A Precise Calorimetric Study of 18-Crown-6 Complexes with Sodium, Potassium, Rubidium, Caesium, and Ammonium Ions in Aqueous Solution

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Synopsis. The complexation of 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) with sodium, potassium, rubidium, caesium, and ammonium ions has been studied by precise titration calorimetry in aqueous solution containing 0.1 mol dm^{-3} $(C_2H_5)_4NCl$ as a constant ionic medium at 25 °C. The calorimetric data were well explained in terms of the formation of the $[M(18\text{-crown-6})]^+$ ($M=Na^+$, K^+, Rb^+, Cs^+, and NH_4^+) complexes, and their formation constants, enthalpies, and entropies were determined. The thermodynamic parameters of the complexes thus obtained are discussed in relation to their structures in solution.

The complexation of 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) with alkali metal ion has been extensively studied in aqueous solution.[1-4] The stability of the complexes varies depending on metal ions. It has been demonstrated by molecular mechanics[5,6] and molecular orbital calculations[7] that the ionic size of the metal ions plays a key role in the stability of the complexes. However, all these calculations are carried out without definite knowledge concerning the solvation number and ring conformation of the complexes. In fact, according to our recent study by solution X-ray diffraction, the 18-crown-6 complexes of some alkali metal ions are extensively solvated in a different manner in aqueous solution.[8] Therefore, stabilities of the metal crown ether complexes in solution must vary also depending on their structure. However, the thermodynamic parameters such as reaction enthalpies and entropies so far obtained are limited[3] and not sufficient for a detailed comparison. More precise and reliable thermodynamic data may be needed for understanding the relationship between structure and stability of the crown ether complexes. In this work, we therefore focused our attention first to widely used 18-crown-6 as a ligand and aimed to determine the precise thermodynamic parameters of the metal complexes by using a precise titration calorimetry system.[9] We found appreciable differences between the thermodynamic parameters thus obtained and those previously reported.[3]

Experimental

Reagents. All Chemicals used were of reagent grade. Nisso 18-crown-6 (99%) was recrystallized once from acetonitrile.[10] 18-Crown-6 acetonitrile solvates thus obtained were dried in a vacuum oven at 35 °C for several days until a constant weight of the compound was attained. Sodium, potassium, rubidium, caesium, ammonium, and tetraethylammonium chlorides were recrystallized once from water and dried in a vacuum oven at 100 °C.

Measurements. Calorimetric measurements were carried out by using a fully automatic on-line calorimetry system at 25 °C. All test solutions contained 0.1 mol dm^{-3} $(C_2H_5)_4NCl$ as a constant ionic medium. A test solution containing alkali chloride or ammonium chloride was titrated with 0.2 mol dm^{-3} 18-crown-6 solution. Heats of complexation at each titration point were corrected for heat of dilution of titrants, which had been determined in advance by separate experiments.

Details of treatments of calorimetric data have been described elsewhere.[9]

Results and Discussion

Typical calorimetric titration curves for potassium and rubidium ions are shown in Fig. 1. The heat of reaction q measured at each titration point is normalized with the volume of the titrant added δv and the concentration of the ligand in the titrant $C_{L,tit}$, and the term $-q/(\delta v C_{L,tit})$ is plotted against C_L/C_M, where C_L and C_M denote the total concentration of the ligand and metal ion, respectively, in solution. The titration curves for all systems were well explained in terms of the formation of $[M(18\text{-crown-6})]^+$ ($M=Na^+$, K^+, Rb^+, Cs^+, and NH_4^+). The formation of $[M(18\text{-crown-6})_2]^+$ ($M=Rb^+$ or Cs^+) in aqueous solution, which has been suggested in some nonaqueous solutions,[4] was rejected in the course of the least-squares calculation. Final results are shown in Table 1, along with the literature values.[2,3] The solid lines in Fig. 1, calculated using the parameters in Table 1, well reproduced the experimental points. The formation constant is the largest for K^+, and practically the same value as that in the literature was obtained in this work. However, the formation constants and enthalpies for other metal ions are appreciably different.

According to molecular mechanics[5,6] and molecular orbital calculations,[7] the sodium ion interacts the most strongly with the 18-crown-6 ligand among alkali metal ions examined. This is reasonable because the metal–oxygen interaction energy may decrease in the order Na>K>Rb>Cs, in parallel with decreasing hydration energy of metal ions.[11] However, the potassium complex is the most stable among the alkali metal complexes examined in aqueous solution. This has been explained simply in terms of the cavity size of 18-crown-6 which fits best to the potassium ion.[2,3]

In crystal, it has been established that the sodium complex prefers the C_1 conformation,[12] while the potassium, rubidium, and caesium complexes prefer the D_{3d} conformation (Fig. 2).[13-16] According to solution X-ray diffraction of $[M(18\text{-crown-6})]^+$ in aqueous solution,[8] the sodium and potassium complexes have the C_1 and D_{3d} symmetries, respectively, as well as in crystal. These metal ions are accommodated in a cavity of 18-

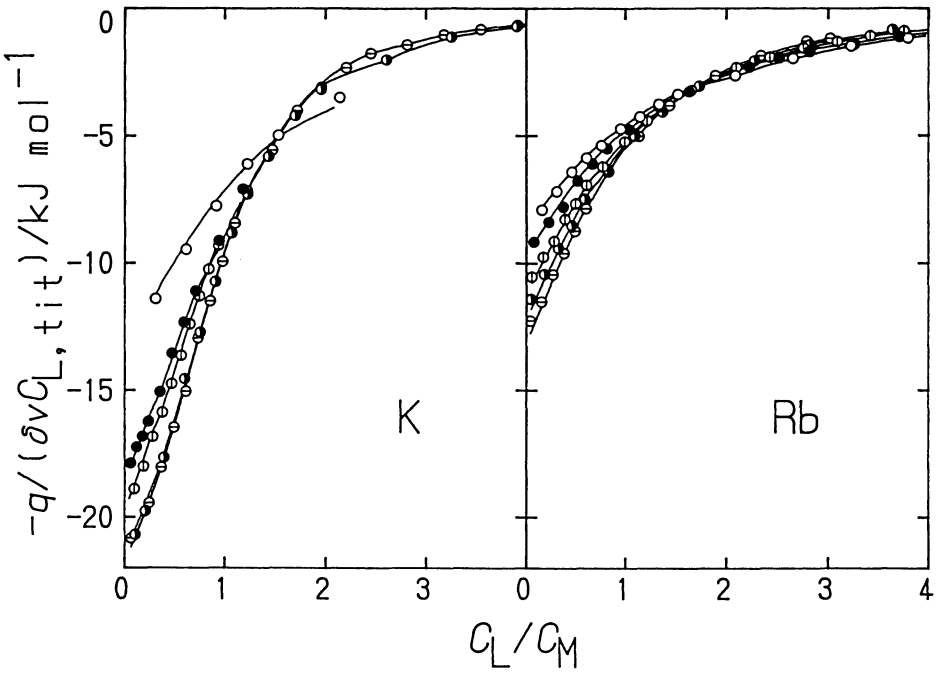

Fig. 1. Calorimetric titration curves for potassium and rubidium ions and 18-crown-6 solutions containing 0.1 mol dm^{-3} $(C_2H_5)_4NCl$ at 25 °C. Concentrations of metal ions in initial test solutions, $C_{M,init}$/ mmol dm^{-3} are 8.009 (○), 20.80 (●), 26.16 (⊕), 37.58 (◑), and 40.02 (⊖) for potassium solutions and 25.80 (○), 33.01 (●), 44.36 (⊕), 53.80 (◑), and 64.89 (⊖) for rubidium solutions.

Table 1. Least-Squares Refinements of Formation Constants, log(K_1/ mol^{-1} dm^3), and Enthalpies, ΔH_1°/ kJ mol^{-1}, of 18-Crown-6 Complexes in Aqueous Solution Containing 0.1 mol dm^{-3} $(C_2H_5)_4NCl$ as a Constant Ionic Medium at 25 °C

	Na	K	Rb	Cs	NH_4
r[a]	102	138	152	167	
ΔG_h°[b]	−410	−337	−316	−283	−320
log K_1	0.57(0.08)	2.04(0.01)	1.40(0.01)	0.92(0.02)	1.03(0.03)
	<0.3[c]	2.06[c]	—	0.8[c]	1.1[c]
	0.80[d]	2.03[d]	1.56[d]	0.99[d]	1.23[d]
ΔH_1°	−13.8(1.8)	−26.3(0.2)	−20.9(0.2)	−19.3(0.5)	−14.1(0.6)
	−9.41[d]	−26.0[d]	−16.0[d]	−15.85[d]	−9.79[d]
ΔS_1°	−35	−49	−43	−47	−28
R[e]	0.0317	0.0200	0.0179	0.0161	0.0270
N[f]	54	94	136	66	60

Values in parentheses refer to three standard deviations.
a) Effective ionic radius in pm quoted from R. D. Shannon, *Acta Crystallogr., Sect. A,* **32**, 751 (1976). b) The Gibbs energy of hydration in kJ mol^{-1} quoted from Ref. 11. c) Ref. 2. d) Ref. 3. e) Hamilton R factor. f) The number of calorimetric data points.

crown-6, and it has been suggested that the C_1 conformation is less stable by ca. 35 kJ mol^{-1} than the D_{3d} conformation.[5] Evidently, the conformational energy difference is larger than the difference between ΔH_1° values for the formation of [M(18-crown-6)]$^+$ (M=Na, K). Therefore, the smaller stability of [Na(18-crown-6)]$^+$ relative to that of [K(18-crown-6)]$^+$ may be originated from the difference in the ligand conformation, i.e., the stabilization energy of the sodium complex is reduced due to the unfavorable ligand conformation.

Unlike the potassium ion, the caesium ion with a relatively large ionic radius is not accommodated in, but is located out of the cavity of the ligand.[1] Although there is no direct structural evidence, the same may apply to the rubidium complex. So these metal complexes have significantly different structures. However, all these complexes may have the similar conformation, so that the difference in the conformational energies among these metal complexes may not be significant. The stability of [M(18-crown-6)]$^+$ decreases in the order of increasing ionic radius of metal ions, $K^+ > Rb^+ > Cs^+$. Also, the reaction enthalpy becomes less negative in the same order, though the change is not significant (Table 1). Such a result may be explained simply in terms of a decreasing electrostatic interaction between metal ions and the ligand with

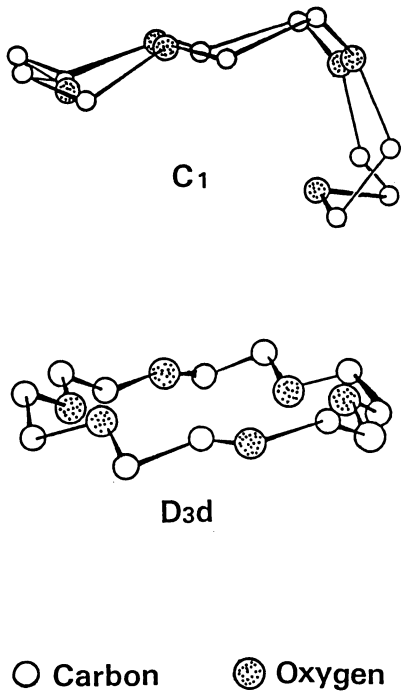

Fig. 2. The C_1 and D_{3d} conformations of 18-crown-6.

increasing ionic radii of metal ions. In other words, an unmatched ionic size of metal ions to the ligand cavity may not be an essential factor for the stability of the crown complexes in solution.

Despite that the ammonium ion has a similar ionic size and hydration energy to the potassium ion, the stability of $[NH_4(18\text{-crown-}6)]^+$ is significantly smaller than that of $[K(18\text{-crown-}6)]^+$, and the corresponding ΔH° and ΔS° values of the former complex are both less negative. The ammonium complex in crystal has the D_{3d} symmetry like the potassium complex, but the ammonium ion is located at 100 pm out of the 18-crown-6 ligand in crystal, i.e., the ammonium ion is bonded with three oxygen atoms of the ligand and one water molecule.[17] Therefore, the structure of the ammonium complex is different from that of the potassium complex, but is rather similar to that of the caesium complex. We postulate that the structure of $[NH_4(18\text{-crown-}6)]^+$ in solution is essentially the same as that in crystal, and the ammonium ion prefers a tetrahedral arrangement about the ion. Accordingly, the ammonium ion is prevented from entering the cavity and also from constructing a sufficient hydration shell, which may lead to a weak interaction of 18-crown-6 with the ammonium ion relative to the potassium ion.

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