

Short Communication

Conductance Studies of the [222] Cryptate Ligand in Methanol

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Much of the previous work on cryptate complexes of alkali and alkaline earth cations has been carried out in aprotic solvents.^{1,2,3} More recently, Abraham *et al.* have determined the heats of complex formation in methanol⁴ and the thermodynamic parameters of transfer of the complexed ions from water to methanol.⁵

From the change in pH which is observed when alkali-metal ions, complexed with the [222] cryptate ligands,* are dissolved in water, it is evident that hydrolysis of the ligand, and perhaps of the cryptate complex, occurs. In order to observe the effect of the ligand on ion-pair formation and on the characteristic ion-size parameter R or a in a hydroxylic solvent, we have measured the conductances of $[M^+222]$ halides ($M^+ = Na^+$ or K^+) in methanol at 25 °C. The data have been analysed by the equations of Lee and Wheaton⁶ and of Fuoss and Hsia.⁷ Previous work on the cryptates has shown that the ion-pair association constants K_A are usually very much smaller than those of the corresponding M^+X^- salts, except for $[Na^+222]I^-$ in methyl cyanide;³ in this case, however, K_A is very small for both the complexed and the uncomplexed species, and its evaluation is imprecise by any available method. Formation constants of $[Li^+222]$ complexes in water, methanol and pyridine have been compared.⁸

Experimental. The sodium and potassium salts were A. R. reagents, re-crystallised and dried before complexing. The cryptate complexes were prepared by treating a solution of the

corresponding salt in methanol with an equivalent quantity of the [222] ligand, purified as described previously,⁵ and dissolved in the methanol. The solvent was evaporated; the complexed salt was recrystallised from acetone and kept under vacuum for several days. Analyses of these complexes for carbon, hydrogen and nitrogen have been reported.⁵

For conductance measurements, methanol was purified by refluxing with magnesium and iodine, and then fractionally distilled; it was stored under a nitrogen atmosphere.

Apparatus and procedure. Conductances were measured in a calibrated Hartley-Barrett type conductivity cell with bright platinum electrodes, at 25 ± 0.01 °C, by means of a Wayne-Kerr Type 8642 transformer ratio-arm bridge, at a fixed frequency of 1592 Hz.

All conductances were measured under a nitrogen atmosphere, and were corrected for the conductance of the solvent. Solutions were prepared by adding weighed aliquots of a stock solution of the ligand complex to a weighed quantity of solvent in the cell.

Results. The number of data points and the range of concentration for each of the complexes are recorded in Table 1. Analysis of the data by the Lee-Wheaton equation is summarised in Table 2, and by the Fuoss-Hsia equation (in the form allowing for ion-pair formation) in Table 3.

Discussion. In both treatments, 'best-fit' values of Δ_o , K_A , and a distance parameter R or a , are recorded.

Table 1. Data on solutions in methanol.^a

	10 ⁴ Concentration range, mol dm ⁻³	No. of data points
$[Na^+222]Cl^-$	1.77–9.75	11
$[Na^+222]Br^-$	0.808–9.39	12
$[Na^+222]I^-$	2.69–10.09	10
$[K^+222]Cl^-$	0.812–10.5	14
$[K^+222]Br^-$	0.716–8.40	14
$[K^+222]I^-$	2.73–15.70	11

*We adopt the same nomenclature for the ligand and its cation complexes as Abraham *et al.*⁵

^aThe full conductance data are available from the authors.

Table 2. Analysis of conductance results by the equation of Lee and Wheaton.⁶

Solute	$K_A/\text{mol}^{-1}\text{dm}^3$	R/nm	$\Delta_o/\text{ohm}^{-1}\text{mol}^{-1}\text{cm}^2$	$\lambda_o(\text{ML}^+)^a$	$b(\text{ML}^+)/\text{nm}^b$	$\delta(\Delta c)^c$	$\Delta\lambda^\circ/\text{ohm}^{-1}\text{mol}^{-1}\text{cm}^2{}^d$
1. $[\text{Na}^+222]\text{Cl}^-$	32	0.74	96.6	44.25	0.62	0.01	0.97
2. $[\text{Na}^+222]\text{Br}^-$	65	0.97	100.4	43.95	0.60	0.32	1.27
3. $[\text{Na}^+222]\text{I}^-$	58	0.68	108.5	45.72	0.58	0.13	-0.51
			Mean value	44.6 ± 1			
4. $[\text{K}^+222]\text{Cl}^-$	23	1.40	94.1	41.8	0.64	0.02	10.65
5. $[\text{K}^+222]\text{Br}^-$	26	0.84	99.5	43.1	0.62	0.04	9.35
6. $[\text{K}^+222]\text{I}^-$	27	0.94	104.7	41.9	0.60	0.03	10.46
			Mean value	42.2 ± 0.8			

^a Based on the anion conductances λ° in methanol at 25 °C: ⁹ 52.36 (Cl^-), 56.45 (Br^-), 62.78 (I^-). ^b Sum of Stokes radii (nm) from $b_i = (8.201 \times 10^{-9}) |Z_j| / \eta \lambda_i^\circ$, with $\eta = 0.005445$.¹⁰ ^c Standard deviation of calculated Λ_c values. ^d $\Delta\lambda^\circ = \lambda^\circ(\text{M}^+) - \lambda^\circ(\text{M}^+222)$ with λ° in methanol at 25 °C: 45.21 (Na^+), 52.38 (K^+).

Table 3. Analysis of conductance results by the equation of Fuoss and Hsia.⁷

	$\Lambda_o/\text{ohm}^{-1}\text{mol}^{-1}\text{cm}^2$	$K_A/\text{mol}^{-1}\text{dm}^3$	a/nm	$\lambda^\circ(\text{ML}^+)/\text{ohm}^{-1}\text{mol}^{-1}\text{cm}^2$	δ	$\Delta\lambda^\circ$
1. $[\text{Na}^+222]\text{Cl}^-$	96.6	32	0.82	44.2	0.03	1.01
2. $[\text{Na}^+222]\text{Br}^-$	100.6	68	0.86	44.2	0.21	1.06
3. $[\text{Na}^+222]\text{I}^-$	108.4	54	0.70	45.6	0.12	-0.39
			Mean value	44.7 ± 0.9		
4. $[\text{K}^+222]\text{Cl}^-$	94.1	25	1.38	41.7	0.06	10.68
5. $[\text{K}^+222]\text{Br}^-$	99.5	23	0.69	43.1	0.05	9.33
6. $[\text{K}^+222]\text{I}^-$	104.6	20	0.32	41.8	0.05	10.58
			Mean value	42.2 ± 0.8		

The significance of the R_i values has been explained by analogy with the Gurney co-sphere radii.¹² Outside this distance from the centre of an ion the continuum model of the solution is adopted, and the free solvent value for the dielectric constant (32.62⁹) is assumed. At distances of separation $\leq R_i$, the co-spheres of ions overlap and the ions are defined as associated; in the present cases such ion-pairs do not contribute to the conductance of the solution. The a -values (Table 3) represent the centre-to-centre distance of contact ion-pairs.

The two equations give closely similar values of Λ_o and K_A , with the exception of K_A for $[\text{K}^+222]\text{I}^-$ in Table 3, which is anomalously small for the potassium salts.

The fitting of the experimental data by the Lee-Wheaton equation is considered to be satisfactory for these large complexed cations. Of course either equation gives a much better fit to the conductances of the alkali halides in water or in methanol with $\delta < 0.02$.

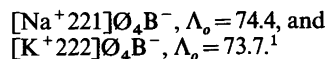
The mean differences in cation limiting conductance in methanol solution are:

$$\lambda_{\text{K}^+}^\circ - \lambda_{\text{Na}^+}^\circ = 7.2 \text{ ohm}^{-1} \text{ mol}^{-1} \text{ cm}^2{}^{11}$$

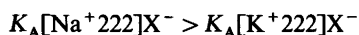
$$\lambda_{[\text{K}^+222]}^\circ - \lambda_{[\text{Na}^+222]}^\circ = -2.4 \text{ ohm}^{-1} \text{ mol}^{-1} \text{ cm}^2$$

(this work)

This inversion suggests that the species complexed by the [222] ligand is the unsolvated ion. From the lower Λ_o values for the complexed ions, and from the R -values we conclude that complexed Na^+ and K^+ ions are associated with co-spheres of partially-oriented solvent molecules, that of the K^+ ion being the larger. This seems also to be true for the solutes



Removal of the solvation shell of the cation results in increased interionic attraction; and the K_A values are larger than for the corresponding halides in methanol. The smaller co-sphere of the $[\text{Na}^+ 222]$ cation results in



However as would be expected for large singly-charged cations, K_A is small; in the extreme case of $[\text{Na}^+ 222]\text{Br}^-$, even in 10^{-3} molar solution, the degree of association is only 4.3%.

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