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DETERMINATION OF COMPLEX STABILITIES WITH NEARLY INSOLUBLE HOST MOLECULES. PART II. COMPLEXATION OF ALKALI AND ALKALINE EARTH METAL CATIONS WITH DIBENZO CROWN ETHERS IN AQUEOUS SOLUTION

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An experimental method was developed to determine the stability constants with nearly insoluble ligands in homogeneous solution. This method was tested using dibenzo crown ethers, which have a very low solubility in aqueous solution. The stability constants for the complexation of alkali and alkaline earth metal cations with different dibenzo crown ethers were determined in aqueous solution. Owing to the complex formation the total concentration of the ligand in solution increases. Dibenzo crown ethers absorb in the ultraviolet spectral range, hence the increase in the ligand concentration can be easily detected. Without the knowledge of the molar absorptivities of the ligands and of the corresponding complexes and of the solubilities, the stabilities of the complexes formed can be calculated under certain assumptions. To verify these assumptions, the solubilities of the dibenzo crown ethers and the molar absorptivities were determined. The kinetics of the solubilization process of the ligands was followed by spectrophotometric measurements.

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INTRODUCTION

The different experimental techniques that are suitable for studying the complexation of cations by non-cyclic, macrocyclic and macrobicyclic ligands have already been mentioned in Part I of this paper.[1]

The first report in the literature about the increase in solubility of a macrocyclic ligand due to interactions with cations goes back to the discovery of the crown ethers by Pedersen,[2] who wrote, 'Dibenzo-18-crown-6 is only slightly soluble in methanol at room temperature. Since it contains no phenolic or other acidic group, it was surprising that its solubility in methanol is greatly increased by the addition of sodium hydroxide. This puzzle was solved by the discovery that most methanol-soluble salts of the alkali and alkaline earth metals have the same effect. Hence, it is not the hydroxyl ion that is responsible for the increased solubility but the cations which operate by complexing with the polyether.' These observations were not used as a basis for studying the reactions between nearly insoluble ligands and salts quantitatively.

However, from the increase in the solubility, the stability constants of complexes of nearly insoluble ligands with cations can be calculated by means of a spectrophotometric method using some assumptions, as shown in Part I.[1] The ligand dibenzo-18-crown-6 and the cryptand (222BB) were used to test the assumptions made and to compare the results with values in the literature. To obtain more experimental results about this new method, the complexation reactions of other dibenzo crown ethers with alkali and alkaline earth metal cations were studied in this work. Unfortunately, no stability constants for these ligands in aqueous solution have been reported.[3, 4]

EXPERIMENTAL

The crown ethers dibenzo-15-crown-5 (DB15C5) (Janssen), [2,4]dibenzo-18-crown-6 ([2,4]DB18C6) (Acros), dibenzo-18-crown-6 (DB18C6) (Merck), dibenzo-24-crown-8 (DB24C8) (Merck) and dibenzo-30-crown-10 (DB30C10) (Fluka) were of the highest purity commercially available. The purity of the ligands was >99%, as proved by their melting points and elemental analyses. Ligands with lower purity were recrystallized several times. The structures of the crown ethers are shown in Figure 1.

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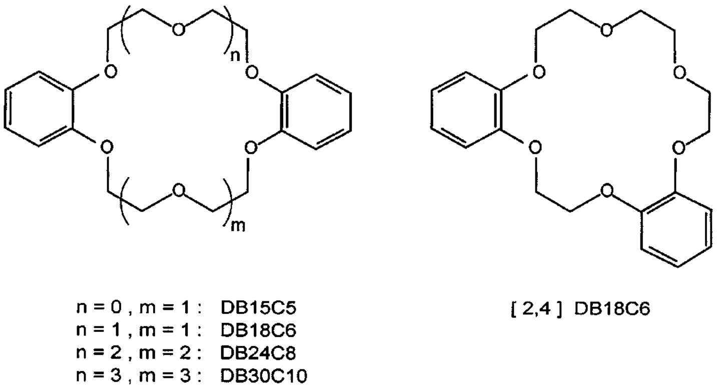

Figure 1. Structures of the dibenzo crown ethers

The salts NaCl, KCl, RbCl, CsCl, $CaCl_2$, $SrCl_2$ and $BaCl_2$ were of the highest purity commercially available. As solvent, doubly distilled water was used.

The solid ligand was added to solutions of the salts (2×10^{-3}–2×10^{-2} mol l^{-1}). The amount of the solid ligand was high enough to ensure the complete saturation of the solutions. The spectra of the solutions were recorded after at least one day. Before absorbance measurements, the saturated solutions were passed through a membrane filter (polycarbonate, 0·4 μm). All solutions were thermostated at 25 °C. The increase in absorbance due to complex formation is shown in Figure 2.

The molar absorptivities of the pure ligands and their complexes were determined at 274 nm for solutions with known ligand concentrations. These values were used to calculate the solubilities of the ligands from the absorbance of solutions saturated with the ligands.

For the measurement of the rates of solubilization, the solid ligands were added to 200 ml of pure water and stirred. The UV spectra were recorded after several time intervals. The increase in absorbance as a function of time is shown in Figure 3.

All spectrophotometric measurements were made using a Varian Cary 5E spectrophotometer.

RESULTS AND DISCUSSION

Kinetics of solubilization and solubilities of the ligands

One of the main problems with these measurements is to decide whether the solubilization has reached an equilibrium state or not. In Figure 3 the absorptivities of dibenzo crown ethers in aqueous solutions are shown as a function of time. After 10 h most of the ligand solutions have reached equilibrium and the further increase in the absorptivities during an additional 14 h is small. Only in the case of

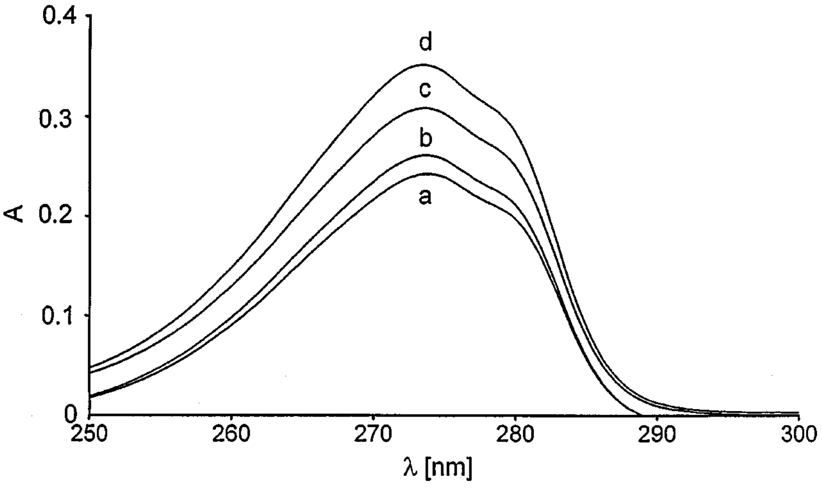

Figure 2. UV spectra of saturated solutions of the ligand [2,4]DB18C6 in the presence of different concentrations of KCl, (a) 2×10^{-3}, (b) 6×10^{-3}, (c) $1{\cdot}4\times10^{-2}$ and (d) 2×10^{-1} M, in aqueous solution at 25 °C

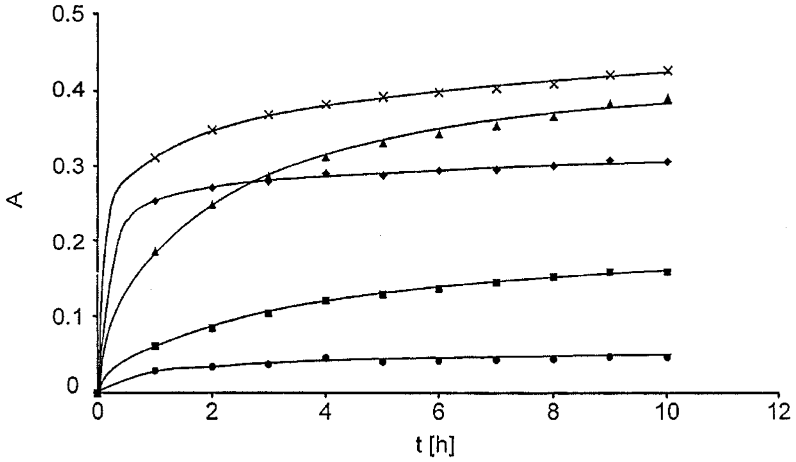

Figure 3. Changes in the absorbance A at 274 nm due to the solubilization of the dibenzo crown ethers, (▲) DB15C5, (●) DB18C6, (◆) [2,4]DB18C6, (×) DB24C8 and (■) DB30C10, in aqueous solution at 25 °C

DB15C5 does it take nearly 24 h before the solution is saturated with the ligand. The smallest ligand examined, with two benzene groups and five ether donor atoms, dissolves more slowly than the other ligands.

The rate constants k for the dissolution of the ligands can be calculated using the equation

$$[\mathrm{L}] = [\mathrm{L}]_{\mathrm{sat}}(1 - e^{-kt}) \tag{1}$$

The values of k are given in Table 1. The solubility of the ligands has no influence on the rate constant. With the exception of DB15C5, the values of k for the other ligands are nearly identical. DB15C5 shows the most hydrophobic character of all the ligands examined. Therefore, the contact between the solid ligand and the solvent molecules is rather poor.

The solubilities of the dibenzo crown ethers are of the same order of magnitude (see Table 1). Only for two dibenzo crown ethers are solubilities available in the literature for comparison.[5–7]

Treatment of the experimental data

The mathematical models for the treatment of the experimental data have already been discussed in detail in Part I.[1] The formation of a 1:1 complex between a ligand L and a cation M^{n+} is given by the equation

$$\mathrm{L} + \mathrm{M}^{n} \rightleftharpoons \mathrm{LM}^{n+} \tag{2}$$

The stability constant K is defined as

$$K = \frac{[\mathrm{LM}^{n+}]}{[\mathrm{L}][\mathrm{M}^{n+}]} \tag{3}$$

The experimentally measured absorptivities A' for a constant optical path length d is given by equation (4) if only the ligand and the complex formed absorb at a given wavelength:

$$A = A'/d = \varepsilon_1[\mathrm{L}] + \varepsilon_2[\mathrm{LM}^{n+}] \tag{4}$$

where ε_1 and ε_2 are the molar absorptivities of the ligand

Table 1. Rate constants of dissolution k (min^{-1}) and solubilities $[\mathrm{L}]_{\mathrm{sat}}$ ($\mathrm{mol\ l}^{-1}$) of dibenzo crown ethers in aqueous solution at 25 °C

Parameter	DB15C5	DB18C6	[2,4]DB18C6	DB24C8	DB30C10
$k \times 10^{-3}$	3·3±0·1	4·8±0·3	4·9±0·3	5·2±0·3	4·6±0·1
$[\mathrm{L}]_{\mathrm{sat}} \times 10^{-5}$	8·3±0·2	1·7±0·1[a] 2[b] 1·3[c]	6·3±0·3	9·0±0·40 8·6[d]	4·0±0·1

[a] From Ref. 1.
[b] From Ref. 5.
[c] From Ref. 6.
[d] From Ref. 7.

Table 2. Molar absorptivities ε (l mol^{-1} cm^{-1}) at 274 nm of the dibenzo crown ethers and of the salt complexes in aqueous solutions at 25 °C

Cation	DB15C5	DB18C6[a]	[2,4]DB18C6	DB24C8	DB30C10
—	5143 ± 141	4682 ± 68	4936 ± 221	4801 ± 242	4281 ± 65
Na^+	4908 ± 127	4780 ± 276	5444 ± 209	4771 ± 166	4243 ± 50
K^+	5088 ± 180	4760 ± 308	5319 ± 126	4612 ± 124	4209 ± 27
Rb^+	5073 ± 156	4961 ± 241	5430 ± 34	4861 ± 211	4270 ± 19
Cs^+	5095 ± 178	4980 ± 197	5138 ± 230	4748 ± 143	4213 ± 42
Ca^{2+}	5214 ± 295	4795 ± 232	5047 ± 205	4582 ± 105	4270 ± 26
Sr^{2+}	5192 ± 281	4578 ± 235	5075 ± 176	4522 ± 106	4410 ± 155
Ba^{2+}	5953 ± 179	4232 ± 156	6427 ± 114	5577 ± 91	4479 ± 14

[a] From Ref. 1.

and the complex, respectively. If the solution is saturated with the ligand, the first term in equation (4) is constant:

$$A_0 = \varepsilon_1 [\mathrm{L}]_{\mathrm{sat}} \tag{5}$$

Using equation (3) and the equations of the material balances, one obtains

$$A/A_0 - 1 = \frac{(\varepsilon_2/\varepsilon_1)K}{1 + K[\mathrm{L}]_{\mathrm{sat}}}\, c_{\mathrm{salt}} \tag{6}$$

Plotting $A/A_0 - 1$ as a function of the total salt concentration c_{salt}, one expects a straight line with slope b. From this slope, the stability constant of the complex formed in solution can be calculated:

$$K = \frac{b}{(\varepsilon_2/\varepsilon_1) - b[\mathrm{L}]_{\mathrm{sat}}} \tag{7}$$

Using the following assumptions, it is possible to calculate stability constants from equation (7) without knowing the molar absorptivities and the solubility of the ligand: (a) the molar absorptivities of the host molecule ε_1 and the complex formed ε_2 are nearly identical:

$$\varepsilon_2/\varepsilon_1 \approx 1$$

and (b) the solubility of the ligand is low:

$$b[\mathrm{L}]_{\mathrm{sat}} \ll 1$$

If both assumptions are valid, the slope b is identical with the stability constant K.

Test of the assumptions

The solubilities of the ligands in aqueous solution are calculated from the absorptivities A_0 of saturated solutions using the molar absorptivities ε_1 of these ligands. The results are summarized in Table 1. The concentrations of the ligands in the saturated solutions are of the order of 10^{-5}–10^{-4} mol l^{-1}. If the stability constants of the complexes formed in aqueous solutions are not higher than 10^3 l mol^{-1} then the assumption $b[\mathrm{L}]_{\mathrm{sat}} \ll 1$ is fulfilled.

The molar absorptivities of the ligands and of the complexes are given in Table 2. Owing to the complexation only minor changes in the molar absorptivities are observed. This is not surprising because the π-electrons of the benzene groups are not directly involved in the complex formation. Some small changes take place due to the ion–dipole interactions of the oxygen donor atoms attached to

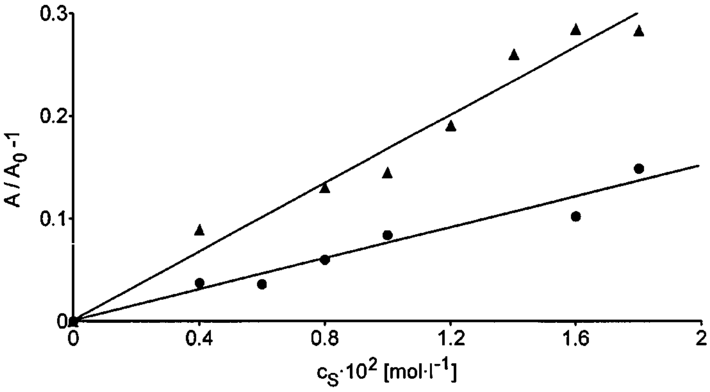

Figure 4. Plot of $A/A_0 - 1$ at 274 nm of saturated solutions of the ligand [2,4]DB18C6 as a function of the total salt concentration c_S [(▲) Na^+ and (●) Cs^+] in aqueous solution at 25 °C

Table 3. Stability constants, log[K (1 mol^{-1})], for the complex formation of dibenzo crown ethers with different cations in aqueous solutions at 25 °C, with correlation coefficients from linear regression analysis using equation (6) in parentheses

Cation	DB15C5	DB18C6[a]	[2,4]DB18C6	DB24C8	DB30C10
Na^+	0·83 ± 0·08 (0·892)	1·09 ± 0·05	1·24 ± 0·06 (0·966)	1·06 ± 0·11 (0·941)	1·12 ± 0·08 (0·966)
K^+	0·95 ± 0·6 (0·882)	1·60 ± 0·04	1·34 ± 0·03 (0·997)	0·91 ± 0·09 (0·904)	1·08 ± 0·05 (0·881)
Rb^+	0·85 ± 0·06 (0·891)	0·89 ± 0·09	0·92 ± 0·04 (0·905)	1·02 ± 0·04 (0·883)	1·32 ± 0·08 (0·970)
Cs^+	0·05 ± 0·04 (0·885)	0·74 ± 0·07	0·84 ± 0·12 (0·957)	1·41 ± 0·03 (0·959)	1·60 ± 0·07 (0·991)
Ca^{2+}	0·19 ± 0·05 (0·921)	0·47 ± 0·26	0·52 ± 0·11 (0·835)	0·84 ± 0·10 (0·846)	1·13 ± 0·08 (0·855)
Sr^{2+}	0·65 ± 0·07 (0·998)	0·75 ± 0·12	1·04 ± 0·07 (0·901)	1·11 ± 0·07 (0·986)	1·39 ± 0·09 (0·943)
Ba^{2+}	0·69 ± 0·09 (0·959)	1·75 ± 0·05	1·32 ± 0·03 (0·967)	1·13 ± 0·05 (0·972)	1·54 ± 0·07 (0·933)

[a] From Ref. 1.

the benzene rings with the complexed cations. The complex formation with Ba^{2+} has an influence upon the values of the molar absorptivities. In this case the ratio $\varepsilon_2/\varepsilon_1$ varies from 0·9 to 1·3. In general, the assumption $\varepsilon_2/\varepsilon_1 \approx 1$ is valid.

Stability constants of dibenzo crown ether complexes

In Figure 4, the absorbance of solutions saturated with the ligand [2,4]DB18C6 are shown as a function of the salt concentration. Owing to the complex formation, the total concentration of the ligand in solution increases.

From equation (6), one expects a straight line by plotting $A/A_0 - 1$ at a constant wavelength as a function of the total salt concentration. This is shown for the ligand [2,4]DB18C6 and some salts in Figure 4. The slope b is identical with the stability constant K if the assumptions made are valid. This has already been shown.

The stability constants for the complexes formed with alkali and alkaline earth metal cations are given in Table 3. The dibenzo crown ethers do not show pronounced selectivity. The ligands DB18C6 and [2,4]DB18C6 show nearly identical complexation behaviour. The cavities of the ligands with more than six oxygen donor atoms are too large to fit optimally with one of the cations. Hence the cations with the largest dimensions are complexed most strongly. In aqueous solution none of the ligands form very stable complexes.

CONCLUSION

The results reported clearly demonstrate the possibility of calculating stability constants of alkali and alkaline earth metal cations with nearly insoluble ligands. If the solubility of the ligands is low and therefore the molar absorptivities cannot be measured experimentally, the stability constants of the complexes may be calculated from the increase in absorbance.

A further advantage of this method is that only small amounts of a ligand are necessary to obtain information about the strength of the complexes formed.

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