From molecules to electrolytes. Electrochemical and thermodynamic aspects of the interaction of phenol and resorcinol based calixarenes with amines

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<u>Abstract</u> An important consequence of the interaction of calix(n)arenes and amines is the generation of new electrolytes resulting from proton transfer reactions from the calix(n)arene molecule to the amine. A brief account on the contributions made in this area is presented. This is followed by recent electrochemical (conductimetric and potentiometric) and thermodynamic studies on the interaction of a phenol–based–calixarene and amines in non–aqueous media. The thermodynamics of extraction of amines by p–tert butyl calix(8)arene in the water–benzonitrile solvent system is discussed taking into account the parameters which contribute to the overall process. The results obtained from conductimetric and spectrophotometric studies on the interaction of a resorcinol–based calixarene and amines are presented.
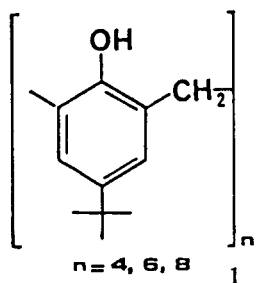
INTRODUCTION

For many years our research interests have been mainly concerned with thermodynamic aspects of macrocyclic chemistry involving cryptands (refs. 1–15) and crown ethers (refs. 15&16) as synthetic hosts and various guest substrates (mainly cations). Particular emphasis has been placed on thermochemical aspects of the binding process including the characterisation of the host, the guest and the resulting complex in solution. As a logical extension of these activities, in recent years the range of macrocyclic ligands investigated has been expanded to involve cyclodextrins (refs. 17&18), cyclams (ref. 19) and calixarenes (refs 19–21). The applications of calorimetry (macro and micro) to the study of host–guest interactions in solution been recently discussed in (ref. 22). This paper concerns calixarenes and, therefore, it seems appropriate to mention that there are two thermodynamic aspects of calixarene chemistry that are currently investigated at Surrey. The first one is related to the interactions of calixarene derivatives and metal cations in 'allosteric guest' media. Based on recent thermodynamic studies on the complexation of a calixarene ester derivative known as n–butyl p–tert butyl calix(4)arene tetraacetate and metal cations in benzonitrile, it was suggested that the terminology 'allosteric guests' (refs. 19&23) should be introduced in calixarene chemistry to refer to solvents which interact with the hydrophobic cavity producing conformational changes which alter the selectivity of the hydrophilic cavity of the ligand. This terminology is based on the analogous behaviour shown by calix(4)arene derivatives with those molecules known as 'allosteric ligands' in enzymology.

The second aspect of interest is that related to the interactions of calix(n)arenes and their derivatives with neutral species.

In this paper, a brief account is first given on the contributions so far made in the area of calixarene chemistry involving amines. This is to be followed by electrochemical (conductimetric and potentiometric) and thermodynamic studies on the interactions of parent calixarenes and amines in non–aqueous media. The thermodynamics of the extraction process involving amines in the water–benzonitrile solvent system is discussed. Finally, recent conductimetric and spectrophotometric studies on the interaction of a resorcinol based calixarene with amines in chloroform are presented.

BACKGROUND INFORMATION

The interaction of calix(n)arenes 1 and amines was first reported by Bauer and Gutsche in 1985 (ref. 24) on the basis of NMR studies using aliphatic amines in several reaction media ($CDCl_3$, CD_3CN and d_6 acetone). These studies revealed that the reaction in acetonitrile and acetone proceeds with the transfer of a proton from the calixarene to the amine followed by ion–pair formation in the form of an endo–calix complex. In chloroform, a complex of different structure to those found in acetonitrile and in acetone was suggested. Using various amines, equilibria data for both processes in acetonitrile were derived from UV measurements (refs. 25 & 26). More recently, Böhmer and Vicens (ref. 27) have discussed the interactions of triethylamine with calix(4)arenes containing one *p* nitrophenol unit using dioxane as the reaction medium. The formation of an amine–calix(4)arene (ion–pair) adduct was reported. Based on the similar stabilities observed for adducts formed between the cyclic tetramer and the corresponding linear trimer with triethylamine in dioxane, it was concluded that similar interactions take place between this amine and the cyclic tetramer and the same amine and the linear trimer. Therefore, for this calix(4)arene, formation of an endo–calix complex with the amine did not occur in dioxane. The results obtained by Gutsche and by Böhmer are very interesting and in no way contradictory since they reflect the medium effect on these reactions. The question that remains unanswered is what is the role of the solvent? It is expected that, in solvents of such low dielectric constants as chloroform and dioxane, most of the species in solution are to be found as ion–pairs. In addition, it is known that dioxane interacts with phenol and thermodynamic data for the hydrogen intermolecular bond OH....O (phenol–dioxane) have been reported (ref. 28). Therefore, similar interactions are expected to be found between this solvent and calixarenes and if so, the reaction medium is likely to compete with the amine for interactions with the ligand. As a result, it is unlikely that in this solvent a distinction could be established between the interactions of amines with the cyclic tetramer relative to the linear trimer.

Another aspect to consider is the interaction of the solvent with the hydrophobic cavity of calix(4)arenes in their cone conformation. This is particularly relevant to the formation of endo–calix complexes with amines. Indeed, in cases where the solvent resides in the cavity of the ligand, unless the energy requirements are met for the solvent to be removed from it, the formation of endo–calix complexes is unlikely to occur. Undoubtedly, solvation plays a significant role in these processes and therefore, there is now the need for the thermodynamic characterisation of the host, guest and the resulting complex in various solvents in order to derive transfer data (refs. 11,13&19) which are essentially a measure of the differences in solvation of a solute in two solvents.

A further report on the interaction of *p*–tert butyl calix(n)arene (n=4,8) with a variety of cyclic amines, including diamines in acetonitrile is that by Görmar and Seiffarth (ref. 29) using U.V. spectrophotometry. The formation of 1:2 amine–calix(n)arene complexes were found for diamines. A series of stability constants were reported by these authors, although no indication was given as to which process the data are referred to.

ELECTROCHEMICAL STUDIES

Much of our present knowledge about electrolyte solutions is the result of conductivity. For systems where the starting compounds (calixarene and amine) are neutral species (which may interact by proton transfer reactions to give electrolytes) conductance measurements provide a useful means to detect the extent of ion formation in solution. Fig. 1 shows conductimetric titration curves for *p*–tert butyl calix(8)arene (Calix 8) and various amines in benzonitrile at 298.15K. This solvent was selected because, unlike acetonitrile (solvent commonly used), a phase separation between benzonitrile and water can be achieved and therefore, direct partitioning of amines in this solvent system is feasible.
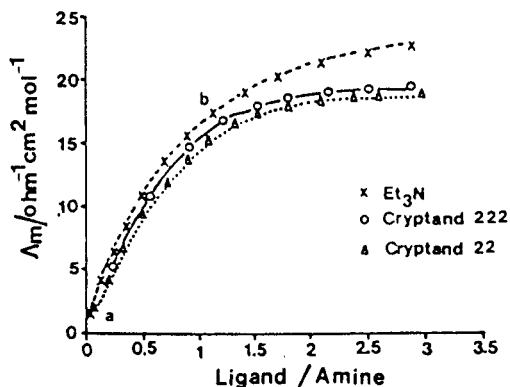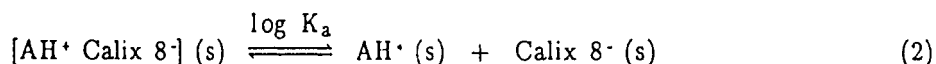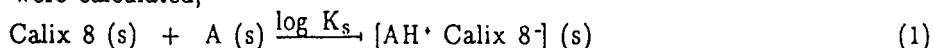
n = 4, 6, 8

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Fig. 1. Conductimetric titration of Calix 8 and amines in benzonitrile at 298.15 K

The results shown in Fig. 1 unambiguously demonstrate that
(i) as the reaction proceeds from (a) to (b), proton transfer from Calix 8 to the amine occurs, since an increase in conductivity could be only attributed to ion formation in solution.
(ii) For these adducts, 1:1 amine–Calix 8 stoichiometries are found. Among the amines considered, the cryptands have distinctive properties relative to other cyclic and non–cyclic amines because each nitrogen can take up a proton. However, conductance data reveals that in the complexation of Calix 8 with cryptands in benzonitrile, only one proton is transferred. This statement is based on the similar conductances observed for Calix 8 with cryptands relative to other amines (where only one proton can be involved). This is further corroborated by potentiometric studies discussed below.

From the initial portion of the experimental titration curves of relatively diluted solutions of Calix 8 and amines (A) in benzonitrile (s), equilibria data for the following processes at 298.15K, were calculated,

$$\text{Calix 8 (s)} + \text{A (s)} \xrightarrow{\log K_s} [\text{AH}^+ \text{Calix 8}^-] \text{ (s)} \tag{1}$$

$$[\text{AH}^+ \text{Calix 8}^-] \text{ (s)} \xrightleftharpoons{\log K_a} \text{AH}^+ \text{ (s)} + \text{Calix 8}^- \text{ (s)} \tag{2}$$

Combination of (1) and (2) leads to data for process

$$\text{Calix (8) (s)} + \text{A (s)} \xrightarrow{\log K'_s} \text{AH}^+ \text{ (s)} + \text{Calix 8}^- \text{ (s)} \tag{3}$$
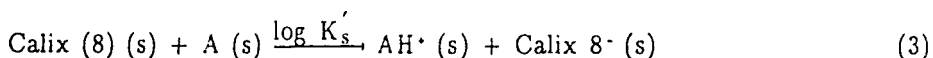
These data are reported in Table 1.
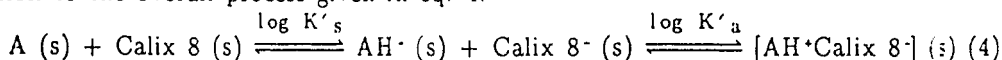
TABLE 1.   Equilibria data of *p*–tert butyl calix(8)arene and
           amines in benzonitrile at 298.15K (conductimetric method).

Amines	$\log K_s$ [a]	$\log K_a$ [b]	$\log K'_s$ [c]
Cryptand 222	3.70 ± 0.20[d]	-2.52 ± 0.09[d]	1.10[d] ± 0.22[d]
Cryptand 22	3.24 ± 0.18	-2.62 ± 0.07	0.62 ± 0.19
Triethylamine	3.98 ± 0.18	-1.56 ± 0.10	2.42 ± 0.21

[a] eq. (1); see text, [b] eq. (2); see text, [c] eq. (3); see text;
[d] ref. 21

The data obtained from conductance measurements show that, for cryptands, the major contribution to the overall process given in eq. 4.

$$\text{A (s)} + \text{Calix 8 (s)} \xrightleftharpoons{\log K'_s} \text{AH}^+ \text{ (s)} + \text{Calix 8}^- \text{ (s)} \xrightleftharpoons{\log K'_a} [\text{AH}^+ \text{Calix 8}^-] \text{ (s)} \tag{4}$$

results from ion–pair formation and for triethylamine from the proton transfer reaction. These results have been now corroborated by potentiometric titrations.

POTENTIOMETRIC STUDIES

Benzonitrile is a weaker acid and a weaker base (autoprotolysis constant, $K_s = 10^{-34.3}$ at 298.15K) than acetonitrile ($K_s \simeq 10^{-33}$; ref. 30) and therefore, its acidic and basic properties are much weaker than water. The extended pH scale of benzonitrile ($pK_s = 34.3$) makes this solvent suitable for potentiometric titrations; particularly when dealing with multidissociable species. This is reflected in the potentiometric titration curve of *p*–tert butyl calix(8)arene and the tetramethylammonium hydroxide base in benzonitrile at 298.15K shown in Fig. 2.
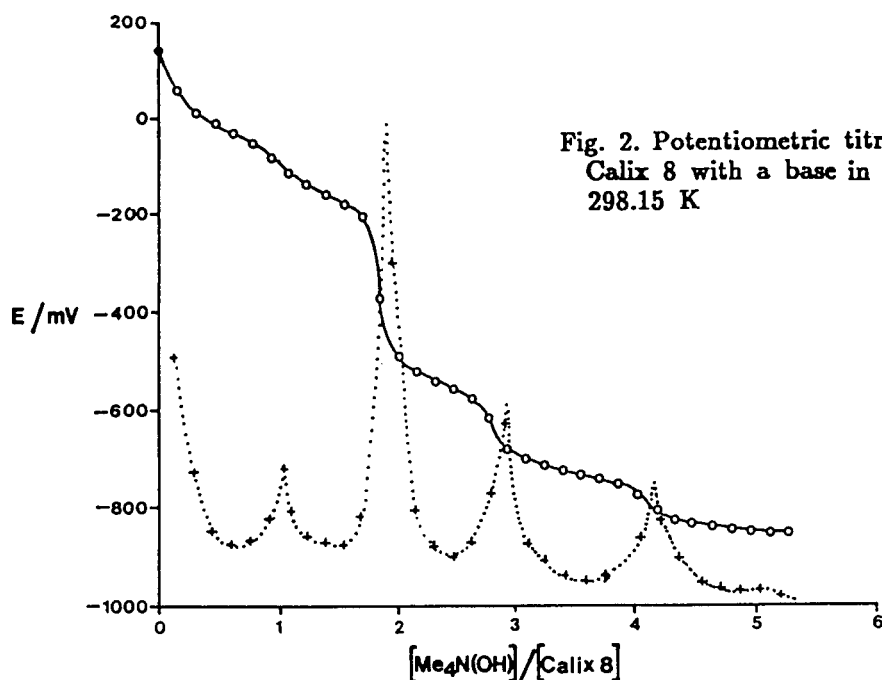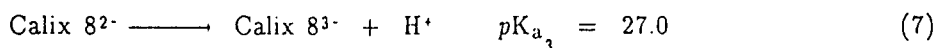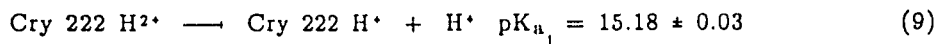
Fig. 2. Potentiometric titration curve of Calix 8 with a base in benzonitrile at 298.15 K

The titration curve shows four inflection points which correspond to the release of four protons from calix(8)arene. However, the most striking feature of Fig. 2 is the substantial potential drop observed in the second dissociation step relative to the rather slight inflection observed for the release of the first proton. This unusual behaviour appears to indicate that the formation of the monoanion of Calix 8 may induce conformational changes which facilitates the release of the second proton. We are now carrying out ^{1}H NMR studies to obtain structural information about it. Titration data were analysed using a computer program (MINIQUAD) to calculate the dissociation constants for the following processes (eqs. 5–8).

$$\text{Calix 8} \longrightarrow \text{Calix 8}^- + \text{H}^+ \qquad pK_{a_1} = 17.42 \pm 0.07 \qquad (5)$$

$$\text{Calix 8}^- \longrightarrow \text{Calix 8}^{2-} + \text{H}^+ \qquad pK_{a_2} = 20.01 \pm 0.08 \qquad (6)$$

$$\text{Calix 8}^{2-} \longrightarrow \text{Calix 8}^{3-} + \text{H}^+ \qquad pK_{a_3} = 27.0 \qquad (7)$$

$$\text{Calix 8}^{3-} \longrightarrow \text{Calix 8}^{4-} + \text{H}^+ \qquad pK_{a_4} = 30.4 \qquad (8)$$
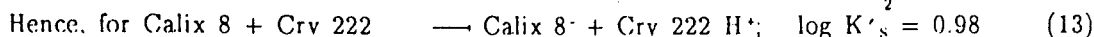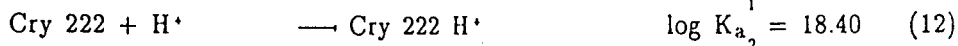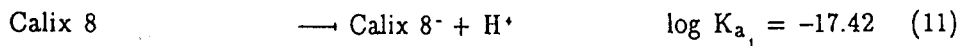
These values were obtained on the basis of several experimental titration data with very small differences between observed and calculated values for pK_{a_1} and pK_{a_2}. Values for the third (pK_{a_3}) and fourth dissociation (pK_{a_4}) are not as reliable due to the low acidities.

The results show that in benzonitrile, the first dissociation for p–tert butyl calix(8)arene occurs at a rather neutral pH on the scale for this solvent. Similar potentiometric studies involving amines were undertaken. Thus, for cryptand 222, (Cry 222) the dissociation constants (expressed as pK_a values) in benzonitrile for the following processes were determined.

$$\text{Cry 222 H}^{2+} \longrightarrow \text{Cry 222 H}^+ + \text{H}^+ \qquad pK_{a_1} = 15.18 \pm 0.03 \qquad (9)$$

$$\text{Cry 222 H}^+ \longrightarrow \text{Cry 222} + \text{H}^+ \qquad pK_{a_2} = 18.40 \pm 0.05 \qquad (10)$$

Therefore, for the process illustrated in eq. 3, log K'_s can be calculated from

$$\text{Calix 8} \longrightarrow \text{Calix 8}^- + \text{H}^+ \qquad \log K_{a_1} = -17.42 \qquad (11)$$

$$\text{Cry 222} + \text{H}^+ \longrightarrow \text{Cry 222 H}^+ \qquad \log K_{a_2} = 18.40 \qquad (12)$$

$$\text{Hence, for Calix 8 + Cry 222} \longrightarrow \text{Calix 8}^- + \text{Cry 222 H}^+; \quad \log K'_s = 0.98 \qquad (13)$$

Therefore, log K'_s = 0.98 is in good agreement with the value obtained by the conductimetric (log K'_s = 1.18; see Table 1) method.

THERMODYNAMIC STUDIES

As pointed out before (refs. 19&21) the recent review by Izatt et al. (ref. 31) reflects the lack of thermodynamic data in the area of calixarene chemistry. It may be correctly argued that thermodynamics do not provide structural information. On the other hand, provided that suitable methods are used to derive accurate data, any model proposed must fit the experimental thermodynamic data. Thus, Table 2 provides log K_s and derived Gibbs energies, $\Delta_c G^\circ$; enthalpies; $\Delta_c H^\circ$ and entropies; $\Delta_c S^\circ$ for the process represented by eq. 1 involving Calix 8 and various amines in benzonitrile at 298.15K.

TABLE 2. Thermodynamic data for the interaction of *p*–tert butyl calix(8) arene and amines in benzonitrile at 298.15 K

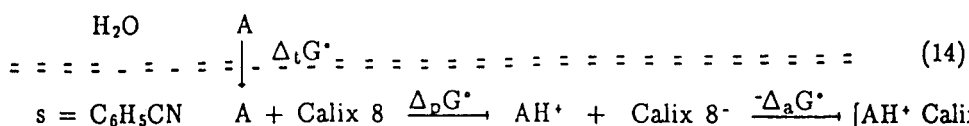| Amine	log K_s	$\Delta_c G^\circ$/ kJ mol^{-1}	$\Delta_c H^\circ$/ kJ mol^{-1}	$\Delta_c S^\circ$/ JK^{-1}mol^{-1}
Cryptand 222	3.84±0.06[a]	−21.92[a]	−57.29±0.67[a]	−118.6[a]
Cryptand 22[b]	3.15±0.04[a]	−17.98[a]	−37.34±0.81[a]	−65.0[a]
Et$_3$N	3.97±0.24[a]	−22.66[a]	−34.50±2.20[a]	−39.7[a]
Atropine	3.30±0.10	−18.84[a]	−30.55±0.70	−39.3[a]

[a] Ref. 21, [b] 1,10 diaza–18–crown 6

Excellent agreement is found between the log K_s values obtained by titration calorimetry for these amines and Calix 8 in benzonitrile, and those derived from conductimetric measurements (Table 1). In all cases, the process is enthalpically controlled and takes place with a considerable loss of entropy which may be partly due to the interaction of two components to give a single component (ion–pair). As far as the $\Delta_c H^\circ$ values are concerned, these data reflect the distinctive properties of cryptand 222 (intermolecular cavity) relative to cryptand 22 (loop); triethylamine and atropine. In fact, the enthalpy value for cryptand 222 is about twice that of atropine. This result strongly suggests that the proton is sitting in the cavity of cryptand 222 and therefore, interacting with the donor atoms of the ligand. It is expected that this effect would be reflected to a lesser extent for cryptand 22 which may be regarded as a circular array of oxygen and nitrogen atoms. This interpretation makes chemical sense since the hydrophilic environment provided by the cavity of cryptand 222 would be more suitable for the proton than the poor solvating medium offered by the solvent. ¹³C NMR studies confirmed that the proton is residing in the cavity of the ligand. A detailed interpretation of the NMR data will be reported shortly.

EXTRACTION OF AMINES BY *p*-TERT BUTYL CALIX(8)ARENE

In a solvent extraction process (direct partition) involving water and benzonitrile, the two solvents would be mutually saturated and therefore, it may be argued that thermodynamic data referred to benzonitrile in its pure state would differ from corresponding data in the saturated solvent. However, for systems constituted by two solvents whose mutual solubility is very low; such as water–dichloromethane (ref. 32); water–nitrobenzene (ref. 33) as well as water–benzonitrile (ref. 34); it has been demonstrated that thermodynamic data in the pure solvent are in excellent agreement with data in the water–saturated solvent. Therefore, the extraction of amines by *p*–tert butyl calix(8)arene in the water–benzonitrile solvent system is discussed on the basis of data referred to the pure solvent.

Since *p*–tert butyl calix(8)arene is rather insoluble in water, the extraction of amines by this ligand from water to benzonitrile may be schematically represented by

$$H_2O \qquad A$$

$$= = = = - = - = =\Big|- \underline{\Delta_t G^\bullet} = \qquad (14)$$

$$s = C_6H_5CN \qquad A + Calix\ 8 \xrightarrow{\Delta_p G^\bullet} AH^+ + Calix\ 8^- \xrightarrow{-\Delta_a G^\bullet} [AH^+ Calix\ 8^-]$$

where $\Delta_t G^\bullet$ denotes the transfer Gibbs energy for the amine from water to benzonitrile and $\Delta_p G^\bullet$ and $\Delta_a G^\bullet$ are the Gibbs energies for the processes given by eqs. (3) and (2); respectively. Therefore, the overall Gibbs energy; $\Delta_{ext} G^\bullet$; is given by

$$\Delta_{ext} G^\bullet = \Delta_t G^\bullet\ (A)\ (H_2O \to s) + \Delta_p G^\bullet\ (s) - \Delta_a G^\bullet\ (s) \qquad (15)$$

Data for the individual processes as well as Gibbs energy for the overall extraction of various amines by Calix 8 from water to benzonitrile at 298.15K is given in Table 3.

TABLE 3.   Gibbs energy data in kJ mol⁻¹ for the extraction of amines by *p*–tert butyl calix(8)arene from water to benzonitrile at 298.15K

Amine	$\Delta_t G^{\bullet\ a}$	$\Delta_p G^\bullet$	$-\Delta_a G^\bullet$	$\Delta_{ext} G^\bullet$
Cryptand 222	7.24[b]	−6.16[c]	−14.38[f]	−13.30
Cryptand 22	7.14	−3.54[d]	−14.96[f]	−11.36
Atropine	−4.23	−2.45[e]	−16.38[d]	−23.06
1–Aminoadamantane	−5.68	−3.25[e]	−15.16[d]	−24.09

[a] This work is derived from solubility measurements of the appropriate amine in H_2O and in C_6H_5CN. In water corrections were applied to account for hydrolysis of amines, [b] From ref. 34, [c] Conductimetric (Table 1) and potentiometric values (see text), [d] Conductimetric method, [e] Conductimetric and potentiometric methods. [f] From Table 1.

The Gibbs energy values for the extraction process, $\Delta_{ext} G^\bullet$ shown in Table 3 clearly reflect that these amines are more favourably transferred to the organic phase in the presence of *p*–tert butyl–calix(8)arene than in its absence. Indeed, in all cases $\Delta_{ext} G^\bullet$ are more negative than $\Delta_t G^\bullet$ values. However, the main contribution to the overall extraction is given by the ion–pair formation process ($-\Delta_a G^\bullet$) between the calixarene anion and the protonated amine. It is clear from this table that the higher extraction data ($\Delta_{ext} G^\bullet$ more negative) for atropine and 1–aminoadamantane relative to the cryptands are largely due to the favourable transfer of the former amines relative to the latter. From $\Delta_{ext} G^\bullet$ values K_{ext} values were calculated and as a result it was found that in the presence of *p*–tert butylcalix(8)arene; 1– aminoadamantate is more favourably transferred by factors of about 1.5, 77 and 170 relative to atropine; cryptand 222 and cryptand 22, respectively. These data are now being corroborated by the direct partition of amines in the presence of the octamer in the organic phase.
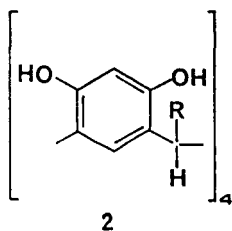
Similar calculations can be applied to the extraction of electrolytes by calixarene derivatives (provided that these derivatives are rather insoluble in water). In this case, relevant parameters to be considered are i) the transfer of the electrolyte from water to the organic phase, ii) The stability constant of the cation and the ligand in the organic phase, iii) Ion pair formation of the uncomplexed and complexed cations with the appropriate anion in the non–aqueous phase. Factors which contribute to the overall extraction of electrolytes from

water by macrocyclic ligands have been previously discussed by us (ref. 4). Research on the extraction of cations by various calixarene derivatives is in progress (ref. 23).

It has been often inferred that if a ligand selectively binds a guest (cation) in a non–aqueous solvent, this ligand would selectively extract that particular guest from water. On this basis, correlations have been made between extraction and stability constant data (ref. 35). The above discussion demonstrates that there are factors other than stability constant data which contribute to the overall extraction process. These have not yet been considered in the field of calixarene chemistry. Therefore, we conclude that this is the first study in which the different parameters which contribute to the overall process are quantitatively assessed for systems involving these ligands.

INTERACTION OF A RESORCINOL-BASED CYCLOTETRAMER AND AMINES

2

Very recently we found by classical calorimetry that the resorcinol dodecanol tetramer **2** (ref. 36) interacts with amines in chloroform and in benzonitrile. Although very low conductances are observed, the presence of ions in solution is detected when the amines are titrated with the tetramer, as reflected in the conductimetric titration curve (Fig. 3) at 298.15 K. The conductimetric titration curves suggest that these amines are likely to undergo homoconjugation in solution and therefore, the highest Λ_m values are observed when triethylamine and cryptand 222 are 50% neutralised. For the former amine, this was confirmed by UV spectrophotometry (Fig. 4) which indicated a 3:1 tetramer: amine stoichiometry. The results obtained with triethylamine are concomitant with a 3:1 resorcinol: tri–n–butylamine adduct reported in the literature (ref. 37) in which a single phenolic group of a pair of resorcinol molecules acts as both as a donor and acceptor.
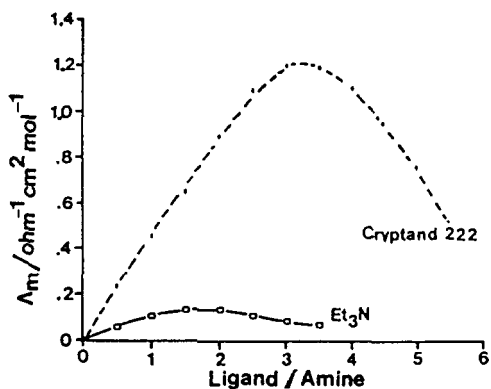

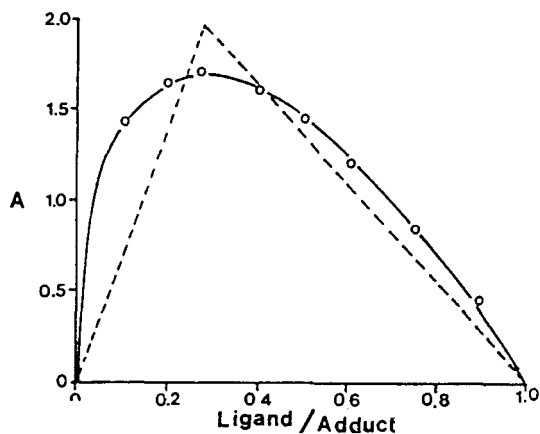Fig. 3. Conductimetric titration curve of 2 with amines in chloroform at 298.15 K

Fig. 4. Continuous variation plot for the formation of 2–triethylamine adduct in chloroform

We are now attempting to analyse the conductimetric titration curves to derive equilibria data for the different processes taking place. Other studies involve ^{13}C NMR and ^{1}H NMR as well as the thermodynamics associated to these processes.

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