tible to conformational changes, which is consistent with the expected effect of the cyclohexo groups on ring rigidity.

The log K values in Table III for the reactions of Sr^{2+}, Ba^{2+}, and Pb^{2+} with II, IIIa, and IIIb are much larger than the corresponding values for the reactions of these metal ions with IV.[17] In addition, the Pb^{2+}–IV complex is reported to be less stable than the Ba^{2+}–IV complex, which is the opposite trend to that seen in Table III for II, IIIa, and IIIb. The results of Shchori et al.[17] with IV suggest that the effect of substitution of two benzo groups on II is to markedly lower complex stability for bivalent, but not univalent (Figure 1) metal ions and to reverse the Pb^{2+}, Ba^{2+} stability order. On the other hand, the data in Figure 2 generally show trends opposite to these for IIIa and IIIb when compared with II.

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Calorimetric Titration Study of the Interaction of Some Uni- and Bivalent Cations with Benzo-15-crown-5, 18-Crown-6, Dibenzo-24-crown-8, and Dibenzo-27-crown-9 in Methanol–Water Solvents, at 25 °C and $\mu = 0.1$[1]

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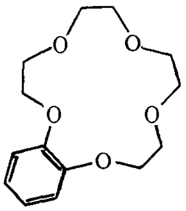
Abstract: The interaction between Na^+, K^+, Rb^+, Cs^+, Ca^{2+}, Sr^{2+}, and Pb^{2+} and the cyclic polyethers benzo-15-crown-5, 18-crown-6, dibenzo-24-crown-8, and dibenzo-27-crown-9 in CH_3OH–H_2O solvents has been studied using a calorimetric titration procedure. Log β_i, ΔH_i, and ΔS_i values are calculated in those instances where sufficient amounts of heat were produced. Complexes having 1:1 metal–ligand stoichiometry resulted with these ligands except for the Rb^+ and K^+-benzo-15-crown-5 systems at 70 and 80 wt % CH_3OH, which were found to be 1:2. As the cyclic polyether ring size increases, the ΔS values for the 1:1 reaction of a given cation become more negative, suggesting increased ligand conformational change upon complex formation.

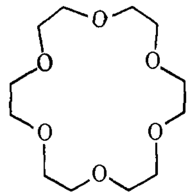
Following the initial observation of Pedersen[2] that certain cyclic polyethers selectively complex cations, extensive research has been conducted on the ability of compounds of this class to complex univalent and bivalent metal ions.[3] A striking result of this work was the observation that in aqueous solution certain of the cyclic polyethers (e.g., 18-crown-6) show marked cation selective behavior, while others (e.g., 15-crown-5[4] and dicyclohexo-24-crown-8[5]) do not. Also, stoichiometry other than 1:1 is observed[2b-d,3] under certain conditions. For example, when the cation is much larger than the ligand cavity, 1:2 cation to ligand complexes may be formed.

In the present investigation, the interactions of several uni- and bivalent cations with ligands I–IV in solvents of several H_2O–CH_3OH compositions have been studied by a calorimetric titration procedure. Log β_i, ΔH_i, and ΔS_i values are calculated in those experiments where sufficient heat was produced. These thermodynamic values are used to evaluate the following factors as they affect complex stability and/or the formation of complexes with other than 1:1 stoichiometry: (1) the composition of the solvent; (2) the ratio of cation diameter to polyether ring cavity diameter; (3) the number of potential cation coordination sites in the ring; and (4) the flexibility of the ring. These and other factors which determine the magnitude of log β_i values for the formation of cation–cyclic polyether complexes have been presented and discussed.[6-9]



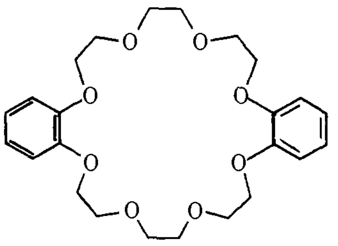
I

benzo-15- crown-5



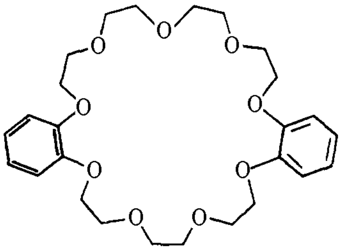
II

18-crown-6



III

dibenzo-24-crown-8



IV

dibenzo-27-crown-9

Experimental Section

Materials. The following chemicals were used in the study; NaCl, $CaCl_2 \cdot 6H_2O$, and $BaCl_2 \cdot 6H_2O$ (Baker and Adamson, ACS reagent); KCl (Matheson, Coleman, and Bell, ACS reagent), RbCl (Apache Chemicals, 99.9%); CsCl (J. T. Baker Chemical Co., 99.9%); $SrCl_2 \cdot 6H_2O$ (Baker Analyzed reagent); $Co(ClO_4)_2 \cdot 6H_2O$, $Cu(ClO_4)_2 \cdot 6H_2O$, $Pb(ClO_4)_2 \cdot 3H_2O$, and $Zn(ClO_4)_2 \cdot H_2O$ (G. Frederick Smith Chemical Co., reagent); $Cd(ClO_4)_2 \cdot 6H_2O$ (Alfa Inorganics); NH_4Cl (Fisher, reagent); methanol (Baker and Adamson Special Reagent Code 1217). Compound II (Peninsular Chemical Research, Inc., 99%) was used without further purification, while the remaining cyclic polyethers (I, III, and IV) were synthesized in our laboratories from reagent grade chemicals using the following procedures.

Compound I was prepared from catechol and 1,11-dichloro-3,6,9-trioxaundecane[2b] using the procedure given by Pedersen;[2b] mp 79–79.5 °C (lit.[2b] 79–79.5 °C). Compound III was prepared from catechol and 1,2-bis(2-chloroethoxy)ethane (Eastman) with potassium hydroxide as base, following the procedure used by Pedersen;[2b] mp, 102–103 °C;[10] NMR ($CDCl_3$) δ 3.85 (s, 8 H), 3.91 (m, 8 H), 4.18 (m, 8 H), and 6.91 (s, 8 H). Anal. Calcd for $C_{24}H_{32}O_8$: C, 64.27; H, 7.19. Found: C, 64.17; H, 7.06.

The preparation of compound IV was accomplished using the following procedures. A mixture of 20 g (0.1 mol) of catechol mono-2-tetrahydropyranyl ether,[11] 12 g of sodium hydroxide, and 50 ml of dimethyl sulfoxide was stirred under nitrogen at room temperature for 1 h. 1,11-Dichloro-3,6,9-trioxaundecane[2b] (35 g, 0.15 mol) was slowly added and the mixture was stirred at room temperature for an additional 3 h. Water was added to dissolve the solid and the mixture was extracted with diethyl ether. The ether extract was condensed to 100 ml, 50 ml of 7 M HCl was added, and the mixture was stirred overnight. The aqueous layer was separated, washed with ether, and the combined ether layers were washed with a 10% aqueous NaOH solution. The NaOH extract was saturated with CO_2 and continuously extracted with ether in a liquid–liquid extractor. The ether extract was dried over anhydrous $MgSO_4$ to give 23.0 g (89% yield) of residue which gave a positive test for phenol and exhibited one large peak in the vapor-phase chromatograph. The residue was stirred with 10.3 g of NaOH in 50 ml of dimethyl sulfoxide for 30 min. 1,2-Bis(2-chloroethoxy)ethane (25.5 g, 1.5 equiv, 0.13 mol) was added dropwise and the mixture was stirred for an additional 3 h. Water was added to dissolve the solid and the aqueous solution was extracted with ether to give a 4:1 mixture of 1,2-bis(2-chloroethoxy)ethane and IV. The aqueous layer was further extracted with heptane continuously in a liquid–liquid extractor. The heptane extract, upon cooling, gave white crystals. Recrystallization from ether–hexane yielded 6.4 g of IV: mp 81.5–82.0 °C; NMR ($CDCl_3$) δ 6.77 (s, 12 H), 3.96 (m, 8 H), 4.18 (m, 8 H), and 6.90 (s, 8 H). Anal. Calcd for $C_{26}H_{36}O_9$: C, 63.40; H, 7.37. Found: C, 63.48; H, 7.50.

Solution Preparation. The solvents were prepared from weighed amounts of methanol and boiled, doubly distilled water. Salt solutions (0.004–0.008 M or 0.15–0.25 M) were prepared by dissolving the appropriate weight of each salt in the methanol–water solvents. The NaCl, KCl, RbCl, and CsCl salts were dried at 120 °C for 24 h prior to weighing. The $Pb(ClO_4)_2$ solution was standardized gravimetrically by precipitation of $PbCrO_4$. The $SrCl_2$ and $CaCl_2$ solutions were standardized by Mohr titration. The $BaCl_2$ solution was standardized volumetrically by observing the end point when a solution of barium "rhodizonate" was converted to barium sulfate.

The cyclic polyether solutions were prepared by dissolving known weights of I, II, III, and IV in the appropriate solvent to give final concentrations of 0.1 or 0.01 M.

Procedure and Calculations. The calorimetric determinations were made at 25 °C using a Tronac precision titration calorimeter (Tronac, Inc., Orem, Utah).[12-15] The cyclic polyether solutions were titrated into the metal ion solutions whenever possible. However, in the cases of III and IV, where the solubilities of the cyclic polyethers were not sufficient to give measurable results, the procedure was reversed and the metal ion solutions were titrated into the cyclic polyether solutions. Heat of dilution corrections were made by titrating solutions of the cyclic polyether or metal ion solutions into the solvent.

The method used to calculate log K and ΔH values from the calorimetric data using a nonlinear least-squares technique has been described.[16] In most cases, the equation

$$M^{n+} + L = ML^{n+} \quad \beta_1 = K_1 = [ML^{n+}]/[M^{n+}][L] \qquad (1)$$

was found to adequately describe the reaction occurring in the calorimeter. However, for the reaction of K^+ with I in 60, 70, and 80% CH_3OH and Rb^+ with I in 70% CH_3OH, eq 1 did not adequately describe the experimental data. Use of eq 1 and

$$M^{n+} + 2L = ML_2^{n+} \quad \beta_2 = K_1K_2 = [ML_2^{n+}]/[M^{n+}][L]^2 \qquad (2)$$

gave results in all cases which could be satisfactorily fitted to the experimental heat values. However, there was not sufficient heat generated in the titration of K^+ with I in 60% CH_3OH (because of low solubility of I) to allow calculation of reliable log β_1 and log β_2 values. Data collected by the reverse titration of I with K^+, where the heat is not limited by solubility, are not sensitive to the presence of 1:2 species; hence, no log β values were calculated for the K^+–I system in 60% CH_3OH. Log β_1 values for the Na^+–I system at 70 wt % CH_3OH calculated from heat data obtained using either Na^+ or I as

Table I. Log β_i, ΔH_i, and ΔS_i Values for the Interaction of Cyclic Polyether Compounds with Several Univalent and Bivalent Metal Ions at 25 °C and $\mu = 0.1$[a]

Ligand	M^{n+}	Solvent composition, wt % CH_3OH in H_2O[b]	Log β_i	i	ΔH_i, kcal/mol	ΔS_i, cal/(deg mol)
I	Na^+	0	0.4[c]			
		20	0.72 ± 0.03	1	−1.77 ± 0.02	−2.6
		40	1.17 ± 0.12	1	−2.63 ± 0.11	−3.5
		60	1.64 ± 0.04	1	−3.78 ± 0.08	−5.2
		70	1.99 ± 0.10	1	−3.82 ± 0.07	−3.7
		80	2.26 ± 0.02	1	−8.32 ± 0.03	−17.6
	K^+	0	0.38 ± 0.10	1	−2.33 ± 0.10	−6.1
		20	1.20 ± 0.10	1	−1.8 ± 0.2	−0.5
		40	1.92 ± 0.04	1	−2.51 ± 0.03	0.4
		70	1.5 ± 0.3	1	*d*	
			4.15 ± 0.02	2	−13.9 ± 0.2	−27.6
		80	2.2 ± 0.2	1	*d*	
			4.80 ± 0.05	2	−15.50 ± 0.13	−30.0
	Rb^+	70	1.8 ± 0.2	1	*d*	
			3.77 ± 0.05	2	−12.0 ± 1.5	−23.5
	Cs^+	70	1.70 ± 0.01	1	−2.43 ± 0.05	−0.4
	NH_4^+	70	*e*			
	Ca^{2+}, Sr^{2+}, Ba^{2+}	70	*e*			
	Pb^{2+}	70	2.04 ± 0.01	1	−5.11 ± 0.02	−7.8
	Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}	70	*e*			
II	Na^+	70	2.76 ± 0.02	1	−4.89 ± 0.01	−3.8
	K^+	70	4.33 ± 0.05	1	−9.68 ± 0.01	−12.7
	Rb^+	70	3.46 ± 0.10	1	−9.27 ± 0.05	−15.3
	Cs^+	70	2.84 ± 0.01	1	−8.09 ± 0.01	−14.1
	Ca^{2+}	70	2.51 ± 0.02	1	−4.27 ± 0.02	−2.8
	Sr^{2+}	70	5.0 ± 0.1	1	−7.49 ± 0.01	−2.5
	Ba^{2+}	70	6.0[f]	1	−10.66 ± 0.01	−8.5
	Pb^{2+}	70	6.5[f]	1	−9.19 ± 0.01	−1.1
III	Na^+	70	1.54 ± 0.01	1	−7.75 ± 0.02	−18.9
	K^+	70	2.42 ± 0.01	1	−8.54 ± 0.01	−17.6
	Rb^+	70	2.55 ± 0.01	1	−8.72 ± 0.02	−17.6
	Cs^+	70	2.48 ± 0.01	1	−8.93 ± 0.02	−18.6
IV	Na^+	70	1.50 ± 0.01	1	−11.74 ± 0.01	−32.5
	K^+	70	2.86 ± 0.01	1	−9.50 ± 0.01	−18.8
	Cs^+	70	1.42 ± 0.02	1	−6.14 ± 0.06	−14.1

[a] Values are the averages taken from four to six determinations. The uncertainties are given as the standard deviation of the mean. [b] These solutions have the following dielectric constants: 0% (78); 20% (70); 40% (61); 60% (52); 70% (47); 80% (43); and 100% (33). [c] Estimated from data in Figure 1, see text. [d] No value calculated, see text. [e] No significant amount of heat was produced, indicating that either $\Delta H = 0$ or no significant amount of reaction took place. [f] Estimated from data in Figure 2, see text.

titrant were the same within experimental uncertainty, indicating that only one species is present in this case.

Results

The results of the study are given in Table I. Log β_i, ΔH_i, and ΔS_i values are given where the heat generated was sufficient to allow these quantities to be calculated or where they could be estimated by other means. The mixing of Na^+ and I in aqueous solution did not produce sufficient heat to allow calculation of a K value. However, extrapolation of the plot of log β_1 for the 1:1 Na^+–I reaction vs. the reciprocal of the solvent dielectric constant, D, (Figure 1) allows the estimation of log K for aqueous solution as 0.4. The reactions of Ba^{2+} and Pb^{2+} with II in 70 wt % CH_3OH were quantitative and we were unable to calculate log β_1 values from the calorimetric data. An estimate of the log β_1 values for these reactions was made from the plot of log K vs. cation radius given in Figure 2. In this plot, a nearly constant difference is seen between the log β_1 values in aqueous and 70 wt % CH_3OH solvent for reaction 1 where L = II. Assuming that similar differences exist in the cases of Ba^{2+} and Pb^{2+} in going from H_2O to 70 wt % CH_3OH, values of log K in 70 wt % CH_3OH for the reaction of these cations with II are estimated to be 6.0 and 6.5, respectively.

The β_1 values for K^+–I interactions in 70 and 80 wt % CH_3OH and Rb^+–I interaction in 70 wt % CH_3OH have large uncertainties associated with them. The uncertainty in β_1 in each case originates in the attempt to apportion the β_2 values between their constituent K_1 and K_2 values where $K_2 > K_1$.[17] Because of the uncertainties in the consecutive constants, no attempt was made to calculate ΔH_i values for the consecutive reactions.

Discussion

Medium Effect on Stability and Stoichiometry of Benzo-15-Crown-5 Complexes. The free energy change for the electrostatic process involving a separation of charged species in a dielectric medium is inversely related to the dielectric constant.[18] If the bonding between uncharged cyclic polyethers and charged cations is electrostatic in nature, as has been suggested,[2,8] one might expect to see a similar dependence of the free energy change on the dielectric constant of the solvent. The plot in Figure 1 of log β_1 vs. $1/D$ is nearly linear, suggesting large electrostatic contributions as would be expected for the binding of Na^+ and K^+ to this ligand. Above 60 wt % CH_3OH 1:2 K^+ complexes are formed. Log β_1 data for

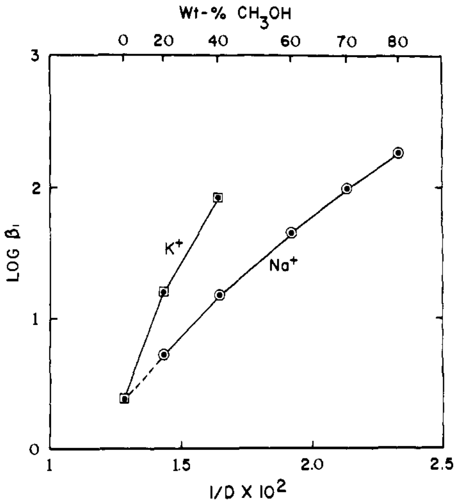


Figure 1. Plot of log β_1 for the reaction $M^+ + L = ML^+$ (L = benzo-15-crown-5) vs. the reciprocal of the dielectric constant.

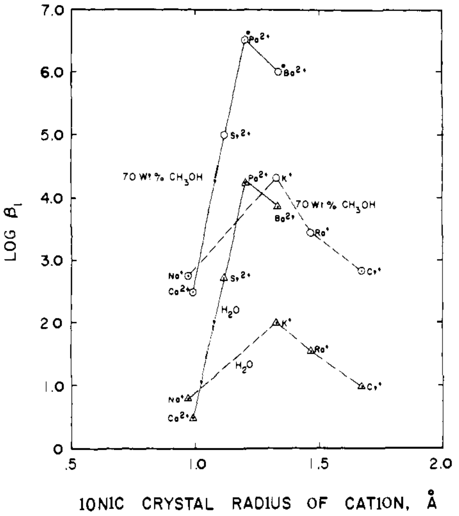


Figure 2. Plot of log β_1 for the reaction $M^{n+} + L = ML^{n+}$ (M^+ - - - , M^{2+} —, L = 18-crown-6) in aqueous and 70 wt % CH_3OH solvents. An asterisk denotes an estimated value, see text.

these complexes are not included in Figure 1, since factors other than the dielectric constant, such as selective cation solvation, solvent structure changes, and ion pairing, may become important for these systems.

The heat produced from the interaction of Na^+ with I in aqueous solution was not large enough to calculate log β and ΔH values, although extrapolation of the data in Figure 1 indicates that log β_1 is approximately the same for the Na^+ and K^+ complexes. This result is consistent with the finding[4] that log K_1 values for the reaction in aqueous solution of Na^+ and K^+ with 15-crown-5 are nearly the same (0.70 and 0.74, respectively).

There is a marked increase in ΔH_1 for the reaction of Na^+ with I in going from 70 to 80% CH_3OH. Although there is no evidence for 1:2 complex formation as is the case with K^+ in solvents with more than 60% CH_3OH, this large increase in ΔH_1 must reflect changes occurring in the structure of the solvent mixture or in the solvation properties of the cyclic polyether and cation at this solvent composition.

Medium Effect on Stabilities of 18-Crown-6 Complexes. Log β_1 values for the reaction of II with uni- and bivalent cations in aqueous solution have been published.[4] The results in Table I allow comparisons to be made between log β_1 values valid in aqueous and 70 wt % CH_3OH solvents. The log β_1 values are plotted in Figure 2, where it is seen that the curves generally are parallel, but shifted approximately 2.0 log β_1 units higher in the methanol solvent. The positions of maximum stability for each charge type remain approximately the same. As the methanol fraction of the solvent increases, the quantity of heat liberated per mole and the log β_1 values (Figure 1) both increase for Na^+. The interaction of K^+ with I shows similar behavior with the exceptions that sufficient heat is generated in aqueous solution to estimate a log β_1 value, and 1:2 complexes are formed between K^+ and I in 70 and 80% CH_3OH solvents. The selectivity of benzo-15-crown-5 for K^+ over Na^+ increases as wt % CH_3OH increases in these CH_3OH-H_2O solvents. Similar results are reported by Lehn and Sauvage[19] for the case of Na^+ and K^+ interaction with several cryptates, selectivity by these ligands for K^+ being greater in 95% CH_3OH than in water. The structure of the 1:2 complex formed between K^+ and I in 70 and 80% CH_3OH is not known. However, it is likely that a "sandwich" type arrangement exists with the K^+ located between the two ligands as has been observed for the 1:2 potassium iodide-benzo-15-crown-5 crystal.[20] The calorimetric data for the reaction of K^+ with cyclic polyethers having larger ring sizes, II, III, and IV, show only 1:1 complexes, suggesting that in these ligands, the K^+ is positioned in the polyether cavity. It is not apparent why a 1:2 complex does not form in the case of the Cs^+-I interaction in the 70% methanol solvent. However, since the experimental data were adequately fit by reaction 1 alone, the contribution from reaction 2 is assumed to be small in this case.

Comparison of ΔH_1 and ΔS_1 values for univalent (Na^+, K^+, Rb^+, Cs^+) and bivalent (Sr^{2+}, Ba^{2+}, Pb^{2+}) cation interaction with II in aqueous[4,21] and 70 wt % CH_3OH solvents shows that, with the exceptions of Rb^+ and Cs^+, the increase in log β_1 is almost entirely due to an increasingly favorable ΔH_1 change, the change in ΔS_1 going from aqueous to 70% CH_3OH solvent composition remaining essentially constant. In the cases of Rb^+ and Cs^+, $-\Delta S_1$ changes of 10 and 6 cal/(deg mol), respectively, are seen compared to 0, 1.2, 2.1, 2.1, and 3.1 for Na^+, K^+, Sr^{2+}, Ba^{2+}, and Pb^{2+}, respectively. Values of ΔS_1 for the 70% CH_3OH solvent were more negative than those in the aqueous solvent in all cases.

Previous studies[4,21] have shown that entropy changes for 1:1 metal complexation with 15-crown-5 and 18-crown-6 in aqueous solution are generally small (<-10 cal/(deg mol)) and negative. Several factors contribute to ΔS, including relative contributions of cation and ligand dehydration, and ligand conformation changes upon complexation. In the small ring compounds, ligand conformation changes are likely small and the small ΔS_1 changes suggest that the solvation effects are also minimal. However, there should be an increase in ring flexibility with increasing free ligand ring size, resulting in more negative ΔS_1 values upon complexation. The data in Table I are generally consistent with this expectation. For example, comparison of ΔS_1 values valid in 70 wt % CH_3OH for formation of 1:1 complexes of Na^+, shows ΔS_1 to be nearly constant for I and II, but to be markedly more negative for the larger ring compounds III and IV. The small ΔS_1 values in the cases of I and II suggest that the structures of these ligands are relatively rigid and do not lend themselves to significant conformational changes. This observation is consistent with the x-ray structure observed by Bush and Truter for the Na^+-I complex.[22] Values of ΔS_1 for the reaction of Na^+ with II and other 18-crown-6 and 15-crown-5 ligands in aqueous solution are likewise numerically small (<-10 cal/(deg mol)).[4] The ΔS_1 values for the reactions of III and IV with Na^+ are substantially more negative, suggesting that significant conformational changes may be important in the formation of these complexes.

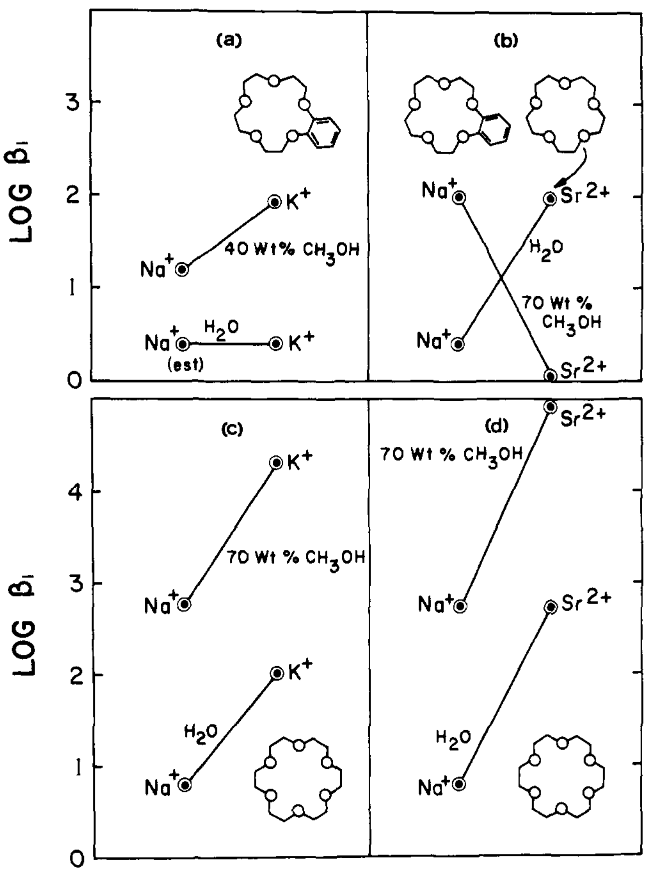


Figure 3. Plot of log β_1 for the reaction $M^{n+} + L = ML^{n+}$ for several cation pairs in H_2O-CH_3OH solvents.

Effect of Ring Size and Solvent Composition on Complex Stability. The absence of a reaction between the alkaline earth metal ions—Ca^{2+}, Sr^{2+}, and Ba^{2+}—and benzo-15-crown-5 in 70 wt % CH_3OH is interesting, since these cations react with 18-crown-6 in this solvent and with 15-crown-5 in aqueous solution.[4] Change in solvent composition from water to water-methanol mixtures results in different cation selectivity patterns for 15-crown-5 and 18-crown-6 ligands. These differences are seen in part in Figures 1 and 2 and are further illustrated in Figure 3, where log β_1 values for 1:1 reactions of several pairs of cations with 18-crown-6 and benzo-15-crown-5 (15-crown-5 in the case of Sr^{2+}, Figure 3b) are compared. There is a regular increase for either the Na^+,K^+ or Na^+,Sr^{2+} pair in the case of 18-crown-6, but for benzo-15-crown-5 differentiation between either K^+ and Na^+ or Sr^{2+} and Na^+ is enhanced in the CH_3OH solvent. This is especially true of the Na^+/Sr^{2+} case where selectivity of Na^+ over Sr^{2+} (or other alkaline earth cations) is markedly enhanced by increasing the fraction of the CH_3OH component of the solvent.

Pedersen[2b] observed that a complex is more stable (higher log β value) the greater the number of potential coordination sites in the ring, provided the sites are coplanar and symmetrically distributed. The two ligands in the present study which fit these requirements are I and II, ligand III (and presumably IV as well) being cylindrically symmetrical according to Pedersen. The log β_1 values for I and II (Table I) confirm Pedersen's statement.

Examination of the ΔH_1 data for the reaction of Na^+, K^+, and Cs^+ with I and II in 70 wt % CH_3OH show $-\Delta H_1$ to become more positive in the case of each cation with an increase of one donor atom in the polyether ring as would be expected if the magnitude of ΔH_1 is related to the number of metal-donor atom bonds. The larger ring compounds do not show a corresponding increase in ΔH_1 with ring size except in the case of Na^+. The ΔH_1 and ΔS_1 data in Table I taken together, however, show interesting and consistent changes as a function of ligand cavity size (15-crown-5 through 27-crown-9) for the alkali metal ions. Between H_2O and 70 wt % CH_3OH there is a large change in ΔH_1 (−3.82 to −11.74) and in ΔS_1 (−3.7 to −32.5) for the case of Na^+, which is consistent with the change which might be expected from an increase in cavity size with a consequent increase in the number of donor atoms and in ligand flexibility. This observation is interesting in connection with x-ray crystallographic data for the K^+-dibenzo-30-crown-10 complex, where extensive ligand conformation change between the complexed and uncomplexed ligand is found.[22] Of the two cations, Na^+ has the greater charge density and the ΔH_1 and ΔS_1 values in Table I suggest that it may be more effective than K^+ in ordering the large cyclic polyether ring. With the 27-crown-9 ring, the largest negative ΔH_1 and ΔS_1 values are found with Na^+, the latter quantity indicating that a greater ligand conformation change is required to accommodate the smaller alkali metal ion. The favorable ΔH_1 value, however, is more than balanced in the case of Na^+ by the large negative ΔS_1 value resulting in a smaller log β_1 value (1.50) than that (2.76) found for formation of the K^+-18-crown-6 complex. The need for large conformational changes to accommodate the cation with correspondingly large negative ΔS_1 changes in the case of the more electronegative Na^+ could account for the large selectivity of K^+ over Na^+ by macrocyclic compounds of large ring size such as valinomycin and nonactin.[8] For example, the difference in the log K values for the interaction in CH_3OH of K^+ and Na^+ with valinomycin is 4.3, while the corresponding difference in the log K values for the reaction of these cations with the relatively inflexible dibenzo-18-crown-6 is 0.3[23]

References and Notes

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