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THE FLUORIDE DILEMMA
Thermodynamics of anion recognition by calixpyrroles

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The implications of environmental contamination by fluoride on human health call upon the need for the development of monitoring systems for the 'in situ' detection of fluoride in contaminated sources and new technologies approaches for their removal. This paper reports recent work on the design of calixpyrrole receptors selective for the fluoride anion. The various steps undertaken for the thermodynamic characterization of these receptors and their anionic complexes are discussed. Thus based on thermodynamic data, the medium and ligand effects on selectivity are quantitatively assessed using representative calixpyrrole derivatives.

Keywords: *calixpyrrole receptors, detection of fluorides, environmental contamination*

Introduction

Supramolecular chemistry [1, 2] is concerned with the interaction of two or more chemical species held together by intermolecular forces (ion-dipole, dipole-dipole, hydrogen bonding, van de Waal forces, etc.) [2] to give the supermolecule. The main actors in the formation of the complex are the receptor (macrocyclic host) and the substrate (ionic or neutral species) or guest. Recognition (selectivity shown by the macrocycle for one species relative to another), translocation (nature of the guest is altered upon complexation with host) and transport (allowing guest to pass through media that it would not normally be able to do by itself) are the key features in supramolecular chemistry [1].

Although the roots of supramolecular chemistry dates back to the end of the XIX. centrury [2], the earliest recognized examples of synthetic supramolecular structures were the complexes formed from crown ethers and metal ions [3]. Since then numerous macrocycles have been synthesized [2, 4] and these are able to complex with a variety of ionic and neutral (in some cases) species. Among these are the cryptands [1], which differ from the crown ethers (mostly characterized by the presence of a hole) in that these are tri-dimensional molecules with a hydrophilic cavity. Calix[*n*]arenes [*n*=5, 6] are compounds with a cup-like structure that through functionalisation of the lower rim give rise to a hydrophobic and a hydrophilic cavity. The presence of two cavities allows complexation with neutral species (through the hydrophobic cavity) and metal cations in the hydrophilic cavity.

Condensation of resorcinol with aldehyde under acid catalysed conditions leads to the formation of resorcarenes [7]. Their most stable conformation is also bowl-shaped (tetramer). The above macrocycles are better known for their cation complexing properties. Anion complexing agents remain less well developed due to a number of factors clearly stated in an excellent paper by Dietrich [8].

Calixpyrroles, a more recent addition to the assortment of macrocycles are able to recognize anions selectively [9, 10]. Thus their basic ring structure resembles that of porphyrins. Due to their resemblance with calixarenes, Sessler's group [10] assigned the term 'calixpyrrole' for the ability of these macrocycles to enter hydrogen bond formation through the pyrrole NH groups. The structures of these macrocycles are shown in Chart 1.

We have extensively reported the thermodynamics of complexation of ions with crown ethers [11–13], cryptands [14–16] and more recently calixarenes [17–21], resorcarenes [22, 23] and calixpyrroles [24].

The extraction properties of macrocyclic ligands, mainly calixarenes, have been previously discussed by us [26, 27]. Particularly interesting is the potential that these ligands may offer (by their attachment to naturally occurring materials, polymerization, etc.) for the development of technological approaches for the removal of pollutants from water. On the other hand, these can be used for the production of monitoring systems for the 'in situ' detection of polluting ions in contaminated sources.

Among polluting anions, fluoride has been a matter of concern for a long time. In agriculture a

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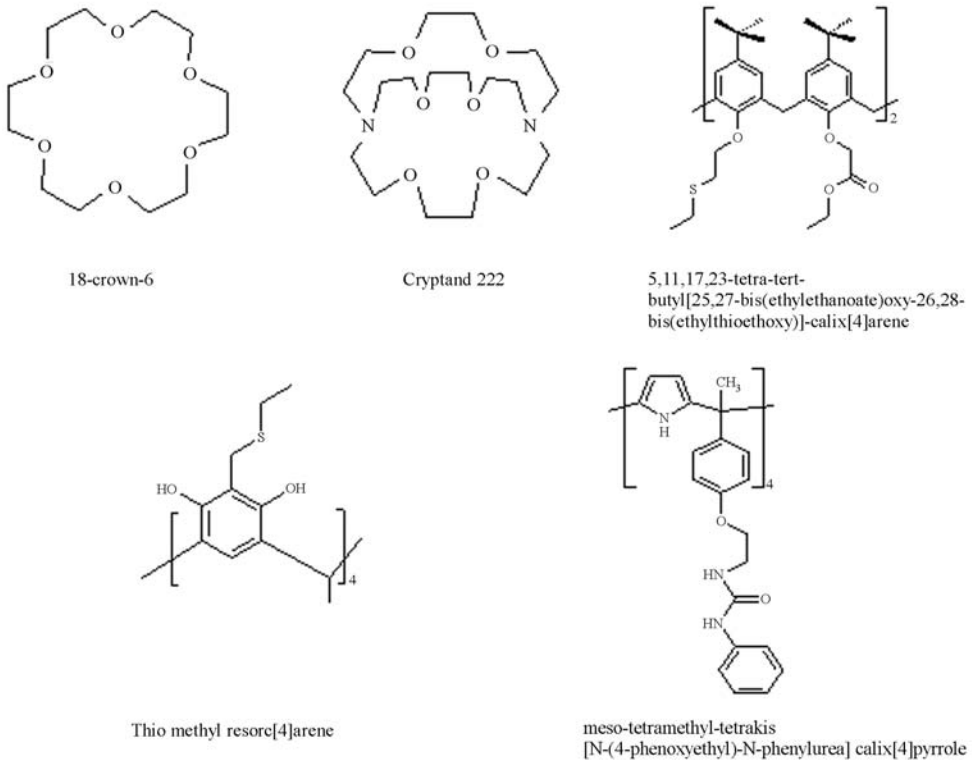


Chart 1 macrocyclic ligands

great deal of pesticides are characterised by the presence of significant quantities of fluoride leading to pollution in areas close to the processing plants [28]. Fluorides are also by-products of the phosphate fertilizer industry [29]. Fluoride toxicity leads to dental, skeletal and systematic fluorosis. For a detailed account on the implications of fluoride contamination in human health, readers are referred to the literature [30–32]. Undoubtedly there is a need for designing selective fluoride receptors. Some of the research carried out at the Thermochemistry Laboratory on calix[4]pyrrole and its derivatives and their interaction with the fluoride anion are now discussed.

Research strategy

Scheme 1 shows the steps undertaken in our laboratory to derive the thermodynamic parameters of complexation of macrocycles and different guests in different media. Thus following the synthesis and characterization of the macrocycles (microanalysis, NMR, mass spectrometry and whenever possible X-ray diffraction studies), ^{1}H and ^{13}C NMR interactions are carried out in order to gain information on

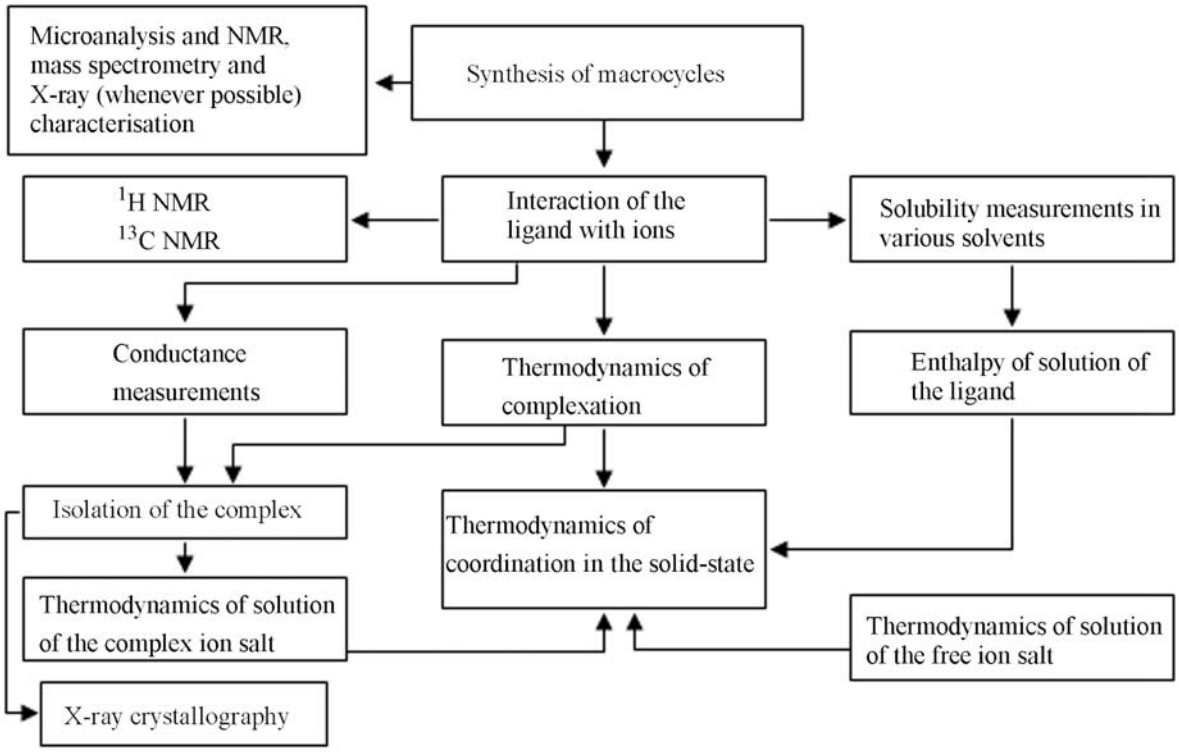
- The structural changes that the receptor undergoes upon complexation and
- The active sites of interaction of the receptor with the guest species in solution.

However the derivation of thermodynamic data requires a great deal of ancillary information in order to formulate a process which is representative of events taking place in solution. Thus conductometry is used for two purposes.

- To determine the range of concentrations at which electrolytes (free and complex) are predominantly in their ionic forms in solution. Thus conductance measurements at different concentrations are carried out. Molar conductances, Λ_m, are calculated and plotted *vs.* $c^{1/2}$, where 'c' is the concentration of the solution on the molar scale.
- Conductometric titrations of metal-ion salts with the receptor in the appropriate medium. A plot of Λ_m *vs.* ligand/metal cation concentration ratio allows to establish the composition of the complex. The shape of the titration curve provides information on the strength of complexation and therefore on the possibility of isolating the metal-ion complex and proceed with solution and X-ray diffraction studies.

For receptors that are likely to undergo dimerisation (or polymerisation) particularly in aprotic media, partition experiments are carried out in order to establish the speciation in solution.

Once the species in solution and the complex composition are identified, the process is characterized thermodynamically using various methods to de-



Scheme 1 Studies leading to the thermodynamics of complexation of macrocycles and ionic species in non-aqueous media

rive the stability constant (hence standard Gibbs energy of complexation, $\Delta_c G^0$). The selection of the method depends on the magnitude of the stability constant as described elsewhere [17]. Whenever possible stability constants reported by our group are the outcome of at least two independent analytical approaches. Enthalpies of complexation are obtained from titration calorimetry (macro and micro).

In addition to the thermodynamics of complexation, a detailed investigation of the solution thermodynamics of reactants and product is undertaken for two purposes.

- To check the accuracy of the solution and the complexing thermodynamic data, through the calculation of corresponding data for the coordination process (reactants and product are in their pure physical state). As explained earlier [33], these should be the same (within the experimental error) independently of the solvent from which these data are derived. In addition, the counter-ion effect (expected to be absent in the complexation process in solution in accord with the equation representative of the process) can be substantial in the coordination process.
- To assess the medium effect on the binding of macrocyles and ionic species through the calculation of the thermodynamics of transfer of reactants and product. Transfer data reflect the differences in solvation of the participating species in one medium relative to another. Therefore the effect of solvation of reactants and product on the complexation process can be quantitatively assessed.

Calix[4]pyrrole fluoride interactions

^{1}H NMR investigations

Starting with calix[4]pyrrole 1 (Chart 2) a detailed thermodynamic investigation was undertaken involving this ligand and halide anions in dipolar aprotic media. These studies confirmed previous statements from Sessler's group regarding the selective behaviour of this ligand for anions [23]. Then, 2, a derivative of 1 with a lower rim resembling that of parent calixarenes was synthesised and characterised [34]. This ligand was polymerised and used as an extracting agent for anions. Thus a recyclable polymer is now available which can be regarded as a new decontaminating agent for the removal of polluting anions from water. More recently we reported [35] a new double cavity calix[4]pyrrole derivative, 3. This receptor showed an enhanced capacity for the fluoride anion in solution. The effect of the introduced cavity and its capacity to interact with anions have been demonstrated elsewhere.

Particularly interesting is the outcome of investigations carried out by two calix[4]pyrrole isomers, 4-αααββ and 4-αβαβ [36] which were clearly identi-

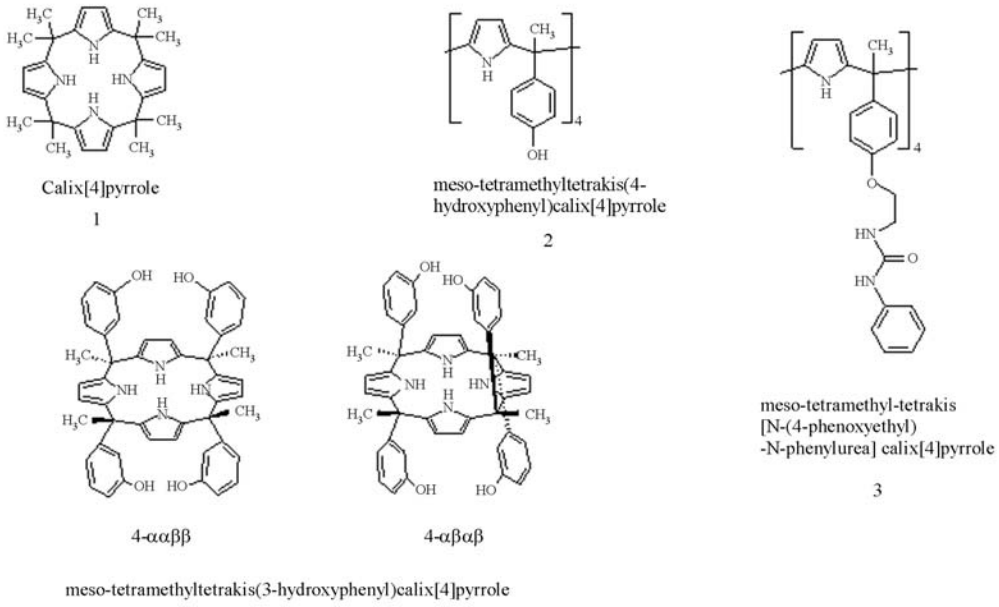


Chart 2 Calix[4]pyrroles

fied by ^{1}H NMR studies. Indeed these studies carried out in various deuterated solvents demonstrated the structural differences between the two isomers. For the 4-αααββ conformational isomer, the pyrrol rings of this ligand are located in two different environments, one situated between the phenol groups in the *cis* conformation while the other pyrrole is sitting between the ones in the *trans* conformation. This is not the case for the 4-αβαβ isomer for which only a singlet is observed for the NH proton at 8.79 and 8.07 ppm for the OH proton, a doublet for the H_{pyr} at 6.02 ppm and a singlet at 1.85 ppm for the methyl group located in the bridge between pyrrole rings. The phenolic group shows chemical shifts at 2.05 ppm (triplet), 6.57 ppm (singlet). ^{1}H NMR measurements on the interaction of these ligands with anions in CD_3CN show that the most significant changes are observed in the pyrrolic and OH protons upon complexation of 4-αβαβ with anions. In fact a lineal relationship is found when the Δδ values (ppm) of the pyrrolic protons are plotted *vs.* the electronegativities of the halide anions as shown in Fig. 1. This pattern is quite typical of the behaviour of calix[4]pyrroles and anions in CD_3CN. The sequence found is that observed for the single-ion transfer Gibbs energies ($\Delta_t G^0$) of halide anions from a dipolar aprotic solvent (acetonitrile) to a protic medium [37] (data based on the Ph_4AsPh_4B convention). In this particular case, the protic medium is represented by the receptor capable of hydrogen bond formation through the pyrrolic protons.

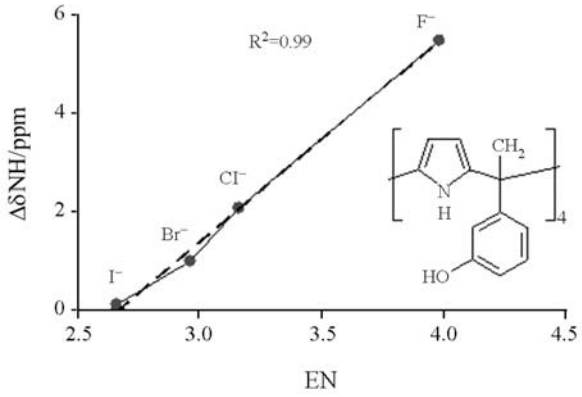


Fig. 1 Relationship between Δδ (ppm) of the pyrrolic protons of αβαβ-calix[4]pyrrole derivative and anion electronegativities (EN) in CD_3CN at 298 K

Conductometric investigations

Representative examples of conductometric curves for the titration of fluoride and dihydrogen phosphate anions (tetra-*n*-butylammonium counter-ion) with 4-αααββ in acetonitrile at 298.15 K are shown in Fig. 2, where Λ_m values are plotted *vs.* the ligand/anion concentration ratio. As far as $H_2PO_4^-$ is concerned, the data show that two anions are hosted by the receptor upon complexation. Complexes of moderate stability are found as assessed from the curvature of the titration curve in N,N-dimethylformamide. The breaks observed at 0.5 and 1 receptor: anion ratio, indicate the formation of a 1:2 and a 1:1 complex, respectively. These results are striking and demonstrate clearly that the medium effect is such that complexes of different composition are formed with the fluoride ion in moving from one to another solvent. On the other hand, it should be observed that for the $H_2PO_4^-$ anions, two

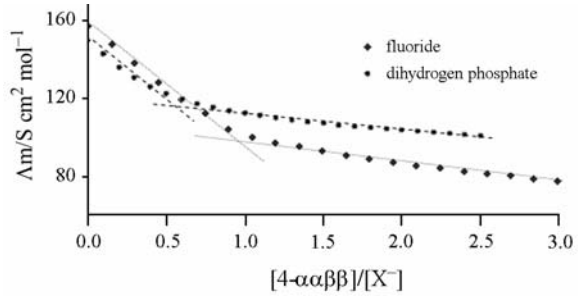


Fig. 2 Conductometric curves for the titration of anions (tetra-*n*-butylammonium counter-ion) with 4-αααββ in acetonitrile at 298.15 K

ions are taken up per unit of ligand in acetonitrile while in N,N-dimethylformamide, this receptor discriminates against this anion.

Unlike 4-αααββ, the 4-αβαβ takes up two units of fluoride per unit of calixpyrrole in acetonitrile and the same composition is found for the $H_2PO_4^-$ anion in this solvent.

Having established the composition of the complex and considering previous information regarding the range of concentration at which the salts are in their ionic forms in the relevant media, we proceeded with the thermodynamic characterisation of these systems.

Thermodynamics of complexation

Table 1 lists the stability constants, logK_s, standard Gibbs energies $\Delta_c G^0$, enthalpies $\Delta_c H^0$ and entropies, $\Delta_c S^0$, of complexation of 4-αααββ and 4-αβαβ isomers with the fluoride anion in acetonitrile (MeCN) at 298.15 K. For comparison purposes, corresponding data for the parent receptor, 1, are also included [24].

It is quite clear from these data that as far as these ligands are concerned, 1, is more selective for the fluoride anion than 4-αααββ and 4-αβαβ as reflected in the stability constants reported in Table 1. However the 4-αααββ ligand has an enhanced capacity to uptake fluoride in acetonitrile than other receptors. The question to be asked is why this is so for these two isomers?

The difference between these two isomers is structural and therefore the variations observed in their capacity to uptake fluoride can be related to the conformation of the ligands and the position of the binding sites within each ligand. Based on the NMR data, it is suggested that the absence of a signal for the OH proton of the 4-αααββ upon complexation implies that the OH groups of this ligand in CD_3CN are driven closely to each other as to enter hydrogen bond formation. This would lead to a more pronounced deshielding effect of this proton resulting in its drift out of the range of the spectra. Being involved in hydrogen bond formation, the possibility of the OH protons to complex a second anion is non existent. This is also reflected in the greater loss of entropy and gain in enthalpy observed for this system relative to corresponding data involving the 4-αβαβ isomer and this anion in acetonitrile. This is not the case for the latter receptor as no evidence of hydrogen bond formation was shown in the ^{1}H NMR spectrum. Therefore these protons are free to interact with a second anion in this solvent.

Complexation data in N,N-dimethylformamide (DMF) reported in Table 1 are those involving the interaction of 4-αααββ derivative and the fluoride anion. Unlike in MeCN, in DMF the capacity of this ligand to take up fluoride is enhanced to an extent that two anions are taken up per unit of ligand. Unlike acetonitrile (protophobic dipolar aprotic solvent), N,N-dimethylformamide is a protophilic dipolar aprotic solvent and therefore able to interact with the phenolic OH groups of the ligand. Therefore the formation of a hydrogen bond between these groups is unlikely to occur. In fact the lower enthalpic stability and the gain in entropy observed for the complexation of 4-αααββ and fluoride in N,N-dimethylformamide provide a clear indication that strong desolvation of the ligand and the monofluoride complex occur upon the formation of the 1:1 and the 1:2 complexes respectively in this solvent. Indeed while the stabilities of the 1:1 complex in these solvents are quite similar, remarkable variations are found in their enthalpic and entropic contributions.

Table 1 Thermodynamic parameters of complexation of αααββ, αβαβ calixpyrroles with fluoride in acetonitrile and N,N-dimethylformamide at 298.15 K [34]

Ligand	L:F$^-$	logK_s	$\Delta_c G^0$/kJ mol^{-1}	$\Delta_c H^0$/kJ mol^{-1}	$\Delta_c S^0$/J mol^{-1} K^{-1}
			Acetonitrile		
1	1:1	6.21	–35.4	–43.5	–27
4-αααββ	1:1	3.08	–17.6	–97.1	–267
4-αβαβ	1:1	5.00	–28.5	–31.4	–10
	1:2	4.72	–27.0	–61.5	–116
			N,N-dimethylformamide		
αααββ	1:1	3.4	–19.2	–13.6	19
	1:2	3.2	–18.2	–7.4	35

In an attempt to interpret the medium effect in enthalpic terms, the transfer enthalpies for the reactants and the product are considered as shown in the following thermodynamic cycle based on Eq. (1) [38] where $P^0=G^0$, H^0, S^0.

$$\Delta_c P^0(s_1) - \Delta_c P^0(s_2) = \Delta_t P^0(\mathrm{L})(s_1 \rightarrow s_2) + \Delta_t P^0(\mathrm{X}^-)(s_1 \rightarrow s_2) - \Delta_t P^0(\mathrm{LX}^-)(s_1 \rightarrow s_2) \quad (1)$$

where L, X^- and LX^- are the notations used to indicate ligand, free and complex anion respectively. In Eq. (1), s_1, is the reference solvent and s_2, any other solvent. In Eq. (2), s_1=MeCN and s_2=DMF

$$\begin{array}{ccc} \alpha\alpha\beta\beta(\mathrm{MeCN}) + \mathrm{F}^-(\mathrm{MeCN}) & \xrightarrow[-97\ \mathrm{kJ\ mol^{-1}}]{\Delta_c H^0} & \alpha\alpha\beta\beta\mathrm{F}^-(\mathrm{MeCN}) \\ \downarrow \Delta_t H^0\ -21.6\ \mathrm{kJ\ mol^{-1}} & \downarrow \Delta_t H^0\ -41.7\ \mathrm{kJ\ mol^{-1}} & \downarrow \Delta_t H^0\ 20.2\ \mathrm{kJ\ mol^{-1}} \\ \alpha\alpha\beta\beta(\mathrm{DMF}) + \mathrm{F}^-(\mathrm{DMF}) & \xrightarrow[-13.6\ \mathrm{kJ\ mol^{-1}}]{\Delta_c H^0} & \alpha\alpha\beta\beta\mathrm{F}^-(\mathrm{DMF}) \end{array} \quad (2)$$

The general concept behind the complexation process in different media is that the best solvating medium for the reactants is the poorest one for complexation. The implication of this statement is that the solvent plays a key role in the binding process. Data in Table 2 shows that the lower enthalpic stability in DMF relative to MeCN is due to the higher solvent-reactants and the lower solvent-product interactions in this solvent relative to MeCN.

Calixpyrrole-dihydrogen phosphate interactions

Table 2 shows the thermodynamic parameters of complexation of 4-αααββ and 4-αβαβ calixpyrroles and the dihydrogen phosphate anion in acetonitrile at 298.15 K. Also included in this table are corresponding data for the parent calix[4]pyrrole. Judging from the stability constant values given in this table, the 4-αβαβ isomer shows a greater affinity for $H_2PO_4^-$ than the 4-αααββ. In fact the stability of the former for the formation of the 1:1 complex does not differ significantly from that of the parent calix[4]pyrrole [24], 1. Given that the enthalpy values associated with the 1:1 complexes of these isomers are quite close, the higher stability of this anion with 4-αβαβ relative to 4-αααββ is mainly attributed to the favourable entropy of the former relative to the latter.

Computer modelling calculations shows that the arrangement of minimum energy for these systems is that which each $H_2PO_4^-$ anion (through its negatively charged oxygen atom) is hydrogen bonded to two pyrrole NH functionalities of the calixpyrrole receptor. Therefore the striking feature of these results is reflected in the overall enthalpy data for these two ligands and $H_2PO_4^-$ in MeCN which are quite close to that previously reported by us for 1 and this anion in this solvent [24]. For the 1:1 complex, molecular modelling calculations suggest that the four NH moieties of the pyrrole units of the receptor participate in hydrogen bond formation with the negatively charged oxygen of the $H_2PO_4^-$ anion. Given that the $\Delta_c H^0$ values for these isomers and this anion in each individual process (1:1 and 1:2; receptor:anion ratio) are approximately half of the $\Delta_c H^0$ value for 1 and $H_2PO_4^-$, it follows that there is an additive enthalpic contribution of NH–O^- bonds between these isomers and this anion in MeCN and therefore enthalpy data are suitable reporters of the number of hydrogen bonds that the receptor can form upon complexation with $H_2PO_4^-$ in MeCN. Further work is in progress to assess the possibility of growing suitable crystals for X-ray diffraction studies. Although these studies are referred to the solid state, some useful insight into calixpyrrole $-H_2PO_4^-$ interactions will assist further these investigations.

Calixpyrrole: fluoride vs. dihydrogen phosphate

Given that 'selectivity' is one of the main features in supramolecular chemistry, stability constants given in Tables 1 and 2 are used to calculate quantitatively, the selectivity factors of the calix[4]pyrrole for fluoride

Table 2 Thermodynamic parameters of complexation of αααββ and αβαβ calixpyrroles with dihydrogen phosphate in acetonitrile at 298.15 K

Ligand	L:$H_2PO_4^-$	logK_s	$\Delta_c G^0$/kJ mol^{-1}	$\Delta_c H^0$/kJ mol^{-1}	$\Delta_c S^0$/J mol^{-1} K^{-1}
		Acetonitrile			
1	1:1	5.0	–28.5	–48.1	–66
4-αααββ	1:1	3.6	–20.5	–24.5	–13
	1:2	2.5	–14.4	–22.6	–28
	overall	6.1	–34.9	–47.1	–41
4-αβαβ	1:1	4.8	–27.4	–20.2	25
	1:2	4.7	–15.2	–29.9	–50
	overall	9.5	–42.6	–50.1	–25
		N,N-dimethylformamide			
No complexation takes place					

relative to $H_2PO_4^-$, $S_{F^-,H_2PO_4^-}$ in acetonitrile (Eq. 3). These are shown in Table 3.

$$S_{F^-/H_2PO_4^-} = \frac{K_s(F^-)}{K_s(H_2PO_4^-)} \quad (3)$$

The data indicate that 1 is more selective for fluoride relative to $H_2PO_4^-$ by a factor of 16.2. This selectivity factor is significantly reduced by the replacement of 1 by 4-αβαβ in MeCN. On the other hand 4-ααββ is more selective for $H_2PO_4^-$ relative to fluoride by a factor of 3.3.

Quantitative evaluation of the ligand effect on the selectivity of the fluoride and dihydrogen phosphate anions are listed in Table 4. These data reflects that among these receptors, 1 is more selective for the fluoride anion by factors of 1349 and 16.2 relative to the 4-ααββ and the 4-αβαβ isomer in acetonitrile. Although the ligand effect on the $H_2PO_4^-$ anion follows the same trends as that found for fluoride, less pronounced changes are observed in the selectivity factors for this anion.

Table 3 Anion effect: selectivity factors[a] of Calix[4]pyrroles for the fluoride relative to the dihydrogen phosphate anion in acetonitrile at 298.15 K

	$S_{F^-,H_2PO_4^-}$ [a]	$S_{(MeCN)}$ [a]
1	16.2	–
4-ααββ	0.30	–
4-αβαβ	1.60	1.7 (enhanced capacity)

[a]From logK_s values in Tables 1 and 2

Table 4 Ligand effect: selectivity factors[a] of Calix[4]pyrrole for the fluoride anions and dihydrogen phosphate relative to the isomers in acetonitrile at 298.15 K

	$S_{L_1}, S_{L_2}(F^-)$[a]	$S_{L_1}, S_{L_2}(H_2PO_4^-)$[a]
1	1	1
4-ααββ	1349	~25.0
4-αβαβ	16.2	1.6

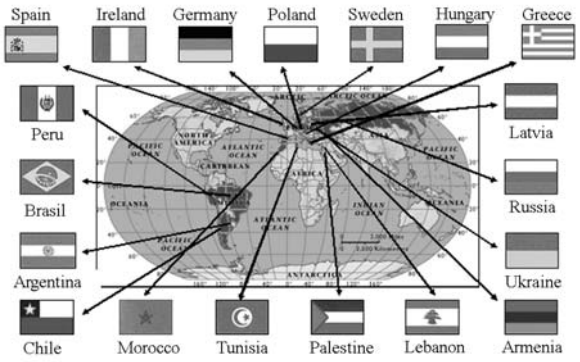
[a]From logK_s values in Tables 1 and 2

Conclusions

From the above discussion the following conclusions are drawn *i*) calixpyrroles are selective receptors for anions. For a full account on a variety of these ligands and their affinity for fluorides, readers are referred to the literature [32], *ii*) the results shown in this paper clearly demonstrate the effect of the medium on the interaction of calixpyrroles with anions. The most representative example is that for these isomers in their interaction with $H_2PO_4^-$. While in acetonitrile, two anions are taken up per unit of ligand, these receptors discriminates against this anion in N,N-dimethylformamide. Changes in the composition of the complex are also observed. Thus the capacity of 4-ααββ for the fluoride anion is enhanced in N,N-dimethylformamide leading to the formation of a 1:2 (ligand:anion) complex relative to acetonitrile. In this medium the hosting capacity of the receptor is reduced to an extent that a 1:1 complex is formed [36], *iii*) additional thermodynamic studies are required to further explore the possibility of using enthalpy data to quantify the extent of hydrogen bond formation between these isomers and various guests, *iv*) polymerisation of receptor 3 has been accomplished and its extraction properties are now being investigated.

Appendix

This paper is dedicated to the memory of my great colleague and friend, Professor Lisardo Nuñez Regueira, to whom I had the privilege of meeting many years ago. We have collaborated in research, teaching, organization of international conferences in South America. It is for this reason and in honour to his outstanding human qualities that in this part I will briefly summarize some of the social aspects that I am currently involved and the progress so far made in projects linked with the Developing World.



International cooperation

International activities, social impact

The writer is strongly of the view that there is a need to include in scientific programmes social objectives. There are here two aspects to consider. The first one involves the development of innovative technology based on fundamental science, technological development and eventual commercialisation which leads to employment and decrease in poverty. The second and much faster approach is the incorporation of charity organisations in research programmes.

- The implementation of MSc programmes in Peru in Industrial Chemistry (National University of San Agustin), Environmental Chemistry (Catholic Uni-

versity of Santa Maria) and Extraction of Strategic Metals (National University of Altiplano) with a total number of 65 graduates at Master level [39].
- The training of people at PhD level (12 in Perú and 6 in Argentina).
- The implementation of research laboratories in Perú with donations from the University of Surrey, Kent and Lund as well as from funds provided by the European Commission.
- The upgrading of the Analytical Chemistry Laboratory at the National University of the South (Argentina) [40].
- Inauguration of the Chemical Laboratory in Arequipa, Perú [40].

The international cooperation developed through the years will allow to expand these activities to other regions of the world.

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