STUDIES ON IRON(III) REMOVAL FROM CHLORIDE AQUEOUS SOLUTIONS BY SOLVENT EXTRACTION AND TRANSPORT THROUGH POLYMER INCLUSION MEMBRANES WITH D2EHPA

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The removal of iron(III) from chloride acidic aqueous solutions in solvent extraction and transport through polymer inclusion membranes (PIMs) has been studied. D2EHPA was used as the extractant/ion carrier in these processes. The extraction of Fe(III), Mn(II), Ni(II), Cu(II) and Co(II) with 0.5 M D2EHPA was: 73.4 %, 11.2 %, 15.3 %, 7.8 % and 23.9 %, respectively. Separation factors (S) for metal ions were calculated and reported. The transport across PIM containing cellulose triacetate (CTA) as the support and o-nitrophenyl octylether (ONPOE) as the plasticizer was found to be the effective and selective method of Fe(III) ions removal from aqueous chloride solutions containing Mn(II), Ni(II), Cu(II) and Co(II) ions. The stability of PIMs was also studied. Present studies indicate that the transport across PIM has the long term integrity.

key words: iron(III), D2EHPA, solvent extraction, polymer inclusion membranes

INTRODUCTION

Iron(III) is present in the solutions after hydrometallurgical processes of recovering a number of nonferrous metal ions such as nickel(II), cobalt(II) and copper(II). The removal of iron(III) from aqueous solutions is a very difficult. Studies on application of tributyl phosphate (TBP) in selective removal of iron(III) from
solution containing manganese(II), copper(II), nickel(II) and cobalt(II) by solvent extraction and transport through polymer inclusion membranes processes were studied (Pospiech and Walkowiak 2005). The commercial cationic and neutral extractants have been proposed for the extraction in order to separate iron(III) from other metal ions. Several publications have dealt with the application of organophosphorus acids and the derivatives of organophosphorus compounds in separation of iron(III) from aqueous chloride and sulphate solutions, i.e. di(2-ethylhexyl)phosphoric acid (D2EHPA) and di(2-ethylhexyl)phosphonic acid (PC - 88A) (Lupi and Pilone 2000; Biswas and Begum 1998, 1999, 2001; Jayachandran and Dhake 1997), tributyl phosphate (TBP) and methyl \textit{iso}-butyl ketone (MIBK) (Saji and Reddy 2001), trioctylphosphine oxide (TOPO) and Cyanex 923 (Saji et al. 1998; Gupta et al. 2003). Separation of iron(III) and nickel(II) from a spent FeCl$_3$ by solvent extraction using Alamine 336, MIBK and PC 88A as extractants were also investigated (Lee et al. 2005). Comparative study of iron(III) separation from zinc sulphate-sulphuric acid solutions by D2EHPA was performed (Principe and Demopoulos 2004). Separation of iron(III), copper(II) and zinc(II) from a mixed sulphate/chloride solution was carried out using the extractants TBP, LIX 84I and Cyanex 921 in kerosene (Sarangi et al. 2007).

The supported liquid membranes (SLM) and polymer inclusion membranes (PIMs) are used to separate different metal ions such as copper(II), nickel(II), cobalt(II), iron(III) and zinc(II) (Gill et al. 2000, Pospiech and Walkowiak 2007; Parhi and Sarangi 2008; Walkowiak and Kozlowski 2009). Transport of iron(III) through SLM with the phosphine oxide (Cyanex 921) as ion carrier is a very effective method of removal of iron(III) from aqueous solutions (Alguacil and Alonso 2000). For concentration of Cyanex 921 higher than 0.26 M, permeability coefficient was found to be 23 $\mu$m/s and the transport process was controlled by the diffusion in the aqueous stagnant film. Iron(III) can be selectively transported from 2.0 M HCl aqueous solutions containing chromium(VI) by using SLM containing the phosphine oxide (Cyanex 923) as a carrier (Alguacil and Martinez 2000).

The long-term stability of the SLM is a major problem for its wide scale industrial applications. In general, the PIMs are analogous to SLMs in terms of mechanism of ion transport but show better stability as compared to SLM (Scindia et al. 2005). One of the important aspects of PIMs is the distribution of organic carrier in the polymer matrix, which determines their transport efficiency (Tripathi et al. 2003). PIMs have been reported to have better mechanical properties than traditional SLMs and good chemical resistance. The addition of plasticizers is reported to improve the compatibility of the carrier with the polymer, and additionally improve the brittleness and elasticity by creating a polymeric solution. Although PIMs have a higher internal viscosity than SLMs, it has been reported that, for a number of systems the fluxes across both types of membranes are comparable. In other cases higher fluxes of transport across PIMs have been investigated (Salazar-Alvarez et al. 2005, Gardner et
al. 2004). A number of new types of PIMs using various cellulose derivatives were described. These membranes have been characterized with respect to their durability against hydrolysis under alkaline and acidic conditions.

Recently, the transport of metal ions by polymer inclusion membranes has been reviewed (Nghiem et al. 2007). The competitive transport of metal ions such as Cr(VI), Cd(II), Zn(II), Sr(II), Cs(I), and Co(II) across PIMs was investigated (Kozlowski et al. 2002, 2007, 2008).

The present work examines the possibility of iron(III) separation from solution containing manganese(II), copper(II), nickel(II), and cobalt(II) by solvent extraction and transport through polymeric inclusion membranes processes with D2EHPA as the extractant/ion carrier. The effect of extractant concentration, the kinetics and efficiency parameters of transport through polymer inclusion membranes have been investigated. The stability of polymer inclusion membranes has also been studied.

**EXPERIMENTAL**

**REAGENTS**

Inorganic chemicals, i.e. iron(III), manganese(II), nickel(II), cobalt(II), and copper(II) chlorides, sodium chloride, and hydrochloric acid were of analytical grade and were purchased from POCh (Gliwice, Poland). Organic reagents, i.e. cellulose triacetate (CTA), o-nitrophenyl octyl ether (ONPOE), di(2-ethylhexyl)phosphoric acid (D2EHPA) and dichloromethane were of analytical reagent grade (Fluka) and used without further purification. Distilled kerosene was used as the diluent in solvent extraction. The density of plasticizer, i.e. ONPOE, was 1.04 g cm$^{-3}$. Aqueous solutions were prepared with twice distilled water, with a conductivity of 0.1 $\mu$S m$^{-1}$.

**PROCEDURE**

**SOLVENT EXTRACTION**

Solvent extraction was carried out using equal volumes of both phases (10 cm$^3$ each) which were mechanically shaken (200 min$^{-1}$) for 20 minutes at the constant temperature (25 $\pm$ 2 $^\circ$C). The metal ions content in the aqueous phase has been determined by means of AAS Solar 939 (Unicam) spectrophotometer, while the pH value has been measured with a CX-731 (Elmetron) pH-meter. The concentration of metals in the organic phase was calculated from the mass balance.
POlYMER INCLUSION MEMBRANE

Organic solutions of cellulose triacetate (CTA), ion carriers (D2EHPA), and plasticizer (ONPOE) in dichloromethane were prepared. A portion of solution was poured into a membrane mold comprised of a 6.0 cm glass ring attached to a glass plate with CTA-dichloromethane glue. The organic solvent was allowed to evaporate overnight and the resultant membrane was separated from the glass plate by immersion in cold water. The membrane was soaked in 0.10 M HCl aqueous solution for 12 hours and stored in distilled water.

MEMBRANE TRANSPORT EXPERIMENTS

The transport across PIMs was carried out in a permeation cell in which the membrane film was tightly clamped between two cell compartments. The effective membrane area, which was exposed to both phases, was 3.14 cm². Both, the source and receiving aqueous phases (50 cm³ each) were stirred at 600 rpm with synchronous motors. The PIM transport experiments were conducted at room temperature (22-25 °C). The permeation of iron(III) was monitored by periodical sampling (0.1 cm³ each) of the source phase. After appropriate dilution, samples were analyzed by an atomic absorption spectrophotometer. The source phase acidity was controlled by pH-meter (Cx-731 Elmetron, with a combined pH electrode, EFH-136, Hydromet, Poland), pH was kept constant by adding to the source phase periodically aqueous solution of 2.0 M HCl.

RESULTS AND DISCUSSION

The solvent extraction of Fe(III) from aqueous chloride solutions containing Mn(II), Ni(II), Co(II), and Cu(II)

The extraction behavior of 0.10 M Fe(III), 0.30 M Mn(II), 0.020 M Ni(II), 0.010 M Cu(II), 0.0020 M Co(II) from 1.0 M hydrochloric acid and 2.0 M sodium chloride with D2EHPA in kerosene as the solvent has been studied. The composition of this aqueous solution is very similar to aqueous solutions after leaching of polymetallic nodules (Jana 1993). Percent extraction of Fe(III) increased with increasing extractant concentration in organic phase (Fig. 1).

As it can be seen from this figure extraction of Fe(III) was the highest for 0.5 M D2EHPA and equal to 73.4 %. Extraction of others metal ions was much lower. Extraction of Mn(II), Ni(II), Cu(II) and Co(II) with 0.5 M D2EHPA was low and amounted to: 11.2 %, 15.3 %, 7.8 % and 23.9 %, respectively. The values of selectivity coefficients are presented in Table 1.
Studies on iron(III) removal from chloride aqueous solutions by solvent extraction and transport ...

Fig. 1. The dependence of Fe(III), Mn(II), Ni(II), Cu(II) and Co(II) extraction percent (% E) from chloride solution on D2EHPA concentration. Organic phase: 0.1 - 0.5 M D2EHPA in kerosene. Aqueous phase: of 0.10 M Fe(III), 0.30 M Mn(II), 0.020 M Ni(II), 0.010 M Cu(II), 0.0020 M Co(II), 1.0 M HCl and 2.0 M NaCl.

Table 1. Selectivity coefficients of Fe(III) over Mn(II), Ni(II), Co(II) and Cu(II) for different D2EHPA concentrations in solvent extraction process. Conditions of experiments as in Fig. 1.

<table>
<thead>
<tr>
<th>Selectivity coefficient, ( S )</th>
<th>D2EHPA, M</th>
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<tbody>
<tr>
<td></td>
<td>0.1</td>
</tr>
<tr>
<td>( S_{Fe(III)/Mn(II)} )</td>
<td>1.50</td>
</tr>
<tr>
<td>( S_{Fe(III)/Ni(II)} )</td>
<td>1.13</td>
</tr>
<tr>
<td>( S_{Fe(III)/Co(II)} )</td>
<td>2.21</td>
</tr>
<tr>
<td>( S_{Fe(III)/Cu(II)} )</td>
<td>0.79</td>
</tr>
</tbody>
</table>

The selectivity of Fe(III) over the other metals ions is a very important process parameter. The investigation found that the selectivity coefficient depends on the extractant concentration in organic phase. The results indicate that the selectivity coefficient increases with increasing D2EHPA concentration.

In this project a preliminary attempt was to find out which iron(III) species are preferably extracted. Literature reports that iron(III) forms various chloride complexes with increase of chloride concentration in aqueous phase. Dependence of the fractions of Fe\(^{3+}\)-Cl\(^-\) (\( \alpha \) \cdot 100%) on chloride ions concentration in aqueous solution (on the ground of the values of stability constants of metal-ion complexes at constant ionic strength I = 4.0 for Fe(III), *Stability Constans of Metal-Ion Complexes, Part A: Inorganic Ligands, Pergamon Press*) was presented in Fig. 2.
The results presented in Fig. 2 indicate that at 4.0 M Cl⁻ concentrations in the aqueous solution, iron(III) exists as 0.70 % Fe³⁺, 22.47 % FeCl₂⁺ and 76.83% FeCl₃⁺. The difference in extraction behaviour of these metals was attributed to the fact that the extraction of Fe(III) is favored from chloride media under these conditions in comparison with other metal ions. It would be possible to separate iron(III) and manganese(II), nickel(II), cobalt(II) and copper(II).

**TRANSPORT OF IRON(III) ACROSS POLYMER INCLUSION MEMBRANES FROM AQUEOUS CHLORIDE SOLUTIONS**

**THE KINETICS OF PIM TRANSPORT**

The polymer inclusion membranes transport of iron(III) from aqueous solution containing 0.10 M Fe(III), 0.30 M Mn(II), 0.020 M Ni(II), 0.010 M Cu(II) and 0.0020 M Co(II), in 1.0 M HCl and 2.0 M NaCl was also studied. D2EHPA as the ion carrier was used. The polymer inclusion membrane contained: 0.0375 g CTA, 2.0 M ion carrier (based on plasticizer and carrier) and 2.66 cm³ ONPOE/1 g CTA. The inclusion membrane composed of: CTA – 19.28 %, ONPOE – 53.47 % and D2EHPA – 27.25 %. The kinetics of PIM transport was calculated by a first order reaction rate:

\[
\ln \left( \frac{c}{c_i} \right) = -kt
\]
Studies on iron(III) removal from chloride aqueous solutions by solvent extraction and transport ...

where: \( c \) is the metal ion concentration (M) in the source phase at some given time, \( c_i \) is the initial metal ion concentration (M) in the source phase, \( k \) is the rate constant (s\(^{-1}\)), and \( t \) is the time of transport (s).

To calculate the \( k \) value, a plot of \( \ln(c/c_i) \) versus time was prepared. The rate constant value for the duplicate transport experiment was averaged and standard deviation was calculated. The initial input flux (\( J_i \)) was determined as equal to:

\[
J_i = \frac{V}{A} \cdot k \cdot c_i
\]  

(2)

where \( V \) is volume of the aqueous source phase (m\(^3\)), and \( A \) is an area of effective membrane (m\(^2\)).

The results obtained for the iron(III) transport into distilled water as the receiving phase are presented in Fig. 3.

Fig. 3. Kinetics of 0.10 M Fe(III) transport through PIM with 2.0 M D2EHPA. Receiving phase: distilled water; PIM: 0.0375 g CTA, 2.66 cm\(^3\) ONPOE/1 g CTA.

As it can be seen from this figure the initial flux was equal to 15.87 \( \mu \text{mol m}^{-2} \text{s}^{-1} \). To calculate the \( k \) value, the plot of \( \ln(c/c_i) \) versus time was made. The relation of \( \ln(c/c_i) \) versus time is linear, which was confirmed by high values of determination coefficients \( (r^2) \). The value of this coefficients was equal to 0.98. In this experiment of polymer inclusion membrane transport no manganese(II), nickel(II), copper(II) and cobalt(II) ions were detected in the receiving phase. That shows that under the conditions of the experiment iron(III) can be effectively separated from other metal ions present in this source aqueous phase with investigated ion carrier.
LONG TERM STABILITY OF THE POLYMER INCLUSION MEMBRANES

Membrane stability was also investigated by performing three transport cycles in 72 h. After each cycle, the solutions were removed from the permuation cell and the membrane was washed: feed and strip compartments were filled with fresh distilled water (30 min.). The stability of PIMs in the transport of iron(III) was studied using D2EHPA as the carrier. We used the same membrane with 2.0 M D2EHPA. The flux of Fe(III) varied slightly at the beginning, but after three cycle the flux decreased considerably. Results are summarized in Table 2.

Table 2. Values of the permeability coefficient \( P \) after each cycle in Fig. 4

<table>
<thead>
<tr>
<th>Cycle number</th>
<th>Permeability coefficient, ( P (\mu m s^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.158</td>
</tr>
<tr>
<td>2</td>
<td>0.142</td>
</tr>
<tr>
<td>3</td>
<td>0.111</td>
</tr>
</tbody>
</table>

The fact that stability of liquid membrane depended on different parameters (Szpakowska and Nagy 1997) suggested that solute-solvent (and polymer solvent) interactions play a dominant role in membrane stability. The influence of different experimental conditions on the transport rate allowed to establish various factors determining membrane stability. One of the major factors is that the membrane solvent and the organic carrier are lost to the aqueous phase, limiting the durability of the membrane. Several authors have reported that polymer inclusion membranes show good long – term stabilities, although in general lower fluxes can be obtained with this kind of membranes due to their high viscosity (Aguilar et al. 2001).

CONCLUSION

Di(2-ethylhexyl)phosphoric acid (D2EHPA) used as extractants in solvent extraction process allow for selective removal of iron(III) from acidic aqueous solutions containing Mn(II), Ni(II), Co(II), and Cu(II). The investigation indicated that the selectivity coefficient depended on the extractant concentration in organic phase. Also, transport across polymer inclusion membranes with D2EHPA as the ionic carrier, orto-nitrophenyl octylether (ONPOE) as the plasticizer, and cellulose triacetate as the support into hydrochloric acid aqueous solution as the receiving phase was found to be very selective for iron(III) removal from acidic aqueous chloride solutions containing Mn(II), Ni(II), Co(II), and Cu(II). No other metals excluding Fe(III) were detected in the receiving aqueous phase.
The results of this study show that in order to achieve long-term stability of the PIM the organophosphorous acid (D2EHPA) as the ion carrier can be used.

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