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Thermodynamics of solvent extraction of alkali metal and alkylammonium cations with alkyl calix[6]aryl esters

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Alkyl calix[6]aryl esters were found to exhibit significant enthalpy-entropy compensation effect (α = 0.92) in solvent extraction of alkali metal and alkylammonium cations. The methyl ester 1 and debutylated ethyl ester 4 showed larger α values that might result in inferior binding affinity compared with the ethyl ester 2.

Calixarenes have received much attention recently as a versatile building block for the design of intriguing biomimetic host systems.[1] Ester, amide, ketone, and many other ligating functional groups have been introduced in an effort to endow this versatile compound class with ionophoric properties.[2-4] Of these, the ester derivatives of *p-tert*-butylcalix[6]arene are known to have high affinity toward alkali metal ions, alkylammonium, and related cations,[5-7] and the binding properties were found strongly dependent upon the nature of alkyl side chain of the ester function.[2,7] Particular interest is that methyl ester **1** and debutylated ester **4** exhibit markedly reduced binding efficiency compared to ethyl and higher homologues up to *n*-butyl ester derivative.[2,7] In this paper we report the thermodynamic properties for the extraction of alkali metal and alkylammonium guests by ester derivatives of calix[6]arenes aiming to elucidate the related binding processes.

Esters **1-4** were prepared according to the reported procedures.[2] Thermodynamic parameters for the extraction of alkali metal and alkylammonium picrates (ΔG_{ex}, ΔH_{ex}, and ΔS_{ex}) were obtained by solvent extraction experiments (CH_2Cl_2:H_2O) at four different temperatures ranging from 5 °C to 25 °C (5.0, 11.0, 18.0, and 25.0 °C).[8] The logarithm of the extraction constant (K_{ex}) was plotted against the inverse temperature (1/T) to give the enthalpy and entropy changes of extraction as slope and intercept, respectively.[9] Representative plots for the extraction of some alkylammonium guests by **2** are illustrated in Figure 1. Each point in the plot is obtained by triplicate measurements (reproducibility is better than ± 5%). The thermodynamic quantities thus obtained of ΔG_{ex}, ΔH_{ex}, and $T\Delta S_{ex}$ are summarized in Table 1. As can be seen from Table 1, all the tested esters exhibited peak selectivity toward methyl or ethylammonium picrate. They generally displayed exothermic behavior, and positive entropy gain except for the case of some alkali metal and butylammonium picrates. It is of interest to note that the ethyl and *n*-propyl esters, **2** and **3**, have almost identical thermodynamic quantities toward most of the employed guests. However, there is a discernible difference in binding behavior between **2**, **3** and **1**, **4**. Generally the trend in stability pattern of the complexes of **2** and **3** follows the change in enthalpy terms, while that of **1** and **4** follows the entropy changes.

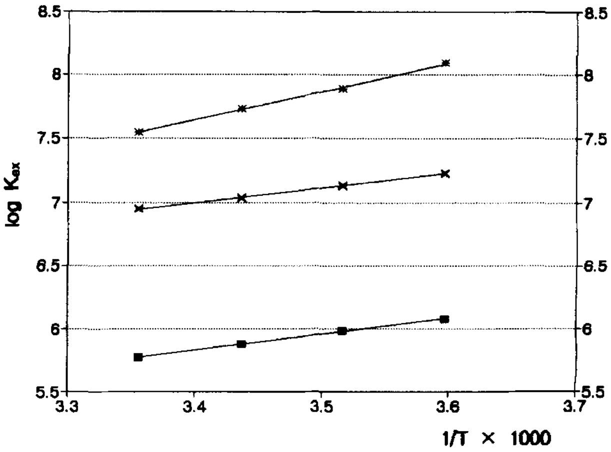

Figure 1 Typical plots of log K_{ex} versus 1/T for the solvent extraction of ammonium (■), ethylammonium (✳), and *n*-butylammonium (X) picrates with **2**.

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Table 1 Thermodynamic quantities (kcal/mol) for the extraction of metal and alkylammonium picrates with ester derivatives of calix[6]arenes[a]

Ligands	*Guest*	ΔG_{ex}	ΔH_{ex}	$T\Delta S_{ex}$
1	K^+	-7.5	-5.9	1.6
	Rb^+	-7.5	-6.2	1.2
	Cs^+	-8.1	-6.9	1.2
	NH_4^+	-6.5	-7.5	-1.0
	Me	-8.3	-6.1	2.2
	Et	-8.5	-4.3	4.2
	n-Pr	-7.7	-1.7	6.0
	n-Bu	-7.3	-3.2	4.1
	iso-Bu	-7.0	-4.4	2.6
	sec-Bu	-6.9	-4.2	2.7
	tert-Bu	-6.6	-6.5	0.1
	$N(CH_3)_4^+$	-7.1	-4.3	2.8
	Benzyl	-7.9	-4.0	3.9
2	Na^+	-7.8	-4.3	3.5
	K^+	-9.2	-11.6	-2.5
	Rb^+	-9.0	-11.2	-2.2
	Cs^+	-10.0	-12.4	-2.4
	NH_4^+	-7.9	-5.8	2.1
	Me	-10.3	-10.1	0.2
	Et	-10.6	-8.4	2.2
	n-Pr	-9.5	-5.3	4.2
	n-Bu	-8.8	-5.0	3.8
	iso-Bu	-8.4	-4.4	4.0
	sec-Bu	-8.3	-4.5	3.8
	tert-Bu	-7.5	-4.4	3.1
	$N(CH_3)_4^+$	-8.8	-5.3	3.6
	Benzyl	-9.2	-7.1	2.1
3	Na^+	-7.1	-6.9	0.3
	K^+	-8.2	-9.8	-1.5
	Rb^+	-8.2	-9.7	-1.5
	Cs^+	-9.2	-11.4	-2.2
	NH_4^+	-7.8	-6.5	1.2
	Me	-10.3	-9.8	0.5
	Et	-10.4	-8.6	1.8
	n-Pr	-9.4	-5.6	3.8
	n-Bu	-8.7	-4.9	3.8
	iso-Bu	-8.3	-4.2	4.1
	sec-Bu	-8.4	-4.1	4.3
	tert-Bu	-7.7	-4.3	3.4
	$N(CH_3)_4^+$	-8.8	-6.4	2.4
	Benzyl	-9.1	-7.8	1.1
4	K^+	-7.6	-8.8	-1.2
	Rb^+	-8.8	-10.2	-1.5
	NH_4^+	-7.5	-5.3	2.2
	Me	-8.6	-7.2	1.4
	Et	-8.0	-5.4	2.6
	n-Pr	-8.0	-5.2	2.8
	n-Bu	-8.1	-5.5	2.6
	iso-Bu	-7.0	-8.5	-1.5
	sec-Bu	-6.5	-14.2	-7.7
	tert-Bu	-6.6	-13.0	-6.4
	$N(CH_3)_4^+$	-7.2	-10.1	-2.9
	Benzyl	-8.2	-6.4	1.8

[a] Extraction condition: [Ligand] = 3.5×10^{-3} M, [alkali metal or alkylammonium picrate] = 7.0×10^{-5} M, H_2O/CH_2Cl_2 = 5.0 mL/5.0 mL, at the temperature range of 5.0 - 25.0 °C.

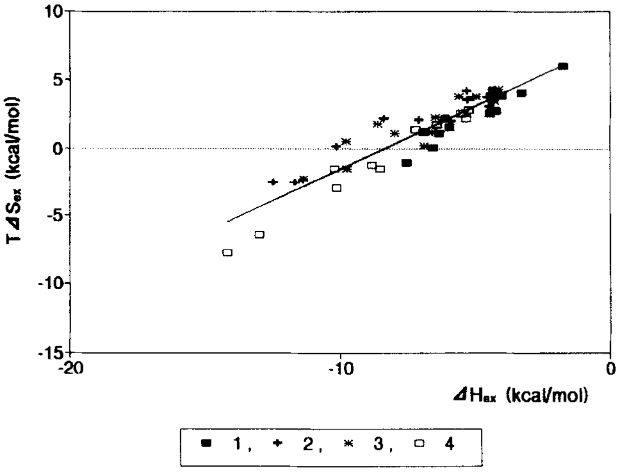


Figure 2 Plot of $T\Delta S_{ex}$ versus ΔH_{ex} for the extraction of alkali metal and alkylammonium cations with calix[6]arene ester ligands.

Recently, Inoue *et al.* have pointed out that a unique enthalpy-entropy compensation relationship holds for complexation involving ion-dipole interaction.[10] To apply this idea to the present system, a plot of ΔH_{ex} versus $T\Delta S_{ex}$ for all the obtained results was made. The plot gave a fairly good straight line (Figure 2), and the α and $T\Delta S_{ex}°$ values, estimated from the slope and intercept of the plot, are given in Table 2. The α value (0.92) suggests that a significant enthalpy-entropy compensation effect[10] does operate for the solvent extraction of alkali metal and alkylammonium cations by calix[6]arene-based ester ligands. That is a large part (92%) of the enthalpic gain from the host-guest interaction; it is canceled by entropic loss from the accompanying large conformational change of calix[6]arene esters. The compensation effect of calix[6]arene esters is (bearing in mind that the experimental conditions are not identical to the present system) much larger than that operating in metal ion binding by tetrameric ethyl ester **5** (α = 0.63).[11] This observation is explicable by the relatively flexible nature of calix[6]arene derivatives compared with the well-established, limited conformational freedom of calix[4]arene derivatives fixed in cone conformation.

Meanwhile, ester ligands derived from calix[6]arenes showed relatively larger $T\Delta S_{ex}°$ values of around 7.5 to 8.9, compared to the other ligand systems reported so far (2.3−7.1)[10] as well as calix[4]arenes (2.68). That means the calix[6]arene ligands might undergo much larger conformational reorganization and extensive desolvation upon complex formation, which is characteristic of the flexible and three-dimensional complex that is formed in this case.

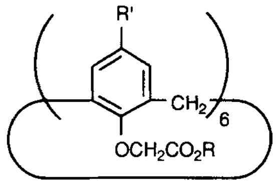
To examine the complexation behavior of individual ester ligands more thoroughly, a plot of ΔH_{ex} versus $T\Delta S_{ex}$ was made for each ligand.[12] Although the number of data points for the plot is not large (12-14 points), there is a discernible difference in the behavior of **2**, **3** and **1**, **4**. Their respective values of α and $T\Delta S_{ex}°$ are obtained from each plot and also summarized in Table 2.

Table 2 Slope (α) and intercept ($T\Delta S_{ex}^o$) of ΔH_{ex}—$T\Delta S_{ex}$ plots

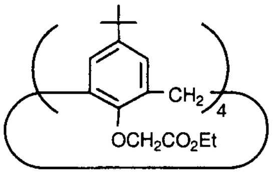
Ligands	*R*	α	$T\Delta S_{ex}^o$
Overall (**1** – **4**)	0.93	0.92 ± 0.05	7.69 ± 1.02
1	0.94	1.08 ± 0.11	7.85 ± 0.64
2	0.96	0.80 ± 0.07	7.51 ± 0.73
3	0.92	0.85 ± 0.10	7.63 ± 0.90
4	0.99	1.15 ± 0.06	8.93 ± 0.59
5[a]	0.95	0.63 ± 0.08	2.68 ± 1.19

[a] Estimated with the results taken from reference 11.

Esters **2** and **3** exhibited nearly same α and $T\Delta S_{ex}^o$ values, which means that they have almost identical complexation behavior toward the alkali metal and alkylammonium cations, at least from the thermodynamic point of view. The α value of ca. 0.8 for **2** and **3** is similar to the reported value for crown ethers (0.77).[10] However, the methyl ester **1** and debutylated ethyl ester **4** have significantly larger α values (1.08 and 1.15, respectively). All the results obtained clearly suggests that the methyl and debutylated ligands, **1** and **4**, have experienced much larger enthalpy-entropy compensation effects, which might originate in the greater conformational flexibility of host **1** and **4** compared to **2** and **3**. The greater flexibility of **1** and **4** is detrimental to complex formation and likely to result in inferior binding properties compared with the esters **2** and **3**.



	R	**R'**
1	Me	*t*-Bu
2	Et	*t*-Bu
3	*n*-Pr	*t*-Bu
4	Et	H



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REFERENCES

1 (a) Gutsche, C.D. *Calixarenes*; Monographs in Supramolecular Chemistry; Stoddart, J.F., Ed.; Royal Society of Chemistry: Cambridge, 1989. (b) Vicens, J., Böhmer, V., Eds.; *Calixarenes, a Versatile Class of Macrocyclic Compounds*; Kluwer: Dordrecht, 1991.

2 Arnaud-Neu, F.; Collins, E.M.; Deasy, M.; Ferguson, G.; Harris, S.J.; Kaitner, B.; Lough, A.J.; McKervey, M.A.; Marques, E.; Ruhl, B.L.; Schwing-Weill, M.J.; Seward, E.M. *J. Am. Chem. Soc.* **1989**, *111*, 8681.

3 (a) Arduini, A.; Pochini, A.; Reverberi, S.; Ungaro, R.; Andreetti, G.D.; Ugozzoli, F. *Tetrahedron* **1986**, *42*, 2089. (b) Cobben, P.L.H.M.; Egberink, R.J.M.; Bomer, J.G.; Bergveld, P.; Verboom, W.; Reinhoudt, D.N. *J. Am. Chem. Soc.* **1992**, *114*, 10573.

4 Shinkai, S. *Tetrahedron* **1993**, *49*, 8933.

5 Chang, S.-K.; Hwang, H.-S.; Son, H.; Youk, J.; Kang, Y.S. *J. Chem. Soc., Chem. Commun.* **1991**, 217.

6 Shinkai, S.; Koreishi, H.; Ueda, K.; Arimura, T.; Manabe, O. *J. Am. Chem. Soc.* **1987**, *109*, 6371.

7 Han, S.Y.; Kang, M.-H.; Jung, Y.E.; Chang, S.-K. *J. Chem. Soc., Perkin Trans. 2* **1994**, 835.

8 Takeda, Y. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 931.

9 Inoue, Y.; Amano, F.; Okada, N.; Inada, H.; Ouchi, M.; Tai, A.; Hakushi, T.; Liu, Y.; Tong, L.-H. *J. Chem. Soc., Perkin Trans. 2* **1990**, 1239.

10 Inoue, Y.; Hakushi, T.; Liu, Y. In *Cation Binding by Macrocycles*; Inoue, Y.; Gokel, G.W. Eds.; Marcel Dekker: New York, 1990; Chapter 1.

11 Calculated for the results of calorimetric studies of **5** and its metal ion complexes in acetonitrile and in methanol solution. Danil de Namor, A.F.; Apaza de Sueros, N.; McKervey, M.A.; Barrett, G.; Arnaud Neu, F.; Schwing-Weill, M.J. *J. Chem. Soc., Chem Commun.* **1991**, 1546.

12 (a) Inoue, Y.; Hakushi, T.; Liu, Y.; Tong, L.-H.; Shen, B.-J.; Jin, D.-S. *J. Am. Chem. Soc.* **1993**, *115*, 475. (b) Inoue, Y.; Liu, Y.; Tong, L.-H.; Shen, B.-J.; Jin, D.-S. *J. Am. Chem. Soc.* **1993**, *115*, 10637.