

# Removal of Zn(II) from chloride acidic solutions with hydrophobic quaternary salts

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The equilibrium of zinc(II) extraction from hydrochloric acid solutions with phosphonium and ammonium quaternary salts and their application as carriers in polymer inclusion membranes were studied. The most efficient was the extraction of zinc with the use of chlorides and bromide of ammonium and phosphonium salt (more than 90%). Quaternary ammonium and phosphonium chlorides and bromide are efficient extractants of zinc(II) from hydrochloric acid solutions. Two-fold molar excess of extractant over Zn(II) is necessary for efficient extraction (100%). Solvent extraction power of the extractants studied decreases with increasing hydrophobicity of the anion in the following sequence: QPCL > QPBr > QPBis > QACL > QABF<sub>4</sub> > QPBF<sub>4</sub> > QPPF<sub>6</sub> > QPNtf<sub>2</sub>. A solution of 1 M H<sub>2</sub>SO<sub>4</sub> is chosen as the best stripping phase from the technological and economical point of view. Transport across polymeric inclusion membrane enables concentration of the stripping solution; however it takes a very long time.

**Keywords:** Zinc(II) extraction, quaternary salts, polymer inclusion membranes.

## INTRODUCTION

Protection of the natural environment is one of the most important issues of the contemporary world. Although the zero charge and harmless technologies are the ideal solution, in some industrial fields they are not achievable. Then, the only solution is to reduce waste streams dumped into the environment and recycle or recover the chemicals.

Construction industry is nowadays based on the use of steel elements that are threatened with corrosion. There are a few methods developed to protect steel from corrosion, one of them is hot-dip galvanizing. This method is applied on industrial scale because the hot-dip galvanized elements are very resistant and well protected from the unfavorable atmospheric conditions. Pickling is one of the steps of preparation of steel surface for galvanizing. Waste streams generated after pickling contain mainly zinc and iron ions (5 – 150 g/dm<sup>3</sup>) and must be recycled or utilized. Selective zinc recovery from spent pickling solutions is an important issue in Poland, where there are more than 50 hot-dip galvanizing plants. Zinc(II) content in the waste streams should not exceed 2 mg/dm<sup>3</sup><sup>1</sup>. Therefore, the treatment of spent pickling solutions is a key issue in hot-dip galvanizing plants. Regeneration of the solutions enables recycling of pickling acid and recovery of metals.

Liquid-liquid extraction is one of the methods applied for treatment of spent pickling solutions<sup>2</sup>. There are many commercial extractants (solvating, base and acidic) used for zinc(II) recovery from hydrochloric acid solutions. The criteria of extractant suitability for spent pickling solution regeneration confirmed by Australian researchers<sup>3</sup> are as follows: good phase disengagement after extraction and stripping, high selectivity of zinc(II) extraction over iron(II) and easy zinc(II) stripping with water.

As a result of an increasing number of literature records on ILs, we propose recovery of zinc and iron ions from spent pickling solutions with phosphonium quaternary salts (classified as ILs). Some reports concerning phosphonium ILs in extraction systems have been available to-date, and

these agents are considered to be prospective for substance separation. Quaternary organic salts, called ionic liquids, are liquid at 100°C, and consist of organic cation and organic or inorganic anion<sup>4</sup>. Depending on the cation and anion used, the properties of ILs, i.e. their viscosity, cloud point and solubility in water, can vary. It is the anion that influences the hydrophobicity of ILs. Most of ionic liquids containing a chloride anion are miscible in water, while those comprising PF<sub>6</sub><sup>-</sup> or N(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub><sup>-</sup> are highly hydrophobic. A great advantage of ILs is their easiness to replace the anion that makes it possible to design compounds with required properties, suited to the particular system<sup>5, 6</sup>.

It is the aim of this work to study the equilibrium of zinc(II) extraction from hydrochloric acid solutions with phosphonium and ammonium quaternary salts, and to apply them as carriers in polymer inclusion membranes.

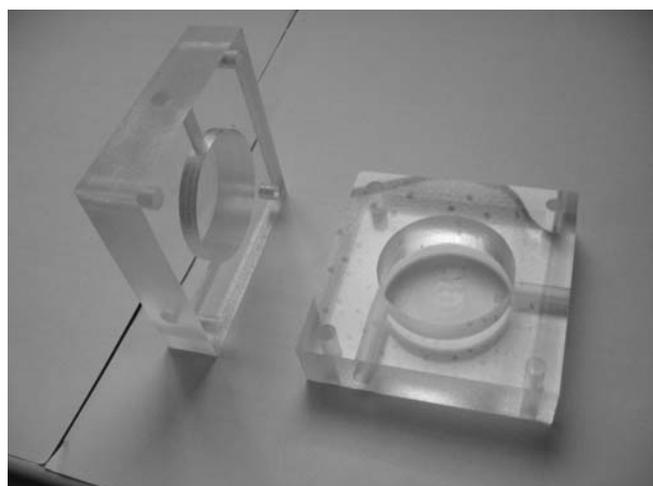
## EXPERIMENTAL

The structures of the applied quaternary salts are presented in Table 1. They are abbreviated as QP (quaternary phosphonium) or QA (quaternary ammonium) and the appropriate anion. All the quaternary salts were diluted in toluene (0.2 M). Their concentrations were suggested by the results of our study of trihexyl(tetradecyl)phosphonium chloride<sup>7</sup>.

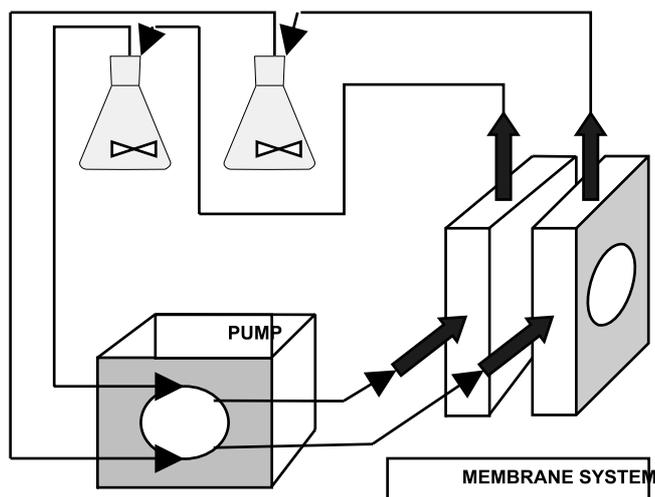
Model aqueous feed contained 5 g/dm<sup>3</sup> (0.077 M) Zn(II); 1.8% (0.58 M) HCl; 5 M Cl<sup>-</sup> (chloride content was adjusted with NaCl). All the chemicals were used as received.

Solvent extraction was carried out in a typical way at 20°C. The same volumes of both phases 5 cm<sup>3</sup> were mechanically shaken in separatory funnels, then left to stand for separation. Volume ratio of 1 gave twofold excess of extractant to the metal ion extracted. The aqueous phase was analyzed for zinc(II) content, and the organic phase was taken for stripping. Several solutions of salts and acids were used as zinc(II) strippants from the loaded organic phase.





a)



b)

Figure 1. a) Measurement module (sandwich type) and b) polymer inclusion membrane system

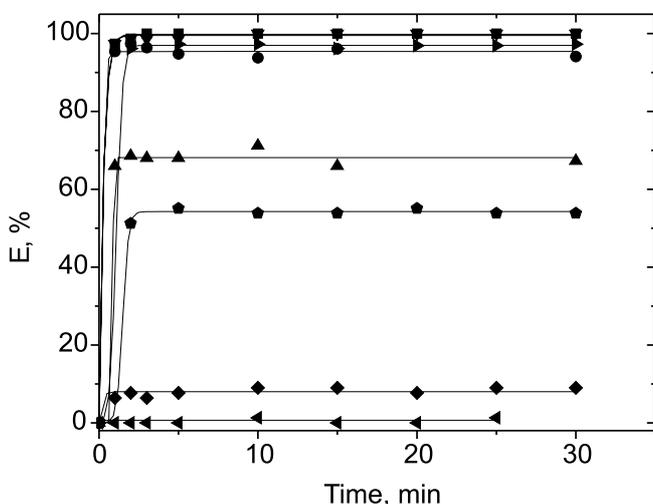


Figure 2. Extraction of Zn(II) vs. time with 0.2 M QPCL (■), QACL (●), QPBr (▼), QPNtf<sub>2</sub> (►), QABF<sub>4</sub> (▲), QPBF<sub>4</sub> (●), QPBis (◆), QPPF<sub>4</sub> (◄) (Aqueous feed: 5 g/dm<sup>3</sup> Zn(II), 1.8% HCl, 5 M Cl<sup>-</sup>)

composed of a big organic anion originated from Cyanex 272, well known as zinc(II) extractant from sulfates, extracts efficiently zinc(II) from chlorides. Salts with more hydrophobic anions (BF<sub>4</sub><sup>-</sup>) extract about 60% of Zn(II) ions, while the most hydrophobic, Ntf<sub>2</sub><sup>-</sup> and PF<sub>6</sub><sup>-</sup>, extract only up to 1 and 10%, respectively.

The extraction isotherms for zinc(II) are steep for small concentrations of metal ion and reach plateau for each organic phase (Fig. 3). Their nonlinear character means that a chemical reaction occurs in the systems studied. It is possible to load QPBr and QPCL with zinc(II) to a maximum capacity near 7 g/dm<sup>3</sup>. The isotherms for quaternary ammonium salts are not so steep as for quaternary phosphonium salts, and zinc(II) content in the loaded organic phase slightly decreases from 6.5 g/dm<sup>3</sup> to 6.2 g/dm<sup>3</sup> for Cl<sup>-</sup> and BF<sub>4</sub><sup>-</sup> anions, respectively. Solvent extraction of zinc(II) with QPPF<sub>6</sub> is weak, only 1.5 g/dm<sup>3</sup> Zn(II) is transported to the organic phase. QPBr and QPCL are the best extractants in the system studied. 0.2 M solution of extractant removes 0.1 M Zn(II) from the feed, which indicates that twofold molar excess of extractant over Zn(II) is necessary for efficient extraction.

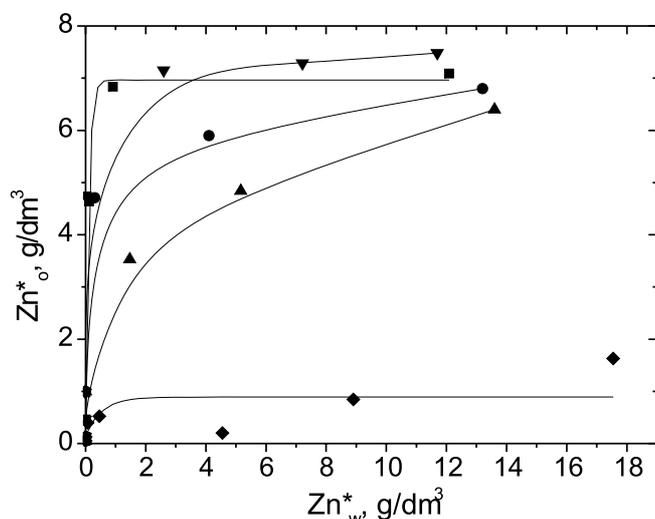


Figure 3. The isotherms of zinc(II) extraction with 0.2 M QPCL (■), QPBr (▼), QACL (●), QABF<sub>4</sub> (▲), QPPF<sub>4</sub> (◆) (Aqueous feed: 0.05 – 20 g/dm<sup>3</sup> Zn(II), 1.8% HCl, 5 M Cl<sup>-</sup>)

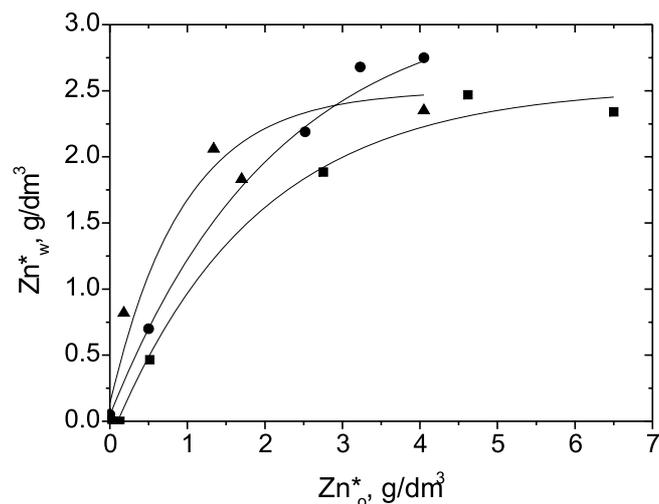
### Classical stripping

Various stripping phases were tested to strip zinc(II) from the loaded organic phases: 1 M H<sub>2</sub>SO<sub>4</sub>, 1 M Na<sub>2</sub>SO<sub>4</sub>, 1; 5 and 6 M HCl, 1 M KSCN, water, 0.05 M EDTA, ammoniacal buffer pH 10. The stripping efficiency for one step of stripping is presented in Table 2. Zinc(II) was stripped from four organic phases (QPCL, QPBr, QACL, QABF<sub>4</sub>) loaded up to 5 g/dm<sup>3</sup>.

The results indicate EDTA solution as the best strippant from among quaternary ammonium salts (100%). Stripping from QPCL is less efficient (near 50%). However zinc(II) forms with EDTA strongly bounded complex that makes it difficult to separate pure metal from this stripping solution. From the technological point of view, EDTA was not used in further stripping investigation. Moreover, it is much more expensive than H<sub>2</sub>SO<sub>4</sub>, which is also an efficient strippant (near 50%). It means that at least two steps of stripping are necessary to efficiently recover zinc(II) from the organic phases studied with this acid. Application of 1 M H<sub>2</sub>SO<sub>4</sub> is economically justified and enables further treatment of zinc(II) sulfate.

**Table 2.** Stripping efficiency from the loaded organic phases for various stripping solutions

Stripping solution	Stripping efficiency from the loaded organic phase, %			
	QPCI	QPBr	QACl	QABF <sub>4</sub>
1 M H <sub>2</sub> SO <sub>4</sub>	40.6	27.4	43.8	41.2
1 M Na <sub>2</sub> SO <sub>4</sub>	35.0	30.1	39.2	33.0
1 M HCl	2.8	0.0	2.0	4.0
5 M HCl	1.4	0.0	–	–
1 M KSCN	0.0	0.0	–	–
H <sub>2</sub> O	16.8	15.5	0.0	0.0
0.05 M EDTA	59.3	–	100	100
6 M HCl	–	0.0	–	–
Buffer pH 10	100	100	–	–

**Figure 4.** The isotherms of zinc(II) stripping with 1 M H<sub>2</sub>SO<sub>4</sub> from loaded QPCI (■), QPBr (●), QACl (▲) (Organic phase loaded to ~ 8 g/dm<sup>3</sup> Zn(II))

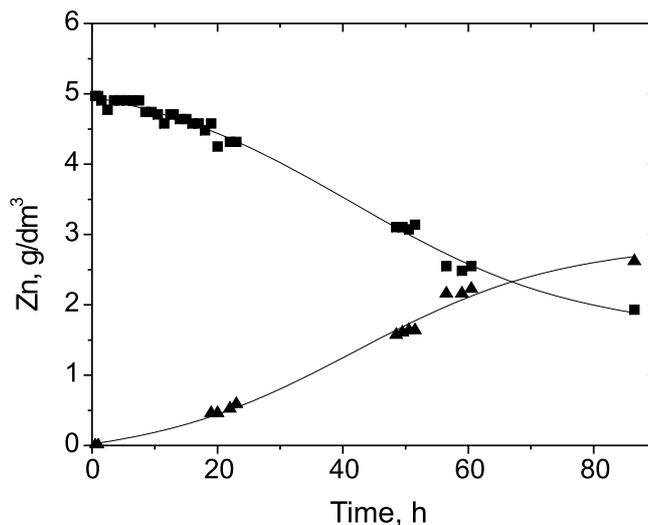
Thus, stripping isotherms are shown for 1 M H<sub>2</sub>SO<sub>4</sub> as stripping phase (Fig. 4). They indicate that zinc(II) can be stripped most efficiently from QACl (almost 2.8 g/dm<sup>3</sup> Zn(II)). However, stripping from loaded QPCl and QPBr enables recovery of 2.5 g/dm<sup>3</sup> of zinc(II). Stripping isotherms are not linear ones.

#### Extraction-stripping in PIM

Equilibrium studies point that quaternary phosphonium chloride is an efficient organic phase for zinc(II) extraction from hydrochloric acid solution. However, it must be applied in solution with toluene to overcome problems with high viscosity of the phosphonium chloride itself. To eliminate the diluent the authors carried out studies in polymer inclusion membranes containing QPCl as a carrier. PIM enables simultaneous extraction-stripping process in small module. Flow rates of the feed and stripping solution were equal to 0.25 cm<sup>3</sup>/s. QPCl concentration in the membrane amounted 20%.

Preliminary investigation with 20% of QACl as a carrier showed that long time of the experiment is a drawback of the technique. After more than 60 hours, the concentration of zinc(II) in the feed decreased to half of the initial value. Change in zinc(II) content in the stripping phase is slower than in the feed.

The authors are aware that CTA is susceptible to hydrolysis in a contact with H<sub>2</sub>SO<sub>4</sub><sup>13,14</sup>. Thus, as a next step of the investigation on PIM, PVC will be applied as a polymeric matrix.

**Figure 5.** Change of zinc(II) concentration in time during membrane extraction-stripping process in the feed (■), and the stripping solution (▲) (Aqueous feed: 5 g/dm<sup>3</sup> Zn(II), 1.8% HCl, 5 M Cl<sup>-</sup> flow 0.25 cm<sup>3</sup>/s, Stripping solution: 1 M H<sub>2</sub>SO<sub>4</sub>, flow 0.25 cm<sup>3</sup>/s, PIM carrier: QPCl 20%)

#### CONCLUSIONS

1. Quaternary ammonium and phosphonium chlorides and bromide are efficient extractants of zinc(II) from hydrochloric acid solutions.
2. Extraction equilibrium is achieved in 5 minutes. Twofold molar excess of the extractant over Zn(II) is necessary for efficient extraction (100%).
3. Extraction power of the extractants studied decreases with increasing hydrophobicity of the anion in the following sequence: QPCl > QPBr > QPBis > QACl > QABF<sub>4</sub> > QPBF<sub>4</sub> > QPPF<sub>6</sub> > QPNtf<sub>2</sub>.
4. 1 M H<sub>2</sub>SO<sub>4</sub> is chosen as the best stripping phase from the technological and economical points of view.
5. Transport across polymeric inclusion membrane enables concentration of the stripping solution, however it takes very long time.

#### ACKNOWLEDGEMENT

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