1674 © 1989 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 62, 1674—1676 (1989) [Vol. 62, No. 5

Formation of Solvent-Separated Ion Pairs in Calixarene Ester-Alkali Picrate Complexes

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(Received December 5, 1988)

Synopsis. Association constants (K_a) of calix[n]arene esters ($\mathbf{1}_n$: n=4, 6, 8) for alkali picrates have been determined in tetrahydrofuran and compared with the $\mathbf{1}_n$-induced bathochromic shifts of the absorption maxima of alkali picrates. It has been established that (1) $\mathbf{1}_n$'s mostly form the 1:1 complexes with alkali metal cations, (2) the K_a values for $\mathbf{1}_n$ are generally smaller than those for crown ethers, and (3) the certain M^+–$\mathbf{1}_n$ complexes are considerably solvent-separated because of the "encapsulation effect" of the calixarene cavity. This is the first example for the systematic investigation on the relation between K_a and the geometry of the calixarene ester complexes.

Calixarenes are cyclic oligomers made up of phenol units. It has been found that the ester derivatives ($\mathbf{1}_n$'s) show the ionophoric nature and capable of binding alkali metal, alkaline earth metal, and diazonium ions are crown ethers do.[1–6] In particular, the tetramer ($\mathbf{1}_4$) exhibits the markedly high Na^+ selectivity.[1–5,7] Arduini et al.[2] proposed on the basis of the ^{1}H NMR measurements that Na^+ is "encapsulated" in the cavity constructed with the ionophoric $-OCH_2COO-$ groups (Fig. 1). Here, two questions occur to us which are both related to the essential behaviors of $\mathbf{1}_n$ as ionophores: that is, if $\mathbf{1}_n$ really forms the encapsulated complexes as illustrated in Fig. 1, then (i) do they form only the 1:1 metal/$\mathbf{1}_n$ complexes but not the 1:2 metal/$\mathbf{1}_n$ sandwich complexes as seen for certain crown ethers? and (ii) do they show the characteristics of solvent-separated ion pairs? Recently, Inoue et al.[8] suggested an interesting idea that the bathochromic shift of the absorption band of the picrate anion, extracted into the organic phase with a macrocyclic ligand from aqueous metal picrate solutions, serves as a convenient measure for evaluating the ion pair tightness in solution. We thus studied the spectroscopic behaviors of alkali picrates (M^+Pic^-) in tetrahydrofuran (THF) in the absence and the presence of $\mathbf{1}_n$ and estimated the stoichiometry and the nature of the ion pairs.

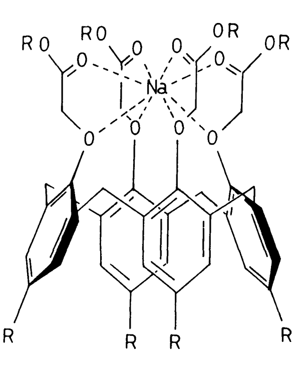
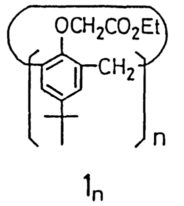


Fig. 1. Encapsulation of Na^+ by $\mathbf{1}_4$.



$\mathbf{1}_n$

Experimental

Preparations of $\mathbf{1}_4$ (25,26,27,28-tetrakis(ethoxycarbonylmethoxy)-*p*-*t*-butylcalix[4]arene), $\mathbf{1}_6$ (37,38,39,40,41,42-hexakis(ethoxycarbonylmethoxy)-*p*-*t*-butylcalix[6]arene), and $\mathbf{1}_8$ (49,50,51,52,53,54,55,56-octakis(ethoxycarbonylmethoxy)-*p*-*t*-butylcalix[8]arene) were described elsewhere.[1–6] All the spectroscopic measurements were carried out at 30 °C in THF.

Results and Discussion

The λ_{max} of M^+Pic^- shifted to longer wavelengths with a few isosbestic points with increasing $\mathbf{1}_n$ concentrations. The spectral change is similar to that in the presence of crown ethers.[9] From a plot of the absorbance for the new λ_{max} vs. $\mathbf{1}_4$ concentration we could determine the stoichiometry (by the molar ratio method) and the K_a (by the Benesi–Hildebrand plot). When the spectral change was relatively small, we employed the continuous variation method (absorbance for the new λ_{max} vs. $[M^+Pic^-]/([M^+Pic^-]+[\mathbf{1}_n])$ to determine the stoichiometry. However, the spectral changes observed for Li^+–$\mathbf{1}_n$(n=4, 6, 8), K^+–$\mathbf{1}_4$ and Cs^+–$\mathbf{1}_4$ were still too small to determine the stoichiometry. The results are summarized in Tables 1—3.

It is seen from Table 1 that $\mathbf{1}_n$'s mostly form the 1:1 complexes with alkali metal cations. This implies that metal cations are bound deeply in the cavity, the complexes being classified as a "nest-in-type". In crown ether chemistry, "perch-on-type" complexes, which frequently lead to the formation of 1:2 metal/crown sandwich complexes, result when the size of metal cations is greater than the cavity size. The metal selectivity in Table 3 suggests that the cavity

Table 1. Stoichiometry of $\mathbf{1}_n$-Alkali Picrate (M^+Pic^-) Complexes

$\mathbf{1}_n$	M^+Pic^-			
	M^+=Li^+	Na^+	K^+	Cs^+
n=4	a)	1:1	a)	a)
n=6	a)	1:1	1:1	1:1
n=8	a)	1:1	1:1	1:1

a) The spectral change was too small to determine the stoichiometry.

Table 2. Bathochromic Shifts ($\Delta\lambda$, nm) of λ_{max}[a)]

Ionophore	M^+Pic^-			
	M^+=Li^+	Na^+	K^+	Cs^+
$\mathbf{1}_4$	1	31	2	0
$\mathbf{1}_6$	1	6	25	20
$\mathbf{1}_8$	1	1	11	6
18-Crown-6	1	29	13	5
Cryptand 222	—	31	29	25

a) The λ_{max} values of M^+Pic^- in the absence of $\mathbf{1}_n$ are 343 nm for Li^+, 351 nm for Na^+, 357 nm for K^+, and 362 nm for Cs^+.

Table 3. Association Constants (K_a)

Ionophore	log K_a for M^+Pic^-[b)]			
	M^+=Li^+	Na^+	K^+	Cs^+
$\mathbf{1}_4$	3.00	3.95	3.08	1.60
$\mathbf{1}_6$	2.78	3.15	4.13	4.52
$\mathbf{1}_8$	2.08	2.61	3.11	3.08
18-Crown-6[a)]	3.72	4.29	5.33	4.91
Cryptand 222	—	6.69	8.38	6.61

a) The measurements were carried out mainly at [18-crown-6]/[M^+Pic^-]<2.0 so that the K_a values reflect those for the 1:1 complexes. b) K_a=[$M^+Pic^-\cdot\mathbf{1}_n$]/[$M^+Pic^-$][$\mathbf{1}_n$].

sizes of $\mathbf{1}_4$ and $\mathbf{1}_6$ are comparable with those of 15-crown-5 and 18-crown-6, respectively. Hence, the formation of the sandwich complex with $\mathbf{1}_n$ is expected, if it exists, for Cs^+–$\mathbf{1}_4$. Although the stoichiometry for this complex could not be determined even by the continuous variation method, the Benesi-Hildebrand plot (at [$\mathbf{1}_4$]/[Cs^+Pic^-]=10—100) used assuming the formation of the 1:1 complex gave a good linear relationship (r>0.98). Probably, this complex also consists of 1:1 Cs^+/$\mathbf{1}_4$. It is known that calix[8]arene derivatives having a large cavity are capable of including two guest molecules.[10,11)] In the present system, however, we could not find any evidence for the formation of 2:1 M^+/$\mathbf{1}_8$ complexes.

The λ_{max} for M^+Pic^- in the absence of $\mathbf{1}_n$ shifted to longer wavelengths in the order of $Li^+ < Na^+ < K^+ < Cs^+$. This order reflects the looseness of the ion pairs. The bathochromic shifts of λ_{max} induced by the addition of $\mathbf{1}_n$ are recorded in Table 2. The largest shift (31 nm) was attained for Na^+–$\mathbf{1}_4$. This shift is comparable with that induced by cryptand 222 and even greater than that induced by 18-crown-6, supporting the formation of the solvent-separated ion pair.[9,12)] The significant bathochromic shifts were also observed for K^+, Cs^+–$\mathbf{1}_6$ (20—25 nm). In contrast, the shifts induced by $\mathbf{1}_8$ were generally small. Presumably, even though M^+ is entrapped in the cavity of $\mathbf{1}_8$, the M^+–Pic^- interaction can still exist because of the flexible, large cavity.

Comparison of Table 2 with Table 3 reveals that these two recognition patterns are surprisingly similar: that is, the greater the K_a, the larger bathochromic shift occurs. This means that the stable $\mathbf{1}_n$ complex encapsulates M^+ deeply in the cavity resulting in the solvent-separated ion pair. The largest K_a was attained for Cs^+–$\mathbf{1}_6$ but not for Na^+–$\mathbf{1}_4$. This implies that Na^+Pic^- bound to $\mathbf{1}_4$ is considerably solvent-separated but the complex is not so stable as that of Cs^+–$\mathbf{1}_6$. The discrepancy is probably related to the rigid nature of the calix[4]arene skeleton which is the origin of the sharp Na^+ selectivity: that is, the cavity of $\mathbf{1}_4$ is so small and so rigid that the Na^+–Pic^- interaction is efficiently shut down by the encapsulation of Na^+. On the contrary, $\mathbf{1}_6$ having the moderately rigid skeleton rather gives the stable complexes although the metal selectivity becomes inferior to that of $\mathbf{1}_4$.

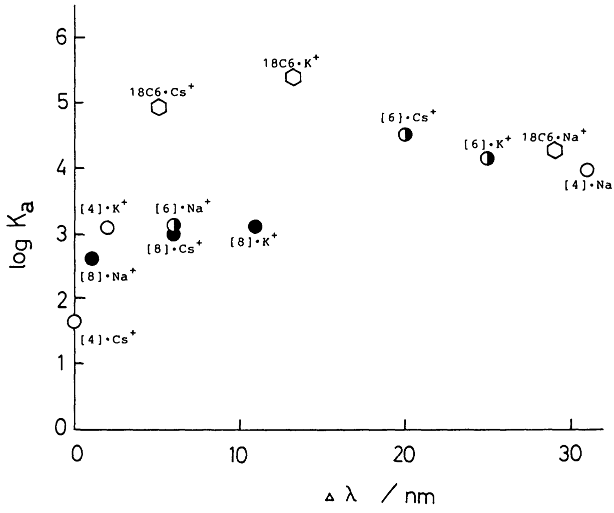


Fig. 2. log K_a vs. $\Delta\lambda$ map. In the figure $\mathbf{1}_n$'s are abbreviated with [n].

Based on these foregoing findings, we illustrated a log K_a vs. $\Delta\lambda$ map (Fig. 2). The map explicitly clarifies several novel facets of the M^+–$\mathbf{1}_n$ complexes. Firstly, 18-crown-6 forms the considerably stable K^+ and Cs^+ complexes but they are less solvent-separated. In contrast, the K_a for Na^+ is smaller than these but the ion pair is much more solvent-separated. Secondly, the K_a values for $\mathbf{1}_n$ are generally smaller than those for 18-crown-6. Nevertheless, certain complexes (e.g., Na^+–$\mathbf{1}_4$, K^+–$\mathbf{1}_6$, and Cs^+–$\mathbf{1}_6$) result in the solvent-separated ion pairs in which the bathochromic shifts greater than 20 nm are observed. This indicates that the solvent-separatedness of these complexes is comparable with that of the cryptand complexes. The unusual power of $\mathbf{1}_n$ is ascribed to the "encapsulation effect", which appears most clearly in $\mathbf{1}_n$ having the small, rigid skeleton. Thirdly, the $\mathbf{1}_8$ complexes give the log K_a=2.8±0.3 for Na^+, K^+, and Cs^+. The nonselective nature suggests that the ion complexation with $\mathbf{1}_8$ occurs according to an "induced-fit" manner. Lastly, the Cs^+–$\mathbf{1}_4$ complex, a combination of the large alkali metal cation and the small calixarene cavity, did not cause any bathochromic shift but slightly increased the absorbance. The K_a estimated from this absorbance increase was only 40 $dm^3\,mol^{-1}$. The data visualize the Cs^+–$\mathbf{1}_4$ complex geometry: $\mathbf{1}_4$ weakly interacts with Cs^+ but cannot encapsulate Cs^+ enough to interfere with the Cs^+–Pic^- interaction.

In conclusion, the present study systematically demonstrated that (i) calixarene esters $\mathbf{1}_n$'s mostly form the 1:1 complexes with alkali metal cations and (ii) they have a tendency to produce the solvent-separated ion pairs. Thus, small Na^+ ion is easily encapsulated leading to the solvent-separated ion pairs, whereas large Cs^+ ion is exposed to solvent media leading to the contact ion pairs. Further investigation on the reactivities and the geometries of these solvent-separated ion pairs is currently continued in our laboratories.

This research was supported by the Grant-in-Aid from the Ministry of Education, Science and Culture. We thank Miss Sayuri Edamitsu (Nagasaki University) and Miss Tomoko Nakane (Kyushu University) for technical assistance.

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12) In order to obtain a further insight into the $\mathbf{1}_n \cdot M^+Pic^-$ ion pairs we measured the ^{23}Na NMR in THF/THF-d_8 mixed solvent at 30 °C. We unexpectedly found that the peak for Na^+ (added as M^+Pic^- (6.8×10^{-3} mol dm^{-3})) is invariably broadened in the presence of $\mathbf{1}_n$: for example, the T_2 values, which can be directly calculated from the peak width ($T_2 = (\pi\delta_{\nu 1/2})^{-1}$ where $\delta_{\nu 1/2}$ denotes the half height line width in Hz) are 7.08×10^{-4} s in the absence of $\mathbf{1}_n$, 1.62×10^{-5} s in $\mathbf{1}_4$ (140 mmol dm^{-3}), 2.11×10^{-5} s in $\mathbf{1}_6$ (470 mmol dm^{-3}), and 3.18×10^{-5} s in $\mathbf{1}_8$ (340 mmol dm^{-3}). Such a broadening effect was not found for Na^+ bound to cyclic polyethers: $T_2 = 8.85 \times 10^{-4}$ s in 18-crown-6 (340 mmol dm^{-3}) and 1.47×10^{-3} s in cryptand 222 (670 mmol dm^{-3}). The similar observation was reported by Jin and Ichikawa: paper presented at the 57th Annual Meeting of the Chemical Society of Japan, Sendai, 1988, September.