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Selective solvent extraction of some heavy metal ions from aqueous solutions by octafunctionalized resorcin[4]arenes

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Abstract: This paper presents the results of the study on the extraction capacity of 1,8,15,22-tetra(1-heptyl)resorcin[4]arene and its octasubstituted derivatives containing thiophosphoryl, ester and amide groups in the presence of Pb(II), Zn(II), Cd(II) and Cr(III) in solvent extraction process. Effects of the structure and concentration of the resorcinarene extractant and the composition of the aqueous phase as well as its acidity on the efficiency and selectivity of removal of the examined metal ions from model aqueous solutions were determined. The 1:1 stoichiometry for complexes formed between Pb(II) and Cr(III) and the octasubstituted resorcin[4]arenes was determined by classical slope analysis and loading test.

Keywords: solvent extraction, lead, chromium, calixresorcinarene, metal removal

1. Introduction

Intensive use of heavy metals in the production processes of many industries leads to environmental pollution of surface waters, from which toxic metal ions can enter the soil and groundwater that are the source of drinking water for plants, animals and humans. Drinking water contaminated with compounds of heavy metals may lead to many serious diseases of cardiological, neurological or immunological nature, and various types of cancer (Ming-Ho, 2005; Jaishankar et al., 2014).

High concentrations of metals such as lead, zinc, cadmium and chromium are found, *e.g.* in galvanic sludges and wastewater as a result of surface treatment of metal products, including removal of old galvanic coatings and electrochemical processes of new coatings application (Rubel et al., 2009). Both chemical and physicochemical processes of removal of heavy metals are applied in the treatment of galvanic wastewater, and chemical precipitation is the most commonly used method, especially in small galvanization plants. Although this process is relatively simple and cheap, it is also harmful from the ecological point of view as it generates very large amounts of waste in the form of heavy metal hydroxides or sulfides. Additionally, the rate of galvanic wastewater purification from heavy metals in Poland is still too low concerning the highest permissible concentrations of these metals in treated industrial wastewater as defined in the Regulation of the Polish Minister of Infrastructure and Construction dated 28 September, 2016 (Ordinance, 2016).

Solvent extraction is one of the most popular hydrometallurgical techniques for the removal of heavy metals from post-production solutions, and its efficiency mainly depends on the conditions of its conduction and the nature of the extractant (Cole and Sole, 2003; Cox, 2004; Kislik, 2012). So far, many extraction systems have been examined in terms of their potential use for efficient extraction of heavy metal ions from aqueous solutions, both model (Pospiech and Changes, 2005; Bouabdallah et al., 2006; Touati et al., 2008; Kumar et al., 2009; Lertlapwasin et al., 2010; Konczyk et al., 2013; Daryabor et al., 2017) and real ones (Ismael and Carvalho, 2003; Silva et al., 2005; Kul and Çetinkaya, 2010; Marszałkowska et al., 2010; Innocenzi and Veglio, 2012; Balesini-Aghdam, 2019). Studies have demonstrated that the optimization of chemical composition of the aqueous and organic phases, the

time and temperature of the process, as well as process supporting with additional factors such as microwave radiation (Ikeda et al., 2016) or ultrasounds (Daryabor et al., 2017), allow to obtain high extraction efficiency. However, the key element of each extraction system is the usage of a proper chemical compound playing the role of an extractant, characterized by high efficiency and selectivity of complexing/decomplexing of metal ions. A wide variety of extractants, both classical and commercially available, as well as newly synthesized compounds with simple or complex structures, of acidic, basic or inert character were used for heavy metal ions extraction. The applied extraction systems often enabled an efficient separation of some metal ions but the selectivity of the process was not satisfactory in many cases. Therefore, there is still a need to search for efficient and selective extractants of heavy metal ions.

In recent years, macrocyclic extractants from the group of calixarenes, considered to be the third generation (after crown ethers and cyclodextrins) of macrocyclic compounds, gained popularity (Gutsche, 2008; Roundhill et al., 2009; Ohto, 2010; Adhikari et al., 2013; Konczyk et al., 2016a; Konczyk et al., 2016b). Calixarenes and their derivatives (heteracalixarenes, heterocalixarenes, calixresorcinarenes) were used to remove metal ions, including Pb(II), Zn(II), Cd(II) and Cr(III), in liquid-liquid and liquid-solid extraction processes (Konczyk et al., 2016a). Compared to calixarenes, there are not so many studies on the use of calixresorcinarenes for the separation of heavy metal ions. The presence of twice the number of hydroxyl groups in resorcinarene molecule and their different locations provide a wide variety of possibilities for their modification and creation of new ligands differing with molecular shape, macrocyclic cavity size, and chemical character. Therefore, it is possible to design a resorcinarene molecule characterized by a good affinity to the ions of a particular metal. Resorcinarenes can adopt four symmetrical arrangements: crown (rccc), boat (rcct), chair (rctt), and saddle (rtct) (Miao et al., 2003). The type of conformation depends on the substituents added in the lower and/or upper rims of the macrocyclic ring. Ligands modified by bulky substituents in the lower rim usually adopt stable cone conformation. In turn, modification of the molecule by the functionalizing hydroxyl group or the ortho-positions in the upper rim of the resorcinol units favors the formation of boat conformation (Velásquez-Silva et al., 2017). It was found that the octasubstitution of hydroxyl protons in the resorcin[4]arene molecule by sulfonyl and phosphoryl groups transforms the initial crown conformation into a stereochemically flexible boat one (Kalchenko et al., 1998). The rapid pseudorotation process involving site exchange of benzene rings with coplanar and perpendicular orientation was observed in the solution. Moreover, the longer moieties attached to the macrocyclic ring are much more flexible than the shorter ones and allow free rotation of the chelating groups for metal ion binding. Such preorganization of the molecule can lead to the formation of a cavity of a size enabling complexation of metal ions.

In our previous papers, heptylresorcin[4]arene-based ligands bearing four carboxyl (Konczyk et al., 2013) or diethoxyphosphoryl groups (Konczyk et al., 2016b) in the upper rim of the molecule were used in solvent extraction process for Pb(II), Cd(II), Zn(II) and Cr(III) removal from acidic aqueous solutions containing these metal ions. Under the applied extraction conditions, the carboxylated ligand was highly effective and selective toward Pb(II) with separation factor values of 51.5 and 23.4 for Pb(II)/Zn(II) and Pb(II)/Cd(II) pairs of ions, respectively. In the case of thiophosphorylated resorcin[4]arene, effective separation of Cr(III) from Cd(II) and Zn(II) with a separation factors equal to 77.0 and 24.9 was achieved for Cr(III)/Cd(II) and Cr(III)/Zn(II) pairs of ions, respectively.

In the present work, a three heptylresorcin[4]arene-based extractants modified in the upper rim of the molecule by eight thiophosphorylated, ester or amide groups were tested as extractants for Pb(II), Zn(II), Cd(II) and Cr(III). The extractability of ligands was compared to non-functionalized heptylresorcin[4]arene reported in the paper (Konczyk et al., 2016b). The process conditions for the best effective separation of the studied metal ions were adjusted and the stoichiometry of the extracted metal-ligand complexes was estimated.

2. Materials and methods

2.1. Reagents

Deionized water with an average conductivity at 20°C not exceeding 0.08 $\mu\text{S}/\text{cm}$ and the following compounds of analytical purity: lead(II) nitrate - $\text{Pb}(\text{NO}_3)_2$ (POCH), zinc nitrate - $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$

(POCH), cadmium nitrate - $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (ACROSS), chromium(III) nitrate - $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (ACROSS), nitric acid and [2-[4-(2-hydroxyethyl)-1-piperazinyl] ethanesulfonic acid - HEPES (SIGMA) were used for preparation of aqueous solutions.

Four extractants from the group of resorcin[4]arenes with the structures shown in Fig. 1, obtained according to (Markovsky et al., 1996; Maslennikova et al., 1996; Konczyk et al., 2016b), and chloroform of analytical grade (POCH) as a solvent, were used for preparation of organic phases.

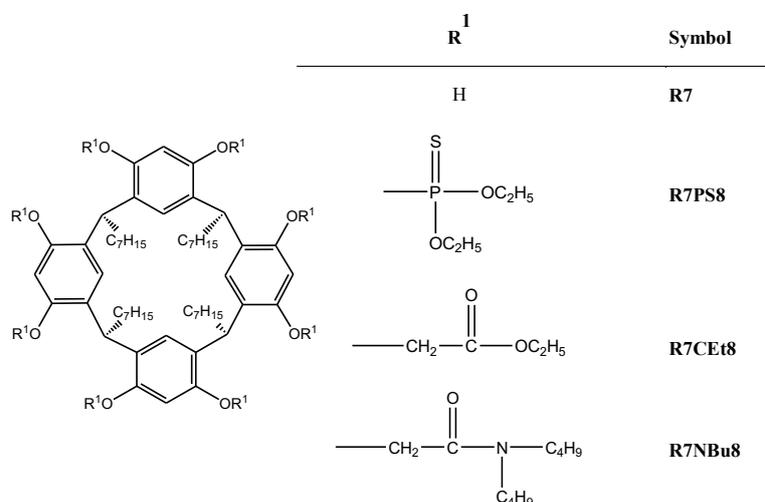


Fig 1. The chemical structures of extractants

2.2. Solvent extraction procedure

The solvent extraction of Pb(II), Zn(II), Cd(II) and Cr(III) was carried out from one-component (containing only one type of these metal ions) and multi-component (containing all of these metal ions) nitrate solutions at a concentration of $5.0 \cdot 10^{-4}$ M (M means $\text{mol} \cdot \text{dm}^{-3}$), prepared by metal salts dissolved in 0.10 M HNO_3 - 0.10 M HEPES buffer (stock solutions of the metal concentration $1.0 \cdot 10^{-2}$ M were prepared, then they were diluted to the desired concentration with 0.1 M HNO_3 (solution A) and with 0.1 M HEPES buffer of pH 5.20 (solution B); solutions A and B were arbitrarily mixed to achieve the desired pH). The organic phase was solution of extractants in chloroform at a concentration of $5.0 \cdot 10^{-3}$ M, except for the study on an effect of the extractant concentration in the organic phase. Here, solutions of the examined resorcinarenes were used at five different concentrations in the range of $5.0 \cdot 10^{-4}$ - $1.0 \cdot 10^{-2}$ M. Equal volumes (5 cm^3) of the aqueous and organic phase were placed in conical flasks, and the contents of the flasks were shaken on an IKA shaker (KS 4000ic control model) at $25 \pm 0.1^\circ\text{C}$ at a frequency of 200 rpm in the optimal time of 2 hours, then the flasks were set for 12 hours. Both phases were then separated and the equilibrium pH was measured using Elmetron pH Meter (CX-505) with the ERH-12-6 combination electrode. The concentration of metal ions in the aqueous phase was measured by atomic absorption spectrometry (AAS) using the Solaar 939 spectrometer (Unicam). The concentration of metal ions in the organic phase was determined as the difference between the initial and equilibrium concentrations of metal ions in the aqueous phase. An organic phase containing the complexes of the examined metals with resorcinarenes was used in the process of metal ions stripping into the aqueous phase. Concentration of nitrate ions in the aqueous phase was determined by ion chromatograph equipped with suppressed conductivity detector (Dionex ICS-3000, Thermo Scientific). Each experiment was repeated three times and the mean value of the metal ions concentration was taken for calculations and plots preparation.

Based on the obtained equilibrium concentrations of metals in the aqueous and organic phases, the values of the ratio of their distribution between these phases (D) were calculated. The efficiency of the extraction was determined by the percentage of extraction ($\%E$):

$$\%E = \frac{D}{D + \frac{V_{aq}}{V_{org}}} \cdot 100\% \quad (1)$$

where V_{aq} and V_{org} determine the volumes of the aqueous and organic phases, respectively.

In turn, the selectivity of the examined metal ions extraction was expressed by the selectivity coefficient (S) using the following equation:

$$S = \frac{D_{M1}}{D_{M2}} \quad (2)$$

where D_{M1} and D_{M2} determine the distribution ratios of two different metals M1 and M2, respectively.

2.3. Stripping procedure

Stripping of metal ions from the post-extraction organic phase was carried out under conditions used during the extraction, using the solutions of nitric acid at concentrations in the range of 0.01 – 1.0 M as the aqueous phase.

An organic phase containing the complexes of the examined metals with resorcinarenes was used in the process of metal ions stripping into the aqueous phase. Concentration of nitrate ions in the aqueous phase was determined by ion chromatograph equipped with suppressed conductivity detector (Dionex ICS-3000, Thermo Scientific). Each experiment was repeated three times and the mean value of the metal ions concentration was taken for calculations and plots preparation.

3. Results and discussion

3.1. Effect of functional groups of calix[4]resocinarene

In order to determine the extraction capacity of the resorcin[4]arenes with respect to Pb(II), Zn(II), Cd(II) and Cr(III), solvent extraction from one-component nitrate solutions of these metals at a concentration of $5.0 \cdot 10^{-4}$ M and pH = 5.0 to an organic phase constituting $5.0 \cdot 10^{-3}$ M resorcinarene solution in chloroform was performed. The selection of extractant solution concentration was based on the fact that the use of organic phase in the form of solutions containing more than $5.0 \cdot 10^{-3}$ M **R7PS8** and **R7CEt8** resulted in an emulsification of the aqueous phase, which made it impossible to determine the concentration of examined metal ions in the aqueous phase after extraction.

The obtained extraction efficiency series of the examined metal ions from aqueous one-component solutions using resorcin[4]arenes are as follows:

- for **R7** and **R7PS8**: Pb(II) > Cr(III) > Cd(II) > Zn(II)
- for **R7CEt8** and **R7NBu8**: Cr(III) > Pb(II) > Cd(II) > Zn(II)

The results of the study (Fig. 2) indicate that the efficiency of extraction of Pb(II), Zn(II), Cd(II) and Cr(III) by non-functionalized resorcin[4]arene **R7** containing heptyl chains attached to methylene bridges of the lower rim of the molecule, is low and does not exceed 15%, irrespective of the aqueous phase composition.

Substitution of the resorcin[4]arene molecule with amide groups (**R7NBu8**) slightly increased an efficiency of the examined ions extraction compared to the non-functionalized resorcinarene **R7**. In turn, the attachment of ester (**R7CEt8**) and thiophosphoryl groups (**R7PS8**) into the resorcin[4]arene molecule caused a distinct increase in Pb(II) and Cr(III) extraction. The highest efficiency of Pb(II) extraction (79%) was recorded in the extraction system with an organic phase containing resorcinarene **R7PS8**, while the highest efficiency of Cr(III) extraction (74%) was obtained for the organic phase solution in the form of resorcinarene **R7CEt8**. For Cd(II), the highest degree of separation (28.5%) was obtained for one-component solutions at pH 5.0, using the organic phase in the form of chloroform solution of thiophosphorylated ligand **R7PS8**. In turn, Zn(II) ions were extracted using resorcinarenes to a small extent (%E < 7%).

Different extraction properties of macrocyclic compounds tested in the presence of Pb(II), Zn(II), Cd(II) and Cr(III) are most often attributed to the best fit of ion diameter (236 pm for Pb(II), 190 pm for Cd(II), 150 pm for Zn(II) and 124 pm for Cr(III) (Wulfsberg, 1991)) to the diameter of the macrocyclic cavity (Bartsch, 1999) and/or the presence of oxygen, sulfur and nitrogen donor atoms in the macrocycle molecule, which, according to the theory of Hard and Soft Acids and Bases (HSAB), introduced by Pearson (1963) may be an important factor affecting the efficiency and selectivity of the extractant. Bartsch et al. (1999) demonstrated that alkali metal cations are efficiently transported by bulk liquid membranes containing lariat crown ethers when the ratio of metal ion diameter to crown cavity diameter is in the range of 0.8 – 0.9.

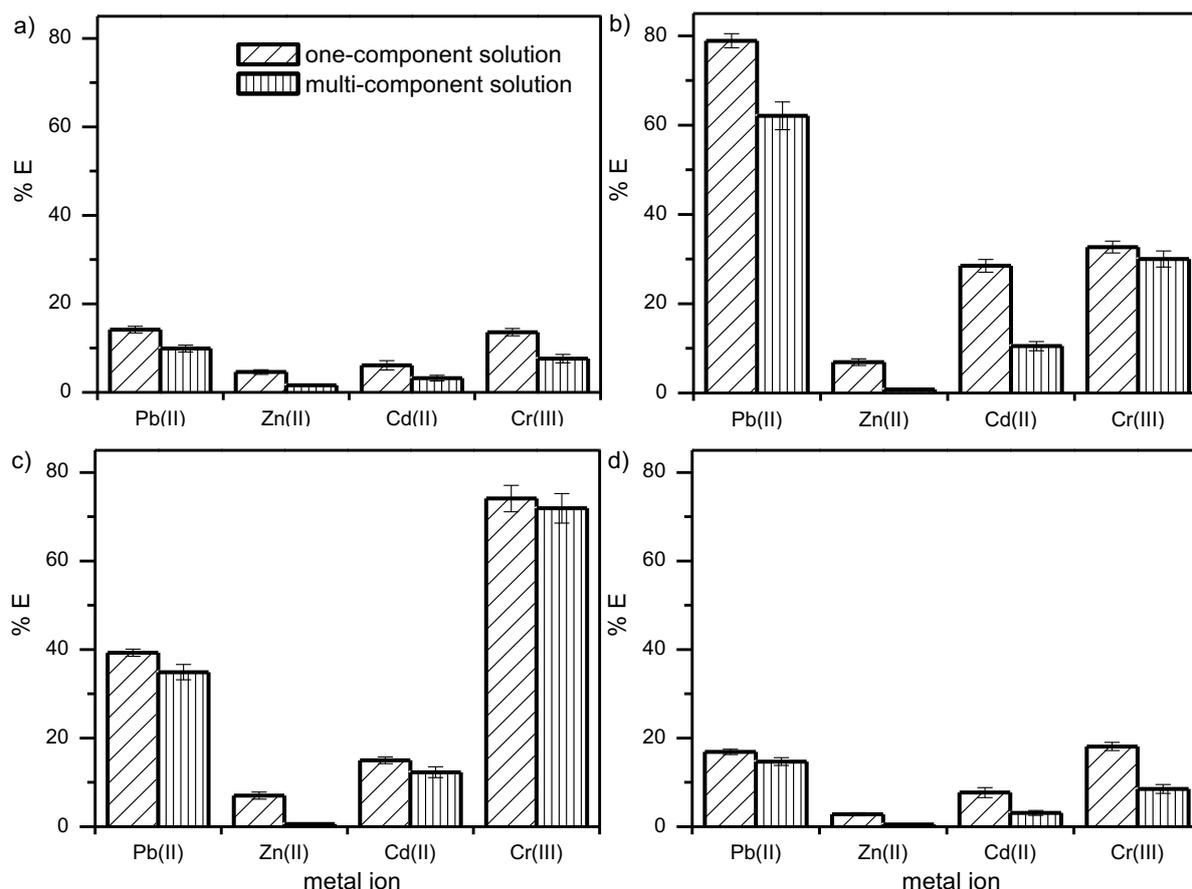


Fig. 2. Effectiveness of Pb(II), Zn(II), Cd(II) and Cr(III) extraction from one- and multi-component solutions using resorcin[4]arene **R7** (a), **R7P8** (b), **R7CEt8** (c) and **R7NBu8** (d); aqueous phase: $5.0 \cdot 10^{-4}$ M solution of the metal ions, pH = 5.0; organic phase: $5.0 \cdot 10^{-3}$ M resorcin[4]arene solution in chloroform

In turn, according to the HSAB theory, the Cr^{3+} cations belong to a group of hard Lewis acids that form strong ionic bonds with hard Lewis bases with donor oxygen atoms. Cd^{2+} cations are soft Lewis acids that easily form covalent bonds with soft Lewis bases containing donor sulfur and nitrogen atoms. In turn, Pb^{2+} and Zn^{2+} ions are intermediate acids with both hard and soft acids properties, thus they should be easily extracted by compounds with oxygen, sulfur and nitrogen donor atoms.

Although hard ligands, including alkylphosphates, carboxylic acids and esters, according to HSAB theory should exhibit a higher affinity for hard Cr(III) cations than for intermediate Pb(II) cations, the applied resorcinarenes efficiently extracted also Pb(II) ions. In turn, sulfur-containing ligands **R7PS8** are softer Lewis bases than ligands containing oxygen, and these ligands should interact preferentially with soft metal ions such as Cd(II). The obtained results indicate that the HSAB theory for octasubstituted resorcin[4]arenes could not explain their affinity to the heavy metal ions. If the ligand contains several coordination atoms competing for a place in the coordination sphere of a metal cation, the influence of many different steric factors, for example additional intra- and intermolecular bonding, the electron effects of substituents, should be considered (Pickering, 1986).

Similar behavior described for some of the macrocyclic extractants from the group of crown ethers containing O-donors, was related to the electron configuration of the Pb(II) cation ($d^{10}s^2$), causing its sphericity (Paar and Pearson, 1983), and consequently formation of lower-symmetry hydroocations as compared to octahedral hydroocations of Cd(II), Zn(II) and Cr(III) (Safin et al., 2008).

The $\text{Pb(II)} > \text{Cd(II)} > \text{Zn(II)}$ series of extraction efficiency obtained for the examined resorcinarenes is consistent with the Pickering's series presenting the binding force of soft and intermediate acids: $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Co}^{2+} > \text{Fe}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+}$ (Swain et al., 1983) and is related to the differences in the so-called absolute hardness of cations expressed numerically as 8.5 for Pb(II), 10.3 for Cd(II) and 10.8 for Zn(II) (Persson, 2010).

A significant phenomenon that can also affect the transition of metal ions from the aqueous to organic phase is their dehydration. Since the energy of Pb(II) ions dehydration (1425 kJ/mol) is lower than the energy of Cd(II) (1806 kJ/mol), Zn(II) (2044 kJ/mol) and Cr(III) dehydration (4402 kJ/mol) (Wulfsberg, 1991), from the point of view of thermodynamics, Pb(II) ions should be extracted as the first.

3.2. Effect of agitation time

In order to determine the optimal time of the process allowing to establish the equilibrium of the system, the study on solvent extraction of Pb(II), Cd(II), Zn(II) and Cr(III) from multi-component solutions of pH=5.0 was conducted, changing the time of phases contact (t) from 5 to 240 minutes. The efficiency of Pb(II), Zn(II), Cd(II) and Cr(III) extraction increased with phase mixing time and reached a constant value for all extraction systems after 120 minutes. Further mixing of the phases caused minor changes in metal ions extraction rate within the measurement error range of $\pm 3\%$. The obtained results are similar to those obtained for the Cr(III)-tetraheptylresorcin[4]arene system (Konczyk et al., 2016b), for which a 2-hour mixing time was sufficient to reach equilibrium. In the case of ionized tetracarboxylated resorcin[4]arene derivative used in Pb(II) ions extraction, the equilibrium state of the system was reached faster (optimum mixing time = 1 h) (Konczyk et al., 2013).

3.3. Effect of aqueous phase composition

Actual aqueous solutions such as surface waters or industrial wastewater typically contain more than one type of metal ions. Therefore, an effect of the presence of all examined metal ions in the aqueous phase was determined by their extraction from an equimolar solution containing $5.0 \cdot 10^{-4}$ M Pb(NO₃)₂, Cd(NO₃)₂, Zn(NO₃)₂ and Cr(NO₃)₃ with pH = 5.0. The results of this study are shown in Fig. 2.

The simultaneous presence of all the examined metal ions in the solution caused a significant decrease in the extraction of Pb(II), Zn(II) and Cd(II), especially in the case of the use of the thiophosphorylated **R7PS8** extractant, and only a slight decrease in the efficiency of Cr(III) extraction, which concurrently led to an increase in the selectivity of Cr(III) extraction compared to Pb(II), Zn(II) and Cd(II).

3.4. Effect of metal ions concentration in aqueous phase

An effect of Pb(II) and Cr(III) concentration in the aqueous phase on the effectiveness of their separation by solvent extraction using **R7PS8** and **R7CEt8** resorcinarenes in the form of $5.0 \cdot 10^{-3}$ M solutions in chloroform was determined. The aqueous phase was a one-component solution of the examined ions at concentrations in the range of $1.0 \cdot 10^{-4}$ – $2.5 \cdot 10^{-3}$ M and pH = 5.0.

Under the extraction conditions employed, a slight decrease in the efficiency of Cr(III) ions extraction was observed with an increase in their initial concentration in the feed phase to $1.0 \cdot 10^{-3}$ M; a further increase in Cr(III) concentration resulted in the formation of a third phase in the extraction system. In turn, an increase in the initial concentration of Pb(II) caused a significant decrease in these ions extraction. Changes in the percentage of Pb(II) release as a function of their initial concentration in an extraction with thiophosphorylated resorcinarene **R7PS8** are presented in Fig. 3. These changes may be because, in the case of diluted aqueous solutions of the metals tested, the amount of active sites binding the extractant relative to the amount of metal cations is higher than in the more concentrated solutions. At the beginning of the process, the rate of metal ions transfer to the organic phase is high but over time, the layer of "excess" ions is probably formed at the boundary of phases, and these ions cannot be captured by resorcinarene molecule and bound in the form of a complex with a specific stoichiometry, resulting in decreased extraction efficiency. Moreover, hydrolyzed Cr(III) forms are usually better extracted by acid carriers (Lanagan and Ibana, 2003), and since the degree of Cr(III) hydrolysis decreases with their increasing concentration in aqueous solutions (Kocaoba and Akcin, 2002), they are better extracted from more diluted solutions.

Similar cases of a decrease in metal ions extraction efficiency with its concentration increase were recorded in the literature, for example during Pb(II) and Cd(II) adsorption on thiomethyl-methoxyphenyl-resorcin[4]arene (Utomo et al., 2012), in a transport of Cr(III) through thick layer

membranes containing dinonyl-naphthalenesulfonic acid (Religa et al., 2009) and solvent extraction of Sr(II) ions using dicyclohexane-18-crown-6 ether (Hafizi et al., 2009).

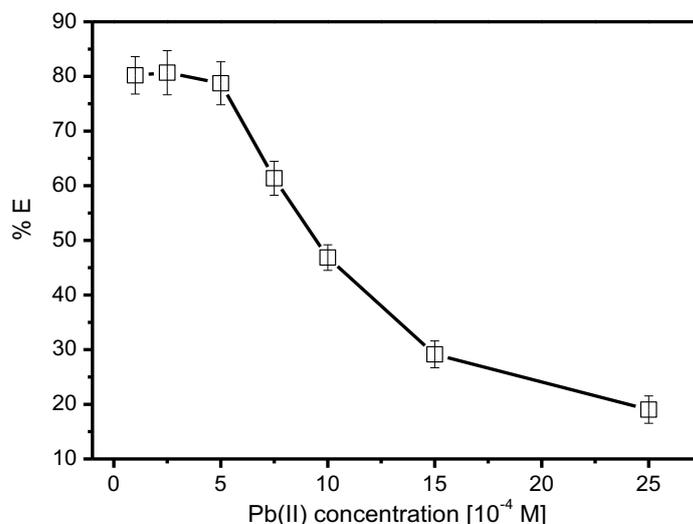


Fig. 3. An effect of Pb(II) concentration on the efficiency of their extraction with resorcinarene **R7PS8**; aqueous phase: solution of Pb(II), pH = 5.0; organic phase: $5.0 \cdot 10^{-3}$ M **R7PS8** solution in chloroform

3.5. Effect of aqueous phase acidity

The selectivity of solvent extraction process is an important parameter from both an ecological and an economic point of view, since obtaining the post-extraction aqueous solutions containing ions of single metals gives the opportunity to reuse them in technological processes and, thus, hazardous waste can become a valuable product. In this aspect, also an effect of aqueous phase acidity on the efficiency and selectivity of Pb(II), Zn(II), Cd(II) and Cr(III) removal from aqueous solutions in the extraction systems containing resorcin[4]arenes was determined. These tests were carried out under the conditions described in the section *Solvent extraction procedure*, using an equimolar solution of Pb(II), Cd(II), Zn(II) and Cr(III) ions with varying pH ranging from 1.0 to 5.0.

In the case of non-functionalized resorcinarene **R7**, no significant effect of aqueous phase acidity on the examined metal ions extraction was observed, and the maximum efficiency of the process, achieved for metal ions solution with pH 5.0, did not exceed 10% for Pb(II), 8% for Cr(III), 4% for Cd(II) and 2% for Zn(II). An increase in the pH of the aqueous phase from 1.0 to 5.0 also slightly affected the extraction of Cd(II) and Zn(II) ions using all examined functionalized resorcinarenes and Pb(II) and Cr(III) ions

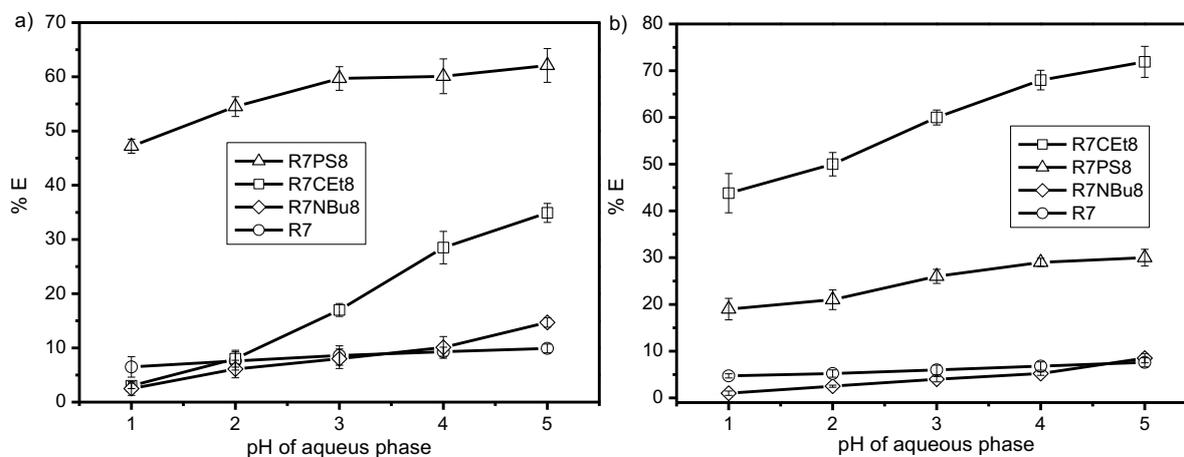


Fig. 4. An effect of aqueous phase acidity on the efficiency of Pb(II) (a) and Cr(III) (b) extraction from multi-component solutions using resorcin[4]arenes; aqueous phase: $5.0 \cdot 10^{-4}$ M solution of Pb(II), Cd(II), Zn(II) and Cr(III); organic phase: $5.0 \cdot 10^{-3}$ M resorcin[4]arene solution in chloroform

when using amide extractant **R7NBu8**. The maximum increase in Cd(II) extraction efficiency with an increase in the pH of the aqueous phase obtained during an extraction with **R7PS8** was only 10%. In the case of extraction systems containing extractants functionalized with non-ionizable thiophosphoryl and ester groups, a more significant influence of aqueous phase acidity on the extraction efficiency of Pb(II) (Fig. 4a) and Cr(III) (Fig. 4b) was observed, and the changes in the degree of separation of these ions with an increase in solution pH were not as rapid as those observed for resorcinarene containing ionizable carboxyl groups (Konczyk et al., 2013).

Such behavior of the ligands can be due to the presence of proton-sensitive moieties in their molecules. During the extraction process, complex formation of the metal cations and nitrate anions in the water phase and protonation of the ligand by nitric acid (e.g. extraction of HNO₃ by the ligand L) may occur. Upon increasing the acidity of the aqueous solution, the amount of protonated ligand increases resulting in lower distribution ratios of the metal ions. Therefore, two different extraction mechanisms are possible, depending on the acidity: a cation exchange mechanism at lower acidity, and a solvation mechanism at higher acidity (Chen et al., 2019).

3.6. Extraction selectivity

Aqueous phase acidity also significantly affected the selectivity of examined resorcin[4]arenes. The values of selectivity coefficients of Pb(II) ions extraction toward Cd(II), Zn(II) and Cr(III) calculated based on the values of the metal distribution ratio (*D*) between the organic and aqueous phases with different pH from equation 2 are summarized in Table 1. The selectivity of Pb(II) extraction with respect to Cd(II) and Zn(II) increased with an increasing acidity of the aqueous phase for all functionalized resorcinarenes in Pb(II) > Cd(II) > Zn(II) series, thus, despite the presence of binding thiophosphoryl, ester and amide groups in resorcin[4]arenes molecule, the selectivity series did not change.

Table 1. The selectivity coefficients of Pb(II) over Zn(II), Cd(II) and Cr(III) with different acidity of aqueous phase; aqueous phase: 5.0 · 10⁻⁴ M solution of Pb(II), Cd(II), Zn(II) and Cr(III); organic phase: 5.0 · 10⁻³ M resorcin[4]arene solution in chloroform

| Extractant | Metal ion (M) | $S_{Pb(II)/M}$ ($*S_{Cr(III)/Pb(II)}$) | | | | |
|---------------|------------------|--|----------|----------|----------|----------|
| | | pH = 1.0 | pH = 2.0 | pH = 3.0 | pH = 4.0 | pH = 5.0 |
| R7PS8 | Cd(II) | 9.1 | 11.5 | 13.5 | 13.6 | 14.0 |
| | Zn(II) | 151.3 | 178.5 | 189.6 | 214.3 | 233.9 |
| | Cr(III) | 3.9 | 4.5 | 4.2 | 3.9 | 3.8 |
| R7CEt8 | Cd(II) | 16.2 | 3.1 | 46.0 | 56.4 | 60.6 |
| | Zn(II) | 19.2 | 94.9 | 243.1 | 763.4 | 1159.0 |
| | Cr(III) | 6.9* | 1.4* | 1.3 | 2.6 | 3.3 |
| R7NBu8 | Cd(II) | 4.1 | 4.2 | 4.7 | 5.3 | 5.4 |
| | Zn(II) | 6.9 | 10.9 | 14.7 | 19.0 | 29.2 |
| | Cr(III) | 4.1 | 2.9 | 1.7 | 1.5 | 1.9 |

The most effective separation of Pb(II) ions from the other ions present in the aqueous phase can be obtained using resorcinarene **R7CEt8** with ester groups, and the highest values of Pb(II)/Cd(II) (60.6) and Pb(II)/Zn(II) selectivity coefficients (1159.0) were obtained for aqueous phases at pH 5.0, while the best separation conditions in case of Pb(II)/Cr(III) ions were achieved for aqueous phase at pH 1.0 ($S_{Cr(III)/Pb(II)} = 6.9$).

In the available literature, there are no reports concerning the ability of resorcinarene derivatives for an extraction of metal ions examined in the present study but the results obtained can be compared with the recently studied calixarenes. Tetra-carboxylic poly-5-allylocalix[4]arene used by Handayani et al. (2011) adsorbed Pb(II), Cd(II) and Cr(III) with an efficiency decreasing in series Cr(III) > Pb(II) > Cd(II). Calix[4]arene with four carboxyl groups efficiently and selectively separated Pb(II) from acidic Pb(II), Cd(II) and Cu(II) solutions in the series Pb(II) > Cd(II) > Cu(II), while its ester derivative did not extract Pb(II) and only in small degree extract Cd(II) and Cu(II) (Toumi et al., 2008). In turn, Dung and Ludwig (1999) extracted Pb(II), Cd(II) and Zn(II) from nitrate solutions using *t*-buthylcalix[4]-crown-6

derivatives obtained the selectivity determined in the series Pb(II) > Zn(II) > Cd(II) regardless of whether the carboxyl or ester groups were attached.

3.7. Effect of extractant concentration in organic phase

In order to determine the optimal concentration of the extractant, solvent extraction ($t = 2$ h; $c_M = 5.0 \cdot 10^{-4}$ M; pH = 5.0) of Pb(II) and Cr(III) to the solutions of resorcin[4]arenes **R7PS8** and **R7CEt8** at concentrations in the range of $5.0 \cdot 10^{-4} - 1.0 \cdot 10^{-2}$ M was performed. It was observed that the efficiency of the examined ions extraction increases with extractant concentration (c_L) and reaches a maximum value of 62% for the extraction of Pb(II) in the extraction system containing $5.0 \cdot 10^{-3}$ M **R7PS8** solution as an organic phase (Fig. 5) and 72% in the case of Cr(III) extraction using $5.0 \cdot 10^{-3}$ M solution of **R7CEt8**.

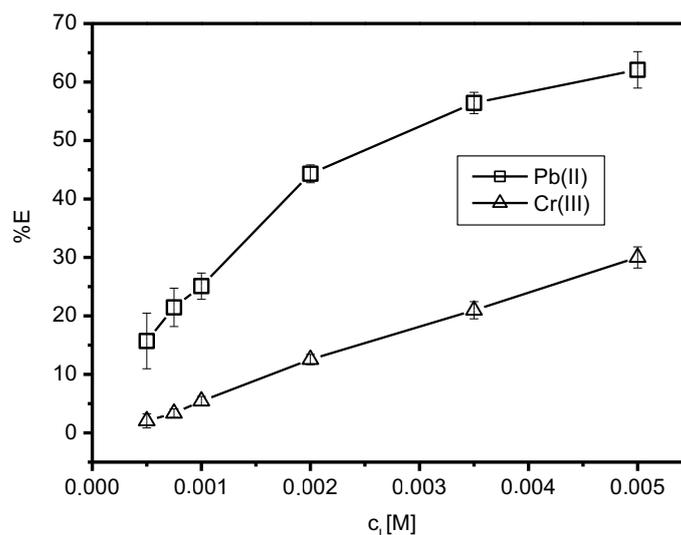


Fig. 5. An effect of **R7PS8** extractant concentration in organic phase on Pb(II) and Cr(III) extraction efficiency; aqueous phase: $5.0 \cdot 10^{-4}$ M solution of Pb(II), Cd(II), Zn(II) and Cr(III), pH = 5.0; organic phase: **R7PS8** solution in chloroform

The use of organic phases in the form of solutions of the examined resorcinarenes at a concentration above $5.0 \cdot 10^{-3}$ M resulted in the formation of an emulsion at the phases boundary. Determination of the concentration of the examined metal ions in the aqueous phase after an extraction was possible after an addition of 0.2 cm^3 of *n*-decanol but due to the significant effect of the modifier on Pb(II) extraction efficiency (Konczyk et al, 2013), the results obtained for these solutions were not taken into account when determining the relationships $\log D = f(\log c_L)$.

3.8. Stoichiometry of metal-resorcin[4]arene complex

In the case of inert extractants having the ability to form an inert complex in the organic phase with metal ions by replacing water molecules in metal aqua-complex with own, more lipophilic molecules according to equation:



the expressions on the extraction constant (K_{ex}) and the distribution ratio can be presented in the form of equations 4 and 5, respectively:

$$K_{ex} = \frac{c_{MX_nL_m(ORG)}}{c_{M^{n+}(AQ)} \cdot c_{X^-(AQ)}^n \cdot c_{L(ORG)}^m} \quad (4)$$

$$D = \frac{c_{MX_nL_m(ORG)}}{c_{M^{n+}(AQ)}} = K_{ex} \cdot c_{X^-(AQ)}^n \cdot c_{L(ORG)}^m \quad (5)$$

and the stoichiometric coefficients in the chemical reaction 3 can be determined by the relationship 6:

$$\log D = \log K_{ex} + n \log c_{X(aq)}^- + m \log c_{L(org)} \quad (6)$$

At a constant pH of the aqueous phase, the logarithmic relationship of metal ions distribution ratio between the aqueous and organic phase on the extractant concentration is a linear function with a slope corresponding to the number of extractant molecules that bind to one metal cation. The $\log D = f(\log c_L)$ relationships obtained for the extraction of Pb(II) and Cr(III) using resorcinarenes **R7PS8** (Fig. 6) and **R7CEt8** were described by regression equations with high values of determinants ($r^2 \geq 0.9930$) and low standard deviation errors (s.d. ≥ 0.046), indicating a high level of statistical significance of the obtained values of the slope values of these straights (\log - \log values in Table 2), corresponding to the 1:1 stoichiometry for metal-resorcin[4]arene complexes.

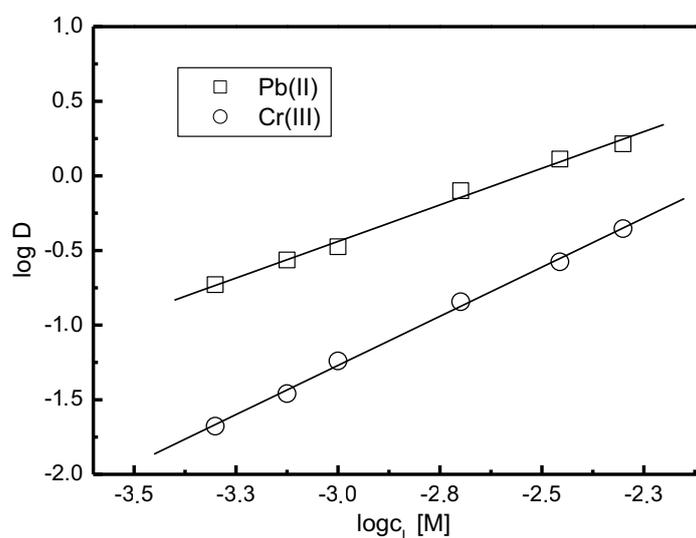


Fig. 6. Log-log dependence of the distribution ratio of Pb(II) and Cr(III) on the total **R7PS8** extractant concentration in organic phase; aqueous phase: $5.0 \cdot 10^{-4}$ M solution of Pb(II), Cd(II), Zn(II) and Cr(III), pH = 5.0; organic phase: $5.0 \cdot 10^{-4}$ – $5.0 \cdot 10^{-3}$ M **R7PS8** solutions in chloroform

The results obtained were confirmed by loading test, depicting the relationship of the stoichiometric concentration of metal in an organic phase ($c_{eq(org)}$) on the initial concentration of the extractant (c_L) as a function of the initial concentration of metal ions in the aqueous phase (c_0).

An increase in the initial concentration of the examined metal ions in the aqueous phase is accompanied by their loading increase to the organic phase until a constant value corresponding to the number of metal ions forming the resorcinarene complex is obtained. The relationships obtained for the extraction of Pb(II) and Cr(III) with the ester derivative of **R7CEt8** are shown in Fig. 7. Similar curves were obtained for octathiophosphorylated resorcinarene **R7SP8**, and the obtained maximum values of the degree of Pb(II) and Cr(III) loading are presented in Table 2 as “*l.test*” values. The maximum loading capacity of 5 mL $5.0 \cdot 10^{-3}$ M resorcinarene solution in chloroform was found to be 476.1 mg Pb(II) and 94.9 mg Cr(III) for **R7PS8**, and 699.7 mg Pb(II) and 60.0 mg Cr(III) for **R7CEt8**.

Both the results obtained using slope analysis and loading test clearly indicate that the reaction observed during an extraction of Pb(II) and Cr(III) from the aqueous solution at pH = 5.0 using octasubstituted resorcin[4]arenes is accompanied by the formation of metal-resorcinarene complexes

Table 2. Stoichiometry of metal-resorcin[4]arene complexes (M : L).

| Metal ion | Method | R7PS8 | R7CEt8 |
|-----------|----------------|-------|--------|
| Pb(II) | <i>log-log</i> | 0.98 | 1.38 |
| | <i>l.test</i> | 0.92 | 1.14 |
| | M : L | 1 : 1 | 1 : 1 |
| Cr(III) | <i>log-log</i> | 1.32 | 1.11 |
| | <i>l.test</i> | 0.90 | 0.79 |
| | M : L | 1 : 1 | 1 : 1 |

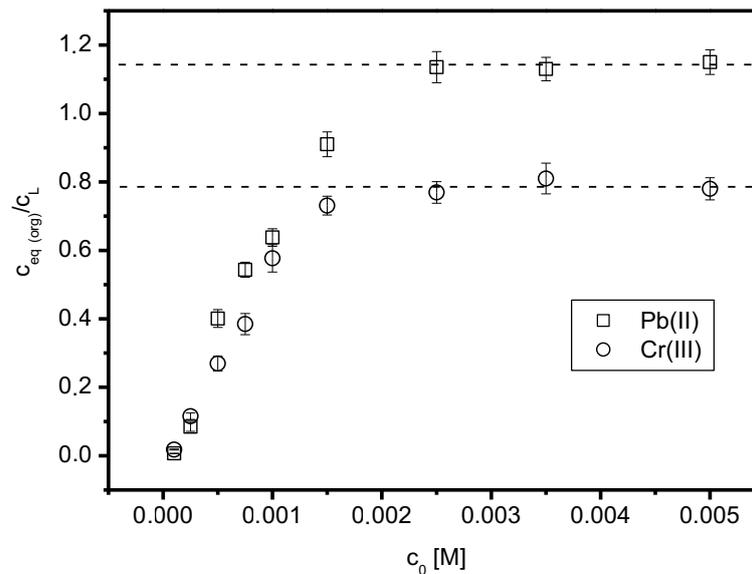
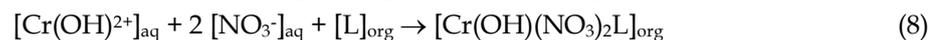


Fig. 7. The loading test of Pb(II) and Cr(III) in the extraction with **R7CEt8**; aqueous phase: $1.0 \cdot 10^{-4}$ - $5.0 \cdot 10^{-3}$ M solution of Pb(II) or Cr(III), pH = 5.0; organic phase: $5.0 \cdot 10^{-3}$ M **R7CEt8** solution in chloroform

with a 1:1 stoichiometry and likely coordination of metal ions with ligands by oxygen or sulfur atoms. Similar results have been obtained for extraction of UO_2^{2+} ions by organophosphorus-functionalized pillar[5]-arenes with $[\text{UO}_2(\text{NO}_3)_2]$ as the extracted species in which uranium is coordinated to the phosphoric oxygens (Chen et al., 2019).

Lead in acidic solutions is most commonly found in the form of ions in the +2 oxidation state. Where the solution contains less than 1 mg Pb^{2+} in 1 dm³, the dominant forms are $\text{Pb}(\text{OH})^+$, $\text{Pb}(\text{OH})_{2(\text{aq})}$ and $\text{Pb}(\text{OH})_3^-$, while in solutions with a higher lead content, hydroxocations are formed: $\text{Pb}_3(\text{OH})_4^{2+}$, $\text{Pb}_4(\text{OH})_4^{4+}$, $\text{Pb}_6(\text{OH})_8^{4+}$, $\text{Pb}_3(\text{OH})_3^{3+}$ and $\text{Pb}_6\text{O}(\text{OH})_6^{4+}$ (Sylva and Brown, 1980; Breza and Manova, 2002; Powell et al., 2009). In the case of Cr^{3+} ions, their concentrations and forms of occurrence depend on the chemical and physical processes present in the aquatic environment. In the absence of a complexing agent other than H_2O or OH^- , Cr(III) in acidic environment (pH < 4) form aqua-complexes $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, and in diluted solutions with a pH in the range of 4–10, as a result of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ hydrolysis, the following complexes are formed: $[\text{Cr}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$, $[\text{Cr}(\text{OH})_2(\text{H}_2\text{O})_4]^+$ and $\text{Cr}(\text{OH})_{3(\text{aq})}$. In the aqueous solution at concentrations above $1.0 \cdot 10^{-6}$ M Cr(III), multiple-core complexes $[\text{Cr}_2(\text{OH})_2(\text{H}_2\text{O})_8]^{4+}$, $[\text{Cr}_3(\text{OH})_4(\text{H}_2\text{O})_9]^{5+}$, $[\text{Cr}_4\text{O}(\text{OH})_5(\text{H}_2\text{O})_{10}]^{5+}$ and $[\text{Cr}_4(\text{OH})_6(\text{H}_2\text{O})_{10}]^{6+}$ can be formed (Takeno, 2005).

Knowing the stoichiometry of the complexes and knowing that in acidic aqueous environment with pH 5.0 lead is present in the form of Pb^{2+} ions (Sylva and Brown, 1980), while chromium under these conditions is present as $\text{Cr}(\text{OH})^{2+}$ (about 70%), $\text{Cr}(\text{OH})_2^+$ (about 16%) and Cr^{3+} (about 8%) (Stünzi and Marty, 1983; Ramos et al., 1995), the reactions observed at the boundary of phases during an extraction of Pb(II) and Cr(III) ions from aqueous solutions of pH 5.0 using inert resorcinarenes **R7PS8** and **R7CEt8** (L) can be presented according to general equation 3 in the form of equations 7–10.



The participation of nitrate ions in the above reactions was confirmed by the measurement of these ions concentration in the aqueous phase before and after extraction process by using ion chromatography; lower concentration of NO_3^- was found in the aqueous phase after the extraction. However, more details are needed to determine the extraction site for these anions in the complex. Taking into account the stability constants (β) of each of the chromium species, the total chromium(III) concentration in the aqueous phase can be expressed as follows:

$$[\text{Cr}(\text{III})]_{\text{aq}} = [\text{Cr}^{3+}]_{\text{aq}} + [\text{Cr}(\text{OH})^{2+}]_{\text{aq}} + [\text{Cr}(\text{OH})_2^+]_{\text{aq}} = [\text{Cr}^{3+}]_{\text{aq}} + \beta_1 \cdot [\text{OH}^-] \cdot [\text{Cr}^{3+}]_{\text{aq}} + \beta_2 \cdot [\text{OH}^-]^2 \cdot [\text{Cr}^{3+}]_{\text{aq}} \quad (11)$$

3.9. Pb(II) and Cr(III) stripping from organic phase

Stripping of Pb(II) and Cr(III) from organic phase containing resorcinarenes **R7PS8** and **R7CEt8** to the solutions of nitric acid at concentrations in the range of 0.01 - 1.00 M was also performed. The changes in the stripping efficiency of Pb(II) and Cr(III) bound in the organic phase with **R7PS8** depending on HNO₃ concentration is presented in Fig. 8.

It was observed that the efficiency of examined ions stripping (*BE*) increases with an increasing acid concentration and reaches a maximum value for 1.0 M HNO₃ solution. Under these process conditions, it was possible to quantitatively recover Pb(II) from the organic phase containing resorcinarene **R7SP8** and 96% from the phase containing resorcinarene **R7CEt8**. In turn, Cr(III) were not extracted at all to the nitric acid solutions from the organic phases containing **R7PS8** and **R7CEt8**. Thus, the used extraction system with **R7SP8** makes it possible to obtain an aqueous solution containing exclusively Pb(II).

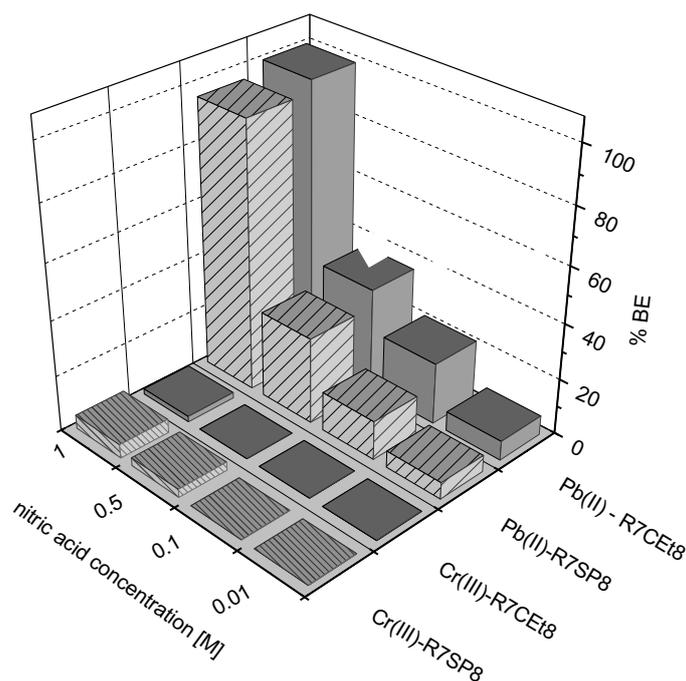


Fig. 8. Efficiency of Pb(II) and Cr(III) stripping as a function of nitric acid concentration; organic phase: chloroform solutions of **R7PS8** or **R7CEt8** loaded with the metal ions; aqueous phase: HNO₃ solution of concentration from 0.1 to 1.0 M

4. Conclusions

The study allowed to evaluate the suitability of selected resorcin[4]arenes for the efficient and selective extraction of Pb(II), Zn(II), Cd(II) and Cr(III) from aqueous solutions in solvent extraction. The results show that the extraction efficiency and selectivity of the examined ions using non-functionalized resorcin[4]arene is lower than that in the case of an application of resorcin[4]arenes containing thiophosphorylated or ester functional groups in the molecule. Better properties of the functionalized resorcinarenes for the extraction of Pb(II) and Cr(III) compared to Zn(II) and Cd(II) can be explained by both the theory of the best metal cation fitting to the macrocyclic cavity and the HSAB theory. The highest level of Pb(II) and Cr(III) separation was obtained for solutions of pH = 5.0, for the systems with an organic phase in the form of chloroform solution of thiophosphoryl and ester resorcin[4]arene derivative, respectively. An increase in Pb(II) and Cr(III) concentration results in a decrease in removal efficiency of these ions from the aqueous phase, thus, the proposed process can only be practically applied for the purification of water and wastewater with a low content of these ions. As a result of the reaction on the aqueous/organic phase boundary, complexes of Pb(II) and Cr(III) with resorcinarenes with 1:1 stoichiometry are formed. It is possible to quantitatively strip Pb(II) ions from the organic phase

containing octatophosphorylated heptylresorcin[4]arene derivative to 1.0 M nitric acid solution without stripping of Cr(III).

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