Desalination and Water Treatment
www.deswater.com

26 (2011) 72–78
February

1944-3994/1944-3986 © 2011 Desalination Publications. All rights reserved
doi: 10/5004/dwt.2011.2112

Removal of heavy metal ions from aqueous solution by azocalix[4]arene

Özlem Özen Karakuş[a,*], Serkan Elçin[a], Mustafa Yilmaz[b], Hasalettin Deligöz[a]

[a]*Faculty of Science-Arts, Department of Chemistry, Pamukkale University, Denizli, Turkey*
Tel. +90 258 296 3613; email: oozen@pau.edu.tr.
[b]*Faculty of Science, Department of Chemistry, Selçuk University, Konya, Turkey*

Received 25 November 2009; Accepted 7 May 2010

ABSTRACT

This study presents the preparation, characterization, and sorption properties of new chromogenic azocalix[4]arene based oligomers (1a, 2a and 3a) towards some selected heavy metal (Ag^+, Hg^+, Hg^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+} and Cr^{3+}) cations. These compounds have been synthesized via polycondensation reactions involving 25,27-diethylacetoxy-26,28-dihydroxy-5,17-bis(4-nitrophenylazo)calix[4]arene (1), 25,27-diethyl acetoxy-26,28-dihydroxy-5,17-bis(4-ethylphenylazo)calix[4]arene (2), or 25,27-diethyl acetoxy-26,28-dihydroxy-5,17-bis(4-bromophenylazo)calix[4]arene (3) with 1,4-bisamino methyl benzene. Two-phase sorption properties of azocalixarene oligomers (1a, 2a and 3a) towards the selected metal cations are reported. The binding properties of these oligomers towards the selected metal cations were observed to be higher than those of monomeric analogs. It is suggested that this increased binding ability arises from highly rigid azo (–N=N–) group moiety at the upper rim of calix[4]arene in the oligomeric skeleton.

Keywords: Azocalixarene; Batch sorption; Calix[4]arene; Heavy metals; Oligomer; Polyamide

1. Introduction

Heavy metal contamination of various surface waters or groundwater is a great concern due to the toxic effect of heavy metal ions on plants, animals and human beings [1–3]. Therefore, effective removal of heavy metal ions from water or various industrial effluents is crucially important and has attracted considerable research and practical interest. Many methods, such as chemical precipitation, ion exchange, reverse osmosis and sorption, etc., have been used to remove heavy metal ions from various aqueous solutions [4–6]. Among the stated methods sorption has increasingly received more attention in recent years due to its relative simplicity, cost efficiency and high effectivity in removing heavy metal ions, especially at low to medium metal ion concentrations from wastewater [7,8].

Macromolecules are widely used in host–guest chemistry for the construction of various receptors for charged and neutral molecules. Calix[*n*]arenes, cyclic oligomers of phenolic units linked through the ortho positions, are a fascinating class of macrocycles [9]. Chemical modification of *upper* or *lower rim* of these compounds has turned this class of synthetic ionophores into effective extractants for transferring anionic [10], cationic [11,12] or neutral molecules from aqueous solution into an organic layer. During the last few decades they have attracted much attention as ionophores in supramolecular receptors.

The complexation properties of these molecules appear to be highly dependent on the nature and number of donor atoms as well as the conformation of the calix[4]arene moiety [13,14]. Therefore, a variety of sophisticated anion complexing ligands containing a calix[4]arene backbone have been designed and synthesized to be used as selective anion extractants [15,16]. These molecules are generally amine or amide substituted

---

*Corresponding author.

Presented at the International workshop on urbanisation, land use, land degradation and environment (ULE 2009), 28 September – 1 October 2009, Denizli, Turkey

calix[4]arene derivatives which are capable of interacting with anions by hydrogen bonds [17]. Recently, we have reported calix[4]arene based receptors which can effectively bind to anions and be useful in various applications such as laboratory, clinical, environmental, and industrial based analyses [18,19].

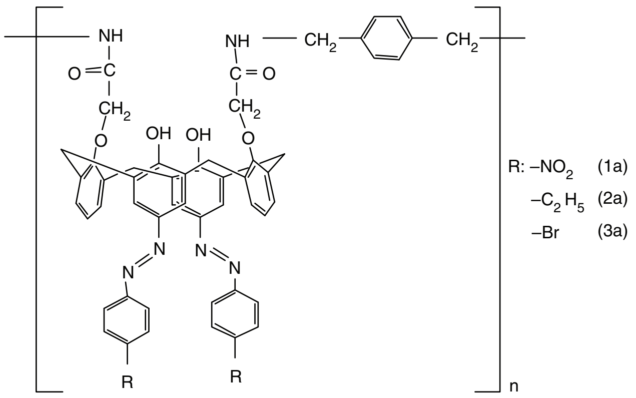
Azocalixarenes, bearing single conjugated chromophore azo (–N=N–) groups in their *p*-positions, are attached to ester or ether subunits at either the *upper* or the *lower rim* of the calixarene macrocyclic ring [20]. The esteric or etheric receptors based on the azocalixarene platform may have the potential applications in preparation, separation, and analysis of enantiomers. In this regard, investigations on the synthesis and characterized recognition properties of azocalix[4]arene derivatives have attracted considerable attention [21–24].

Transition metal (Ag^+, Hg^+, Hg^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Cr^{3+}) cations are recognized as highly toxic, which makes their presence in environmental waters or soils undesirable. Since they are not degradable, such metals can be accumulated in the environment and produce toxic effects in plants and animals even at very low concentrations. Heavy metal ion removal from waters has been an important subject of extensive technological research and application of recovering processes. Therefore, separation of these trace metals is vital due to their potential health and ecological [25].

In our earlier studies, we have synthesized polymeric calix[*n*]arene derivatives and investigated their selective extraction of transition metal ions [26–29]. Afterwards we have synthesized chromogenic azocalix[4]arene derivatives containing amid group at *lower rim* and investigated selectivities of these derivatives in extraction of transition metal cations [30].

Our research group formerly reported high selectivity of azocalix[4]arene derivatized ligands in extracting the alkaline earth (Sr^{2+}) and the transition metal (Ag^+, Hg^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Cr^{3+}) cations. This has been assessed by extraction studies with metal picrates from aqueous solution into chloroform [31].

Generally, it has been accepted that calixarene-based ionophores frequently show superior ion selectivity with respect to crown ether-based ionophores [32]. The objective of this study is to investigate and compare the extraction properties of diethyl ester derivatives of *di*-azocalix[4]arene (1, 2 and 3) and their azocalix[4] arene-oligomers (1a, 2a and 3a). Transition metal cations has also been introduced to induce azo groups in the oligomers, because azocalix[4] arene oligomers are used as stationary phase in separating metal ions. Interested synthetic oligomers have potential application in separating metal ions. They are also perfect candidates for recognition especially in separation of transition metal cations. Thus this property will be highly focused in the future studies our research group.



Scheme 1. Sorbents used in this work.

This study presents the preparation, characterization, and sorption properties of new chromogenic azocalix[4]arene oligomers (1a, 2a and 3a) towards some selected heavy metal (Ag^+, Hg^+, Hg^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+} and Cr^{3+}) cations (Scheme 1).

2. Materials and methods

2.1. Apparatus

Melting points of compounds are determined by Schorp-APAII digital melting point apparatus in a sealed capillary and reported without correction. ^{1}H-NMR spectra are referenced to tetramethylsilane (TMS) at 0.00 ppm as an internal standard and recorded with a Bruker 200 MHz spectrometer at room temperature (25 ± 1°C). Infrared (IR) spectra are recorded on a Mattson 1000 Fourier Transform Infrared (FTIR) spectrometer by using KBr pellets. UV-vis spectra are obtained on a Shimadzu 160A UV-Visible recording spectrophotometer. The elemental analyses are performed in Laboratories of TUBITAK (Scientific and Technical Research Council of Turkey).

Molecular weight determinations are performed by gel permeation chromatography (GPC) in tetrahydrofuran (THF) at 30 °C using an Agilent (HP) GPC with refractive index detector, with a solvent flow rate of 0.6 ml/min and a sample concentration of 2.0 mg/ml. The micro columns are calibrated using a set of narrow polydispersity polystyrene standards. M_{an} and M_w are calculated in customary fashion with routine Millennium software on a PC, which controlled the entire GPC apparatus.

2.2. Reagents

Analytical thin layer chromatography (TLC) tests are performed on precoated silica gel plates (SiO_2, Merck PF254), while silica gel 60 (Merck, particle size 0.040–0.063 mm, 230–240 mesh) is used for preparative column chromatography. All chemicals used are of analytical grade purity and used without further purification. Some solvents in crystallization are retained in the analytical samples. Best fits between the analytical values and appropriate fractional increments of solvents were used. All aqueous solutions are prepared with deionized water which have been passed through a Human Power I Plus I + UV water purification system.

2.3. Synthesis

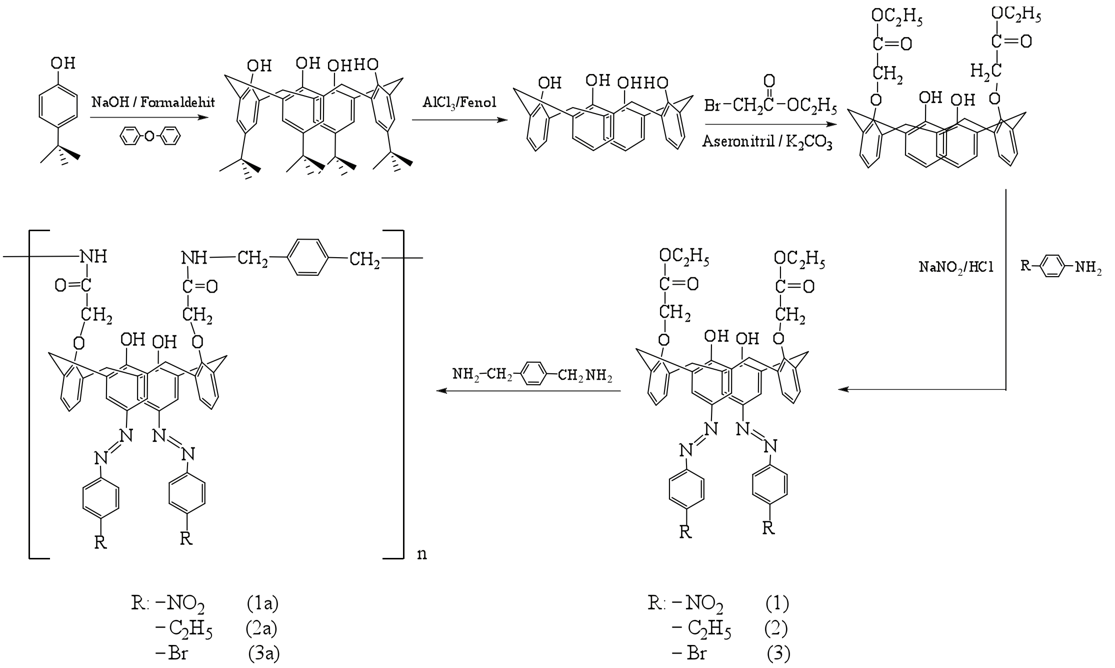
p-tert-Butylcalix[4]arene [33], calix[4]arene [34] and 25,27-diethylacetonyloxy-26,28-dihydroxycalix[4]arene [35] are synthesized as described by a previously reported method. The synthesis of calix[4]arene was performed using the method of Gutsche et al. [33,34]. In our previous work, we have investigated the azo coupling reactions of diethylester calix[n]arene with 4-nitro, 4-ethyl or 4-bromobenzenediazonium chlorides. The series of three novel azocalix[4]arene derivatives described herein were synthesized according to the method described by Deligoz et al. [23]. All reactions have been proceeded smoothly producing the corresponding azo compounds in acceptable yields.

2.3.1. Synthesis of 25,27-diethylacetoxy-26,28-dihydroxy-5,17-(4-nitrophenylazo) calix[4]arene (1) [23]

A solution of 4-nitrophenyldiazonium chloride, which is prepared from 4-nitroaniline (0.5 g, 3.62 mmol), sodium nitrite (0.31 g, 4.49 mmol) and *conc*. HCl (4 ml) in water (3 ml), is added slowly to a cold (5 °C) solution of 25,27-diethylacetoxy-26,28-dihydroxycalix[4] arene (1.0 g, 1.67 mmol) in DMF-H_2O (13 ml, 8:5, v/v). After waiting for two hours addition of sodium acetate trihydrate (0.62 g, 5.10 mmol) gave a dark brown suspension which than is filtered, washed with water [yield, 1.20 g (81%)] followingly. Purification of sample by column chromatography (1:1/v:v EtOAc:Hexane) yielded an orange product. (yield, 0.90 g (62%), m.p. 165 °C). [Found: C: 65.10; H: 4.69; N: 9.10]; $C_{48}H_{42}N_6O_{12}$ requires C: 64.42; H: 4.72; N: 9.39. IR (KBr) ʋ: 3480 cm^{-1} (–OH), 1757 cm^{-1} (–C=O), 1466 cm^{-1} (–N=N–), 1209 cm^{-1} (C–O). ^{1}H-NMR (DMSO-d_6, 25 °C) δ_H: 1.3 (6H, t, $-CH_3$), 3.4–4.5 (d, 8H, J = 13.4 Hz, Ar–CH_2–Ar), 4.3 (q, 4H, $-CH_2-CH_3$), 4.7 (s, 4H,–CH_2–C=O), 6.7–6.8 (m, 8H, ArH–NO_2), 6.9–7.1 (m, 10H, Ar–H), 7.5 (s, 2H, OH).

2.3.2. Synthesis of 25,27-diethylacetoxy-26,28-dihydroxy-5,17-(4-nitrophenylazo) calix[4]arene (1) [23]

A solution of 4-nitrophenyldiazonium chloride, which is prepared from 4-nitroaniline (0.5 g, 3.62 mmol), sodium nitrite (0.31 g, 4.49 mmol) and conc. HCl (4 ml) in water (3 ml), is added slowly to a cold (5 °C) solution of 25,27-diethylacetoxy-26,28-dihydroxycalix[4]arene (1.0g, 1.67 mmol) in DMF-H_2O (13 ml, 8:5, v/v). After waiting for two hours addition of sodium acetate trihydrate (0.62 g, 5.10 mmol) gave a dark brown suspension which than is filtered, washed with water [yield, 1.20g (81%)]



Scheme 2. Synthesis of azocalix[4]arene oligomers.

followingly. Purification of sample by column chromatography (1:1/v:v EtOAc:Hexane) yielded an orange product. (yield, 0.90 g (62%), m.p. 165 ºC). [Found: C: 65.10; H: 4.69; N: 9.10]; $C_{48}H_{42}N_6O_{12}$ requires C: 64.42; H: 4.72; N: 9.39. IR (KBr) υ: 3480 cm^{-1} (–OH), 1757 cm^{-1} (–C=O), 1466 cm^{-1} (–N=N–), 1209 cm^{-1} (C–O). ^{1}H-NMR (DMSO-d_6, 25 °C) δ_H: 1.3 (6H, t, –CH_3), 3.4–4.5 (d, 8H, *J*=13.4 Hz, Ar–CH_2–Ar), 4.3 (q, 4H, –CH_2–CH_3), 4.7 (s, 4H,–CH_2–C=O), 6.7–6.8 (m, 8H, ArH–NO_2), 6.9–7.1 (m, 10H, Ar–H), 7.5 (s, 2H, OH).

2.3.3. Synthesis of 25,27-diethylacetoxy-26,28-dihydroxy-5,17-(4-ethylphenylazo) calix[4]arene (2)

Azocalix[4]arene 2 is prepared by using 4-ethylaniline in water/HCl as described above. It is filtered, washed with water and dried under vacuum respectively [yield, 1.12 g (77%)]. Purification of sample by column chromatography (1:1/v:v EtOAc:Hexane) yielded a yellow product (yield, 0.78g (53%), mp. 165 ºC). [Found: C: 72.10; H: 5.89; N: 6.39]; $C_{52}H_{52}N_4O_8$ requires C: 72.54; H: 6.09; N: 6.51. IR (KBr) υ: 3426 cm^{-1} (–OH), 1748 cm^{-1} (–C=O), 1458 cm^{-1} (–N=N–), 1194 cm^{-1} (C–O). ^{1}H-NMR (DMSO-d_6, 25 °C) δ_H: H: 1.3 (t, 6H, –CH_3), 1.4 (t, 6H, CH_3.), 2.7 (q, 4H, CH_2–CH_3), 3.5–4.5 (d, 8H, J=13.4 Hz, Ar–CH_2–Ar), 4,3 (q, 4H, CH_2–CH_3), 4.7 (s, 4H, –CH_2–C = O), 6.8–7.0 (m, 8H, ArH–C_2H_5), 7.3–7.7 (m, 8H, Ar–H), 8.2 (s, 2H, OH).

2.3.4. Synthesis of 25,27-diethylacetoxy-26,28-dihydroxy-5,17-(4-bromophenylazo) calix[4]arene (3)

Azocalix[4]arene 3 is prepared by using 4-bromoaniline in water/HCl as described above. It is filtered, washed with water and dried under vacuum respectively [yield, 1.21 g (76%)]. Purification of sample by column chromatography (1:1/v:v EtOAc:Hexane) yielded a dark yellow product. (yield, 0.79 g (50%), mp. 146 °C). [Found: C: 60.90; H: 4.29; Br: 16.50; N: 5.93]; $C_{48}H_{42}Br_2N_4O_8$ requires C: 59.89; H: 4.40; Br: 16.60; N: 5.82. IR (KBr) υ: 3426 cm^{-1} (–OH), 1752 cm^{-1} (–C=O), 1468 cm^{-1} (–N=N–), 1195 cm^{-1} (C–O). ^{1}H-NMR (DMSO-d_6, 25 °C) δ_H: 1.3 (t, 6H, –CH_3), 3.4–4.5 (d, 8H, *J*=13.4 Hz, Ar–CH_2–Ar), 4.3 (q, 4H, –CH_2–CH_3), 4.7 (s, 4H, –CH_2–C=O), 6.6–7.8 (m, 8H, ArH–Br), 6.9–7.1 (m,10H, Ar–H), 7.5 (s, 2H,–OH).

2.3.5. Preparation of azocalix[4]arene-oligomer 1a [36]

1.0 g (0.11 mmol) of 25,27-diethylacetoxy-26,28-dihydroxy-5,17-(4-nitrophenylazo) azocalix[4]arene (1) and 15 equivalent moles of 1,4-bisaminomethyl benzene in toluene-methanol (1:1/v:v) solution is refluxed by using a double-necked round bottom flask. After 30 h the solution is dried under vacuum. Resulting residue is dissolved in chloroform before extracting with 1 N H_2SO_4 and H_2O respectively. The solid phase is separated from organic phase and obtained yellow product. (yield, 0.92 g (87%), mp. 238–240 °C). IR (KBr) υ: 3376 cm^{-1} (–OH), 1664 cm^{-1} (–C=O), 1465 cm^{-1} (–N=N–), 1219 cm^{-1} (C–O). ^{1}H-NMR (DMSO-d_6, 25 °C) δ_H: 3.4–4.3 (bd, 8H, *J*=13.4 Hz, Ar–CH_2–Ar), 4.5 (m, 4H, –CH_2–NH), 4.7 (bs, 4H, –CH_2–C=O), 6.6–6.8 (m, 8H, ArH–NO_2), 7.0–7.3 (m, 10H, calix–Ar–H), 7.4, (m, 8H, Ar–H), 8.0 (bs, 2H, OH), 9.0 (bs, 2H, NH).

2.3.6. Preparation of azocalix[4]arene-oligomer 2a

Azocalix[4]arene-oligomer 2a is prepared by using compound 2 as described in previous section. It is appeared as a yellow product. (yield, 0.60 g (57%), mp. 218–220 °C). IR (KBr) υ: 3377 cm^{-1} (–OH), 1670 cm^{-1} (–C=O), 1465 cm^{-1} (–N=N–), 1218 cm^{-1} (C–O). ^{1}H-NMR (DMSO-d_6, 25 ºC) δ_H: 3.4–4.2 m, (8H, *J*=13.4 Hz, Ar–CH_2–Ar), 4.5 (m, 4H,–CH_2–NH), 4.7 (bs, 4H, –CH_2–C=O), 6.6–6.8 (m, 8H, ArH–C_2H_5), 7.0–7.3 (m, 10H, calix–Ar–H), 7.4, (m, 8H, Ar–H), 8.0 (bs, 2H, OH), 9.0 (bs, 2H, NH).

2.3.7. Preparation of azocalix[4]arene-oligomer 3a

Azocalix[4]arene-oligomer 3a is prepared by using compound 3 as described in previous section. It is appeared as a yellow product. (yield, 0.87 g (83%), mp. 283–285 ºC). IR (KBr) υ: 3320 cm^{-1} (–OH), 1663 cm^{-1} (–C=O), 1464 cm^{-1} (–N=N–), 1110 cm^{-1} (C–O). ^{1}H-NMR (DMSO-d_6, 25 ºC) δ_H: 3.3–4.0 (bd, 8H, *J* = 13.4 Hz, Ar–CH_2–Ar), 4.2 (bq,4H,–CH_2–NH), 4.4 (bs, 4H, –CH_2–C=O), 6.6–6.8 (m, 8H, ArH–Br), 7.0–7.3 (m, 10H, calix–Ar–H), 7.4, (m, 8H, Ar–H), 8.5 (s, 2H, OH), 9.0 (s, 2H, NH).

2.4. Batch Sorption

Picrate extraction experiments were performed by using Cram procedure [37]. The azocalix[4]arene-oligomers 1a, 2a and 3a (1.0×10^{-2} g) were separately mixed with 10 ml of aqueous picric acid (2,4,6-trinitrophenol) and transition metal salt (M^{2+} $(NO_3)_2$) solution. Resulting suspension was shaken at room temperature for 20 min in a closed glass flask. The sorbent was removed by filtration before measurements. The sorption experiments and absorbance measurements were performed on each cation attached azocalix[4]arene oligomer system three times. Shimadzu 160A UV-Visible recording spectrophotometer was used to determine the concentration of the picrate remained in the aqueous phase after the sorption.

The salts used for the sorption, $AgNO_3$, $HgNO_3$, $Hg(NO_3)_2$, $Co(NO_3)_2$, $Ni(NO_3)_2$, $Cu(NO_3)_2$, $Cd(NO_3)_2$ and $Cr(NO_3)_2$, were used as reagent grade. The transition metal picrates were prepared by stepwise addition of 1.0×10^{-3} mol l^{-1} metal nitrate solution to 2.5×10^{-5} mol l^{-1} aqueous picric acid solution. Resulting suspension was shaken at room temperature for 1 h.

The sorption percentage of ions (S) was calculated using the equation

$$S\,(\%) = [(C_i - C_e)/C_i] \times 100$$

where C_i and C_e are initial and final concentrations of metal picrates before and after sorption respectively.

3. Results and discussions

3.1. Results and characterization of the products

The main focus of this work is to design new azocalixarene based ionophores which can effectively bind cations and be useful in various applications such as laboratory, clinical, environmental, and industrial based analyses. To achieve the desired goal, *p-tert*-butylcalix[4]arene has chosen as precursor. A synthetic strategy has been developed to enable its derivatization. Such a synthetic route is depicted in Scheme 2. The substitution of calix[4]arene at its *lower rim* has been carried out in the presence of potassium carbonate and sodium iodide in dry acetonitrile with bromoethylacetate. Alternatively, the syntheses of azocalix[4]arenes 1, 2 and 3 are based on the previously published procedures to afford the cone conformations in 62, 53 and 50% yield, respectively [23].

Reported procedures have been followed for the preparation of azocalix[4]arenes 1, 2 and 3. Compounds of azocalix[4]arene oligomers 1a, 2a and 3a were synthesized as shown in Scheme 2. Besides traditional organic spectroscopic identification (FT-IR and ^{1}H-NMR) of all these azocalix[4]arenes, NMR spectral analysis of azocalix[4]arene-oligomers 1a, 2a and 3a confirmed their structures to be in *cone* conformation.

The preparation of *di*-azocalix[4]arenes has been reported in the literature [28] but now we have prepared them with better yields. Thereafter, azocalix[4]arenes 1, 2 and 3 were used as precursors for the synthesis of oligomer supported azocalix[4]arene ionophores (1a, 2a and 3a) by polycondensation reactions. Azocalix[4]arene-oligomers 1a, 2a and 3a were prepared by heating 1, 2 and 3 with 1,4-bisaminomethyl benzene in toluene-ethanol (1:1, v/v) for 30 h under inert atmosphere in 87, 57 and 83% yield, respectively.

Azocalix[4]arene oligomers 1a–3a were also characterized by FT-IR and ^{1}H-NMR spectroscopy. The formation of amide bands of calix[4]arene oligomers (1a, 2a and 3a) was confirmed by the appearance of the characteristic amide bands at about 1663–1670 cm^{-1} in their IR spectra, and by the disappearance of ester carbonyl band at 1752–1758 cm^{-1} in the IR spectra.

The molecular weight of azocalix[4]arene-oligomers 1a–3a were determined by GPC in THF against polystyrene standards. The number average molecular weight (M_w) of 1a–3a were found to be 2938, 2837 and 3134 g/mol, respectively. This value indicates the presence of three azocalix[4]arene units in the oligomeric skeleton.

^{1}H-NMR spectroscopy is a versatile tool for the identification of azocalix[4]arene conformations [20]. The ^{1}H-NMR spectra of azocalix[4]arene 1, 2 and 3 are those of a typical AB pattern for the methylene bridge protons (Ar–CH_2–Ar) of the calixarene moiety at 3.4 and 4.5 ppm (J=13.4 Hz) for all three compounds which indicates that all of them exists in cone conformation. Alternatively, ^{1}H-NMR spectrum of azocalix[4]arene 1 contains aromatic meta protons at δ=6.7 ppm (J=8.6 Hz) and aromatic ortho protons at δ=6.8 ppm (J=8.6 Hz), which indicate that the azo coupling reactions of *p*-nitroaniline for azocalixarene 1 has been occurred.

3.2. Batch sorption

Industrial processes introduce up to a million different pollutants into the atmosphere and the aquatic ecosystem. Heavy metals are one group of these substances, although not all of them are considered to be harmful to humans. Toxic heavy metal ions are important because of their high toxicity and presence in soils and waters. The azocalix[4]arene molecule is a macrocycle used effectively in the complexation of the heavy metal pollutants.

Different functionalized azocalixarenes are potentially excellent starting materials for the selective designing of new materials. In the present work the preparation of *di*-functionalized azocalix[4]arene at the *upper rim* and its conversion to the 1,4-bisamino methyl benzene and finally its metal sorption are reported. In order to find the transportation rate of metal cations from aqueous phase to organic phase metal picrates have been formed by using picric acid. This has enabled us detection of metal picrates with UV-vis spectroscopy. Azocalix[4]arenes are potentially capable of forming stable complexes with metal ions [9].

Transportation experiments for picrate salts were carried out with a H_2O–$CHCl_3$ liquid-liquid or liquid-solid phase transfer system using the diazo coupling calix[n]arene and diazo compounds as cation carriers. The results of the cation transportion experiments are in good agreement with those of the two-phase extraction measurements.

The ionophoric properties of oligomers 1a–3a towards the transition metal cations were investigated by the picrate sorption method [37]. These data were obtained by using chloroform solutions of the ligands in extracting metal picrates from aqueous solution. Equal volumes (10 ml) of aqueous solutions of metal picrates (2×10^{-5} M) and solutions of azocalix[4]arene derivatives (1×10^{-3} M) in chloroform were vigorously shaken at 25 °C for an hour. After the completion of phase separation, absorbance values have been measured three times. The equilibrium concentration of picrate in aqueous phase has been determined as 354 nm (λ_{max}). The results expressed as percentage of

Table 1
Extraction/sorption of metal picrates with ligands[a]

	Picrate salt sorption (%)							
Ligand	Ag^+	Hg^{2+}	Hg^+	Co^{2+}	Ni^{2+}	Cu^{2+}	Cd^{2+}	Cr^{3+}
1	3.39	25.82	21.08	–	2.27	2.56	1.21	18.81
2	–	28.63	21.17	2.58	3.78	3.74	1.46	18.93
3	5.27	26.59	15.98	2.14	1.89	3.44	4.39	17.69
1a	74.26	69.91	82.51	67.04	70.01	70.60	71.63	62.50
2a	82.18	76.42	87.83	81.28	77.91	83.74	86.68	74.00
3a	78.50	61.29	66.55	75.21	71.80	70.71	73.41	72.38

[a] $H_2O/CHCl_3$ = 10/10 ml (v/v): picric acid = 2×10^{-5} m, [ligand] = 1×10^{-3} m or 0.1 g oligomer, [metal nitrate] = 1×10^{-2} m; 298 K, 1 h contact time. Experimental error was ± 2%.

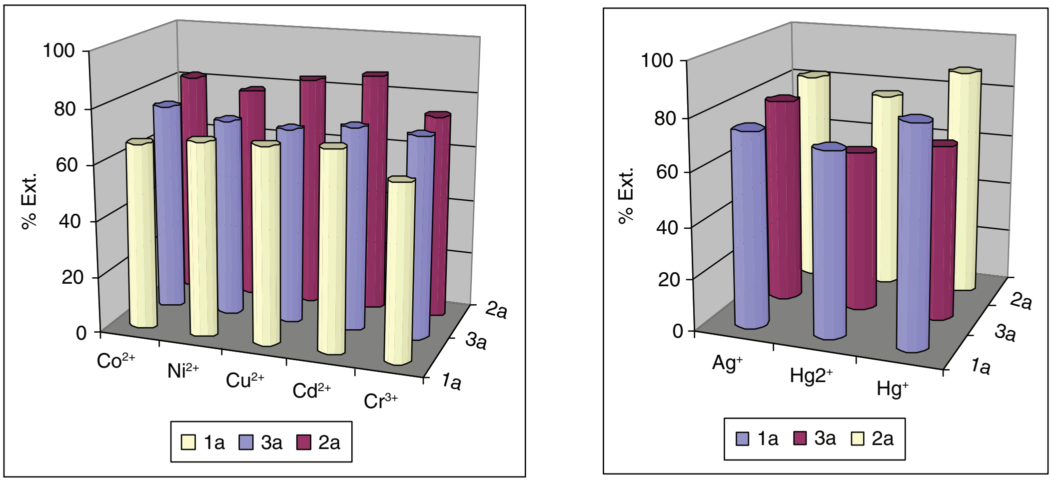


Fig. 1. Sorption percentage of the metal picrates with 1a–3a at 25 ºC.

cation sorption (S %) are collected in Table 1 and shown graphically in Fig. 1. Under the lights of the results, it was observed that azocalix[4]arenes were effective sorbents. The sequence of sorption efficiency of azocalix[4]arene (2a) for heavy metal cations was $Cd^{2+} > Cu^{2+} > Co^{2+} > Ni^{2+} > Cr^{3+}$. Consequently, grafting of azo groups with calix[4]arene is a useful approach for heavy metal sorption. It was clearly found out that –N=N– group has tendency to form polarizable complex through transition metal ions due to cation-π interactions. Thus it is suggested that this increased binding ability arises from highly rigid azo (–N=N–) group moiety at the upper rim of calix[4]arene in the oligomeric skeleton.

4. Conclusion

This work describes the preparation, characterization, and sorption properties of new chromogenic azocalix[4]arene based oligomers (1a, 2a and 3a) towards some selected heavy metal (Ag^+, Hg^+, Hg^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+} and Cr^{3+}) cations. The spectroscopic data indicated that these compounds (1–3) adopt the cone conformation. The extraction ability of the azo (–N=N–) groups moiety of calix[4]arene/derivatives and their corresponding oligomers 1a, 2a and 3a have been studied. It is observed that the oligomers (1a–3a) are better extractants than corresponding monomers (1–3). Oligomers captured selected metal cations more efficiently than monomeric analogs The binding properties of the oligomers toward these selected metal cations were observed higher than those of monomeric analogs. This is a particularly important feature if it is desirable to recover the particular metal in pure form and reuse the extractant. The calixarene based receptors could be proved to find remarkable applications in the design of chemical sensors, using an electrochemical transduction/as conventional ion selective electrodes (ISE) and solid-state sensors (ISFETs).

Acknowledgement

We thank to the Scientific and Technical Research Council of Turkey (TUBITAK-Grand No. 107T770) for financial support of this work.

References

[1] D.C.K. Ko, J.F. Porter and G. McKay, Ind. Eng. Chem. Res., 42 (2003) 3458–3469.

[2] A.K. Meena, G.K. Mishra, P.K. Rai, C. Rajagopal and P.N. Nagar, J. Hazard. Mater., B, 122 (2005) 161–170.

[3] A. Ozcan, A.S. Ozcan, S. Tunali, T. Akar and I. Kiran, J. Hazard. Mater., B, 124 (2005) 200–208.

[4] S. Memon and M. Yilmaz, J. Macromol. Sci. Pure., 39(1–2) (2002) 63–73.

[5] A. Mellah, S. Chegrouche and M. Barkat, J. Colloid Interf. Sci., 296 (2006) 434–441.

[6] D.R. Raut, P.K. Mohapatra, S.A. Ansari, A. Sakar and V.K. Manchanda, Desalination, 232 (2008) 262–271.

[7] A.R. Hajipour, S. Habibi and A.E. Ruoho, Polym. Int., 58 (2009) 630–639.

[8] M. Tabakcı and M. Yılmaz, J. Hazard. Mater., 151 (2009) 331–338.

[9] C.D. Gutsche and J.F. Stoddart, In Calixarenes Revisited. Monographs in Supramolecular Chemistry; (Ed.); The Royal Society of Chemistry, London (1998) 149–167.

[10] O. Ediz, M. Tabakci, S. Memon, M. Yilmaz and D.M. Roundhill, Supramol. Chem., 16 (2004) 199–204.

[11] H. Deligöz, M. Tavasli and M. Yılmaz, J. Polym. Sci. Pol. Chem., 32 (1994) 961–2964.

[12] A. Yilmaz, S. Memon and M. Yılmaz, J. Polym. Sci. Pol. Chem., 37 (1999) 4351–4355.

[13] F. Arnaud-Neu, G. Barrett, S.J. Harris, M. Owens, M.A. McKervey, M.-J. Schwing-Weill and R. Schwinte, Inorg. Chem., 32 (1993) 2644–2650.

[14] T. Tuntulani, P. Thavornyutikarn, S. Poompradub, N. Jaiboon, V. Ruangpornvisuti, N. Chaichit, Z. Asfari and J. Vicens, Tetrahedron, 58 (2002) 10277–10285.

[15] M. Dudic, P. Lhoták, I. Stibor, H. Dvoráková and K. Lang, Tetrahedron, 58 (2002) 5475– 5482.

[16] S.E. Matthews and P.D. Beer, Supramol. Chem., 17 (2005) 411–435.

[17] D.M. Roundhill, H.F. Koch, Chem. Soc. Rev., 31 (2002) 60–67.

[18] E. Akceylan, M. Yilmaz and R.A. Bartsch, J. Macromol. Sci. Pure., 43 (2006) 477–486.

[19] S. Memon, M. Tabakci, D.M. Roundhill and M. Yilmaz, React. Funct. Polym., 66 (2006) 1342–1349.

[20] H. Deligöz, (Review Article) J. Incl. Phenom. Macro., 55 (2006) 197–218.

[21] H.M. Chawla, S.P. Singh, S.N. Sahu, and S. Upreti, Tetrahedron, 62 (2006) 7854–7865.

[22] H.M. Chawla, S.P. Singh, and S. Upreti, Tetrahedron, 62 (2006) 2901–2911.

[23] H. Deligöz and N. Ercan, Tetrahedron, 58 (14) (2002) 2881–2884.

[24] T.L. Kao, C.C. Wang, Y.T. Pan, Y.J. Shiao, J.Y. yen, C.M. Shu, G.H. Lee, S.M. Peng and W.S. Chung, J. Org. Chem., 70 (2005) 2912–2920.

[25] M. Ak, D. Taban and H. Deligöz, J. Hazard. Mater., 154 (1–3) (2008) 51–54.

[26] A. Akdoğan, M. Deniz (Tavaslı), S. Cebecioğlu, A. Şen and H. Deligöz, Separ. Sci. Technol., 37 (4) (2002) 973–980.

[27] H. Deligöz, Supramol. Chem., 15(5) (2003) 317–321.

[28] H.K. Alpoğuz, A. Kaya and H. Deligöz, Separ. Sci. Technol., 41 (2006) 1155–1167.

[29] Ö.Ö. Karakuş and H. Deligöz, J. Incl. Phenom. Macro., 61 (2008) 289–296.

[30] I. Dumazet-Bonnamour, Hatem Halouani, F. Oueslati and R. Lamatine, C.R. Chimie, 8 (2005) 881–891

[31] H. Deligöz and E. Erdem, J. Hazard. Mater., 154 (1–3) (2008) 29–32.

[32] M. Takeshita and S. Shinkai, Bull. Chem. Soc. Jpn., 68 (1995) 1088–1097

[33] C.D. Gutsche and M. Iqbal, Org. Synth., 68 (1990) 234–238.

[34] C.D. Gutsche, M. Iqbal and D. Stewart, J. Org. Chem., 51 (1986) 742–745.

[35] C.D. Gutsche and L.G. Lin,Tetrahedron, 42 (1986) 1633–1640.

[36] A. Hamdi, Y.H. Lee, Y. Kim, D.K.A. Kusumahastuti, K. Ohto, R. Abidi and J. Vicens, Tetrahedron Lett., 50 (2009) 540–543.

[37] K.G. Koening, G.M. Lein, P. Stuckler, T. Kaneda and D.J. Cram, J. Am. Chem. Soc., 101 (1979) 3553–3556.