Extraction and Solution Thermodynamics of Complexation of Alkali and Alkaline-earth Cations by Calix[4]arene amides

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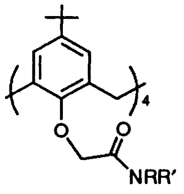
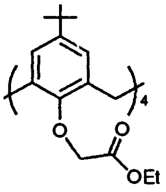
The extracting properties of nine new calix[4]arene tetraamides towards the entire alkali cation series and strontium have been determined. One of the amides bearing propargyl (prop-2-ynyl) residues on the nitrogen atoms has also been tested in complexation in methanol for the same cations. The enthalpies and entropies of complexation of alkali and alkaline-earth cations by the diethyl and pyrrolidinyl tetraamides in methanol and of alkali cations by the diethyl tetraamide in acetonitrile have been determined for the first time from calorimetric measurements. The data are compared with data for calixarene esters and solvent effects are discussed in the light of earlier results.

Of the many calix[4]arenes chemically modified at the lower rim, ester,[1-7] ketones[2-4] and amides[8,9] have attracted particular attention because these derivatives display strong extracting and complexing properties towards alkali cations, with a marked preference for Na$^+$. Their ability to discriminate selectively amongst these cations has been ascribed to their preorganized cone conformation leading to cone complexes as depicted by the X-ray structure of the potassium complexes of the *p-tert*-butylcalix[4]arene tetradiethylamide (**1**).[8] Calix[4]arene amides also show a strong affinity for alkaline-earth cations[9] with a high selectivity for calcium or strontium over magnesium. Transport of alkali thiocyanates, from an aqueous source phase to an aqueous receiving solution, through a bulk liquid membrane of dichloromethane, has been recently shown to be facilitated by calix[4]arene amides.[10] Up to now only two members of the amide family have been studied: the *p-tert*-butylcalix[4]arene tetradiethylamide (**1**) and the *p-tert*-butylcalix[4]arene tetrapyrrolidinylamide (**2**). We now report a study of the extraction, from water into dichloromethane, of alkali and strontium picrates by nine new amide derivatives (compounds **3**–**11**) in order to determine whether the Na$^+$/K$^+$ selectivity can be tuned by varying the nature of the residues R and R′ attached to the amide function, as was observed in the calix[4] ester series.[11] Because one of the derivatives, the dipropargyl amide **9**, showed an atypical extraction profile, its complexing properties in methanol towards alkalis and strontium have also been studied. In an attempt to understand better the complexation process, we also present the results of the first calorimetric study of alkali and alkaline-earth complexes of compounds **1** and **2** in methanol and of alkali complexes of **1** in acetonitrile. The complexation enthalpy, ΔH_c, and entropy, ΔS_c, terms are compared with previous results obtained with the *p-tert*-butylcalix[4]arene ethylester (**12**)[12] and discussed in terms of solvation effects and preorganization of the ligands. Our conclusions are compared with those of molecular dynamics simulations performed in water and acetonitrile and recently published.[13,14]



1 R = R′ = Et
2 = [CH$_2$]$_4$
3 = Pr
4 = Bu
5 = Pentyl
6 = Hexyl
7 = Octyl
8 = CH=CH$_2$
9 = C≡CH
10 = CH$_2$Ph
11 R = Et, R′ = CH$_2$Ph



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Experimental

Synthesis of Amides.—Diethylamide **1** and pyrrolidinylamide **2** were known compounds, the former having been prepared by Arduini *et al.*[8] from *p-tert*-butylcalix[4]arene and chloro-*N*,*N*-diethylacetamide in the presence of sodium hydride, and the latter by us[9] using the known tetraacid chloride **13**[11] and pyrrolidine in dry tetrahydrofuran (THF). The latter route was used here to make new amides **3**–**11**.

General Procedure.—To a stirred solution of triethylamine (4.20 mmol) and the appropriate secondary amine (5.25 mmol) in dry THF (15 cm^3) under nitrogen at room temperature was added dropwise a solution of tetraacid chloride **13** (1.05 mmol) in dry THF (10 cm^3). The mixture was stirred for 24 h and then filtered. The filtrate was concentrated to dryness and the resulting residue was taken up in dichloromethane and washed with cold water. Evaporation of the solvent, followed by purification by crystallisation, afforded the amide in an analytically pure state. The following amides were thus prepared.

n-Propylamide **3**. (72%), mp 187–189 °C (ethanol–dichloromethane); ν_{max}(KBr)/cm^{-1} 1658; δ_H(300 MHz; CDCl$_3$) 0.86 (t, 24 H), 1.07 (s, 36 H), 1.50 (m, 16 H), 3.20 (m, 20 H), 5.01 (s, 8 H), 5.24 (d, *J* 11.0 Hz, 4 H) and 6.77 (s, 8 H); δ_C(75 MHz; CDCl$_3$) 11.3, 11.5, 20.9, 22.1, 31.4, 32.4, 33.7, 47.5, 48.4, 71.6, 125.2, 133.6, 144.1, 154.0 and 169.3 (Found: C, 74.6; H, 9.2; N, 4.6. Calc. for $C_{76}H_{116}N_4O_8$: C, 75.2; H, 9.6; N, 4.6%).

n-Butylamide **4**. (75%), mp 193–194 °C (ethanol–dichloromethane); ν_{max}(KBr)/cm^{-1} 1658; δ_H(300 MHz; CDCl$_3$) 0.91 (t, 24 H), 1.07 (s, 36 H), 1.28 (m, 16 H), 1.48 (m, 16 H), 3.20 (m, 20 H), 4.97 (s, 8 H), 5.23 (d, *J* 12.8 Hz, 4 H) and 6.75 (s, 8 H); δ_C(75

MHz; $CDCl_3$) 13.9, 20.0, 20.3, 29.9, 31.1, 31.6, 32.4, 33.7, 45.5, 46.6, 71.5, 125.2, 133.6, 144.1, 153.9 and 169.5 (Found: C, 75.8; H, 9.6; N, 4.0. Calc. for $C_{84}H_{132}N_4O_8$: C, 76.1, H, 10.0; N, 4.2%).

n-Pentylamide **5**. (60%), mp 110–111 °C (ethanol–dichloromethane); ν_{max}(KBr)/cm^{-1} 1659; δ_H(300 MHz; $CDCl_3$) 0.88 (t, 24 H), 1.09 (s, 36 H), 1.25 (m, 32 H), 1.55 (m, 16 H), 3.30 (m, 20 H), 5.00 (s, 8 H), 5.21 (d, *J* 14.0 Hz, 4 H) and 6.86 (s, 8 H); δ_C(75 MHz; $CDCl_3$) 14.1, 22.5, 22.6, 27.5, 28.9, 29.0, 29.7, 31.4, 32.4, 33.7, 44.8, 46.9, 71.4, 125.1, 133.6, 144.1, 153.9 and 169.4 (Found: C, 76.4; H, 9.9; N, 3.8. Calc. for $C_{92}H_{148}N_4O_8$: C, 76.8; H, 10.4; N, 3.9%).

n-Hexylamide **6**. (55%), mp *ca.* 90 °C (decomp.) (ethanol–dichloromethane); ν_{max}(KBr)/cm^{-1} 1657; δ_H(300 MHz; $CDCl_3$) 0.90 (t, 24 H), 1.07 (s, 36 H), 1.25 (m, 48 H), 1.46 (m, 16 H), 3.20 (m, 20 H), 5.00 (s, 8 H), 5.21 (d, *J* 13.0 Hz, 4 H) and 6.79 (s, 8 H); δ_C(75 MHz; $CDCl_3$) 14.0, 22.5, 26.5, 26.8, 29.0, 29.7, 31.2, 31.2, 31.6, 32.3, 33.6, 45.9, 46.7, 71.4, 125.1, 133.6, 144.0, 153.8 and 169.3 (Found: C, 77.7; H, 10.4; N, 3.7. Calc. for $C_{100}H_{164}N_4O_8$: C, 77.5; H, 10.7; N, 3.6%).

n-Octylamide **7**. (75%), viscous oil; ν_{max}(film)/cm^{-1} 1645; δ_H(300 MHz; $CDCl_3$) 0.88 (t, 24 H), 1.07 (s, 36 H), 1.29 (m, 64 H), 1.46 (m, 16 H), 1.60 (m, 16 H), 3.23 (m, 20 H), 4.98 (s, 8 H), 5.20 (d, *J* 12.0 Hz, 4 H) and 6.76 (s, 8 H); δ_C(75 MHz; $CDCl_3$) 14.1, 22.7, 27.0, 27.3, 27.9, 27.9, 29.1, 29.4, 29.6, 29.7, 31.4, 31.4, 31.9, 32.3, 33.7, 46.1, 47.0, 71.5, 125.2, 133.7, 144.1, 153.8 and 169.4.

Allylamide **8**. (56%), mp 168–170 °C (ethanol–dichloromethane); ν_{max}(KBr)/cm^{-1} 1663; δ_H(300 MHz; $CDCl_3$) 1.07 (s, 36 H), 3.16 (d, *J* 12.8 Hz, 4 H), 3.91 (d, *J* 4.9 Hz, 8 H), 3.96 (d, *J* 5.8 Hz, 8 H), 5.02 (s, 8 H), 5.07 (d, *J* 12.8 Hz, 4 H), 5.17 (2 d, *J* 9.7, 4.0 Hz, 16 H), 5.76 (m, 8 H) and 6.77 (s, 8 H); δ_C(75 MHz; $CDCl_3$) 31.4, 32.1, 33.7, 47.3, 48.0, 71.3, 116.7, 117.9, 125.2, 133.4, 133.5, 133.7, 144.3, 153.5 and 169.7 (Found: C, 75.8; H, 7.9; N, 4.5. Calc. for $C_{76}H_{100}N_4O_8$: C, 76.2; H, 8.4; N, 4.7%).

Propargylamide **9**. (83%), mp 218–220 °C (ethanol–dichloromethane); ν_{max}(KBr)/cm^{-1} 1658; δ_H(300 MHz; $CDCl_3$) 1.08 (s, 36 H), 3.22 (d, *J* 13.0 Hz, 4 H), 3.55 (s, 8 H), 4.35 (s, 16 H), 5.01 (d, *J* 13.0 Hz, 4 H), 5.06 (s, 8 H) and 6.80 (s, 8 H); δ_C(75 MHz; $CDCl_3$) 30.9, 31.4, 33.8, 71.5, 72.2; 72.7, 76.8, 77.2, 125.4, 133.5, 144.8, 153.1 and 169.2 (Found: C, 77.2; H, 6.7; N, 4.5. Calc. for $C_{76}H_{84}N_4O_8$: C, 77.3; H, 7.2; N, 4.7%).

Benzylamide **10**. Mp 210.5–212.0 °C (ethanol–dichloromethane), δ_H(500 MHz; $CDCl_3$) 1.09 (s, 36 H), 3.07 (d, *J* 13.0 Hz, 4 H), 4.40 (s, 8 H), 4.44 (s, 8 H), 5.06 (d, *J* 13.0 Hz, 4 H), 5.18 (s, 8 H), 4.44 (s, 8 H), 5.06 (d, *J* 13.0 Hz, 4 H), 5.18 (s, 8 H), 6.76 (s, 8 H), 7.05 (bs, 16 H) and 7.17 (bs, 24 H) (Found: C, 81.0; H, 7.1; N, 3.6. Calc. for $C_{108}H_{116}N_4O_8$: C, 81.2; H, 7.3; N, 3.5%).

Ethylbenzylamide **11**. (73% yield), mp 198–199 °C (ethanol–dichloromethane), δ_H(300 MHz; $CDCl_3$) 1.00 (t, 12 H), 1.08 (s, 36 H), 3.28 (d, *J* 13.0 Hz, 4 H), 3.30 (q, 8 H), 5.10 (m, 12 H), 6.79 (t, 4 H), 6.82 (s, 8 H), 7.18 (t, 8 H) and 7.23 (d, 8 H); δ_C(75 MHz; $CDCl_3$) 13.7, 31.4, 32.2, 33.8, 40.4, 47.5, 71.4, 125.3, 127.0, 127.9, 128.3, 129.6, 133.6, 144.4, 152.2 and 169.8 (Found: C, 77.8; H, 7.9; N, 4.0. Calc. for $C_{88}H_{108}N_4O_8$: C, 78.3; H, 8.1; N, 4.2%).

Physicochemical Measurements.—Materials. The solvents methanol (Carlo Erba, max. 0.01% water) and acetonitrile (SDS, purex, analytical grade) were used without further purification. The supporting electrolyte used in the stability constant determinations, either Et_4NCl (Fluka, purum) or Et_4NClO_4 (Fluka, purum) according to the experimental method, was first recrystallised from methanol and acetone and dried under vacuum, for 24 h at ambient temperature.

The metallic salts were chosen according to their solubilities in the solvents studied and to the techniques employed: LiCl (Fluka, purum), NaCl (Merck, p.a.), KCl (Merck, p.a.), RbCl (Fluka, puriss.), CsCl (Merck, p.a.), $Ca(ClO_4)_2 \cdot 4H_2O$ (Fluka purum), $Sr(NO_3)_2$ (Merck, p.a.) and $Ba(ClO_4)_2$ (Prolabo, p.a. were used for spectrophotometric and calorimetric measurements in methanol, $LiClO_4$, $NaClO_4$ (Prolabo, Rectapur) $KClO_4$ (Prolabo, Normapur), $RbClO_4$ (Sigma) and CsNO (Fluka, purum) for all types of measurements in acetonitrile except CsI (Janssen Chimica) for calorimetry. All these salts were dried under vacuum for 24 h before use. The stock solutions of all of them except the alkalis were standardised by complexometric titrations with EDTA in the presence of the appropriate indicators.[15]

The preparation of alkali and strontium picrates employed in extraction experiments has already been reported.[9]

Extraction. The extraction measurements from water to dichloromethane were performed according to the following procedure: 2.5×10^{-4} mol dm^{-3} aqueous picrate (5 cm^3) and 5 cm^3 of a 2.5×10^{-4} mol dm^{-3} solution of calixarene in CH_2Cl_2 were vigorously agitated in a stoppered glass tube with a mechanical shaker for 2 min, then magnetically stirred in a thermostatted water bath at 20 ± 0.1 °C for 30 min and finally left standing, for a further 30 min. The concentration of picrate ion remaining in the aqueous phase was then determined spectrophotometrically as previously described.[9] Blank experiments showed that no picrate extraction occurred in the absence of calixarene.

Stability constant measurements. When the stability constants β, defined by the concentration ratio $[ML^{n+}]/[M^{n+}] \cdot [L]$ (M^{n+} = cation, L = ligand) were not too high (log $\beta < 5$), they have been determined by UV absorption spectrophotometry at 25 °C according to the procedure already described in detail.[9]

The stability of the Rb^+ complex of ligand **1** in acetonitrile was determined using competitive potentiometry involving the silver cation [log β = 5.5 for $Ag(\mathbf{1})^+$] as already described.[9] The stabilities of the Li^+, Na^+ and K^+ complexes with **1** in acetonitrile were too high to be determined by the same procedure.

The high stability of the sodium complex of **9** in methanol has also been determined using competitive potentiometry involving the silver cation [log $\beta = 6.1 \pm 0.1$ for $Ag(\mathbf{9})^+$]. However, contrary to the procedure generally followed where a solution of the ligand is added to a mixture of Ag^+ and the cation under investigation and because of the low solubility of **9** in methanol, a 10^{-3} mol dm^{-3} solution of $NaClO_4$ was added to a 1:1 mixture of **9** and $AgClO_4$ ($C_L = C_{Ag} = 10^{-4}$ mol dm^{-3}).

Calorimetric measurements. The calorimetric determinations were made at 25 °C, using a precision isoperibol titration calorimeter (Tronac 450, Orem, Utah). The calorimeter was equipped with a 2 cm^3 burette linked by teflon tubes to the reaction vessel and connected to a computing system which allowed precise injections of the titrant during an accurately known amount of time. The whole assembly was then immersed into the calorimeter bath and left for several minutes until thermal equilbrium was reached. The burette was connected to a motor the rotating rate of which (400 steps. s^{-1}) corresponded to a burette delivery rate of 0.333 cm^3 s^{-1}. For solubility reasons the metallic salts (C_M) were titrated into 50 cm^3 solution of calixarene (C_L). The concentration ranges were $5 \times 10^{-4} \leqslant C_L \leqslant 10^{-3}$ mol dm^{-3} and $0.01 \leqslant C_M \leqslant 0.113$ mol dm^{-3} in methanol, and in acetonitrile $2.5 \times 10^{-4} \leqslant C_L \leqslant 5 \times 10^{-4}$ mol dm^{-3} and $0.005 \leqslant C_M \leqslant 0.02$ mol dm^{-3}. The temperature *versus* time curve was automatically converted into a heat *versus* mole of titrant added curve, then automatically corrected by an appropriate programme. An electrical calibration (Joule effect) was made after each experiment. This instrument is entirely computerized and all the heat evolved by the reaction is automatically corrected for the different

Table 1 Percentage extraction (%E) of alkali and strontium picrates into CH_2Cl_2 at 20 °C. Arithmetic mean of several experiments—standard deviation on the mean: $\sigma_{N-1} \leqslant 1$

Compound	R = R′	Li^+	Na^+	K^+	Rb^+	Cs^+	$S(Na^+/K^+)$	Sr^{2+}
1	Ethyl[a]	62.5	95.5	73.7	24.0	11.8	1.29	86.3
2	Pyrrol[a]	47.8	91.1	57.5	16.1	11.2	1.58	72.1
3	Propyl	71.6	95.0	79.6	33.3	9.7	1.19	78.5
4	Butyl	67.7	92.0	78.4	37.8	14.8	1.17	74.0
5	Pentyl	69.9	93.0	80.9	37.3	14.4	1.15	76.6
6	Hexyl	71.2	87.6	77.2	36.9	26.2	1.13	68.4
7	Octyl	74.6	94.8	84.6	48.3	28.4	1.12	65.0
8	Allyl	40.1	91.5	63.7	16.0	6.4	1.44	53.4
9	Propargyl	8.6	76.0	11.4	3.9	2.8	6.67	2.4
10	Benzyl	36.5	79.8	56.1	14.4	11.5	1.42	27.9
11	R = Ethyl R′ = Benzyl	50.2	95.0	68.7	24.1	15.1	1.38	58.8

[a] From ref. 9.

Table 2 Logarithms of the stability constants β of alkali complexes of ligand **9** in methanol at 25 °C, I = 0.01 mol dm^{-3} (Et_4NCl)

Ligands	Li^+	Na^+	K^+	Rb^+	Cs^+
9	3.8 ± 0.2[a]	6.6 ± 0.1[b]	3.5 ± 0.1[a]	2.8 ± 0.5[a]	1.4 ± 0.5[a]

[a] Spectrophotometric determinations. [b] Potentiometric determination, I = 0.01 mol dm^{-3} (Et_4NClO_4).

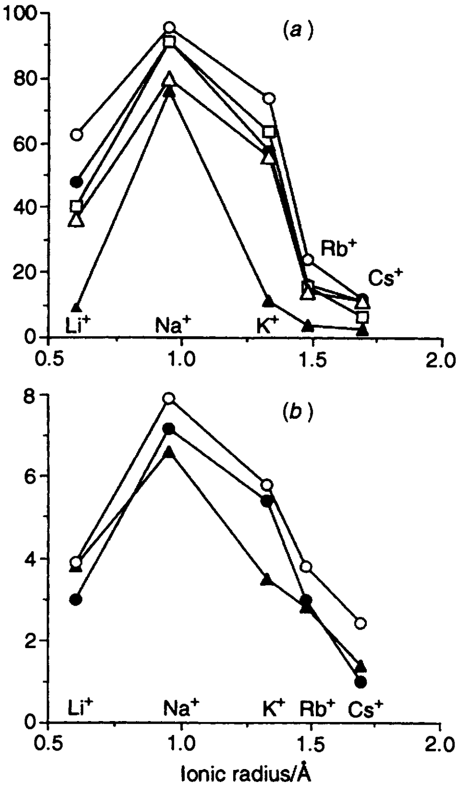

Fig. 1 (*a*) Percentage cation extracted (%E) from water to dichloromethane of alkali picrates and (*b*) logarithms of the stability constants β in methanol *vs.* the cation ionic radius r for the complexation of alkali cations by some calixarene tetraamides: (○) ethyl; (●) pyrr; (□) allyl; (▲) propargyl; (△) benzyl

additional heats (non-chemical heat effects). Heat-of-dilution corrections were made by titrating the metal ion solution into the solvent.

Where log β was known from other techniques to be higher than 5, the number of moles of the metallic salt added to the ligand solution was equal to the number of moles of the complex formed and the measured heat directly related to the complexation enthalpy ΔH_c. ΔS_c could then be derived from the expression $\Delta G_c = \Delta H_c - T\Delta S_c$, knowing $\Delta G_c = -RT \ln \beta$.

Where log β was lower than 5, log β and ΔH_c could be refined simultaneously using two different programs based on a least-squares analysis of the calorimetric data: the program FS101 provided by Tronac and the general program Sirko.[16] Both programs gave the same results. In general the values of log β determined from calorimetry were in good agreement with those previously determined from spectrophotometric measurements. The same ΔH_c values were also obtained when log β values were fixed during the refinement to the values found by spectrophotometry.

The accuracy and reproducibility of the calorimetric measurements were checked by determining the enthalpies of complexation of Na^+ and K^+ with 18-crown-6 in methanol. In this case and in contrast to our experiments with calixarenes, the crown ether was titrated into the metal ion solution. The values found were Na^+, $\Delta H_c = -35.82$ kJ mol^{-1} and K^+, -56.43 kJ mol^{-1}, respectively, in excellent agreement with the literature data.[17] The stability constant of the sodium complex was found to be 4.32 log units, also in excellent agreement with the literature data.[17]

Results and Discussion

Extraction and Complexation of Alkali and Strontium Cations. Effect of Substituent Variation.—The results given in Table 1 as the percentage cation extracted, %E, correspond to the mean values of at least five independent experiments. The variations of %E with the ionic radius of the cations are illustrated in Fig. 1(*a*) for selected derivatives.

All the tetraamide derivatives show a high extraction level for alkali cations, sodium being always the best extracted. Li^+ is slightly less well extracted than K^+, but much more than Rb^+ and even more than Cs^+. As already observed with the ethyl and pyrrolidinyl derivatives, amides are better extracting agents than esters, but less selective. For instance, the Na^+/K^+ extraction selectivity factor S, expressed as the ratio of the percentages extraction of sodium over potassium, is only 1.17 for the n-butyl derivative **4** instead of 12.5 for the n-butyl ester analogue.[11] Within the alkyl derivatives, the nature of the substituent has a small but significant influence on the extraction level. However, for a given cation, there is no regular variation of %E with the alkyl substituents as the number of carbon atoms increases. With regard to the Na^+/K^+ selectivity,

Table 3 Thermodynamic parameters of complexation of alkali complexes with calix[4]arene tetraethyl ester **12** and tetraamides **1** and **2** in methanol and aceonitrile at 25 °C

		Methanol					Acetonitrile				
Ligands		Li^+	Na^+	K^+	Rb^+	Cs^+	Li^+	Na^+	K^+	Rb^+	Cs^+
1	log K	4.1 ± 0.2 (3.9)[b]	(7.9 ± 0.1)[c]	(5.8 ± 0.1)[c]	3.8 ± 0.1 (3.8)[b]	2.5 ± 0.1 (2.4)[b]	⩾8.5	⩾8.5	⩾8.5	5.7 ± 0.1[e]	3.5 ± 0.1[f]
	$-\Delta G_c$/kJ mol^{-1}	22.2 ± 0.6[b]	45.0 ± 0.6	33.1 ± 0.6	21.6 ± 0.6[b]	14 ± 1[b]	⩾48.4	⩾48.4	⩾48.4	32.5 ± 0.6	19.9 ± 0.6
	$-\Delta H_c$/kJ mol^{-1}	7 ± 2	50.6 ± 0.8	42.4 ± 0.2	17.5 ± 0.8	9 ± 3	55 ± 2	79 ± 4	64 ± 2	37.2 ± 0.8	26 ± 2
	$T\Delta S_c$/kJ mol^{-1}	15 ± 3	−6 ± 1	−9.3 ± 0.8	4 ± 1	5 ± 4	⩾ −6.6	⩾ −30.6	⩾ −15.6	−5 ± 1	−6 ± 3
	ΔS_c/J K^{-1} mol^{-1}	50 ± 10	−20 ± 3	−31 ± 3	13 ± 3	17 ± 13	⩾ −22	⩾ −103	⩾ −52	−17 ± 3	−20 ± 10
2	log K	(3.0 ± 0.05)[b]	(7.2 ± 0.05)[c]	(5.4 ± 0.1)[c]	3.1 ± 0.2 (3.0)[b]	(⩽1)[b]					
	$-\Delta G_c$/kJ mol^{-1}	17.1 ± 0.3	41.0 ± 0.3	30.8 ± 0.6	17.1 ± 0.6[b]						
	$-\Delta H_c$/kJ mol^{-1}	−6 ± 1	34.3 ± 0.8	32.6 ± 0.4	11 ± 1	*d*					
	$T\Delta S_c$/kJ mol^{-1}	23 ± 1	7 ± 1	−2 ± 1	6 ± 2						
	ΔS_c/J K^{-1} mol^{-1}	77 ± 3	23 ± 3	−6 ± 3	20 ± 6						
12	log K[g]	2.6	5.0	2.4	3.1	2.7	6.4	5.8	4.5	1.9	2.8
	$-\Delta G_c$/kJ mol^{-1}	14.84	28.54	13.7	17.66	15.38	36.53	33.11	25.69	10.85	15.98
	$-\Delta H_c$/kJ mol^{-1}[a]	−5.05	45.6	14.22	—	—	48.78	61.55	43.85	18.67	11.48
	$T\Delta S_c$/kJ mol^{-1}[a]	19.89	−17.06	−0.52	—	—	−12.25	−28.44	−18.16	−7.82	4.5
	ΔS_c/J K^{-1} mol^{-1}[a]	66.7	−57.2	−1.7	—	—	−41.1	−95.4	−60.9	−26.2	15.1

[a] From ref. 12. [b] Spectrophotometric determination from ref. 9. [c] Potentiometric determination from ref. 9. [d] No measurable heat other than heat of dilution. [e] This work, potentiometric determination. [f] This work, spectrophotometric determination. [g] From ref. 4.

Table 4 Thermodynamic parameters of complexation of alkaline-earth cations with the tetraamides **1** and **2** in methanol, at 25 °C

Ligands		Ca^{2+}	Sr^{2+}	Ba^{2+}
1	log K^a	$\geqslant 9.0$	$\geqslant 9.0$	7.2 ± 0.1
	$-\Delta G_c$/kJ mol^{-1}	$\geqslant 51.3$	$\geqslant 51.3$	41.0 ± 0.6
	$-\Delta H_c$/kJ mol^{-1}	25.0 ± 0.5	10.0 ± 0.5	-2.5 ± 0.4
	$T\Delta S_c$/kJ mol^{-1}	$\geqslant 26.3$	$\geqslant 41.3$	43 ± 1
	ΔS_c/J K^{-1} mol^{-1}	$\geqslant 88.2$	$\geqslant 138.6$	144 ± 3
2	log K^a	$7.8 + 0.1$	8.1 ± 0.1	6.8 ± 0.1
	$-\Delta G_c$/kJ mol^{-1}	44.5 ± 0.6	46.2 ± 0.6	38.8 ± 0.6
	$-\Delta H_c$/kJ mol^{-1}	10.0 ± 0.5	*b*	-7.7 ± 0.8
	$T\Delta S_c$/kJ mol^{-1}	34 ± 1		46 ± 1
	ΔS_c/J K^{-1} mol^{-1}	116 ± 3		196 ± 3

[a] From ref. 9. [b] No measurable heat other than heat of dilution.

the *S* values are found to be very close to each other. However a slight but systematic decrease of *S* is observed with the increasing number of carbon atoms in the substituent, from 1.29 for the ethyl derivative **1** to 1.12 for the octyl derivative **7**.

The presence of the other substituents, containing multiple bonds such as allyl or propargyl, or with cyclic structures like benzyl or pyrrolidinyl, decreases the extraction levels of all the cations, especially of K^+ with respect to Na^+. The steric properties of the latter may increase the relative rigidity of the ligands and the electron withdrawing character of the former (their Taft electronic parameters σ^* are 0.56 and 2.18 for the allyl and propargyl groups, respectively)[18] reducing the basicity of the carbonyl groups, may account for these observations. Moreover, the fact that the extraction level of K^+ is more affected than that of Na^+ contributes to an increase of the Na^+/K^+ selectivity. For instance for the benzyl derivative **10** the selectivity is 1.42, whereas for the mixed compound **11** the selectivity is intermediate between those of compounds **1** and **10**. The propargyl derivative (compound **9**) with $S = 6.67$ is the most selective amide of the entire group.

The lower affinity of **9** for the alkali cations is also reflected in complexation as shown in Table 2, which contains the logarithms of the stability constants of the 1 : 1 complexes, and in Fig. 1(*b*), which shows the variations of log β along the series for ligands **1**, **2** and **9**. In the case of Na^+, for which the procedure of determination was different (see Experimental), the refinements were clearly improved if we assumed the presence of an additional NaL_2 species ($\log K_2 = \log[NaL_2{}^+]/[NaL^+][L] = 5.6$). To our knowledge this is the first case where a complex of a calix[4]arene amide may be present. Fig. 1 shows that the complexation and extraction selectivity patterns of ligand **9** in the alkali series are parallel, with a marked preference for Na^+. The increase in the Na^+/K^+ selectivity observed in extraction is confirmed in complexation as $S' = \beta\ (NaL)/\beta\ (KL)$ is 1258 with ligand **9** and only 126 for **1**.

The influence of the R substituent on extraction is more important for strontium than for the alkalis. The levels are still high, although lower than those for sodium, when R is an alkyl group, but decrease significantly with the allyl and benzyl derivatives and dramatically with the propargyl derivative for which %*E* is close to zero. This trend is also visible in complexation where an average value of $\log \beta = 3.3 \pm 0.1$ has been found from spectrophotomeric and potentiometric measurements. Although in the latter case the procedure employed was that as for sodium, there was no evidence of the formation of ML_2 species.

Thermodynamic Parameters of Complexation.—The values of ΔG_c, ΔH_c and ΔS_c of complexation of alkali cations by ligands **1** and **2** in methanol and by ligand **1** in acetonitrile are listed in Table 3. Corresponding values for the *p*-*tert*-butylcalix[4]arene tetraethylester **12** in both solvents are included for comparison purposes.[12] The corresponding parameters for the complexation of alkaline-earth cations in methanol by ligands **1** and **2** are reported in Table 4. ΔH_c values are the arithmetic means of at least two independent determinations and the confidence intervals correspond to the standard deviation on the mean, $\pm\sigma_{N-1}$. The precision on the $T\Delta S_c$ and ΔS_c terms have been calculated taking into account the precision on log β and hence ΔG_c.

Complexation of alkali cations in methanol. For Cs^+ and ligand **1**, the lack of accuracy in ΔH_c can be explained by (*i*) the low degree of complex formation at the end of the titration (< 48%), resulting from its low stability and the low solubility of the cesium salt, and (*ii*) the low heat evolved by the complexation process. For Li^+ and ligand **2**, a small endothermic change was observed, corresponding to the balance between the heat of complexation and the heat of dilution. In this case it was impossible to refine simultaneously log β and ΔH_c. Therefore log β was assigned to the value determined by spectrophotometry. The heat generated by complexation of Cs^+ by the tetrapyrrolidinyl amide **2** was not sufficient to allow the determination of ΔH_c and hence ΔS_c.

With both ligands **1** and **2** and all the alkali cations, except Li^+, the complexation process is enthalpy controlled: ΔH_c values are negative, the most negative ones being for Na^+ in both cases. The entropy values may be favourable ($\Delta S_c > 0$) as in the case of Rb^+ with both ligands, Cs^+ with **1** and Na^+ with **2**, or unfavourable ($\Delta S_c < 0$) in the other cases. The formation of the Li^+ complex of ligand **1** is accompanied by favourable enthalpy and entropy terms, but the ΔG_c is entropy controlled. With ligand **2** the complexation process is entropy driven only as $\Delta H_c > 0$.

The solution calorimetry of Na^+ and K^+ complexes of the tetraethylester **12**, which we have previously reported,[12] shows the same type of stabilization of these complexes and their homologues as the tetradiethylamide **1**. However the Li^+ complex of **12** is enthalpically destabilized and it is noteworthy that it has $-\Delta H_c$ and $T\Delta S_c$ values very close to those of $Li2^+$. Fig. 2, which gives a graphical representation of the variation of $-\Delta G_c$, $-\Delta H_c$ and $T\Delta S_c$ in the series, enables a better comparison to be visualised between the three ligands.

First, for both calixarene amides **1** and **2**, the same trends are observed along the series: an exothermic maximum is observed for Na^+ and there is a decrease in ΔS_c from Li^+ to K^+ and thereafter an increase for Rb^+ and Cs^+. The enthalpy terms are always more favourable with compound **1** (ΔH_c more negative) whereas the entropy terms are always more favourable with the pyrrolidinyl amide **2** (higher ΔS values). This may be related to a more important desolvation of the cations imposed by higher steric hindrance and greater rigidity of the ligand due to the presence of the pyrrolidinyl substituents. Thus the higher stability of the alkali complexes of **1** as compared with their homologues of **2** is of enthalpic origin.

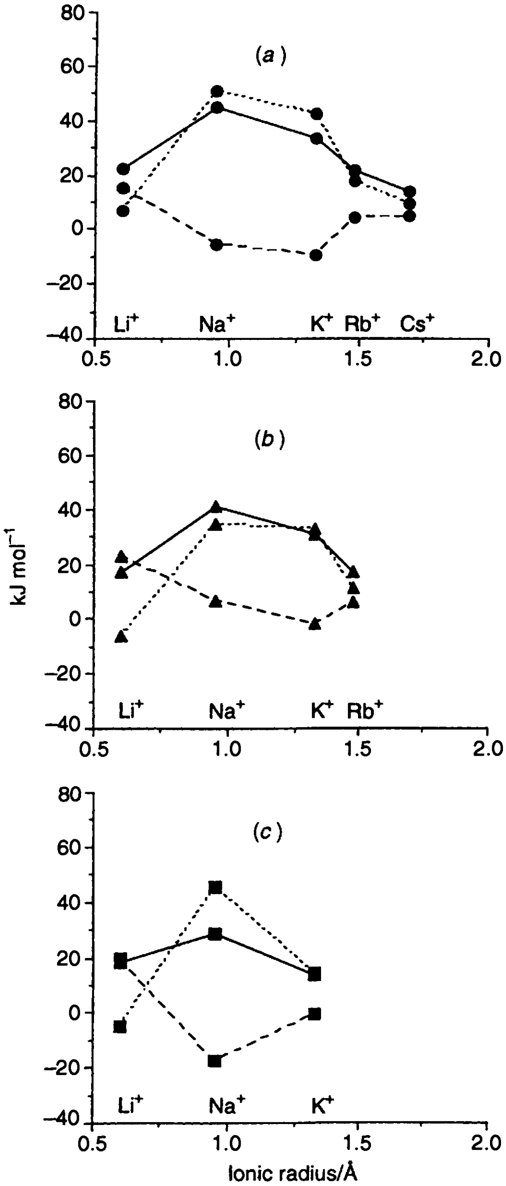

Fig. 2 Variation of the thermodynamic parameters ΔG_c, ΔH_c and $T\Delta S_c$ in methanol *vs.* the cation ionic radius *r* for the complexation of alkali cations by (*a*) ligand **1**, (*b*) ligand **2** and (*c*) ligand **12**: (——) $-\Delta G_c$; (· · · ·) $-\Delta H_c$; (— — —) $T\Delta S_c$

Secondly, for the ethylester **12**, which is strictly comparable to **1** only, the trend in ΔH_c is similar, with a maximum for Na^+, but the enthalpy terms are always less negative, especially with K^+. This could be partly due to the lower basicity of the carbonyl groups in esters. There is also a decrease in $T\Delta S_c$ from Li^+ to Na^+, followed by an increase for K^+.

Thirdly, the greater stability of $Na1^+$ over $Na12^+$ complexes is due to a more favourable ΔH_c value (−50.6 instead of −45.60) and to a less unfavourable ΔS_c (−18.7 instead of −57.2). The extra stabilisation of $K1^+$ with respect to $K12^+$ is due to an enthalpy effect only, which overcomes an even more unfavourable entropy term. Thus the lower Na/K selectivity of amides is mainly due to the high ΔH_c value for the K^+ complex.

Complexation of alkali cations by **1** *in acetonitrile.* For Li^+, Na^+ and K^+ it was possible to determine a lower limit only of $\log\beta$ and consequently of $-\Delta G_c$ and $T\Delta S_c$ because of the excessive stability of these complexes in this solvent. This limit (8.5 log units) corresponds to the highest $\log\beta$ value which could be derived from competition reactions with Ag^+. In the case of Cs^+, ΔH_c was obtained either by simultaneous refinement of ΔH_c, $\log\beta$ and the enthalpy of dilution of the cation, or from displacement reaction (1), produced by titrating

$$Cs1^+ + Na^+ \longrightarrow Na1^+ + Cs^+ \qquad (1)$$

a mixture of 1 : 50 molar ratio of ligand and caesium iodide with a solution of $NaClO_4$. As the sodium complex is much stronger than the caesium complex, one can assume, at each point of the titration, that the formation of $Na1^+$ is quantitative and that the heat evolved is directly related to the difference ΔH_c ($Na1^+$) $-\Delta H_c$ ($Cs1^+$). The values of ΔH_c ($Cs1^+$) obtained by these two methods fully agreed and the mean value is given in Table 3. The stability order for the alkali complexes of **1** in acetonitrile is, strictly speaking, reduced to the following sequence: $K^+ > Rb^+ > Cs^+$.

However, it was possible to measure in each case the enthalpies of complexation (Table 3), which were all favourable. As in methanol, there is an exothermic maximum for Na^+. As regards to the entropy changes along the series, it is not possible to draw any firm conclusions as only lower limits are available for the first three cations. Nevertheless, when these limits are considered [Fig. 3(*a*)], a decrease can be noticed from Li^+ to Na^+ followed by an increase for K^+ and Rb^+. For Rb^+ and Cs^+, the entropy terms, which are in these cases accurately determined, are of the same order of magnitude and slightly unfavourable. In the case of the tetraethylester **12** in the same medium [Fig. 3(*b*)],[12] a similar type of variations had been found for $-\Delta H_c$ and $T\Delta S_c$, although $-\Delta H_c$ values were much lower. The ΔS_c values become more unfavourable going from Li^+ to Na^+ and thereafter increase for the larger cations.

Comparison between methanol and acetonitrile. Figs. 2 and 3 enable the comparison of the thermodynamic parameters for the amide derivative **1** in methanol and acetonitrile. With the amide **1**, the stability of the complexes, $-\Delta G_c$, is always higher in acetonitrile than in methanol, especially for the lithium complex. $-\Delta H_c$ values are also higher and thus more favourable, in acetonitrile whereas $T\Delta S_c$ values, where they could be well established, are always lower, becoming even unfavourable. Therefore the higher stability of the complexes in acetonitrile is of enthalpic origin. On the other hand, the variations of $-\Delta H_c$ along the series have the same patterns in methanol as in acetonitrile, with a maximum at Na^+. As regards to the variations of $T\Delta S_c$, no strict comparison can be made as only limit values are available for Li^+, Na^+ and K^+ in acetonitrile, although it also seems to display a minimum (see above).

In contrast, with the ester **12** [Figs. 2(*c*) and 3(*c*)], the stabilities of the complexes are not always higher in acetonitrile than in methanol. If there is still a dramatic increase in stability with Li^+, the Rb^+ complex is less stable in acetonitrile and the Cs^+ complex has the same stability in both solvents. Here again it is difficult to compare further ΔH_c and $T\Delta S_c$ values, as they could not be determined in methanol for Rb^+ and Cs^+. However, where the data are available, $-\Delta H_c$ is higher and $T\Delta S_c$ lower in acetonitrile than in methanol, as was observed with the amide complexes. Moreover, the variations of $-\Delta H_c$ and $T\Delta S_c$ in both solvents display a maximum and a minimum at Na^+, respectively.

From these observations different questions can be addressed: (1) why are $-\Delta H_c$ and $T\Delta S_c$, respectively, higher and lower in acetonitrile than in methanol; (2) how does one explain the variation of $-\Delta H_c$ and $T\Delta S_c$ in the series for a given ligand; (3) what is the origin of the higher stability of Li^+ complexes in acetonitrile?

As stated by Lehn *et al.*,[19] the enthalpies of complexation are a measure of the changes in energy of the bonds between the cation and either the ligand or the solvent, the changes in inter-

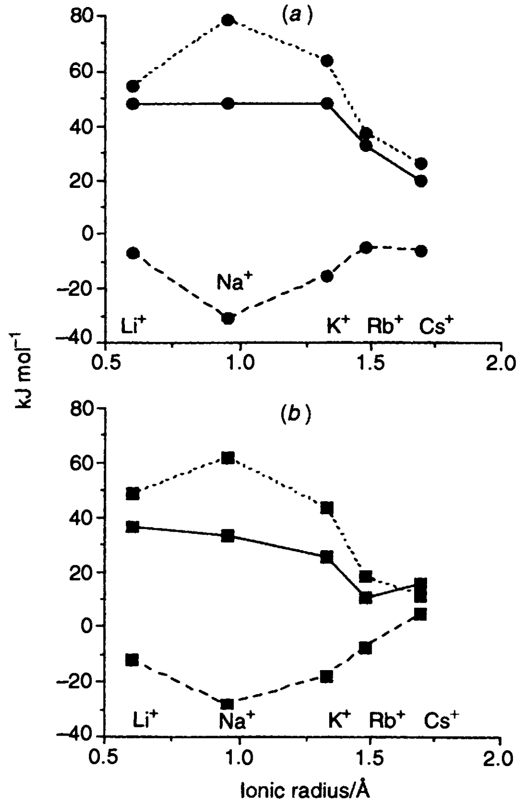

Fig. 3 Variation of the thermodynamic parameters ΔG_c, ΔH_c and $T\Delta S_c$ in acetonitrile *vs.* the cation ionic radius *r* for the complexation of alkali cations by (*a*) ligand **1** and (*b*) ligand **12**: (——) $-\Delta G_c$; (· · · ·) $-\Delta H_c$; (— — —) $T\Delta S_c$

binding site repulsion, the ligand solvation and its steric deformation by the cation. The entropy terms are mainly related to conformational changes and solvation effects, which involve the solvation of the cation, the ligand and the complexes. The answer to the first question should be mainly related to the solvation of the cation and of the ligand. In acetonitrile, the ligands and cations are expected to be less solvated than in methanol, in agreement with the Gutmann's donor numbers of the solvents (14.1 and 23.5, respectively).[20] Accordingly, the cation–ligand interactions are favoured in acetonitrile over the cation–solvent and the ligand–solvent interactions, resulting in more favourable enthalpies. The entropy changes in the aprotic solvent are lower mainly because of the less important release of solvent molecules upon complexation in acetonitrile. However, when looking more closely at the solvation of the cations along the series, the logarithms of the transfer activity coefficients, log γ, from methanol to acetonitrile, is very high for Li^+ (4.55) and then decreases for Na^+ (0.95), K^+ (−0.37), Rb^+ (−0.59) and Cs^+ (−0.81).[21] This means that K^+, Rb^+ and Cs^+ are slightly more solvated in acetonitrile than in methanol and thus slightly less favourable to the cation–ligand interactions. Moreover, going from methanol to acetonitrile with ester **12**, does not lead to an increase of stability of the Rb^+ and Cs^+ complexes. These results suggest that, with the amide derivative, the lower solvation of the ligand in acetonitrile should be the predominant factor to explain the higher stability of the complexes in this solvent. According to Wipff's molecular dynamic simulations,[14] the fact that acetonitrile does not solvate carbonyls as much as methanol does, allows the complexes to adopt mostly 'closed type' structures where the cation is shielded from the solvent. No simulation has been made in methanol, but the properties of methanol are very close to those of water and to a first approximation we can reasonably transpose to methanol the results of the simulations in water.

With regard to the second question, the solvation of the cation in methanol as well as in acetonitrile, within the alkali series, decreases in going from Li^+ to Cs^+. By assuming a total desolvation of the cations upon complexation, one would expect a decrease of ΔS_c from Li^+ to Cs^+. With ligand **1**, this is observed in fact for the first three cations only and not for the larger ones.

When comparing the stability of a series of complexes of the same ligand in a given solvent, the solvation of this ligand has of course not to be considered. On the contrary, the solvation of the complex, which certainly differs from that of the free ligand, should be an important factor to be taken into account. The complex is likely to interact with the solvent through the complexed cation, at the lower rim, and at the upper rim by inclusion of a solvent molecule in the lipophilic cone. With increasing cation size, the structures of the complexes become more likely to be 'open', making possible the interaction of the cation with the solvent. This assumption, supported by molecular dynamics simulations in water,[13] would result in an increase of the solvation of the complexes from Li^+ to Cs^+ and hence an additional loss in entropy especially for the larger cations. Such an effect is however not observed experimentally. The inclusion of one molecule of solvent at the upper rim is well known from crystallographic studies of calix[4]arene derivatives.[22] In solution, NMR studies of the tetraethylester **12** in acetonitrile showed a 'shaping effect' which may result from the presence of one acetonitrile molecule inside the cone.[12] Moreover, molecular dynamic simulations on the tetradiethylamide in water and acetonitrile are consistent with the presence of one molecule of solvent inside the cone of the ligand in all the complexes except the Li^+ complex in water.[13,14] Thus in both solvents, except in the case of Li^+ in methanol, the change in solvation (at the upper rim) between the ligand and the complexes should be constant along the series and there may be no particular entropy contribution from these effects.

Therefore it is clear that the different solvation effects as depicted above cannot account alone for the entropy variation along the alkali series, at least after K^+. On the other hand, molecular dynamics simulations in water show that a complex in solution can be seen as an equilibrium between several conformations, the number and the stability of which should increase when going from Li^+ to Cs^+. In other words, the degrees of freedom of the systems ligand–cation would increase with the size of the cation, resulting in an entropy gain along the series. This effect might be responsible for the trend in entropy change on going from Na^+ to K^+ for the tetraethylester in methanol, and from K^+ to Rb^+ and Cs^+ for the corresponding amide derivative (ligand **1**) in the same solvent.

As regards to the enthalpy variations in the series, the interactions between the donor sites of the ligand and the cation are expected to become weaker with the increasing size of the cation, *i.e.* decrease in charge density, and the solvation of the carbonyls is expected to be higher, resulting in a decrease of the enthalpies of complexation for the larger cations. Moreover, results of molecular dynamics simulations concerning the contribution of the carbonyls to the binding of the cation have been explained assuming optimal linear arrangements with only small cations and more 'tangential coordination' with larger cations.[13,14]

Concerning the third question, Li^+ seems to show exceptional behaviour, whatever the ligand and the solvent. First, the entropic contribution is always much higher for the lithium complexes than for the other complexes. In methanol the stability is even entropy controlled for $Li2^+$ and $Li12^+$. This property can be related to the importance of solvation of this smallest cation. With the ester derivative **12**, there is also a

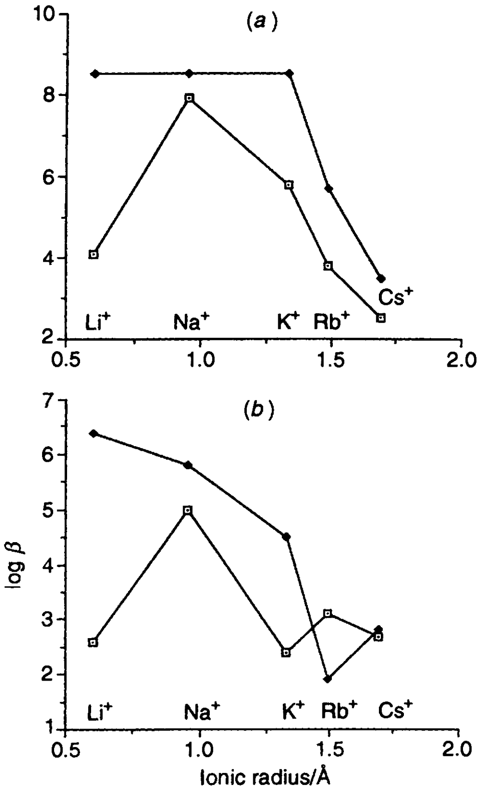

Fig. 4 Comparison of the logarithms of the stability constants β in methanol (□) and acetonitrile (◆) for alkali complexes of (*a*) ligand **1** and (*b*) ligand **12**

change in the selectivity pattern from methanol to acetonitrile, due in particular to the high stability of the Li^+ complex in acetonitrile [Fig. 4(*b*)]. With the amide derivative **1**, it is difficult to draw firm conclusions since only lower limits of $\log\beta$ are available for Li^+, Na^+ and K^+. Nevertheless the stability of the Li^+ complex is much higher than in methanol. This corresponds to a dramatic increase of $-\Delta H_c$.

Complexation of alkaline-earth cations in methanol. In the case of Sr^{2+} which forms a strong complex with ligand **2** ($\log K = 8.1$), no measurable heat other than heat of dilution was observed, which should be an indication that $-\Delta H_c$ is very close to zero. With calcium and strontium and ligand **1**, only a lower limit of the entropy of complexation can be given, $-\Delta G_c$ being too high to be accurately determined either by spectrophotometry or competitive potentiometry. With both ligands, the heat generated by complexation of magnesium was not sufficient to allow the determination of ΔH_c.

With both ligands and all the alkaline-earth cations studied, the complexation process is entropy controlled. For Ca^{2+} and Sr^{2+} and ligand **1** and Ca^{2+} with **2**, the stabilization also results from favourable enthalpy terms. However the absolute value of the enthalpy, which is much lower than for alkalis, decreases in the series as expected from the diminishing charge density with the increasing size of the cation and ΔH_c becomes even positive, hence unfavourable, with Ba^{2+}. ΔS_c values increase with the increasing size of the cations for compound **2**. These trends are more difficult to assess with ligand **1** as only lower limits can be given for ΔS_c values in the case of Ca^{2+} and Sr^{2+}. The slight Sr^{2+} over Ca^{2+} selectivity of ligand **2** is due to a more favourable entropy term.

The low values of enthalpy for both ligands with alkaline-earth cations could be explained by the importance of the solvation of these cations in methanol. The energy gain from the ligand–cation interactions is of the same order of magnitude as the energy expense for the cation desolvation. At the same time, the high number of solvent molecules released from the cations upon complexation gives reason for the high values of entropy.

The trends of enthalpy and entropy changes along the series can be explained by the same observations as those made for the alkali cations.

Conclusions

The extracting and complexing properties of nine new calixarene-amides (compounds **3**–**11**) have been investigated in order to see if the complexation abilities and selectivities could be modulated by changing the nature of the substituents on the nitrogen atoms of the amide functions. Remarkable differences are observed in the extraction profiles of derivatives bearing substituents with different electronic properties, whereas similar profiles are noticed when the substituents have similar electronic properties, as in the case of the alkyl derivatives. The solution calorimetric study, carried out with the two compounds **1** and **2**, shows the importance, not always considered as it should be, of the ligand solvation in the complexation process. The higher stability of **1** in acetonitrile with respect to methanol is mainly explained by the interactions between the carbonyls and the solvent, which are higher in methanol than in acetonitrile. Another interesting observation is the good agreement between our experimental results and the conclusions drawn from computer investigations on similar systems. For example, the new idea that a complex could be seen as an equilibrium between different conformations could perfectly explain the trends found for the entropy changes in methanol. These results show that molecular dynamic simulations, while they should not be seen as a microscopic picture of reality, do provide a valid support for the interpretation of experimental data.

Acknowledgements

Part of this work has been performed within the European Union RTD Programme on Nuclear Waste Management and Storage (Contract F12W-CT90-0062). The authors thank the EU for financial support.

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Paper 4/06123C
Received 7*th October* 1994
Accepted 28*th October* 1994