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LOG *K*, Δ*H*, AND *T*Δ*S* VALUES FOR THE REACTION OF SEVERAL UNI- AND BIVALENT METAL IONS WITH SEVERAL UNSUBSTITUTED CYCLIC POLYETHERS AND THEIR BENZO-SUBSTITUTED DERIVATIVES

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ABSTRACT

Log K, ΔH, and $T\Delta S$ values valid in methanol at 25°C have been determined calorimetrically for the interaction of several uni- and bivalent metal ions with benzo-15-crown-5 (B15C5), benzo-18-crown-6 (B18C6), dibenzo-18-crown-6 (DB18C6), dibenzo-21-crown-7 (DB21C7), dibenzo-24-crown-8 (DB24C8), and dibenzo-27-crown-9 (DB27C9). In addition, log K, ΔH, and $T\Delta S$ values have been determined under the same conditions for interactions of Tl^+ with 15-crown-5 (15C5), 18-crown-6 (18C6), and 21-crown-7 (21C7) and for interactions of Pb^{2+} with 15C5 and 21C7.

For the interaction of a given cation with large ring macrocycles, e.g., DB24C8 and DB27C9, log K values are usually lower than with macrocycles whose cavity radius closely matches the cation radius. Generally, log K and $-\Delta H$ values decrease in the series un-, monobenzo-, dibenzo-substituted macrocycle. Log K values decrease in this series more for bivalent than for univalent cations.

INTRODUCTION

Log K, ΔH, and $T\Delta S$ values for cation–macrocycle interaction have been compiled [1,2]. These data show that macrocycles can bind a large variety of uni-, bi- and trivalent cations. The stabilities of cation–macrocycle complexes depend on a number of parameters involving the cation (ionic radius, ionic charge, type), macrocycle (cavity radius, number and type of donor atoms, ring substituents, etc.) and medium (solvent, temperature, etc.). Considerable effort has been expended in identifying these parameters and in evaluating them [1–4].

Lamb et al. [3] have shown the effect of macrocycle ring size and donor atom type on log K, ΔH, and $T\Delta S$ for the reaction of several uni- and

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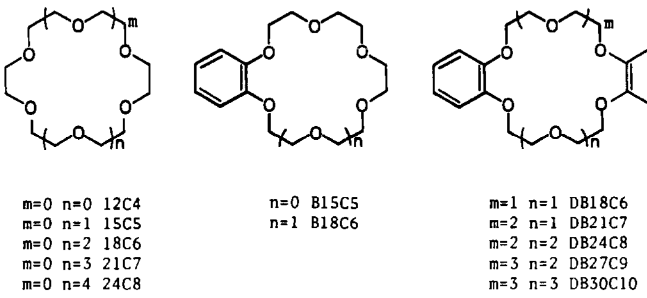

Fig. 1. Macrocycles used in this study.

bivalent cations with macrocyclic crown ethers in methanol solvent. A significant conclusion of this study was that the selectivity of a given macrocyclic ligand for a cation is enhanced by a good fit of the cation in the ligand cavity only for cations small enough to enter the ligand cavity. For cations larger than the macrocyclic radius, relative size is less important. More recently, it has been further observed that the ratio of the cation ionic radius to the crown ether cavity radius cannot be used as a single predictor of the selectivity of crown ethers for cations [5,6].

The intent of the present study is to expand upon our earlier work [3] in order to examine additional uni- and bivalent cation–crown ether interactions in methanol as a function of crown ether ring size and ring substituent. A variety of uni- and bivalent cations is included in the study in order to evaluate the cation parameters referred to earlier.

EXPERIMENTAL

Materials

Reagent grade salts used in this study and the suppliers are: NaCl and KCl (Mallinckrodt); $AgNO_3$ (Sargent-Welch); $TlClO_4$ and $TlNO_3$ (ICN); RbCl and $Sr(ClO_4)_2 \cdot 6H_2O$ (Alfa); RbCl (Fisher); CsCl and $Ba(ClO_4)_2$ (Research Organic/Inorganic Chemical Corp.); $Pb(ClO_4)_2 \cdot 3H_2O$ (G. Frederick Smith); $Pb(NO_3)_2$ and $Ca(NO_3)_2 \cdot 3H_2O$ (Aldrich, gold label); $Ca(NO_3)_2$ (B & A). The ligands, B15C5, 18C6, B18C6, DB18C6, 21C7, DB21C7, DB24C8, and DB27C9, were obtained from Parish Chemical Company and used without further purification. Each of the crown ethers was standardized by calorimetric titration to an end point against an appropriate metal salt [7], and found to be at least 90% pure.

Procedure

The titration calorimetric technique used for determining log K, ΔH, and $T\Delta S$ values has been described previously [8]. The technique involves measurement of temperature changes for a reaction as a function of moles of titrant added. The ΔH and log K values for the reaction are computed using a least-squares fit of the data. In the case of the Cs^+–B18C6 system, reactions of stoichiometry 2:1 and 1:1 were detected and resolved. In the case of Pb^{2+}–18C6, log K was too large (> 5.5) to measure using our methods. Three to five independent experimental determinations were made for each metal–macrocycle combination.

RESULTS AND DISCUSSION

Log K, ΔH, and $T\Delta S$ values valid in methanol at 25°C for the M^{n+}–crown ether systems studied are listed together with literature data for these and related M^{n+}–macrocycle interactions in Table 1. In general, log K data determined in the present study agree well with those few values reported earlier.

The cation radii in Table 2 are taken from Shannon [9] as determined by X-ray crystallography for oxides of coordination number six. Macrocycle cavity radii have either been determined by X-ray crystallography [10] or estimated from Corey–Pauling–Koltun space-filling models [11]. Cavity radii of 27C9 and 30C10, have not been estimated since the flexibility of these large macrocycles make the concept of a well-defined cavity less meaningful.

Effect of cation charge

Generally, crown ethers [11,12] and cryptands [4,11,13] show greater selectivities among 2+ than among 1+ cations. This has been attributed to the greater range of solvation energies of 2+ cations [11]. Evaluation of ΔH and $T\Delta S$ values for K^+ and Ba^{2+} interactions with 18C6 illustrates another interesting difference between 1+ and 2+ cations. K^+ and Ba^{2+} have nearly identical ionic crystal radii [9]; however, K^+–18C6 interaction gives a more favorable enthalpy change and a less favorable entropy change ($\Delta H = -56.1$ kJ mol^{-1}, $T\Delta S = -21.5$ kJ mol^{-1}) than Ba^{2+}–18C6 interaction ($\Delta H = -43.55$ kJ mol^{-1}, $T\Delta S = -3.34$ kJ mol^{-1}) [1,3]. Data in Table 1 show that for M^+ and M^{2+} of similar sizes, M^+–crown ether interactions usually give more favorable ΔH and less favorable $T\Delta S$ values than corresponding M^{2+} interactions. M^+ and M^{2+} cation pairs of similar sizes in Table 2 are: K^+–Ba^{2+}; Ag^+–Sr^{2+}; and Na^+–Ca^{2+}. The smaller solvation energies of 1+ cations probably account for their more favorable ΔH values of complexation. More favorable $T\Delta S$ values for 2+ relative to 1+ cations probably result from the larger number of bound solvent molecules released upon desolvation of 2+ cations in the formation of the M^{n+}–crown ether complex. Other factors not considered here, such as complex solvation,

TABLE 1

Log K, ΔH (kJ mol^{-1}), and $T\Delta S$ (kJ mol^{-1}) for reaction of uni- and bivalent cations with several unsubstituted, mono-, and dibenzo-substituted crown ethers in methanol at 25°C [a]

Cation	Parameter	12C4	15C5	B15C5	18C6	B18C6	DB18C6	21C7	DB21C7	24C8	DB24C8	DB27C9	DB30C10
Li^+	log K		[b]		[b]			[b]					> 0
Na^+	log K	1.47	3.48	2.89	4.36	4.21	4.5	1.73	2.40	2.35	2.25	2.41	2.1
				±0.03 [c]		±0.02 [c]						± 0.05 [c]	
		2.29 [d]	3.30	3.05	4.38	4.03	4.36	2.54					2.0
		1.41	3.14	3.37	4.46	4.5	4.36						
		2.20 [d]	2.4 [d]	2.87	4.32	4.35	4.36						
		1.7	3.25		4.35		4.4						
			3.30		4.35								
			1.44 [d]		4.32								
			3.24										
			3.27										
			3.31										
	ΔH	−12.6	−20.9	−18.6	−35.1	−34.6	−31.2	−43.4				−19.0	−17
				±0.3 [c]		±0.3 [c]						± 1.9 [c]	
		−28.0 [d]	−22.6		−31.38								
			−23.01										
	$T\Delta S$	−4.17	−1.00	−2.1 [c]	−10.3	−10.6 [c]	−5.61	−33.4				−5.27 [c]	
		−15.1 [d]	−3.76		−6.488								
			−5.149										
K^+	log K	1.59	3.77	[c]	6.06	5.29	5.1	4.22	4.19	3.53	3.45		4.60
						±0.02 [c]			± 0.03 [c]		± 0.10 [c]		
		0.56 [d]	2.71 [d]	2.8	6.18	5.2	5.00	4.35	4.30	3.48	3.57		
		1.74	3.35	3.15 [d]	6.08	5.27	5.08	4.41			3.6		
		1.58	2.65 [d]		6.20	5.7	5.00						
		0.15 [d]	3.61		6.1	5.05	4.8						
			1 [d]		5.93		5.00						
			3.1		6.08		5.05						
			2.9 [d]		6.10								
			3.34										
			2.21 [d]										
			3.43										
			3.3 − 3.6										
			3.34										
	ΔH	−21.3	−32.2		−56.1	−44.85	−40.04	−35.94	−34.6		−31.1		
						±0.13 [c]			± 0.3 [c]		± 1.2 [c]		
			−33.9 [d]		−53.14						−35.3		
			−32.6										
			−36.8 [d]										
			−32.22										

	$T\Delta S$	−12.3	−10.7		−21.5	−14.6^{c}	−10.93	−11.8	−10.7^{c}		−11.4^{c}		
			−18.4^{d}		−18.00						−14.7		
			−13										
			−22^{d}										
			−11.72										
Rb^+	$\log K$				5.32	4.48	4.36	4.86			3.86		4.6
						±0.02^{c}	±0.01^{c}						
					5.73	4.62	4.23				3.85		
					5.35	5.1							
	ΔH				−50.6	−43.0	−28.6	−40.4			−39.4		−53
						±0.3^{c}	±0.7						
	$T\Delta S$				−20.2	−17.4^{c}	−3.72^{c}	−12.7			−17.2		
Cs^+	$\log K$		2.62	1.91	4.79	3.95	3.55	5.01	4.25	4.15	3.85	3.67	4.2
						±0.04^{c}			±0.03^{c}		±0.10^{c}	±0.04^{c}	
			2.18	2.03	2.06^{d}	2.33	2.92^{d}	5.02	4.20		3.84	3.74	
						±0.17^{c,d}							
											3.78		
					4.49	3.66			1.9^{d}				
					4.62	4.1							
					1.30^{d}								
	ΔH		−31.9		−47.2	−42.30		−46.77	−44.10		−37.9	−41.97	−47
						±0.79^{c}			±0.67^{c}		±1.3^{c}	±0.88^{c}	
			−49.0		−13.9^{d}	−43					−36.8		
						±14^{c,d}							
	$T\Delta S$		−17.4		−19.9	−19.7^{c}		−18.1	−19.8^{c}		−15.9^{c}	−21.0^{c}	
					−2.1^{d}	−30^{c,d}					−14.6		
Ag^+	$\log K$		3.62	2.63	4.58	4.23	4.04	2.46	2.41			2.47	
				±0.06^{c}		±0.01^{c}			±0.05^{c}			±0.02^{c}	
					4.57								
	ΔH		−27.53	−17.9	−38.3	−39.7		−28.9	−7.61			−14.0	
				±0.7^{c}		±0.3^{c}			±0.42^{c}			±0.1^{c}	
	$T\Delta S$		−6.86	−2.85^{c}	−12.1	−15.6^{c}		−14.8	6.15^{c}			0.08^{c}	
Tl^+	$\log K$		3.31	^{e}	5.34	4.37	3.92	4.55	4.03		3.40		4.5
			±0.02^{c}		±0.02^{c}	±0.02^{c}		±0.01^{c}	±0.03^{c}		±0.17^{c}		
					4.6		3.80						4.4
					5.26								
	ΔH		−36.4		−45.65	−39.1		−40.1	−36.9		−30.0		−46
			±1.0^{c}		±0.54^{c}	±0.3^{c}		±0.1^{c}	±0.5^{c}		±1.0^{c}		
	$T\Delta S$		−18^{c}		−15.1^{c}	−14.2^{c}		−14.1^{c}	−13.8^{c}		−10.6^{c}		

TABLE 1 (continued)

Cation	Parameter	12C4	15C5	B15C5	18C6	B18C6	DB18C6	21C7	DB21C7	24C8	DB24C8	DB27C9	DB30C10
Mg^{2+}	log *K*		^{b}		^{b}								
Ca^{2+}	log *K*		2.18 2.55 2.1^{d} 2.36		3.86 3.90	2.28 ± 0.02^{c} 3.50		2.80		2.66			
	ΔH		−6.07 −11.7 20.1^{d}		−11.5	−8.62 ±0.54^{c}							
	$T\Delta S$		6.35 2.8 32.2^{d}		10.5	4.39^{c}							
Sr^{2+}	log *K*		2.63		> 5.5	5.12 ±0.02^{c} 4.92		1.77					
	ΔH		−19.6		−36.0	−19.6 ±0.1^{c}		−29.7					
	$T\Delta S$		−4.62			9.58^{c}		−19.6					
Ba^{2+}	log *K*				7.04	5.48 ±0.04^{c} 5.35	4.28	5.44	4.21 ± 0.01^{c}		4.04 ±0.03^{c}		
	ΔH				−43.55	−37.2 ±0.2^{c}	−21.2	−28.5	−21.1 ± 0.2^{c}		−24.6 ± 0.5^{c}		
	$T\Delta S$				−3.34	−5.94^{c}	3.31	2.6	2.9^{c}		−1.5^{c}		
Pb^{2+}	log *K*		3.56 ±0.03^{c} 2.00 ±0.02^{c,d}	2.36^{c}	> 5.5^{c}	5.49 ±0.01^{c}		3.76 ±0.03^{c}	1.97 ± 0.02^{c}		2.34 ± 0.10^{c}		
	ΔH		−28.4 ±0.8^{c} −21.1 ±0.5^{c,d}	−21.5^{c}	−37.5 ±0.2^{c}	−32.0 ±0.4^{c}		−20.6 ±0.3^{c}	−15.1 ± 0.3^{c}		−23.0 ± 2.9^{c}		
	$T\Delta S$		−8.08^{c} −9.67^{c,d}	−8.03^{c}		−0.63^{c}		0.84^{c}	−3.8^{c}		−9.67^{c}		

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[a] Log *K*, ΔH, and $T\Delta S$ values are for 1:1 macrocycle–cation interactions unless otherwise noted. All data are taken from ref. 1 unless otherwise noted. Corresponding log *K*, ΔH, and $T\Delta S$ values are listed in order.

[b] No measurable heat other than heat of dilution indicating that ΔH and/or log *K* are very small [3].

[c] This work.

[d] Data are for 2:1 macrocycle–cation interaction and follow corresponding 1:1 macrocycle–cation interaction in Table 1.

[e] Reaction of stoichiometry other than 1:1 which was not resolved; this work.

[f] Heat produced but insufficient to calculate log *K* or ΔH; this work.

[g] Heat produced but insufficient to calculate log *K* or ΔH [3].

TABLE 2
Cation ionic radii for several uni- and bivalent cations [9]

Cation	Radius (Å)	Cation	Radius (Å)
Mg^{2+}	0.720	Pb^{2+}	1.19
Li^{+}	0.76	Ba^{2+}	1.35
Ca^{2+}	1.00	K^{+}	1.38
Na^{+}	1.02	Rb^{+}	1.52
Ag^{+}	1.15	Tl^{+}	1.50
Sr^{2+}	1.18	Cs^{+}	1.67

Macrocycle cavity radii (Å)

15C5 (0.86–0.92) [a] (0.85) [b]	21C7 (1.7) [b]
18C6 (1.34–1.43) [a] (1.38) [b]	24C8 (2.0) [b]

[a] From X-ray crystallographic data [10].
[b] From Corey–Pauling–Koltun models [11].

ligand desolvation, and ligand conformational change, probably make contributions to these terms as well.

Effect of solvent

The selectivity of macrocycles for one cation over a second cation of different charge may be altered significantly by changing the solvent in which the reaction occurs. For example, DB18C6 is selective for Ba^{2+} over K^+ in H_2O, but the reverse is true in CH_3OH [1]. Selectivities of post-transition cations over alkali cations may also be changed as a function of solvent.

The univalent cations, Ag^+ and Tl^+, have smaller increases in log K values from H_2O to CH_3OH than do alkali cations. For example, the difference in log $K(CH_3OH)$ and log $K(H_2O)$ for Ag^+–18C6 interaction is 3.08 log K units [1]. The same difference for Na^+–18C6 interaction is 3.56 log K units [1]. The log $K(H_2O)$ value for Ag^+–18C6 interaction, 1.50, is larger than that expected [2] based on the ionic radius of Ag^+ as determined by Shannon (Table 2) while the log $K(CH_3OH)$ value is unpredictably low [11]. In the cases of Tl^+ and Rb^+, which have nearly equal radii, the difference in log $K(CH_3OH)$ and log $K(H_2O)$ for Tl^+–18C6 interaction is 3.07 log K units compared to 3.76 log K units for Rb^+ [1]. Tl^+ has much more affinity for 18C6 in H_2O than Rb^+, but in CH_3OH their affinities for 18C6 are nearly equal [1].

The smaller increase in log K values for Ag^+ and Tl^+ from H_2O to CH_3OH is due to solvation effects in the two solvents. The free energy of transfer from H_2O to CH_3OH for single ions, ΔG^0_{tr}, may be used as a measure of a cation's relative solvation energies in H_2O and CH_3OH. Smaller differences in cation–macrocycle complex stabilities between H_2O and CH_3OH will occur for smaller absolute values of ΔG^0_{tr}. The ΔG^0_{tr} values (kcal/mol) of +1.8 and +1.0 for Ag^+ and Tl^+, respectively, are less positive than the ΔG^0_{tr} values of +2.0, +2.4, +2.4, and +2.3 for Na^+, K^+, Rb^+, and Cs^+, respectively [14]. These ΔG^0_{tr} values should account for the smaller differences in log $K(CH_3OH)$ and log $K(H_2O)$ for Ag^+ and Tl^+ interactions with 18C6 because they indicate that Ag^+ and Tl^+ have higher solvation energies in CH_3OH relative to H_2O than do Na^+, K^+, Rb^+, and Cs^+. The increased solvation of Ag^+ in CH_3OH relative to alkali cations is a major factor in accounting for the lower than expected log K value of Ag^+ in CH_3OH, because more energy is expended for Ag^+ in the desolvation step. Higher than expected log K values for the interactions of Ag^+ and Tl^+ with macrocycles in H_2O may be a result of covalent bonding contributions in the cases of these cations.

Effect of ring size

The selectivity order in CH_3OH of 15C5 for 1+ cations from Table 1 is $K^+ > Ag^+ > Na^+ > Tl^+ > Cs^+ > Li^+$. Of these cations, only Li^+ is small enough to enter the cavity of 15C5, but Li^+ is too small to achieve optimal interaction with the oxygen donor atoms. The low log K and ΔH values for Li^+–15C5 interaction are probably due to the latter factor coupled with the high solvation energy of Li^+. Among the other cations, the ionic radius of Na^+ most closely corresponds to the cavity radius of 15C5, although it is slightly larger. However, the larger K^+ is bound more strongly than Na^+ by 15C5. The lower affinity of Na^+ than K^+ for 15C5 is probably a result of the greater solvation energy of Na^+ [3]. For 2+ cations, 15C5 is selective for both Sr^{2+} and Pb^{2+} over Ca^{2+}, even though the ionic radius of Ca^{2+} most closely matches the cavity radius of 15C5. The selectivity of Sr^{2+} and Pb^{2+} over Ca^{2+} may also be explained on the basis of the higher solvation energy of the smaller cation, Ca^{2+}. Mg^{2+}, like Li^+, is small enough to enter the cavity of 15C5, but too small to achieve optimal interaction. The high solvation energy of Mg^{2+} undoubtedly contributes to its extremely weak affinity for the ligand. Literature data in Table 1 also show that K^+–12C4 interaction gives a larger log K_1 value than Na^+–12C4 interaction. From these results it can be concluded that 12C4 and 15C5 macrocycles do not exhibit selectivities for the cation whose ionic radius is closest to the cavity radius of the macrocycle.

It was found that among 1+ cations, 18C6 is selective for K^+ and 21C7 is selective for Cs^+ [3]. Values of ΔH and $T\Delta S$ indicate that the K^+–18C6 and the Cs^+–21C7 complexes are enthalpy-stabilized. In these complexes, K^+ fits the cavity of 18C6 best, while Cs^+ fits the cavity of 21C7 best [3]. The log K data for Tl^+ show it to interact less with 18C6 than K^+ and less with 21C7 than Cs^+. These results are predictable considering that the ionic radius of Tl^+ is slightly larger than the cavity radius of 18C6 and slightly smaller than the cavity radius of 21C7. However, of these two ligands, 18C6 binds Tl^+

most strongly. The difference in radii between Tl^+ and the cavity of 18C6 is less than that between Tl^+ and the cavity of 21C7. For 2+ cations, both 18C6 and 21C7 are selective for Ba^{2+} over other bivalent cations. On the basis of size relationships, these results can be explained by the better fit of Ba^{2+} in the cavities of these crown ethers. Log K data were not obtained for Pb^{2+}–18C6 interaction in CH_3OH, but the log K value for this interaction in H_2O is higher than it is for the corresponding Ba^{2+} interaction [1,2]. This is surprising on the basis of size relationships because Pb^{2+}, being smaller than Ba^{2+}, would not be expected to fit the cavity of 18C6 as well as Ba^{2+}. The result may be due either to greater covalent bonding contributions in the case of Pb^{2+} or to solvation effects. Frensdorff reported log K values for K^+–24C8 and Cs^+–24C8 interactions in CH_3OH [15]. Gokel et al. [5] have also reported log K values for Na^+–24C8, K^+–24C8 and Ca^{2+}–24C8 systems in CH_3OH. These log K values for M^{n+}–24C8 interactions are lower than those for M^{n+}–21C7 interactions. This is expected in the case of 24C8 because of a decrease in the cation ionic radius-to-cavity radius ratio.

Where data are available, the log K values in Table 1 for M^{n+}–dibenzo-substituted crown ether interactions decrease successively in the series, DB18C6, DB21C7, DB24C8, and DB27C9 for all of the cations studied except Na^+, Ag^+, Tl^+, Cs^+, and Pb^{2+}. The log K values would be expected to decrease, except for that pertaining to Cs^+–DB21C7 interaction, because of a decrease in the ratio of cation ionic radius to crown ether cavity radius. However, log K values for Na^+ and Ag^+ increase slightly from DB21C7 to DB27C9 and that for Pb^{2+} from DB21C7 to DB24C8. The unexpected magnitude of the log K values in the cases of Na^+, Ag^+, and Pb^{2+} may be a result of the ability of large crown ethers to wrap around relatively small cations and form stable complexes [3]. M^{n+}–DB30C10 interactions give log K values in every case higher than would be expected on the basis of size relationships. Crystal structure data of the K^+–DB30C10 complex show that the ligand completely wraps around K^+ so that all ten oxygen donor atoms of the ligand coordinate to K^+ [16]. The results in Table 1 show that complex stability as well as selectivity is generally decreased when the cavity radius becomes larger than the radius of 21C7. Therefore, it is concluded that the size relationship does not hold for large crown ethers.

Effect of benzo ring substituents

Attachment of a benzene ring to the periphery of a crown ether results in lower oxygen donor atom basicity (electron density) and, therefore, lower cation–crown ether complex stabilities [17]. We have determined log K, ΔH, and $T\Delta S$ only for the interactions of Na^+, Ag^+, and Pb^{2+} with B15C5. For each of these cations, the log K and $-\Delta H$ values in Table 1 are lower for B15C5 than for 15C5. The loss of electron density in the B15C5 cavity results in lower log K and $-\Delta H$ values for M^{n+}–B15C5 interactions. The above argument also applies to the finding that log K and $-\Delta H$ values decrease from 18C6 to B18C6 for every cation studied except for the $-\Delta H$ values in the case of Ag^+–crown ether interactions. Addition of a second benzo group to B18C6 to form DB18C6 results in log K and $-\Delta H$ values that decrease in every instance studied, except for the log K values of Na^+. Crystal structure data of the Na^+–18C6 complex show Na^+ coordinated to all six oxygen atoms of 18C6 and to one H_2O molecule. One of the oxygen atoms of the ring coordinates above the plane of the complex [18]. On the other hand, crystal structure data of the Na^+–DB18C6 complex show Na^+ coordinated to all six DB18C6 oxygen atoms lying in the same plane. In addition, two H_2O molecules coordinate Na^+, one from above and one from below the plane of the complex [16]. The log K values in Table 1 for Na^+–DB18C6 interaction are similar in magnitude to those for Na^+–18C6 interaction. It might be reasoned that coordination of Na^+ by 18C6, rather than DB18C6, requires extra desolvation of the cation. The loss of free energy incurred for this extra desolvation is offset by the loss of free energy incurred when the more electron-deficient DB18C6 complexes Na^+. The Na^+–DB18C6 interaction results in a more favorable $T\Delta S$ value compared to those for Na^+–18C6. Usually, dibenzo-substituted crown ethers have more positive $T\Delta S$ terms with a given cation than un- or monobenzo-substituted crown ethers. This is consistent with the idea that less conformational change is allowed for M^{n+}–DB18C6 interactions because of the rigidity of the DB18C6 molecule.

Generally, log K values decrease more for 2 + than for 1 + cations of comparable sizes in the series un-, mono-, dibenzo-substituted crown ether. For example, the difference in log K values between Ba^{2+}–18C6 and Ba^{2+}–B18C6 interactions is 1.56 log K units. The same difference for K^+–18C6 and K^+–B18C6 interactions is only 0.77 log K units. The difference in log K values between Ba^{2+}–B18C6 and Ba^{2+}–DB18C6 interactions is 1.20 log K units. The same difference between K^+–B18C6 and K^+–DB18C6 interactions is only 0.2 log K units. The selectivity of 18C6 for Ba^{2+} has been reduced significantly in the case of B18C6 and has been reversed in the case of DB18C6 reactions. Log K data in H_2O also decrease more for 2 + than for 1 + cations of comparable sizes in the above series [1]. The decrease in electron density in the cavities of mono- and dibenzo-substituted crown ethers results in a loss of M^{n+} attraction for the ligand and a corresponding less stable complex. As the ligand loses electron density the free energy of attraction of M^{n+} for the ligand decreases more for 2 + than for 1 + cations as can be calculated using eqn. (1) [11]

$$\Delta G = \frac{n\mu_1 Ze}{r_x^2} \tag{1}$$

where n is the number of donor atoms in the ligand, μ_1 is the dipole moment of the donor atom group in the ligand, Z is the charge on the metal ion, e is the charge on the electron, and r_x is the cation–dipole distance. Equation (1) represents the free energy for the electrostatic gas phase interaction of M^{n+} with the ligand. According to eqn. (1), ΔG and, therefore, log K should decrease more for 2+ than for 1+ cations in the series un-, mono-, dibenzo-substituted crown ethers. The experimental data substantiate this theory with only a few exceptions. The $-\Delta H$ values also generally decrease more for 2+ than for 1+ cations in the same series as would be expected.

CONCLUSIONS

18C6, B18C6, DB18C6, 21C7, and DB27C9 show selectivities among univalent cations studied for the cation whose ionic radius best matches the cavity radius of the crown ether. 18C6, 21C7, DB21C7, and DB24C8 show selectivities among bivalent cations studied for the cation whose ionic radius best matches the cavity radius of the crown ether. The cation radius-to-cavity radius relationship is not the determining parameter for the observed selectivities of the other cation–crown ether systems studied. It has generally been observed from data determined in this study and from literature data in Table 1 that, as macrocycle cavity radii become larger than cation radii, both complex stabilities and selectivities are decreased.

It has been found for all cations studied that log K and $-\Delta H$ values for cation–crown ether interactions decrease in the series un-, mono-, dibenzo-substituted crown ether (except log K in the case of Na^+–DB18C6 and $-\Delta H$ in the case of Ag^+–B18C6 interactions). This is attributed to the electron-withdrawing power of benzo groups. Log K and $-\Delta H$ values also decrease more for 2+ than for 1+ cations through the same series.

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