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# Extraction and separation of In(III), Ga(III) and Zn(II) from sulfate solution using extraction resin

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## Abstract

The separation of In(III), Ga(III) and Zn(II) from sulfate solution has been studied using an extraction resin containing 2-ethylhexyl phosphoric acid mono(2-ethylhexyl) ester (P507 extraction resin). The effect of pH on the extraction of each metal was determined. Extraction isotherms were then constructed at selected pH. Results show that In(III) is first extracted from aqueous solutions at pH 2.0 using this resin while Ga(III) and Zn(II) are co-extracted at pH 3.0. Their separation can be carried out using HCl of different concentrations as eluants. The saturation adsorption capabilities of indium(III) and gallium(III) were evaluated as 47.2 and 31.0 mg/g or 0.41 and 0.44 mmol/g, respectively. The molar ratio of metal ion: P507 reagent on resin was about 1:3. 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 a multi-component solution.

*Keywords:* Separation; Indium(III); Gallium(III); Zinc(II); Extraction resin; P507

## 1. Introduction

The demands for indium and gallium have increased in recent years because they can be used in semiconductor materials such as InP or GaAs. However, there are no discrete reserves of In and Ga, and their global distributions are very sparse. The two metals show similar chemical behavior, and one significant source for them is zinc refinery residue (Nishihama et al., 1999; Zou and Chen, 2002). Due to the strategic importance of these elements, research efforts on their mutual separation and recovery are completely justified. Liquid–liquid extraction has been applied to the practical separation and recovery of indium and gallium from the residue (Paiva, 2001; Mihaylov and Distin, 1992; Jayachandran and Dhadke, 1998; Iyer and Dhadke, 2001; Lee et al., 2002; Zhang et al., 2003). However, the main drawback of the solvent extraction process is related to the loss of extractant resulting from its partial dissolution in the aqueous phase, which may cause environmental hazards and economic limitations. Ion exchange technology can be considered as an alternative method. However it also has some drawbacks: slow adsorption and desorption rates, poor selectivity and requirement of concentrated electrolytes for desorption. Furthermore, the development of highly selective chelating ion exchange resins entails a very tedious and time-consuming search for highly selective functional groups (Casatillo et al., 1999). Therefore, there is a growing interest in the development of new methods for the separation and recovery of indium and gallium.

Since the mid of 1970s, extraction resins (previously called Levextrel resins) have acquired great importance as a technique with interesting features for the recovery and chromatographic separation of metal ions because

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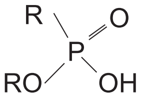
they bridge the gap between two separation techniques of solvent extraction and ion exchange (Marinsky and Marcus, 1981; Jia et al., 2004). They combine the advantages of solid ion exchange for processing highly diluted solutions with the specific properties of the extractants. They exhibit a high distribution ratio and selectivity characteristic of the extractants dissolved in a liquid organic phase combined with the simplicity of equipment and operation characteristic of solid ion exchange technology. Consequently, the resins are very suitable for recovering or scavenging a specified metal ion with high selectivity, for which conventional solvent extraction is unfavorable. They are much easier to use than solvent extraction systems and less expensive than chelating resins (Gonzalez et al., 2001). Furthermore, the extraction characteristics of the resin can be evaluated from previous data on the solvent extraction.

In the past few years, the application of extraction resins in metal extraction and separation processes has focused on hydrometallurgical and analytical applications, and in most cases related to rare metals applications (Wang et al., 2002; Cortina, 1998; Juang, 1999; Marinsky and Marcus, 1997). However, a few types of extraction resins were used in separation and recovery of indium and gallium. The purpose of this study is to investigate the different adsorption and elution behaviors of indium, gallium, and zinc from sulfate solution with an extraction resin containing 2-ethylhexyl phosphoric acid mono (2-ethylhexyl) ester (P507 extraction resin), and to investigate their separation.

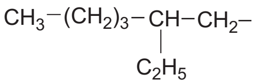
## 2. Experimental

### 2.1. Reagents and analyses

P507 extraction resin was obtained from Beijing Research Institute of Chemistry Engineering and Metallurgy, Ministry of Nuclear Industry, China. The chemical structure of this extractant is as follows:



where *R*:



$$CH_3-(CH_2)_3-\underset{\displaystyle C_2H_5}{\underset{|}{CH}}-CH_2-$$

The elemental analysis of P507 extraction resin showed that the amount of phosphorus contained in the tested resin was 4.02% or 1.30 mmol/g. Indium, gallium and all other chemicals used were of analytical grade and purchased from Shanghai Chemical Reagent Company, China.

The concentration of indium(III) or gallium(III) in a single-component solution was determined spectrophotometrically with a GBC UV–Vis 916 spectrophotometer(Australia) (Zhuzhou Smelter, 1979a; Otomo, 1965). The concentration of zinc(II) in a single metal solution was determined by titration with EDTA at high concentration and by a GBC UV–Vis 916 spectrophotometer at low concentration (Zhuzhou Smelter, 1979b). The concentrations of indium(III), gallium(III) and zinc (II) in multi-component solution were analyzed by using Thermo Jarrell Ash ICP–IRIS Advantage 1000(U.S.A.).

### 2.2. Experimental procedures

#### 2.2.1. Batch test of indium(III), gallium(III) and zinc(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 solution was mixed and shaken in a stoppered glass flask submerged in a thermostatted water bath (Yoshizuka et al., 1990). Based on the preliminary experiments (data not shown), the equilibrium time in the adsorption of indium(III), gallium(III) and zinc(II) was maintained at 2.5, 2.0 and 1.5 h, respectively. The amount of metals adsorbed per gram of 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 a 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).

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

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

#### 2.2.2. Column test for adsorbing and stripping metals

For continuous extraction, extraction resins 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 metal in 0.1 mol/L sodium sulfate and the pH was controlled at the optimum pH for