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Coordination Chemistry Reviews
190–192 (1999) 283–295

COORDINATION CHEMISTRY REVIEWS

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Solution thermodynamics of pyridinocalix(4)arenes and monovalent cations

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Accepted 17 February 1999

Contents

Abstract

Recent work on pyridinocalix(4)arenes and monovalent cations (Li^+, Na^+, K^+, Rb^+ and Ag^+) using various techniques (^{1}H-NMR, conductance measurements, potentiometry, titration microcalorimetry and X-ray diffraction) is reviewed. In doing so representative data on the solution Gibbs energies of geometrical isomers of pyridinocalix(4)arenes in a variety of solvents and on the thermodynamics of complexation of pyridinocalix(4)arenes and alkali–metal and silver cations in dipolar aprotic media (acetonitrile and benzonitrile) are discussed. The importance of selecting a suitable solvent for complexation studies

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PII: S0010-8545(99)00071-5

involving ionic species is particularly emphasised.

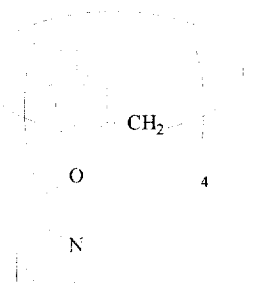
Keywords: Solution thermodynamics; Pyridinocalix(4)arenes; Monovalent cations

1. Introduction

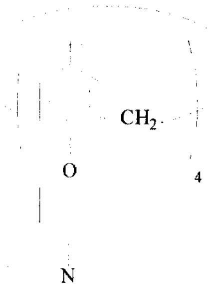
The last few decades have witnessed increasing synthetic developments in the area of Macrocyclic Chemistry [1]. For many years our research has been focused on the solution thermodynamics of macrocycles and their complexes. Thus in 1977 we reported [2] a thermochemical cycle involving cryptand 222 and alkali-metal cations (Na^+ and K^+) in water and in methanol, taking into account the transfer parameters from the reference solvent (water) to methanol of the free and complex cations and the ligand. The main aim of these investigations was to assess the medium effect on the complexation process. Several studies in different media [3–5] led to a linear correlation between complexation entropies, $\Delta_c S^\circ$ involving cryptands and univalent cations and solvation entropies, $\Delta_{solv} S^\circ$ of these cations in dipolar aprotic solvents [6]. We have recently demonstrated that the effective shielding of cryptand 222 with univalent cations in these solvents weakens considerably for bivalent cations and breaks completely with the lanthanides [7]. Other studies from our laboratory are those concerning with the thermodynamics of crown ethers and metal cations [8,9] as well as the interaction of cyclodextrins with anions [10], sulphonamides [11] and monosaccharides [12]. Among the macrocycles so far synthesised, calixarenes, products of the condensation of *p*-substituted phenol and formaldehyde in basic medium have attracted much interest [13–17]. Indeed research undergoing in this area is very intensive and these compounds have found a wide range of applications to the extent that numerous patents have been published in recent years [18]. During this period of development a lot has been learnt about the chemistry of calixarenes and much remains to be investigated. Our contributions involve solution studies of parent calixarenes and their interaction with amines [19–21], calixarene ester derivatives and their metal–ion complexes [22]. More recently a series of lower rim functionalised calix(4)arenes containing different pendant groups including tertiary aliphatic and alicyclic amines have been synthesised at Surrey [23,24] (Fig. 1). Several reports on the thermodynamics of these systems can be found in the literature [25–27]. The solution thermodynamics of parent calixarenes and their upper and lower rim derivatives as well as their complexation with ionic and neutral species have been recently reviewed by our group [28]. Research undergoing at Surrey in the field of calixarene chemistry involves:

1. complexation with calixarene derivatives with monovalent, bivalent [29] and tervalent [29] cations in different media;
2. anion complexation involving calixarene amido derivatives [30];
3. coordination enthalpies derived from solution and complexation data [31].

This paper reviews some of the recent work carried out in our laboratory on the thermodynamics involving calix(4)arene derivatives containing pyridino (**1a**, **1b**, **1c**) pendant arms and metal cations [32].



1a



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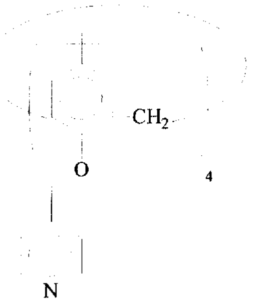

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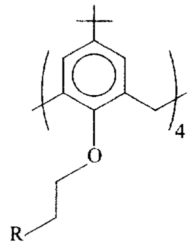

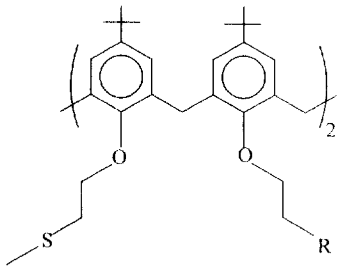

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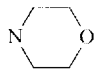
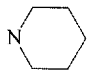
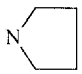
$N(CH_3)_2$	
$N(CH_2CH_3)_2$	
$N(iPr)_2$	

Fig. 1. Structures of *p-tert*-butylcalix(4)arenes containing different pendant groups synthesised at Surrey.

2. Pyridinocalix(4)arenes

In 1989 with the aim of extending the coordination chemistry of calixarene derivatives to transition metal cations, Pappalardo et al. [33] reported the synthesis of **1a**. It should be emphasised that most of the synthetic and structural contributions involving pyridino calixarenes are due to the contributions of this group [34–43]. Pappalardo et al. [41] also investigated (i) the ability of **1a** to extract alkali-metal cations in the water–dichloromethane solvent system (both solvents are mutually saturated) and (ii) the interaction of **1a** with alkali-metal cations. For this purpose, NMR measurements were carried out in $CDCl_3$.

As far as extraction is concerned, these authors demonstrated that in the solvent system under study, the ability of **1a** to extract alkali-metal cations from water in a given set of experimental conditions is relatively poor. As previously stated [44], several individual processes are involved in the overall extraction of metal cations from the aqueous to the organic phase in the presence of the ligand. Therefore, the data reported (although interesting from the point of view of the applications and uses of these ligands in extraction processes) are not necessarily representative of the selective behaviour of this ligand for metal cations in solution. As far as the NMR studies are concerned, these investigations demonstrated that the process (or processes) involving this derivative and alkali-metal cations in deuterated chloroform is kinetically slow to the extent that after several days, changes in the NMR were observed. The authors attributed the slow kinetics observed to the process of complexation. We considered that the extent of electrolyte dissociation in chloroform is very small. Therefore, ion-pairs rather than ionic species are likely to predominate in solution at least for the uncomplexed salt in this solvent. Little is known about the behaviour of calixarene derived salts in solution and a lot need to be investigated on these systems. Based on these observations we proceeded with solution thermodynamic studies involving **1a** as well as their geometrical isomers, **1b** and **1c** and some of this work is now reviewed.

2.1. Standard solution Gibbs energies

Representative data for the standard solution Gibbs energies of **1a**–**1c** at 298.15 K in protic (methanol, MeOH; ethanol, EtOH; 1-propanol, 1-PrOH and 1-butanol, 1-BuOH) and in dipolar aprotic (*N*,*N*-dimethylformamide, DMF; acetonitrile, MeCN; benzonitrile, PhCN;) solvents are listed in Table 1. These data were derived from solubilities of these compounds in these solvents only for cases in which the exposure of the solute to a saturated atmosphere of the solvent did not lead to solvate formation. Gibbs energy data are referred to the standard state (1 mol dm^{-3} of saturated solution). The process is represented by Eq. (1) where PyrCalix(4) denotes **1a**, **1b** and **1c**.

Table 1
Solution ($\Delta_s G°$) and Transfer ($\Delta_t G°$) Gibbs energies of pyridinocalix(4)arenes in protic and dipolar aprotic solvents at 298.15 K[a]

$\Delta_s G°$ (kJ mol^{-1})[b]			
Protic solvents[c]	**1a**	**1b**	**1c**
MeOH	16.59	7.86	10.13
EtOH	12.80	8.86	11.79
1-PrOH	9.39	–	–
1-BuOH	8.15	15.03	–
Dipolar aprotic solvents			
DMF	15.56	11.91	16.67
MeCN	19.35	14.00	16.01
PhCN	11.30	8.68	11.49
$\Delta_t G°$ (kJ mol^{-1}) (MeCN → s)[b]			
S			
MeOH	−2.76	−6.14	−5.88
EtOH	−6.55	−5.14	−4.22
1-PrOH	−9.96	–	–
1-BuOH	−11.20	1.03	–
DMF	−3.79	−2.09	0.66
MeCN	0	0	0
PhCN	−8.05	−5.32	−4.52

[a] Abbreviations, MeOH, methanol; EtOH, ethanol; 1-PrOH, propan-1-ol; 1-BuOH, butan-1-ol; DMF, N,N dimethylformamide; MeCN, acetonitrile; PhCN, benzonitrile.

[b] Data from Ref. [32].

[c] (**1a**), Solubility increases; (**1b** and **1c**), solubility decreases.

$$\mathrm{PyrCalix(4)(sol.)} \rightarrow \mathrm{PyrCalix(4)(s)} \qquad (1)$$

where, sol. and s denote the solid and solution respectively. The usefulness of these data has been described elsewhere [32]. Solvation changes in moving from one solvent to another reflecting the shift in the equilibrium position as a result of the medium effect are observed in the standard transfer Gibbs energies. These are calculated taking acetonitrile as the reference solvent. Therefore, representative data also included in Table 1 are referred to the process,

$$\mathrm{PyrCalix(4)(MeCN)} \rightarrow \mathrm{PyrCalix(4)(s)} \qquad (2)$$

Data listed in Table 1 show that as the distance between the phenolic oxygens and the pyridyl nitrogens is altered in moving from **1a** to **1c**, significant solvation changes occur. Since the standard Gibbs energy, $\Delta_t G°$ is related to the transfer constant, K_t, it was therefore possible to calculate the changes in the equilibrium constant in moving from one solvent to another. The two different patterns observed in the transfer of **1a** from acetonitrile to the alcohols relative to those for **1b** and **1c** are striking. Thus, while the $\Delta_t G°$ values of **1a** become more negative from methanol to 1-butanol, the opposite is true for **1b** and **1c**. These values reflect that for **1a**, the interactions between this ligand and the solvent are stronger as the hydrophobic nature of the aliphatic alcohol increases. This sequence is just the reverse for **1b** and **1c**. It was suggested that the trend observed for **1b** and **1c** in these solvents was expected taking into account that the acidity of the proton donor and the basicity of the proton acceptor contribute to the strength of hydrogen bond formation. There is also evidence that the pyridine ring interacts with the alcohols via hydrogen bond formation. As far as these derivatives are concerned, the pK_a values in methanol at 298.15 K have shown that the affinity of **1c** for the proton is higher than that of **1b** which, in turn is more basic than **1a**. While it was stated that the only conclusion that could be drawn from the $\Delta_t G^\circ$ values is that as far as the alcohols are concerned BuOH is the best solvator for **1a** and MeOH for **1b** and **1c**, the results clearly demonstrate that the position of the pyridyl nitrogens relative to the phenolic oxygens alters significantly the solvation of these ligands in protic solvents. In dipolar aprotic solvents, benzonitrile is the best solvator for these ligands. It has been previously stated [26] that solvent effects are better reflected in the enthalpy and entropy associated to these processes than in the Gibbs energy term. Therefore, the availability of these data will provide further insight into the nature of these interactions. Having enough background information regarding the solubility of these ligands in the various solvents, complexation studies were undertaken in acetonitrile and benzonitrile, since data are available for alkali-metal cations and other calixarene derivatives in these solvents. Taking into account the observations reported in the literature regarding the slow kinetics associated with the interaction of **1a** and alkali-metal cations in $CDCl_3$ as detected from NMR measurements, the same technique was adopted to investigate the complexation of this ligand and metal cations including silver (using perchlorate as the counter-ion) in CD_3CN. Thus ^{1}H-NMR measurements taken at different time intervals (30 min to 10 days) revealed that in this solvent, the kinetics of the process involving these systems is fast. No changes were observed in the ^{1}H-NMR spectra after 30 min. (For details regarding the synthesis and characterisation of **1a** in the cone conformation as well as complexation studies, readers are referred to the original sources). The following gives a brief summary of the techniques used for complexation studies for these systems.

3. Conductance measurements

Conductance measurements are currently carried out in our laboratory to determine the composition of the complexes formed between macrocycles and ionic species in solution [45,48]. A representative example is given in Fig. 2 where molar conductances (Λ_m) are plotted against ligand: cation ratio for the system Li^+ and **1a** in acetonitrile (2i) and in benzonitrile (2ii) at 298.15 K. These results show that the complex stoichiometry is 1:1. This was also observed for all univalent cations (including Ag^+) and **1a** in these solvents. The sharp break observed for the conductimetric titration curve (Fig. 2) for Li^+ and **1a** was also found for Na^+,

Ag^+ and this ligand in MeCN and PhCN, reflecting that the complexes formed are relatively strong. For K^+ and Rb^+ continuous variations were found in the Λ_m values by altering the ligand: metal cation ratio. These were taken as an indication that the ability of **1a** to interact with the larger cations is weak. Again, experimental

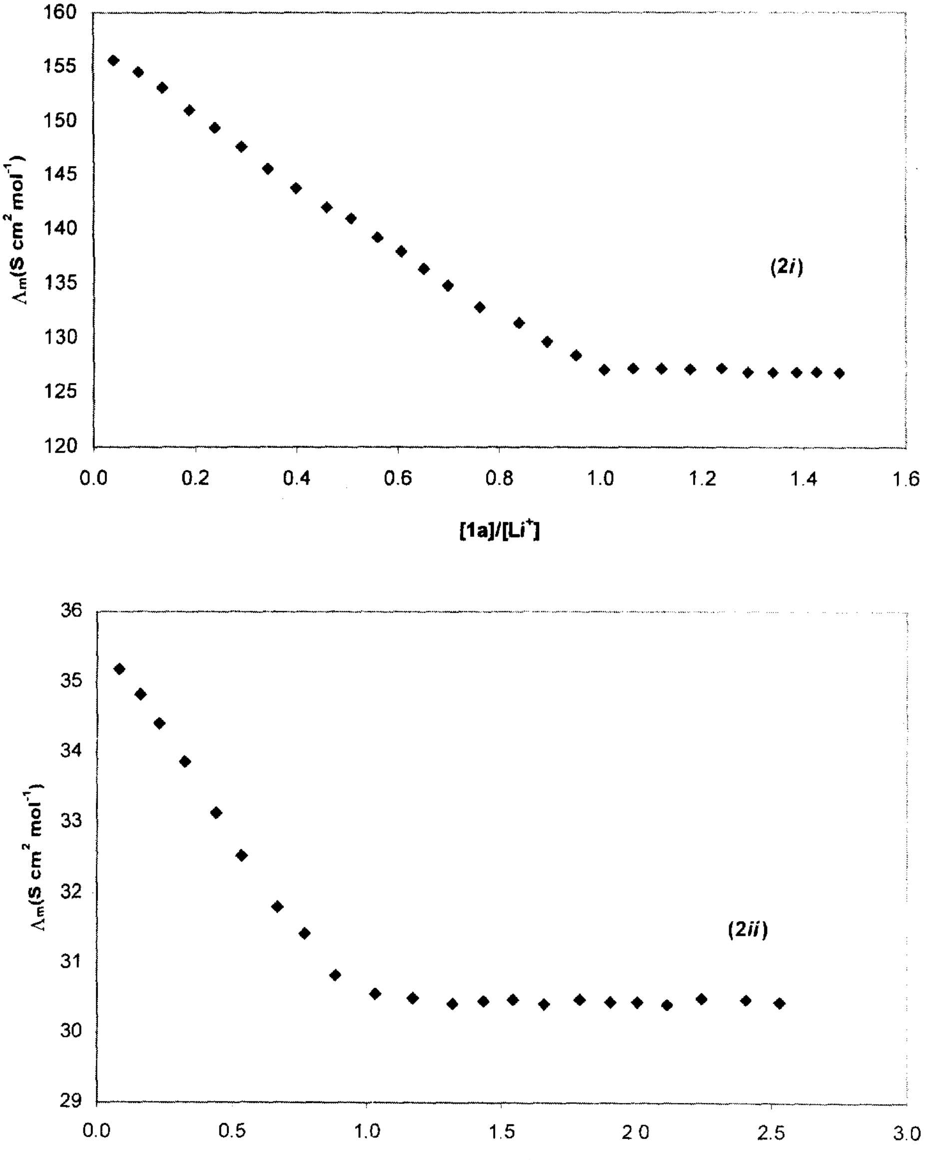


Fig. 2. Conductimeteric curves for the titration of **2a** with $LiClO_4$ in acetonitrile (2*i*) and in benzonitrile (2*ii*) at 298.15 K.

work carried out with **1b** and **1c** with Ag^+ in acetonitrile indicate that unlike **1a**, the interaction of these ligands with this cation in MeCN is also weak. As far as **1b** and **1c** are concerned, no changes in conductance besides dilution were observed when either **1b** or **1c** were added to salts containing alkali-metal cations in these solvents. This observation was also noted by Pappalardo et al. [41] by ^{1}H-NMR measurements in $CDCl_3$ using **1b**.

An important point to stress regarding conductance measurements is that these are quite informative. Thus, the decrease in conductance observed by adding the ligand to the solution of the metal-ion salt was attributed to the lower mobility of the metal-ion complex (a large cation) relative to the free cation. Although it may be argued that this behaviour is expected, there is enough evidence in the literature (for systems involving less bulky ligands and Li^+ in MeCN) indicating that this is not always the case [8,9]. Therefore it is useful to investigate the conductimetric behaviour of macrocycle based electrolytes relative to that involving the free cation salt provided that both of them contain the same counter-ion in a given solvent and at the required temperature.

Another relevant information from these measurements was that concerning the kinetics of the complexation process. Thus for all the metal cations investigated with **1a** in these solvents, soon after the addition of the ligand to the metal-ion salts, stable readings were observed in the conductimeter indicating that fast kinetics is associated with these processes. As far as acetonitrile is concerned, these findings further corroborate the results obtained from ^{1}H-NMR measurements.

A further scope of this technique is the use of conductance data for the derivation of the stability constant associated with the complexation process and this has been discussed elsewhere [45]. The following section outlines thermodynamic aspects of the complexation process involving (i) **1a** and alkali-metal cations in acetonitrile and benzonitrile and (ii) the interaction of geometrical isomers (**1a**, **1b**, **1c**) with the silver cation in acetonitrile.

4. Thermodynamics of complexation. Titration microcalorimetry

Calorimetry is a useful technique for the derivation of the stability constant and enthalpy associated with the complexation process provided that the strength of complexation (as reflected by the stability constant; $\log K_s$) is not too high in the medium under study. Instrumental developments in this area [46] have provided us with calorimeters of high sensitivity which in addition possess the capacity to monitor fast and slow processes. Such is the case with the isothermal titration microcalorimeter (Thermal Activity Monitor, TAM) designed by Wadsö et al. [46]. It was the availability of this equipment which made these measurements possible. Indeed, attempts to obtain data for these systems in acetonitrile by classical titration calorimetry failed due to the low solubility of **1a** in this solvent. Similar difficulties were encountered with the latter technique in studies involving the interaction of calixarene derivatives and lanthanide cations [47] since the rate of

Table 2
Thermodynamics of complexation of pyridinocalix(4)arenes and metal cations in dipolar aprotic media at 298.15 K

Cation	Solvent	Ligand	Log K_s	$\Delta_c G^\circ$ (kJ mol^{-1})	$\Delta_c H^\circ$ (kJ mol^{-1})	$\Delta_c S^\circ$ (J K^{-1} mol^{-1})
Li^+	MeCN	**1a**	5.95[a]	−33.96[a]	−23.91[a]	33.7[a]
Li^+	PhCN	**1a**	5.10[a]	−29.11[a]	−33.77[a]	−15.6[a]
Na^+	MeCN	**1a**	5.49[a]	−31.34[a]	−25.61[a]	19.1[a]
Na^+	PhCN	**1a**	4.74[a]	−27.06[a]	−24.43[a]	8.8[a]
K^+	MeCN	**1a**	3.14[a]	−17.92[a]	−18.47[a]	−1.9[a]
K^+	PhCN	**1a**	3.61[a]	−20.61[a]	−8.78[a]	39.7[a]
Rb^+	MeCN	**1a**	2.58[a]	−14.73[a]	−15.50[a]	−2.7[a]
Ag^+	MeCN	**1a**	5.09[b]	−29.06[b]	−19.04[b]	33.6[b]
Ag^+	MeCN	**1c**	2.63[b]	−15.03[b]	−25.63[b]	−35.6[b]

[a] Ref. [48].
[b] Ref. [32].

complexation for some of these systems can be relatively slow. Again, this was overcome by the use of titration microcalorimetry as assessed by Danil de Namor and Jafou [47]. Representative data for the thermodynamics associated with **1a** and monovalent metal cations are those in acetonitrile and in benzonitrile at 298.15 K shown in Table 2. Data for **1c** and the silver cation are also listed in Table 2. In cases where the stability constants are relatively high, these data were checked by potentiometry (direct for silver and competitive for other cations). For details see original sources [32,48]. Thermodynamic data are referred to the process:

$$M^+(s) + PyrCalix(4)(s) \rightarrow M^+PyrCalix(4)(s) \qquad (3)$$

No such response was found for **2a** and Cs^+ in MeCN or for Rb^+ and Cs^+ in PhCN in the microcalorimeter. In addition conductance changes were not detected when this ligand was added to metal-ion salts containing these cations in these solvents. As far as calorimetry is concerned it may be correctly argued that if the enthalpy associated with the process is 0, the lack of heat does not necessarily imply that complexation does not occur. A similar argument can be applied to conductance measurements given that if the mobility of both, free and complex salts is approximately the same, very small changes in conductance will be observed, although this is unlikely to occur. Although we put forward the suggestion that this ligand is likely to form very weak complexes with these metal cations, further research is required on these systems. Having stated this, it is clear from the data listed in Table 2, that the selectivity of **1a** for metal cations in MeCN follows the sequence:

$$Li^+ > Na^+ > Ag^+ > K^+ > Rb^+$$

As far as PhCN is concerned, the same sequence was found for Li^+, Na^+, K^+ (data for Ag^+ and **1a** in this solvent are not yet available). Following previous studies by Danil de Namor et al. log K_s values were used to assess quantitatively the selective behaviour of **1a** for lithium relative to other metal cations in MeCN and PhCN [3–5]. Based on transfer Gibbs energies for these cations from acetonitrile to benzonitrile based on the Ph_4AsPh_4B convention [22] it was concluded that as far as complexation Gibbs energies are concerned, the competitive effect of the ligand and the solvent for the cation was not shown, at least to the same extent as for the complexation process involving these cations and cryptand 222 in dipolar aprotic media [6]. This conclusion is also applicable to calix(4)arene esters and alkali-metal cations in these solvents as previously demonstrated. Data listed in Table 2 show that for all these cations with the exception of K^+ and **1a** in PhCN these processes are enthalpy controlled. In MeCN among the alkali-metal cations, the enthalpic stability is at its maximum for Na^+ and **1a** while in PhCN this is observed for lithium and this ligand. The two opposite trends observed in the complexation entropies in acetonitrile ($\Delta_c S^\circ$ becomes more negative down the group) relative to benzonitrile (increasingly more positive from Li^+ to K^+) were analysed in terms of the solvation entropies of alkali-metal cations in these solvents and the entropies of calixarenate formation, $\Delta_{cf}S^\circ$ where the metal cation is transferred from the gas phase (g), (Eq. (4))

$$M^+(g) + \text{PyrCalix(4)(s)} \rightarrow M^+\text{PyrCalix(4)(s)} \qquad (4)$$

It was suggested that the changes found in the $\Delta_{cf}S^\circ$ values for the various alkali-metal cations were likely to be attributed to the differences in the solvation of the ligand and the metal–ion complexes in these solvents and these are now under investigation. As far as the data for silver and these ligands (**1a** and **1c**) in acetonitrile are concerned, striking differences were observed in the thermodynamics of complexation as shown in Table 2. Thus for **1a** and Ag^+, the balance between enthalpy and entropy (both favourable) leads to a relatively high stability for complex formation (see log K_s and $\Delta_c G^\circ$ for this system, Table 2). However, the higher enthalpic stability observed for Ag^+ and **1c** in MeCN relative to **1a**, is overcome by the loss of entropy accompanying this process. As a result, the complex formed between **1c** and Ag^+ in acetonitrile is weak as observed in the stability constant and derived Gibbs energy of complexation listed in Table 2. The higher affinity of **1a** for silver relative to **1c** in this solvent was attributed to the cooperative effect of both donor atoms (phenolic oxygen and pyridyl nitrogen) in the complexation of this ligand and the silver cation. This was corroborated by ^{1}H-NMR measurements involving this ligand and silver in CD_3CN where considerable shift changes were reported for the β and γ pyridyl protons in the presence of this cation with respect to that of the free ligand. In addition, the resonance arising from the oxygen methylene protons was found to be affected by a deshielding influence attributed to some interaction between the phenolic oxygens and the silver cation. ^{1}H-NMR measurements for **1c** and Ag^+ in CD_3CN did not lead to significant changes in the spectrum as compared with that of the free ligand and therefore it was not possible to draw any definite conclusion for this system.

It was noted that the stability constant (hence $\Delta_c G^\circ$) of Ag^+ and **1a** in acetonitrile is not dramatically different from that on Na^+ and this ligand in this solvent as shown in Table 2. However differences are observed in the enthalpic and entropic contributions for these systems. It is well established that specific interactions take place between the silver cation and acetonitrile due to back donation of electrons to a antibonding orbital of the nitrile group [49]. As a result Ag^+ is better solvated in MeCN than Na^+ and if so the former is likely to undergo higher desolvation upon complexation than the latter. This statement is concomitant with the drop in enthalpic stability and the gain in entropy observed in the complexation of Ag^+ and **1a** relative to Na^+ and this ligand in acetonitrile. Having stated this, a detailed analysis of the complexation process involving these cations and this ligand requires thermodynamic information on the ligand and the metal-ion complexes in a wide variety of solvents and this research is now in progress.

On the basis of the relatively high stability of lithium, sodium and silver with **1a** in acetonitrile (as assessed from the log K_s values given in Table 2), attempts were made to isolate the metal-ion complex salts. Suitable crystals for X-ray diffraction studies were obtained for sodium and silver and a brief description is given. For full details, readers are referred to the original source [32].

5. X-ray diffraction studies

The X-ray structure of these compounds [32,48] was investigated by O.E. Piro, Universidad Nacional de la Plata, (Argentina) and E.E. Castellano, Instituto de Física de San Carlos, Universidad de Sao Paulo, (Brazil). Thus, the sodium **1a** perchorate monoacetonitrile salt shows three different complexes in the lattice, two sited on fourfold axes and one on a twofold axis. In all cases, the ligand is found in a 'cone' conformation with the sodium sitting in the hydrophilic cavity and interacting with four phenolic oxygens and four pyridyl nitrogens while one molecule of acetonitrile was found in the hydrophobic cavity. As far as the silver **1a** perchlorate monoacetonitrile complex is concerned, again the ligand hosts the cation in its hydrophilic cavity through interaction with the phenolic oxygens and the pyridyl nitrogens and as in the sodium complex, a molecule of acetonitrile is found in the hydrophobic cavity. We are now proceeding with the solution thermodynamics of these complexes. In doing so and in the light of the three different complexes found in the lattice of the sodium **1a** perchlorate complexes, advanced NMR techniques are being used to identify whether or not these species are present in solution.

6. Final remarks

Several techniques (^{1}H-NMR, conductivity, potentiometry and calorimetry) were explored in the study of the interactions involved in the complexation of pyridinocalix(4)arenes and monovalent metal cations in acetonitrile and benzonitrile. The results show that, in these solvents, the rate of complexation of **1a** and these metal cations is fast. These studies demonstrated that from the thermodynamic view point, the significance of the data relies entirely on the identification of the speciations in solution. In this respect, it should be stressed that a great deal of scrutiny and detail are required regarding the behaviour of electrolytes in solution in thermodynamic studies involving ionic species. A direct implication of this statement is that particular attention should be paid to the appropriate selection of the solvent in complexation studies.

Acknowledgements

I thank my co-workers whose names appear in the list of publications. Particular thanks are due to EU, DG-XII for financial support.

References

[1] J.M. Lehn, Supramolecular Chemistry, VCH, Weinheim, 1995.
[2] M.H. Abraham, A.F. Danil de Namor, W.H. Lee, J. Chem. Soc. Chem. Commun. (1977) 893
[3] A.F. Danil de Namor, L. Ghousseini, J. Chem. Soc. Faraday Trans. I 80 (1984) 2843; 81 (1985) 781.
[4] A.F. Danil de Namor, L. Ghousseini, W.H. Lee, J. Chem. Soc. Faraday Trans. 81 (1985) 2495.
[5] A.F. Danil de Namor, L. Ghousseini, T. Hill, J. Chem. Soc. Faraday Trans. 82 (1986) 349.
[6] A.F. Danil de Namor, J. Chem. Soc. Faraday Trans. 84 (1988) 2441.
[7] A.F. Danil de Namor, D. Kowalska, J. Phys. Chem. 101 (1997) 1643.
[8] A.F. Danil de Namor, M.A. Llosa Tanco, M. Salomon, C.Y. Ng, J. Phys. Chem. 98 (1994) 11796.
[9] A.F. Danil de Namor, C.Y. Ng, M.A. Llosa Tanco, M. Salomon, J. Phys. Chem. 100 (1996) 14485.
[10] A.F. Danil de Namor, R. Traboulssi, D.F.V. Lewis, J. Am. Chem. Soc. 112 (1990) 8442.
[11] A.F. Danil de Namor, D.A. Pacheco Tanaka, L. Nuñez Regueira, I. Gomez Orellana, J. Chem. Soc. Faraday Trans. 88 (1992) 1665.
[12] A.F. Danil de Namor, P.M. Blackett, M.C. Cabaleiro, J.M.A. Al Rawi, J. Chem. Soc. Faraday Trans. 90 (1994) 845.
[13] C.D. Gutsche, in: J.F. Stoddart (Ed.), 'Calixarenes'; Monographs in Supramolecular Chemistry, Royal Society of Chemistry, London, 1989.
[14] J. Vicens, V. Böhmer (Eds.), Calixarenes. A Versatile Class of Macrocyclic Compounds, Kluwer, Dordrecht, The Netherlands, 1991.
[15] J. Vicens, Z. Asfari, J.M. Harrowfield (Eds.), Calixarenes 50th Anniversary. Commemorative Volume, Kluwer, Dordrecht, The Netherlands, 1994.
[16] C.D. Gutsche, Aldrichim. Acta 28 (1995) 3.
[17] V. Böhmer, Angew. Chem. Int. Ed. Engl. 34 (1995) 713.
[18] R. Perrin, R. Lamartine, M. Perrin, Pure Appl. Chem. 65 (1993) 1549.
[19] A.F. Danil de Namor, M.T. Garrido, L. Muñoz, D.A. Pacheco Tanaka, F.J. Sueros Velarde, M.C. Cabaleiro, J. Chem. Soc. Chem. Commun. (1992) 855.
[20] A.F. Danil de Namor, D.A. Pacheco Tanaka, F.J. Sueros Velarde, J.D. Cardenas Carcia, M.C. Cabaleiro, J.M.A. Al Rawi, J. Chem. Soc. Faraday Trans Biophys. Chem. Special Issue 89 (1993) 2727.
[21] A.F. Danil de Namor, J. Wang, I. Gomez Orellana, F.J. Sueros Velarde, D.A. Pacheco Tanaka, J. Incl. Phen. Mol. Recognit. Chem. 19 (1994) 371.
[22] A.F. Danil de Namor, E. Gil, M.A. Llosa Tanco, D.A. Pacheco Tanaka, L.E. Pulcha Salazar, R.A. Schulz, J Wang, J. Phys. Chem. 99 (1995) 16776, 16781.
[23] A.F. Danil de Namor, F.J. Sueros Velarde, M.C. Cabaleiro, J. Chem. Soc. Faraday Trans. 92 (1996) 1731.

[24] A.F. Danil de Namor, R.G. Hutcherson, F.J. Sueros Velarde, A. Alvarez-Larena, J.L. Briansó, J. Chem. Soc. Perkin Trans. I (1998) 2933.
[25] A.F. Danil de Namor, R.G. Hutcherson, F.J. Sueros Velarde, M.L. Zapata-Ormachea, L.E. Pulcha Salazar, I. Al Jammaz, N. Al Rawi, Pure Appl. Chem. 70 (1998) 769.
[26] A.F. Danil de Namor, M.L. Zapata-Ormachea, R.G. Hutcherson, J. Phys. Chem. 102 (1998) 7839; J. Phys. Chem. 103 (1999) 366.
[27] A.F. Danil de Namor, F.J. Sueros Velarde, R.G. Hutcherson, O.E. Piro, E.E. Castellano, J. Chem. Soc. Faraday Trans. 94 (1998) 1257.
[28] A.F. Danil de Namor, R.M. Cleverley, M.L. Zapata-Ormachea, Chem. Rev. 98 (1998) 2495.
[29] A.F. Danil de Namor, A.F. Aguilar Cornejo, O. Jafou, work in progress.
[30] A.F. Danil de Namor, C. Rondon Fudinaga, J.D. Cardenas Garcia, O. Jafou, G. Andreou, work in progress.
[31] A.F. Danil de Namor, M.A. Llosa Tanco, L.E. Pulcha Salazar, D. Kowalska, J. Villanueva Salas, R.A. Schulz, J. Chem. Soc. Faraday Trans. 94 (1998) 3111.
[32] A.F. Danil de Namor, O.E. Piro, L.E. Pulcha Salazar, A.F. Aguilar Cornejo, N. Al Rawi, E.E. Castellano, F.J. Sueros Velarde, J. Chem. Soc. Faraday Trans. 94 (1998) 3097.
[33] F. Bottino, L. Giunta, S. Pappalardo, J. Org. Chem. 54 (1989) 5407.
[34] S. Pappalardo, F. Bottino, L. Giunta, M. Pietraskiewicz, J. Karpiuk, J. Incl. Phen. Mol. Recognit. Chem. 10 (1991) 387.
[35] S. Pappalardo, L. Giunta, M. Foti, G. Fergusson, J.F. Gallagher, B. Kaitner, J. Org. Chem. 57 (1992) 2611.
[36] P. Neri, M. Foti, G. Fergusson, J.F. Gallagher, B. Kaitner, M. Pons, M.A. Molins, L. Giunta, S. Pappalardo, J. Am. Chem. Soc. 114 (1992) 7814.
[37] G. Fergusson, J.F. Gallagher, S. Pappalardo, J. Incl. Phen. Mol. Recognit. Chem. 14 (1992) 349.
[38] P. Neri, S. Pappalardo, J. Org. Chem. 58 (1993) 1048.
[39] F. Bottino, S. Pappalardo, J. Incl. Phen. Mol. Recognit. Chem. 19 (1994) 85.
[40] G. Fergusson, J.F. Gallagher, L. Giunta, P. Neri, S. Pappalardo, M. Parisi, J. Org. Chem. 59 (1994) 42.
[41] S. Pappalardo, G. Fergusson, P. Neri, C. Rocco, J. Org. Chem. 60 (1995) 4576.
[42] S. Pappalardo, New J. Chem. 20 (1996) 465.
[43] S. Pappalardo, G. Fergusson, J. Org. Chem. 61 (1996) 2407.
[44] A.F. Danil de Namor, F.J. Sueros Velarde, A.R. Casal, A. Pugliese, M.T. Goitia, M. Montero, F. Fraga López, J. Chem. Soc. Faraday Trans. 93 (1997) 3955.
[45] B.G. Cox, H. Schneider, Coordination and Transport Properties of Macrocyclic Compounds in Solution, Elsevier, Amsterdam, 1992.
[46] I. Wadsö, Chem. Soc. Rev. 26 (1997) 79.
[47] A.F. Danil de Namor, O. Jafou, (1999) to be submitted.
[48] A.F. Danil de Namor, E.E. Castellano, L.E. Pulcha Salazar, O.E. Piro, O. Jafou, Phys. Chem. Chem. Phys. 1 (1999) 285.
[49] O. Popovich, R.P. Tomkins, Non-aqueous Solution Chemistry, Wiley, New York, 1981.