A comparison of different experimental techniques for the determination of the stabilities of polyether, crown ether and cryptand complexes in solution

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(Received October 16, 1991; revised January 31, 1992)

Abstract

Conductometric, potentiometric and calorimetric titrations were performed to determine the stability constants of the alkali, alkaline earth and Ag(I) complexes with pentaethyleneglycol dimethylether, 18-crown-6 and the cryptand (222) in methanolic solutions. In the cases where no direct information about the stability constants could be obtained from these measurements indirect methods were used. The experimental techniques are discussed in detail. The stability constants obtained by the different experimental methods are in good agreement.

Introduction

Many experimental techniques have been described in the literature for the study of complex formation of cations with inorganic and organic ligands [1–5]. For many years computers were used for the evaluation of experimental data and their treatment became more and more sophisticated [6].

The formation of crown ether and cryptand complexes can be studied by all techniques already described in the literature. In practice, however, only some of them are used because most have been developed for aqueous solutions [7] and not for organic solvents. Because the macrocyclic and macrobicyclic ligands are able to shield the complexed cations more or less from the surrounding solvents other solvents than water are chosen for complexation studies. One expects to get more information about the influence of solvents on these reactions.

A compilation of stability constants of crown ether and cryptand complexes gives numerous values in different solvents together with the known reaction enthalpies [8]. However, as the experimental conditions may vary a direct comparison is not strictly achieved.

Therefore it seemed necessary to study some complexation reactions by different experimental techniques in detail and to compare the results. As ligands a noncyclic polyether, the crown ether 18-crown-6, and the cryptand (222) were chosen, because the stabilities of the complexes formed with these ligands are known to differ by several orders of magnitude [8]. Thus, the advantages and disadvantages of the most common experimental methods can be shown and discussed. Using methanol as solvent a comparison with already published data is possible because upto now most stability constants have been measured in this solvent.

Experimental

The ligands 2,5,8,11,14,17-hexaoxaoctadecane (PG; Riedel-de Haen), 18-crown-6 (Merck) and the cryptand (222) (Merck) were used without further purification. The following anhydrous salts: $NaNO_3$ (Merck), KJ (Merck), RbJ (Merck), $RbNO_3$ (Merck), CsF (Ventron), $AgNO_3$ (Merck), $Ca(NO_3)_2$ (BDH), $Sr(NO_3)_2$ (Ventron) and $Ba(ClO_4)_2$ (Merck) were dried under vacuum prior to use. Tetraethylammonium perchlorate (TEAP) and tetraethylammonium nitrate (TEAN) (Fluka) were recrystallized and dried under vacuum. The alkali tetraphenylborates were prepared and purified as described in the literature [9]. Heptafluorobutyrates were prepared by adding the solid alkaline earth hydroxides to a concentrated aqueous solution of heptafluorobutyric acid (Aldrich) until no dissolution of the hydroxide could be observed. The solution was filtered and evaporated. The residue was washed with methylene chloride and dried *in vacuo*. Dry methanol (Merck, max. 0.01% H_2O) was used as solvent.

Measurements of the conductivity were performed using a Methrom conductometer 660. The cell constant of the set up was estimated to be 0.7624 cm^{-1}. The following ion-selective electrodes were chosen for potentiometric titrations: Na^+ (Methrom EA 109-Na), K^+ (Ingold pK201-S7) and Ag^+ (Methrom EA 282).

0020-1693/92/$5.00

For the calorimetric titrations a Tronac model 450 calorimeter was used.

Conductometric and calorimetric titrations were performed at least three times. The ranges of concentrations used and the experimental errors are given in the discussion of each experimental technique.

Results and discussion

The stability constant for the formation of a 1:1 ligand–cation complex is defined as

$$K=[ML^{n+}]/[M^{n+}][L]$$

The material balances in this case are given by

$$c_M=[M^{n+}]+[ML^{n+}]$$

$$c_L=[L]+[ML^{n+}]$$

The concentrations c_M and c_L denote the total concentrations of the salt and the ligand. $[M^{n+}]$, $[L]$ and $[ML^{n+}]$ are the actual concentrations of the uncomplexed cation, of the uncomplexed ligand and of the complex formed during the titration, respectively.

Activity corrections are necessary if the ionic strength varies during the titrations. As a first approximation it may be assumed that the activity coefficients of the cation and the complex are equal and the activity coefficient of the neutral ligand is zero. Thus, no corrections have to be taken into account. Another possibility is to perform the measurements at a high ionic strength. Under this circumstances the ionic strength is nearly constant during the titration. It is also necessary to know that the supporting electrolyte does not participate in the reaction studied. For this reason tetraalkylammonium salts are normally used as supporting electrolytes. However, at high concentrations the formation of ion-pairs can occur [10]. Fortunately it is known from results obtained in acetone and methanol as solvents that the stability of the ion-pairs does not affect the calculated stability constants of crown ether [11] and cryptand complexes [12].

At low values of the ionic strength I the Debeye–Hückel equation

$$\log f_i=-Az_i^2I^{1/2}/(1+BaI^{1/2})$$

is valid to calculate activity coefficients f_i [13]. z_i is the valency of the cation and anion, respectively. The constants A and B can be calculated from the absolute temperature T and the dielectric constant ϵ of the solvent

$$A=(2\pi N/1000)^{1/2}\times e^3/(2.303(k\epsilon T)^{3/2}) \qquad (\mathrm{mol^{-1/2}\ l^{1/2}\ K^{3/2}})$$

$$B=(8\pi Ne^2/1000k\epsilon T)^{1/2} \qquad (\mathrm{mol^{-1/2}\ cm^{-1}\ l^{1/2}\ K^{1/2}})$$

with the Avogadro number N, Boltzmann's constant k and the protonic charge e. The ion size parameter a in the Debeye–Hückel equation for dilute solutions is in the order of 4 Å [14].

A direct comparison of the values of the stability constants estimated at ionic strengths below $I=0.05$ M is possible since it is known that under these experimental conditions the complex formation constants remain reasonably constant [15].

The stability constants determined by means of different experimental techniques are summarized in Table 1 for the non-cyclic ligand PG, in Table 2 for the crown ether 18-crown-6, and in Table 3 for the cryptand (222).

Conductometric titrations

If the mobility of the uncomplexed cation and of the complex are different the complex formation should result in changes of conductivity during a titration. However, serious problems arise by dilution of the salt solution. Even in dilute methanolic solutions not all salts are completely dissociated [17]. Thus the mathematical treatment of conductivity data becomes complicated. Accordingly, stability constants evaluated from titrations with varying salt concentrations [18] have been questioned [19]. This problem can be eliminated by adding the pure ligand to the salt solution [20, 21]. Thus, only very small changes in the salt concentration have to be taken into account.

Another elegant way to avoid any dilution effect of the salt solution is also described in the literature [22, 23]. The ligand solution contains the same salt concentration as the titrated salt solution. For this study the concentration of the ligand was 0.015–0.02 M and the salt concentration $1.0–2.0\times10^{-3}$ M. Since the ionic strength remains constant no corrections for changes in ion activity are necessary. The observed equivalent conductances Λ_{obs} is given by the sum of the equivalent conductance of the cation Λ_+, the crown ether complex Λ_c and the anion Λ_-

$$\Lambda_{obs}=\alpha\Lambda_+ +(1-\alpha)\Lambda_c+\Lambda_- \tag{1}$$

with $\alpha=[M^{n+}]/c_M$.

Using the mass balances and the definition of the complex stability one gets the following expression

$$\alpha=[-(K[c_L-c_M]+1)+([K(c_L-c_M)+1]^2 +4Kc_M)^{1/2}]/2Kc_M \tag{2}$$

The anion conductivity can be neglected because it is known not to associate with the free cation and because it is also assumed not to associate with the cation–ligand complex. As a consequence the equivalent conductivity of the anion remains constant throughout the titration. The best value of Λ_c is calculated by a least-squares analysis of the equation given for Λ_{obs}. The error square

TABLE 1. Stability constants (log K, K in M^{-1}) for the reaction of the ligand 2,5,8,11,14,17-hexaoxaoctadecane with cations in methanol at 25 °C

Value	Na^+	K^+	Rb^+	Cs^+	Ag^+	Ca^{2+}	Sr^{2+}	Ba^{2+}
log K^a	[d]	2.40	2.07	1.72	[d]	2.29	2.53	2.31
log K^b	1.54	2.07	1.98	1.76	1.80	[e]	[e]	2.59
log K^c	[f]	[f]			[f]			

[a]Conductometric titration. [b]Direct calorimetric tritration. [c]Direct potentiometric titration. [d]Changes in the conductivity too small during the titration. [e]No heat produced during the calorimetric titration. [f]Change of the potential too small during the titration.

TABLE 2. Stability constants (log K, K in M^{-1}) for the reaction of the crown ether 18-crown-6 with cations in methanol at 25 °C

Value	Na^+	K^+	Rb^+	Cs^+	Ag^+	Ca^{2+}	Sr^{2+}	Ba^{2+}
log K^a	4.42	>5.5	5.35	4.37	4.67	3.74	>5.5	>5.5
log K^b	4.32	>5	5.32	4.44	4.58	3.87	>5	>5
log K^c	4.35	6.15			4.65			
log K^d		6.29	5.82				6.84	7.31
		6.07	5.57					7.38
log K^e						3.94[f]		
						3.99[g]		

[a]Conductometric titration. [b]Direct calorimetric titration. [c]Direct potentiometric titration. [d]Calorimetric competitive titration. [e]Potentiometric competitive titration. [f]With the Ag^+ electrode. [g]With the K^+ electrode.

TABLE 3. Stability constants (log K, K in M^{-1}) for the reaction of the cryptand (222) with cations in methanol at 25 °C

Value	Na^+	K^+	Rb^+	Cs^+	Ag^+	Ca^{2+}	Sr^{2+}	Ba^{2+}
log K^a	>5	>5	>5	4.04	>5	>5	>5	>5
log K^b	>5	>5	>5	3.95	>5	>5	>5	>5
log K^c	7.95	9.82			12.23			
log K^d	7.31					8.16	[e]	[e]
log K^f	7.97[g]	10.49[g]	9.10[g]			8.14[g]	11.75[h]	12.9[h]

[a]Conductometric titration. [b]Direct calorimetric titration. [c]Direct potentiometric titration. [d]Calorimetric competitive titration. [e]Dissociation of the complex is too slow. [f]Potentiometric competitive titration. [g]With the Ag^+ electrode. [h]With the Ag^+ electrode from ref. 16.

sum over the n data points is given by

$$U(\Lambda_c)=\sum_{i=1}^{n}(\Lambda_{obs,\,i}-(\alpha_i\Lambda_+ +(1-\alpha_i)\Lambda_c))^2 \qquad (3)$$

The best value of Λ_c for a given titration is that which minimizes $U(\Lambda_c)$. At that value we have

$$\delta U(\Lambda_c)/\delta\Lambda_c=0 \qquad (4)$$

or

$$\sum_{i=1}^{n}(\Lambda_{obs,\,i}-(\alpha_i\Lambda_+ +(1-\alpha_i)\Lambda_c)(\alpha_i-1)=0 \qquad (5)$$

For the unknown equivalent conductivity of the complex formed one gets

$$\Lambda_c=\sum_{i=1}^{n}(\Lambda_{obs,\,i}-\alpha_i\Lambda_+)(1-\alpha_i)\Bigg/\sum_{i=1}^{n}(1-\alpha_i)^2 \qquad (6)$$

Using eqn. (6) and assuming a value of the stability constant it is possible to calculate a value for the equivalent conductivity of the complex. With this value the error square sum is calculated. By systematical variation of the stability constant K one value for Λ_c is found which minimizes $U(\Lambda_c)$.

The experimentally measured equivalent conductivities for the titration of sodium tetraphenylborate with the ligand 18-crown-6 in methanolic solution are summarized in Table 4. For comparison calculated values of the equivalent conductivity assuming different values of the complex stability are given too. The minimum value of the error square sum is found for log $K=4.42$ with the sum of the equivalent conductivities of the sodium complex and the anion

$$\Lambda_c+\Lambda_-=62.53\ \mathrm{S\ cm^2\ mol^{-1}}$$

TABLE 4. Experimental equivalent conductivities Λ_{exp} (S cm^2 mol^{-1}) for the titration of sodium tetraphenylborate (2.00×10^{-3} M) with the ligand 18-crown-6 in methanol at 25 °C and calculated equivalent conductivities Λ_{calc} assuming different complex stabilities K

c_L/c_M	Λ_{exp}	Λ_{calc}		
		log K=4.00	log K=4.42	log K=5.00
0.000	68.81	68.81	68.81	68.81
0.078	68.41	68.31	68.33	68.34
0.154	67.91	67.83	67.86	67.89
0.228	67.46	67.36	67.41	67.45
0.302	67.01	66.90	66.96	67.02
0.373	66.56	66.47	66.53	66.59
0.444	66.11	66.05	66.11	66.18
0.515	65.71	65.65	65.69	65.77
0.580	65.31	65.26	65.32	65.38
0.645	64.96	64.90	64.95	64.99
0.710	64.61	64.57	64.59	64.62
0.775	64.26	64.26	64.26	64.26
0.840	64.01	63.99	63.94	63.92
0.900	63.71	63.74	63.69	63.62
0.960	63.51	63.53	63.46	63.36
1.035	63.26	63.31	63.24	63.15
1.080	63.11	63.19	63.14	63.07
1.140	63.01	63.06	63.03	63.00
1.195	62.91	62.95	62.95	62.96
1.250	62.86	62.86	62.89	62.94
1.305	62.81	62.79	62.85	62.92
$\Lambda_c+\Lambda_-$		62.06	62.53	62.83
$U(\Lambda_c)\times10^2$		7.43	2.77	9.40

This value is slightly smaller than that found for the uncomplexed salt

$$\Lambda_+ + \Lambda_- = 68.81 \text{ S cm}^2\text{ mol}^{-1}$$

The equilibrium constant for a given reaction can be determined by conductometric titrations if the magnitude of K and of the equivalent conductivities are within certain limits. Using the stated values of the equivalent conductivities of sodium tetraphenylborate and its 18-crown-6 complex the influence of the complex stability upon the measured equivalent conductivity is shown in Fig. 1. For reactions with log $K<1$ the changes become very small and with log $K>6$ all curves will nearly look identical. For reliable calculation of stability constants from experimental data the values of K should be in the range mentioned above. The dependence upon the differences between the equivalent conductivities of the salt and the corresponding complex is obvious. Figure 2 shows curves for a constant value of log K and a given equivalent conductivity of the salt while the value of the equivalent conductivity of the complex is varied. If the difference between both equivalent conductivities is small only minor changes of the measured equivalent conductivity will occur. It follows that in order to obtain sufficient changes during titration the lower the K value is, the higher the differences of the equivalent conductivities must be. To fulfil this condition the anion should contribute as little as possible to the overall conductivity because the other individual conductivities are given by the reaction studied. Thus, big organic anions such as the tetraphenylborate ion are preferable because they have only small values of the equivalent conductivities [24, 25].

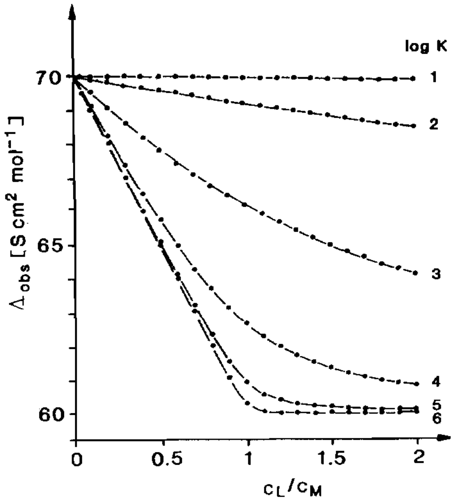

Fig. 1. Influence of the complex stability (log K, K in M^{-1}) upon the expected equivalent conductivities Λ_{obs} (S cm^{2+} mol^{-1}) due to complex formation during the titration of a salt (Λ=70 S cm^{2+} mol^{-1}) with a ligand (equivalent conductivity of the complex Λ_c=60 S cm^{2+} mol^{-1}).

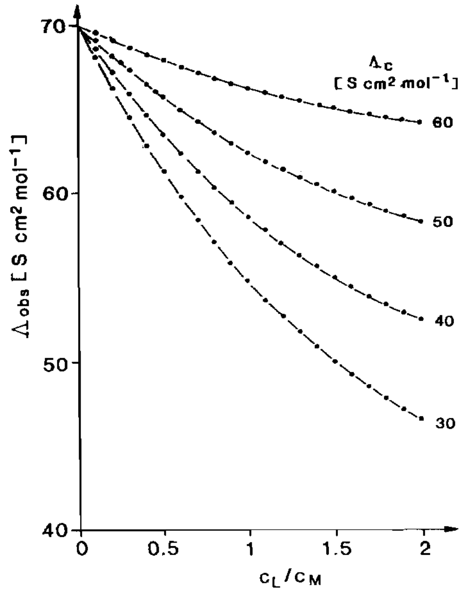

Fig. 2. Influence of the values of the equivalent conductivity of the complex formed (Λ_c, in S cm^{2+} mol^{-1}) upon the observable equivalent conductivities during the titration of a salt (Λ=70 S cm^{2+} mol^{-1}) with a ligand solution for a given complex stability of log K=3.

Due to the high accuracy of conductivity measurements the reproducibility of the stability constants calculated from the experimental data is at least log $K = \pm 0.03$.

Calorimetric titrations

Nearly all chemical reactions are accompanied by temperature changes. Therefore, calorimetric methods have many applications in analytical chemistry [26] and for the determination of equilibrium processes [27, 28].

The method and theory of calorimetric titrations and the calculation of equilibrium constants has already been discussed in detail [29–31]. However, it seems necessary to repeat some of the fundamentals of calorimetric titrations, because the reliability of this method has been questioned recently [32].

In a typical calorimetric titration a ligand solution (0.06–0.08 M) is added continuously to a solution (40 ml) containing the salt ($4\text{–}6 \times 10^{-3}$ M) in the reaction vessel. Since the buret delivery rate has been determined separately the concentrations of the ligand and of the salt in the reaction vessel can easily be calculated.

After appropriate corrections for all non-chemical heat effects the measured heat Q_t at any time during the titration is related to the number of moles of products formed in all chemical reactions taking place in the reaction vessel $\Delta n_{i,\,t}$ and the corresponding reaction enthalpies ΔH_i by the following equation

$$Q_t = \sum_{i=1}^{t} \Delta n_{i,\,t} \Delta H_i \qquad (7)$$

Δn_t is a function of the corresponding stability constant. If only one reaction takes place the stability constant and the reaction enthalpy ΔH can be calculated by a least-squares analysis. The error square sum over t data points is given by

$$U(\Delta H) = \sum_{i=1}^{t} (Q_t - \Delta n_t \Delta H)^2 \qquad (8)$$

The value of the reaction enthalpy which minimizes the error square sum is defined by

$$\Delta H = \sum_{i=1}^{t} \Delta n_t Q_t \Big/ \sum \Delta n_t^2 \qquad (9)$$

Similar to the procedure outlined for the evaluation of data from conductometric titrations one calculates Δn_t for an assumed value of the stability constant. Using eqn. (9) it is possible to obtain a value for the reaction enthalpy which is then used to calculate the error square sum. A systematically variation of the stability constant leads to a value of the reaction enthalpy which minimizes $U(\Delta H)$.

Since the ionic strength changes during the titration, corrections for the activity coefficients at each data point are necessary. This is done using the Debeye–Hückel equation which has been discussed before.

A description of the complete calculation procedure in more detail together with a FORTRAN program for the calculation of K and ΔH from calorimetric titrations including the mentioned corrections has already been published [33]. A version of this program in BASIC was used for the evaluation of the experimental data.

The accuracy of the calorimeter used has already been proven and reported by the measurement of a standard reaction [34].

The simultaneous calculation of the stability constant and the reaction enthalpy from one thermogram, however, is only possible if both values are within certain limits. The effect of the value of the stability constant for a given reaction enthalpy on the heat produced during titration is shown in Fig. 3. If log K values exceed 5.5 the curvature of the thermograms differ only slightly from one to another. Therefore, this is the upper limit of the stability constants. It is not possible to give an exact lower limit, however, it depends also on the value of the reaction enthalpy. The influence of the reaction enthalpy on the thermogram is demonstrated for a constant value of the complex stability in Fig. 4. Thus, for the lower K only with higher ΔH is a sufficiently curved thermogram obtained. If log $K > 5.5$ only the reaction enthalpy can be calculated. In this case the number of moles of the complex formed is equal to the number of moles of the titrant added to the solution in the reaction vessel. From this linear change of Q during the titration period ΔH is easily obtained.

Even in cases where no direct information about the composition of the complexes formed in solution is available calorimetric titrations give some reliable thermodynamic data [35]. As long as the thermogram shows

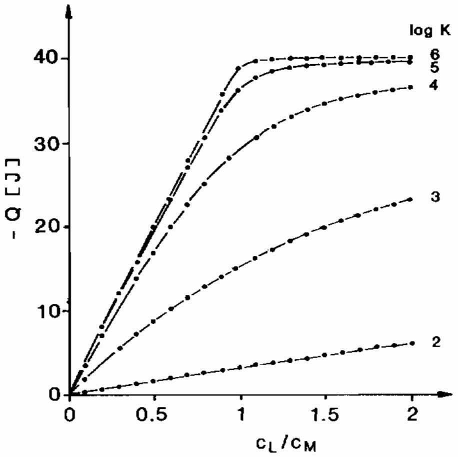

Fig. 3. Effect of the values of the stability constant on the expected heat Q (J) during a calorimetric titration of a salt solution (1×10^{-3} M) with a ligand solution for a given reaction enthalpy of $\Delta H = -40$ (kJ mol^{-1}).

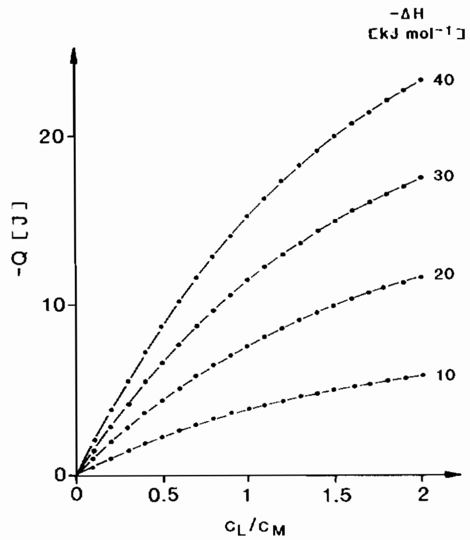

Fig. 4. Influence of the values of the reaction enthalpy on the measurable heat Q (J) during a calorimetric titration of a salt solution (1×10^{-3} M) with a ligand solution for a given stability constant of log $K=3$.

no curvature from the start of the titration there is no experimental evidence for a deviation from a complete complex formation. Although this point has been questioned [32] it is verified by the experiment. The concentrations of the ligand and salt solutions can be arranged so that this titration period is sufficiently long. The only assumption one has to make in order to calculate ΔH is that each mole of the component added to the reaction vessel is complexed by x moles of the component inside the reaction vessel. Thus the number of moles n of the complex formed is equal to the number of moles m of the component titrated into the reaction vessel

$$\Delta H = Q/n \tag{10}$$

If this assumption is incorrect and the complex formation is incomplete one gets for x species formed in solution

$$\sum_{i=1}^{x} \Delta H_i = Q \Big/ \sum_{i=1}^{x} n_i \tag{11}$$

Thus a variation of the concentrations of ligand and cation should result in different overall reaction enthalpies because the number of moles n_i of the different species formed depends on the ratio of ligand to cation.

The temperature change during the calorimetric titrations is rather small with $T=0.01$ K. As a result the stability constants remain unaffected. The experimental reproducibility of the stability constants and reaction enthalpies is in the order of log $K = \pm 0.05$ and $\Delta H = \pm 1$ kJ mol^{-1}. From thermograms with log $K > 5$ the accuracy of the ΔH values is even better.

Calorimetric competitive titrations

In order to extend the range of measurable stability constants to values higher than log $K=5$ calorimetric competitive titrations can be performed [36, 37]. This method has already been tested to some extent to demonstrate the reliability of the results obtained [38].

Two types of competitive titrations have been used to obtain the results given in Tables 2 and 3.

(i) A ligand L_1 (0.08 M) is titrated into a solution containing another ligand L_2 (0.02–0.04 M) and a cation M^{n+} (5×10^{-3} M). The following reaction takes place

$$L_1 + L_2M^{n+} \rightleftharpoons L_1M^{n+} + L_2$$

The stability constant K_1 is given by

$$K_1 = \frac{[L_1M^{n+}][L_2]}{[L_1][L_2M^{n+}]}$$

(ii) A salt solution M_1^{n+} (0.08 M) is titrated into a solution of a ligand L (5×10^{-3} M) and another salt M_2^{n+} (0.02–0.04 M). In this case the following reaction can be observed

$$M_1^{n+} + LM_2^{n+} \rightleftharpoons LM_1^{n+} + M_2^{n+}$$

with

$$K_2 = \frac{[LM_1^{n+}][M_2^{n+}]}{[M_1^{n+}][LM_2^{n+}]}$$

The anions have been omitted for clarity since they do not take part in the reactions if the salts can be assumed to be completely dissociated under the experimental conditions.

The observed heat of reaction is now related to the number of moles of the complexes L_1M^{n+} or LM_1^{n+}, respectively formed during these titrations. The further treatment of the experimental data from calorimetric competitive reactions is identical compared with that already described for calorimetric titrations.

In a few cases the dissociation reaction of the complexes already formed is slow, thus the burette delivery rate has to be reduced to insure that during the titration the competitive reaction has always reached its equilibrium state [38]. In particular the dissociation reactions of alkaline earth cryptates are known to be extremely slow [12] so the stability of these complexes cannot be estimated in this way.

However, the main problem of this method is to find a competitive reaction which results in values of log K_1 or log $K_2 < 5$ and negative reaction enthalpies. For this reaction the stability constant and the reaction enthalpy should already be known. If for one ligand or one cation one or more competitive calorimetric titrations gives values of log $K < 5$ it is possible to calculate the unknown stability constant and to compare the result. The reliability of the indirectly obtained stability constant and reaction enthalpy can be determined by comparison with the directly measured reaction enthalpy.

The following may serve as example. The stability constant of the complex between 18-crown-6 and K^+ cannot be measured directly by calorimetric titrations. The titration of solutions of K^+ into solutions containing 18-crown-6 (18C6) and Na^+ or Cs^+ gives thermograms suitable for the calculation of stability constants and reaction enthalpies

1. $K^+ + 18C6Na^+$:

   $\log K = 1.97$ and $-\Delta H = 22.5$ (kJ mol^{-1})

2. $K^+ + 18C6Cs^+$:

   $\log K = 1.63$ and $-\Delta H = 6.9$ (kJ mol^{-1})

By combination with data for the formation of the complexes with Na^+ and Cs^+ one gets for the formation of the K^+ complex

1. $\log K = 6.29$ and $-\Delta H = 56.5$ (kJ mol^{-1})
2. $\log K = 6.07$ and $-\Delta H = 56.8$ (kJ mol^{-1})

The value of the reaction enthalpy obtained from direct calorimetric titration is: $-\Delta H = 56.1$ (kJ mol^{-1}).

The reactions studied by competitive calorimetric titrations to determine the stability constants for the formation of complexes with the crown ether 18C6 and the cryptand (222) given in Tables 2 and 3 are summarized in Table 5.

The accuracy for stability constants estimated by calorimetric competitive titrations is found to be $\log K = \pm 0.1$.

Potentiometric titrations

During the titration of a salt solution with a ligand solution the concentration of the free cation changes due to complex formation. Using ion-selective electrodes it is possible to calculate the actual activity of a cation during titration. Most commercially available ion-selective electrodes however are damaged in solvents other than water. Therefore in the present study only glass electrodes for sodium and potassium ions and a silver electrode for silver ions are used.

TABLE 5. Reactions studied by calorimetric competitive titrations and indirectly estimated stability constants ($\log K$, K in M^{-1}) and reaction enthalpies ΔH (kJ mol^{-1}) and the direct measured reaction enthalpies ΔH_{dir} (kJ mol^{-1})

Measured reaction	Calculated reaction	$\log K$	$-\Delta H$	$-\Delta H_{\mathrm{dir}}$
$K^+ + 18C6Na^+$	$K^+ + 18C6$	6.29	56.5	56.1
$K^+ + 18C6Cs^+$	$K^+ + 18C6$	6.07	56.8	56.1
$(222) + 18C6Rb^+$	$Rb^+ + 18C6$	5.57	49.9	49.6
$Rb^+ + 18C6Na^+$	$Rb^+ + 18C6$	5.87	47.1	49.6
$Sr^{2+} + 18C6Ca^{2+}$	$Sr^{2+} + 18C6$	6.84	31.4	37.2
$Ba^{2+} + 18C6Na^+$	$Ba^{2+} + 18C6$	7.31	47.4	48.5
$Ba^{2+} + 18C6Ag^+$	$Ba^{2+} + 18C6$	7.38	48.4	48.5
$K^+ + (222)Na^+$	$Na^+ + (222)$	7.90	34.4	36.2
$K^+ + (222)Ca^{2+}$	$Ca^{2+} + (222)$	8.16	22.7	22.0

The experimental setup has already been described in the literature in detail [39]. A salt solution (0.8–1.5×10^{-3} M) is titrated with a solution containing the ligand (0.015–0.025 M). All potentiometric titrations are performed at a constant ionic strength of $I = 0.05$ M. TEAP or TEAN are used as inert electrolytes. Under these experimental conditions the activity coefficients are constant. Therefore it is not necessary to assume that the activity coefficients are equal to one [40].

The activity of the uncomplexed cation $[M^{n+}]$ in solution is calculated from the measured potential E by the Nernst equation

$$[M^{n+}] = c_M \times 10^{(E - E_1)/D} \tag{12}$$

E_1 is the potential between the ion-selective electrode and the reference electrode before the titration. The constant D is defined by

$$D = -2.303RT/nF = -59.16/n \text{ (mV)} \tag{13}$$

with the gas constant R, the temperature T, the Faraday constant F and the charge of the cation n.

Since the total concentrations of the cation c_M and ligand c_L are known the concentrations of the complex $[LM^{n+}]$ formed

$$[LM^{n+}] = c_M - [M^{n+}] \tag{14}$$

and of the free ligand [L]

$$[L] = c_L - c_M + [M^{n+}] \tag{15}$$

can be calculated.

Using these equations the activities of all species in solution for the case of 1:1 complex formation are known. Thus the stability constant is easily obtained from the measured electrochemical potential. This stability constant is only valid for the given ionic strength. However, it has been shown by Smetana and Popov that the values of the stability constant remain unaffected upto an ionic strength of $I = 0.05$ M [15].

Some experimental data for a potentiometric titration of a solution containing $AgNO_3$ with the cryptand (222) together with the calculated stability constants are given in Table 6. The experimental potentials at ligand concentrations higher than the salt concentrations can be used directly to calculate the stability constant. Under this circumstances only 1:1 complexes between the cryptand (222) and Ag^+ will form. So each experimental value can be used to calculate the stability constant of this reaction. As it can be seen the accuracy of the stability constant is very good.

TABLE 6. Experimentally measured potential E (mV) of a potentiometric titration of solution ($V = 20$ ml) containing $AgNO_3$ (1.04×10^{-3} M) with the cryptand (222) and the calculated stability constant (log K, K in M^{-1}) with a zero potential $E_1 = -0.4$ mV at 25 °C

c_L/c_M	E	log K
9.123	599.8	12.217
8.643	598.4	12.220
8.163	596.9	12.223
7.683	595.4	12.228
7.203	593.5	12.228
6.722	591.6	12.231
6.242	589.5	12.233
5.762	587.1	12.235
		12.227 ± 0.006

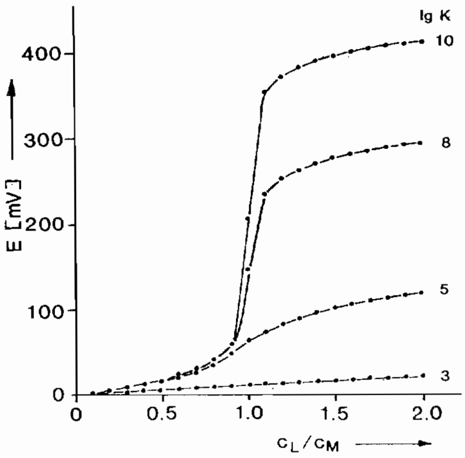

Fig. 5. Potential changes E (mV) during a potentiometric titration for different values of the stability constant K.

Obviously no problems occur with the calculation of high values of stability constants from potentiometric titration data. To show the influence of the value of the stability constant upon the titration curves, some calculated curves are shown in Fig. 5. The potential changes at the equivalent points increase with increasing stability constants. Below a value of log $K = 3$ the titration curves show no equivalent point. They appear nearly as a straight line. Curves obtained only by dilution of the salt solution have a nearly identical shape.

The experimental reproducibility of stability constants is in the order of log $K = \pm 0.02$.

Potentiometric competitive titrations

In all cases where no ion-selective electrodes exist competitive potentiometric titrations may be performed to measure the complexation of a cation directly in an organic solvent. All ions for which ion-selective electrodes are available can be used as auxiliary ions if their complexes are more stable than the complexes with other cations. If this condition is not fulfilled no exchange reaction between the cations will take place.

If the cation for which an electrode can be used is M_1^+ the following reaction is expected to take place

$$M_1^+ + LM^{n+} \rightleftharpoons LM_1^+ + M^{n+}$$

From the measured potentials during titration the actual concentrations of the cation M_1^+ are derived. They can be used to calculate the concentrations of all other species as described before. By combination with the separately estimated stability constant for the formation of the LM_1^+ complex the stability constant of LM^{n+} is obtained. This method is known from the literature for Ag^+ ions [39] and for Na^+ ions [40]. A salt solution (1×10^{-3} M) for which an ion-selective electrode exists is titrated with a solution containing the ligand (1×10^{-2} M) and the other salt (2×10^{-2} M). TEAP or TEAN are used to keep the ionic strength constant during titration.

If the kinetic of the dissociation of the complex LM_1^+ is slow no real titration is possible. A solution of the complex is mixed with a solution containing Ag^+ or another cation and the mixture is left until the equilibrium is reached. The equilibration time may vary from some minutes to months [16].

The reproducibility of the values of the stability constants obtained from potentiometric competitive titrations is in the order of log $K = \pm 0.05$.

Conclusions

Common experimental methods used to study the complex formation with non-cyclic, macrocyclic and macrobicyclic ligands in organic solvents have been discussed in some detail. Further methods such as UV–Vis spectrophotometry, polarography or NMR spectroscopy have already been described in the literature [7].

As can be seen from Tables 1, 2 and 3 the stability constants estimated by different experimental techniques agree very well. However, in order to get reliable results one has to decide which method to choose for a given system by sharp scrutiny of the response for the quantity to be observed. For stability constants smaller than 10^5 conductometric or calorimetric titrations may be used. The advantage of calorimetric measurements is that the stability constants together with the reaction enthalpies can be calculated from one experiment. Potentiometric titrations give good results if the stability constants are higher than 10^3. For systems where these methods fail competitive potentiometric or calorimetric titrations should be used.

TABLE 7. Stability constants (log K, K in M^{-1}) for the complexation of K^+ by different ligands in methanol at 25 °C

Pg	18-crown-6	cryptand (222)
2.02[a]	6.15[a]	9.82[a]
2.01[a]	6.29[a]	10.49[a]
2.1[b]	6.07[a]	10.8[q]
2.2[c]	6.10[e]	10.41[r]
2.20[d]	6.06[f]	
	6.18[g]	
	6.02[h]	
	6.0[i]	
	6.10[k]	
	5.93[l]	
	6.08[m]	
	6.18[n]	
	6.08[o]	
	6.09[p]	

[a] This work. [b] Ref. 41. [c] Ref. 42. [d] Ref. 43. [e] Ref. 44. [f] Ref. 45. [g] Ref. 46. [h] Ref. 47. [i] Ref. 48. [k] Ref. 49. [l] Ref. 50. [m] Ref. 51. [n] Ref. 52. [o] Ref. 53. [p] Ref. 40. [q] Ref. 54. [r] Ref. 55.

To compare the results from this work with data from the literature stability constants for the complexation of K^+ with the ligands examined as an example are summarized in Table 7. For all three ligands the stability constants measured are in absolute agreement with the values from the literature. The same is true for all other cations examined.

Acknowledgement

Financial support by the Minister of Science and Technology of Nordrhein-Westfalen is gratefully acknowledged.

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