Complexation of Li$^+$, Na$^+$ and K$^+$ Ions by [222], [222D], [221], [221D] Cryptands in Acetonitrile at 25 °C: Conductometric Determination of the True Thermodynamic Formation Constants

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Abstract. A new method is presented for the analysis of precise conductance data to obtain the true thermodynamic formation constants of macrocyclic–cation complexes. The method, based on the Lee–Wheaton theory on mixed electrolytes, takes into consideration the ion pair formation of both the uncomplexed and complexed cations and avoids the use of the simple additivity assumption of the conductances of two electrolytic species present in salt/ligand/solvent systems. The method has been applied to determine the thermodynamic complexation constants of lithium, sodium and potassium ions with the cryptands [221], [222] and their decyl derivatives [221D], [222D] in acetonitrile. The results show that the presence of an alkyl chain in the molecular structure of the cryptands decreases the macrocyclic–cation complexation constant with respect to the values obtained for the parent compounds by almost an order of magnitude. Such a finding has been explained in terms of the asymmetric position in the space of the oxyethylenic bridges of the macrocyclic ligand promoted by the presence of the linked hydrocarbon chain. The above explanation has been confirmed by the anomalous behavior of both the ion-pair association constants of complexed salts and their limiting molar conductivity.

Key words: conductivity, ion–cryptand complexes, thermodynamic formation constants in acetonitrile, lithium, sodium and potassium perchlorates.

1. Introduction

Crown ethers and cryptands, originally synthesized by Pedersen [1] and Lehn [2] respectively, are characterized by a negatively charged internal cavity able to host metal cations of suitable size. After their synthesis, the equilibrium formation constants, enthalpy and entropy changes, and rate constants for the complexation of many cations with a variety of macrocyclic ligands derived from these classes of compounds were reported by many researchers, working with both aqueous

and nonaqueous solvents and using a variety of experimental techniques. For a comprehensive review of this subject see references [3–5].

In a previous paper [6] it was shown that, for a given system, complexation constants reported in the literature determined from NMR, calorimetry, polarography, conductance and potentiometric measurements often differ significantly from treatments which account for ion pair formation of both the uncomplexed and the complexed cation [6, 7]. This is particularly true for systems containing solvents of low dielectric constant. In our previous studies it was found that precise conductivity data can be effectively used to determine the contribution of ion pair formation of both uncomplexed or free cations, and ion pairs formed between an anion and the macrocyclic complexed cation. In the present communication the method is extended to alkali metal perchlorate–*diazabicyclo* cryptand ([221] and [222]) systems in acetonitrile.

For the determination of the '*true*' or '*thermodynamic*' complexation constant, K_r, of a metal ion M^+ with a ligand X, the equilibria to be considered are:

$$K_a = [M^+ \cdot A^-]/([M^+][A^-]f^2) \tag{1}$$

$$K_{a2} = [MX^+ \cdot A^-]/([MX^+][A^-]f^2) \tag{2}$$

$$K_r = [MX^+]/([M^+][X]) \tag{3}$$

where A^- is the anion, f is the mean activity coefficient and K_a and K_{a2} are the association constants of the $[M^+ \cdot A^-]$ and $[MX^+ \cdot A^-]$ ion pairs, respectively. To account for the above equilibria a method of analysis of the conductance data has been recently proposed by one of us [7]. In this treatment, the observed conductance Λ of a salt–ligand–solvent ternary system was treated as a sum of the contributions from the molar conductivity of the electrolyte, Λ_1, and complexed salt, Λ_2.

$$\Lambda = \alpha^*\Lambda_1 + (1 - \alpha^*)\Lambda_2 \tag{4}$$

where $\alpha^* = [M^+]/[A^-]$. By neglecting interactions between the different cations present in solution (M^+ and $M^+ \cdot X$), Equation (4) was readily analyzed using the Fuoss–Hsia equation [8] with the Fernandez–Prini–Justice expansion [9] and the equilibrium constants in Equations (1)–(3) determined from the derived parameters Λ_1 and Λ_2. This method, although more accurate than the previous simpler method proposed by Evans *et al.* [10], is a first-order approximation which assumes the conductance of the two electrolytes (MA and MXA) to be additive. In reality the long range electrostatic interactions within the Debye–Hückel atmosphere surrounding the reference ion in binary electrolyte–solvent systems are affected by the presence of a second electrolyte. Thus relaxation and electrophoretic fields in ternary systems (two cations and a common anion in the present case) cannot be

obtained by the simple additivity rule. In other words, the additivity of the conductances of binary systems can be considered as a first-order approximation in treating these more complex ternary systems.

The Lee–Wheaton (LW) theory [11, 12] on electrolyte solutions overcomes this approximation by considering the effect of the long range electrostatic interactions between the different ionic species on the ionic mobility of each ion constituting the electrolytic system. Taking these effects into account, the LW conductivity equations constitute an improved method for determining the thermodynamic complexation constants of metal cations with macrocyclic ligands. This improved treatment based on LW treatnient of conductivity data for multicomponent electrolyte solutions is presented in this paper and is applied to the determination of the complexation constants of Li^+, Na^+ and K^+ cations with [222], [222D], [221] and [221D] cryptands in acetonitrile at 25 °C.

2. Experimental

2.1. MATERIALS

4,7,13,16,21,24 Hexaoxa-1, 10-diazabicyclo [8,8,8] hexacosane **[222]**, *4,7,13,16, 21-Pentaoxa-1,10-diazabicyclo[8,8,5]tricosane* **[221]**, and their decyl derivatives *5-Decyl-4,7,13,16,21,24 Hexaoxa-1,10-diazabicyclo[8,8,8]hexacosane* **[222D]** and *5-Decyl-4,7,13,16,21-Pentaoxa-1,10-diazabicyclo [8,8,5] tricosane* **[221D]** were used as received from Merck. The molecular structures of the above compounds are reported in Figure 1. *Acetonitrile* (U.V. spectroscopic reagent grade from Fluka) was further purified by refluxing over phosphorus pentoxide and then fractionally distilled. The physical properties determined for the purified product (density ρ = 0.77650 g cm^{-3}, viscosity η = 0.3436 mPa s, dielectric constant ϵ = 36.05, and specific conductance χ_0 = 0.05×10^{-6} S cm^{-1}) were in agreement with literature values [13, 14]. *Lithium, sodium and potassium perchlorates* (commercial reagent grade products) were recrystallized 4 times from conductivity water [$\chi_0 = 1 - 2 \times 10^{-7}$ (S cm^{-1})] and dried at 150 °C in a vacuum oven. The dried salts were kept in a desiccator containing P_2O_5.

2.2. APPARATUS AND METHODS

The complete description of the apparatus used to measure the density, viscosity and dielectric constant of the acetonitrile has been published elsewhere [15]. Conductance measurements were carried out with an accuracy of $\pm$ 0.05% using a Wayne Kerr Model 6425 Precision Component Analyzer. The electrical resistance of solutions, measured at 1, 2, 5, 10 kHz, were extrapolated to infinite frequency for the usual correction. A Chiu–Fuoss type conductance cell [16] with Pt electrodes was used. The cell constant, k_c = 0.31443 $\pm$ 0.00001 cm^{-1}, was determined with KCl aqueous solutions according to the method described by Lind, Zwolenik and Fuoss [17]. The temperature of the cell, checked with an F 25 Automatic System
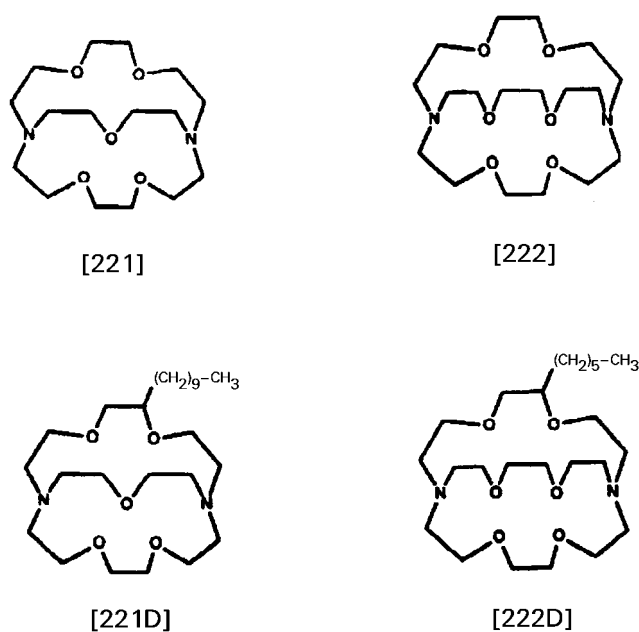
Figure 1. Molecular structures of [221], [221D], [222] and [222D].

Laboratory digital thermometer, was maintained at 25 ± 0.002 °C in a 120 L volume oil thermostat equipped with a Heto PT-CBII temperature controller.

The conductance runs were carried out as follows: weighed amounts of ligand solution were placed into the conductivity cell and its resistance determined after thermal equilibrium. Then successive weighed amounts of stock electrolyte solution were added using air-tight Hamilton glass syringes, the resistance being measured after each addition. In some cases, the conductances of the system initially containing a known amount of electrolyte in the pure solvent were measured. Then the ligand was added stepwise in weighed increments and the conductance determined after each addition of the stock ligand solution.

2.3. RESULTS

Molar conductivities Λ (S cm^2 mol^{-1}) were calculated from the electrolyte specific conductance χ using the relations:

$$\Lambda = 1000(\chi - \chi_0')/C_s \tag{5}$$

$$\chi_0' = \chi_0 + \alpha C_L \tag{6}$$

where C_s and C_L are the molar concentrations of the electrolyte and ligand, respectively, χ_0 is the specific conductance of the pure solvent and α is an empirical constant experimentally determined by measuring the specific conductance of a

ligand solution of known concentration. The experimental molar conductances, Λ, for the ternary systems (electrolyte + ligand + solvent) are summarized in Table I where C_s and C_L have the same meaning as in Equations (5) and (6), and C_s/C_L is the electrolyte/ligand molar ratio.

3. Data Analyses

The Lee–Wheaton equation for the equivalent conductivity of the ion j in a solution containing s ions is:

$$\lambda_j = \lambda_j^0 \left\{ 1 + z_j \sum_j \chi_j^p \sum_v \tau_v \chi_v^p [A_v^p(\tau)(\beta\kappa) + B_v^p(\tau)(\beta\kappa)^2 + C_v^p(\tau)(\beta\kappa)^3] \right\}$$
$$- |z_j|(\kappa\tau)/(1+\tau)\{1 + V_j^{(1)}(\tau)(\beta\kappa) + V_j^{(2)}(\tau)(\beta\kappa)^2 + P_j^{(5)}\tau/6\} \qquad (7)$$

where all the terms are as defined in the original papers [11, 12]. Since $\tau = \kappa R$ the equation involves a distance of closest approach R which is assumed to be the same for all pairs of oppositely charged ions. Treating our systems as a mixture of two electrolytes, i.e., two cations with a common anion, the total conductance, Λ, of the system depends on the following parameters:

$$\Lambda = \Lambda(\lambda_{M^+}^\circ, \lambda_{MX^+}^\circ, \lambda_{A^-}^\circ, K_a, K_{a2}, K_f, R) \qquad (8)$$

where $\lambda_{M^+}^\circ, \lambda_{MX^+}^\circ, \lambda_{A^-}^\circ$ are the ionic limiting conductance obtained from Equation (7), K_a and K_{a2}, the ion pair association constants of free and complexed cation with the common anion, from equilibria 1 and 2, respectively, K_f the formation constant of complexed cation from equilibrium 3, and R is the average closest approach distance for the $[M^+ \cdot A^-]$ and $[MX^+ \cdot A^-]$ ion-pairs. Equation (8) shows that the total conductivity is dependent upon seven dependent variables. To reduce the number of adjustable parameters in the conductivity Equations (7) and (8), the parameters $\lambda_{M^+}^\circ$, $\lambda_{A^-}^\circ$ and K_a, are fixed at those values obtained from conductivity data for the simpler binary MA–solvent systems. Thus only the four adjustable parameters $\lambda_{MX^+}^\circ$, K_{a2}, K_f, R are required to solve Equation (8).

Equation (8) was solved with an appropriate BASIC program formulated to yield values of $\lambda_{MX^+}^\circ$, K_{a2}, K_f and R for fixed values of $\lambda_{M^+}^\circ$, $\lambda_{A^-}^\circ$ and K_a. Initial input to the program from a data file are the measured conductance data followed by the known values for $\lambda_{M^+}^\circ$, $\lambda_{A^-}^\circ$ and K_a and estimated values of $\lambda_{MX^+}^\circ$, K_{a2}, K_f and R. Using these initial values for the adjustable parameters, the concentrations of each neutral and ionic species at equilibrium are calculated from Equations (1)–(3) using the mass balance relations

$$[MA]_0 = [M^+] + [MX^+] + [M^+ \cdot A^-] + [MX^+ \cdot A^-] \qquad (9)$$

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Table I. Molar conductivities at 25 °C of alkali metal perchlorates in acetonitrile as a function of concentration of the ligands [221], [222], [221D] and [222D].

Λ	$10^4\,C_s$	$10^4\,C_L$	C_s/C_L	Λ	$10^4\,C_s$	$10^4\,C_L$	C_s/C_L
				$LiClO_4$			
	[221]				**[222]**		
156.67	9.526	22.000	0.433	155.33	18.443	2.967	6.216
152.97	18.517	21.268	0.870	154.21	18.443	6.200	2.975
150.96	27.607	20.529	1.345	153.13	18.443	9.247	1.994
149.41	35.072	19.922	1.760	152.10	18.443	12.429	1.484
147.75	42.426	19.323	2.195	150.98	18.443	15.691	1.175
146.02	50.279	18.685	2.691	150.19	18.443	18.791	0.981
144.50	57.500	18.097	3.177	150.17	18.443	21.847	0.844
143.16	64.171	17.555	3.655	150.16	18.443	24.797	0.744
141.97	70.356	17.052	4.126				
140.89	76.184	16.577	4.596				
	[221D]				**[222D]**		
138.71	8.944	23.633	0.378	136.39	8.641	19.881	0.435
134.75	17.989	22.830	0.788	135.46	15.472	18.748	0.825
135.44	26.320	22.081	1.191	136.30	20.736	17.875	1.160
137.70	34.370	21.377	1.608	138.80	26.473	16.924	1.564
138.42	41.400	20.754	1.995	139.82	31.752	16.048	1.979
138.47	48.332	20.139	2.400	140.17	36.140	15.320	2.359
138.19	54.084	19.628	2.756	140.22	40.157	14.654	2.740
137.86	59.797	19.122	3.127	140.13	44.356	13.958	3.178
137.33	65.980	18.573	3.552	139.91	48.074	13.341	3.604
138.79	71.145	18.115	3.927				
				$NaClO_4$			
	[221]				**[222]**		
157.02	6.505	22.214	0.293	161.20	17.732	3.031	5.850
152.41	15.320	21.454	0.714	158.67	17.732	5.974	2.968
150.97	24.753	20.641	1.199	155.97	17.732	9.132	1.941
151.20	33.912	19.851	1.708	153.33	17.732	12.220	1.451
150.40	42.084	19.146	2.198	150.91	17.732	15.978	1.110
149.57	49.050	18.546	2.645	148.71	17.732	18.149	0.977
148.65	55.229	18.013	3.066	148.64	17.732	21.374	0.830
147.72	61.506	17.472	3.520	148.63	17.732	24.836	0.714
146.79	67.698	16.938	3.997				

Table I. Continued

Λ	$10^4 C_s$	$10^4 C_L$	C_s/C_L	Λ	$10^4 C_s$	$10^4 C_L$	C_s/C_L
	[221D]				**[222D]**		
141.33	14.168	23.052	0.615	139.22	19.380	17.375	1.115
139.35	23.621	22.135	1.067	142.99	23.998	16.437	1.460
143.63	32.945	21.226	1.554	145.08	28.564	15.509	1.842
145.05	43.557	20.201	2.156	146.06	32.090	14.793	2.169
145.10	53.999	19.189	2.814	146.59	35.175	14.166	2.483
144.58	62.619	18.324	3.434	146.96	38.537	13.482	2.858
144.10	70.649	17.574	4.020	147.16	42.044	12.770	3.295
143.26	78.293	16.832	4.651				
142.63	85.069	16.175	5.259				
141.87	92.408	15.464	5.976				
			KClO$_4$				
	[221]				**[222]**		
160.20	2.955	21.420	0.138	162.57	22.607	3.803	5.944
158.58	4.855	20.549	0.236	159.62	22.607	7.579	2.983
157.34	6.671	19.716	0.338	156.66	22.607	11.380	1.987
156.22	8.558	18.851	0.454	153.84	22.607	15.080	1.499
155.46	10.044	18.170	0.553	150.54	22.607	19.347	1.168
154.78	11.464	17.519	0.654	148.16	22.607	23.448	0.966
154.28	12.625	16.987	0.743	148.11	22.607	27.351	0.827
153.79	13.758	16.467	0.835	148.06	22.607	31.972	0.707
153.36	14.789	15.995	0.924				
153.20	15.266	15.776	0.968				
	[221D]				**[222D]**		
146.70	2.222	23.472	0.095	145.44	3.722	19.444	0.187
144.74	4.405	22.534	0.195	144.10	5.787	19.069	0.303
143.56	6.170	21.776	0.283	143.15	7.554	18.383	0.411
142.50	7.997	20.992	0.381	142.19	9.508	17.625	0.539
141.63	9.752	20.238	0.482	141.33	11.647	16.795	0.693
140.97	11.185	19.623	0.570	140.66	13.459	16.092	0.836
140.36	12.597	19.016	0.662	140.11	14.973	15.505	0.966
139.82	13.898	18.458	0.753	141.29	16.015	15.100	1.060
139.34	15.143	17.923	0.845				
138.95	16.317	17.419	0.937				

Units; A (S cm^2 mol^{-1}) ; C_s and C_L (cm^3 mol^{-1}).

$$[X]_0 = [X] + [MX^+] + [MX^+ \cdot A^-] \tag{10}$$

and

$$[M^+] + [MX^+] = [A^-] \tag{11}$$

from the electroneutrality requirement. In Equations (9) and (10) $[MA]_0$ and $[X]_0$ are the initial concentrations of the salt and ligand, respectively. Solving the system with respect to $[A^-]$, we obtain a third-order equation that can be solved by the Newtor–Raphson method [18]. Then from the value of $[A^-]$ the concentrations of all remaining species in solution are easily determined.

The mean activity coefficient f in the equilibrium Equations (1) and (2) are obtained from

$$\ln f = -\beta k/2(1 + kR) \tag{12}$$

where, $\beta/2$ is the Bjerrum distance [19]:

$$\beta/2 = e^2/2\epsilon kT \tag{13}$$

and k is the Debye distance [20] given by:

$$k = [8\pi e^2[M^+]N/1000\epsilon\kappa]^{1/2}. \tag{14}$$

In Equations (12)–(14), ϵ is the static dielectric constant of the solvent, T the temperature (Kelvin), κ the Boltzman constant (1.38×10^{-6} erg/degree), e the electron charge (4.80×10^{-10} u.e.s.), N the Avogadro number, and R is the Gurney distance [21]. By using a grid search method [22] the program solves Equation (8) by changing the variable parameters $\lambda^\circ_{MX^+}$, K_{a2}, K_f and R in the direction which minimizes the variance U, defined as:

$$U = \sum (\Lambda_{cal} - \Lambda_{sper})^2/(N - 3). \tag{15}$$

Standard deviations for the adjustable parameters are obtained using Sillen's pit-mapping method [23]. The method of analysis of conductance data for ternary systems proposed in the present paper enables one to calculate complex formation constants up to a limit of around 10^{12} mol^{-1} dm^3. For K_f values greater than this limit, the iterative program does not converge. This limitation of 10^{11} to 10^{12} mol^{-1} dm^3 for K_f was reported previously [6, 7, 18] and found to be due to difficulty in locating the precise minimum in the pit of the U vs. K_f plot, i.e., at large values of K_f, the shape of the pit becomes very flat and insensitive to values of U (Equation (15)). In contrast, we have not observed any lower limit to the determination of K_f values by our method. In those instances where K_f is very large, the BASIC program is stopped and values of $K_f > 10^{12}$ mol^{-1} dm^3 are assumed.

Table II. Conductometric parameters of LiClO$_4$, NaClO$_4$ and KClO$_4$ in acetonitrile at 25 °C.

Electrolyte	$\Lambda°$ S cm^2 mol^{-1}	K_a dm^3 mol^{-1}	$10^8 R$ cm	$100\sigma/\Lambda°$
LiClO$_4$	173.27 ± 0.03	18.4 ± 0.1	7.0 ± 0.2	0.01
NaClO$_4$	180.53 ± 0.06	17.3 ± 0.2	7.7 ± 0.4	0.02
KClO$_4$	187.77 ± 0.07	28.5 ± 0.1	5.5 ± 0.3	0.02

Table II summarizes the conductometric parameters for the binary systems obtained analyzing previous binary solution data [6] with the Lee–Wheaton equation. The results are in full agreement with those previously obtained [6] by analyzing the same set of data with the Fuoss-Hsia equation using the Fernandez–Prini and Justice expansion. Data from Table II were used as fixed parameters to calculate the complexation constants, the ion pair association constants and the limiting conductance of the alkali metal cations complexed by [221], [222], [221D] and [222D] ligands reported in Table III. Included in Table III are the complexation constants from literature for comparison.

4. Discussion

Inspection of Table III reveals that for the few cases where the comparisons are possible, literature data differ from the present results, in some cases by two to three orders of magnitude. While the orders of selectivity are in agreement, the results from the present treatment of conductivity data are, where precise comparisons are possible, lower than literature values which neglect ion pair formation of the salt MA and the complex salt MXA. Such a finding constitutes another example substantiating the importance of considering ion pairing equilibria in determining the true thermodynamic formation constants of the inclusion complexes. The reason for these abnormally large K_f values is the fact that, by neglecting ion pair formation, it is assumed that all decreases in the 'free' cation concentration, [M$^+$], are simply due to formation of the complex MX$^+$. By neglecting the formation of MA and MXA ion pairs, the concentration of MX$^+$ is therefore overestimated, and the resulting '*apparent*' K_f value can be orders of magnitude higher than the true K_f value (see also Ref. [6] for quantitative details).

In Table IV the Pauling ionic radii of lithium, sodium and potassium are reported, together with the cavity radii of [222] and of [221]. As can be seen from Figure 2, the complexation constants exhibit maximum values when the ionic radius matches the ligand cavity size, as expected from the empirical '*lock and key*' rule. With the exception of the cases where $K_f > 10^{12}$ mol^{-1} dm^3, this figure also shows that for a given cation, the complexation constants obtained with [221]

Table III. Conductometric parameters of $LiClO_4$, $NaClO_4$ and $KClO_4$ with [221], [222], [221D] and [222D] in acetonitrile at 25 °C.

Electrolyte	Λ_2° S cm^2 mol^{-1}	K_{a2} dm^3 mol^{-1}	K_f dm^3 mol^{-1}	$10^8 R$ cm	$\log K_f$	$100\sigma/\Lambda^\circ$	$\log K_f$ (lit)
			[221]				
LiClO$_4$	167.01 ± 0.01	8.81 ± 0.04	$(1.32 \pm 0.5)10^6$	10.88 ± 0.02	6.12	0.02	–
NaClO$_4$	166.14 ± 0.02	12.53 ± 0.06	$>10^{12}$	10.45 ± 0.03	>12	0.03	11.22 [24]
KClO$_4$	166.24 ± 0.01	9.13 ± 0.03	$(4.29 \pm 0.2)10^7$	10.92 ± 0.02	7.63	0.01	9.46 [24]
			[221D]				
LiClO$_4$	148.89 ± 0.02	13.77 ± 0.07	$(8.18 \pm 2)10^5$	10.65 ± 0.04	5.91	0.05	–
NaClO$_4$	154.05 ± 0.02	16.22 ± 0.09	$>10^{12}$	12.33 ± 0.04	>12	0.04	–
KClO$_4$	150.89 ± 0.01	15.20 ± 0.04	$(8.16 \pm 0.2)10^6$	18.56 ± 0.04	6.91	0.01	–
			[222]				
LiClO$_4$	163.66 ± 0.01	5.2 ± 0.1	$(1.62 \pm 0.1)10^6$	8.2 ± 0.1	6.21	0.02	6.7 [25]
NaClO$_4$	162.89 ± 0.01	10.69 ± 0.08	$(1.39 \pm 0.7)10^7$	8.26 ± 0.05	7.14	9.03	10.9 [25]
KClO$_4$	163.62 ± 0.02	6.99 ± 0.09	$>10^{12}$	8.24 ± 0.07	>12	0.04	11.4 [26]
			[222D]				
LiClO$_4$	149.41 ± 0.01	15.90 ± 0.06	$(1.93 \pm 0.1)10^5$	6.51 ± 0.03	5.28	0.02	–
NaClO$_4$	152.36 ± 0.01	17.03 ± 0.08	$(2.80 \pm 0.5)10^6$	8.40 ± 0.01	6.44	0.03	–
KClO$_4$	151.69 ± 0.01	7.41 ± 0.09	$>10^{12}$	14.4 ± 0.1	>12	0.04	–

Table IV. Ionic Pauling radius and cryptands cavity radius.

Cation	Ionic radius (Å)	Cryptand	Cavity radius (Å)
Li$^+$	0.78		
Na$^+$	0.98	[221]	1.0–1.1
K$^+$	1.33	[222]	1.3–1.4

or [222] differ by almost an order of magnitude from the values obtained for the corresponding decyl derivatives. This feature was unexpected since the cavity size of ligands was not expected to be greatly affected by the presence of the alkyl chain. As pointed out by Lehn [27], cryptands have a rather flexible skeleton that allows the formation of stable inclusion complexes, even in some cases where the nominal ligand cavity size is different from that of cations. For cryptand [222] the three oxyethylenic chains forming the cavity of the macrobicyclic compound are equivalent as to their length and number of oxygen atoms; thus they are symmetrically located in space to form a molecule of spherical shape into which cations can be inserted. However, the case differs for [222D], where one of the three oxyethylenic chains contains the hydrophobic decyl chain. In this case, the interaction between the hydrophobic decyl chain and the polar environments of both solvent and the intercalating cation produce an asymmetrical distribution in oxyethylenic bridge distances modifying the charge distribution inside the negative cavity of the decyl cryptate compound. Thus smaller K_f values are observed for lithium and sodium ions with [222D] with respect to the values obtained with [222]. The same argument can be applied to [221] and [221D] compounds with respect to lithium and potassium ions.

Figure 3 compares the ion pair association constant of uncomplexed and complexed cations. As can be seen in this figure, ion pair formation with uncomplexed cations is greater than that of the complexed ones. Such a feature can be easily explained considering the screening of the cation electrical charge due to the macrocyclic molecule surrounding the hosted cation. Figure 3 also shows that the cations complexed by [221] or [222] have smaller ion pair association constants than those obtained for the ligand containing the decyl chain. Such results can be explained considering that for the [221D] or [222D] ligands the asymmetric distribution of oxyethylenic bridges surrounding the encapsulated cation sterically favors the anion approach to the hosted cation.

We consider next the transport properties of both uncomplexed and complexed salts. Figure 4 compares the limiting equivalent conductance of lithium, sodium and potassium perchlorates in acetonitrile with and without addition of cryptands. The analysis of the figure shows that the equivalent conductances of the three electrolytes in pure acetonitrile are well differentiated and decrease in the order expected for decreasing cation solvation. The trends of the equivalent conductances
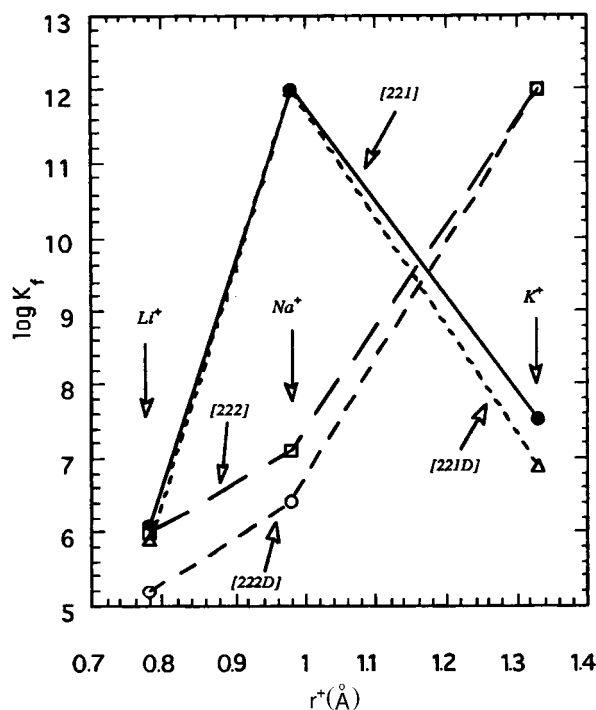
Figure 2. log K_f as a function of Pauling ionic radius. The lines in the figures represent guides for visual comparison.

of the three electrolytes in the presence of [221] or [222] are different as $\Lambda°$ for each salt-cryptand system are nearly equal. This result can be easily rationalized if we consider that in the complexation process significant cation desolvation accompanies intercalation into the ligand cavity. Thus the hydrodynamic cationic species in solution is mainly characterized by ligand size rather than by the size of the uncomplexed or solvated cation. Some peculiarities occur with the cryptand decyl derivative. As can be seen from Tables III and V and Figure 4, the molar conductivities of the salts complexed by [221D] or [222D] are significantly reduced. The major cause of this effect can certainly be attributed to the larger sizes of the crytand decyl derivatives, but some cation effects appear to have a minor influence, as discussed below.

Further information on the sizes of the particles that are hydrodynamically equivalent to the ions can be obtained from the Stokes radii, $r^{\pm}$, calculated from the ionic limiting conductance, λ, using the relation;

$$r^{\pm} = Fe/1800\pi\lambda_0^{\pm}\eta = (0.819/\lambda_0^{\pm}\eta) \cdot 10^{-8}$$

where F is the Faraday, e is the electron charge, η is the macroscopic viscosity of the solvent and all other symbols have their usual meaning. The ionic limiting
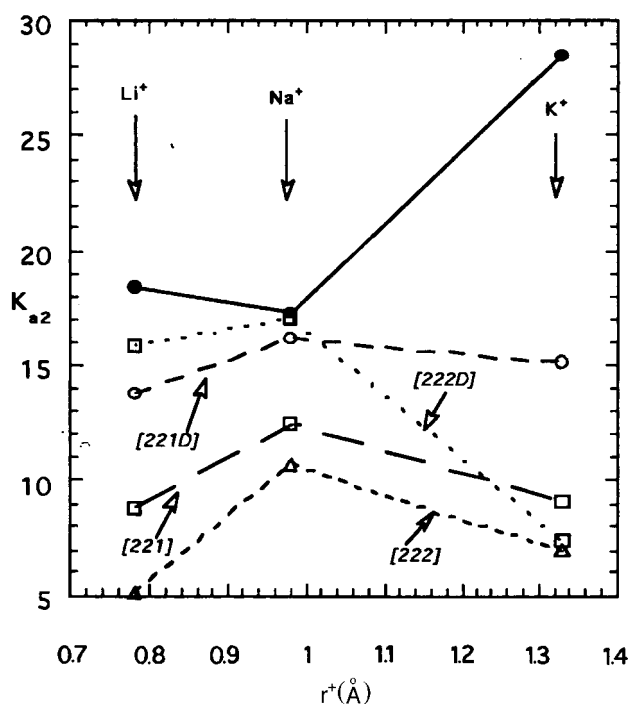
Figure 3. Ion pair association constants for complexed cations compared with the ion pair association constants of uncomplexed cations (solid line). The lines in the figures represent guides for visual comparisons.

Table V. Limiting ionic conductance and Stokes radii of Li^+, Na^+, K^+, and ClO_4^- with [221], [222], [221D] and [222D] in acetonitrile at 25 °C.

Cation	λ°	$r^\pm$	λ°	$r^\pm$	λ°	$r^\pm$	λ°	$r^\pm$	λ°	$r^\pm$
			[221]		[221D]		[222]		[222D]	
Li^+	69.5	3.4	63.2	3.8	45.1	5.3	60.0	4.0	45.6	5.2
Na^+	76.7	3.1	62.3	3.8	50.2	4.8	59.1	4.0	48.5	4.9
K^+	84.0	2.8	62.4	3.8	47.1	5.1	58.8	4.0	47.9	5.0

Units: λ°, S cm^2 mol^{-1}, $r^\pm$, 10^{-8} cm.

conductances have been obtained by applying the Kohlraush rule to the limiting conductances reported in Tables II and III and using the value 103.8 S cm^2 mol^{-1} reported by Kay *et al.* [14] for the limiting ionic conductance of ClO_4^- in acetonitrile. From the results, which are summarized in Table V, it is seen that differences in ionic solvation relate to the charge density of cations. Lithium ion in pure acetonitrile, in spite of its smaller Pauling radius (see Table V) has a Stokes radius that is around 20 and 40% larger than the values obtained for sodium and potassium ions, respectively. Cationic complexation by [221] and [222], cancel out such dif-
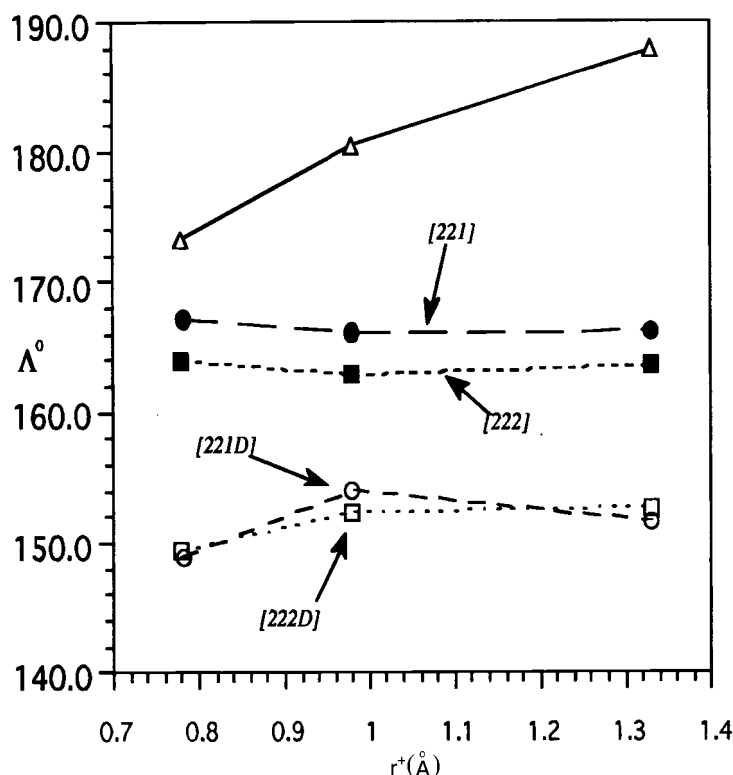
Figure 4. Comparison of the limiting equivalent conductance of the complexed and uncomplexed salts (solid line). The different salts are identified by the Pauling (crystal) radius of the cation reported on the *x* axis. The lines in the figures represent guides for visual comparison.

ferences and unique values of 3.8 Å and 4.0 Å are obtained for the hydrodynamic radii of Li^+, Na^+ and K^+ ions complexed by [221] and [222], respectively. This suggests that all the alkali cations considered in the present work, and in particular Li^+, are essentially completely desolvated upon entering the cavity of [221] or [222]. The situation in the presence of [221D] or [222D] is quite similar, but there does seem to be a cation influence on the hydrodynamic radius, particularly for Li^+. Such a result can be rationalized assuming that given the asymmetrical distribution of oxyethylenic bridges in the molecular structure of the $[221D]M^+$ or $[222D]M^+$ complexes, short range interactions between the intercalated lithium cation and bulk solvent molecules are still possible.

Acknowledgements

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