

RECOVERY OF INDIUM IN A HOLLOW FIBER MEMBRANE PERTRACTOR

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Abstract

In the present work, the recovery of indium from sulfate media using a continuous-type membrane pertractor with hollow fiber geometry was investigated as a study of the feasibility of the industrial application of this pertraction technique. Separation and enrichment of indium with di-(2-ethylhexyl) phosphoric acid in kerosene in hollow fiber-in-fiber membrane pertractor were carried out simultaneously. A series of experiments on the pertraction of indium was performed to investigate the effect of various experimental conditions on the permeation rate. The mechanism of indium pertraction through three-phase membrane system can be explained by diffusion model accompanied by two interfacial reactions.

Key words

Membrane Pertraction, Indium, Permeability, D2EHPA, Hollow Fiber.

1. Introduction

The development of high technology in electronics is expected to cause an increase in demand for indium for industrial applications. Indium is commonly encountered in hydrometallurgical zinc production process at relatively low concentration in aqueous media. One of the widely practiced method for indium recovery is solvent extraction [1]. Di-(2-ethylhexyl) phosphoric acid (abbreviated as D2EHPA) is the typical well-known extractant that has been frequently used [2-3]. Conventional solvent extraction employs dispersion of one phase as drops in another phase and subsequent coalescence of dispersed phase and phase separation. This mode of operation frequently leads to solvent loss by emulsion formation. The loss of costly extractants or chelating agents in indium recovery is detrimental to the process economics. It seems worthwhile to examine possibility of replacement conventional solvent extraction equipment by a membrane contactor providing dispersion-free operation. Supported liquid membrane device has already been studied [4] for indium separation, as well as the separation together with copper in dual membrane extraction [5], and pertraction process [6]. The present paper deal with the influences chemical species concentrations on indium permeation process in a hollow fiber-in-fiber configuration of pertraction module.

2. Experimental

Aqueous solutions of indium ions were prepared by dissolving indium in 500 mol/m³ (Na,H)SO₄, which means that the total sulfate content was kept constant. The organic solutions were prepared by dissolving D2EHPA (Fluka) as a chelating agent in kerosene.

Equilibrium measurements. The distribution ratios of indium ions were measured as follows. Equal volumes of the aqueous and organic solution of known concentrations were shaken in a separating funnel and allowed to attain equilibrium. After about 1 h, the phases were separated and the aliquots of both phases were pipetted to determine the distribution ratio of indium ion.

The indium concentration was determined by atomic absorption spectrophotometry (PYE Unicam SP 9). Prior to chemical analysis indium in the organic phase were stripped with 3 mol/dm³ nitric acid.

Permeation experiments. Simultaneous removal and recovery of indium were done using a hollow fiber-in-fiber module. A schematic of the experimental setup is shown in Fig. 1.

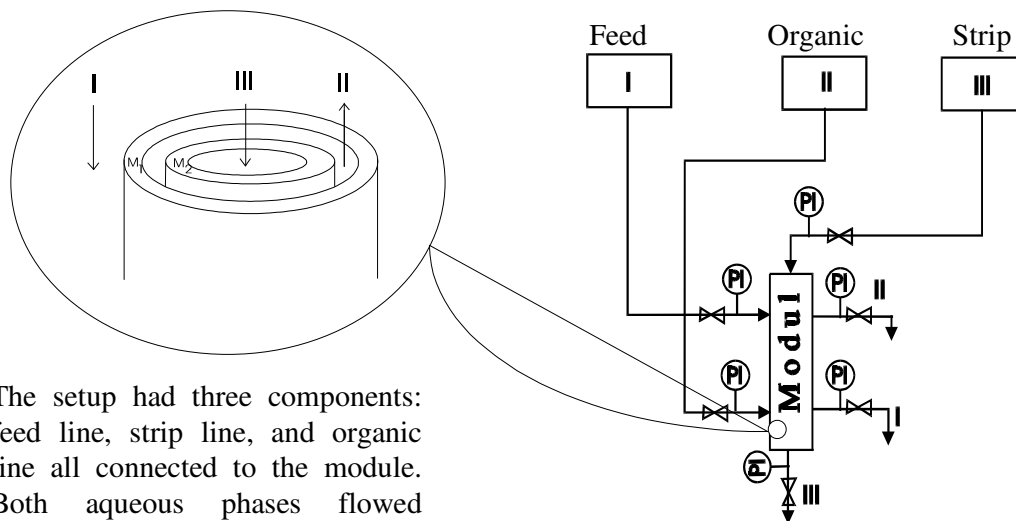


Fig. 1. Apparatus for pertraction

The setup had three components: feed line, strip line, and organic line all connected to the module. Both aqueous phases flowed through tube and the shell side co-currently and the organic extractant flowed counter-currently through the annular space. Since, the fibers were hydrophilic, the aqueous phases wetted the pores in the fiber wall. The phase interfaces were located at the wall of fibers on the organic side by keeping the pressures of the aqueous phases slightly lower than that of the organic phase. The mode of operation was once-through. Aqueous feed and organic solutions were prepared as in the distribution measurements. Strip solution was sulfuric acid in de-ionized water. Concentration of indium was determined using AAS, and pH was controlled by pH-meter (Iscra MA 5725).

3. Results and discussion

Permeation rate is expected to be determined by extraction equilibrium constants, individual mass transfer resistances, and by chemical species concentrations.

3.1. Extraction equilibrium

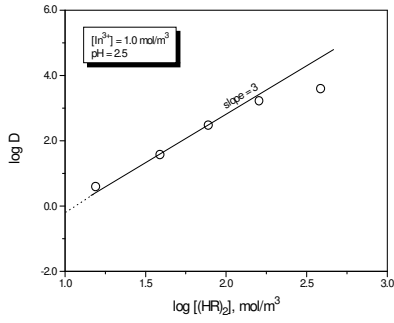


Fig.2. Equilibrium distribution between aqueous and organic phase vs.

D2EHPA concentration.

The extraction of In^{3+} -ions from sulfate media with D2EHPA is expressed as follows:



where $(\text{HR})_2$ is the dimer of the D2EHPA in an organic phase. By modification of eq. (1) can be obtained:

$$\log D = \log K_{\text{ex}} + 3\text{pH}_{(\text{aq.})} + 3\log[(\text{HR})_2]_{(\text{org.})} \quad (2)$$

where D is the distribution coefficient of indium $[\text{InR}_3(\text{HR})_3]_{(\text{org.})}/[\text{In}^{3+}]_{(\text{aq.})}$, and K_{ex} denotes extraction equilibrium constant. The experimental results are plotted in Fig. 2. and Fig. 3. According to eq. (2), and extraction equilibrium constant was obtained. Polymerization of D2EHPA in the organic phase limits the range of linearity in Fig. 2. In Fig. 3. the distribution coefficient decreases monotonically with increasing aqueous acidity. This confirms that extraction is principally dominated by the ion-exchange reaction in which hydrogen ions are liberated.

3.2. Permeation kinetics of indium

From the experimental results, the apparent permeability for indium for extraction end stripping step, $P_{\text{ex,s}}$ is obtained as follows:

$$P_{\text{ex,s}} = E_{\text{ex,s}} \cdot Q_{\text{I,II}} / n \cdot \pi \cdot d_{1,2} \cdot L_{1,2} \quad (3)$$

where $E_{\text{ex,s}}$ is the extent of indium extracted/stripped, $Q_{\text{I,II}}$ is the volumetric flow rate, n , $d_{1,2}$ and $L_{1,2}$ are number, the diameters and the effective lengths of the hollow fibers at the interfaces. Fig. 4. Shows the relation between the permeability of indium, $P_{\text{ex,s}}$ and pH of the feed aqueous phase.

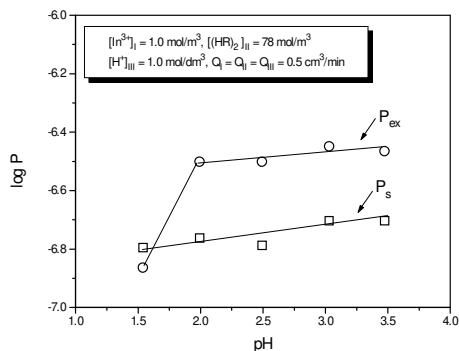


Fig. 4. The permeability of indium vs. pH in the feed.

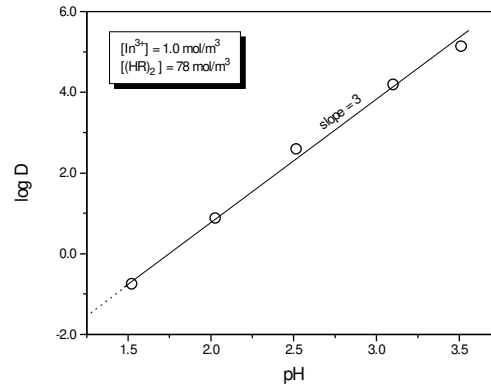


Fig. 3. Equilibrium distribution of indium vs. pH.

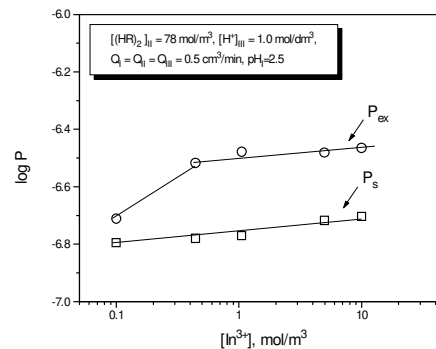


Fig. 5. The permeability of indium vs. indium concentration in the feed.

In the low pH range, the slope of this relation is almost 3. According to this, P is affected by pH. At higher pH, there is no effect of pH on P_{ex} , it is suggested that permeation rate is

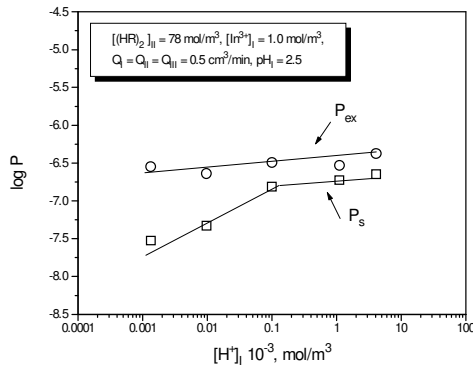


Fig. 7. The permeability of indium hydrogen ion in the strip.

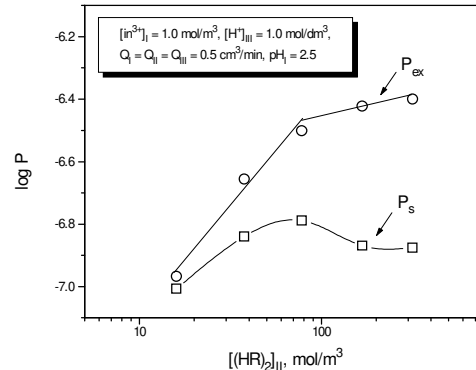


Fig. 6. The permeability of indium vs. D2EHPA concentration in the organic.

controlled by diffusion of the chemical species in the wide range at higher pH. Significant differences between extraction step permeability and stripping step permeability can be explained by no effect of pH on reversible chemical reaction in eq. (1) taking place at the organic-strip interface. The effect of the concentration of the In^{3+} in the aqueous phase on P_{ex} and P_s is shown in Fig. 5. It is found that P_{ex} is proportional to the In^{3+} concentrations at relatively low concentrations, but P_s and P_{ex} at high concentration are almost independent on In^{3+} concentration. Fig. 6. Shows the effect of dimmeric D2EHPA concentration on P_{ex} . It is evident, the P_{ex} values approach a constant value with increasing $(HR)_2$ concentration in organic phase, in the same manner as at pH. The J_s increase with carrier concentration, reaching a maximum at 80 mol/m^3 , and then decreases at higher concentrations (Fig. 6). In Fig. 7. the dependence of $P_{ex,s}$ on hydrogen strip concentration were shown. Since, P_{ex} is not affected until very low concentration is reached. This implies that hydrogen strip concentration is greatly in excess of the required stoichiometric quantity at higher concentration than 0.1 mol/dm^3 . The stripping is much slower than extraction that can be explained by a relatively slow decomposition of In -D2EHPA complex at the organic-strip interface. In this study, effects of the membrane and individual film mass transfer resistances which variation can be done by changing the flow rates and membrane parameters on pertraction kinetics are not considered. However, it could be expected that at diffusion controlled regime, the influence of these parameters can not be neglected.

4. Conclusion

It was clarified that the pertraction mechanism of indium-ion through a hollow fiber-in-fiber type membrane contactor can be explained by a diffusion model accompanied by two interfacial chemical reactions. The extraction rate was controlled by an interfacial reaction at low pH and low In^{3+} concentration in the feed phase and very low $(HR)_2$ concentration in the organic phase. The extraction rate was diffusion limited in wide range at higher pH and higher In^{3+} in the feed and $(HR)_2$ concentration in the organic phase, respectively. The effect of composition of strip solutions on extraction step kinetics can be neglected. The stripping rate was controlled by an interfacial reaction rate at very high and low $(HR)_2$ concentration in the organic phase and low hydrogen concentration in the strip and by the diffusion when hydrogen in the strip solutions is high enough.

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