Complex Formation of Alkaline Earth Cations with Benzo-15-Crown-5 and some 18-Crowns in Methanol, Dimethylformamide and Dimethyl sulfoxide Solutions

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Abstract

The complexation of alkaline earth cations by benzo-15-crown-5, 18-crown-6, 1,10-diaza-18-crown-6 and dibenzo-18-crown-6 has been studied in methanol, dimethylformamide and dimethyl sulfoxide solutions by means of a competitive spectrophotometric technique using murexide as a metal ion indicator. The selectivities and stabilities of the resulted 1:1 complexes were found to be strongly solvent dependent. There is an inverse relationship between the stabilities of the complexes and Gutmann donicity of the solvents. In all solvents used, the stability of alkaline earth complexes with various 18-crowns increase in the order $Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$, while the formation constants of benzo-15-crown-5 complexes vary in the order $Ca^{2+} > Sr^{2+} > Mg^{2+}$. It was found that the alkaline earth–18-crown interaction is strongly dependent upon the nature of substituents on the ring; the stability of the resulting complexes with the same cation vary in the order 18-crown-6 > 1,10-diaza-18-crown-6 > dibenzo-18-crown-6.

Introduction

The synthesis of macrocyclic polyethers known as crowns by Pedersen, and the observation of the affinity of these ligands to alkali and alkaline earth cations [1], have led to intensive efforts to understand the factors which control the thermodynamic and kinetic stability of the resulted complexes in solution [2]. Most of the research works in this area has been focused on alkali–crown ether complexes and, in comparison, information on the corresponding alkaline earth complexes is much less available. Furthermore, the majority of such studies on alkaline earth–crown ether complexation have been carried out in water and water–methanol mixtures and information in non-aqueous media is quite sparse [2].

It was of interest to us to study the effects of variables such as crown ether ring size, ring substituent and ring flexibility, and especially the solvent properties on the selectivity and stability of crown ether complexes with alkaline earth cations. We have recently reported the results of the study of alkaline earth complexes with dibenzo-30-crown-10 in some non-aqueous solutions [3]. In this paper we report the study of Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} complexes with benzo-15-crown-5 and some 18-crowns (Fig. 1) in methanol, dimethylformamide and dimethyl sulfoxide solutions by a competitive spectrophotometric technique, using murexide as a metal ion indicator [4].

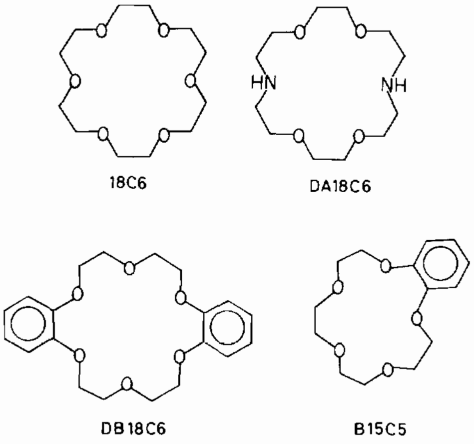

Fig. 1. Structure of crown ethers.

Experimental

Benzo-15-crown-5 (B15C5) was synthesized by a slight modification of Pedersen's method [1]. The product was recrystallized from reagent grade acetone and vacuum dried. 18-crown-6 (18C6, Aldrich) was further purified by preparing the acetonitrile complex which was recrystallized from acetonitrile. The weakly bonded solvent was removed under vacuum. Dibenzo-18-crown-6 (DB18C6, Parish) was

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recrystallized from benzene; 1,10-diaza-18-crown-6 (DA18C6, MCB) was recrystallized from n-heptane. After recrystallization, both ligands were dried under vacuum for several days.

Methanol (MeOH, Baker), dimethylformamide (DMF, Fisher) and dimethyl sulfoxide (DMSO, Fisher) were purified and dried by the previously described methods [5]. Reagent grade magnesium chloride, calcium chloride, strontium nitrate (all from Merck Co.), barium chloride (Fluka) and murexide (Merck) were dried over P_2O_5 *in vacuo* for 72 h. All spectra were obtained with a Model 34 Beckman UV–Vis Spectrometer at 25 ± 1 °C.

The formation constants of alkaline earth–murexide complexes were determined by the absorbance measurements at several wavelengths of the spectra of solutions in which varying concentration of metal ions (1.0×10^{-5}–1.0×10^{-4} M) were added to a fixed concentration of murexide (2.0×10^{-5} M) in different solvents. The alkaline earth–murexide formation constants in MeOH, DMF and DMSO are reported elsewhere [6]. The formation constants of various alkaline earth–crown ether complexes were determined by recording the spectra of a series of solutions containing varying amounts of the crown ethers and fixed concentrations of metal ions and murexide. Attainment of equilibrium was checked by the observation of no further change in the spectra after several hours. Errors associated with the formation constants were reported as ± standard deviations.

Results and Discussion

The calculated formation constants of all resulting complexes between Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} ions and different crown ethers (Fig. 1) in MeOH, DMF and DMSO solutions are presented in Table 1. The corresponding reported values in methanol and aqueous solutions are also included for comparison. The selectivity behavior of different crown ethers towards alkaline earth cations in methanol solution is shown in Fig. 2, and the relationships between the stabilities of alkaline earth–18-crown-6 complexes and crystal radii of the cations in various solvents are plotted in Fig. 3. It is seen from Table 1 that, in most cases, our results show a satisfactory agreement with those reported in the literature (and obtained by different techniques).

All of the solvents used in this study have relatively high dielectric constants (Table 1) and at the very low salt concentrations at which we worked (10^{-4}–10^{-5} M), the amount of ion pairing with free alkaline earth cations, and especially with large complex ions, is negligible. Therefore, the nature of the anion should not influence the complexation reactions.

TABLE 1. Formation Constants of Different Alkaline Earth–Crown Ether Complexes in MeOH, DMF and DMSO Solutions at 25 °C

Ligand	Solvent	D^a	DN^b	Log K_f			
				Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
B15C5	MeOH	32.7	19.7	2.27 ± 0.07	2.66 ± 0.06	2.42 ± 0.08	
	DMF	36.7	26.6	<2.0	2.32 ± 0.08	2.15 ± 0.06	
	DMSO	46.7	29.8	<2.0	2.12 ± 0.05	<2.0	
18C6	MeOH	32.7	19.7	3.61 ± 0.06	4.25 ± 0.10	5.64 ± 0.12	7.15 ± 0.13
					3.86[c]	>5.5[c]	7.04[c]
	DMF	36.7	26.6	2.50 ± 0.05	3.03 ± 0.07	4.23 ± 0.10	5.29 ± 0.12
	DMSO	46.7	29.8	2.22 ± 0.06	2.49 ± 0.07	3.63 ± 0.10	4.68 ± 0.10
	H_2O	78.5	33.0	–	1.8[d]	2.73[e]	3.87[e]
DA18C6	MeOH	32.7	19.7	3.40 ± 0.06	3.89 ± 0.07	4.75 ± 0.11	5.98 ± 0.10
					3.87[f]	5.99[f]	6.12[f]
	DMF	36.7	26.6	2.37 ± 0.06	2.70 ± 0.06	4.00 ± 0.07	4.25 ± 0.09
	DMSO	46.7	29.8	2.06 ± 0.07	2.35 ± 0.08	3.24 ± 0.09	3.45 ± 0.08
	H_2O	78.5	33.0			2.57[g]	2.98[g]
DB18C6	MeOH	32.7	19.7	2.33 ± 0.07	2.83 ± 0.08	3.45 ± 0.08	4.40 ± 0.09
						3.55[h]	4.28[i]
	DMF	36.7	26.6	<2.0	2.02 ± 0.07	2.37 ± 0.08	3.25 ± 0.07
	DMSO	46.7	29.8	<2.0	<2.0	2.08 ± 0.07	2.62 ± 0.09
	H_2O	78.5	33.0			1.0[i]	1.95[j]

[a] *D* = dielectric constant, ref. 7. [b] *DN* = donor number, ref. 7. [c] Ref. 8. [d] Ref. 9. [e] Ref. 10. [f] Ref. 11. [g] Ref. 12. [h] Ref. 13. [i] Ref. 14. [j] Ref. 15.

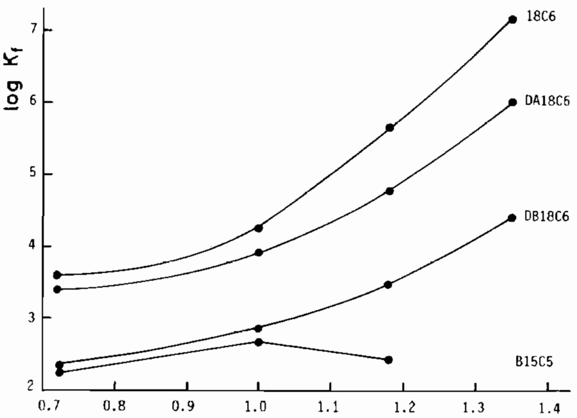

Fig. 2. The selectivity behavior of different crown ethers toward alkaline earth cations in methanol solution.

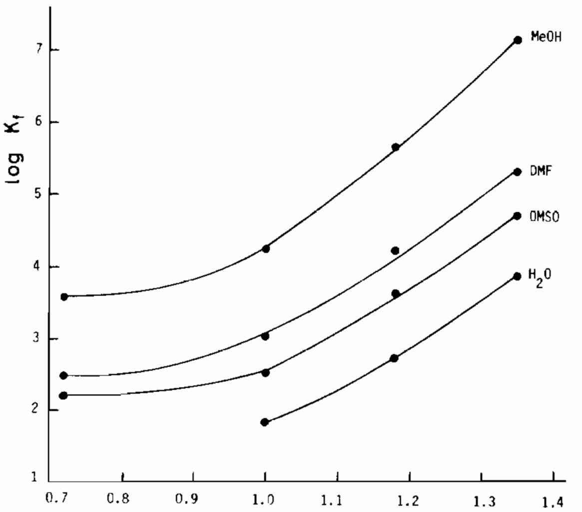

Fig. 3. Stability constants of alkaline earth–18C6 complexes *vs.* ionic radii of the cations in various solvents.

From Table 1, it is immediately obvious that the nature of solvent has a very important effect on the stability and selectivity of the resulting complexes. In all cases, the stability of the complexes increase with decreasing the solvating power of the solvents, as expressed by the Gutmann donor number [7]. Methanol is the solvent with the lowest donicity and, therefore, shows the least competition with the ligand molecules for cations which in turn results in the most stable complexes in the series. The results in water which is a better donating solvent than those used in this study follow nicely the lines of the argument. We have previously observed the same type of solvent effect on the complexation of macrocyclic ligands [3, 16–20].

The selectivities of various 18-crowns for Ba^{2+} over Ca^{2+} ion in different solvents are listed in Table 2. It is seen that the selectivity is invariably influenced by the solvent properties as well as the rigidity of the ligand molecules used. With the same macrocycle, the Ba^{2+}/Ca^{2+} selectivity increases by decreasing the solvent donicity. On the other hand, the selectivity of DB18C6, with a considerably more rigid structure than the 18C6 or DA18C6 ligands, varies much less with the solvent in comparison with that of other 18-crowns. The same effect has already been reported in the literature for the case of alkali complexes with 18-crowns [21].

TABLE 2. The Selectivities of Different 18-Crowns for Ba^{2+} Ion over Ca^{2+} Ion in Various Solvents at 25 °C

Ligand	$K_f(Ba^{2+})/K_f(Ca^{2+})$			
	MeOH	DMF	DMSO	H_2O
18C6	794.3	182.0	154.9	117.5
DA18C6	123.0	35.5	12.6	
DB18C6	37.1	17.0		

The stability of alkaline earth complexes with various 18-crowns in all solvents used, increases in the order Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}, while the formation constants of B15C5 complexes vary in the order Ca^{2+} > Sr^{2+} > Mg^{2+}. Barium ion with an ionic radius of 1.35 Å [22] nicely fits inside the cavities of 18-crowns with radii of 1.3–1.6 Å [23]. Other cations with smaller ionic sizes are too loose for the cavities of these ligands, resulting in weaker complexes. On the other hand, the cavity of the B15C5 macrocycle (0.85–1.1 Å in radius) matches properly with the Ca^{2+} ion size (r = 1.0 Å), while the smaller Mg^{2+} ion (r = 0.72 Å) and larger Sr^{2+} ion (r = 1.18 Å) would fail to achieve the best fit condition.

However, it should be noted that the thermodynamic stability constants are not just a measure of the absolute strength of the complexes, an understanding from the 'ion-in-the-hole' model [2], but a measure of the relative strength as compared to the ionic solvation. Thus it is only for the weakly solvated larger ions (such as Ba^{2+} ion) that the cation size can be considered primarily responsible for the complexing characteristics. While, in the case of smaller cations like Mg^{2+} ion, the cation is so strongly solvated that considerably more energy must be expended in the desolvation step than for the larger cations. Contributions of the solvent–complex and even solvent–ligand interactions on the stability of the resulting complexes cannot be ignored. It has been shown that in some solvents there are rather strong interactions between the macrocyclic ligands and solvent molecules [24, 25], in which the extent of interaction depends on the structure of the solvent. It is clear that such interactions can modify the complexing abilities of the macrocyclic ligands in solution.

Comparison of the data given in Table 1 shows that among the 18-crowns used, where the ring frame remains the same, alkaline earth–crown interaction is strongly a function of the nature of substituents on the ring which control the electron-pair donicity as well as the flexibility of the ligand molecules. The substitution of two oxygen atoms by two nitrogens in the 18C6 macrocyclic ring significantly decreases the stability of the alkaline earth complexes. Similar results have been reported in the case of alkali–crown complexes [17, 23]. Figure 2 shows that the effect is most pronounced in the case of the barium complex. These results are not unexpected since the Ba^{2+} ion is the hardest acid among the alkaline earth cations and consequently would interact less strongly with the nitrogen atoms of the ring as soft bases.

The effect of substitution of two benzo groups on the 18C6 ring is to markedly lower the complex stability of the alkaline earth complexes. It should be noticed that the introduction of two electron withdrawing benzo groups reduces the donicity of the oxygen atoms in the ring and hence reduces the cation–crown interaction. On the other hand DB18C6 is a more rigid molecule than 18C6, so that the existence of two bulky benzo groups on the ring of 18C6 would prevent the macrocyclic molecule wrapping itself around the cation. Combination of the two mentioned factors causes a drastic decrease in the stability of alkaline earth complexes with DB18C6 in comparison with corresponding complexes with 18C6 and even DA18C6.

The above results strongly emphasize the variability of factors which affect the stability of a macrocyclic complex. While the relative sizes of the macrocyclic cavity and of the cation play an important role, they are certainly not the unique, and not always the most important, factors which determine the stabilities of macrocyclic crown ether complexes. The nature of the solvent–cation, solvent–complex and solvent–ligand interactions as well as the relative donor abilities of the heteroatoms of the macrocyclic ring and the ring flexibility are also of considerable importance.

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