

*Received April 18, 2012; reviewed; accepted July 11, 2012*

## LEAD(II) REMOVAL FROM AQUEOUS SOLUTIONS BY SOLVENT EXTRACTION WITH TETRACARBOXYLRESORCIN[4]ARENE

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**Abstract:** A novel tetracarboxylresorcin[4]arene was synthesized and its selective complexing ability towards Pb(II) ions was examined. The influence of several parameters such as pH of aqueous phase, agitation time, extractant and modifier concentrations on solvent extraction of Pb(II) ions from the aqueous nitrate phase into chloroform organic phase was studied. The stoichiometry of the formed metal-ligand complexes was established by slope analysis. Pb(II) ions were quantitatively extracted in the form of 2:1 Pb(II)-resorcin[4]arene complex from aqueous solutions of pH 5.5 to the solution of ligand in chloroform. Competitive solvent extraction experiments in the presence of Zn(II) and Cd(II) ions were also carried out and high selectivity of the extractant towards Pb(II) over Zn(II) and Cd(II) was found. The selectivity order was: Pb(II) >> Cd(II) > Zn(II).

**Keywords:** solvent extraction, lead(II), zinc(II), cadmium(II), resorcinarene

### Introduction

For many years solvent extraction has been one of the most used techniques for the removal and separation of heavy metal ions in the industrial scale processes. The general advantage of solvent extraction over traditional methods used for wastewaters treatment (chemical precipitation, coagulation-flocculation, ion exchange, adsorption, membrane filtration) is highly selective metal recovery from aqueous solutions (> 500 mg/dm<sup>3</sup>) during continuous operations. The efficiency of metal ion extraction depends on many parameters such as ligand structure, solution pH, type of solvent, temperature and time of process, however the extractant ability to form a metal-ligand complex has a crucial effect on the process selectivity. Therefore, results of wide studies dealing with extractive removal and separation of Pb(II) ions with the use of

commercially available chemicals *e.g.* di(2-ethylhexyl)phosphoric acid – D2EHPA (Holdich and Lawson, 1985; Gherasim et al., 2011), CYANEX (Menoyo et al., 2001; Kozłowska et al. 2007), tributyl phosphate – TBP (Arous et al., 2010), aromatic hydroxyoximes – LIX (Rodriguez et al., 1997) and newly synthesized macrocycles such as lariat and crown ethers (Kalmykov et al., 1998; Walkowiak and Kozłowski, 2009), calixarenes and calixcrowns (Roundhill et al., 2009) as extractants carried out in various extraction systems were reported.

Calix[n]arene-based compounds with different groups such as carboxylic, ester, amide, thioamide and acetylhydrazide moieties functionalizing phenolic oxygen atoms of calixarene or thiacalixarene platform were applied for Pb(II) extraction. It was noted that calixarenes functionalized with proton-ionizable groups such as carboxylic acids have a better complexing ability towards lead ions than their analogs with non-ionizable (*e.g.* ester) groups or non substituted hydroxyl groups (Toumi et al., 2008). Many researchers have found that carboxyl derivatives of calix[n]arenes are efficient extractants of lead ions and that the number of attached carboxylic groups, conformational structure of these ligands and cavity size of basic skeleton play a crucial role in a Pb(II) ions complexation. Mono-, di- (Yang et al., 2011; Park et al., 2010), tetra- (Ohto et al., 1999) and pentaacids (Adhikari et al., 2010) were used as a Pb(II) complexing agents and it was observed that incorporation of more proton-ionizable groups to the calixarene skeleton enhanced its binding affinity and selectivity towards Pb(II) ions. Ohto et al. (1999) reported high efficiency and selectivity of Pb(II) extraction over Zn(II), Cu(II), Fe(III) and Al(III) by tetracarboxylcalix[4]arene with following selectivity orders: Pb(II) > Fe(III) > Cu(II) > Zn(II).

The results presented by Park et al. (2010) show that the mixed calix[4]arene possessing two carboxylic and two butyloxy groups on the narrow rim occurring in 1,3-alternate, partial cone (with butyl groups up) and cone conformations was an efficient extractant of lead ions at equilibrium pH of aqueous phase equal to 5.0, but the change of isomeric forms to partial cone with carboxyl groups decreased the complexing ability of this ligand.

One of the most promising and intensively studied class of macrocycles related to calixarenes are calix[n]resorcinarenes, named also resorcin[n]arenes. They are products of the acid-catalyzed condensation reaction of resorcinol with an aldehyde. Resorcinarenes differ from calixarenes in the spacing of the phenolic hydroxyl groups (the upper wide rim) and have more functionalization sites in the molecule (from 2 to 16 sites for resorcin[4]arenes) than calixarenes, therefore the different extractive properties of resorcinarenes towards metal ions than those of calixarenes should be expected. Although many resorcin[n]arenes (usually  $n = 4, 6$ ) were synthesized (Kozłowski et al., 2010), there are only very few examples of their separation properties towards metal ions, especially transition and post-transition metal ions (Jain and Kanaiya, 2011). Podychaev et al. (2009) quantitatively extracted Pb(II) ions from nitrate aqueous solution (pH = 6.0) containing  $2.5 \cdot 10^{-4}$  M picric acid to chloroform phase with tetranonylcalix[4]resorcinarene bearing acetylhydrazone groups. Only non-

ionizable resorcin[4]arenes modified by methylene bridges were applied for Pb(II) ions removal in membrane extraction by using polymer inclusion membranes; in this process the transport of about 80% Pb(II) ions to nitric acid was observed (Benosmane et al., 2009; 2010). In the analogy to calixarenes, resorcinarenes with attached proton-ionizable carboxylic groups should be more efficient and selective extractants for Pb(II) ions in comparison to corresponding non-ionizable compounds.

We synthesized tetracarboxylresorcin[4]arene and studied its extraction behavior towards Pb(II) ions. The influence of parameters such as the agitation time, the ligand and modifier concentrations and pH of aqueous phase on process efficiency was discussed. Selectivity of the ligand towards Pb(II) was also evaluated by a competitive extraction with Pb(II), Zn(II) and Cd(II) ions.

## Experimental part

### Reagents

Tetracarboxylresorcin[4]arene  $R(\text{COOH})_4$  was synthesized in two steps. In the first step involving the acid catalyzed condensation of resorcinol with dodecanal, the undecylresorcin[4]arene was obtained (Schantwinkel et al., 2008). This compound was functionalized by  $\alpha$ -bromoacetic acid in the presence of NaH in dry THF, according to procedure similar to that described by Demirel et al. (2003). The structure of the compound presented in Fig. 1 was confirmed by  $^1\text{H}$  NMR spectroscopy (500MHz,  $\text{DMSO-d}_6$ ),  $\delta$ : 0.825 (t, 12H,  $J = 7,5$  Hz,  $\text{CH}_3$ ), 1.12–1.125 (m, 72H,  $\text{CH}_3(\text{CH}_2)_9$ ), 1.824 (m, 8H,  $\text{CH}_2\text{CH}$ ), 4.24 (m, 4H,  $\text{ArCHAr}$ ), 4.51 (s, 8H,  $\text{OCH}_2\text{COOH}$ ), 6.30 (s, 4H,  $\text{ArH}$ ), 6.38 (s, 4H,  $\text{ArH}$ ), 8.80 (s, 4H,  $\text{ArOH}$ )

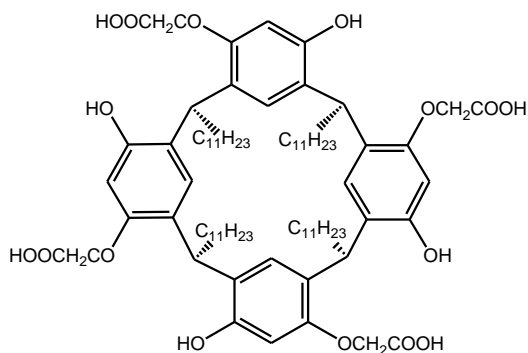


Fig. 1. Structure of  $R(\text{COOH})_4$

The HPLC grade chloroform ( $\text{CHCl}_3$ ) used as the ligand solvent was provided from POCH (Gliwice, Poland). The other organic chemicals were of commercially available reagent grade and were used without further purification.

All aqueous solutions were prepared using analytical reagent grade chemicals (POCH, Across) and deionized water (conductivity – 0.10  $\mu\text{S}/\text{cm}$ ). Solutions of Pb(II), Zn(II) and Cd(II) were prepared by dissolving appropriate amounts of  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Zn}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$  and  $\text{Cd}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$  in water.

### Solvent extraction procedure

The solvent extraction experiments were carried out at room temperature in a stopped glass flask at 1:1 volume ratio of aqueous and organic phases. The chloroform phase of  $\text{R}(\text{COOH})_4$  and aqueous phase containing metal nitrate were agitated by mechanical shaker with a constant stirring rate 600 rpm. The phases were separated after the mixture was settled for 12 h and the metal ion concentrations were determined in aqueous phase using flame atomic absorption spectrometer (Solar 939, Unicam). Metal ion concentrations in the organic phase  $[M^{2+}]_{org}$  were calculated from the difference of the metal ion concentrations in the aqueous phase before  $[M^{2+}]_{aq,0}$  and after extraction  $[M^{2+}]_{aq}$  and the following equations for the percent extraction %*E* (Eq. 1) and the metal distribution ratio between organic and aqueous phases *D* (Eq. 2) calculation were applied:

$$\% E = \frac{[M^{2+}]_{aq,0} - [M^{2+}]_{aq,eq}}{[M^{2+}]_{aq,0}} \cdot 100 \%, \quad (1)$$

$$D = \frac{[M^{2+}]_{aq,0}}{[M^{2+}]_{aq,eq}}. \quad (2)$$

The pH of aqueous phase was adjusted by adding a small amount of  $\text{HNO}_3$  and measured with Elmetron CX-731 pH-meter. The pH value of aqueous solutions after solvent extraction was taken as the equilibrium pH.

## Results and discussion

### Effect of *n*-decanol

During preliminary experiments of solvent extraction from  $5 \cdot 10^{-4} \text{ M}$  Pb(II) (pH = 5.0) aqueous nitrate solution by  $\text{R}(\text{COOH})_4$  dissolved in  $\text{CHCl}_3$  at  $5 \cdot 10^{-4} \text{ M}$  concentration, the formation of emulsion at the interface of aqueous and organic phases was observed. This phenomenon in extraction systems is known and described in the literature, especially for alkali metal ions extraction from nitrate aqueous solutions with macrocycles (Delmau et al., 2005). Most of the available evidence on third phase formation suggests that it may be due to limited dissolution of extractant after its protonation when contacted with acidic aqueous phase and that the addition of a modifier, e.g. a long chain alcohol usually prevented the third phase appearance, therefore *n*-decanol

was added to organic phase. Our investigations revealed that the third phase can be removed after addition of 20% of n-decanol, but such modification resulted in a decrease of the extraction efficiency of Pb(II) ions. The effect of n-decanol content in organic phase on extractability of tetracarboxylresorcinarene was studied. Results are shown in Fig. 2.

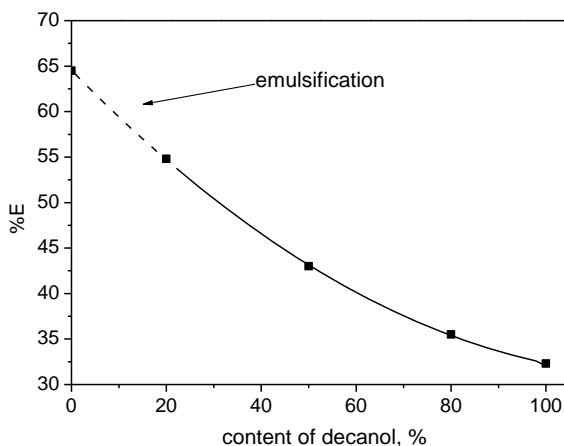


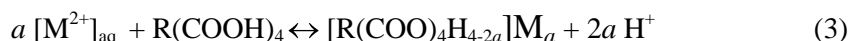
Fig. 2. Effect of n-decanol on percentage extraction of Pb(II) by  $R(\text{COOH})_4$  ( $[\text{Pb}(\text{II})] = 5 \cdot 10^{-4} \text{ M}$ ,  $\text{pH} = 5.0$ ;  $[R(\text{COOH})_4] = 5 \cdot 10^{-4} \text{ M}$ ; contact time: 1 h)

### Effect of agitation time

The solvent extraction experiments were carried out for  $1 \cdot 10^{-3} \text{ M}$   $R(\text{COOH})_4$  solution in  $\text{CHCl}_3/n$ -decanol (4/1) and aqueous phase containing  $5 \cdot 10^{-4} \text{ M}$   $\text{Pb}^{2+}$  ( $\text{pH} 5.5$ ) at agitation times ranging from 5 to 180 min. The Pb(II) extraction percentage increased with the contact time and reached the plateau of 55% within 50–70 min. The further agitation of solutions caused the slight decrease of the extraction efficiency, nevertheless, these changes are within the range of the experimental error estimated to be approximately  $\pm 2\%$ . To ensure equilibrium, 1 h contact time was maintained during the extraction studies.

### Effect of pH

The efficiency of extraction of metal cations by acidic-type extractants depends on the deprotonation of extractant molecules and the formation of metal-ligand complex. Extraction process for divalent metal ions with tetracarboxylresorcin[4]arenes at the aqueous/organic interface can be written as follows:



where  $R(\text{COOH})_4$  and  $[R(\text{COO})_4\text{H}_{4-2a}]M_a$  denote extractant and metal-ligand complex, respectively. This equation shows that the acidity of aqueous phase plays a significant role in extraction process, therefore the effect of initial pH of aqueous phase containing  $5 \cdot 10^{-4}$  M Pb(II) in the range 1.5–6.0 was determined. The extraction of Pb(II) ions in the higher pH may not be precise because of the metal ions hydrolysis and the hydroxide precipitation that can interfere with the metal-ligand complex formation and cause decline of process efficiency. As shown in Fig. 3, the increase of pH to 5.5 caused the enhancement of process efficiency to ca. 60%, however with the further increase in pH efficiency slightly declines. Pb(II) extraction at low pH seems to be caused by the occurrence of strong intermolecular hydrogen bonding and protonation of most hydroxyl groups in the  $R(\text{COOH})_4$  molecule. When there is sufficient excess of  $\text{H}^+$  ions in the strongly acidic solution in comparison to metal ion, most of oxygen pair electrons coordinate rather with  $\text{H}^+$  than with metal cations. In the case of the high pH of aqueous solution, where limited amount of  $\text{H}^+$  ions is present, the interaction between oxygen lone pair electrons of  $R(\text{COOH})_4$  and vacant orbital of Pb(II) is possible. Similar profile of percent Pb(II) loading to the organic phase versus pH of aqueous phase was found for dimetoxycalix[4]arene di(carboxylic acid) with cone conformation (Park et al., 2010). However, these results differ from those obtained by Ohto et al. (1999) for methylbutylcalix[4]arene with four acetic acid groups and Adikhari et al. (2010) for *t*-butylcalix[5]arene with five acetic acid moieties, where a quantitative removal of Pb(II) ions from acidic solutions of pH above 2.0 was observed. It is probably caused by the differences in the geometrical arrangement of carboxyl groups in calixarene and resorcinarene molecules and their dissociation.

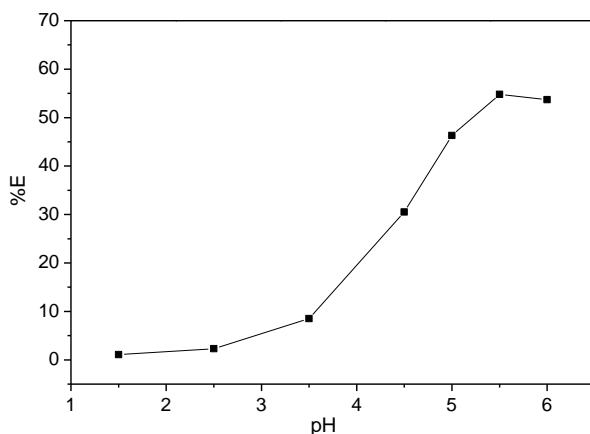


Fig. 3. Effect of pH on the Pb(II) extraction ( $[\text{Pb(II)}] = 5 \cdot 10^{-4}$  M;  $[\text{R}(\text{COOH})_4] = 1 \cdot 10^{-3}$  M; the contact time: 1 h)

### Effect of extractant concentration

The solvent extraction of Pb(II) with extractant concentration in the range from  $5 \cdot 10^{-4}$  to  $1 \cdot 10^{-2}$  M under the best conditions of agitation time and aqueous phase pH was investigated. It was observed that the Pb(II) extraction efficiency increased with the resorcinarene concentration increase and reached maximum values of 99% for  $R(\text{COOH})_4$  in  $\text{CHCl}_3/\text{n-decanol}$  (4/1 vol.) mixture at the  $1 \cdot 10^{-2}$  M concentration. Fig. 4 shows the logarithmic relation of the Pb(II) distribution ratio between aqueous and organic phases vs. extractant concentration. The slope of obtained straight line was determined to be  $1.66 \pm 0.04$  what can indicate that two metal ions are extracted by one ligand molecule, and complexes  $R(\text{COO})_4\text{Pb}_2$  are formed.

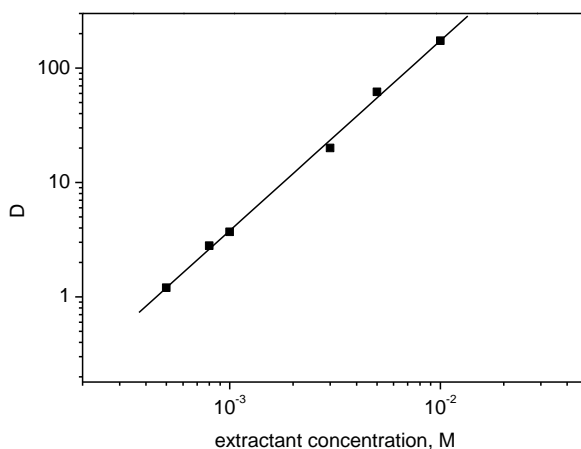


Fig. 4. Effect of extractant concentration on the distribution coefficient  
 ( $[\text{Pb}(\text{II})] = 5 \cdot 10^{-4}$  M, pH = 5.5)

The extraction ability of macrocyclic carrier is optimized by the structural modifications both within the ring and terminal groups, that can be either hydrophobic alkyl chains or ionizable, hydrophilic units. The complexation ability with metal ion may proceed by electrostatic interaction with aromatic rings (size-recognition) as well as by the cation- $\pi$  interaction. For the explanation of Pb(II) complexation mechanism by  $R(\text{COOH})_4$ , a further evidence, *e.g.* by determination of crystallographic structure of the ligand and its complex with Pb ions is required.

### Competitive solvent extraction of Pb(II), Zn(II) and Cd(II)

The competitive solvent extraction of Pb(II), Zn(II) and Cd(II) ions from  $5 \cdot 10^{-4}$  M aqueous nitrate solutions into chloroform/n-decanol (4/1 vol.) phase containing  $1 \cdot 10^{-3}$  M resorcinarene  $R(\text{COOH})_4$  as an extractant was also carried out. The obtained values of percent extraction show that  $R(\text{COOH})_4$  can be used for selective removal of Pb(II) over Cd(II) and Zn(II) ions. The relatively high separation of Pb(II) ions was observed

in the competitive solvent extraction from aqueous solution in pH range 4.0–6.0 (Fig. 5).

The efficiency and selectivity of metal ions extraction decreased in the order  $\text{Pb(II)} \gg \text{Cd(II)} > \text{Zn(II)}$ . The selectivity coefficients  $S$  calculated as  $D_{\text{Pb(II)}}/D_{\text{Cd(II) or Zn(II)}}$  at different pH's of aqueous phase are presented in Table 1.

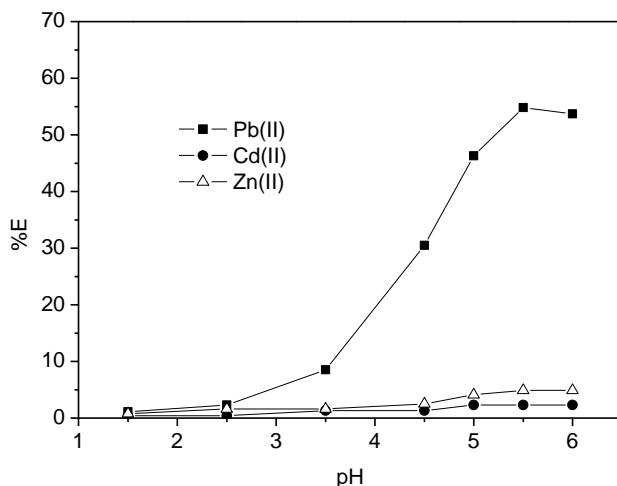


Fig. 5. Competitive solvent extraction of Pb(II), Cd(II) and Zn(II) ions, ( $[\text{M(II)}] = 5 \cdot 10^{-4} \text{ M}$ ;  $[\text{R(COOH)}_4] = 1 \cdot 10^{-3} \text{ M}$ ; the contact time: 1 h)

Table 1. Selectivity coefficients at different pH's of aqueous phase (process conditions in Fig. 5)

| $S$                | pH   |      |      |       |       |       |       |
|--------------------|------|------|------|-------|-------|-------|-------|
|                    | 1.5  | 2.5  | 3.5  | 4.5   | 5.0   | 5.5   | 6.0   |
| $S_{\text{Pb/Cd}}$ | 1.38 | 1.39 | 5.56 | 17.41 | 20.20 | 23.44 | 22.40 |
| $S_{\text{Pb/Zn}}$ | 2.97 | 6.01 | 6.81 | 32.30 | 36.68 | 51.53 | 49.24 |

The increase of pH resulted in higher selectivity coefficients. The highest  $S$  values were obtained for a pair Pb(II) / Zn(II) ions at pH 5.5. The successful separation Pb(II) by  $\text{R(COOH)}_4$  was achieved. The excellent extraction behavior of applied extractant towards Pb(II) ions results probably from better fitting of large Pb(II) cations to cavity size of resorcinarenes than in the case of smaller cations, *i.e.* Cd(II) and Zn(II).

## Conclusions

The tetracarboxylresorcin[4]arene was found to be an efficient and selective extractant for lead(II) solvent extraction from nitrate aqueous solutions. The best efficiency of the solvent extraction was obtained for one-hour agitation time of aqueous phase at pH



5.5 and organic phase containing  $R(\text{COOH})_4$  as the extractant ( $5 \cdot 10^{-4}$  M), n-decanol (20% vol.) as the organic phase modifier and chloroform as the diluent. Under these conditions the separation of Pb(II) over Cd(II) and Zn(II) ions with high selectivity coefficients equal to 23.4 and 51.5, respectively, was achieved.

## Acknowledgments

This work is part of the projects No. N N209 441539 and N N209 762940. The authors acknowledge Polish Ministry of Science and Higher Education and National Science Centre for financial support of these projects.

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