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Hydrogen Bonding and Solvent Effects on Complexation of Alkali Metal Cations by Lower Rim Calix[4]arene Tetra(*O*-[*N*-acetyl-D-phenylglycine methyl ester]) Derivative

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Abstract

Complexation of alkali metal cations with 5,11,17,23-tetra-*tert*-butyl-26,28,25,27-tetrakis(*O*-methyl-D-α-phenylglycylcarbonylmethoxy)calix[4]arene (**L**) was studied by means of spectrophotometric, conductometric and potentiometric titrations at 25 °C. The solvent effect on the binding ability of **L** was examined by using two solvents with different affinities for hydrogen bonding, viz. methanol and acetonitrile. Despite the presence of intramolecular NH···O=C hydrogen bonds in **L**, which need to be disrupted to allow metal ion binding, this calix[4]arene amino acid derivative was shown to be an efficient binder for smaller Li^+ and Na^+ cations in acetonitrile (lg $K_{\mathrm{Li}\mathbf{L}} > 5$, lg $K_{\mathrm{Na}\mathbf{L}} = 7.66$), moderately efficient for K^+ (lg $K_{\mathbf{KL}} = 4.62$), whereas larger Rb^+ and Cs^+ did not fit in its hydrophilic cavity. The complex stabilities in methanol were significantly lower (lg $K_{\mathrm{Na}\mathbf{L}} = 4.45$, lg $K_{\mathbf{KL}} = 2.48$). That could be explained by different solvation of the cations and by competition between the cations and methanol molecules (via hydrogen bonds) for amide carbonyl oxygens. The influence of cation solvation on complex stability was most pronounced in the case of Li^+ for which, contrary to the quite stable $\mathrm{Li}\mathbf{L}^+$ complex in acetonitrile, no complexation was observed in methanol under the conditions used.

Introduction

Calixarene derivatives are capable of host-guest interactions with different ions and neutral molecules [1–5]. Their ionophoric affinity towards metal cations depends on the substituents on phenolic oxygens forming a hydrophilic cavity at the calixarene lower rim, as well as on the size of the cavity. The size is mainly determined by the number of the repeating phenolic units comprising the macrocycle. The most common are calix[4]arene and calix[6]arene derivatives. Among the alkali metal cations the former have been shown to strongly bind smaller cations (Li^+, Na^+), whereas the latter are more selective with respect to the larger ones. Calixarenes with carbonyl-containing substituents, which include calixarene ketones, esters or amides, are effective receptors for alkali and alkaline-earth cations. In derivatives having substituents with both a hydrogen-bond acceptor (carbonyl group) and a hydrogen-bond donor (e.g. –NH– group in secondary amides), circular intramolecular hydrogen bonds are formed which have a strong influence on their ionophoric activity [6–12]. A few calix[4]arene derivatives of this kind carrying amino acid or peptide substituents have been recently suggested [9] to serve as synthetic models for the selectivity filter of the potassium channel in the cell membrane. The calix[4]arene investigated in the present paper, namely 5,11,17,23-tetra-*tert*-butyl-26,28,25,27-tetrakis-(*O*-methyl-D-α-phenylglycylcarbonylmethoxy)calix[4]arene (**L**, Figure 1) [7], is also an amino acid derivative. The structure of that compound in chloroform was investigated by means of IR and NMR techniques. It was shown to exist in stable cone conformation with a noncovalently organized cavity at the lower rim which was formed by circular intramolecular amidic NH···O=C hydrogen bonds. The ^{1}H NMR studies of Na^+ and K^+ complexation with **L** led to the conclusion that intramolecular hydrogen bonds were broken upon complexation (Figure 1). Competition between the cation and NH protons for amide carbonyl oxygen atoms was suggested to play an important role in the complexation process. The X-ray structure analysis of the $[\mathrm{Na}\mathbf{L}]ClO_4$ complex revealed sodium ion coordination by four ether and

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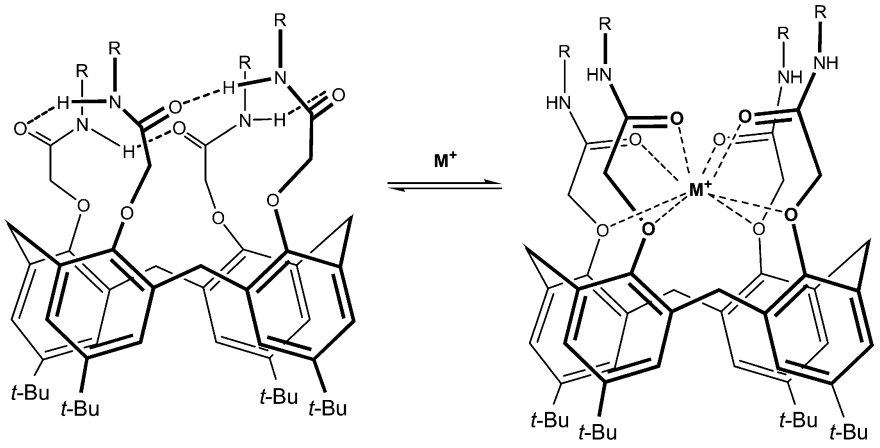

R = $CHPhCOOCH_3$

Figure 1. Schematic presentation of the complexation of metal ion by calix[4]arene derivative **L** (cf. [6, 9]).

four carbonyl oxygen atoms from four amino acid subunits [7].

In this paper the investigations have been extended to quantitative comparison of the abilities of **L** for binding different alkali metal cations using spectrophotometric, conductometric and potentiometric methods. The solvent effect on the binding properties of **L** has also been a matter of our interest. For that purpose two solvents with different affinities for hydrogen bonding, i.e. methanol and acetonitrile, were examined.

Experimental

Materials

5,11,17,23-tetra-*tert*-butyl-26,28,25,27-tetrakis-(*O*-methyl-D-α-phenylglycinecarbonyl-methoxy)calix[4]arene was prepared according to the procedure described elsewhere [7]. The solvents, methanol (Aldrich, spectrophotometric grade) and acetonitrile (Merck, Uvasol) were used without further purification. The ionic strength was kept constant by addition of Et_4NCl (Fluka) and Et_4NClO_4 (Fluka) in methanol and acetonitrile solutions, respectively. The salts used for the investigation of **L** complexation in methanol were chlorides (LiCl, NaCl, KCl, CsCl, Merck, p.a.; RbCl, Aldrich, 99+%). Perchlorates ($LiClO_4$, $NaClO_4$, $KClO_4$, Merck, p.a.) and nitrates ($RbNO_3$, Merck, p.a.; $CsNO_3$, Merck, puriss.) were used for titrations in acetonitrile.

Spectrophotometry

UV titrations were performed at (25.0 ± 0.1) °C by means of a Varian Cary 5 spectrophotometer equipped with a thermostatting device. The spectral changes of **L** solution (V_0 = 2.0 cm^3; $c = 1 \times 10^{-4}$ to 2.4×10^{-4} mol dm^{-3}, I_c = 0.01 mol dm^{-3}) were recorded upon stepwise addition of an alkali salt solution ($c = 10^{-3}$ to 10^{-2} mol dm^{-3}, I_c = 0.01 mol dm^{-3}) directly into the measuring quartz cell (l = 1 cm). In some cases spectrophotometric titrations were performed under the same conditions using optical fibres (V_0 = 20.0 cm^3, l = 1 cm). Absorbances were sampled at 1 nm intervals. Titrations for each M^+/**L** system were repeated three or four times. The obtained spectrophotometric data were processed using the SPECFIT program [13].

Conductometry

Conductometric titrations were carried out at (25.0 ± 0.1) °C by means of a Jenway 4020 conductometer. The cell constant, (1.060 ± 0.001) cm^{-1}, was determined using 0.1 mol dm^{-3} aqueous KCl solution. The alkali salt solution (V_0 = 20.0 cm^3, $c_0 = 1 \times 10^{-4}$ to 2×10^{-4} mol dm^{-3}) was titrated with ligand solution (1×10^{-3} mol dm^{-3}) in a closed, thermostatted titration vessel up to the n(**L**)/n(M^+) ratio of approximately 5. The measured conductivities were corrected for the conductivity of the solvent.

Potentiometry

The stability constant of NaL^+ complex in acetonitrile was determined by potentiometric titration of 30.0 cm^3 $NaClO_4$ solution ($c_0 = 1 \times 10^{-4}$ mol dm^{-3}) with solution of **L** ($c = 1 \times 10^{-3}$ mol dm^{-3}) in a thermostatted titration vessel. The ionic strength of both solutions was set to 0.01 mol dm^{-3} by Et_4NClO_4. A sodium-selective glass electrode (Metrohm) was used as indicator electrode, and the reference electrode, Ag/AgCl (Metrohm), was filled with 0.01 mol dm^{-3} Et_4NCl solution in acetonitrile. The working and reference half-cells were connected with a salt bridge containing 0.01 mol dm^{-3} Et_4NClO_4 and were thermostatted at (25.0 ± 0.1) °C. A Methrohm 713 pH meter was used for the emf. measurements. The cell was calibrated by the incremental addition of $NaClO_4$ solution (0.01 mol dm^{-3}) to 30.0 cm^3 of 0.01 mol dm^{-3} solution of Et_4NClO_4. The

Nernst-like behaviour was observed, with the slope of emf. vs p[Na] plot being for all experiments about −58 mV. Titration was repeated three times and the obtained data were analysed with the SUPERQUAD program [14].

Results and discussion

Stability constants of the 1:1 NaL^+ and KL^+ complexes in methanol were determined spectrophotometrically. Stepwise addition of NaCl or KCl solutions into ligand solution led to a hypochromic effect on the larger part of the ligand UV spectrum, accompanied by the occurrence of well-defined isosbestic point(s). As an example, spectrophotometric titration of **L** with Na^+ is shown in Figure 2. Stability constants calculated by processing titration data are given in Table 1. Addition of Li^+, Rb^+ or Cs^+ chlorides into methanol calixarene solution had no significant effect on the absorbance of L, indicating that no observable complexation took place. To check these findings, complexation was also followed by conductometric titrations of alkali metal salt solutions with **L**. In agreement with the spectrophotometric observations, there were no significant changes in molar conductivities of LiCl, RbCl and CsCl solutions upon addition of **L**.

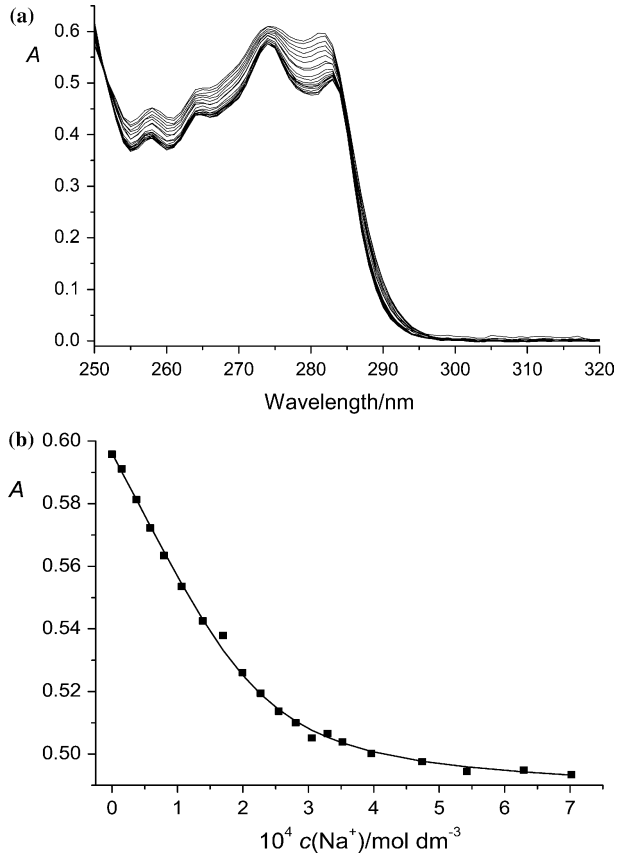

Figure 2. (a) Spectrophotometric titration of **L** ($c = 2.38 \times 10^{-4}$ mol dm^{-3}) with NaCl in methanol. $l = 1$ cm; $I_c = 0.01$ mol dm^{-3} (Et_4NCl); $t = (25.0 \pm 0.1)$ °C; $c(Na^+) = 0$ (top curve) -7.64×10^{-4} mol dm^{-3} (bottom curve); the spectra are corrected for dilution. (b) Dependence of absorbance at 282 nm on NaCl concentration. ■ experimental;—calculated.

Table 1. Stability constants of complexes of alkali cations with **L** in methanol and acetonitrile. $I_c = 0.01$ mol dm^{-3}; $t = (25.0 \pm 0.1)$ °C

Cation	lg (K/mol^{-1} dm^3) ± SE	
	Methanol	Acetonitrile
Li^+	–[a]	>5[c]
Na^+	4.45 ± 0.02[b]	7.66 ± 0.01[d]
K^+	2.48 ± 0.03[b]	4.62 ± 0.06[b]
Rb^+	–[a]	–[a]
Cs^+	–[a]	–[a]

[a] Addition of Li^+, Rb^+ and Cs^+ salts into calixarene solution had no significant effect on the absorbance of **L**. Likewise, in conductometric titrations of Li^+, Rb^+ and Cs^+ solutions with **L** no significant changes of molar conductivity were observed.[b] Spectrophotometric determination.[c] Estimated by spectrophotometry and conductometry. [d] Potentiometric determination.SE = standard error of the mean.

The UV spectral changes observed upon addition of $LiClO_4$, $NaClO_4$ or $KClO_4$ to **L** acetonitrile solution were basically similar to those described above. The only stability constant we were able to determine by spectrophotometric titration in acetonitrile was that of the KL^+ complex (Table 1). In the titrations of **L** with $LiClO_4$ and $NaClO_4$ a linear relationship of A (corrected for dilution) vs $n(M^+)$ was observed up to the ratio $n(M^+)/n(\mathbf{L}) \approx 1$ (n denotes total amount), followed by a break in the titration curve (Figure 3). That indicated strong complexation and formation of 1:1 (M^+:**L**) complexes (corresponding stability constants could only be estimated, Table 1). These results were confirmed by conductometric titrations where molar conductivity decreased almost linearly with the amount of ligand added. At the ratio $n(\mathbf{L})/n(M^+) \approx 1$ a break in the titration curve was again noted (Figure 4). Decrease in molar conductivity was due to lower electric mobility of the larger ML^+ complex compared to the free cation. As the size of the conducting complex is mainly determined by the (large) size of the ligand, the molar conductivities of different ML^+ complexes could be expected to be similar. Indeed, the molar conductivity assessed from the conductivity data after the break point (Figure 4) was approximately 120 S cm^2 mol^{-1} for both $[LiL]ClO_4$ and $[NaL]ClO_4$.

The addition of Rb^+ and Cs^+ into acetonitrile calixarene solution did not cause any significant changes in its UV spectrum. There was, likewise, almost no change in molar conductivities of $RbNO_3$ and $CsNO_3$ during titration of their acetonitrile solutions with **L**. Both findings led to the same conclusion as in the case of methanol, i.e. complexation between larger cations and **L** was weak or non-existent.

As the stability constant of the NaL^+ complex in acetonitrile was too high for spectrophotometric determination, direct potentiometry using a sodium-selective glass electrode was applied (Table 1). In Figure 5, the potentiometric curve representing the titration of

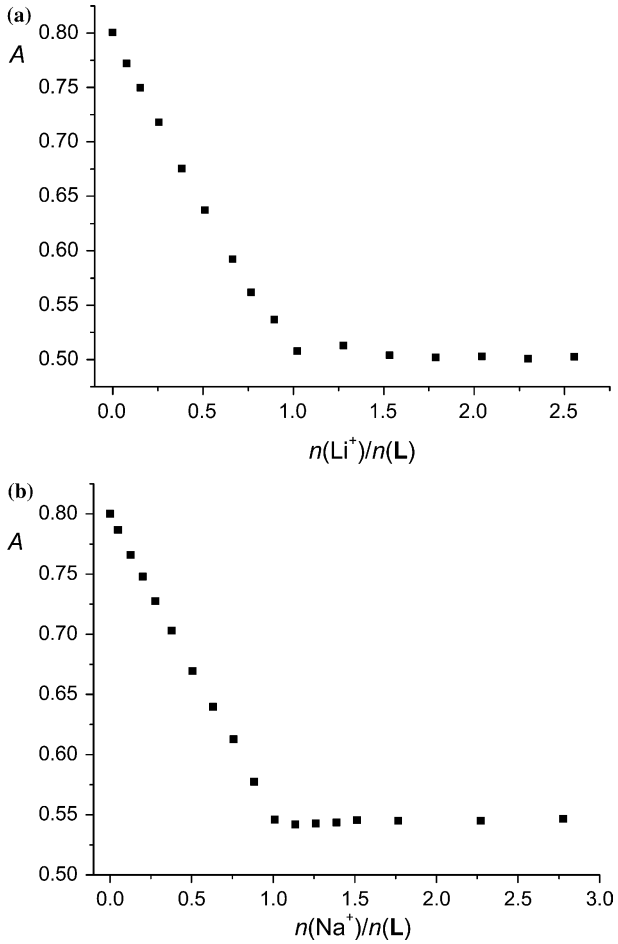

Figure 3. Dependence of **L** solution absorbance at 282 nm on (a) $n(LiClO_4)/n(\mathbf{L})$ ratio, (b) $n(NaClO_4)/n(\mathbf{L})$ ratio. Solvent: acetonitrile; l = 1 cm; I_c = 0.01 mol dm^{-3} (Et_4NClO_4); t = (25.0 ± 0.1) °C.

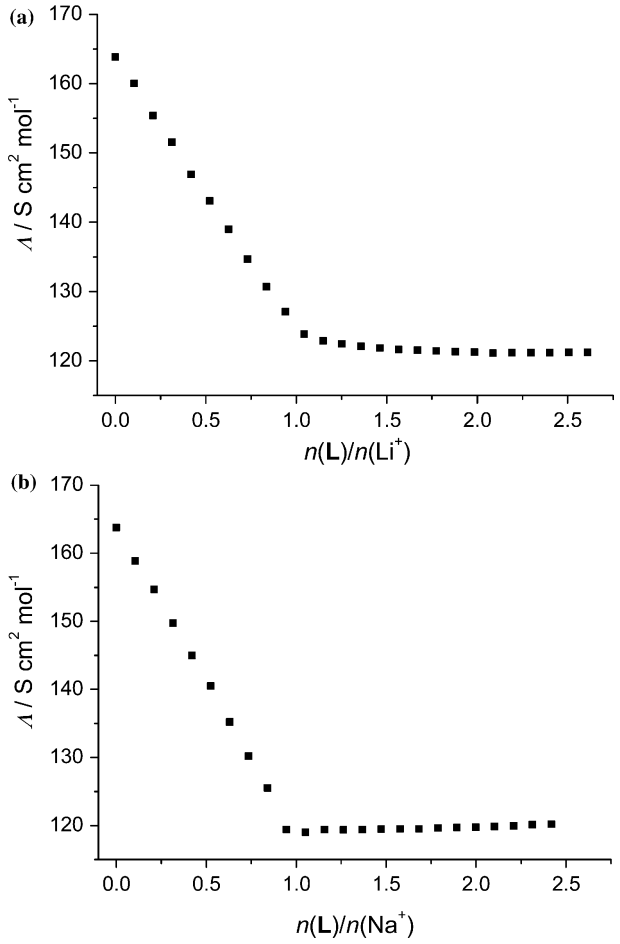

Figure 4. Conductometric titration of (a) $LiClO_4$, (b) $NaClO_4$with **L** in acetonitrile; t = (25.0 ± 0.1) °C.

$NaClO_4$ with **L** shows a p[Na] jump at the 1:1 **L**/Na^+ ratio, which agrees with the results of spectrophotometric and conductometric measurements.

In order to compare the binding affinity of **L** for alkali cations with that of some other calix[4]rene derivatives (amides, ester and ketones) [15–19], the corresponding stability constants are listed in Table 2. It should be noted that in some cases there is a serious disagreement between the data obtained by various authors using different techniques to follow the complexation. The problem has been pointed out by de Namor et al. [3, 20] who argued that many thermodynamic data for calixarene-cation systems needed to be revisited. Although we agree with that, in this work we rely on the data available in the literature to assess the difference in ionophoric activities between several calix[4]arenes with respect to the nature of the substituents at their lower rim.

The data presented in Table 2 indicate that the complexes of alkali cations with tertiary amide derivatives of calix[4]arene are more stable than those with the ketone or ester derivatives in either methanol or acetonitrile. That can be explained by the increased basicity of the amide carbonyl oxygens. However, although herein investigated calixarene is also an amide derivative, the $\mathbf{ML}^+$ stability constants are considerably lower than those of the tertiary amide complexes. The reason can be found in the presence of circular intramolecular hydrogen bonds mentioned earlier, which need to be disrupted in order to allow change in orientation of amide groups into a position favourable for complexation. Consequently, competition between the cations and NH protons for amide carbonyl oxygen atoms leads to lower stability of the complexes formed [6–12] which appears to be comparable to that of ketone and ester derivatives (Table 2).

A strong influence of the solvent on the complexing properties of calix[4]arenes can be seen by inspecting the data in Tables 1 and 2. The stability constants in acetonitrile are generally several orders of magnitude higher than in methanol. That is mainly due to the different solvation of the species taking part in the complexation reaction, i.e. free cation, free ligand, and complex. In the case of **L** in acetonitrile, which is characterized by a proton-accepting property, one could expect the formation of intermolecular hydrogen bonds with amide NH-groups leading to the weakening of intramolecular NH···O=C bonds and hence making carbonyl oxygens available for complexation of the metal ion. On the contrary, methanol with its proton-donating ability has an opposite effect. By forming hydrogen bonds with

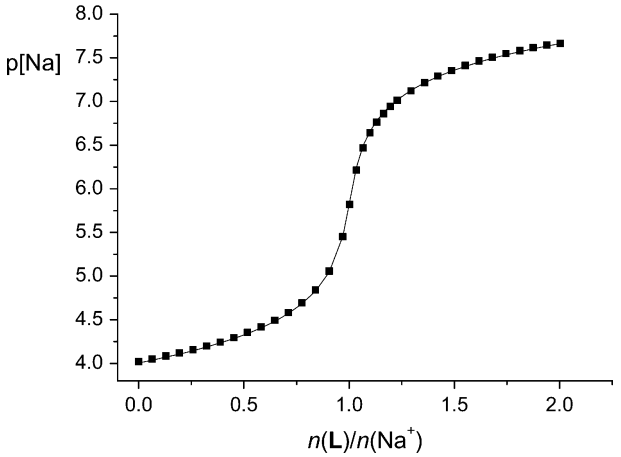

Figure 5. Potentiometric titration of $NaClO_4$ with **L** in acetonitrile. $c_0(Na^+) = 1 \times 10^{-4}$ mol dm^{-3}; $V_0 = 30.0$ cm^3; $c(\mathbf{L}) = 9.7 \times 10^{-4}$ mol dm^{-3}; $I_c = 0.01$ mol dm^{-3} (Et_4NClO_4); $t = (25.0 \pm 0.1)$ °C. ■ experimental: — calculated.

Table 2. Stability constants of complexes of alkali cations with different calix[4]arene derivatives in methanol and acetonitrile at 25 °C

R[a]	Lg (K/mol^{-1} dm^3)									
	Methanol					Acetonitrile				
	Li^+	Na^+	K^+	Rb^+	Cs^+	Li^+	Na^+	K^+	Rb^+	Cs^+
I	3.9[b]	7.9[b]	5.8[b]	3.8[b]	2.4[b]	≥8.5[c]	≥8.5[c]	≥8.5[c]	5.7[c]	3.5[c]
II[b]	2.98	7.16	5.4	3.0	≤1					
III[d]	2.6	5.0	2.4	3.1	2.7	6.4 6.1[e]	5.8 7.53[e]	4.5 4.04[e]	1.9 2.05[e]	2.8 –[e, f]
IV[d]	2.7	5.1	3.1	3.6	3.1	5.8	5.6	4.4	1.7	3.7 –[f, g]
V[d]						6.3	6.1 8.89[g]	5.1	4.5	5.6 –[f, g]
VI[h]	–[f]	4.45	2.48	–[f]	–[f]	> 5	7.66	4.62	–[f]	–[f]

[a] Substituents on phenolic oxygens: **I** = $-CH_2CON(C_2H_5)_2$; **II** = $-CH_2CON(CH_2)_4$; **III** = $-CH_2COOC_2H_5$; **IV** = $-CH_2COCH_3$; **V** = $-CH_2COPh$; **VI** = $-CH_2CONHCHPhCOOCH_3$. [b] Ref. [15]. [c] Ref. [16]. [d] Ref. [17]. [e] Ref. [18]. [f] No complexation was observed. [g] Ref. [19]. [h] This work.

amide carbonyl oxygens, methanol molecules efficiently compete with the cation for its binding sites. As a result, the stability constants are lower in methanol than in acetonitrile solutions. The influence of cation solvation is most pronounced in the case of lithium complexation by **L**. While LiL^+ is very stable in acetonitrile, its presence has been hardly observed in methanol solutions, or not at all (Table 1). As a hydrogen bonding solvent, methanol strongly solvates small cations [21], thus making substitution of its molecules by ligand binding sites thermodynamically unfavourable. The difference in solvation of a solute in various media can be quantitatively estimated by means of the respective Gibbs energies of transfer ($\Delta_t G$) from one solvent to another. The $\Delta_t G$/kJ mol^{-1} values for transfer of alkali cations from methanol to acetonitrile are: Li^+, 25.9; Na^+, 5.4; K^+, −2.1; Rb^+, −3.3; Cs^+, −4.6. The values were calculated by combining Gibbs energies of transfer of cations from water to methanol or acetonitrile tabulated in Ref. [22] ($\Delta_t G$(MeOH–MeCN) = ($\Delta_t G$(H_2O–MeCN)–$\Delta_t G$(H_2O–MeOH)). These data suggest that the solvation of the lithium ion is much stronger in MeOH than in MeCN, that sodium ion solvation is still stronger in MeOH, but that the opposite holds for the other alkali cations. Therefore, the low affinity of **L** towards Li^+ in methanol as compared to acetonitrile can be partly accounted for by the relatively strong solvation of this cation in MeOH. Naturally, the cation solvation effect is present in the complexation of the other alkali metal ions, but it is not as dominant as in the case of lithium.

When comparing stabilities of different ML^+ complexes in the same solvent, apart from cation solvation, that of the complex should also be taken into account. We cannot say much about this aspect on the basis of the data presented in this paper. However, closeness of molar conductivities (which are affected by solvation) of the LiL^+ and NaL^+ complexes (Figure 4) do not indicate a significant difference in solvation between the two species.

Another well-known factor with a direct impact on complex stability is compatibility of the cation and calixarene hydrophilic cavity sizes. As seen in Table 1, ligand **L**, being calix[4]arene, accepts well smaller cations, i.e. Li^+ (in MeCN) and Na^+. Its affinity towards K^+ is moderate, whereas Rb^+ and Cs^+ are too large to fit into the hydrophilic cavity. Ligand selectivity for one particular cation with respect to others is usually expressed as the ratio of the stability constants of the corresponding complexes. Here we compare the binding affinity of **L** for Na^+ to its affinity for the other alkali cations in the two solvents. According to Table 1, Na^+/Li^+, Na^+/Rb^+ and Na^+/Cs^+ selectivities are very high in methanol, while the K_{NaL}/K_{KL} ratio is approximately 100. As only the lower limit of the LiL^+ stability constant in acetonitrile could be estimated, it is hard to assess even semiquantitatively Na^+/Li^+ selectivity in this solvent. However, **L** remains to be very selective for Na^+ with respect to Rb^+ and Cs^+. The Na^+/K^+ selectivity, possibly the most interesting one, is almost ten times higher in acetonitrile (about 1000) than in methanol. That can be explained by means of the effect of free cation solvation assuming that a possible difference between solvations of NaL^+ and KL^+ complexes in a given solvent can be neglected. Since the hydrophilic cavity is more suitable for accommodating Na^+ than K^+ in either solvent, the higher selectivity for sodium in acetonitrile is due to a smaller difference in the extent of Na^+/K^+ solvation in this solvent than in methanol, as seen from the transfer Gibbs energies given above.

Conclusion

Due to the presence of intramolecular NH···O=C hydrogen-bonding organization the investigated calix[4]arene amino acid derivative was found to have a

lower affinity for alkali metal cations compared to tertiary amide derivatives in both examined solvents, i.e. acetonitrile and methanol. However, in acetonitrile **L** was shown to bind Na^+ and Li^+ cations quite strongly, whereas its affinity for K^+ was moderate. No complexation of larger Rb^+ and Cs^+ cations could be detected in either solvent.

The result of a remarkable influence of the solvent on the complexation abilities of **L** are considerably lower ML^+ stability constants in methanol than in acetonitrile (Table 1). The solvent effect is composite, and includes solvation of all the species involved in the complexation reaction. In the case of Li^+ the difference between its solvation in MeCN and MeOH is great enough to be an important factor leading to a huge difference in the complexation equilibria in the two solvents. As the extent of Na^+ and K^+ solvation does not greatly differ in the two solvents, the lower stability of their complexes with **L** in MeOH is predominantly a consequence of hydrogen bonding interactions of methanol molecules with the cation binding sites of the ligand, i.e. carbonyl oxygens.

The solvation effects in combination with the compatibility in size of the guest cation and calix[4]arene hydrophilic cavity make **L** rather selective for Na^+ with respect to the other alkali cations.

Acknowledgements

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