Calix[4]Pyrrole Derivative: Recognition of Fluoride and Mercury Ions and Extracting Properties of the Receptor-Based New Material

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A calix[4]pyrrole derivative, namely, meso-tetramethyl tetrakis (4-phenoxy methyl ketone) calix[4]pyrrole, **1**, was synthesized and structurally (^{1}H NMR) and thermodynamically characterized. The complexing properties of this receptor with a wide variety of anions and cations in dipolar aprotic media (acetonitrile, propylene carbonate, and dimethyl sulfoxide) were investigated through ^{1}H NMR and conductance studies. The former technique was used to assess whether or not complexation occurs and if so to identify the active sites of interaction of **1** with ions. The composition of the complexes was established by conductance measurements. It was found that in dipolar aprotic solvents, **1** interacts only with two polluting ions (fluoride and mercury). The complexation thermodynamics of **1** and these ions in these solvents is reported. The medium effect on the binding process involving the fluoride ion is discussed taking into account the solvation properties of reactants and the product. Complexes of moderate stability are found. Given that this is an important factor to consider for the recycling of the loaded material in extraction processes, **1** was treated with formaldehyde in basic medium leading to the production of a calix[4]pyrrole based material able to extract fluoride and mercury (II) ions from water. Thus the optimum conditions for the extraction of these ions from aqueous solutions were established. The material is easily recyclable using an organic acid. Final conclusions are given.

1. Introduction

The search for receptors able to interact selectively with polluting ions while discriminating against essential ones is an area of priority concern.

Among the anions, fluoride has received a great deal of attention for a long period of time. However, there are still controversial statements regarding the permissible doses of fluoride ingestion by humans which may vary from one individual to another. It is now well established that a high consumption of fluoride leads to serious health problems. Natural sources are the main providers of fluoride ingestion.[1]

As far as cations are concerned, mercury is recognized as a highly dangerous pollutant by the Environmental Protection Agency (EPA) due to its accumulative and persistent character in the environment and biota. It has been recognized as a potent neurotoxin pollutant. Therefore the design of receptors able to interact with these ions could provide the basis for technological developments for the uptake of these pollutants from water.[2]

Calix[4]pyrrole is obtained from the condensation reaction between pyrrole and ketone in acidic medium. It can be functionalized to produce a number of derivatives.[3,4] Contributions made in this field have been acknowledged elsewhere.[5] Further research on calixpyrroles-based sensors has been recently reported.[6,7] Calix[4]pyrrole as well as some of its derivatives have shown selective properties for the fluoride anion and by proper design, selective receptors for mercury complexation have been reported.[8,9]

However, most of the data available on the thermodynamics of calix[4]pyrroles and anions are limited to stability constants in a few solvents. Only few studies involve the enthalpy and entropy associated to these processes.[10−17] Detailed thermodynamics including thermodynamics of transfer of host, guest, and complex from a reference solvent to another are those reported by Danil de Namor and co-workers.[5,10,12,13,15−17]

On the basis of the above statements, the aim of this work was to design a receptor with short pendant arms in order to accomplish the following:

(i) Alter the ability of compound **2** (meso tetramethyl tetrakis 4-hydroxy phenyl calix[4]pyrrole) to interact with anions other than fluoride. In this way, anion interferences when anchored to an oligomeric framework are avoided.

(ii) Explore its ability to interact with mercury(II).

(iii) Provide a detailed thermodynamic chararacterisation of the complexation process and the solvation contribution to it. In doing so, the thermodynamics of transfer of the reactants and the product from a reference solvent to others are to be considered.

(iv) Immobilize the receptor and assess its potential as a decontaminating agent for the removal of fluoride and mercury (II) from water.

Thus, this paper reports (i) the synthesis and characterization (structural and thermodynamic) of meso-tetramethyl tetrakis-(4-phenoxy methyl ketone) calix[4]pyrrole, **1**; (ii) The cation and the anion complexing properties of this ligand in dipolar aprotic solvents (propylene carbonate, PC, dimethyl sulfoxide, DMSO and acetonitrile, MeCN) with the aim of assessing the medium effect on the complexation process. For this purpose, several techniques have been explored. (iii) The extraction properties under several experimental conditions of a new oligomeric material containing **1** as an anchor group. Whenever possible comparison with existing analogous macrocycles and calix[4]pyrrole-based materials for extraction processes will be established.[18]

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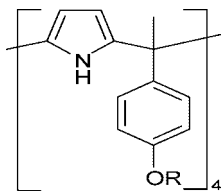
1 R= COCH$_3$

2 R= H

3 R= (CH$_2$)$_2$SCH$_2$CH$_3$

2. Experimental Section

2.1. Chemicals Used. Pyrrole (99%), methane sulfonic acid (99.5%), *p*-hydroxyacetophenone (99%), acetyl chloride (99%), triethyl amine (99%), lithium perchlorate, sodium perchlorate (99%), potassium perchlorate (99%), calcium perchlorate tetrahydrated (99%), magnesium perchlorate (80%), cadmium perchlorate, mercury perchlorate monohydrated (99.99%), tetra-*n*-butylammonium bromide (99%), iodide (97%), nitrate (97%), tris(hydroxymethyl)amino methane (99.9%), formaldehyde (37%), propylene carbonate (99.7%), deuterated dimethylsulfoxide (d$_6$-DMSO), and acetonitrile (CD$_3$CN) were all purchased from Aldrich Chemical Co.

Magnesium sulfate (62−70%), methanol (HPLC grade), diethyl ether (Laboratory reagent), acetic acid (analytical reagent), acetone (analytical reagent), tetrahydrofuran (HPLC grade), acetonitrile, and dimethyl sulfoxide (both HPLC grade were refluxed in a nitrogen atmosphere and distilled over calcium hydride)[19] were purchased from Fisher UK Scientific International.

Rubidium (Alfa Aesar Company) and strontium hydrated perchlorate (K & K laboratory), and tetra-*n*-butylammonium as perchlorate (99%, Fluka Chemical Company), fluoride trihydrated (97%, Fluka Chemical Company), and chloride (97%, Fluka chemical Company) salts were dried over P$_4$O$_{10}$ under vacuum for several days. The absence of a water peak in the NMR spectra upon addition of metal cation salts indicated that these salts were dry.

2.2. Synthesis of meso-Tetramethyl-tetrakis-(4-hydroxyphenyl) Calix[4]Pyrrole. The preparation of meso-tetramethyl-tetrakis-(4-hydroxyphenyl) calix[4]pyrrole was achieved by applying the procedure reported in the literature.[20,21] Thus pyrrole (5 g, 75 mmol) was placed in a 250 mL round-bottom flask equipped with a magnetic stirrer and filled with methanol (100 mL). Methanesulphonic acid (1 mL) was then added to the mixture and stirred for 30 min. This was followed by the stepwise addition of a solution of *p*-hydroxyacetophenone (11 g, 80 mmol) in methanol (50 mL). The reaction mixture was monitored by TLC using a dichloromethane/methanol mixture (9.5:0.5) as the developing solvent and was left to stir overnight. Then the mixture was poured into distilled water (200 mL). An orange color precipitate was obtained. The residue was filtered off, collected, and then dissolved in diethyl ether (400 mL). The solution was filtered gravitationally to remove the black tar obtained. This was recrystallized from acetic acid and left to cool down. Green crystals containing the αααα isomer-acetic acid complex were obtained. The acid was removed by further recrystallization with an acetonitrile/acetone mixture. White crystals of the calixpyrrole derivative (65% yield) were obtained. These were dried in vacuum at 90 °C. ¹H NMR (d$_6$-acetone, 300 MHz 298 K, δ in ppm): 8.75 (s broad, 4H, N*H*); 8.22 (s, 4H, O*H*); 6.78 (d, 8H, Ar*H*; *J* = 9.3 Hz); 6.66 (d, 8H, Ar*H*, *J* = 9.0 Hz); 5.96 (d, 8H, Py*H*, *J* = 2.7 Hz); 1.81 (s, 12 H, C*H*$_3$).

Elemental analysis was carried out at the University of Surrey. Calculated %: C, 77.81; H, 5.99; N, 7.56. Found %: C, 77.60; H, 5.94; N, 7.51.

2.3. Synthesis of meso-Tetramethyl tetrakis-(4-phenoxymethyl Ketone) Calix[4]Pyrrole, 1. The procedure used in the literature[22] for the synthesis of this calix[4]pyrrole receptor was modified. Calixpyrrole (3 g, 4 mmol) was placed in a 250 round-bottom flask and dissolved in tetrahydrofuran (200 mL) and the solution was stirred for 10 min. Acetyl chloride (1.27 g, 16 mmol) and triethylamine (3.27 g, 32 mmol) were added and the solution was stirred for 5 days. The solvent was evaporated and the crude product was dissolved in acetonitrile. The compound was recrystallized using a methanol/acetone (75:100) mixture. It was then collected by filtration and dried in vacuum at 90 °C.¹H NMR (d$_6$-DMSO, 300 MHz, 298 K, ppm): 9.53 (s; 4H, N*H*); 7.02 (d, 8H, Ar*H*); 6.93 (d, 8H, Ar*H*); 5.99 (d, 8H, Py); 3.23 (s, 12H, C*H*$_3$); 1.80 (s, 12H, C*H*$_3$).

2.4. Synthesis of the Oligomer of the Calixpyrrole Derivative, 1. The base catalyzed phenol-formaldehyde procedure was used in the preparation of the calixpyrrole oligomeric material.[23] The calix[4]pyrrole derivative **1** (5 g, 5.18 mmol) was placed in a 500 mL round-bottom flask and dissolved in tetrahydrofuran (100 mL). Formaldehyde (37 wt % in methanol) (5.04 mL, 62.16 mmol) and tetra-*n*-butylammonium hydroxide (15% in methanol) were then added. The reaction was left to stir overnight. The compound was characterized by mass spectroscopy. The molecular weight of the calix[4]pyrrole derivative, **1,** was found to be 909.034 g mol^{-1}. The residual peaks found at *m/z* ratio between 2400 and 2800 indicate the formation of an oligomer (trimer) that is at least three times the molecular weight of the monomer.

2.5. Solubility Measurements. Saturated solutions of **1** were prepared by adding an excess amount of the macrocycle in different solvents (methanol, MeOH; ethanol, EtOH, acetonitrile, MeCN; *N,N*-dimethylformamide, DMF; dimethylsulfoxide, DMSO and propylene carbonate, PC). The solutions were left in a thermostatted bath at 298.15 ± 0.01 K until equilibrium was reached.

Several blank measurements were carried out to ensure the absence of any involatile material in the pure solvent. Samples of the saturated solutions were taken and analyzed gravimetrically by triplicate. Solvation of the macrocycle was checked by placing a small amount of the compound in a saturated atmosphere of the appropriate solvent.

2.6. ¹H NMR Measurements. A Bruker AC-300E pulsed Fourier transform NMR spectrometer was used to characterize **1** and to provide information about its interaction with ions. ¹H NMR measurements were recorded at 298 K. Typical operating conditions for the routine proton measurements involved a pulse or flip angle of 30°, spectral frequency of 300.135 MHz, delay time of 1.60 s, acquisition time of 1.819 s, and line broadening of 0.55 Hz.

A solution of **1** was prepared in the appropriate deuterated solvent and then placed in a 5 mm NMR tube using tetramethylsilane as the internal reference.

The complexation behavior of the ligand toward anions and cations was studied by adding the salts containing the appropriate ion (8.0 × 10^{-3} to 1.6 × 10^{-2} mol dm^{-3}) into the NMR tube containing a solution of **1** dissolved in the same solvent (1.0 × 10^{-3} mol dm^{-3}). Stepwise additions of the salts were made. The chemical shifts were recorded. Changes in the chemical shifts upon addition of the salts relative to the free ligand were calculated.

2.7. Conductance Measurements. For these measurements, a Wayne−Kerr Autobalance Universal Bridge type B642 was used. The conductivity cell constant was determined by the method of Jones and Bradshaw.[24]

Conductometric titrations were carried out in a conductivity cell filled with a weighed volume of the solution of the appropriate anion salt in the solvent of interest (5.00×10^{-5} to 1.00×10^{-4} mol dm^{-3}) and titrated with a solution of **1** (1.00×10^{-3} mol dm^{-3}) in the same solvent using a glass syringe connected to a calibrated automatic burette. Conductance readings at 298.15 ± 0.01 K were recorded after each addition and the molar conductance was calculated. A plot of molar conductance versus the ligand-ion concentration ratio was used to determine the stoichiometry of the complex.

2.8. Calorimetric Measurements. Calorimetric measurements were carried out for two purposes: (i) to obtain the enthalpy of solution of the ligand in various solvents and (ii) to derive the thermodynamic parameters of complexation of this ligand and the relevant ions in various solvents.

(i) Calorimetric Determination of the Enthalpies of Solution of 1 and 2 in Various Solvents. The enthalpies of solution, $\Delta_s H$ (kJ mol^{-1}), of **1** and **2** at different concentrations (3×10^{-5} to 1×10^{-2} mol dm^{-3}) in MeCN, PC, DMF, and DMSO at 298.15 ± 0.01 K were determined calorimetrically using the Tronac 450 calorimeter. Thus glass ampoules (at least six) containing known quantities of the ligand were sealed. These were then placed on the holder at the end of the stirrer and immersed in the desired solvent in the reaction vessel. The system was then placed in a water bath until thermal equilibrium was attained. Ampoules were broken by means of the plunger that goes through the stirrer rod, and the resulting temperature changes were recorded. After each experiment, an electric calibration was performed. The total heat recorded was the sum of the heat of solution and the heat of ampule breaking. The latter was determined by breaking empty ampoules in the same solvent under investigation and recording the heat change. The heat of solution was calculated by subtracting the heat of breaking of the empty ampule from the total heat recorded.

(ii) Determination of the Thermodynamic Parameters of Ion Complexation. The calibration of the machine was carried out using the standard reaction of protonation of an aqueous solution of tris-(hydroxymethyl) aminomethane (THAM) with an aqueous solution of hydrochloric acid (0.1 mol dm^{-3}) at 298.15 K. The value obtained (-47.33 kJ mol^{-1}) was in good agreement with that reported by Wilson and Smith[25] (-47.49 kJ mol^{-1}) at 298.15 K.

Stability constants (log Ks) and enthalpies of complexation, $\Delta_c H$, of the ligand with the fluoride anion at 298.15 K in DMSO, MeCN, and PC were determined by direct calorimetric titrations using the Tronac 450 calorimeter.[26]

For the calorimetric titrations, a solution of the ligand (10^{-4}–10^{-3} mol dm^{-3}) was placed in the vessel (50 cm^3) in the selected solvent and the anion salt (10^{-3}–10^{-2} mol dm^{-3}) was placed in the same solvent in the syringe. The latter was added from a 2 cm^3 burette connected by a silicone tube to the reaction vessel after thermal equilibrium was reached. These experiments were carried out by triplicate. For each solvent, blank experiments were performed to account for dilution effects resulting from the addition of the appropriate anion salt to the solvent placed in the calorimetric vessel.

For the complexation studies involving **1** and Hg^{2+} in MeCN, a solution of **1** (1×10^{-3} mol dm^{-3}) was placed in the vessel (50 cm^3) and the mercury cation salt (5×10^{-2} mol dm^{-3}) in the syringe. The latter was added from a 2 cm^3 burette connected

by a silicone tube to the reaction vessel after thermal equilibrium was reached. These experiments were carried out by triplicate. Blank experiment was performed to account for dilution effects resulting from the addition of the mercury cation to the solvent placed in the calorimetric vessel.

2.9. The Removal of Fluoride and Mercury (II) from Aqueous Solutions. Batch experiments were carried out by adding different amounts of the oligomeric material to test tubes containing a known concentration of sodium fluoride or mercury (II) nitrate in aqueous medium. The solutions were shaken on a vibromixer for a period of 2 min and left overnight in a thermostatted bath at 298.15 K. Once equilibrium was achieved samples for analysis were drawn. Given that the material takes up the cation and the anion simultaneously, initial and equilibrium concentrations of salts were measured for sodium in the case of fluoride using a sodium selective electrode. The initial and equilibrium concentrations of mercury (II) were determined by a volumetric method using EDTA as the complexing agent. Blank experiments using deionized water were carried out.

Concentrations of fluoride and mercury taken up by the material were calculated from the difference between the initial C_i and equilibrium C_{eq} concentrations in solution (mol dm^{-3}). Therefore, the percentage of removal of these ions by the material was calculated by the use of eq 1

$$\% \text{ Extraction} = \frac{(C_i - C_{eq}) \times 100}{C_i} \qquad (1)$$

In order to estimate the uptake capacity of the materials for these ions from aqueous solutions, batch experiments were carried out at 298.15 K at different concentrations of the fluoride (4.00×10^{-3} to 1.00×10^{-1} mol dm^{-3}) and mercury (9.00×10^{-4} to 6.00×10^{-3} mol dm^{-3}) salts using a fixed mass of the material. The uptake capacity, q_{eq} (mmol g^{-1}), or the maximum amount of anion or cation taken up per unit mass of material was calculated from eq 2

$$q_{eq} = \frac{(C_i - C_{eq}) \times V}{m} \qquad (2)$$

In eq 2, m is the mass of the material (g), and V is the volume of the solution (cm^3).

The effect of pH on the removal process was studied by adding a volume (10 cm^3) of the fluoride (1.00×10^{-1} mol dm^{-3}) or mercury (5.00×10^{-3} mol dm^{-3}) salts to the tests tubes containing a fixed amount of the material. The pH of the initial solutions was adjusted using hydrochloric acid (HCl) or ammonium hydroxide (NH$_4$OH) until the desired pH was obtained. The pH range investigated was from 3 to 12. A digital microprocessor pH-meter equipped with a glass electrode was used for these measurements. Two standards buffer solutions of pH = 4.0 and pH = 7.0 were used for calibration.

The kinetics of the process was investigated by carrying out batch equilibrium experiments performed at 298.15 K to evaluate the time required to attain equilibrium. Times from 5 min and 24 h were investigated. Other parameters (mass of the material, initial concentration of the solution, pH and temperature) were kept constant. The equilibrium concentrations of the anion or cation salts versus the equilibration time at 298.15 K were plotted.

All experiments were done under controlled temperature which is 298.15 K.

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TABLE 1: Solubilities and Derived Standard Gibbs Energies of Solution of 1 in Various Solvents[a]

	solubility/mol dm^{-3}			$\Delta_s G^0$/kJ mol^{-1}			$\Delta_t G^0_{(MeCN \to s)}$/kJ mol^{-1}		
solvent	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**
MeCN	$(6.4 \pm 0.6) \times 10^{-4}$	$(9.45 \pm 0.04) \times 10^{-4}$		18.23	17.26		0	0	0
PC	$(1.4 \pm 0.1) \times 10^{-2}$		$(2.64 \pm 0.04) \times 10^{-2}$	10.58		9.01	−7.65		
DMSO	$(2.09 \pm 0.08) \times 10^{-2}$			9.59			−8.64		
DMF	$(1.4 \pm 0.1) \times 10^{-2}$			10.58			−7.65		
MeOH	$(2.6 \pm 0.1) \times 10^{-4}$	$(7.52 \pm 0.02) \times 10^{-2}$	$(1.3 \pm 0.2) \times 10^{-3}$	20.46	6.41	16.51	2.23	−10.85	−7.50
EtOH	$(3.4 \pm 0.5) \times 10^{-4}$	$(3.63 \pm 0.03) \times 10^{-2}$		19.8	8.22		1.57	−9.04	

[a] Transfer Gibbs energies from acetonitrile at 298.15 K. Solvent abbreviation: acetonitrile, MeCN; propylene carbonate, PC; dimethyl sulfoxide, DMSO; *N,N*-dimethylformamide, DMF; methanol, MeOH; ethanol, EtOH.

TABLE 2: Enthalpies of Solution of 1 in Acetonitrile, Propylene Carbonate, and Dimethylsulfoxide at 298.15 K

MeCN		PC		DMSO	
$c^{1/2}$/mol dm^{-3}	$\Delta_s H$/kJ mol^{-1}	$c^{1/2}$/mol dm^{-3}	$\Delta_s H$/kJ mol^{-1}	$c^{1/2}$/mol dm^{-3}	$\Delta_s H$/kJ mol^{-1}
3.00×10^{-5}	−49.26	1.13×10^{-2}	16.62	5.33×10^{-3}	40.50
4.47×10^{-5}	−21.97	1.26×10^{-2}	17.03	5.41×10^{-3}	37.93
6.27×10^{-3}	−12.63	1.62×10^{-2}	23.13	7.50×10^{-3}	26.17
8.74×10^{-3}	−0.50	1.76×10^{-2}	26.77	7.58×10^{-3}	26.04
1.07×10^{-4}	19.97	1.92×10^{-2}	26.93	1.00×10^{-2}	15.53
1.32×10^{-4}	32.16	2.00×10^{-2}	29.60	1.13×10^{-2}	9.32
		2.24×10^{-2}	33.08	1.26×10^{-2}	2.13
				1.31×10^{-2}	3.92
$\Delta_s H^0 =$	−114.4 ± 0.5 kJ mol^{-1}	$\Delta_s H^0 =$	1.39 ± 0.08 kJ mol^{-1}	$\Delta_s H^0 =$	63 ± 1 kJ mol^{-1}

3. Results and Discussion

3.1. Solution Thermodynamics of 1 in Different Solvents. Solubility data for **1** in various solvents are listed in Table 1. These are the result of several analytical measurements carried out on the same saturated solution. The standard deviation of the data is also included in this Table.

In these solvents, no solvate formation was observed when **1** was exposed to a saturated atmosphere of the appropriate solvent. Therefore the standard Gibbs energies of solution, $\Delta_s G^0$ in these solvents were calculated. These data are referred to the standard state of 1 mol dm^{-3}. Taking acetonitrile as the reference solvent, the standard transfer Gibbs energies, $\Delta_t G^0$ of **1** to other solvents are calculated (see Table 1). The results show that these ligands are favorably transferred to other aprotic solvents such as PC, DMSO, and DMF while its solvation in MeCN does not differ significantly from that in the alcohols. These results contrast significantly with those for an analogous receptor, **2** and **3** meso-tetramethyl tetrakis {4-[2-(ethylthio)ethoxy]phenyl}calix[4]pyrrole (see Table 1) which are favorably transferred to the alcohols. Thus the replacement of the phenolic hydrogen (likely to interact strongly with MeOH and EtOH through hydrogen bond formation) by a ketone and sulfur functional groups has altered significantly the solvation properties of **1** relative to **2, 3** and these may have some implications on the complexing properties of this receptor relative to **2** and **3**.

In an attempt to assess the contribution of the enthalpy and entropy to the Gibbs energy of the solution process, calorimetric measurements were carried out. Table 2 reports solution enthalpy data, $\Delta_s H$ for **1** at different concentrations, c_1 of the ligand in acetonitrile, dimethyl sulfoxide, and propylene carbonate at 298.15 K. Since $\Delta_s H$ was found to be concentration dependent, the standard enthalpy of solution, $\Delta_s H^0$ in the appropriate solution at $c = 0$ was calculated from a plot of $\Delta_s H$ against the square root of the ligand concentration, $c^{1/2}$.

As far as **2** is concerned, the enthalpy of solution for this ligand did not change with changes in its concentration and an average value was taken as the standard enthalpy of solution of **2** in these solvents at 298.15 K (Table 3).

TABLE 3: Enthalpies of Solution of 2 in Acetonitrile and *N,N*-Dimethylformamide at 298.15 K

MeCN		DMF	
$c^{1/2}$/mol dm^{-3}	$\Delta_s H$/kJ mol^{-1}	$c^{1/2}$/mol dm^{-3}	$\Delta_s H$/kJ mol^{-1}
5.80×10^{-5}	46.76	9.45×10^{-4}	−46.37
7.29×10^{-5}	46.29	1.51×10^{-4}	−45.97
8.50×10^{-5}	45.74	2.16×10^{-4}	−45.82
1.18×10^{-4}	45.45	2.92×10^{-4}	−44.89
2.04×10^{-4}	45.37	4.16×10^{-4}	−45.99
2.95×10^{-4}	46.76	4.62×10^{-4}	−45.32
4.02×10^{-4}	45.95	5.05×10^{-4}	−46.14
$\Delta_s H^0 =$	46.0 ± 0.6 kJ mol^{-1}	$\Delta_s H^0 =$	−45.8 ± 0.5

TABLE 4: Solution Thermodynamic Parameters of 1 in Various Solvents at 298.15 K[a]

solvent	$\Delta_s G^0$/kJ mol^{-1}	$\Delta_s H^0$/kJ mol^{-1}	$\Delta_s S^0$/J K^{-1} mol^{-1}	$\Delta_t G^0_{(MeCN \to s)}$/kJ mol^{-1}	$\Delta_t H^0$/kJ mol^{-1}	$\Delta_t S^0$/J K^{-1} mol^{-1}
MeCN	18.23	−114.4	−444.8	0	0	0
PC	10.58	1.39	−30.8	−7.65	115.8	414
DMSO	9.59	63	179	−8.64	177.4	624

[a] Derived transfer data from acetonitrile.

Combination of $\Delta_s G^0$ and $\Delta_s H^0$ leads to the calculation of the standard entropy of solution, $\Delta_s S^0$. These data are used to derive the thermodynamic parameters of transfer of **1** from MeCN to PC and DMSO listed in Table 4.

The results show that the favorable transfer of **1** from acetonitrile to PC and DMSO is entropy driven and enthalpically destabilized.

3.2. ¹H NMR Studies on the Interaction of 1 with Ions. The addition of anion salts in DMSO led to a significant downfield change ($\Delta\delta = 2.913$ ppm) in the pyrrolic ring relative to that of the free ligand when the fluoride salt was added. This is a clear indication that this anion interacts with this receptor through hydrogen bond formation between the pyrrolic proton and the fluoride anion. No changes were observed in the ¹H NMR spectrum of **1** in this solvent when other anion salts (chloride, bromide, iodide, hydrogen sulfate, dihydrogen phosphate, and nitrate) were added to the ligand.
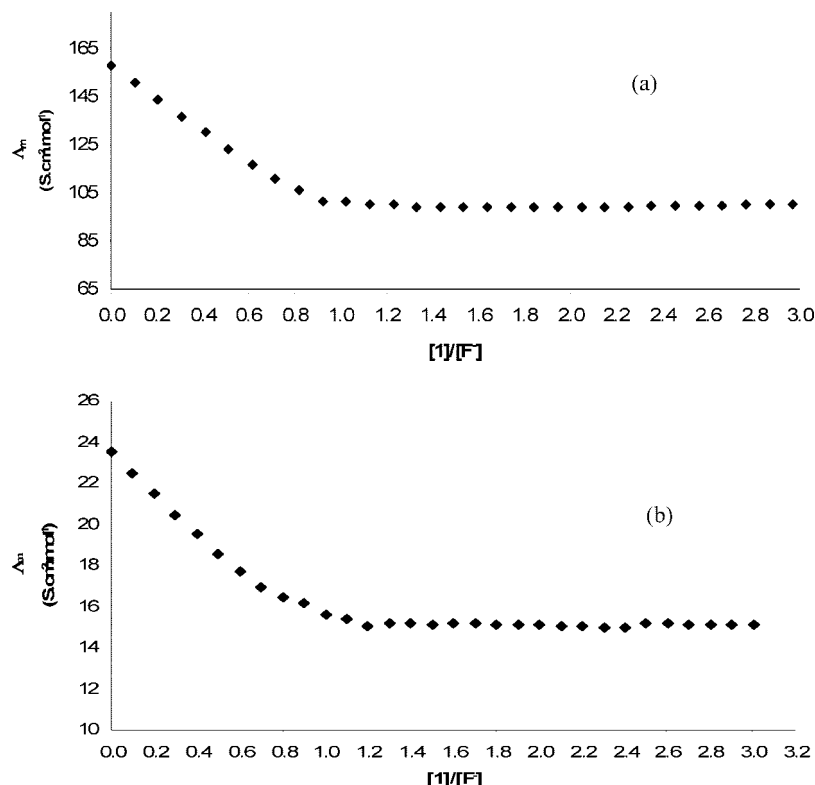
Figure 1. (a) Conductometric titration curve of fluoride (as tetra-*n*-butylammonium) with **1** in MeCN in 298.15 K. (b) Conductometric titration curve of fluoride (as tetra-*n*-butylammonium) with **1** in PC in 298.15 K.

The ^{1}H NMR spectrum of this ligand in CD$_3$CN shows an upfield shift for the fluoride anion due to the conformational changes of the ligand taking place upon complexation. This conformational change results from the orientation of the pyrrole proton, thus shielding this proton from the external magnetic field. However, the significant chemical changes observed for **2** upon the addition of F$^-$, Cl$^-$, Br$^-$, and H$_2$PO$_4^-$ in CD$_3$CN, suggest that **1** is more selective than **2** for interacting with fluoride.

As far as the cations (alkali, alkaline-earth, transition, and heavy metal cations) in CD$_3$CN are concerned, the only significant chemical shift change was observed upon the addition of mercury salt. A significant deshielding effect was observed for the methyl group near the carbonyl suggesting that the complexation occurs through the oxygen atoms of the pendant arms. As compared with **3**, the significant chemical shift changes observed in CD$_3$CN were only upon the addition of Ag$^+$ and Hg^{2+}, showing that **1** has advantage over **3** for being more selective for Hg^{2+} among the cations.[15]

3.3. Conductometric Titrations. These titrations were carried out with the aim of establishing the composition of the complex in these solvents and to obtain a semiquantitative information regarding the strength of complexation. Plots of molar conductance, Λ_m, versus the ligand/anion concentration ratios [**1**]/[F$^-$] in acetonitrile and propylene carbonate are shown in Figure 1a,b, respectively.

The lower mobility of the complex relative to the free anion results in a decrease in conductance as the reaction proceeds due to the relatively large size of the former relative to the latter. In both cases, complexes of 1:1 (ligand/ anion) stoichiometry are formed. The shape of the conductometric curves seems to be indicative of the formation of complexes of moderate stability.

As far as mercury is concerned, the conductometric titration curve for this metal cation and **1** in acetonitrile is shown in
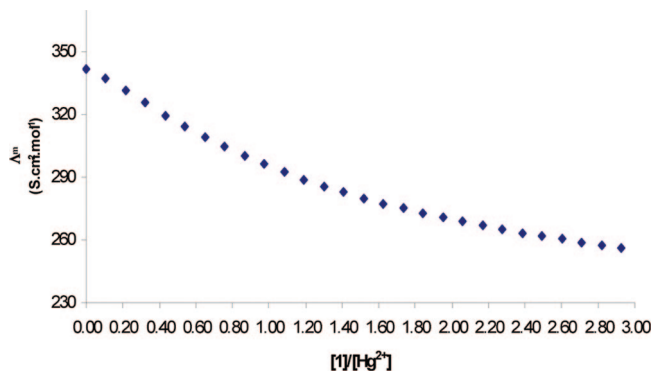

Figure 2. Conductometric titration curve of mercury (as perchlorate) with **1** in MeCN in 298.15 K.

Figure 2. It shows a similar pattern to that for the fluoride anion with a decrease in conductance upon addition of the ligand to the solution containing the cation salt due to the size effect. The composition of the complex is 1:1 (ligand/cation) in acetonitrile.

The next section discusses the thermodynamics of complexation of **1** and the fluoride anion in acetonitrile, propylene carbonate and dimethylsulfoxide together with data involving this receptor and the mercury cation in acetonitrile.

3.4. Thermodynamics of Complexation. Stability constants (expressed as log K_s) and derived standard Gibbs energies, $\Delta_c G^0$ (referred to the standard state of 1 mol dm^{-3} for the reactants and the product), standard enthalpies, $\Delta_c H^0$ and entropies, $\Delta_c S^0$ in various solvents (acetonitrile, propylene carbonate, and dimethylsulfoxide) for the process described by eq 3 involving **1** and the fluoride anion at 298.15 K are listed in Table 5.
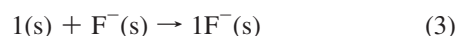
$$\mathbf{1}(s) + F^-(s) \rightarrow \mathbf{1}F^-(s) \qquad (3)$$

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TABLE 5: Stability Constants, Standard Gibbs Energies, Enthalpies, and Entropies of 1 and the Fluoride Anion in Various Solvents and the Mercury(II) Cation in Acetonitrile at 298.15 K

solvents	$\log K_s$	$\Delta_c G^0/$ kJ mol^{-1}	$\Delta_c H^0/$ kJ mol^{-1}	$\Delta_c S^0/$ J mol^{-1} K^{-1}
		F$^-$		
MeCN	3.30 ± 0.04	−19.2 ± 0.2	−81.1 ± 0.5	−203
PC	3.3 ± 0.1	−19.1 ± 0.7	−27.8 ± 0.3	−29
DMSO	3.59 ± 0.02	−20.5± 0.1	−38 ± 1	−63
		Hg^{2+}		
MeCN	5.64 ± 0.03	−32.2 ± 0.2	−118.5 ± 0.5	−289

The results show that (i) the complexation process is enthalpy controlled; (ii) the medium effect is negligible on the stability of the complex as reflected in the similar $\log K_s$ values found in the various solvents. However, the enthalpy and entropy contributions to complex stability vary significantly from one medium to another. It is therefore concluded that the stability of the complexes is the result of a remarkable enthalpy−entropy compensation effect, this is shown in Figure 3 where a linear relationship is found between $\Delta_c H^0$ and $\Delta_c S^0$ values with a slope of 306.8 K. As compared with **2**, the complexation process of **1** with fluoride in acetonitrile was found to be enthalpically more favorable by 48.7 kJ mol^{-1} than that of **2** and this anion. However, the greater loss of entropy in the interaction of **1** with fluoride in this solvent decreases the stability of the complex with this ligand relative to **2** (Table 6).

As far as the interaction of **1** and Hg^{2+} is concerned (also included in Table 5), the reaction is enthalpically controlled. It was found that the 1:1 complexation of **1** and Hg^{2+} in acetonitrile is enthalpically more favorable by 30.6 kJ mol^{-1} than that of **3** and this cation in the same solvent (Table 6) given that there is not a dramatic difference in the loss of entropy in the complexation of mercury (II) and these ligands in this solvent. The stability of the complex is enhanced in moving from **3** to **1**.
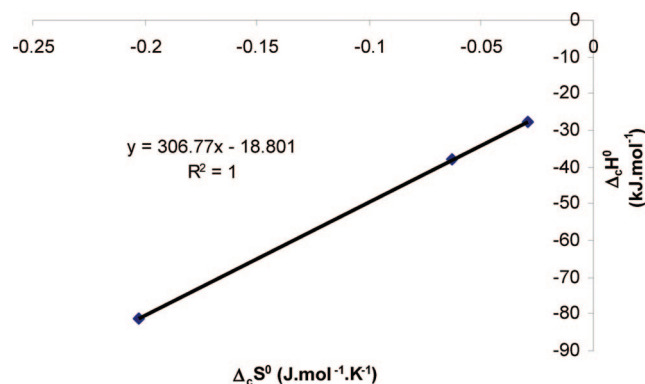

Figure 3. Standard entropy vs standard enthalpy of complexation of **1** and the fluoride anion in different solvents at 298.15 K.

TABLE 6: Thermodynamic Parameters for the Complexation of Fluoride with 1, 2, and Mercury in Acetonitrile with 1 and 3 in Acetonitrile at 298.15 K

| solvents	$\log K_s$	$\Delta_c G^0/$ kJ mol^{-1}	$\Delta_c H^0/$ kJ mol^{-1}	$\Delta_c S^0/$ J mol^{-1} K^{-1}
		F$^-$		
1	3.30 ± 0.04	−19.2 ± 0.2	−81.1 ± 0.5	−203
2	5.44 ± 0.08	−31.1 ± 0.4	−32.4 ± 0.6	−5
		Hg^{2+}		
1	5.64 ± 0.03	−32.2 ± 0.2	−118.5 ± 0.5	−289
3 (1:1)	3.72 ± 0.02	−21.26 ± 0.01	−87.9 ± 0.7	−224

Attempts to assess the factors which contribute to the higher enthalpic stability for the complexation of **1** and the fluoride anion in acetonitrile relative to other solvents are made by the use of the following thermodynamic cycle (eq 4)
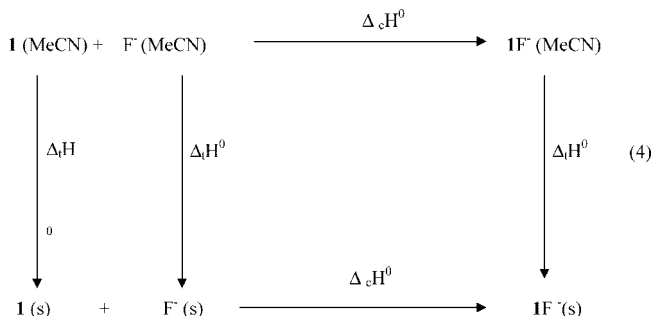
By inserting the appropriate data in eq 4, the results for the MeCN-PC solvent system are first discussed (eq 5). Data for **1** are those reported in Table 3. The $\Delta_t H^0$ (MeCN→PC) for the fluoride anion was obtained from the $\Delta_s H^0$ values for Bu$_4$NF in acetonitrile reported in the literature[8,10,13] and that in propylene carbonate determined in this work (17 ± 1 kJ mol^{-1}). Taking into account the single-ion $\Delta_t H^0$ (MeCN→PC) for the Bu$_4$N$^+$ ion (data based on the Ph$_4$AsPh$_4$B convention[27]) a value of −22.0 kJ mol^{-1} was calculated for the $\Delta_t H^0$ (F$^-$) (MeCN→PC). Using complexation and transfer data for the receptor and the free anion from MeCN to PC, the $\Delta_t H^0$ value for the fluoride complex was obtained.
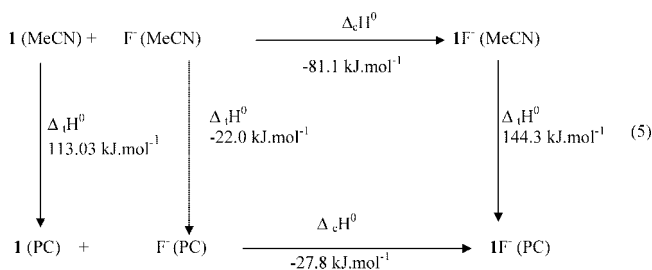
As far as this system is concerned, both, the free and complex fluoride anions contribute favorably to the higher enthalpic stability of complexation in MeCN relative to PC, overcoming the unfavorable input of the receptor (enthalpically more stable in MeCN than in PC). The same pattern is found in the MeCN→DMSO solvent system as shown below (eq 6)
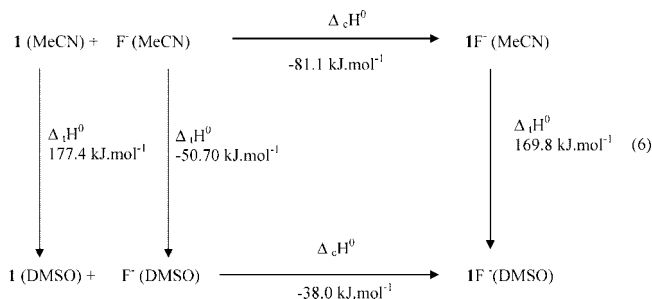
We therefore conclude once again that it is possible to predict the more favorable complexation medium from assessing the solvation properties of reactants and the product in the relevant media. Thus the most favorable solvent for complexation is that
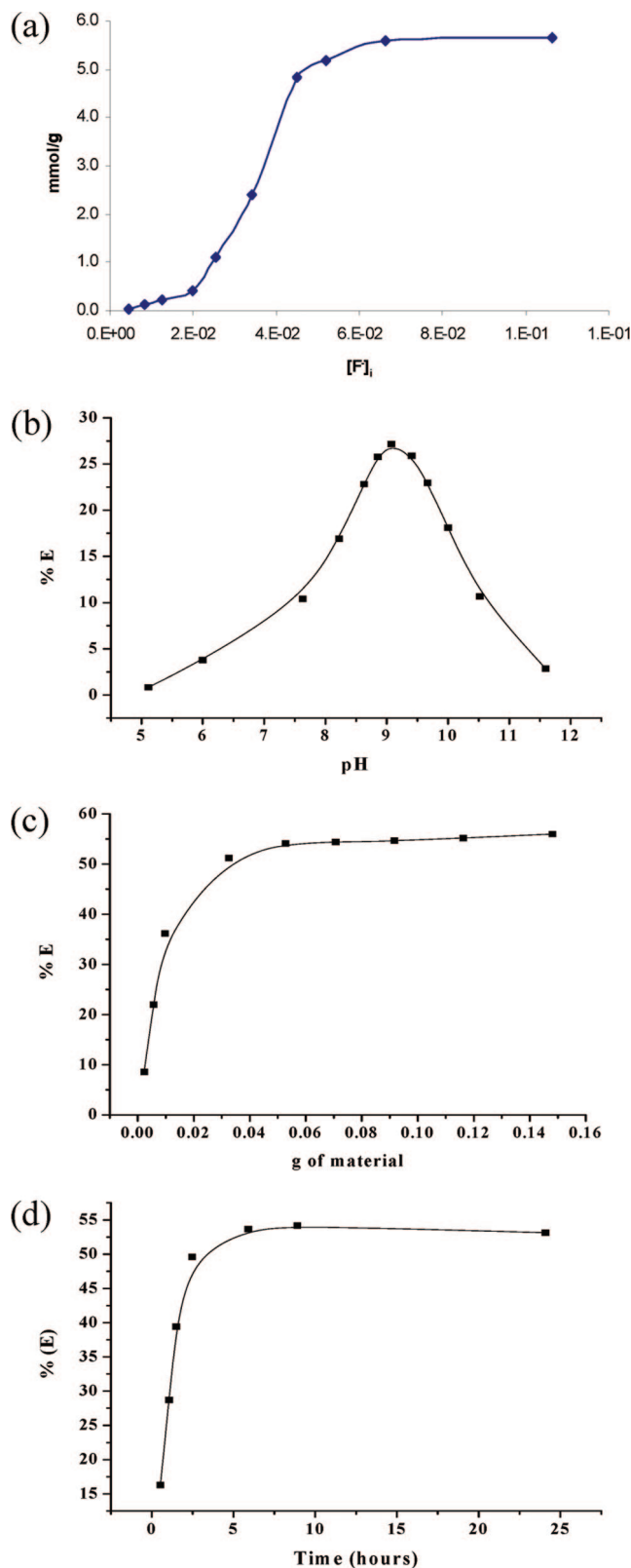
(a)

(b)

(c)

(d)

Figure 4. (a) Uptake isotherm for F⁻ from aqueous solution by the calix[4]pyrrole based material at 298.15 K. (b) Effect of pH on the uptake of F⁻ from aqueous solution by the calix[4]pyrrole based material at 298.15 K. (c) Effect of the mass of calix[4]pyrrole based material on the uptake of the F⁻ anion from aqueous solution at 298.15 K. (d) Kinetics of extraction of the fluoride salt from aqueous solution by the calix[4]pyrrole based material at 298.15 K.

which offers the poorest solvating medium for the reactants and the strongest solvating medium for the complex.
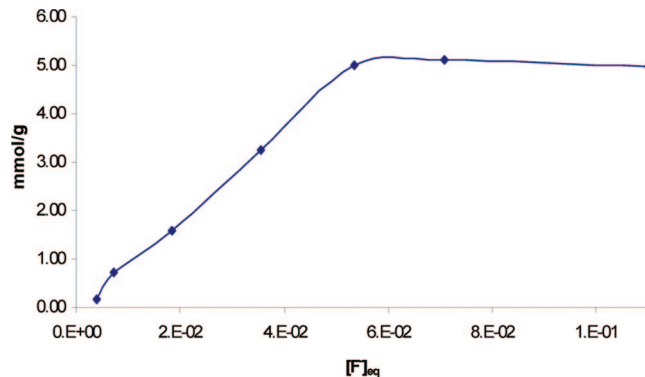

Figure 5. Capacity of calix[4]pyrrole based material to remove fluoride ion from aqueous solution after the regeneration process at 298.15 K.

The above results encouraged us to proceed with the production of a new material containing **1** as anchor group as described in the experimental section. The following section discusses the extracting properties of this material for the removal of fluoride and mercury(II) ions from aqueous solution.

3.5. Extraction Experiments Using a Calix[4]Pyrrole-Based Material. *Capacity of the Material to Uptake Fluoride (As Sodium Fluoride) from Aqueous Solution.* The capacity (maximum quantity of salt extracted from the solution per unit quantity of material) was determined by equilibrating a fixed mass of the calix[4]pyrrole material with the aqueous solutions containing different concentrations of sodium fluoride. Thus Figure 4a shows that the amount of NaF (mmoles) extracted by the material per gram of dry resin is 5.64 mmol/g of material or 214 mg/g of material. It is observed that the degree of extraction of the material is dependent on the concentration of the salt present and on the pH of the solution (see Figure 4b), and it is indeed the latter parameter which determines the sigmoidal shape observed in Figure 4a. Attempts were performed for the removal of fluoride from aqueous solutions using different materials. Some of them showed low capacities compared to our material (214.26 mg g⁻¹) like montmorillonite[28] (0.263 mg g⁻¹), aluminum-impregnated carbon[29] (1.07 mg g⁻¹), algae biosorbent[30] (1.272 mg g⁻¹), α-alumina[31] (2.73 mg g⁻¹), aligned carbon nanotubes[32] (4.5 mg g⁻¹), alum sludge[33] (5.394 mg g⁻¹), while others had moderate capacities like lanthanum-impregnated cross-linked gelatin[34] (21.28 mg g⁻¹), Al³⁺ exchange zeolite[35] (37.54 mg g⁻¹), and La³⁺ exchange zeolite[35] (59.11 mg g⁻¹).

Sodium fluoride is a salt formed from a weak acid (HF, $pK_a =$ 3.45 at 298 K) and a strong base (NaOH) and therefore the pH of the solution is in the alkaline range and will change with changes in salt concentration. Thus an increase in the salt concentration results in a pH increase. This is corroborated by the results shown in Figure 4b, where percentages of extraction (% E) are plotted against the initial pH of the aqueous solution. The results show that the maximum extraction is observed at pH 8−9 when the salt concentration is about 0.1 mol dm⁻³. Other factors considered were the effect of the mass of material used on the extraction process. Thus a plot of % E against the mass of material at a fixed initial concentration of the salt and at 298 K is illustrated in Figure 4c.

Given that the kinetics of the extraction process is a prerequisite for the most effective use of extracting agents, this was investigated by sampling and analyzing the presence of fluoride in the aqueous solution at different intervals of time until equilibrium was reached. Thus Figure 4d shows a plot of
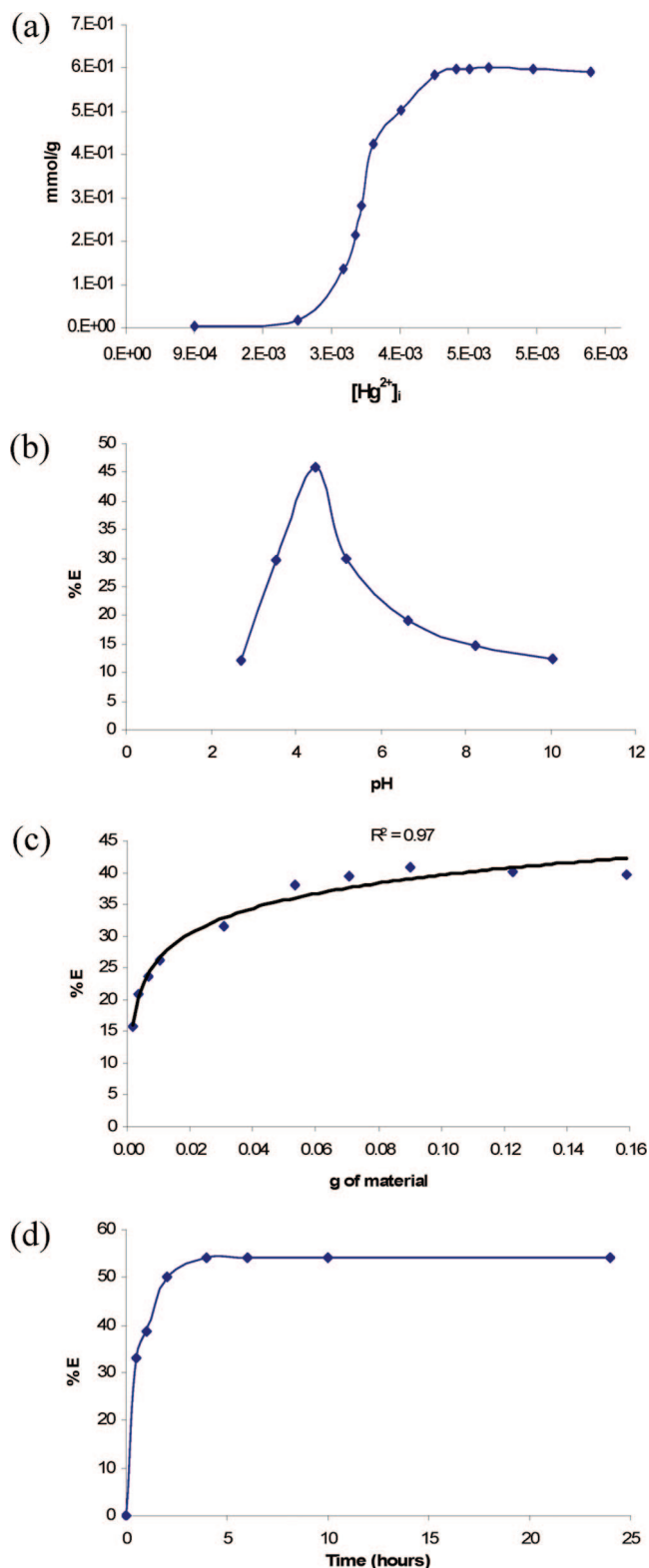
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Figure 6. (a) Uptake isotherm for Hg^{2+} from aqueous solution by the calix[4]pyrrole based material at 298.15 K. (b) Effect of pH on the uptake of Hg^{2+} from aqueous solution by the calix[4]pyrrole based material at 298.15 K. (c) Effect of mass on the uptake of Hg^{2+} from aqueous solution by the calix[4]pyrrole based material at 298.15 K. (d) Kinetics of extraction of the mercury salt from aqueous solution by the calix[4]pyrrole based material at 298.15 K.

% E against time where the amount of the material, the pH and the temperature were kept constant. It is shown that the kinetics of the process is relatively fast. Recycling of the material was carried out by washing it three times with citric acid (0.1 mol

dm^{-3}). After several recycling, the capacity of the material to remove fluoride from aqueous solutions was not altered significantly (Figure 5).

Capacity of the Calix[4]Pyrrole-Based Material to Uptake Mercury from Aqueous Solution. Batch experiments with solutions containing different concentrations of the mercury salt solution were performed at 298.15 K with the aim of determining the capacity of the polymeric material to take up Hg (II) from aqueous solution at 298.15 K. Figure 6a shows the amount of mercury extracted per gram of the oligomeric material.

At equilibrium, the amount of metal cation salt removed per unit mass of the material remains constant (5.91×10^{-1} mmol/g of the material or 118.55 mg/g) despite the increase in the initial concentration of the salt. Another calix[4]pyrrole based material[25,36] showed an uptake capacity of 58.17 mg/g, while capacities of 92.27 and 70.21 mg/g were found for two modified silica compounds.[36]

The effect of the solution pH on the extraction process is shown in Figure 6b where the percentage of extraction is plotted against the initial pH of the aqueous solution. The results show that the maximum extraction is observed at pH 3−5 when the concentration of the mercury solution is about 0.005 mol dm^{-3}.

The effect of the mass of material used on the extraction of mercury from aqueous solution is shown in Figure 6c. The results show that, as expected, the removal efficiency of the material generally increases with increasing the amount of the oligomer. The maximum percentage of mercury removed by this material from aqueous solution under these experimental conditions was about 43−50%.

The kinetics of the extraction process is shown in Figure 6d which is a plot of % E against time showing that the kinetic of the extraction process is fast.

4. Final Conclusions

From the above discussion, it is concluded that.

(i) A calix[4]pyrrole derivative able to interact with two polluting ions, fluoride and mercury has been synthesized and structurally and thermodynamically characterized.

(ii) The base catalyzed phenol-formaldehyde procedure was used to produce a calix[4]pyrrole based new material able to remove two important polluting ions (fluoride and mercury) from water. The conditions for the optimal extraction of these ions from water have been established. The material has several advantage in that (i) high concentration of fluoride and mercury salts can be used in the extraction process, (ii) there is a high capacity for uptaking these ions from aqueous solutions, (iii) the lack of interaction with ions other than fluoride and mercury means that this material is almost free from interference from other ions in solution, and (iv) the recycling of the material requires a straightforward procedure. Indeed this is successfully achieved through the use of an aqueous solution containing a low cost organic acid.

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