Mobilities of cation–macrocyclic ligand complexes

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Abstract - Formation constants for complexion between alkali metal cations and the crown ether 18C6 in the solvent 2-cyanopyridine at 30°C were determined from conductance measurements. The method allows for precise determination of these formation constants up to values of K_f around 10^{11} mol^{-1} dm^3. The method also permits accurate evaluation of association equilibrium constants between the complex species $(M-18C6)^+$ and the anion. The magnitudes of these ion association constants are related to the nature of the solvation of the cation and of the complexed cation. The mobilities of the complexes are also dependent, in part, upon solvation effects. In 2-cyanopyridine the single ion molar conductance of the $(Li-18C6)^+$ complex is greater than that of the uncomplexed cation. Similar behavior is observed for alkali metal complexes with 18C6 and the cryptand 222 in other solvents such as propylene carbonate and propylene carbonate mixtures with dichloromethane.

INTRODUCTION

Since the syntheses of crown ethers by Pedersen (ref. 1) and cryptands by Lehn (ref. 2), the application of macrocyclic ligand chemistry has taken many directions as attested to by the diversity of the subject matter of this symposium and a recent review by Izatt and co-workers (ref. 3) which cites close to 1200 references to publications up to early 1990. A fairly recent application of macrocyclic ligand chemistry has been to nonaqueous electrolyte solutions for use in high energy lithium battery development. Yamaki and Tobishimo (refs. 4,5) and Matsuda et al. (ref. 6) noted that additions of 12C4 and 15C5 not only increases the conductivity of propylene carbonate (PC) solutions containing lithium salts, but also increased the cycling efficiency of the lithium anode. Yamaki and Tobishimo also reported that the lithium ion transport number, t_+, is increased upon the addition of 12C4 to PC. Additions of crown ethers and cryptands to solid state ionically conducting polymers have also been noted to change the transport properties of salts (refs. 7,8), and the nature of the macrocyclic ligand-ion interactions in solid state polymers is a subject of a plenary lecture in this symposium (ref. 9).

The present paper focuses upon the interactions of cations with selected macrocyclic ligands and liquid organic electrolytes. New results for 18C6 with alkali metal salts in 2-cyanopyridine (2CNP) at 30°C are reported and compared to previous results for alkali metal salts in PC and a mixed solvent containing 36 mass % PC in CH_2Cl_2. We have used audiofrequency conductivity measurements to determine the stability (formation) constants for the alkali metal cation-macrocyclic ligand interaction. *This method also yields accurate values for the molar conductivities at infinite dilution and ion association constants for the cation-ligand complexes with various anions.* With the exception of the studies by Boileau et al. on Na and K complexes with the cryptands [221] and [222] in tetrahydrofuran (ref. 10), previous studies involving conductance measurements have neglected this type of ion association. *Our results suggest that a number of cation-macrocyclic ligand complexes undergo ion association and that this phenomenon is highly dependent on the nature of both ion-solvent and ion-macrocyclic ligand interactions.*

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EXPERIMENTAL

The solvent, 2CNP which has a mp of ~28°C, was stored over type 4 molecular sieves at slightly above 30°C for one week. The solvent was then distilled under vacuum, and the distillate further purified by fractional crystallization discarding about 25 % of the liquid. Karl Fischer analyses of the purified 2CNP gave water contents of 15 ± 10 ppm, and the electrolytic conductance at 30°C ranged between $8 \cdot 10^{-9}$ to 1 $\cdot 10^{-8}$ S cm^{-1}. At 30°C, the density of the pure solvent, ρ_0, is 1.0785 kg m^{-3} and it has a viscosity of 0.01816 P and a relative permittivity of 93.77 (ref. 11).

LiAsF$_6$ (USS Agri Chemicals, Electrochemical Grade) and sodium tetraphenylboride, NaBPh$_4$ (Baker, AR grade), were dried under vacuum at around 50-60°C and not treated further. KBPh$_4$ was prepared from NaBPh$_4$ and KCl as described by Kunze and Fuoss (ref. 12). The triflate salt LiCF$_3$SO$_3$ (Aldrich) was recrystallized from an acetone:toluene 1:4 mixture (both solvents were Burdick Jackson Distilled-in-Glass grade). The product was dried at 60°C in vacuum. The Rb and Cs triflates were prepared by metathesis from LiCF$_3$SO$_3$ and either RbF or CsF. These fluorides (Cerac, 99.9 %) were dried under vacuum at 90°C for 15 h. Stoichiometric quantities of RbF or CsF in methanol were mixed with LiCF$_3$SO$_3$ in methanol and filtered to remove LiF. The volume of the filtrate was reduced and then cooled to crystallize the triflate. The product was then recrystallized from methanol and dried under vacuum at 60°C. The cyclic ether (Aldrich) was recrystallized from Burdick and Jackson acetonitrile, washed by decantation with cold (5°C) acetonitrile and placed in vacuum at 30°C for 24 h. All solvents were stored in an argon-filled dry box (oxygen and water contents ≤ 1 ppm), and all salts were stored in a desiccator over P$_2$O$_5$ in a dry room. The dew point in the dry room varied between -35 and -60°C.

All solutions were prepared by weight in the dry room and their densities measured with a Parr DMA 45 digital density meter. Stock solutions were prepared with total salt concentrations, C_{MX}, and total ligand concentrations, C_L, both equal to around 0.05 mol kg^{-1}: i.e. the molar ratio C_L/C_{MX} was around unity. About 20 g of pure 2CNP were placed in a Kraus-type conductivity cell with a cell constant of 0.12155 cm^{-1} (calibrated with aqueous KCl solutions with standard values taken from ref. 13). The cell was placed in a thermostated water bath in the laboratory at 30.0 ± 0.005°C (NIST traceable precision thermometer used). Weighed additions of the 18C6-salt stock solutions were made with air- and liquid-tight plastic syringes and solution resistances determined with a Wayne Kerr model 6425 Precision Component Analyzer and extrapolated to infinite frequency. Conversions of concentrations to volume units utilized the relation $c = \tilde{m}\rho$ where the solution densities were calculated from $\rho = \rho_0 + A\tilde{m}$. The constant A was determined from the densities of the stock solutions (note that the units of $\tilde{m}$ are mol kg^{-1} solution).

RESULTS AND CALCULATIONS

Molar conductivities, Λ/S cm^2 mol^{-1}, were calculated from the infinite frequency electrolytic conductances, κ, after correcting for the pure solvent conductance, i.e. $\Lambda = 1000\kappa/C_{MX}$ where C_{MX} is the total concentration of the alkali metal salt. In fitting the experimental molar conductivities to the theoretical conductance equation (see below), the following equilibria were considered.

$$M^+ + X^- \Leftrightarrow MX \qquad K_a \qquad\qquad [1]$$

$$M^+ + L \Leftrightarrow ML^+ \qquad K_f \qquad\qquad [2]$$

$$ML^+ + X^- \Leftrightarrow MLX \qquad K_{a2} \qquad\qquad [3]$$

In calculating concentrations of all species in eqs. [1-3], the activity coefficients of neutral species were taken as unity, and for charged species the mean molar activity coefficients were calculated from

$$\ln y_{\pm} = \frac{-A\sqrt{I}}{1 + R_y B\sqrt{I}} \qquad\qquad [4]$$

In eq. [4], A and B are the Debye-Hückel constants, R_y is the distance parameter which is assigned the value of the Bjerrum distance q (for 2CNP, $q = 0.294$ nm at 30°C), and I is the ionic strength which is equal to the anion concentration, $[X^-]$, and equal to the sum of the cation and the complexed cation concentrations $[M^+] + [ML^+]$. For specific values of the thermodynamic equilibrium constants K_a, K_f and K_{a2}, the concentrations of all species in solution are calculated using standard techniques from material and charge balance requirements. The basic relation obtained for the cation concentration is the following 5th order polynomial

$$\sum_{j=0}^{5} a_{ij}\left[M_i^+\right]^j = 0 \qquad [5]$$

where a_{ij} are constants containing equilibrium constants and total concentrations C_{MX} and C_L. Eq. [5] is similar to the 6th order polynomial previously derived for the anion concentration (ref. 14). Eq. [5] was solved by the Newton-Raphson iteration method.

The system is treated as a combination of two independent salts, M·X and ML·X. The total molar conductivity, Λ, of the solution is therefore the sum of contributions from M·X designated by Λ_1 and from ML·X designated by Λ_2. In addition, allowance is made for ion pairing of both the simple cation and the complexed cation. The working conductivity equations are therefore

$$\Lambda = \alpha^* \Lambda_1 + \left(1 - \alpha^*\right)\Lambda_2 \qquad [6]$$

where

$$\Lambda_1 = \alpha_1\left\{\Lambda_1^0 - S_1\sqrt{I} + E_1 I \ln I + J_{11}(R_1)I - J_{21}(R_2)I^{3/2}\right\} \qquad [7]$$

and

$$\Lambda_2 = \alpha_2\left\{\Lambda_2^0 - S_2\sqrt{I} + E_2 I \ln I + J_{12}(R_1)I - J_{22}(R_2)I^{3/2}\right\} \qquad [8]$$

Numerical values for the constants required in eqs. [7,8] were taken from (ref. 15). From the above definitions it follows that

$$\alpha^* = \frac{\left[M^+\right]}{\left[X^-\right]} \qquad \alpha_1 = \frac{\left[M^+\right]}{\left[M^+\right]+\left[MX\right]} \qquad \alpha_2 = \frac{\left[ML^+\right]}{\left[ML^+\right]+\left[MLX\right]} \qquad [9]$$

In all calculations, R_1 was equated to the Bjerrum distance q and the conductivity parameters for MX in 2CNP, Λ_1^0 and K_a, were taken from studies on the pure binary system (refs. 11,16) which therefore fixed these parameters for the present calculations. The remaining variable parameters for the ternary system, Λ_2^0, K_f, K_{a2} and R_2 were adjusted by the 'grid-search' method (ref. 17). In this method Λ_1^0 and K_a are fixed as described above and values for the variable parameters Λ_2^0, K_f, K_{a2} and R_2 are initially selected arbitrarily, and then adjusted in a manner which minimizes the variance U which is defined by

$$U = \sum\left(\Lambda_{obsd} - \Lambda_{calcd}\right)^2 \qquad [10]$$

The shape of a plot of U against one of the variable parameters keeping the remaining variable parameters constant is described as a 'pit' with a minimum value designated as U_0 (ref. 18). Following Sillén (ref. 18), the standard deviation for each variable is obtained from the contour of the pit from

$$U = U_0\left(1 + \frac{1}{n-N}\right) \qquad [11]$$

where n is the total number of data sets and N is the degrees of freedom. For a given variable, k, the best value occurs at $U = U_0$ and the standard deviation of k defined as $k \pm \sigma$ is obtained from the points where

$U - U_0 = U_0/(n - N)$ (eq. [11]). This is shown in Fig. 1 where U is plotted as a function of K_f for $CsCF_3SO_3$ + 18C6 in 2CNP. For this plot, the parameters Λ_2°, K_{a2} and R_2 were fixed and K_f varied around the minimum at $U_0 = 0.000177$. From the contour of the pit where $U = 0.000388$ (eq. [11]), we find a standard deviation of $5\cdot10^4$ for K_f. All standard deviations reported below were computed in this manner.
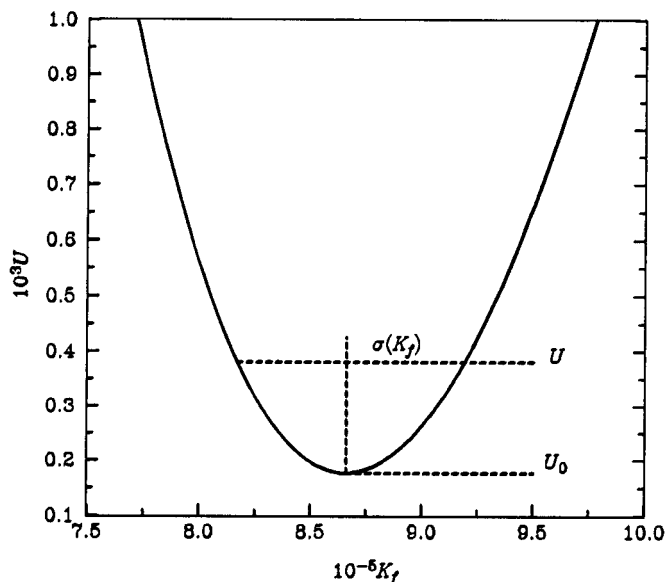

Fig. 1. Calculation of the standard deviation σ for K_f for the [$Cs^+\cdots$18C6] complex. The contour was constructed by varying K_f while keeping the values of Λ_2°, K_{a2} and R_2 constant.

Table 1 lists the derived parameters for MX-18C6 systems in 2CNP obtained in the present study. The derived parameters for the binary MX-2CNP systems required for input into eq. [7] were taken from (refs. 11, 16) and are summarized in Table 2. Fig. 2 is the phoreogram for the LiAsF$_6$-18C6-2CNP system which is typical for systems where the majority of cationic charge carriers is the complexed cation, i.e. for systems for which $K_f > \sim10^3$ mol^{-1} dm^3. Single ion molar conductivities, λ_i°, for simple and complexed ions were also evaluated and are given in Table 3. The division into single ion values was made using the assumption $\lambda^\circ(i\text{-Pent}_3BuN^+) = \lambda^\circ(BPh_4^-)$ (ref. 11).

Table 1. Derived parameters for MX-18C6 systems in 2CNP at 30°C[a]

system	Λ_2°	K_f	K_{a2}	R_2	α_Λ
LiAsF$_6$ – 18C6	33.23 (0.007)	$1.04\cdot10^5$ ($7\cdot10^4$)	----	0.261	0.007
NaBPh$_4$ – 18C6	23.00 (0.01)	$>10^{12}$	----	0.421	0.01
KBPh$_4$ – 16C6	23.91 (0.005)	$>10^{12}$	----	0.393	0.01
RbCF$_3$SO$_3$ – 18C6	32.25 (0.004)	$1.6\cdot10^9$ ($1\cdot10^9$)	3.57 (0.01)	0.560	0.004
CsCF$_3$SO$_3$ – 18C6	31.77 (0.004)	$8.66\cdot10^5$ ($5\cdot10^4$)	2.51 (0.01)	0.632	0.004

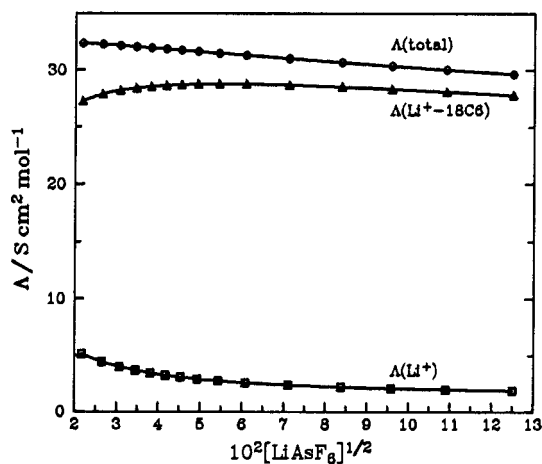[a]Units: Λ/S cm^2 mol^{-1}, K_{a2}/mol^{-1} dm^3, R_2/nm. Values in parentheses are standard deviations, σ.

Fig. 2. Phoreogram for the LiAsF$_6$-18C6-2CNP system at 30°C. Molar conductivities for Li$^+$ and the complex Li$^+$⋯18C6 calculated from eqs. [6]-[9]. [18C6]/[LiAsF$_6$] molar ratio constant at 0.9448.

Table 2. Derived parameters for binary MX-2CNP systems at 30°C[a]

salt	Λ_1°	K_a	R_2	σ_Λ
LiAsF$_6$	32.35	---	0.936	0.02
NaBPh$_4$[b]	24.25	---	0.277	0.009
KBPh$_4$[b]	26.51	0.64	0.456	0.008
RbCF$_3$SO$_3$	35.59	14.04	1.187	0.04
CsCF$_3$SO$_3$	36.16	12.00	0.899	0.005

[a]For units see Table 1 above.
[b]Parameters calculated by present authors using data from (ref. 11).
All other parameters taken from (ref. 16).

Table 3 Single ion molar conductivities in 2CNP at 30°C[a]

cation	λ_i°	complex	λ_i°
Li$^+$[b]	12.08	Li$^+$⋯18C6	12.96
Na$^+$	12.98	Na$^+$⋯18C6	11.74
K$^+$	15.25	K$^+$⋯18C6	12.65
Rb$^+$	18.28	Rb$^+$⋯18C6	14.94
Cs$^+$	18.85	Cs$^+$⋯18C6	14.46

λ_i° units are S cm^2 mol^{-1}. [b]λ_i° from (ref. 11). Other values from (ref. 16).

DISCUSSION

In spite of a very high relative permittivity (93.77 at 30°C), 2CNP is a poor solvator for cations and poorer for anions (refs. 11, 16). Its behavior in general is very similar to the much less polar solvent acetonitrile (AN) (ref. 11), and in fact ion association constants for most salts are close to those in AN (e.g. see refs. 19 - 21). The Walden products, $\Lambda^\circ\eta_o$, for both AN and 2CNP solutions correlate extremely well as shown in Fig. 1 of (ref. 11). Thus for single ion molar conductivities of alkali metal cations, the behavior in 2CNP (Table 3) is similar to that in AN which is similar to that in most other aprotic as well as protic solvents: i.e. where the conductivities increase as the crystal radii increases. Thus single ion $\lambda^\circ(M^+)$ values for the alkali metal cations increase in the order Li$^+$<Na$^+$<K$^+$<Rb$^+$<Cs$^+$ (ref. 22). This order of conductivities is attributed to the degree of solvation where smaller cations with a

high charge density are more strongly solvated than the successive larger cation. As seen in Table 3, while this behavior is followed in 2CNP, there are significant deviations for the mobilities of $M^+ \cdot \cdot 18C6$ complexes. In addition to the observation that $\lambda°(Li^+ \cdot \cdot 18C6)$ is significantly larger than $\lambda°(Na^+ \cdot \cdot 18C6)$, it is also seen that $\lambda°(Li^+ \cdot \cdot 18C6) > \lambda°(Li^+)$. Similar behavior has previously been reported for alkali metal complexes with 18C6 (ref. 14) and 15C5 (ref. 23) in PC, and for these cations with 18C6 and cryptand 222 in a mixed solvent containing 36 mass % PC in CH_2Cl_2 (ref. 24). Data for these macrocylic complexes from (refs. 14, 23, 24) are summarized in Tables 4 and 5, and for comparison, data for the binary systems are summarized in Table 6.

The mobility behavior of 'free' cations compared to complexed cations is certainly influenced by solvation effects as well as by cavity size. With cations much smaller than the size of the macrocylic ligand cavity, conformational changes in the ligand often occur upon complexation. In addition complete or partial desolvation of the cation will occur depending upon cation size and its solvation sphere. For example it is known that 18C6 can exist in two conformations designated as C_i and D_{3d} (refs. 26-28). The C_i conformer is of low strain energy where the oxygen donors lie above and below the mean plane of the

Table 4. Derived parameters for PC solutions at 25°C[a]

system	$\lambda_2°$	K_f	K_{a2}	$\lambda°(M^+)$	$\lambda°(M^+ \cdot \cdot L)$
$LiClO_4 \cdot \cdot 18C6$	27.30	605	---	7.86	8.41
$NaClO_4 \cdot \cdot 18C6$	27.25	$4.46 \cdot 10^5$	---	9.41	8.36
$KSCN \cdot \cdot 18C6$	31.57	$1.03 \cdot 10^6$	0.11	11.80	8.87
$LiClO_4 \cdot \cdot 15C5^b$	27.5	$1.8 \cdot 10^4$	b	7.86	8.6
$NaClO_4 \cdot \cdot 15C5^b$	28.3	$5.0 \cdot 10^3$	b	9.41	9.5
$KClO_4 \cdot \cdot 15C5^b$	26.9	$2.6 \cdot 10^3$	b	11.80	8.0

[a]See Tables 1 and 3 for units. Data taken from (ref. 14) except as noted.
[b]Data from (ref. 23). $\lambda°$ values for the 15C5 complexes calculated by the present authors using $\Lambda°$ from (ref. 23) and $\lambda°(ClO_4^-) = 18.89$ S cm^2 mol^{-1} from (ref. 14). K_{a2} not considered in (ref. 23), but probably not significant.

Table 5. Derived parameters for 36 mass % PC in CH_2Cl_2 at 25°C[a]

system	$\Lambda_2°$	K_f	K_{a2}	$\lambda°(M^+)$	$\lambda°(M^+ \cdot \cdot L)$
$LiClO_4 \cdot \cdot 18C6$	71.32	$2.54 \cdot 10^3$	---	21.5	27.4
$NaClO_4 \cdot \cdot 18C6$	69.62	$7.75 \cdot 10^5$	3.56	23.7	25.7
$KSCN \cdot \cdot 18C6$	75.43	$>10^{12}$	4.76	28.4	30.1
$LiAsF_6 \cdot \cdot 222$	70.76	$3.18 \cdot 10^4$	1.07	21.5	23.7
$NaBPh_4 \cdot \cdot 222$	52.72	$>10^{12}$	---	23.7	26.3
$KSCN \cdot \cdot 222$	72.31	$>10^{12}$	---	28.4	27.0

[a]See above tables for units. All data from (ref. 24). L is the ligand 18C6 or 222.

crown. Li^+ and to some extent Na^+ will undergo radical desolvation as the cation enters the cavity of the macrocyclic ether and occupies a site where the donor oxygens lie above and below the cation. Due to both the charge and position of the donor oxygens, further coordination of the cation by anions or the negative end of the solvent dipole is hindered. Assuming that the 18C6-solvent interaction is comparatively weak, major consequences of this complexation are the increase in the molar conductivity of the complex and a corresponding large decrease in ion association of the type designated by K_{a2} in eq.

Table 6. Derived parameters for binary systems (salt + solvent) at 25°C

salt	PC[a]		36 mass % PC in CH_2Cl_2[b]	
	Λ_1°	K_a	Λ_1°	K_a
$LiClO_4$	26.75	1.2	65.44	0.44
$LiAsF_6$	22.53	---	68.73	12.12
$NaClO_4$	28.30	---	67.61	17.98
$NaBPh_4$	17.30[c]	---	50.24	---
KSCN	34.50	5.42	73.66	32.84

[a]From (ref. 14) and references cited therein.
[b]From (ref. 24). [c]Based on data from (ref. 25).

[3]. In the highly symmetric D_{3d} conformer of 18C6, all the donor oxygens lie in the same plane above the mean plane of the ring, and the cations K^+, Rb^+ and Cs^+ coordinate to a site above the center of an essentially flat hexagon (ref. 27). This configuration allows for specific (axial) interactions between the cation in $M^+ \cdots 18C6$ and solvent dipole and/or anion. Depending upon the extent of solvation which one expects to be in the order $K^+ > Rb^+ \geq Cs^+$, the resulting mobility of the complex may be greater than, equal to or less than that of the 'free' cation (e.g. compare Tables 3-5).

While the above discussions centered around 18C6 complexes, similar concepts apply to cryptands such as 222. This cryptand is known to exhibit three conformations depending upon the position of the nitrogen lone-pairs: these are the exo-exo (or out-out), exo-endo (out-in) and endo-endo (in-in) conformers (refs. 30-31). The endo-endo conformer is the preferred isomer (ref. 32), presumably with the smaller cations. With cations which are too large to fit into the cavity of the cryptand, the cation will coordinate at a site above the cavity and result in conformational changes of the cryptand (33).

CONCLUSIONS

Ion association as represented by eq. [3] can strongly influence measurements of K_f. In strongly coordinating solvents with reasonably high donor numbers and dielectric constants such as PC ($\varepsilon = 64.92$ and dipole moment $\mu = 4.98$ D) where cations are moderately to strongly solvated, there is little or no ion association and it is very reasonable to neglect this effect in the experimental determination of K_f. However in weakly solvating solvents such as 2CNP (although $\varepsilon = 93.77$ and $\mu = 5.1$ D) and AN ($\varepsilon = 35.95$ and $\mu = 3.9$ D), ion association is small but sufficiently large to require consideration of all three equilibria represented by eqs. [1] - [3]. In solvents of low polarity such as THF ($\varepsilon = 7.39$ and $\mu = 1.75$ D), ion association represented by eqs. [1] and [3] is extensive as observed by Boileau et al. (ref. 10) in their study of the KBPh$_4$-222-THF system. The unique NMR study by Khazaeli et al. (29) of the complexation of cesium salts by 18C6 in methylamine ($\varepsilon = 9.0$ at 25°C) also confirms the existence of extensive ion pairing of the complex (eq. [3]). K_{a2} values for the 1:1 $Cs^+ \cdots 18C6$ complex were found to increase according to $SCN^- < I^- < BPh_4^-$.

The neglect of the ion association equilibria in eqs. [1] and [3] can effect the experimental determination of K_f in several ways. Using conductivity data will **underestimate** K_f. Because the ion association given by eq. [1] is generally greater than that of eq. [3], calculated $[M^+]$ concentrations will increase more rapidly then $[M^+ \cdots L]$ concentrations and greater weight will be given to eq. [7] resulting in a value of K_f smaller than the true value. Using the potentiometric titration method with specific ion electrodes will **overestimate** K_f since measurements yield $[M^+]$, and the remaining concentration $C_{tot} - [M^+]$ is assumed to equal $[M^+ \cdots L]$ when in fact it equals $[M^+ \cdots L] + [MX] + [MLX]$. Finally, we would like to point out that while the conductivity method appears to limit the determination of formation constants to values less than around 10^{11} to 10^{12} mol^{-1} dm^3, it allows one to accurately evaluate small values for K_f. For example, the formation constant for the $Li^+ \cdots 18C6$ complex in PC has apparently been difficult to determine by potentiometric titration and calorimetric methods. The value of $K_f = 490$ mol^{-1} dm^3 determined by Smetana and Popov by an NMR method (ref. 34) is in very good agreement with the conductometrically determined value of 605 mol^{-1} dm^3 (see Table 4).

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