Complexation Thermodynamics of Bis(crown ether)s. 2.[1] Calorimetric Titration of Complexation of Potassium Ion with Bis(benzocrown ether)s: Enthalpy–Entropy Compensation

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Calorimetric titrations in methanol–water (8:2) at 25 °C were performed to give the complex stability constants and thermodynamic properties for the complexation of potassium ion with a series of alkyl-bridged bis(benzo-15-crown-5 ether)s **1** and the corresponding oxo derivatives **2**. All bis(crown ether)s were shown to form intramolecular "1:2" sandwich-type complexes. The bis(crown ether)s **1** with an alkyl bridge gave higher complexing abilities in general than the oxo derivatives **2** and the previously reported Schiff base analogues **3** and **4**. The effects of the chain length and derivatization of the bridging chain upon complex stability are discussed. The ΔH–$T\Delta S$ plot gives a good linear relationship as has been demonstrated in the complexation of cations with a variety of glyme/podands, crown ethers, cryptands, and macrocyclic antibiotics. The enthalpy–entropy compensation effect again holds in the complexation with bis(crown ether)s.

A variety of bis(crown ether)s have recently been synthesized and have shown to possess higher binding abilities toward some cations than the corresponding mono crown ethers.[1,6–9] The facile formation of intramolecular "1:2" sandwich complex reasonably accounts for this enhanced binding abilities of bis(crown ether)s especially toward large cations, since two crown ether moieties linked by a bridging chain are intrinsically advantageous in the entropy term as compared with the parent mono crown ethers which have to reduce more degrees of freedom upon regular intermolecular 1:2 complex formation. It is also interesting to compare the complexation behavior of bis(crown ether)s with that of macrocyclic antibiotics, since they bear close analogy in the large conformational change and extensive desolvation caused by encapsulating complexation. However, few thermodynamic studies have been undertaken so far with bis(crown ether)s,[1,7c] and insufficient data are available to us to discuss their complexation behavior from the thermodynamic point of view.

We wish now to report our thermodynamic study on the intramolecular "1:2" complexation of potassium ion with a series of alkyl chain bridged bis(benzo-15-crown-5 ether)s (**1**) and their oxo derivatives (**2**) (Chart I) using titration calorimetry. The cation binding abilities and thermodynamic parameters for the bis(crown ether) complexation are discussed as a function of the length and derivatization of the bridging chain. We also test the validity of the enthalpy–entropy compensation effect which has been demonstrated in the complexation of cations with a variety of glyme/podands, crown ethers, cryptands, and macrocyclic antibiotics.[10]

Experimental Section

Materials. Dioxobis(benzocrown ether)s **2b,e,f** were synthesized in the reaction of benzo-15-crown-5 (**5**) with the appropriate alkanedioic acids in polyphosphoric acid. The Raney nickel reduction of the dioxobis(benzocrown ether)s gave the corresponding polymethylene-bridged bis(benzocrown ether)s **1b,d,e,f**. The detailed syntheses and identifications of these bis(crown ether)s and **1a** have been reported.[11]

The solvent methanol was refluxed over magnesium turnings and then distilled. The purified methanol was mixed with distilled, deionized water [(1.0–1.2) × 10⁻⁶ S/cm] to make a mixed solvent for calorimetry. Analytical-grade potassium thiocyanate was dried in vacuo prior to use.

Apparatus and Procedures. Calorimetric titration experiments were performed at 25 °C by using a Swedish LKB-8721-2 precision calorimeter in a thermostated water bath, which was connected to an Apple II microcomputer for automated titration and data processing.[12] The minimum temperature change detectable by the calorimeter was 8 × 10⁻⁵ °C, or 0.0079 cal.

The principle of measurement is conventional,[13] and one titration gives a set of complex stability constant (K) and enthalpy change (ΔH) simultaneously. The detailed procedures were reported elsewhere.[14] Typically, a potassium thiocyanate solution (0.100 M) was introduced continuously at a rate of 0.4348 mL/min into a bis(crown ether) solution (1.3–1.6 mM) placed in the calorimeter. A titration curve was obtained by plotting the temperature change (measured by E/mV) against the amount of KSCN solution added, from which the values K and ΔH were calculated. The reliability of the whole system was doubly checked by test runs using the reported reaction systems:[14] (i) the enthalpy change (ΔH = −11.34 kcal/mol at 25 °C) upon titration of Tris with hydrochloric acid was consistent with that reported (−11.35 kcal/mol);[15] (ii) ΔH (−6.22 kcal/mol at 25 °C) for the complexation of 18-crown-6 with potassium chloride in aqueous solution was also in good agreement with the reported value (−6.21 kcal/mol).[16]

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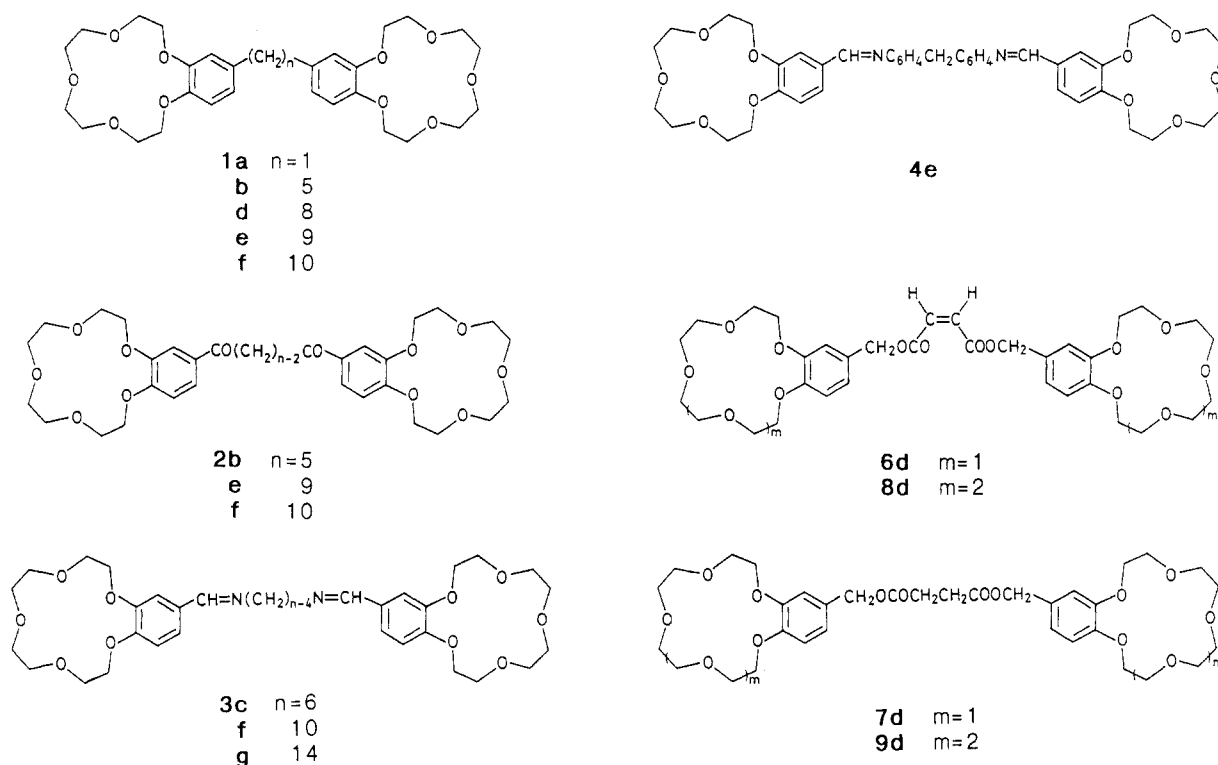
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CHART I

1a n = 1
b   5
d   8
e   9
f   10

2b n = 5
e   9
f   10

3c n = 6
f   10
g   14

4e

6d m = 1
8d m = 2

7d m = 1
9d m = 2

Results

Assuming the 1:1 stoichiometry for the complexation of potassium ion with bis(crown ether)s **1** and **2**, the complex stability constant (K) and the enthalpy change (ΔH) were calculated by using the least-squares method to minimize the U value:

$$U(K,\Delta H) = \sum_{p=1}^{m}(Q_{c,p} - \Delta H \Delta n_p)^2$$

where $Q_{c,p}$ refers to the experimental heat of complexation measured at time p in minutes and Δn_p denotes the amount in moles of the complex formed at time p and is directly related to the stability constant K.

The stability constant K and the enthalpy change ΔH of complexation for each bis(crown ether) were calculated by computer simulation with continuously changing K, i.e., Δn_p, to minimize the U value. The U value was minimized satisfactorily in each case to give the optimized set of K and ΔH shown in Table I, which in turn supports the 1:1 stoichiometry for the complex formation as assumed above.

Discussion

Open- versus Closed-Clam Complex. Although the titration curves are well accounted for in terms of the 1:1 stoichiometry for the complexation reaction, this does not immediately mean the formation of the intramolecular "1:2" sandwich complex between potassium ion and the bis(crown ether). In particular, the bis(crown ether) **1a**, carrying two crown units linked with a bridge as short as one methylene unit, does not seem to give a stable intramolecular "1:2" sandwich complex; examination of a CPK space-filling molecular model indicates that at least a tetramethylene bridge is needed in order to face two crown ether units parallel with each other owing to steric requirement. Indeed, its complex formation constant (log K = 2.92) is substantially lower than those (3.24–4.36) for the polymethylene-bridged bis(crown ether)s **1b–f** but is still much higher than that (1.50) for 1:1 complexation of the parent benzo-15-crown-5 (**5**). This result clearly indicates that, in spite of the short bridging chain,
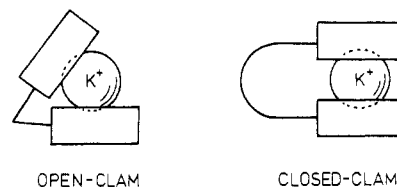
both crown ether units in **1a** cooperatively bind the potassium cation, giving an open-clam-type complex, in which the methylene bridge functions as a hinge, while the other bis(crown ether)s of $n \geq 5$ form intramolecular "1:2" sandwich-type complexes of closed-clam structure.

OPEN-CLAM   CLOSED-CLAM

The large negative entropy change for **1a**, as compared with the other long-chained bis(crown ether)s **1b–f**, may reflect the restricted motion of two crown ether units and the insufficient desolvation in the open-clam complex.

TABLE I: Complex Stability Constant (log K) and Thermodynamic Parameters in kcal/mol for Complexation of Bis(benzo-15-crown-5 ether)s 1–4 and of the Parent Benzo-15-crown-5 (5) with Potassium Ion in Methanol–Water (8:2) at 25 °C

compd	log K	$-\Delta H$	$-\Delta G$	$T\Delta S$	ref
1a	2.92 ± 0.03	15.92 ± 0.05	3.98	−11.94	a
1b	4.36 ± 0.04	10.74 ± 0.13	5.95	−4.79	a
1d	3.24 ± 0.03	14.41 ± 0.23	4.42	−9.99	a
1e	3.40 ± 0.03	13.97 ± 0.02	4.64	−9.33	a
1f	3.68 ± 0.02	13.78 ± 0.06	5.02	−8.76	a
2b	3.47 ± 0.03	8.84 ± 0.25	4.73	−4.11	a
2e	3.31 ± 0.06	11.80 ± 0.20	4.51	−7.28	a
2f	3.13 ± 0.02	12.63 ± 0.50	4.27	−8.36	a
3c	3.14 ± 0.06	18.00 ± 0.66	4.28	−13.72	b
3f	3.56 ± 0.08	16.25 ± 0.22	4.85	−11.40	b
3g	3.12 ± 0.07	17.23 ± 0.44	4.25	−12.98	b
4e	2.79 ± 0.01	16.70 ± 0.06	3.80	−12.90	b
5 (1:2)	4.74 ± 0.04	15.42 ± 0.32	6.45	−8.97	b
	4.80 ± 0.05	15.46 ± 0.13	6.54	−8.92	c
5 (1:1)	1.50 ± 0.01	2.79 ± 0.32	2.05	−0.74	b

a This work; average of more than three independent runs. *b* Reference 1. *c* Izatt, R. M.; Terry, R. E.; Nelson, D. P.; Chan, Y.; Eatough, D. J.; Bradshaw, J. S.; Hansen, L. D.; Christensen, J. J. *J. Am. Chem. Soc.* **1976**, *98*, 7626.

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Chain Length. The length of the polymethylene bridge has a drastic effect upon log K as well as ΔH and ΔS. The stability constant K increases substantially with extending methylene chain length from $n = 1$ to 5, then decreases 1 order of magnitude with further extension to 8, and finally levels off thereafter. This result coincides with the idea that there must be the best compromise chain length/conformation for the sandwich-type complexation, and the trend observed agrees roughly with the previous studies.[6,9a]

It is interesting to discuss the effect of chain length from the thermodynamic point of view. When compared with the minimum stability constant for **1a** ($n = 1$) in the series, the maximum value for **1b** at $n = 5$ is accomplished by the great entropic gain of 7.15 kcal/mol, which far exceeds the enthalpic loss of 5.18 kcal/mol. The formation of a cation–ligand complex diminishes the freedom of both components and is unfavorable intrinsically from the entropic point of view. This decrease in entropy is, however, compensated to large extent by desolvation of both cation and ligand involved. In discussing the complexation phenomenon, to what extent the bound solvent molecules are released upon complexation is one of the most dominant factors to consider. Provided that two crown ether units are conformationally allowed to form a parallel face-to-face sandwich structure, the degree of desolvation upon complexation should be analogous for most bis(crown ether)s, including **1b–f** and **2b–f**. In this context, the considerably large negative entropy change observed for **1a** may be attributed mostly to the incomplete desolvation owing to its open-clam structure. On the other hand, the deviation in $T\Delta S$ obtained for the other polymethylene-bridged bis(crown ether)s of $n = 5$–10 is inferred to originate not from the desolvation difference but from the different degrees of conformational change upon complexation of each bis(crown ether). The minimum entropy changes for **1b**, and **2b** as well, indicate that the chain length of $n = 5$ is conformationally most suitable for the sandwich complexation of both the polymethylene-bridged bis(crown ether)s **1** and its oxo derivatives **2**.

Derivatization. As can be seen from Table I, the oxo derivatives **2** possess more or less lower cation-binding abilities than the corresponding **1**. This is rationalized in general in terms of the reduced electron density of the donor aryloxy oxygens which is caused by the electron-withdrawing carbonyl group attached to the aryl group. When two series **1b,e,f** and **2b,e,f** are compared with each other, the decrease in log K caused by the derivatization is most evident at $n = 5$. The much smaller enthalpic stabilization for **2b** is responsible for its marked decline in log K or $-\Delta G$, while the difference in $T\Delta S$ is relatively small between **1b** and **2b**. At $n = 9$ and 10, the effect of derivatization upon log K is unexpectedly small. Although the enthalpic stabilization is reduced by the derivatization in these cases, the entropy change compensates it to moderate extent, resulting in minimal decrease in log K for **2e,f**. This result suggests that, for the bis(crown ether)s with an unnecessarily long bridge, the electronic effect is partly canceled by the increased conformational rigidity of carbonyl compared with methylene.

Taking into account of our previously reported thermodynamic data for the bis(crown ether) Schiff bases **3**,[1] it is considered that the derivatization at the bridging chain has a leveling effect upon complexing ability; no drastic change, by a factor of 10, is seen in the stability constant K for the modified ligands **2** and **3**. This would simply suggest that the optimized conformation for the sandwich complex is achieved at n not employed in this study, because of the increased conformational rigidity of two C=O or C=N bonds conjugated to the phenyl groups. However, the solvent extraction study[8] on a series of bis(crown ether)s **3** with $n = 6$–14 and 16 revealed that the effect of changing n upon extractability of potassium picrate is minimal only to give a small local maximum of percent extractability at $n = 8$.

Enthalpy–Entropy Compensation. We have reported that good linear relationships are found between ΔH and $T\Delta S$ for the complexation of cations with a variety of synthetic and natural ligands, including glyme/podand, crown ether, cryptand, and macrocyclic antibiotic, and that this linear relationship serves our understanding of the complexation phenomenon.[10] The slope (α)

TABLE II: Thermodynamic Parameters in kcal/mol for Solvent Extraction (H$_2$O/CHCl$_3$) of Potassium and Cesium Ions with Some Bis(benzocrown ether)s 6e–9e at 25 °C[a]

ligand	cation	$-\Delta H$	$-\Delta G$	$T\Delta S$
6d	K$^+$	6.18	5.77	−0.41
7d	K$^+$	8.88	5.73	−3.16
8d	Cs$^+$	11.0	6.57	−4.44
9d	Cs$^+$	12.7	6.47	−6.23

[a] Reference 7c.

TABLE III: Slope (α) and Intercept ($T\Delta S_0$) of the ΔH–$T\Delta S$ Plots for 1:1 and 1:2 Complexations with Various Ligands in the Homogeneous Phase and in Solvent Extraction

ligand	1:1 complexation		1:2 complexation	
	α	$T\Delta S_0$	α	$T\Delta S_0$
glyme/podand[a]	0.86	2.3		
crown ether[a]	0.76	2.4	0.71	2.7
cryptand[a]	0.51	4.0		
antibiotic[a]	0.95	5.6		
bis(crown ether)[b]	1.16	7.1		

[a] Reference 10. [b] This work; this type of ligand forms stoichiometrically 1:1 or intramolecular "1:2" sandwich complex.
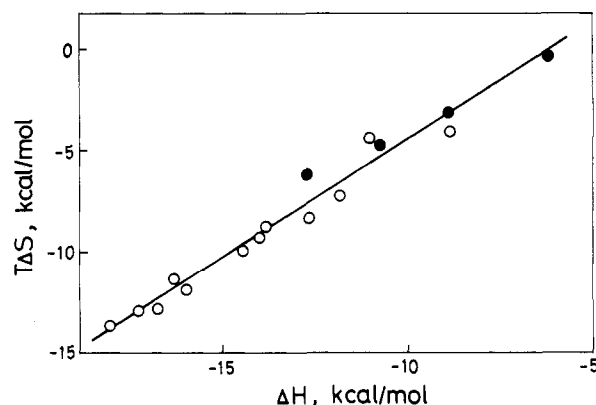

Figure 1. Enthalpy–entropy compensation effect for intramolecular "1:2" complexation of cations with bis(crown ether)s in homogeneous phase (O) and in solvent extraction (●); see Tables I and II for original data.

and the intercept ($T\Delta S_0$), which are characteristic of the type of ligand used, can be rationalized in terms of the change in ligand conformation and the extent of desolvation upon complex formation, respectively.

We test the validity of this enthalpy–entropy compensation effect in the present case, since bis(crown ether) is a new category of ligand which resembles macrocyclic antibiotic in the manner of complexation. However, the available thermodynamic data are fairly limited for the complexation of bis(crown ether)s. In Table II are listed additional thermodynamic parameters obtained in the solvent extraction study with bis(crown ether)s **6d–9d**.[7c] With the data for **1–4** and **6–9** in Tables I and II, the entropy change ($T\Delta S$) is plotted as a function of the enthalpy change (ΔH). As can be seen from Figure 1, the plot gives an excellent linear relationship (correlation coefficient $r = 0.99$) with a slope (α) of 1.16 and an intercept ($T\Delta S_0$) of 7.1; see Table III. This result clearly indicates that the ΔH–$T\Delta S$ compensation effect does hold in the complexation of bis(crown ether)s. Furthermore, the fact that the parameters from solvent extraction are well accommodated in the plot without any evident deviation indicates that, as mentioned previously,[10] a common complexation mechanism must operate in the homogeneous phase and in the solvent extraction. Although there may still remain some ambiguity in comparatively discussing the derived figures (α and $T\Delta S_0$) due to the small sample size ($n = 16$), the largest slope (α) and intercept ($T\Delta S_0$) among the ligands hitherto examined indicate that, upon complex formation, bis(crown ether)s suffer the largest conformational change, which cancels out the enthalpic gain, and

also the most extensive desolvation, which virtually dominates the complex stability. This image coincides nicely with the complexation mechanism of a cation with a bis(crown ether), and the present result again supports our proposal that the complexation phenomenon can be understood well in terms of the enthalpy–entropy compensation effect.

Solvatochromic Behavior of Binary Supercritical Fluids: The Carbon Dioxide/2-Propanol System

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Dependence of the solvatochromic shift for binary supercritical fluid mixtures as a function of modifier mole fraction, temperature, and pressure is discussed. Carbon dioxide/2-propanol binary fluid mixtures were studied at both subcritical and supercritical conditions. The local composition of the cybotactic region was seen to be enriched in organic cosolvent at low pressures. As the pressure or temperature increased, the local composition of the organic cosolvent decreased. A simple theory is developed to describe the local composition of the fluid in the cybotactic region about the solvatochromic probe molecule.

Introduction

The local composition of bulk solvent modifier or cosolvent about a solute in liquid mixtures is an area of active research.[1-7] In supercritical fluids the local composition and local density of solvent molecules about the solute at high dilution can be related to the partial molar volume of the solute in the fluid phase.[8-10] The solvent cluster of supercritical CO_2 about naphthalene corresponds to approximately 80 solvent molecules over multiple solvent shells at 35 °C and 80 bar.[9,10] The effect of an organic cosolvent on the local composition surrounding a solute molecule for binary supercritical fluid solutions has only recently been studied.[10] The enhancement of the organic cosolvent by both specific and nonspecific solute–solvent interactions should provide a basis for understanding solvent modifier effects in supercritical fluids as well as the phenomena of cluster formation in pure and binary supercritical fluid solutions. The specific solute–binary fluid interactions in the local environment of the solute molecule have direct relevance to supercritical fluid extractions,[11,12] chromatographic selectivity,[13-16] and molecular diffusion.[17]

The cybotactic region of the solute molecule (the region of solvent molecules whose structure is influenced by the presence of the solute molecule), is best explored by a technique that does not perturb the local equilibrium composition. The spectroscopic study of the local solvent environment has been applied to liquids[18] and recently to pure supercritical fluids.[19-22] The solvatochromic behavior of the nearest-neighbor solvent shell about a solute, obtained by monitoring their effect on the stabilization of the excited-state dipole of the solute probe molecule, directly provides information on the local composition for pure and binary supercritical fluid systems.

In this paper we report a study of the cybotactic region for a solvatochromic probe molecule and determine the local composition as a function of temperature, pressure, and concentration of organic cosolvent. The specific system chosen for study, CO_2/2-propanol, is also one of significant practical importance. The understanding of solvent structure and composition of the cybotactic region for supercritical fluids provides a basis for bridging the gap between gas-phase and liquid-phase cluster formation and should provide a greater understanding of organized molecular structures in both supercritical fluids and liquids.

Theory

The ground state of a dilute solute probe solvated by a pure supercritical fluid, such as carbon dioxide, will have an equilibrium energy of solvation determined largely by dipole–induced dipole interactions with the solvent molecules. This assumes there are no specific intermolecular interactions such as hydrogen bonding or charge-transfer-complex formation. With the introduction of a polar organic cosolvent (e.g., 2-propanol) to the supercritical fluid, both dipole–dipole and specific intermolecular interactions become possible. Spectroscopic studies of the solvent structure about the solute can be accomplished by the solvatochromic technique. On excitation of the ground state of the solute molecule to the excited state, the dipolar orientation of the solvent molecules remain frozen in their ground-state configuration because the

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