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The synthesis and characterization of azocalix[4]arene based chemosensors and investigation of their properties

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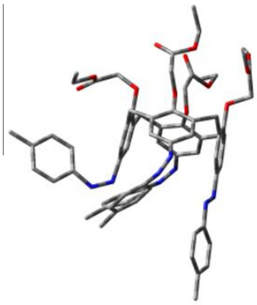
HIGHLIGHTS

- In this study, azocalix[4]arene tetraester derivatives (**4a**–**f**) were synthesized.
- Their thermal decomposition analysis was performed by means of TG, DTA and DTG.
- Azocalix[4]arene derivatives have showed a good selectivity toward Hg^{2+} and Hg^{+} ions.

GRAPHICAL ABSTRACT



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ABSTRACT

In the present study, azocalix[4]arenes were prepared by linking 4-methoxy, 4-methyl, 4-ethyl, 4-chloro, 4-bromo and 4-nitroaniline to calix[4]arene through a diazo-coupling reaction. A new family of azocalix[4]arene tetraester derivatives, (**4a**–**f**), have been prepared with the incorporation of ethyl ester units to azocalix[4]arene. Characterization of the synthesized azocalix[4]arenes was carried using elemental analyses, UV–vis, FT-IR and ^{1}H NMR spectroscopic techniques. The effect of varying pH levels and solvent types on the absorption ability of azocalix[*n*]arenes substituted with electron-donating and electron-withdrawing groups was examined. Thermal decomposition of azocalix[4]arene derivatives (**4a**–**f**) was investigated by means of thermogravimetry (TG), differential thermogravimetry (DTG) and differential thermal analysis (DTA) analyses. In conclusion of the examination of the extraction we found a selectivity characteristic of these compounds toward Ag^{+}, Hg^{+} and Hg^{2+} cations.

Introduction

Calix[4]arenes play an important role in supramolecular chemistry as molecular scaffolds for elaborating sophisticated hosts [1–4]. Functional groups are introduced into the existing calix[*n*]arene framework by a functionalized method either through the “*lower rim*” (the oxygen-position of the phenolic moieties) or the “*upper rim*” (the *p*-position of the aromatic nuclei) [5]. Literature surveys show that the majority of the existing studies have not only focused on the thermal behavior but also concentrated on functionalization [6].

A variety of functional groups have been regio- and stereospecifically introduced on the hydroxy groups of calix[4]arenes as recognition sites by linking moieties through etherification. However, the transformation causes the location of the functional groups to be apart from the calix skeleton [7,8]. This situation makes it difficult for guests to be affected by the steric effects of the calix skeleton and/or to interact with substituents which are present on it (e.g., with residual hydroxy groups or linking hetero atoms). This

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issue may be addressed by cleaving the aryl–oxygen bonds, thereby replacing the hydroxy groups with different functional groups. However, such a transformation is quite difficult for calix[4]arenes because of their steric and electronic environment in proximity to the *lower rim* [9,10], in addition to the poor nuclei fugacity of the phenolic hydroxy group.

Calix[*n*]arenes are extensively used in selective extraction of metals, nuclear waste treatment, catalysis, complexation of fullerenes and neutral molecules. Their synthesis procedure, in addition to their physical characterization techniques (in terms of their physical properties such as melting point, solubility and acid dissociation constant, pKa) are complicated [1,2]. The high melting points of these compounds necessitate a careful investigation of their thermal behavior. Thermal analysis methods have been extensively applied in the field of polymers, solid/liquid interface, carbohydrate chemistry, minerals, energetic materials, pharmaceutical and biochemistry [11–13].

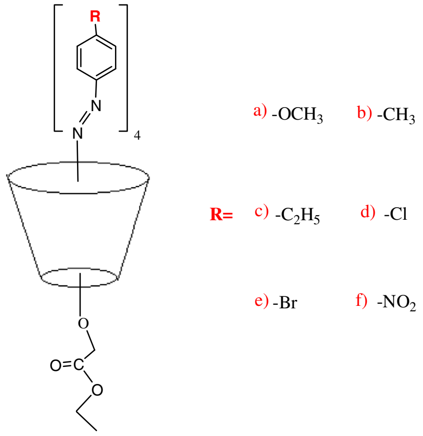
Thermogravimetric analysis is a valuable tool for the determination of inclusion behavior of calix[*n*]arenes with guest molecules such as toluene, xylene, chloroform, acetone, methanol and alkyl ammonium [14,15]. Increasing temperature leads to loss of small functional groups from the main calix[*n*]arene body. As the temperature increases, the chain length of the leaving functional groups increases. Calix[*n*]arenes are good antioxidants of polyolefins such as polypropylene, and polyethylene [16–18]. It is reported that, more than 20,000 ton of phenolic antioxidants were consumed during 1983 for the stabilization of plastics in USA alone. This data clearly reveals the importance of antioxidants in terms of the polymer industry [19]. The present study is concerned with the synthesis of azocalix[*n*]arenes and investigation of their thermal decomposition kinetics.

Schatz et al. studied solid state inclusion of various organic solvent molecules in *p-tert*-butylcalix[*n*]arene [15]. After their study, synthesis and characterization of *p-tert*-butylcalix[6]arene ammonium cation complexes have been reported. A similar study was also reported by Radius et al., who prepared calix[4]arene-supported iron(III) complexes [20].

As reported in [21–23], secondary and tertiary amine complexes of calixresorcinarenes are formed in a solution with a complementary fit with the calix cavity size. Calixresorcinarene forms complexes with amines with a stoichiometry ratio of 1:2 in the solid-state. There are several variations of decomposition structures of azocalixarenes/calixarenes, or azocalixarene metal complexes as shown by X-ray crystallography. These structures present variable positions of various metal cations, some of which fill the cavity by interacting with the electron clouds and the others by forming hydrogen bonds with phenolic oxygens.

Recently, synthesis and theoretical investigation of calix[4]arene derivatives and their complexes, polymeric calix[*n*]arene derivatives and azocalix[*n*]arenes have been reported by our research group [24]. We examined the selective extraction of Fe^{3+} ion from aqueous phase into the organic phase as well as the liquid–liquid extraction of transition metal ions using diazo-coupled calix[*n*]arenes. However, there is still an important need for systems those can explain color changes with ionic or molecular interactions [25–27].

In this study, we have mainly looked into the development of a new class of chromogenic azocalix[4]arene chemosensors. This work focuses on thermal behavior and decomposition of six diazo-coupled azo substituted calix[4]arenes (**4a**–**f**) (Scheme 1). There are an insufficient number of reports on the thermal decomposition analysis of azocalix[4]arene-based compounds so far. Hence, this study has been a research effort to fill this gap in the academic literature.



Scheme 1. Diazo-coupled azocalix[4]arene tetraester derivatives (**4a**–**f**).

Experimental

All reagents and solvents were purchased from Merck, Sigma–Aldrich and Carlo-Erba Company and used without further purification.*p-tert*-Butylcalix[4]arene, calix[4]arene, *p*-substitute phenylazocalix[4]arenes **(3a–f)** 25,26,27,28-tetrakis(ethoxycarbonylmethoxy)-5,11,17,23-tetrakis[(4-methoxyphenyl)azo]calix[4]arene (**4a**), 25,26,27,28-tetrakis (ethoxycarbonylmethoxy)-5,11,17,23-tetrakis[(4-methylphenyl)azo]calix[4]arene (**4b**), 25,26,27,28-tetrakis(ethoxycarbonylmethoxy)-5,11,17,23-tetrakis[(4-ethylphenyl)azo]calix[4]arene (**4c**), 25,26,27,28-tetrakis (ethoxycarbonylmethoxy)-5,11,17,23-tetrakis[(4-chlorophenyl)azo]calix[4]arene (**4 d**), 25,26,27,28-tetrakis(ethoxycarbonylmethoxy)-5,11,17,23-tetrakis[(4-bromophenyl)azo]calix[4]arene (**4e**) and 25,26,27,28-tetrakis(ethoxycarbonylmethoxy)-5,11,17,23-tetrakis[(4-nitrophenyl)azo]calix[4]arene (**4f**) were synthesized as described in previously reported methods [28–34].

Instrumental

Melting points of analyzed compounds were measured using an Electrothermal IA9100 digital melting point apparatus in capillaries sealed under nitrogen and they were used without correction. ^{1}H NMR spectra were referenced to tetramethylsilane (TMS) at 0.00 ppm as the internal standard solution and were recorded on a Bruker 400 MHz spectrometer at room temperature (25 ± 1 °C). IR spectra were recorded by a Mattson 1000 FTIR spectrometer using KBr pellets. UV–vis spectra were obtained by a Shimadzu 1601 UV–Visible recording spectrophotometer. The elemental analyses were performed in the Laboratories of TUBITAK (The Scientific and Technological Research Council of Turkey).

Crystallization solvent was remained in some of the analytical samples and affected the elemental analysis results. In such cases, best fits between the analytical values and appropriate fractional increments of solvents were used.

TG, DTG and DTA curves of analyzed compounds were obtained simultaneously by using a Shimadzu DTG-60H thermal analyzer. The measurements were realized in platinum crucible and flowing air atmosphere ($25\ mL\ min^{-1}$). Potential applications of the calyx[*n*]arenes, such as selective extraction, azo dyes component and antioxidant properties, are realized in air atmosphere. So we chose air atmosphere. The analyzed temperature range was 25–850 °C. The heating rate was set to $10\ °C\ min^{-1}$ and the sample masses were between 3–5 mg. Highly sintered α-Al_2O_3 was used as the reference material. Before carrying out the experiments, it is essential to calibrate the balance for buoyancy effects for the quantitative estimation of mass changes. The material chosen for the investigation of such effects was silver. The temperature was calibrated measuring the melting points of indium and tin provided by Shimadzu.

Preparation of the ligands and the diazotization

p-tert-butylcalix[4]arene, calix[4]arene and azocalix[4]arenes (**3a–f**) were synthesized as described previously [28–32].

Esterification

We have followed the procedure given in references [33,34] in order to carry out the experiments.

*Preparation of 25,26,27,28-tetrakis(ethoxycarbonylmethoxy)-5,11,17,23-tetrakis[(4-methoxyphenyl)azo]calix[4]arene (**4a**)*

The esterification reaction of calix[4]arene (**3a**) (1 g, 1.04 mmol) and ethyl bromoacetate (0.93 mL, 8.32 mmol) has been performed in a suspension of K_2CO_3 (2.15 g, 15.60 mmol) and NaI (1.25 g, 8.32 mmol) in dry acetonitrile (100 mL). The reaction mixture was refluxed for 4 days and subsequently allowed to cool down to room temperature. After evaporating the solvent by using a rotary evaporator, the resulting residue was taken up in $CHCl_3$ (100 mL). The obtained mixture was washed first with 0.5 N HCl (250 mL) and then with water (300 mL). The organic layer was dried with $MgSO_4$. The addition of ethanol (50 mL) yielded the product as a pale orange powder (yield, 1.01 g (74%), mp. 245–246 °C). [Found: C: 66.19; H: 5.61; N: 8.67]; $C_{72}H_{72}N_8O_{16}$ requires C: 66.25; H: 5.56; N: 8.58. IR (KBr) υ: 1755 cm^{-1} (—C═O), 1449 cm^{-1} (—N═N). ^{1}H-NMR ($CDCl_3$, 25 °C) δ_H: 1.31 (t, J = 7.14 Hz, 12H, CH$_2$—$\mathbf{CH_3}$), 3.48 (d, J = 13.72 Hz, 4H, Ar$\mathbf{CH_2}$Ar), 3.80 (s,12H, O—$\mathbf{CH_3}$), 4.24 (q, J = 7,14 Hz, 8H, O—$\mathbf{CH_2}$—CH$_3$), 4.84 (s, 8H, O—$\mathbf{CH_2}$—C═O), 5.02 (d, J = 13.76 Hz, 4H, Ar$\mathbf{CH_2}$Ar), 6.78 (d, J = 9.01 Hz, 8H, Ar**H**), 7.33 (s, 8H, Ar**H**), 7.64 (d, J = 8.98 Hz, 8H, Ar**H**).

*Preparation of 25,26,27,28-tetrakis(ethoxycarbonylmethoxy)-5,11,17,23-tetrakis[(4-methylphenyl)azo]calix[4]arene (**4b**) [34]*

Azocalix[4]arene (**4b**) was prepared as described above, using ethyl bromoacetate with (**3b**) and K_2CO_3/NaI. A pale brown product was obtained (yield, 1.12 g (81%) mp. 276–278 °C, Lit. mp. 283–285 °C).

*Preparation of 25,26,27,28-tetrakis(ethoxycarbonylmethoxy)-5,11,17,23-tetrakis[(4-ethylphenyl)azo]calix[4]arene (**4c**)*

Azocalix[4]arene (**4c**) was prepared as described above, using ethyl bromoacetate with (**3c**) and K_2CO_3/NaI. The product was dark orange color (yield, 0.99 g (73%) mp. 215 °C). [Found: C: 74.26; H: 6.27; N: 8.72]; $C_{76}H_{80}N_8O_{12}$ requires C: 70.35; H: 6.21; N: 8.64. IR (KBr) υ: 1750 cm^{-1} (—C═O), 1465 cm^{-1} (—N═N). ^{1}H-NMR ($CDCl_3$, 25 °C) δ_H: 1.22 (t, J = 7.60 Hz, 12H, Ar—CH$_2$—$\mathbf{CH_3}$), 1.31 (t, J = 7.15 Hz, 12H, CH$_2$—$\mathbf{CH_3}$), 2.64 (q, J = 7.60 Hz, 8H, Ar—$\mathbf{CH_2}$—CH$_3$), 3.50 (d, J = 13.77 Hz, 4H, Ar$\mathbf{CH_2}$Ar), 4.24 (q, J = 7.14 Hz, 8H, O—$\mathbf{CH_2}$—CH$_3$), 4.85 (s, 8H, O—$\mathbf{CH_2}$—C═O), 5.03 (d, J = 13.72 Hz, 4H, Ar$\mathbf{CH_2}$-Ar), 7.11 (d, J = 8.58 Hz, 8H, Ar**H**), 7.36 (s, 8H, Ar**H**), 7.58 (d, J = 8.51 Hz, 8H, Ar**H**).

*Preparation of 25,26,27,28-tetrakis(ethoxycarbonylmethoxy)-5,11,17,23-tetrakis[(4-chlorophenyl)azo]calix[4]arene (**4d**)*

Azocalix[4]arene (**4d**) was prepared as described above, using ethyl bromoacetate with (**3d**) and K_2CO_3/NaI. The resultant product was in orange color (yield, 0.82 g (61%) mp. 214–216 °C). [Found: C: 61.84; H: 4.61; N: 8.36]; $C_{68}H_{60}Cl_4N_8O_{12}$ requires C: 61.73; H: 4.57; N: 8.47. IR (KBr) υ: 1749 cm^{-1} (—C═O), 1464 cm^{-1} (—N—N). ^{1}H-NMR ($CDCl_3$, 25 °C) δ_H: 1.31 (t, J = 7.15 Hz, 12H, CH$_2$—$\mathbf{CH_3}$), 3.50 (d, J = 13.83 Hz, 4H, Ar$\mathbf{CH_2}$Ar), 4.25 (q, J = 7.16 Hz, 8H, O—$\mathbf{CH_2}$—CH$_3$), 4.84 (s, 8H, O—$\mathbf{CH_2}$—C═O), 5.03 (d, J = 13.77 Hz, 4H, Ar$\mathbf{CH_2}$Ar), 7.26 (d, J = 8.83 Hz, 8H, Ar**H**), 7.36 (s, 8H, Ar**H**), 7.58 (d, J = 8.77 Hz, 8H, Ar**H**).

*Preparation of 25,26,27,28-tetrakis(ethoxycarbonylmethoxy)-5,11,17,23-tetrakis[(4-bromophenyl)azo]calix[4]arene (**4e**)*

Azocalix[4]arene (**4e**) was prepared as described above, using ethyl bromoacetate with (**3e**) and K_2CO_3/NaI. A pale brown product was acquired (yield, 0.73 g (56%) mp. 231–232 °C). [Found: C: 54.31; H: 4.09; N: 7.46]; $C_{68}H_{60}Br_4N_8O_{12}$ requires C: 54.42; H: 4.03; N: 7.47. IR (KBr) υ: 1748 cm^{-1} (—C═O), 1463 cm^{-1} (N═N). ^{1}H-NMR ($CDCl_3$, 25 °C) δ_H: 1.31 (t, J = 7.14 Hz, 12H, CH$_2$—$\mathbf{CH_3}$), 3.49 (d, J = 13.84 Hz, 4H, Ar$\mathbf{CH_2}$Ar), 4.24 (q, J = 7.14 Hz, 8H, O—$\mathbf{CH_2}$-—CH$_3$), 4.83 (s, 8H, O—$\mathbf{CH_2}$—C═O), 5.03 (d, J = 13.78 Hz, 4H, Ar$\mathbf{CH_2}$-Ar), 7.35 (s, 8H, Ar**H**), 7.42 (d, J = 8.77 Hz, 8H, Ar**H**), 7.50 (d, J = 8.73 Hz, 8H, Ar**H**).

*Preparation of 25,26,27,28-tetrakis(ethoxycarbonylmethoxy)-5,11,17,23-tetrakis[(4-nitrophenyl)azo]calix[4]arene (**4f**)*

Azocalix[4]arene (**4f**) was prepared as described above, using ethyl bromoacetate with (**3f**) K_2CO_3/NaI. The color of the resultant product was pale brown (yield, 0.69 g (52%), mp. 168–170 °C). [Found: C: 59.91; H: 4.40; N: 12.47]; $C_{68}H_{60}N_{12}O_{20}$ requires C: 59.82; H: 4.43; N: 12.31. IR (KBr) υ: 1756 cm^{-1} (—C═O), 1463 cm^{-1} (—N═N), 1520 cm^{-1} and 1342 cm^{-1} (Ar—NO$_2$). ^{1}H-NMR ($CDCl_3$, 25 °C) d_H: 1.32 (t, J = 7.14 Hz, 12H, CH$_2$—$\mathbf{CH_3}$), 3.54 (d, J = 13.96 Hz, 4H, Ar$\mathbf{CH_2}$Ar), 4.25 (q, J = 7.14 Hz, 8H, O—$\mathbf{CH_2}$-—CH$_3$), 4.87 (s, 8H, O—$\mathbf{CH_2}$—C═O), 5.10 (d, J = 13.93 Hz, 4H, Ar$\mathbf{CH_2}$-Ar), 7.44 (s, 8H, Ar**H**), 7.74 (d, J = 9.04 Hz, 8H, Ar**H**), 8.12 (d, J = 9.03 Hz, 8H, Ar**H**).

Liquid–liquid extraction

A chloroform solution (10 mL) of ligand (10^{-3} M) and an aqueous picric acid solution (10 mL) of metal ions (2×10^{-5} M) were shaken together at 25 °C for duration of an hour. An aliquot of the aqueous solution was taken and its UV spectrum was recorded. UV spectra of the aqueous picric acid solution of metal ions were also recorded for comparison. The initial extraction procedure was repeated twice. The extractability (Ex %) of the metal cations was expressed by means of the following equation:

$$\mathrm{Ex}\% = [(A_0 - A)/A_0] \times 100$$

where A_0 and A are the absorbance values in the absence and presence of ligands, respectively.

Results and discussions

Syntheses and characterizations

It has been generally accepted that calix[*n*]arene based chemosensors a stronger ion selectivity compared to diazo-coupling based chemosensors. In some cases, this characteristic may be enhanced with the use of appropriate functionalities. Our former azocalix[*n*]arene based studies were mostly focused on derivatives with functionalities appended to the *lower rim* [35,36].

Each azocalix[*n*]arene compound carries a single *p*-substituted phenylazo-chromogen group. Each of these chromogen groups contains four free phenolic groups. Azocalix[4]arene compounds are synthesized through diazo coupling reaction of corresponding diazotized amines with calix[4]arenes. Azocalix[4]arene derivatives are carried out through esterification of them.

In the present study, five new *p*-substituted (—OCH$_3$, —C$_2$H$_5$, —Cl, —Br and —NO$_2$) aniline derivatives were prepared. The effect of substituents on the color of azocalix[4]arene ester derivatives (**4a**–**f**) was discussed. Their thermal behaviors, solvent extraction and absorption properties were assessed. Until now there have been no publications about the synthesis and wavelength shift behavior of such compounds. Hence, this study has been a research effort to fill this gap in the academic literature.

This study mainly focuses on five novel (**4c**–**f** and **4a**) and one existent (**4b**) azocalix[4]arene ester derivatives (**4a**–**f**). At first, *p-tert*-butylcalix[4]arene was prepared by reaction of *p-tert*-butylphenol with formaldehyde according to the Gutsche method [28]. Treatment of *p-tert*-butylcalix[4]arene with aluminum chloride gave calix[4]arene according to the method described by Gutsche et al. [29]. In accordance with our former experience [30–32], azocalix[4]arene derivatives have been synthesized from calix[4]arene by diazo coupling with the corresponding aromatic amines. Then we synthesized the diazonium salt derivatives according to the method reported by Morita et al. [30].

The synthesis of azocalix[4]arene tetraester derivatives (**4a**–**f**) have been summarized in four steps starting from simple *p-tert*-butylcalix[4]arene (Scheme 2). All synthetic compounds were checked for their purity levels with thin layer chromatography (TLC). They were characterized by FT-IR and NMR analyses as given in the Experimental Section. Since the terminals of both pendants of these conjugates possess $-CH_2COOC_2H_5$ moieties, it is of interest to study their recognition abilities toward electrophilic coupling and solubilization properties of important molecules, such as aromatic amines and ethyl esters. To elicit the selectivity of these conjugates ($-OCH_3$, $-CH_3$, $-C_2H_5$, $-Cl$, $-Br$ and $-NO_2$) as well as the role of the four aromatic azo arms, appropriate controlled molecular systems were generated by converting phenolic groups into $-COOC_2H_5$ moieties. The diazo-coupling reaction of these, azocalix[4]arenes, namely, $-N{=}N-Phe-R$, and their ethyl ester version, namely, $CH_2COOC_2H_5$, were synthesized and characterized (Scheme 2) and used in the extraction studies.

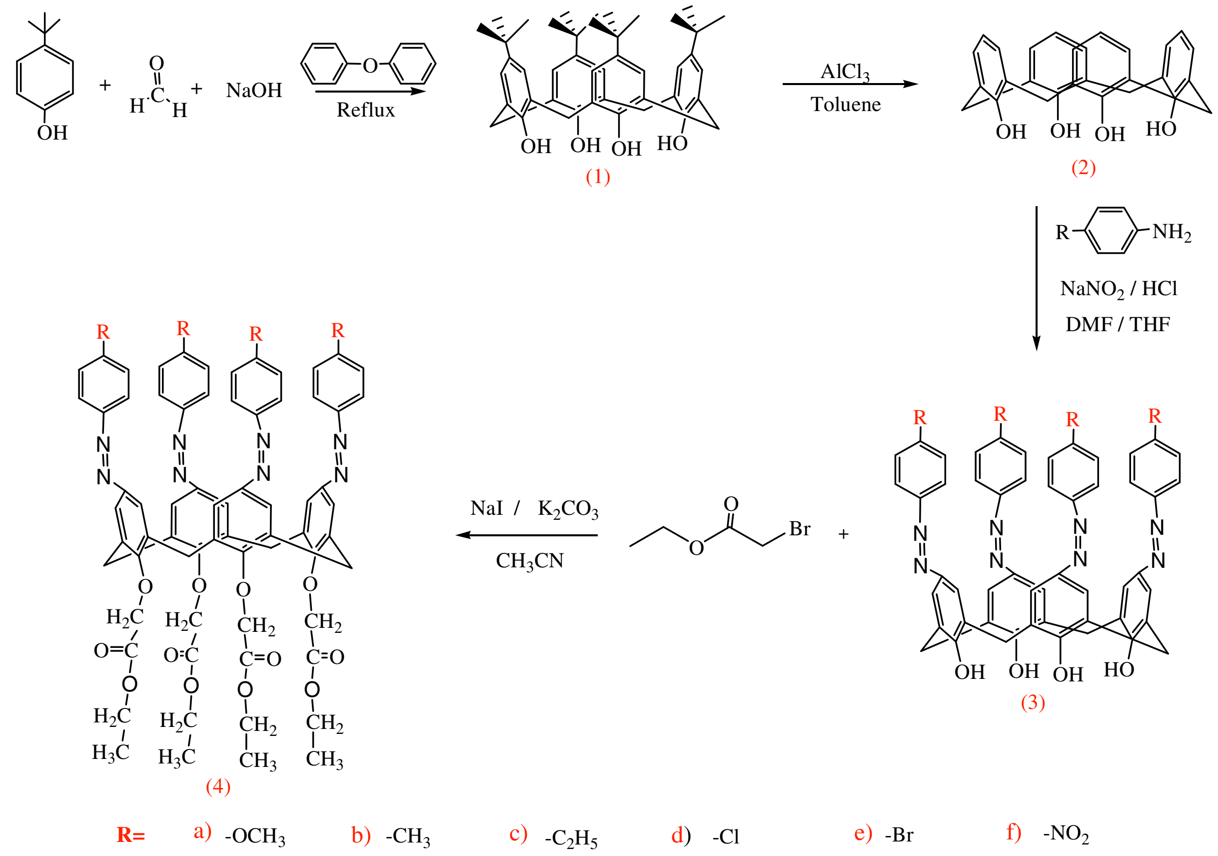
The diazonium salts are excellent electrophiles and they attack any available position on the calix[*n*]arene molecules to yield complex mixtures. Purification of five novel azocalix[4]arene ester derivatives resulted in corresponding residues in 52–81% yields.

The above reaction products were characterized by elemental analysis, FT-IR and ^{1}H-NMR spectral techniques. FT-IR V_{max} values of all products were recorded between 1748–1756 cm^{-1} ($-C{=}O$), 1449–1465 cm^{-1} ($-N{=}N$. The ^{1}H-NMR spectrum of **4a** revealed a triplet peak for methyl protons at 1.31 (**a**), a quartet peak for methylene protons at 4.24 (**b**), two peaks for bridge methylene protons (**AB spin system**) at δ 3.35–3.54 and 5.02–5.10, a singlet peak for methoxy protons at 3.80 (**g**), a singlet peak for carbonyl neighboring methylene protons at 4.84 (**c**).

Conformational studies have been realized by using ^{1}H-NMR spectra method at room temperature. The corresponding details of the structure determination and refinement are given in Fig. 1. The crystal structure of azocalix[4]arene ester derivatives exhibited *cone* conformation and is in conformity with the results obtained by NMR analysis. The structure exhibits rather exposed azo and ester moieties those are amenable for interaction with the incoming species. Similar structural features were observed also with azocalix[4]arene where the terminal $-CH_2CH_3$ ester is poised suitable for interaction.

Solvent effect

UV–vis absorption spectra were measured using a Shimadzu 160A spectrophotometer in the wavelength range 300–700 nm. Absorption spectra of azocalix[4]arenes were measured with various solvents and at different pH levels. The choice of solvent was



Scheme 2. Structure of azocalix[4]arene tetraester derivatives (**4a**–**f**).

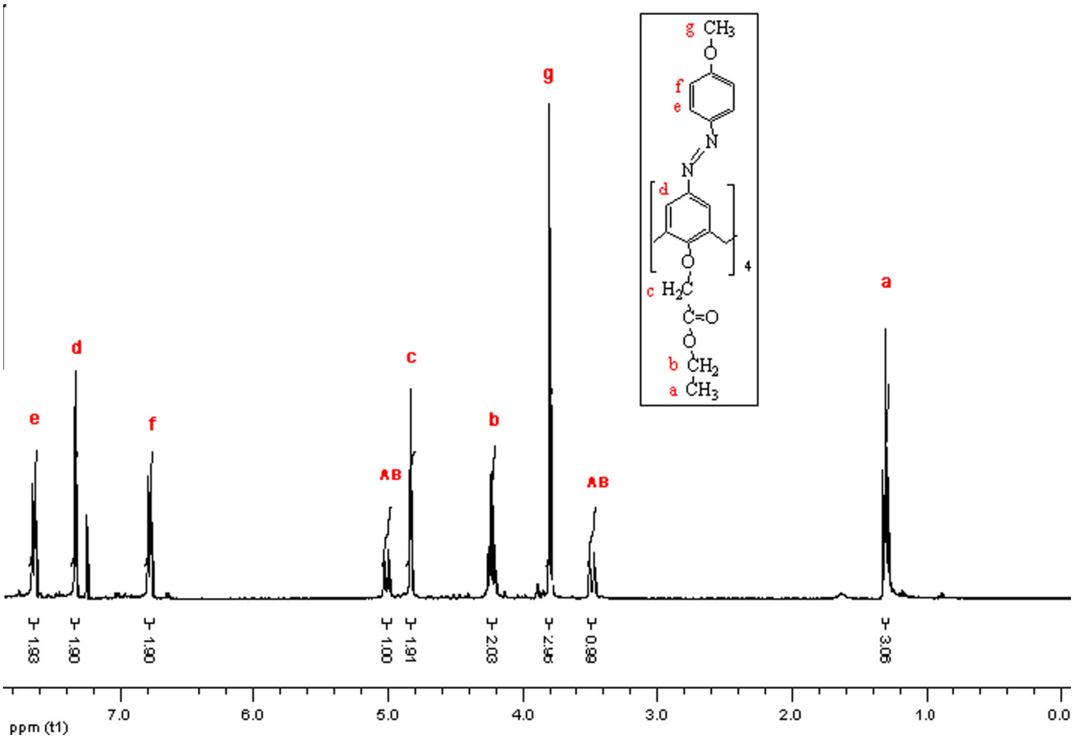


Fig. 1. ^{1}H-NMR spectra of azocalix[4]arene tetraester derivatives (**4a**).

selected based on their polarities. The analysis has been mainly focused on the shift effect of solubility and pH. Effects of substituents have also been considered. More detailed analysis of the effects of various solvents and pH change has been performed only for azocalix[4]arene (**4a**–**f**) solutions.

Typical absorption spectra of azocalix[4]arenes (**4a**–**f**) in different solvents are shown in Fig. 2. It can be seen that the absorption maxima measured in DMF and DMSO solutions are slightly shifted to higher wavelengths (red shift) as compared with the corresponding values measured in other solvents. This shift can simply be explained by the conjugation of substituted azo derivatives in the calixarene structure.

Effect of various pH levels and solution concentrations on the absorption intensities have been studied in a more detailed way. The absorption spectra of azocalix[4]arenes (**4a**–**f**) were recorded in various solvents at a concentration of $\sim 10^{-6}$ to $\sim 10^{-8}$ M; the recorded results are summarized in Table 1. The spectra of azocalix[4]arenes were found to exhibit strong solvent dependency, which did not show regular variation with the polarity of solvents.

It was observed that the absorption spectra of the compounds in chloroform solution generally differ from the absorption spectra in all other solvents. The λ_{max} of the compounds shifted considerably in DMF and DMSO (e.g. for compound **4a** λ_{max} is 345 nm in $CHCl_3$, 349 nm in DMF and 350 nm in DMSO; for compound **4c** is 332 nm in $CHCl_3$, 336 nm in DMF and 338 nm in DMSO; for compound **4e** is 338 nm in $CHCl_3$, 340 nm in DMF and 343 nm in DMSO).

The UV spectra of azocalix[4]arenes (**4a**–**f**) in chloroform solution showed two bands in the region 300–700 nm. The relatively small difference in the λ_{max} may have been caused by the polarity change of the absorbing system due to solvent interactions. Table 1 also shows that the presence of electron-donating or electron-withdrawing groups has not resulted in any marked increase or decrease in the λ_{max} in the visible 300–500 nm.

The effects of concentration, acidity and alkalinity of these azocalix[4]arene derivatives (**4a**–**f**) on their absorption maxima were examined. The λ_{max} values of no compound changed with varying compound concentration.

These compounds existed in an equilibrium state and its evidence is provided by isosbestic points in the visible spectra of the compound **4d** in different solvents (Fig. 3). These compounds (**4a**–**f**) showed one absorption peak in DMF and DMSO. The equilibrium of compounds (**4a**–**f**) in DMF and DMSO may exist between tautomeric form and anionic form.

Solvent extraction

Designation of azocalix[4]arene tetraacetates as receptors is based on their well-recognized complexation abilities. If these compounds are immobilized in the *cone* conformation, they exhibit high complexation affinity toward selected metal cations. To visualize the complexation phenomenon, we appended tetraacetate groups in the opposite direction of the *upper rim* chromophore groups. This functionalization allows the monitoring of complexation phenomenon using UV–vis spectroscopy.

In recent years, the various sensors have been reported for selective and sensitive determination of metals, biomolecules and organic compounds [37–39]. The present study is focused on investigating the ionophoric properties of the *upper rim* functionalized azocalix[4]arene derivatives (**4a**–**f**) toward selected metal cations (Na^+, K^+, Sr^{2+}, Ag^+, Hg^+, Hg^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cr^{3+}, Al^{3+}, La^{3+}). The extraction properties of these compounds (**4a**–**f**) have been evaluated by solvent extraction processes of selected metal picrates (Table 2 and Fig. 4).

An investigation of the ionic recognition properties of synthesized chemosensors in terms of alkaline (Na^+, K^+), alkaline-earth (Sr^{2+}) and transition metal ions (Ag^+, Hg^+, Hg^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+}, Cr^{3+}, Al^{3+} and La^{3+}) was also conducted. Azo group (—N=N—) containing molecular receptors have been expected to exhibit pronounced changes in the course of interaction with transition metal ions. However, the azocalix[4]arenes (**4a**–**f**) showed

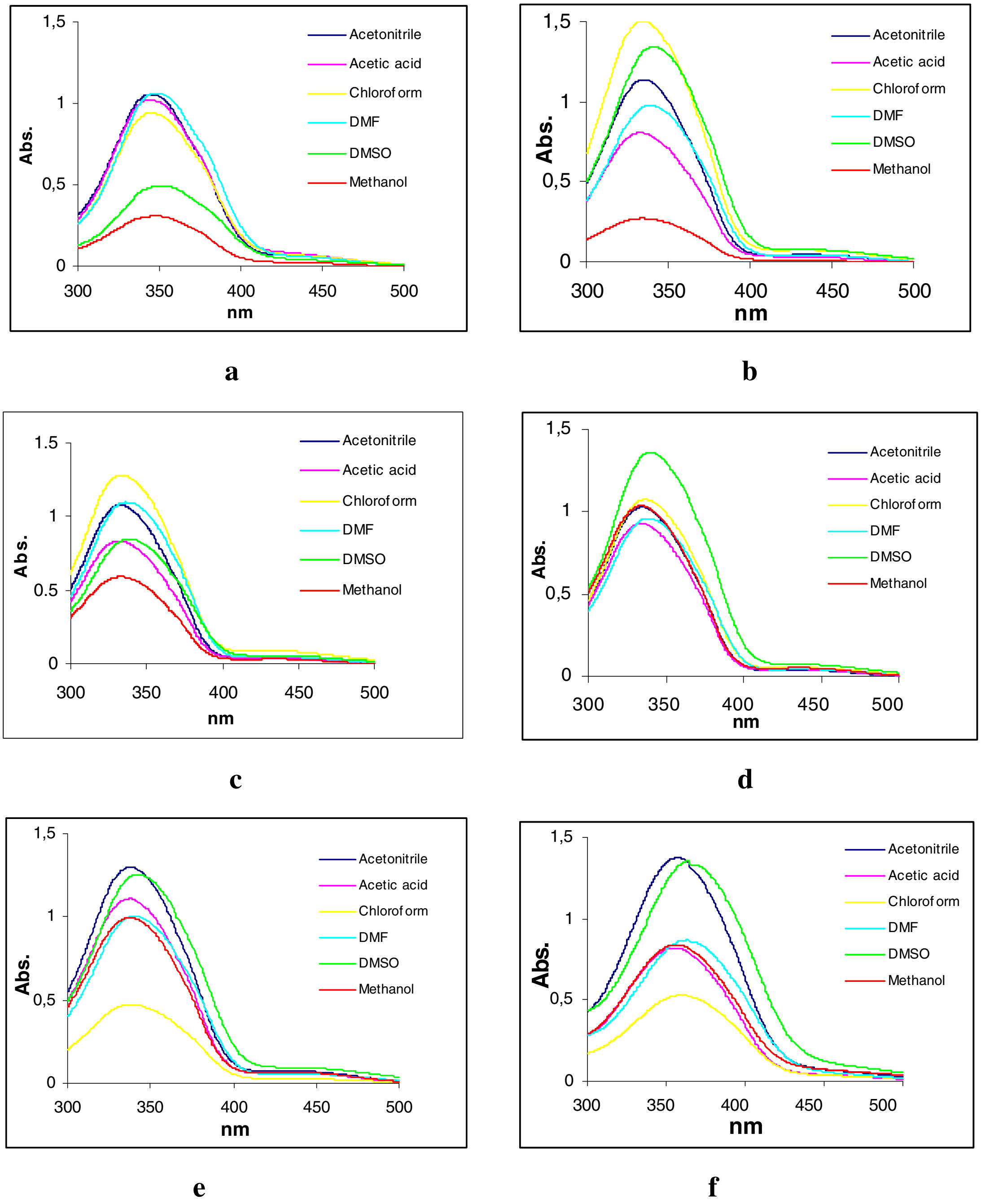


Fig. 2. Absorption spectra of azocalix[4]arene (**4a**–**f**).

Table 1
Influence of solvent on λ_{max} (nm) of azocalix[4]arenes (**4a**–**f**).

Ligands	MeCN	AcOH	$CHCl_3$	DMF	DMSO	MeOH	MeOH + HCl	MeOH + KOH
4a	344	344	345	349 438	350 435	348	353 482	349
4b	334	333	334	339 435	340 434	335	335 458	334
4c	333	332	332	336 435	338 433	333 433	335 441	335
4d	335	335	336	338 437	340 433	334 433	335 434	337 673
4e	338	338	338	340 334	343 433	336 434	338 436	343
4f	358	354	359	364	358	364	357	363

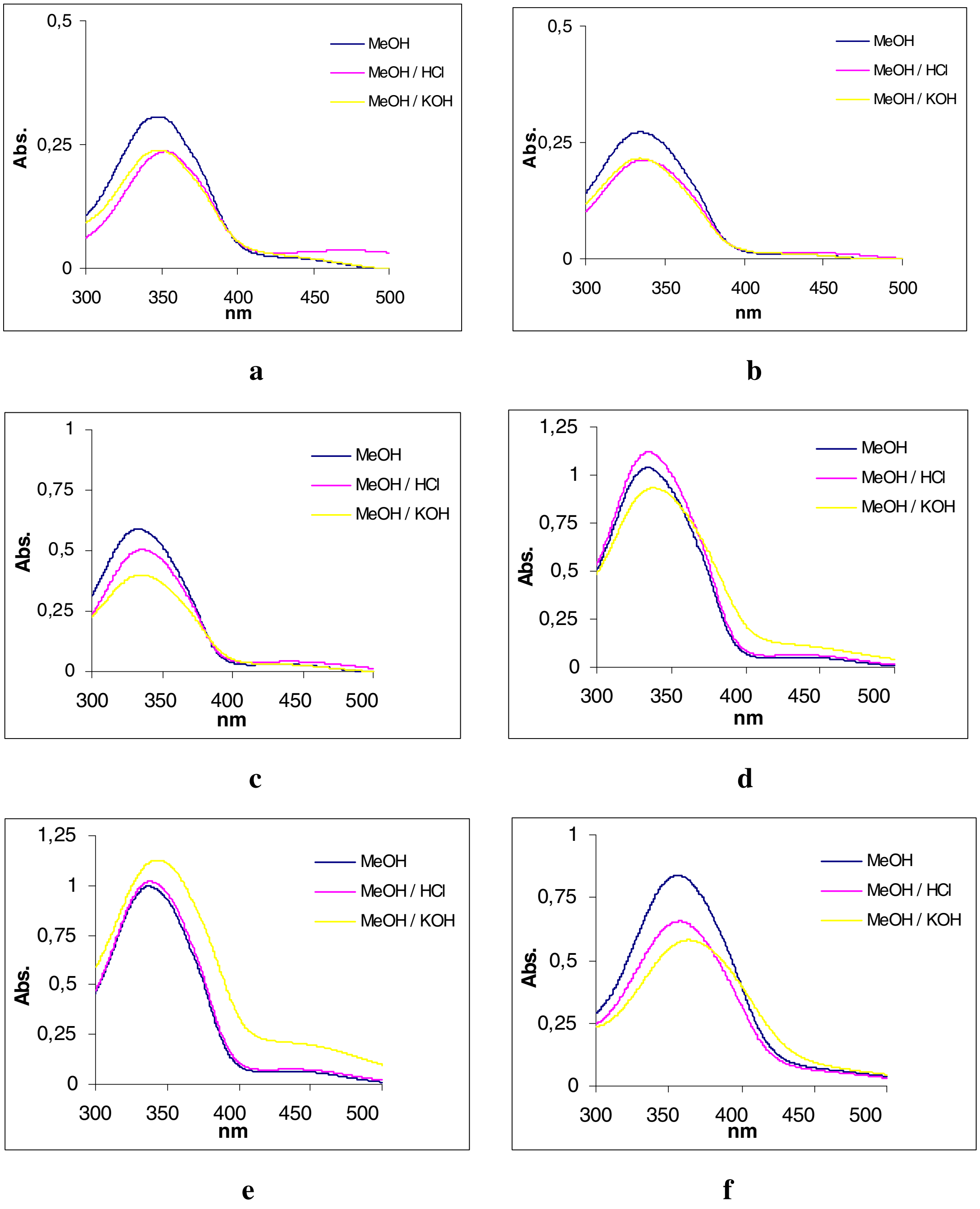


Fig. 3. Effect of acid and base absorption spectra of azocalix[4]arene (**4a**–**f**).

Table 2
Extraction of metal picrates with azocalix[4]arene derivatives **4a**–**f**.[a]

Ligands	Picrate salt extracted (%)													
	Na^+	K^+	Sr^{2+}	Ag^+	Hg^+	Hg^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Pb^{2+}	Zn^{2+}	Cr^{3+}	Al^{3+}	La^{3+}
4a	⩽3.0	⩽3.0	⩽3.0	18.4	15.7	23.8	⩽3.0	⩽3.0	⩽3.0	3.2	⩽3.0	7.9	4.1	⩽3.0
4b	⩽3.0	⩽3.0	⩽3.0	13.2	16.5	26.7	⩽3.0	⩽3.0	⩽3.0	⩽3.0	⩽3.0	6.0	3.9	⩽3.0
4c	⩽3.0	⩽3.0	⩽3.0	13.6	17.0	23.4	5.0	⩽3.0	⩽3.0	⩽3.0	⩽3.0	6.0	⩽3.0	⩽3.0
4d	4.3	⩽3.0	⩽3.0	4.0	19.6	28.7	3.6	⩽3.0	⩽3.0	⩽3.0	⩽3.0	6.9	7.1	3.1
4e	⩽3.0	⩽3.0	⩽3.0	4.2	18.5	28.0	3.5	⩽3.0	⩽3.0	⩽3.0	⩽3.0	6.8	6.9	⩽3.0
4f	⩽3.0	⩽3.0	⩽3.0	5.0	14.4	17.7	3.7	⩽3.0	⩽3.0	4.4	⩽3.0	6.5	3.4	4.0

[a] $H_2O/CHCl_3$ = 10/10 mL (v/v): [picric acid] = 2×10^{-5} M, [ligand] = 1×10^{-3} M, [metal nitrate] = 1×10^{-2} M; 298 K, 1 h contact time. $\alpha \leqslant \pm 2\%$.

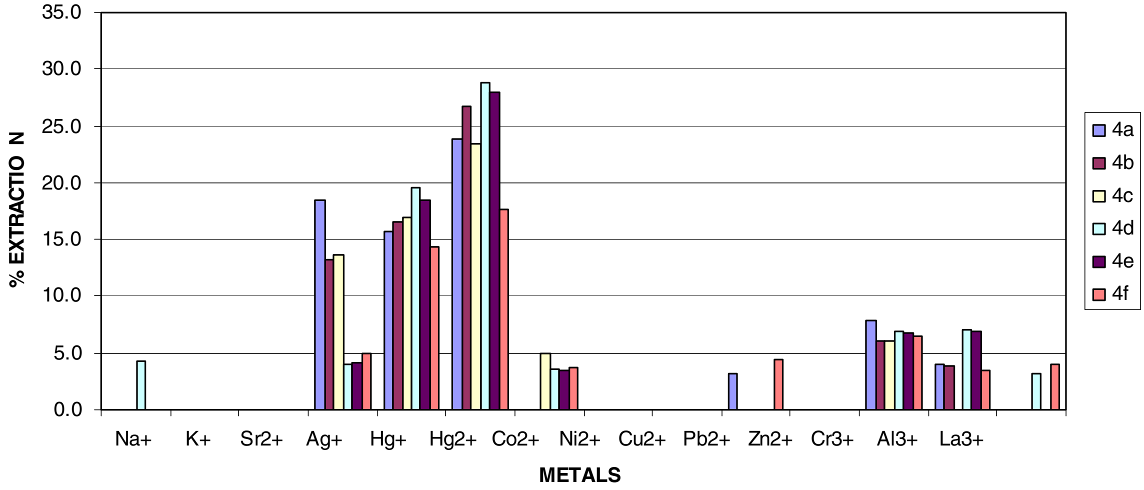


Fig. 4. Extraction percentages of azocalix[4]arene derivatives (**4a–f**).

Table 3
The thermo-analytical results of all compounds (**4a–f**).

Compound	T_i–T_f (°C)	T_{peak} (°C)	Mass loss (%$^{(exp.)}$)	Mass loss (%$^{(theo.)}$)	$T_{melting}$
4a	260–340	317.93	26.58	26.36	249.00
	340–657	572.19	73.91	73.64	
4b	260–346	316.97	26.36	27.72	279.20
	346–665	597.75	73.61	72.28	
4c	260–345	314.49	26.07	26.52	220.05
	345–653	602.87	73.13	73.48	
4d	260–344	321.38	27.55	26.07	218.40
	344–610	539.06	64.50	65.43	
	610–666	642.65	8.20	8.50	
4e	260–327	322.25	23.34	22.98	238.73
	327–612	559.83	66.48	66.56	
	612–802	640.24	9.95	10.47	
4f	260–377	313.22	37.02	38.46	166.71
	377–655	526.97	67.99	61.54	

substantially stronger affinities toward Hg^{2+} compared to the other cations.

Thermal behavior

Thermal analysis plays an important role in studying the structure and stability of calix[*n*]arenes. The determination of thermal stability of calix[*n*]arenes is a very important in terms of finding potential application areas. The thermogravimetric analysis technique provides additional information about structure analysis and molecular interactions [40–42].

In the current study, thermal behavior and thermal stability of novel azocalix[4]arene derivatives (**4a–f**) are investigated. The relationship between thermal stability and substituted groups was determined. The thermo-analytical results are summarized in Table 3. The DTA curves show that all compounds melt before decomposition. Melting points of **4a–f** compounds were identified as 249, 279.20, 220.05, 218.40, 238.73, 166.71 °C, respectively. These values are consistent with melting points which were measured using an Electrothermal IA9100 digital melting point apparatus.

The compounds **4a–c**, **f** decompose in two exothermic stages. The first stage corresponds to the decomposition of ester groups and occurred in 260–352 °C temperature range averagely. Reaction peak temperatures are very close to each other and their average value is 315.65 °C. The second stage is related to the decomposition of complete structure and ends with (67.99–73.91%) experimental mass loss. This value is compatible with average theoretical mass loss (61.54–73.64%). This reaction starts immediately after the end of the first decomposition reaction and completes at 658 °C averagely. The TG and DTA curves of these compounds are given in Fig. 5.

The decomposition of (**4d** and **e**) compounds occur in three stages. The first decomposition stage takes place in (260–344 to 260–327 °C), respectively. Experimental mass loss values are 27.55% (theo: 26.07%) and 23.34% (theo: 22.98%), respectively. In

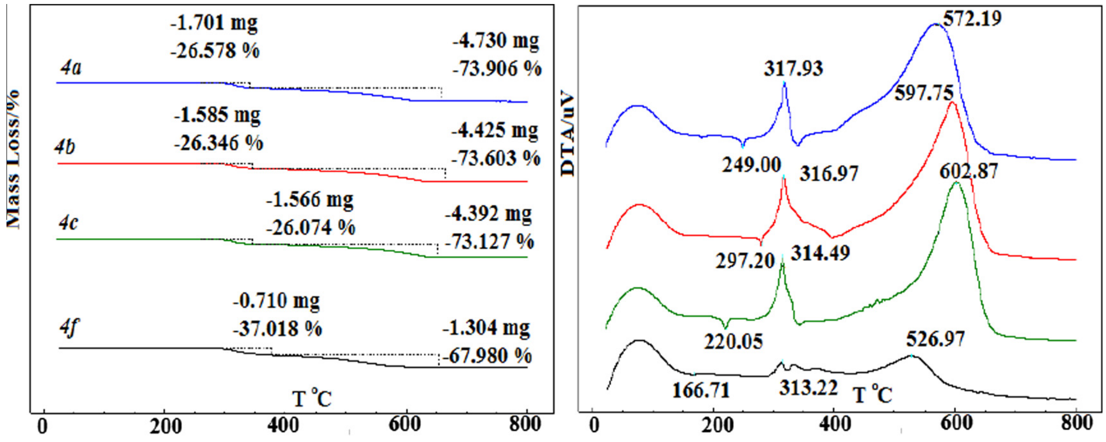


Fig. 5. The TG and DTA curves of (**4a–f**) compounds.

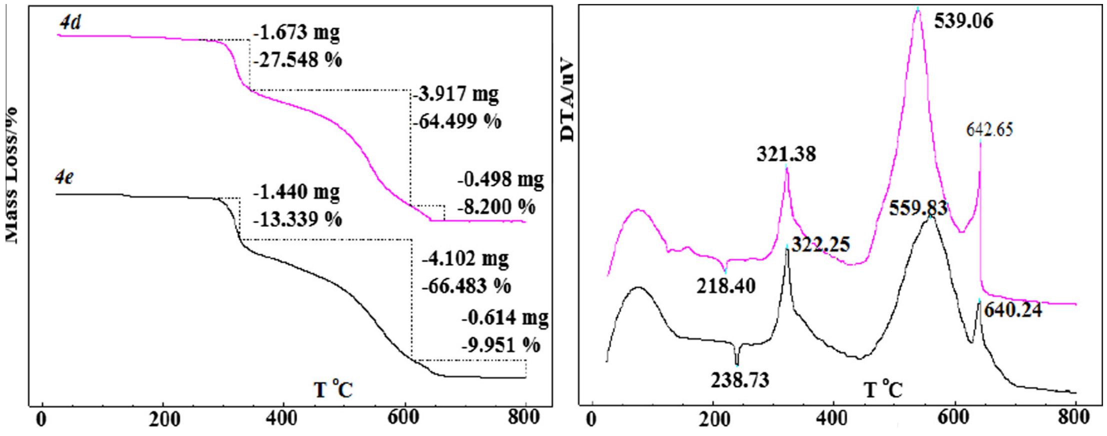


Fig. 6. The TG and DTA curves of (**4d** and **e**) compounds.

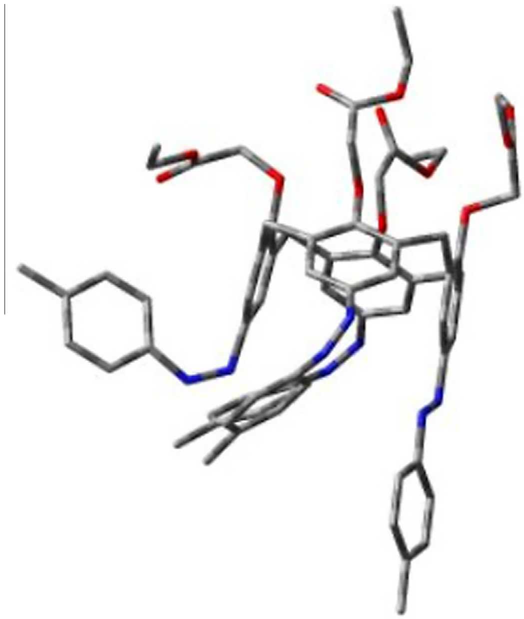


Fig. 7. The optimized structure of (**4b**) molecule.

this stage, fragmentation occurred in ester groups. In the second stage, the decomposition of compound proceeds until it reaches its halogen-benzene structure residue. Peak temperatures of second stage are 539.06 and 559.83 °C, respectively. Final halogen-benzene structure of the compounds decomposes in the last stage. The third exothermic peak of (**4d**) compound is greater than that of (**4e**) compound due to the stronger bond between chlorine and benzene groups. The TG and DTA curves of these compounds are shown in Fig. 6.

Optimization studies

Probable Three-dimensional structure of the (**4b**) molecule, was drawn with GaussView 5.0 molecular imaging program [43] and space settlements of atoms were determined. All theoretical calculations were performed by Gaussian 09W package program [44]. Showed in Fig. 7 the crystal structure of azocalix[4]arene ester derivative (**4b**) exhibited as *cone* conformation.

Conclusions

In summary, the synthesis and characterization of six novel azocalix[4]arene tetraester derivatives (**4a–f**) were studied by means of FT-IR, ^{1}H NMR spectroscopic techniques as well as elemental analysis. These compounds were examined the effect of varying pH levels and solvent types on the absorption ability of azocalix[4]arenes substituted with electron-donating and electron-withdrawing groups. Thermal decomposition of azocalix[4]arene derivatives (**4a–f**) was investigated by means of thermogravimetry (TG), differential thermogravimetry (DTG) and differential thermal analysis (DTA) analyses. In conclusion of the examination of the extraction we found a selectivity characteristic of these compounds toward Ag^+, Hg^+ and Hg^{2+} cations.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2015.01.087.

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