

COMPUTERIZED CONDUCTOMETRIC DETERMINATION OF STABILITY CONSTANTS OF COMPLEXES OF CROWN ETHERS WITH ALKALI METAL SALTS AND WITH NEUTRAL MOLECULES IN POLAR SOLVENTS

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(Received 1st November 1986)

SUMMARY

A computerized conductometric procedure for the determination of stability constants of the complexes of crown ethers (15-crown-5, benzo-15-crown-5 and 12-crown-4) with alkali metal salts in polar solvents is described, based on a microcomputer-controlled titration system. For the control of the experiments from software, a modular computer program was written in FORTH computer language. The procedure is especially suitable for the study of 1:2 metal ion/ligand complexes, which occur frequently with the compounds used. For the study of the interaction between crown ethers and neutral molecules, an indirect procedure is outlined.

Crown ethers and related compounds are capable of forming complexes with many metal salts, with organic salts (such as organic ammonium, arene-diazonium and guanidinium salts) and with many (neutral) organic molecules. For the determination of the (thermodynamic) stability of these complexes, a large variety of methods and procedures has been reported; these have been reviewed [1]. In this laboratory, a polarographic procedure has been developed for the computerized determination of stability constants of CE-complexes with (alkali) metal salts and neutral compounds in polar solvents [2, 3].

The conductance of an electrolyte solution depends on the number and nature of the ionic species present in the solution. In view of the fact that crown ethers form complexes with a variety of cations, and with the assumption that the mobility of the free cations is different from their complexes, conductometry is a technique that can be applied to the study of complexation of cations by crown ethers. For neutral species, the technique cannot be applied as such. An indirect procedure, however, is a possible alternative for the study of the interaction between crown ethers and these species.

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In this paper, the development of a microcomputer-controlled conductometric titration system is described, together with the possible applications of the system to the study of complexation of cations. An indirect procedure for the study of the interaction between neutral species and crown ethers is outlined as well.

Determination of the stability constants

For the conductometric determination of stability constants (or ion-pair association or dissociation constants), the standard procedure involves the measurement of the (specific) conductance of an electrolyte solution as a function of ionic strength or electrolyte concentration. From these measurements, the equivalent conductance (at infinite dilution) and the degree of association between anions and cations can be evaluated by means of the equations describing the conductance of electrolyte solutions in terms of inter-ionic effects, for example the Onsager equation [4] or an extended form of this equation (see, e.g. ref. 5).

In the case of complexation of ionic species by crown ethers that have no acidic and/or basic substituents, it is possible to evaluate the interaction between the species involved by studying the equivalent conductance of the salt solution as a function of the ligand concentration. Therefore, the solutions containing a completely dissociated metal salt and a variable concentration of the crown compound can be regarded as a mixed electrolyte with a common anion at constant ionic strength. In this approach, no corrections for the inter-ionic effects on ionic mobility are necessary, assuming that any changes in interactions are negligible when the solvated cation is converted to the complex with the crown ether. Taking into consideration the possible effects of cations with different mobilities on the mobility of the common anion, some correction term might be necessary. However, these corrections are likely to be very small [6] and can also be neglected.

A second advantage of this approach is the fact that no indifferent salt has to be added in order to obtain constant ionic strength. Therefore, the experiment can be done with diluted systems, thereby minimizing the formation of ion-pairs in solvents of lower dielectric constant.

If only one complex is formed and if the equivalent conductivity of the complex salt MLX_n can be determined experimentally, the stability constant of the complex can be calculated directly from the observed (specific) conductance value and the total concentrations of M and L. This applies only to those cases in which it is possible to measure the conductance of the solution at such excess ligand concentrations L_T that it can be assumed that the concentration of the metal ion M^{n+} is negligibly small, i.e., for stable complexes and/or at large ratio of L_T/M_T . This approach has been used by several authors (see, e.g. refs. 7–16). If more than one complex species is formed, or if the equivalent conductivity of the complex species ML_i cannot be determined experimentally, a general least-squares procedure has to be applied in order to obtain the desired parameters.

The interaction between crown ethers and uncharged species (e.g., urea) can only be studied by means of an indirect procedure. This procedure is similar to the indirect polarographic one described previously [2, 3]. First, the conductometric properties of an indicator system have to be studied. From the conductometric study of the interaction between the indicator compound and the crown compound L, the equivalent conductivity and stability constants of the complex between M and L are evaluated as outlined above (Fig. 1A). Next, the influence of addition of the neutral guest species, U, to a solution of the metal salt M in presence of an arbitrary, but fixed amount of L is investigated. As a result of the (assumed) interaction between U and L, M is displaced from the complex and the observed conductivity will change in the direction of the conductance of the free metal salt. Usually, this will result in an increase of the observed conductance (Fig. 1B). From this change in conductance upon addition of the neutral compound U, the stability constant of the complex between U and the ligand L can be evaluated.

Computer programs for data-acquisition and data-handling

For the over-all control of the experiment and for the calculation of stability constants from the conductance data, two different computer programs were developed.

Computer program for control of the experiment. The experiment was controlled entirely from software by means of a program KONDAT, written in FORTH (FysForth version 03). Some words defined for the control of polarographic experiments (described earlier [3]) were used in this program, while other words were developed specifically for the control of the conductometric experiments.

After the input of some experimental parameters from the keyboard (i.e., the concentrations of metal salt and titrant as well as the total volume of

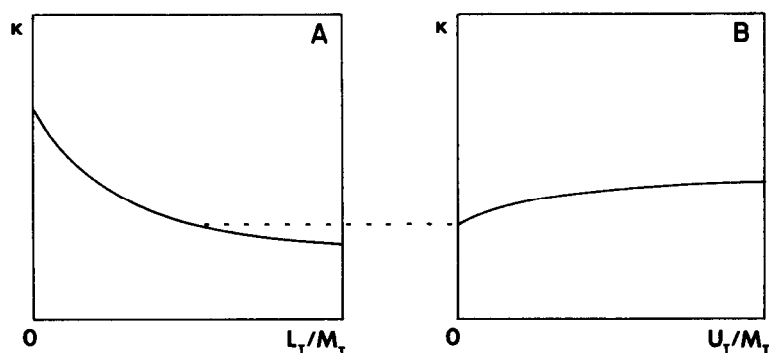


Fig. 1. Indirect conductometric procedure for the determination of stability constants: (A) determination of K_1 ; (B) determination of K_B (cf. Table 1). Specific conductance as a function of the analytical concentration of L or U. M, metal salt; L, crown ether; U, neutral guest species (in competition with M).

titrant to be added to the metal salt solution), data acquisition and storage take place automatically. This task is performed by the apparatus described previously [3]. After each addition of titrant to the metal salt solution, a delay period of 90 s is allowed for mixing and obtaining temperature equilibrium. Next, the conductance of the solution is measured as soon as the observed signal (as obtained from the ADC) has attained a stable level. The input parameters and all the experimental data are recorded on disk in a format that allows the data to be used by both FysForth and Pascal programs.

Computer program for evaluation of the data. For the evaluation of the conductometric data, a non-linear least-squares curve-fitting program KONFIT was developed. The program, written in Pascal, is based on the iterative adjustment of the calculated values of the specific conductance to the observed conductance values by using a modified Simplex procedure [17]. Adjustable parameters are both the stability constants and the equivalent conductivities of all the species present, but the user has the option of excluding any parameter from the refinement procedure. Because the selected mathematical model is only applicable to experiments that are done at constant ionic strength, complexes of the type M_nL were not taken into consideration and only the systems given in Table 1 were used. In the case of models III and IV, the stability constants K_1 and K_2 of the metal/crown ether complexes were incorporated in the program as non-adjustable.

The experimental data are read from the data files created by the FORTH program KONDAT. Input parameters for the program are the initial values for the N parameters to be refined and the step size for the first simplex, which decides the initial surface area in the $(N + 1)$ -dimensional space to be evaluated. The use of Simplex algorithms minimizes the chance of divergence of the refinement procedure, but it is possible that the optimum found is

TABLE 1

Mass-balance equations used in computer program KONFIT for evaluation of conductometric data^a

Model	Reactions	Stability constants	Mass-balance equations
I	M + L ML	$K_1 = (ML)/(M)(L)$	$M_T = (M) + (ML)$ $L_T = (L) + (ML)$
II	M + L ML ML + L ML	$K_1 = (ML)/(M)(L)$ $K_2 = (ML_2)/(ML)(L)$	$M_T = (M) + (ML) + (ML_2)$ $L_T = (L) + (ML) + 2(ML_2)$
III	M + L ML U + L UL	$K_1 = (ML)/(M)(L)$ $K_B = (UL)/(U)(L)$	$M_T = (M) + (ML)$ $U_T = (U) + (UL)$ $L_T = (L) + (ML) + (UL)$
IV	M + L ML ML + L ML ₂ U + L UL	$K_1 = (ML)/(M)(L)$ $K_2 = (ML_2)/(ML)(L)$ $K_B = (UL)/(U)(L)$	$M_T = (M) + (ML) + (ML_2)$ $U_T = (U) + (UL)$ $L_T = (L) + (UL) + (ML) + 2(ML_2)$

^aU is the guest species in competition with M.

TABLE 2

Solutions of the mass-balance equations given in Table 1 in terms of the free ligand concentration [L]

Model	Solution
I	$K[L]^2 + [L](1 + K(M_T - L_T)) - L_T = 0$
II	$K_1 K_2 [L]^3 + [L]^2 (K_1 (1 + K_2 (2 M_T - L_T))) + [L](1 + K_1 (M_T - L_T)) - L_T = 0$
III	$K_1 K_B [L]^3 + [L]^2 (K_1 + K_B + K_1 K_B (U_T + M_T - L_T)) + [L](1 + K_1 (M_T - L_T) + K_B (U_T - L_T)) - L_T = 0$
IV	$K_1 K_2 K_B [L]^4 + [L]^3 (K_1 K_2 (K_B (2 M_T + U_T - L_T) + 1) + K_1 K_B) + [L]^2 (K_1 (K_B (M_T + U_T - L_T) + K_2 (2 M_T - L_T) + 1) + K_B) + [L](K_1 (M_T - L_T) + K_B (U_T - L_T) + 1) - L_T = 0$

only a local optimum [18, 19]. Therefore it is a standard procedure to repeat the fitting procedure once or twice with different starting values and different initial step sizes in order to test if the true optimum is found.

The mass-balance equations of Table 1 can be solved in order to obtain equations for the free ligand concentration [L] (Table 2). For models II–IV, the free ligand concentrations [L] were calculated by means of a Newton–Raphson procedure. Once the value of [L] had been obtained, the concentrations of all the other species involved were calculated from the corresponding equations given in Table 1, by using the estimated values of the stability constants at the current iteration step of the program. The refinement of the parameters is continued until the sum-of-squares of the residuals between calculated and observed values of the conductance for all experimental points is minimized. The output of the program KONFIT comprises the refined parameters, the sum-of-squares and the standard deviation of the data as well as the distribution of the species.

EXPERIMENTAL

Chemicals and instrumentation

12-Crown-4 (Janssen), 15-crown-5, benzo-15-crown-5 and dibenzo-24-crown-8 (all from Merck) were used as obtained. 18-Crown-6 (Merck) was purified from the acetonitrile complex as described by Gold and Rice [20]. Alkali metal chlorides were dried at reduced pressure (3.33 kPa) and a temperature of 323 K for 24 h and stored over phosphorus pentoxide. Double-distilled water was used throughout the experiments. Methanol (Merck) was of analytical-reagent grade (water content 0.05%). Guanidinium hydrochloride (Merck, zur Synthese) was recrystallized from water. All other chemicals were of at least analytical-reagent grade and were used as received.

A Philips PW-9509 conductivity meter was used (accuracy 0.15% full scale

deflection), together with a Philips PW-9510/60 measuring cell; the cell constant (0.85 cm^{-1}) was evaluated by using aqueous solutions of potassium chloride. For the addition of titrant solutions, a Radiometer Autoburette ABU-12a, total volume 2.5 or 25.0 ml, was used. Additions to the titration vessel were done at constant volume increments of 0.01 or 0.1 ml, respectively. The accuracy of the buret is 0.1%. The titration vessel with the conductivity cell was kept at $298 \pm 0.1 \text{ K}$ by using a Tamson thermostat.

The recorder output of the conductivity meter was connected to a Basis 108 microcomputer through a 12-bit ADC [3].

Procedure

Purified nitrogen was passed through an aqueous solution of tetramethylammonium hydroxide in order to remove CO_2 and then through a washing-bottle containing the solvent to be used before it was led into the titration vessel. Nitrogen was passed over the salt solution in this vessel for 30 min in order to remove CO_2 before the experiment was started. No special precautions were taken to exclude the influence of moisture on the water content of the solvent used.

Titration solutions were prepared by dissolution of the sample into a salt solution of the same concentration as present in the titration vessel at the start of the experiment, in order to keep the ionic strength constant during the experiment. The solution in the titration vessel was mixed by means of a magnetic stirrer.

RESULTS AND DISCUSSION

Complexation of alkali metal ions

As a first evaluation of the procedure, the complexation of potassium chloride by 18-crown-6 in water was studied. Upon addition of the crown to the solution of the potassium salt, a decrease of the equivalent conductance

TABLE 3

Complexation of potassium chloride by 18-crown-6 in water. Comparison of manual and computerized method; equivalent conductivities of free and complex salt and logarithmic value of stability constant at 298 K

Method	Δ_{MX} [$\Omega^{-1} \text{ m}^2 \text{ eq}^{-1}$]	Δ_{MLX} [$\Omega^{-1} \text{ m}^2 \text{ eq}^{-1}$]	$\log(K)$
Manual ($n = 5$)			
Range	151.2–153.7	102.2–111.9	2.05–2.18
Mean	152.2	107.5	2.12
S.d.	1.2	3.5	0.05
Computerized ($n = 5$)			
Range	151.3–152.0	109.2–112.1	2.08–2.12
Mean	151.7	110.6	2.10
S.d.	0.3	1.2	0.02

κ was observed, which can be regarded as the effect of the lower mobility of the complex species in comparison with the free potassium ion. The conductometric data were evaluated by means of the program KONFIT based on model I. In Table 3, the results are given for the computerized procedure in comparison to a manual one. It can be seen that the precision of the computerized procedure is better than that of the manual one. The value for the stability constant of the potassium/18-crown-6 complex is in good agreement with literature data [21]. The value for the equivalent conductivity of the free metal salt is slightly larger than the values reported in the literature (for potassium chloride in water at 298 K, this value is 149.86). This was found to be the case for some other systems as well, but no explanation can be given.

Next, the complexation of the sodium and potassium ion by benzo-15-crown-5 in a solvent mixture of methanol and water (7:3 w/w) was studied. This system was chosen in view of the fact that Izatt et al. [22] had reported 1:2 complexation for the potassium ion (a 'sandwich' type of complex in which the metal ion is surrounded by two crown ether molecules) with the stability constant for the 1:2 complex more than 10 times greater than the value of K_1 . Moreover, relatively little quantitative data on this type of complexation could be found in the literature [21, 23–26]. The techniques used in these studies were potentiometry [22, 24, 25], calorimetry [22, 23] and NMR spectroscopy [26]. Ungaro et al. [27] studied the complexation of sodium and potassium by 4'-substituted benzo-15-crown-5 derivatives in acetone by means of conductometry; the existence of 1:2 complexes with the potassium ion was discussed in qualitative terms only. In other papers on

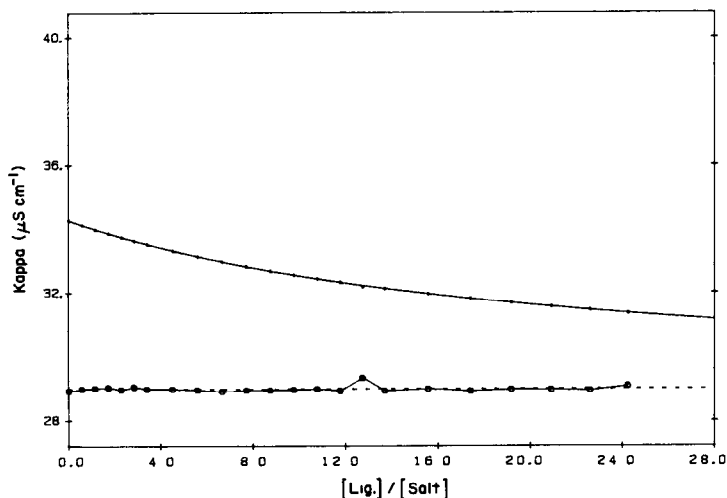


Fig. 2. Conductance of a solution of sodium chloride (0.508×10^{-3} M) in methanol as a function of the concentration of benzo-15-crown-5, showing the experimental points and the calculated curve (upper curve). Deviation between observed and calculated conductance values for the 1:1 model is indicated by the lower curve (enlarged).

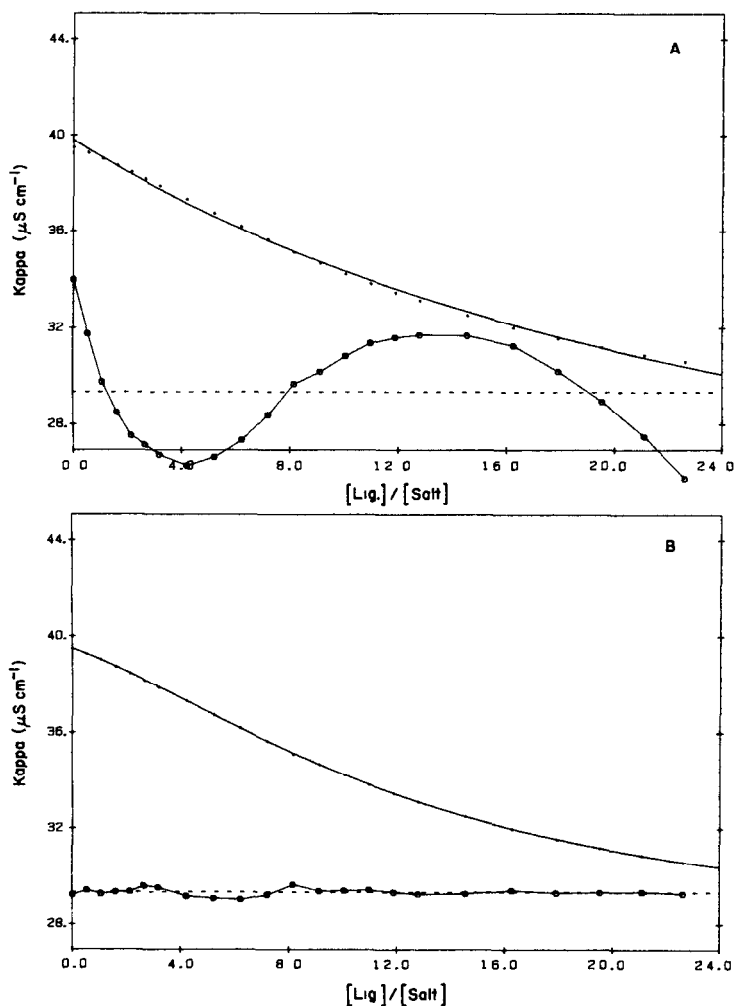


Fig. 3. Conductance of a solution of potassium chloride (0.524×10^{-3} M) in methanol as a function of the concentration of benzo-15-crown-5. The upper (calculated) curve is given with the experimental data points. The lower curves (enlarged) show the deviation between observed and calculated conductance values for the 1:1 model (A) and the 1:2 model (B).

the conductometric study of complexation of alkali metal ions with small crown ethers [12, 13, 28, 29], the formation of 1:2 complexes was discussed in qualitative terms only or not at all.

The conductance of the solutions of sodium and potassium chloride as a function of the concentration of benzo-15-crown-5 in 70% methanol is represented in Figs. 2 and 3. The upper curve in each frame is the calculated curve; the lower curve shows the difference between observed and calculated values. A good fit was obtained with model I in the case of the sodium ion

(Fig. 2). For the potassium ion, however, a characteristic 'deviation plot' was obtained when the data were evaluated according to model I (Fig. 3A), whereas a good fit was obtained by using model II (Fig. 3B). The difference between the 'goodness of fit' for models I and II can be grasped from the calculated standard deviation of the data, but the graphical representation as given in Figs. 2 and 3 is very helpful in this respect. The calculated values of the stability constants and equivalent conductivities of the complex species for the sodium and potassium salts and the other alkali metal chlorides are given in Table 4.

The most remarkable fact is the strong tendency for sandwich complex formation for the potassium ion compared to the other alkali metal ions. Sandwich-type complexes have been reported in the literature for different metal salts with crown ethers having a small cavity such as the 12-crown-4 and 15-crown-5 derivatives, both in the solid state and in solution. As can be

TABLE 4

Stability constants and equivalent conductivities (Λ) of alkali chloride complexes with benzo-15-crown-5 and 15-crown-5 in methanol/water (7:3) at 298 K

Cation	[Salt] (mM)	Λ_{MX}	Λ_{MLX}	Λ_{ML_2X}	$\log(K_1)$	$\log(K_2)$
<i>Benzo-15-crown-5</i>						
Li	0.797	54.8	<50	—	<0.4	—
Na	0.508	67.5	56.7	—	1.97	—
K	0.524	76.0	59.4	52.9	1.97	2.40
Rb	0.516	78.4	65.0	50.5	1.77	1.96
Cs	0.508	79.1	69.0	46.0	1.66	1.02
	0.798	78.5	66.2	44.3	1.55	1.13
<i>15-Crown-5</i>						
Li	0.797	54.8	52.1	—	1.02	—
Na	0.508	67.9	59.4	—	2.32	—
K	0.524	77.0	70.0	55.0	2.79	2.04
Rb	1.138	75.6	71.5	50.0	2.81	1.83
Cs	0.798	78.4	75.4	55.0	2.49	1.48
	1.007	77.9	70.8	52.9	2.22	1.35

TABLE 5

Alkali metal ion diameters and cavity sizes of crown ethers (from ref. 30)

Metal ion	Radius (Å)	Crown ether	Radius (Å)
Li	1.36	14-crown-4	1.2–1.5
Na	1.90	15-crown-5	1.7–2.2
K	2.66	18-crown-6	2.6–3.2
Rb	2.94	21-crown-7	3.4–4.3
Cs	3.34		

seen from the data in Table 5, the potassium ion is too large for the cavity of 15-crown-5. Therefore, the formation of 1:2 complexes is not unexpected. In contrast with this finding, for the larger rubidium and cesium ions the relative amount of 1:2 complexation is less prominent. (Recently, it has been established that cesium picrate, like the sodium salt and unlike the potassium salt, forms a 1:1 complex with benzo-15-crown-5 [31].) Moreover, the sodium ion, which should fit exactly into the cavity of the 15-crown-5 ring, can form a 'sandwich' type of complex with benzo-15-crown-5 if the anion present has unfavourable coordinating properties (see, e.g. ref. 32). Hence it can be concluded that the size/fit concept, often used to explain the selectivity of the crown ethers towards complexation of alkali metal ions, by itself provides insufficient ground for a more quantitative explanation of the observed tendency towards 1:2 stoichiometry.

The stability constants for the alkali metal complexes with the unsubstituted 15-crown-5 (in the same solvent mixture) are also given in Table 4. By comparison with the complexes of the benzo derivative, these complexes are more stable. The ratio of K_1/K_2 is larger for the potassium and rubidium ion and somewhat smaller for the cesium ion. The lower stability of the complexes of the substituted crown ether can be explained by the fact that the catecholic oxygen atoms of the benzo-crown are less basic than the other oxygen atoms in the ring of the crown ether. Moreover, the presence of the benzo group reduces the flexibility of the molecule, thereby diminishing the possible wrapping of the crown around the (partially desolvated) cation in the (sandwich) complex.

The interaction between the alkali metal ions and 12-crown-4, 15-crown-5 and benzo-15-crown-5 was also investigated in pure methanol; the results are presented in Table 6. In comparison with the methanol/water mixture, the complexes of 15-crown-5 and benzo-15-crown-5 are more stable in methanol, while the ratio of K_1/K_2 is larger in methanol than in the methanol/water mixture (except for the complexes of 15-crown-5 with K^+ and Cs^+). The stability of the lithium complexes is very small, even for 12-crown-4. Apparently the solvation of this ion more than balances the binding forces of the crown ethers in these solvents.

From the values of the equivalent conductivities of the free metal ions and their complexes with 12-crown-4, 15-crown-5 and benzo-15-crown-5, the (relative) size of the ionic species can be calculated from the equation

$$r_i = 0.82/\lambda_i^0 \eta$$

where λ_i^0 and η represent the limiting ion conductance and the viscosity of the solvent, respectively [33]. The Stokes radii of the alkali metal ions in water, methanol and methanol/water (7:3) are presented in Table 7. The limiting ionic conductance values for the methanol/water mixture were calculated from the observed equivalent conductance values and the Onsager equation. (For this purpose, the values for the dielectric constant and the viscosity of this solvent mixture were taken as 47.1 and 1.19 cP, respectively.)

TABLE 6

Stability constants and equivalent conductivities of alkali chloride complexes with benzo-15-crown-5, 15-crown-5 and 12-crown-4 in methanol at 298 K

Cation	[Salt] (mM)	Δ_{MX}	Δ_{MLX}	Δ_{ML_2X}	$\log(K_1)$	$\log(K_2)$
<i>Benzo-15-crown-5</i>						
Li	0.561	89.4	89.4	—	— ^a	—
Na	0.515	94.6	90.4	—	2.94	—
	1.029	89.6	84.8	84.6	2.94	2.14
K	0.535	101.4	91.4	86.0	2.96	3.20
					2.68	2.70
Rb	0.516	103.3	87.4	83.1	2.68	2.70
	1.017	102.4	89.3	81.5	—	—
Cs	0.472	108.3	85.1	—	2.20	—
	0.796	108.2	85.2	82.7	2.21	1.53
	1.000	105.3	81.3	80.7	2.15	1.34
<i>15-Crown-5</i>						
Li	0.561	89.3	99.6	—	1.21	—
Na	0.515	94.6	94.6	—	— ^a	—
K	1.089	98.3	90.2	85.8	3.38	2.62
Rb	0.516	105.6	89.4	88.9	2.88	2.23
Cs	0.796	107.5	94.1	87.1	2.78	1.74
	1.001	105.3	93.1	85.6	2.81	1.90
<i>12-Crown-4</i>						
Li	1.028	79.6	—	—	<0.0	—
Na	1.029	89.4	89.2	85.2	2.05	1.73
K	1.047	98.5	92.8	83.9	1.73	0.86
Rb	1.086	100.4	94.4	81.7	1.65	0.87
Cs	0.796	107.4	102.2	82.6	1.60	0.74
	1.001	105.2	100.6	84.0	1.65	0.90

^aNo change in conductance was observed.

TABLE 7

Calculated Stokes radii of free alkali metal ions in water, methanol and methanol/water (7:3) at 298 K

Metal	Stokes radius (Å)		
	Water	Methanol/ water	Methanol
Li	2.38	3.6	3.75
Na	1.84	2.3	3.29
K	1.25	1.8	2.82
Rb	1.18	1.7	2.65
Cs	1.19	1.7	2.43

From Table 7, it can be concluded that the Li^+ and Na^+ ions are more strongly solvated than the other alkali metal ions while, apart from the lithium ion, there is a preferential solvation by the water molecules in the methanol/water mixture.

This can also be concluded from the differences between the equivalent conductivities of the alkali metal ion complexes in methanol and the methanol/water solvent mixture (compare Table 4 with Table 6). In methanol, the differences between the equivalent conductivities of the free metal ions and their complexes are smaller than those in the methanol/water mixture. This suggests that replacement of methanol molecules by the crown ether molecule has a smaller effect on the radius of the complex than the removal of water molecules. It can also be concluded from the data on the equivalent conductivities of the complex species that in the 1:1 complexes of the alkali metal ions with the small crown ethers used, the solvation shell is not completely removed. The equivalent conductivities of the 1:1 complexes of 12-crown-4 and 15-crown-5 differ relatively little from the values of the free cations, whereas the values for the 1:2 complex are significantly lower. Moreover, these latter values are very much the same for all the alkali metal ions (with the exception of the lithium ion) for a certain crown compound. Finally, the equivalent conductivities for the 1:2 complexes of 12-crown-4 are lower than those for 15-crown-5, suggesting that in the latter complexes, the solvation shell is removed to a larger extent than in the case of 12-crown-4.

In Tables 8 and 9, the stability constants of the complexes of 12-crown-4, 15-crown-5 and benzo-15-crown-5 with the alkali metal ions in methanol (and in methanol/water, 7:3) are summarized and compared with literature values. It can be seen that not all data are in good agreement, especially with regard to the values of the stability constant for the ML_2 complexes. This may be caused by the fact that different techniques have been used for the determination of the stability constants. With potentiometric procedures, for example, it is impossible to work with a large excess of ligand, in particular in those cases in which rather stable complexes are being formed ($\log K \geq 3$). Therefore, the relative amount of the ML_2 complex is small and the determination of the value of K_2 is subjected to a large uncertainty (as reported by Michaux and Reisse, for instance [24]). This is also the case for determinations by means of calorimetry; the values reported by Buschmann [46], for example, tend to be high. It is clearly desirable to evaluate the methods and procedures used by the different authors, carefully and critically in order to rate the results reported at their true value.

Complexation of urea

The interaction between urea and some crown ethers was studied by means of the indirect procedure described above. In water, the addition of urea to a solution containing potassium chloride and a 5-fold excess of 18-crown-6 resulted in a very small increase of the observed equivalent conductance of

TABLE 8

Comparison of present and literature values of the stability constants ($\log K_1$ and $\log K_2$) of alkali metal salt complexes with 12-crown-4, 15-crown-5 and benzo-15-crown-5 in methanol at 298 K

Crown	Li		Na			K			Rb			Cs			
	K_1	Ref.	K_1	K_2	Ref.	K_1	K_2	Ref.	K_1	K_2	Ref.	K_1	K_2	Ref.	
12C4	<0	TW ^a	2.0	1.7	TW	1.7	0.9	TW	1.6	0.9	TW	1.6	0.8	TW	
	<1	26	1.7	—	35	1.74	—	35							
	~0 ^b	34	1.47	2.28	24	1.59	0.56	24							
			2.1	1.7	26	1.7	0.7	26							
			1.41	2.20	36	1.58	0.15	36							
15C5	1.2	TW	— ^c		TW	3.4	2.6	TW	2.9	2.2	TW	2.8	1.8	TW	
	1.23 ^b	34	3.25		37	3.61	1.3	24				2.18		38	
			3.24		35	3.59		39				1.89	1.2	40 ^d	
			3.14	2.4	24	3.77	2.71	38				2.62		41	
			3.48		38	3.63	2.45	42 ^e							
			3.39		43 ^d	3.86	2.21	43 ^d							
			3.30		41	3.35	2.65	41							
			3.30	1.44	36	3.1	2.9	48							
			3.27		44	3.34	2.21	36							
			3.31		45	3.34		45							
			3.43	2.40	46	3.43		44							
			3.42	2.77	46	3.85	2.48	46	4.07	2.47	46	3.58	2.53	46	
			B15C5	— ^c	TW	2.9	2.1	TW	3.0	3.2	TW	2.7	2.7	TW	2.2
1.23	43 ^d	3.38			43 ^d	2.90	2.75	43 ^d				1.91		47	
		3.05			48	2.8	3.15	48				2.03		49	
		2.97			3				2.90	2.45	3				
		3.37			47										
		2.87			50										
		3.12			51										
		3.03		2.42	46	3.93	2.57	46	3.97	2.55	46	3.52	2.68	46	

^aThis work. ^bTemperature = 300 K. ^cNot determined (no change in conductance was observed). ^dFound by differential vapour-pressure osmometry. ^eFound by a polarographic method.

TABLE 9

Comparison of present and literature values of the stability constants ($\log K_1$ and $\log K_2$) of alkali metal salt complexes with 15-crown-5 and benzo-15-crown-5 in methanol/water (7:3) at 298 K

Crown	Li	Na	K		Rb		Cs		Ref.
	K_1	K_1	K_1	K_2	K_1	K_2	K_1	K_2	
15C5	1.0	2.3 2.21–2.65	2.8	2.0	2.8	1.9	2.3	1.4	This work 37
B15C5	0.4	2.0 1.99	2.0 1.5	2.4 2.65	1.8 1.8	2.4 1.97	1.6 1.70	1.1	This work 52

the solution. This can be explained by the interaction between urea and the crown ether, because addition of urea to a solution containing only the potassium salt did not have any effect on the conductance. The change in the conductance value observed in the presence of the crown ether, however, was too small to calculate the stability constant of the crown ether/urea complex.

In methanol, no change in conductance was observed upon addition of urea when the sodium/benzo-15-crown-5 couple was used as the indicator system, indicating that the interaction between urea and this crown ether is absent or very weak. For 18-crown-6 and dibenzo-24-crown-8, the difference between the equivalent conductivities of the free metal salt and its 1:1 complex with the crown ether was too small to be used for the indirect procedure. Therefore, it was decided to look for an alternative indicator compound. The guanidinium ion is a suitable species for this purpose because it can be considered as a charged analogue of the urea molecule. (Moreover, the complexation of guanidinium salts in solution has been studied by different authors [53, 54] and the crystal structure of the solid complexes of guanidinium salts with some crown ethers has been elucidated [55, 56].)

When guanidinium hydrochloride served as the indicator compound, it was possible to calculate the stability constant of the urea/18-crown-6 complex in methanol. This value was very small ($\log K = 0.4 \pm 0.1$), but in agreement with results of the polarographic experiments [1, 2]. It was not possible to study the interaction between urea and dibenzo-24-crown-8 by using the guanidinium ion as indicator; the specific conductance of a solution of the guanidinium ion in methanol changed only very little on addition of the crown ether and no reproducible value of the stability constant could be calculated.

Conclusions

The conductometric study of the complexation of metal salts by crown ethers provides a suitable means for determining the stability constants of these complexes. Moreover, additional information concerning the solvation and size of the free and complex species in solution can be obtained from the equivalent conductivities of the species involved.

In principle, it is possible to study the interaction between crown ethers and uncharged compounds by means of an indirect procedure. For this purpose, the availability of a suitable indicator system is a major prerequisite.

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