \text{ pH at constant [HL]}_{R}$$
 (6)

The curves in Figure 1(b) can be described by the following equations:

For In (III): $\log D = -0.296 + 2.991 \text{ pH} (R = 0.999)$ For Ga(III): $\log D = -8.314 + 2.958 \text{ pH} (R = 0.999)$ For Zn (III): $\log D = -5.811 + 2.033 \text{ pH} (R = 0.999)$

As expected, for In ion and Ga ion extraction, both slopes of the curves tended to 3. And for Zn ion extraction, the slope of the curve tended to 2.

Separation power

The selectivity coefficient is usually determined using multi-component solutions and calculated using the ratio between the distribution coefficients of each metal. In the present work, we used previous results (extraction efficiency versus pH with single-component solutions) to get a separation power coefficient (SP).²³ This coefficient was calculated using the following equation:

$$SP = SE_{M1} - SE_{M2} \tag{7}$$

where $SE_{Mi}(\%)$ is the extraction efficiency at selected pH for metal i. When necessary, the values of the distribution coefficients were extrapolated to obtain the corresponding values of the SP. This parameter enables the optimum pH range for metal separation to be predetermined simply and quickly.

Figure 2 gives the results for the SP. A SP greater than 95% may be obtained at a working pH ranging between 1.5 and 2.5 for the separation of In (III) and Ga (III)/Zn (II), and at pH 1.5, In(III) can be completely separated from Ga (III) and Zn(II). On the other hand, the SP for Ga (III)/Zn (II) does not exceed TABLE II

Sorption Using Solvent Impregnated Resin						
Metal	$q_{\rm m} ({\rm mg}/{\rm g})$	b (L/mg)	R			
In	46.8	0.772	0.98			

0.145

33.9

Ga

45%. Thus, this resin can be used to separate In (III) from Ga (III) and Zn(II) at pH 2; however, the separation of the three metal ions cannot be performed in a single-step procedure using this system. It is necessary to add a second treatment step for the separation of Ga (III) from Zn (II).

Effect of temperature on the distribution coefficient of In(iii) and Ga(iii)

The effect of temperature on the adsorption of In(III) and Ga(III) was investigated at the temperature range of 280–308 K. The results are showed in Figure 3.

It was found that both of the distribution coefficients increased with increase of the temperature. The relationship between temperature and the extraction equilibrium constant was examined to estimate the apparent thermodynamic function ΔH for adsorption and extraction reaction. According to Van't Hoff equation,²⁴

$$\log D = (-\Delta H/2.303RT) + C$$
(8)

where *R* is gas constant and *C* is integral constant.

Both of the plots of log *D* versus 1/T are linear. The enthalpy changes of the adsorption of In(III) at pH 2 and Ga(III) at pH 3 were evaluated as 16.9 and 45.6 kJ/mol, respectively, which mean that both of them

are endothermic reactions and the increase of temperature favors the adsorption of the two ions.

Sorption isotherms

0.99

Figure 4 shows sorption isotherms for each resin/ metal system. Each of these curves exhibits a typical Langmuir isotherm shape, characterized by a strong increase in the sorption capacity at low residual metal concentration followed by an asymptotic trend at high residual concentration. The asymptotic value represents the maximum sorption capacity (q_m : mg/g or mmol/g), and the affinity coefficient of the resin for metal ions (coefficient *b* in the Langmuir equation: L/mg or L/mmol) is correlated to the initial slope of the curve (the slope is equal to $q_m b$). Table II summaries the Langmuir coefficients for each resin/metal system.

Stoichometry of sorption of In and Ga ions by the resin

From the results above, the saturation adsorption capabilities of In(III) and Ga(III) evaluated were 46.8 and 33.9 mg/g or 0.41 and 0.49 mmol/g, respectively. The amount of impregnated extractant in the tested resin determined by NaOH titration was 1.31 mmol/g. The molar ratios of In(III) and Ga(III) to D2EHPA on the resin are then determined as 1:3.20 and 1:2.67, respectively. Both are nearly 1:3. Accordingly, the sorption reaction of metal ions by the resin can be described with the following general reaction (eq. (1) can thus be rewritten as):

$$M^{3+} + 3HL_{(R)} \rightleftharpoons ML_{3(R)} + 3H^+$$
(9)

where M^{3+} denotes In^{3+} or Ga^{3+} .

TABLE III				
Effect of Stripping	Experiments for In(III),	Ga(III), and Zn(II)		

	In(III)		Ga(III)		Zn(II)	
Concentration of HCl/ mol/L	Added HC l/ml	Stripping efficiency/%	Added HCl/ml	Stripping efficiency/%	Added HCl/ml	Stripping efficiency/%
0.05	nd ^a	nd	nd	nd	10–90	93.7
0.10	nd	nd	70-100	90.8	5-30	100.4
0.25	100 ^b -500 ^c	82.5	0-30	100.1	5-25	99.7
0.50	10-100	97.8	0-20	100.5		_
1.0	0-25	99.5	0-20	100.3	_	_
2.0	0-20	101.0	d	_		_
3.0	0-20	100.7		_		_
Optimum concentration/						
mol/L		2.0		0.25		0.1

^a Not detectable.

^b The critical volume of HCl added when In(III) first appeared from the efflent solution.

^c The critical volume of HCl added when In(III) just disappeared from the efflent solution.

^d No experiment was conducted.



Figure 5 Mutual flow chart of In(III), Ga(III), and Zn(II).

Stripping experiment

As indicated in Figure 1, In(III), Ga(III), and Zn(II) were hardly adsorbed by D2EHPA SIR at the high acidity. HCl was used as the stripping agent, as its stripping effect is better than that of sulfuric acid and nitric acid according to the preliminary experiments. Table III lists the relationship among HCl concentration and the amount of HCl added as well as elution percentage of loaded metals on the resin. Table III shows that if 0.10 mol/L hydrochloric acid was used to strip adsorbed Ga (III) and Zn (II) adsorbed from the resin, 30 mL hydrochloric acid could strip all of Zn(II). However, stripping of Ga (III) was only observed after 70 mL of hydrochloric acid was added. This means that Ga (III) and Zn(II) adsorbed on the same resin column could be separated by two steps by using different hydrochloric acid concentrations.

Study of In(iii), Ga(iii), and Zn(ii) extraction from multi-component solutions using D2EHPA SIR

As obtained earlier, In(III), Ga(III), and Zn(II) show different extents of extraction at different pH and dif-

ferent extents of stripping at different concentration. Such differences can be exploited to devise a technique to extraction separation of such three ions with D2EHPA SIR in multi-component mixtures. Discontinuous extraction of In, Ga, and Zn was investigated using the flow sheet given in Figure 5.

A multi-component solution containing 0.2 g/L of each metal ion was prepared in Na_2SO_4 (0.1 mol/L). In(III) was first separated from a ternary mixture by only extracted into resin column I quantitatively at pH 2.0, which was then stripped with 2 mol/L HCl quantitatively. Ga(III) and Zn(II) remained in the aqueous solution. Here, the pH of the solution was adjusted to 3.0, and the two ions were coextracted into resin column II. By taking advantage of the difference in stripping concentrations, Zn(II) was first stripped with 0.1 mol/L, and then Ga(III) with 0.25 mol/L. Table IV shows the results of the separation steps. It shows that nearly complete separation of In(III), Ga(III), and Zn(II) was accomplished.

Cyclic properties of the resin

As mentioned earlier, the separation of In, Ga, and Zn can be achieved by controlling the extraction acidity and selecting different concentrations of stripping solution. However, if this type of resin is applied in industrial scale, it is important to research the possibility of using the resin in a repeated operation. Therefore, taking to adsorb and strip In as an example, the cyclic operation of D2EHPA SIR was examined. One continuous operation to adsorb and strip In is regarded as one cycle. The results are shown in Table V. It was evident that the breakthrough curve and the elution curve in the fifth run were not so much different from that in the first run. This indicates that the loss of D2EHPA from the resin is almost neglected. Hence, the cyclic properties of this resin are well.

CONCLUSIONS

The results showed that the SIR containing D2EHPA gave a theoretical separation of In (III), Ga (III), and Zn (II) from dilute solutions by controlling pH and using different concentration eluents. The results obtained in batch systems were confirmed using fixed-bed systems for the continuous recovery of the metals in

Separation of In(III), Ga(III), and Zn(II) from Simulated Solutions					
Ion	Amount taken/mg	Extraction pH	Stripping agent (HCl)/mol/l	Amount recoveried/mg	Recovery/%
In(III)	2.55	2	2.0	2.51	98.4
Zn(II)	35.6	3	0.1	35.0	98.3
Ga(III)	0.262	3	0.25	0.256	97.7

TABLE IN

Times of cycle	Breakthrough volume/mL	Adsorption capability/mg/g	Stripping volume/mL	Striping efficiency/%
0	29	47.5	25	99.5
1	28	47.3	25	99.9
5	28	47.2	25	99.1

 TABLE V

 Cyclic Properties of D2EHPA Solvent Impregnated Resin in Extracting and Eluting In(III)

single-component solutions with this resin. In multicomponent solutions, this resin placed in columns in series enabled In (III) ion to be successively collected at pH 2 in the first column, while Ga(III) and Zn(II) passed through the column system without being adsorbed and then were collected at pH 3 in the second column. HCl solutions (2 mol/L) led to the desorption of In (III) from the first column. The 0.1 and 0.25 mol/L HCl solutions led to the desorption of Ga (III) and Zn(II) from the second column, respectively. The system produced a complete and selective recovery of the three metals.

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