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EXTRACTION PROPERTIES OF TETRAHEPTYLRESORCIN[4]ARENES IN RELATION TO Cr(III) IONS

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Abstract: Resorcin[4]arene-based ligand bearing four heptyl chains at the lower rim of the molecule was prepared and modified by four tetradioxyphosphoryl groups in the upper rim. The compounds obtained were characterized by NMR spectroscopy and their extractability toward chromium(III) ions was studied. The influence of process parameters such as the pH of aqueous phase, agitation time and also extractant's structure and concentration on efficiency of Cr(III) ions solvent extraction is presented. The highest yield of Cr(III) solvent extraction was obtained for two-hour agitation time of $5.0 \cdot 10^{-4}$ M metal solution of pH 5.0 and $5.0 \cdot 10^{-3}$ M chloroform solution of the tetradioxyphosphorylated derivative of heptyl-resorcin[4]arene. Under optimal conditions, competitive solvent extraction of Cr(III), Zn(II), and Cd(II) ions was performed and separation factor values were established as 77.0 and 24.9 for Cr(III)/Cd(II) and Cr(III)/Zn(II) ions pairs, respectively. The stoichiometry of formed metal-ligand complexes 1:1 was found by classical slope analysis method.

Keywords: solvent extraction, resorcin[4]arenes, chromium(III), cadmium(II), zinc ions

Introduction

A large amount of toxic heavy metals present in the natural environment has become a serious problem worldwide and poses a huge threat to human health and life. Most of these metals are released into the environment from anthropogenic sources. Many industries that are involved in electroplating, leather tanning, textile dyeing, and wood preservation employ chromium solutions in their technological processes and release them to surface waters through wastewater discharge (Wolinska et al., 2013). Chromium is an element with specific biological properties that depend on its concentration and oxidation state. Many different forms of chromium occur in environmental waters, but trivalent chromium Cr(III) and hexavalent chromium Cr(VI) have a important biological relevance. Cr(III) ions at low concentration are

considered to be a key nutrient required for the proper metabolism of glucose, lipids and proteins but at high concentrations can lead to DNA damage and hence are regarded as toxic substance. Moreover, Cr(III) can be easily oxidized to Cr(VI) that is a very dangerous allergen, mutagen, and carcinogen, resulting in an increased risk of lung cancer (Dayan and Paine, 2001). Therefore, from human safety point of view, removal of chromium from industrial wastewater is significant to minimize its discharge into the environment. On the other hand, recovery and separation of chromium from other metals present in the wastewater is extremely important from an economic point of view.

Solvent extraction is one of the most effective techniques for the recovery of heavy metal ions and it is widely used in many industries in wastewater treatment. The efficiency of this process depends on many parameters such as ligand structure, pH of aqueous solution, type of organic solvent, temperature, and the duration of process. Although a large number of commercial (Rao and Sastri, 1980; Lanagan and Ibane, 2003, Wionczyk and Apostoluk, 2004; Luo et al., 2013) and newly synthesized compounds (Deligöz and Erdem, 2007; Ohto, 2010) are applied as ligands of metal ions, including Cr(III) ions, in solvent extraction systems, more selective extractants are still required.

Recently, several studies concerning the synthesis, properties, and applications of new macrocyclic extractants for the extractive removal of Cr(III) were published, but no researches have focused on the solvent extraction of Cr(III) using resorcinarene ligands. Jumina et al. (2007, 2011) applied resorcin[4]arenes for solid phase extraction of Cr(III) and Pb(II) ions. *C*-methyl and *C*-4-methoxyphenyl derivatives of resorcin[4]arene were good adsorbents of Cr(III) ions. It was found that the molecular structure of resorcin[4]arene has a significant impact on its adsorptive behavior in relation to the metal ions; a larger uptake of Cr(III) than Pb(II) ions was observed when ligand with *C*-methyl groups was used and a smaller uptake of Cr(III) than Pb(II) when *C*-4-methoxyphenyl derivative was used.

This work is a part of our investigation on the extractive properties of resorcin[4]arene derivatives toward toxic metal ions. In our earlier paper (Konczyk et al., 2010), the extractability of tetracarboxylresorcin[4]arene in relation to Pb(II) ions was presented, and a high selectivity of the extractant toward Pb(II) over Zn(II) and Cd(II) was found. In this study, tetraheptylresorcin[4]arene and its derivative functionalized by four diethoxythiophosphoryl groups at the upper rim were synthesized and applied for Cr(III) solvent extraction. The purpose of this study was to establish the factors determining the efficiency and selectivity of the process and to find the stoichiometry of the formed metal-resorcin[4]arene complexes.

Experimental part

Reagents and apparatus

The HPLC-grade chloroform (CHCl_3) used as the ligand solvent was obtained from POCH (Gliwice, Poland). The other organic chemicals were of commercially available reagent grade of Sigma or Merck and were used without further purification. All aqueous solutions were prepared using chemicals of analytical reagent grade (POCH, Across) and deionized water (conductivity – 0.10 $\mu\text{S}/\text{cm}$). Solutions of Cr(III), Zn(II), and Cd(II) were prepared by dissolving appropriate amounts of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in 0.1 M HNO_3 .

Metal ion concentration in aqueous solutions and the pH of solutions were measured by atomic absorption spectrometer Solar 939 and pH-meter Elmetron CX-731, respectively. ^1H NMR measurements were performed by Bruker Ultrashield Avance II spectrometer in CDCl_3 .

Synthesis of extractants

1,8,15,22-tetra(n-heptyl)-resorcin[4]arene (**1**) was synthesized according to a procedure recorded in (Schantwinkel et al., 2008). The equimolar mixture of 1,3-dihydroxybenzene and octanal in the ethanol medium with concentrated hydrochloric acid was boiled for 24 h. After the evaporation of the volatile compounds, the viscous residue was recrystallized three times from $\text{EtOH}/\text{H}_2\text{O}$ (1:1) mixture. The structure of **1** (Fig. 1) was confirmed by ^1H NMR spectroscopy (500 MHz, CDCl_3), δ : 0.830 (t, $^3J = 7.5$ Hz, 12H, CH_3), 1.150 (m, 24H, $\text{CH}_3-(\text{CH}_2)_3-\text{CH}_2$), 1.250 (m, 16H, $\text{C}_4\text{H}_9-(\text{CH}_2)_2-$), 2.011 (m, 8H, $-\text{CH}_2-\text{CH}$), 4.370 (t, $^3J = 7.5$ Hz, 4H, Ar-CH-Ar), 6.130 (s, 4H, Ar-H), 7.145 (s, 4H, Ar-H), 8.850 (s, 8H, Ar-OH).

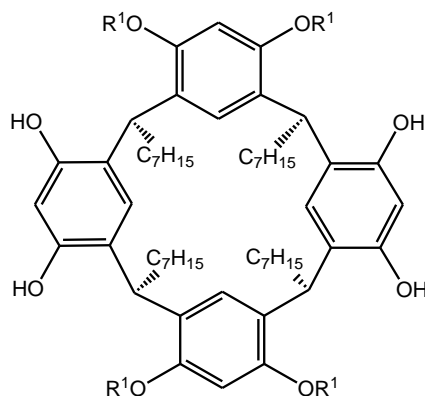


Fig. 1. Molecular structure of extractants **1** ($\text{R}^1 = \text{H}$) and **2** ($\text{R}^1 = \text{P}(\text{O})(\text{OC}_2\text{H}_5)_2$)

For obtaining 3,10,17,24,-tetrahydroxy-5,12,19,26-tetra(diethoxyphosphoryloxy)-1,8,15,22-tetra(n-heptyl)-resorcin[4]arene (**2**) 1 mol of resorcin[4]arene **1** and 4.1 mol

diethyl chlorophosphate and 10.0 mol of dry triethylamine in the dry chloroform medium was boiled for 2 days (control by the TLC method). After evaporating, the viscous residue was solved in the chloroform and washed twice with deionized water. The organic layer was dried over anhydrous sodium sulfate(VI), filtered and evaporated in the vacuum. The rest was recrystallized from hexane. The structure of obtained compound (Fig. 1) was confirmed by ^1H NMR spectroscopy: (500 MHz, CDCl_3), δ : 0.887 (t, $^3J = 7.5$ Hz, 12H), 1.01–1.24 (m, 4OH), 1.28 (t, $^3J = 7.5$ Hz, 24H), 2.12 (m, 8H), 3.70 (m, 16H), 4.38 (t, $^3J = 7.5$ Hz, 4H), 6.16 (s, 4H), 7.20 (s, 4H), 8.901 (s, 4H) and ^{31}P NMR (500 MHz, CDCl_3), δ : 10.09 ppm.

Solvent extraction procedure

The solvent extraction experiments were carried out at temperature 25 ± 0.1 °C in a closed glass flask at 1:1 volume ratio of aqueous and organic phases. The chloroform solution of resorcin[4]arene and aqueous solution containing ions of one metal or three metals (selectivity test) were agitated by mechanical shaker (IKA KS 4000ic control) at various times and rates ranging between 5 – 240 minutes and 100 – 400 rpm, respectively. Next, the mixture was settled for phase separation and the equilibrium concentration of the metal ions was measured using atomic absorption spectrometer (AAS Solar 939). The extractability of resorcin[4]arenes toward the studied metal ions was established as the percent extraction (%E) calculated as follows (1):

$$\%E = \frac{[\text{M}^{n+}]_{\text{org}}}{[\text{M}^{n+}]_{\text{aq},0}} \cdot 100\% \quad (1)$$

Metal ion concentrations in the organic phase ($[\text{M}^{n+}]_{\text{org}}$) were calculated from the difference of the metal ion concentrations in the aqueous phase before ($[\text{M}^{n+}]_{\text{aq},0}$) and after solvent extraction ($[\text{M}^{n+}]_{\text{aq}}$). The separation factors were determined from the following equation:

$$S = \frac{D_{\text{Cr}^{3+}}}{D_{\text{M}^{2+}}} \quad (2)$$

where M^{2+} is the given divalent metal ion and D is the metal distribution ratio between organic and aqueous phases:

$$D = \frac{[\text{M}^{n+}]_{\text{org}}}{[\text{M}^{n+}]_{\text{aq}}} \quad (3)$$

The pH of aqueous phase was adjusted by adding a small amount of nitric acid or tetramethylammonium hydroxide solutions. In back-extraction experiment, after partition of the phases, the aqueous phase was removed and replaced with the same volume of mineral acid (HNO_3 or HCl) solution. Such biphasic system was stirred

within 2 hours and the concentration of Cr(III) ions in aqueous phase was also measured by AAS.

Results and discussion

Extraction ability of resorcin[4]arenes toward Cr(III) ions

In preliminary solvent extraction experiments, the potential extractability of resorcin[4]arenes **1** and **2** toward Cr(III) ions was investigated. For this purpose, the metal ions were extracted from their single $5.0 \cdot 10^{-4}$ M nitrate solutions with pH of 5.0 to chloroform phase containing $1.0 \cdot 10^{-3}$ M of resorcin[4]arene **1** or **2**. It was found that the ligand structure had a strong impact on the Cr(III) removal efficiency. Non-substituted resorcin[4]arene **1** was not effective in transferring Cr(III) ions into organic phase; it extracted only ca. 20% of all chromium cations present in the aqueous phase. However, tetrasubstituted derivative **2** exhibited definitely better extraction ability toward the studied metal ions, which was nearly 95%. Poor extraction capacity of compound **1** can be attributed to non-fitting of the cation into the macrocyclic cavity. In this case, the ratio of Cr(III) ionic radius (0.12 nm, Wulfsberg, 1991) and resorcin[4]arene cavity diameter (0.99 nm, Makinen et al., 2001) is below “the best range” worded by Bartsch (1999) for complexation of alkali metal ions by crown, and lariat ethers and applied by many researchers for interpreting the extraction results obtained in other metal ion/macrocyclic ligand systems (Matulkova and Rohovec, 2005; Ulewicz and Walkowiak, 2006; Benosmane et al., 2009). This indicates that Cr(III) ions are too small to fit into the macrocyclic cavity of resorcin[4]arene formed by intramolecular hydrogen bonds between the OH groups of the resorcinol subunits. Functionalization of compound **1** by four diethoxyphosphoryl groups probably lead to change its conformational flexibilities and ligand preorganization. In a consequence, the oxygen atoms of P=O groups in compound **2** can form a suitable cavity for Cr(III) complexation.

Effect of agitation rate and time

The agitating rate and time of Cr(III) ions extraction from their $5.0 \cdot 10^{-4}$ M aqueous solution of pH 5.0 to $5.0 \cdot 10^{-3}$ M solution of the used resorcin[4]arenes in chloroform was optimized in order to obtain the best extraction percentages indicating the achievement of the process equilibrium. The optimum agitation rate was selected based on the studies of Cr(III) extraction process at five different agitation rates of the phases between 100–400 rpm and constant the other parameters. It was noted that the extraction process was practically independent of agitation rate both in the case of ligand **1** and **2**; only small increase (8%) of the extraction percentage by raising agitation rate from 100 and 200 rpm was observed for ligand **2**. Therefore, an agitation rate of 200 rpm was applied for all studies. In the next experiment, agitating time was changed from 5 to 240 min, while all the other parameters were fixed. From 120 to

240 min of the extraction by both ligand **1** and ligand **2** only slight changes of %E value, ranging in the experimental error $\pm 2\%$, were detected, therefore 2-hour contact time of phases was maintained during the further extraction studies.

Effect of aqueous phase acidity

Cr(III) ions were extracted from solutions at the pH range of 1.0–5.0 to $5.0 \cdot 10^{-3}$ M chloroform solutions of **1** and **2**. The %E of Cr(III) ions slightly increased when the pH of solution was increased and attained a maximum value at pH 5.0 (Fig. 2).

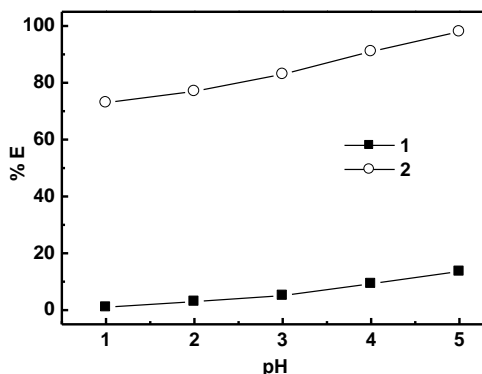
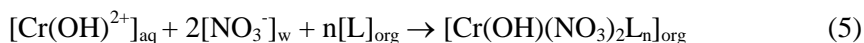


Fig. 2. Extraction percentages of Cr(III) ions by **1** and **2** as a function of pH of aqueous phase

Under these acidic conditions, compound **2** transferred to the organic phase ca. 100% of Cr(III) ions while compound **1** extracted only 10% of these cations. Small changes in %E of Cr(III) with an increased pH indicate that the protonation of phenolic groups of the studied macrocycles did not occur under extraction conditions and the extracted complex was electrically neutral. On the other hand, it is known that chromium(III) may exist in different ionic pH-dependent forms. In more acidic aqueous solutions ($\text{pH} \leq 3.0$), chromium occurs mainly in the form of Cr^{3+} , whereas at pH 5.0, $\text{Cr}(\text{OH})^{2+}$ dominates (ca. 70%) (Ramos et al., 1995). Larger divalent chromium hydroxycations probably better matches the macrocyclic cavity of **2** than trivalent cations; therefore, chromium is more effectively extracted at higher pH than at lower pH. The extraction process for Cr(III) ions with ligand **2** at the aqueous/organic interface can be written as follows (4)-(5):



where aq, org, and L denote the aqueous phase, organic phase, and extractant, respectively.

Effect of ligand concentration

Solvent extraction of Cr(III) at fixed metal ions concentration and with varying concentration of compound **2** under optimal conditions of agitation time and aqueous phase pH was carried out. Effectiveness of Cr(III) extraction increased by increasing the extractant concentration from $5.0 \cdot 10^{-4}$ M to an optimum level of $1.0 \cdot 10^{-2}$ M, in which $5.0 \cdot 10^{-4}$ M of metal ions was quantitatively transferred to the organic phase. Figure 3 shows the logarithmic relation of the Cr(III) distribution ratio between the aqueous and organic phases vs. concentration of extractant **2**.

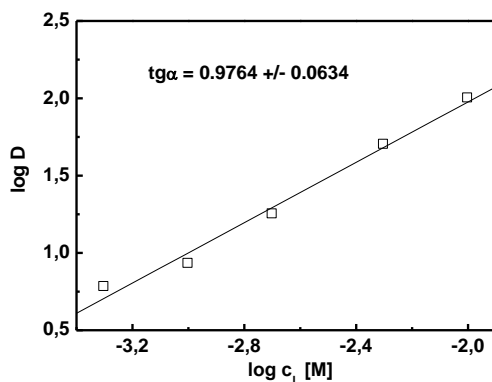


Fig. 3. Effect of ligand concentration on the distribution coefficient ($c_{\text{Cr(III)}} = 5.0 \cdot 10^{-4}$ M, pH = 5.0, L = resorcin[4]arene **2**)

The slope of the best-fit straight line was found to be 0.94 in the investigated system, which indicates the participation of one ligand molecule in the one Cr(III) ion extraction and complexes $\text{Cr}(\text{NO}_3)_3\text{L}$ and $\text{Cr}(\text{OH})(\text{NO}_3)_2\text{L}$ were formed. This stoichiometry agrees with that obtained during Cr(III) ions extraction with 18-crown-6 (Bhar et al., 2013).

Effect of metal ions concentration

The effect of initial metal ions concentration in the aqueous phase on the Cr(III) extraction percentage was also analyzed, keeping the pH constant at 5.0.

As can be seen from Figure 4, the increase of Cr(III) concentration in aqueous phase from $1.0 \cdot 10^{-4}$ to $5.0 \cdot 10^{-3}$ M involves a decrease of the extractability of resorcin[4]arene **2**. The fact is that a higher metal content in the aqueous phase requires a higher concentration of extractant in the organic phase; therefore, the concentration of the extractant used seems to be insufficient to extract the metal ions that are above the concentration of $5.0 \cdot 10^{-4}$ M. Furthermore, the extraction process of Cr(III) ions from more concentrated aqueous solutions is hindered because of the third-phase formation. In consequence, quantitative extraction of Cr(III) ions by ligand **2** is possible only from their dilute aqueous solution of concentration $5.0 \cdot 10^{-4}$ M and

lower. Since higher concentration of the metal is more preferable in the aspect of potential application of the studied extraction process for Cr(III) removal from wastewaters, the metal concentration of $5.0 \cdot 10^{-4}$ M was selected for all experiments.

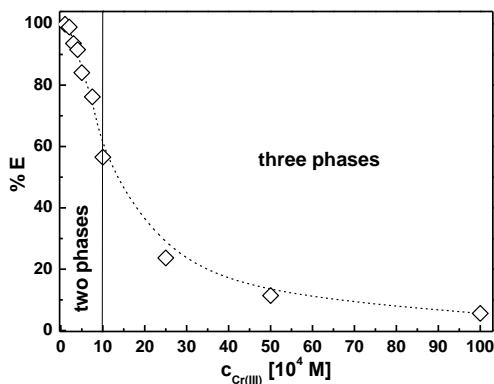


Fig. 4. Effect of Cr(III) ions concentration in aqueous solution on their extraction efficiency by resorcin[4]arene **2**

Competitive extraction of heavy metal ions

The unique property of macrocyclic compounds is their high selectivity for a target metal ions. Therefore, the competitive extraction of Cr(III), Cd(II) and Zn(II) ions from equimolar ($5.0 \cdot 10^{-4}$ M) mixture of their nitrate solution by resorcin[4]arene **2** was also studied. Under optimal conditions of the process, an effective removal and separation of Cr(III) ions over Cd(II) and Zn(II) ions was possible. The extraction yields of Cd(II) and Zn(II) ions by **2** were lower than 15% while Cr(III) extraction was quantitative. According to Pearson's hard and soft acids and bases (HSAB) theory (Pearson, 1963) this can be explained as follows: resorcin[4]arene **2** possessing hard coordination sites (oxygen atoms of phosphoryl groups) is a hard base and has stronger affinity toward Cr(III) ions as a hard Lewis acids compared to Zn(II) and Cd(II) ions that are classified as a borderline and soft Lewis acids, respectively. The transport selectivity order obtained was as follows: Cr(III) \gg Cd(II) $>$ Zn(II) with separation factor values of 77.0 and 24.9 for Cr(III)/Cd(II) and Cr(III)/Zn(II) ions pairs, respectively.

Conclusions

Results of this study revealed that heptylresorcin[4]arene is a poor extractant of Cr(III) ions. However, modification of this molecule by four tetradietoxyphosphoryl groups makes it an efficient and selective ligand that could quantitatively extract Cr(III) ions from their $5.0 \cdot 10^{-4}$ M nitrate aqueous solutions at pH 5.0 in 2-hour solvent extraction process. The extraction of Cr(III) by the applied resorcin[4]arene is strongly

dependent on the agitation time, aqueous phase acidity, and also metal and extractant concentrations. It was found that under optimal conditions of the extraction process, Cr(III) ions could be selectively separated from Cd(II) and Zn(II) ions with a separation factor of 77.0 and 24.9, respectively. The stoichiometric study by using classical slope analysis suggested the formation of extracted species corresponding to mononuclear complexes of chromium with resorcin[4]arene ligand of probable structure $\text{Cr}(\text{NO}_3)_3\text{L}$ and/or $\text{Cr}(\text{OH})(\text{NO}_3)_2\text{L}$. Moreover, further studies are needed to confirm these findings.

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