COMPLEXATION OF ALKALI METAL AND SILVER IONS WITH UNSUBSTITUTED AND DICYCLOHEXANO-SUBSTITUTED 3*m*-CROWN-*m* ETHERS IN DIPOLAR APROTIC SOLVENTS AND ALCOHOLS

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COMPLEXATION OF ALKALI METAL AND SILVER IONS WITH UNSUBSTITUTED AND DICYCLOHEXANO-SUBSTITUTED 3m-CROWN-m ETHERS IN DIPOLAR APROTIC SOLVENTS AND ALCOHOLS

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Formation constants, $K^f(LM^+)$, of the 1:1 complexes of 3m-crown-m ($m = 4, 5, 6$) with Li^+ were estimated in acetonitrile (AN) using a cation selective electrode. Here L refers to the ligand and M^+ to the metal ion. Those of 3m-crown-m ($m = 7, 8, 9, 10$) ligands and their dicyclohexano-substituted analogs with Na^+, K^+ and Rb^+ were found from the solubility of the halide or picrate salt in the presence of excess ligand. Solvents were methanol, isopropanol, n-butanol, AN, acetone and propylene carbonate. The maximum stability of 3m-crown-mM^+ in AN occurs at $m = 5$ for Li^+ and Na^+, and at $m = 6$ for K^+ and Rb^+, corresponding to a close fit of ring hole size and ionic radius. A shallow plateau was observed at $m = 8$ for Na^+ and probably at $m = 10$ for K^+ due to a "wrap around" complex. Extensive solvation of the latter has been inferred from its low ionic mobility, which is discussed in terms of the Zwanzig theory of ionic conductivity. Solubility data of sodium iodate in the presence of dibenzo-18-crown-6 in tetra-ethylammonium perchlorate ($0.04\ mol\ L^{-1}$) in methanol yield $K^f(LNa^+)$ close to that at low ionic strength. Electrochemical methods for estimation of $K^f(LM^+)$ are therefore suitable in the presence of a high concentration of inert electrolyte.

Keywords: 3m-crown-m ethers; alkali metal ions; complexation constants; dipolar aprotic solvents

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INTRODUCTION

It is of analytical and physical chemical interest to utilize one or several crown ethers in a homologous series that have a maximal binding capacity in solution for a given cation. Such crown ethers are valuable in extraction analysis,[1-3] or as a neutral carrier in liquid membrane ion selective electrodes.[4]

The effect of varying the methylene chain length in crown ethers having only four oxygen heteroatoms on the thermodynamics of complexation of Li^+ and Na^+ in methanol (MeOH) was investigated by Inoue *et al.*[5] In general, the best match of cavity size with cation radius, high ring symmetry, rigidity and favorable orientation of the oxygen lone pairs results in large negative values of both ΔH and $-T\Delta S$ of binding as with 14-crown-4, 14C4. In another study,[6] also in MeOH, these authors varied the number of ethyleneoxy units in the series $(CH_2CH_2O)_m$, denoted as 3m-crown-m, or 3mCm.

In dipolar aprotic solvents (DAS) of intermediate dielectric constant, e.g. acetonitrile (AN), solvation of uncomplexed M^+ is considerably less extensive than in MeOH,[7] somewhat simplifying the interpretation of thermodynamic data of complexation. In these solvents ion pairing is minimal. Complexation data in the gas phase,[8] which circumvent solvation effects, are still more readily interpreted. Thermodynamic data of complexation of M^+ with 3m-crown-m or with the corresponding dicyclohexano-substituted crown ethers (DCC3m-crown-m) in DAS in the literature are limited to those ligands with $m = 4-6$. This includes a detailed study[9] of binding of K^+ to 3m-crown-m ethers in AN. It is desirable, therefore, to have a more complete profile of the stability of the complexes vs ligand ring size, encompassing larger crown ethers in these series.

In the present work, stability constants, $K^f(LM^+)$, at 25°C of 3m-crown-m ($m = 4-10$) and those of DCC 3m-crown-m with alkali metal ions and Ag^+ were determined in AN, propylene carbonate (PC), acetone (AC), MeOH, *i*-propanol (*i*-PrOH) and *n*-butanol (*n*-BuOH).

12C4　　　**DCC24C8**　　　**DCC30C10**
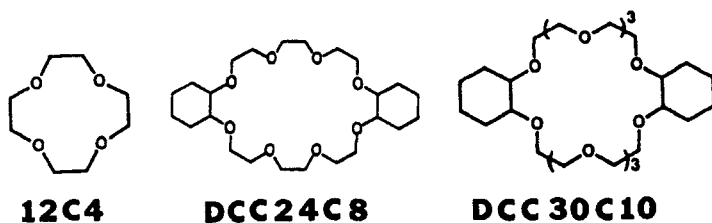
As dibenzo-30-crown-10K$^+$ (DB30C10K$^+$) is symmetrical "wrap around" complex, both in the solid state[10] (two-fold symmetry) and in solution in AN,[11,12] nitromethane[12] and AC,[12] a comparison of the molar electrical conductivities at infinite dilution, $\lambda_0(LM^+)$, of DCC30C10K$^+$, DB30C10K^{+13} and 30C10K$^+$ with that of cryptand 2.2.2K$^+$ (poorly solvated in DAS) sheds light on the solvation of these crown complexes.

Finally, $K^f(DB18C6K^+)$ was estimated in MeOH at a high ionic strength (tetraethylammonium perchlorate, 0.04 mol L^{-1}) in this study. Such solutions are typically used in the polarographic method[14] for estimation of $K^f(LM^+)$.

EXPERIMENTAL

Acetonitrile, propylene carbonate, methanol, i-propanol and n-butanol were purified as previously described.[15] Lithium, sodium, potassium and rubidium chlorides,[16] silver perchlorate,[16] silver nitrate,[17] sodium iodate,[17] tetraethylammonium and silver perchlorates,[17] sodium and potassium tetraphenylborates[18] were products used previously. Rubidium tetraphenylborate was prepared similarly to the potassium salt. 21-crown-7 and 24-crown-8 were synthesized according to Beadle et al.,[19] and 27-crown-9 and 30-crown-10 according to Chênevert and D'Astous.[20] Dicyclohexano-substituted crown ethers were prepared by non-stereoselective hydrogenation of the dibenzo crowns.

The total solubility of lithium, sodium, potassium and rubidium chlorides in the absence or presence of crown ether (1×10^{-3}–2×10^{-2} mol L^{-1}) was determined by evaporating a known volume of the saturated solution to dryness and titrating the residue potentiometrically with silver nitrate in aqueous medium. A Markson sodium ion selective glass electrode was conditioned in LiClO$_4$ in AN (0.01 mol L^{-1}). It was calibrated in LiClO$_4$ solutions (1.5×10^{-4}–1.5×10^{-2} mol L^{-1}), taking ion pairing into account ($K_A = 2.4 \times 10^1$).[21] Electrode response was 55.3 mv/pa(Li$^+$). The three compartment potentiometric cell, potentiometer and Ag/AgNO$_3$ reference electrode were described previously.[18] Conductivity cells and bridge were those used for precise measurements (0.1%).[15]

RESULTS

In all instances, a 1:1 complex, LM$^+$, appears to be formed in this study. Values of $\log K^f(LM^+)$ of the lithium complexes in AN obtained with a Li$^+$

selective electrode are in fair to good agreement with those from the litera-
ture. They are as follows: 12C4Li$^+$ 3.47 ± 0.03 (this work), 4.25 ± 0.46[22]
(^{7}Li NMR), 3.402 ± 0.002[23] (conductance), 3.12 ± 0.06[24] (^{7}Li NMR),
15C5Li$^+$ 5.44 ± 0.08 (this work), 3.600 ± 0.032,[23] 5.34[25] (conductance),
4.8 ± 0.2[24] and 18C6Li$^+$, 2.99 ± 0.06 (this work), 2.34 ± 0.04,[22] 3.727 ±
0.001[23] and 2.30 ± 0.05[24] (K is in mol^{-1} L). Assuming the empirical rela-
tion[13] (equation (1)),

$$^{AN}\Delta^{PC} \log K^f(18C6M^+) = -0.636\Delta G^0_{tr}(18C6)_{AN \rightarrow PC}/RT \ln 10$$
$$-0.674\Delta G^0_{tr}(M^+)_{AN \rightarrow PC}/RT \ln 10, \qquad (1)$$

also holds for Li$^+$ between AN and PC, $\log K^f(18C6Li^+) = 2.55$ in AN,
taking $\log K^f(18C6Li^+) = 2.70 \pm 0.05$ in PC.[26] In equation (1) M$^+$ =
Na$^+$, K$^+$, Rb$^+$ and ΔG^0_{tr} denotes free energy of transfer from AN to PC,
being 1.88 kJ mol^{-1} for 18C6[13] and -0.6 kJ mol^{-1} for Li$^+$.[16] In addition,
$\log K^f(DB18C6Li^+) = 2.26 \pm 0.06$ in AN (this work), which is much larger
than 0.86 reported by Karkhaneei et al.[24]

In this study, the solubility of lithium chloride was found to be
0.0309 mol L^{-1} in AN saturated with DB18C6, as compared to 0.0249 mol
L^{-1} in its absence. As the effect of DB18C6 is small, as expected, and the
system is complex, a reliable value of $K^f(DB18C6Li^+)$ could not be
obtained.

Complexation constants of sodium, potassium and rubidium ions with
3m-crown-m and with the corresponding dicyclohexano-substituted ligands
were estimated from the increase in solubility of appropriate alkali metal
chloride, bromide or picrate. Both uncomplexed ligand and complexed salt,
LMX, are freely soluble. The required total solubility, association constant,
$K_A(MX)$, and solubility product, $K^{sp}(MX)$, of the uncomplexed salts are
tabulated in Table I.

All complexed salts and uncomplexed AgClO$_4$ are considered as com-
pletely dissociated in AN, PC and MeOH under our experimental condi-
tions. In solvents of low dielectric constant, AC, i-PrOH and n-BuOH,
association constants $K_A(MX)$ and $K_A(LMX)$ were derived from the linear
Shedlowsky plots of the conductivity data. Values of $\Lambda_0(NaCl)$ are 15.2
in i-PrOH and 14.5 in n-BuOH, while $\Lambda_0(RbCl) = 17.3$ in both solvents.
Table II lists values of $\lambda_0(LM^+)$ of the complexed alkali metal cations in
AN, taking $\lambda_0(BPh_4^-) = 58.3$.[27] Calculation of $K^f(LM^+)$ from solubility
data of MX in the presence of excess L has been described previously.[17] An
appreciable systematic variation of the $K^f(DCC3mCmM^+)$ with increasing
ligand concentration in AN and PC was observed in this study for the

TABLE I Association constants and solubility products of alkali metal salts in several solvents

Salt	Solvent	Total solubility/ $(\text{mol L}^{-1}) \times 10^4$	$K_A(MX)$ mol^{-1}L	$10^7 K^{sp}$ (MX)	Reference
NaCl	AN	0.85	$\sim 6 \times 10^3$	0.050	18
KCl	AN	1.21	< 10	0.10	18
RbCl	AN	—	a	0.50	18
KBr	AC	2.34	58	0.28	37
NaCl	PC	—	a	0.109	16
KCl	PC	2.75	a	0.724	16
RbCl	PC	7.14	a	4.68	16
NaCl	*i*-PrOH	4.1	$1.0_7 \times 10^3$	0.772	This work
NaCl	*i*-PrOH	5.92	—	—	38
KPi	*i*-PrOH	1.19	5.7×10^3	0.061	37
RbCl	*i*-PrOH	5.29	3.2×10^3	0.721	This work
NaCl	*n*-BuOH	7.81	$1.2_6 \times 10^3$	1.84	This work
NaCl	*n*-BuOH	10.61	—	—	38
KPi	*n*-BuOH	1.31	4.8×10^3	0.074	37
RbCl	*n*-BuOH	4.58	3.2×10^3	0.548	This work

a: electrolyte regarded as completely dissociated.

TABLE II Ionic mobilities $(\text{S cm}^2\text{mol}^{-1})$ and association constants $(\text{mol}^{-1}\text{L})$ of complexed alkali metal salts[a] in various solvents

Solvent	Salt	λ_0^+			$\Lambda_0(IV \cdot MX)$	$K_d(IV \cdot MX)$
		$I \cdot M^+$	$II \cdot M^+$	$III \cdot M^+$		
AN	LNaBPh₄	60.5	55.0	49.2		
AN	LKBPh₄	57.6	56.5	49.5		
AN	LRbBPh₄	58.0	55.2	50.2		
AC	LKBr				177	97
i-PrOH	LNaCl				17.9	97
i-PrOH	LKPi				23.5	310
i-PrOH	LRbCl				18.1	15
n-BuOH	LNaCl				13.1	150
n-BuOH	LKPi				17.3	340
n-BuOH	LRbCl				14.9	80

[a]I = 21C7, II = 27C9, III = 30C10, IV = DCC30C10 mixture of isomers, Pi⁻ = picrate.

majority of the complexes. This behavior may be attributed to different isomers of the ligands, each having its own 1 : 1 complexation constant and not 1 : 2 complexation of a single isomer.[28],*

Table III summarizes values of $\log K^f(LM^+)$, M^+ being Na^+, K^+, Rb^+, and Ag^+ with L being 21C7, 24C8, 27C9, 30C10 and their dicyclohexano-substituted entities. Solvents are MeOH, *i*-PrOH, *n*-BuOH, AN, AC and

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* Although a 1 : 2 complex, DB30C10Na$_2^{2+}$, has been detected in nitromethane, its presence in solvents of higher donicity used in the present study is expected to be minimal. Na⁺ is considerably less solvated in nitromethane than in AN, $\Delta G_{tr}^0(Na^+)_{AN \to NM}$ being 16.55 kJ mol⁻¹.[7]

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TABLE III   Complexation constants of alkali metal ions and Ag^+ with large crown ethers, L, in several solvents at 25°C (K^f in $mol^{-1} L$)

Solvent	L	$\log K^f(LM^+)$				Reference
		LNa^+	LK^+	LRb^+	LAg^+	
MeOH	21C7	1.73 ± 0.11	4.22 ± 0.03	4.86 ± 0.02	2.46 ± 0.04	39
MeOH	21C7	2.46				40
MeOH	21C7		4.41			41
MeOH	DCC21C7[a]				3.87 ± 0.07	This work
MeOH	24C8	2.02 ± 0.08				6
MeOH	DCC24C8[a]	3.51	3.84	3.88	3.60	42
MeOH	DCC24C8[a]				4.40 ± 0.02	This work
MeOH	30C10	2.14 ± 0.07	3.98 ± 0.02			6
MeOH	DCC30C10[a]	2.38 ± 0.13	4.50 ± 0.03		2.97 ± 0.02	This work
i-PrOH	DCC30C10[a]	3.82 ± 0.02	5.93 ± 0.04	5.09 ± 0.04		This work
n-BuOH	DCC30C10[a]	3.80 ± 0.01	5.47 ± 0.05	5.30 ± 0.06		This work
AN	21C7	3.54 ± 0.04	4.60 ± 0.08	4.79 ± 0.04		This work
AN	DCC21C7[a]	5.05	4.98	4.88		This work
AN	24C8	3.90 ± 0.04	3.94 ± 0.06	3.94 ± 0.08		This work
AN	DCC24C8[a]	5.45	5.10	4.84		This work
AN	27C9	3.67 ± 0.06	4.55 ± 0.04	4.02 ± 0.03		This work
AN	30C10	3.6 ± 0.1	4.62 ± 0.09	4.45 ± 0.02		This work
AN	DCC30C10[a]	4.33	4.86	4.75		This work
AC	DCC30C10[a]		4.58 ± 0.06			This work
PC	DCC21C7[a]	5.19	4.73	4.25	7.03 ± 0.04	This work
PC	DCC24C8[a]	5.48	4.79	4.43	7.48 ± 0.06	This work
PC	DCC30C10[a]	4.41	4.66	4.25	6.00 ± 0.03	This work

[a] mixture of isomers.

PC. As expected, a small effect on $K^f(LM^+)$ of substituents on the large macrocycle 30C10 was observed in AN and PC, M^+ being K^+ or Rb^+. As an example, $\log K^f(DB30C10K^+) = 4.83$,[13] $\log K^f(30C10K^+) = 4.62$ and $\log K^f(DCC30C10K^+) = 4.86$ in AN (Table III). Corresponding Na^+ complexes in AN exhibit an increase in $\log K^f(LNa^+)$, 3.20,[13] 3.6 and 4.33, respectively.

The effect of high ionic strength on $K^f(DB18C6Na^+)$ in MeOH is depicted in Table IV, which presents solubility data in MeOH saturated with both sodium iodate and DB18C6. In the absence of $NaIO_3$ the solubility of DB18C6 increases from $1.38 \times 10^{-3} mol L^{-1}$ in pure $MeOH$[17] to $1.88 \times 10^{-3} mol L^{-1}$ in Et_4NClO_4 ($0.043 mol L^{-1}$). The activity coefficient, y_L, in the latter solution is 0.734. Activity coefficients of all other neutral species are assumed to be unity; errors made by this assumption are minimal, as the concentrations of these species are low. In contrast, $y^{\pm 2}$ of $NaIO_3$ in the presence of Et_4NClO_4 is only 0.25, as evaluated from $^{17}K^{sp}(NaIO_3) = 1.50 \times 10^{-7}$ and $[Na^+]$ (equal to $[IO_3^-]$). It is apparent that Et_4NClO_4 exerts only a minor effect on $K^f(LM^+)$ and that electrochemical

TABLE IV   Estimation of $K^f(DB18C6Na^+)$ in tetraethylammonium perchlorate (0.043 mol L^{-1}) in methanol saturated with DB18C6 (L) from solubility of sodium iodate

(mol L^{-1})	$(NaIO_3)_{satd.}{}^a$ (mol L^{-1}) $\times 10^4$	$(NaIO_3)_{satd.}$ Et_4NClO_4 (0.043 mol L^{-1}) (mol L^{-1}) $\times 10^4$	$(NaIO_3)_{satd.}{}^a$ $(L)_{satd.}$ (mol L^{-1}) $\times 10^3$	$(NaIO_3)_{satd.}$ $(L)_{satd.}$ Et_4NClO_4 (0.043 mol L^{-1}) (mol L^{-1}) $\times 10^3$
$C(IO_3^-)$	5.0_θ	8.47	3.59	5.48
$[Na^+]$	4.2	7.7	0.08_5	0.13
$[IO_3^-]$	4.2	7.7	2.84	4.73
$[NaIO_3]$	0.8	0.8	0.08	0.08
$[L]$	0	0	1.38	1.88
$[LNa^+]$	0	0	2.76	4.60
$[LNaIO_3]$	0	0	0.67	0.67
$y^{\pm 2}$	0.83	0.25	0.627	0.25
$K^f(LNa^+)^b$	—	—	$2.3_5 \times 10^4$	$1.9_3 \times 10^4$

[a]Ref. [17]. [b]units: mol^{-1} L.

methods employing a high concentration of a non-electroactive electrolyte can yield reliable values of $K^f(LM^+)$.

DISCUSSION

Values of K^f for the lithium ion complexes with 3m-crown-m in AN, PC and AC are in the order $15C5 \gg 12C4 > 18C6$, which is the same as that in AN-nitromethane mixtures from ^{7}Li NMR.[24] A good match occurs between the ionic radius $(0.73 \,\text{Å}^{29})$ vs. cavity hole radius, r $(15C5) = 0.85 \,\text{Å}.^{30}$ A very good match with 14C4 as ligand was noted by Inoue et al.[5] in MeOH; this ligand affords a more favorable enthalpy and entropy of binding than does 12C4.

Plots of $\log K^f(LM^+)$ in AN vs. 3m of the 1 : 1 complexes of 3m-crown-m or DCC3m-crown-m with Na^+, K^+, and Rb^+ are presented in Figure 1. Values of $\log K^f(LM^+)$ for complexes of small crown ethers were taken from the literature and averaged when more than one value was reported. A maximum occurs at 15C5 for Na^+ $(r(Na^+) = 1.02 \,\text{Å},^{29}$ $r(15C5) = 0.85 \,\text{Å}^{30})$, at 18C6 for K^+ and Rb^+ $(r(K^+) = 1.38 \,\text{Å},^{29}$ $r(Rb^+) = 1.49 \,\text{Å},^{29}$ $r(18C6) = 1.38 \,\text{Å}^{30})$ for the unsubstituted crown ethers. It also occurs at $DCC18C6K^+$. Ionic radii correspond to a coordination number of 6. Cavity radii were derived from CPK models. In the gas phase[8] $18C6Na^+$ is intrinsically more stable than $18C6K^+$. It should be noted that uncomplexed small 3m-crown-m ethers are solvated to a considerable extent by AN.[31] This factor alone would decrease $K^f(LM^+)$. A shallow maximum occurs at $m = 8$
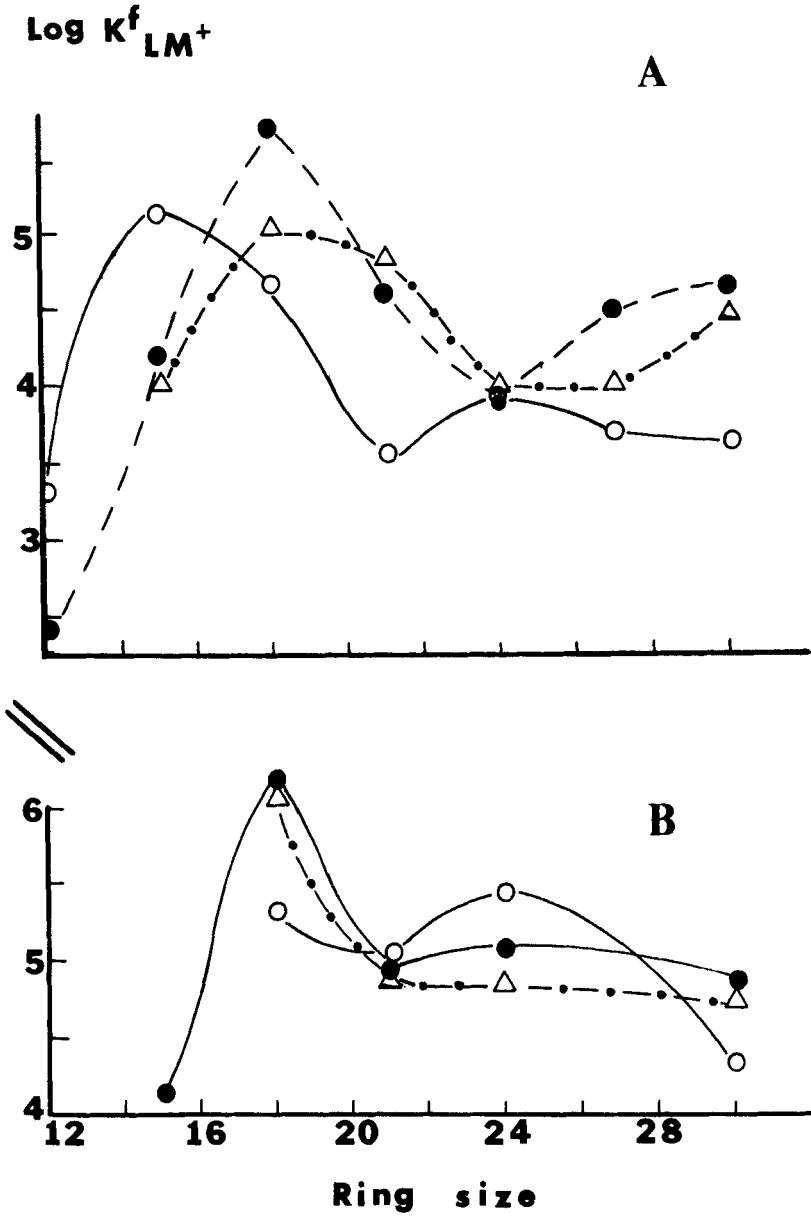
FIGURE 1 Plots of $\log K^f(LM^+)$ in acetonitrile vs ring size ($3m$ in m-crown-m or in DCC$3m$-crown-m). A. unsubstituted, B. dicyclohexano-substituted crown ethers. ($-\bigcirc-$) Na^+, ($-\bullet-$) K^+, ($-\triangle-$) Rb^+.

for Na^+ and presumably at $m = 10$ for K^+ with the larger, flexible unsubstituted and dicyclohexano crown ethers. Such behavior in MeOH has been attributed to "wrap around" complexes by Inoue *et al.*[6]

The following discussion deals with ionic mobilities of complexed alkali metal ions and association constants, $K_A(LMX)$, of the corresponding salts. The crystallographic radius of cryptand 2.2.2.K^+ (C222K^+), 5.00 Å,[32] is practically identical to that of DB30C10K^+, 5.05 Å,[10] as calculated from the average distance between K^+ and the ethoxy carbon atoms. The order of decreasing $\eta\lambda_0(LM^+)$ product in AN is C222K^+(0.196)[33] $\gg$ DB30C10K^+ (0.175)[13] > 30C10K^+(0.169 P-S·cm^{2}mol^{-1}). This is as a consequence of extensive outer sphere solvation of the "wrap around" crown complexes,[13] C222 being poorly solvated. This was also concluded from the difference in ΔG_{tr}^0 of DB30C10K^+ and DB30C10 between DAS of various donor strengths.[13] For example, this difference is $-6.43 + 1.59 = -4.84$ KJ mol^{-1} going from PC to dimethylsulfoxide.

The solvatodynamic radius, r_i, which is the sum of the radius of the unsolvated complex and the thickness of the outer solvation shell, can be estimated from the conductometric λ_0 value using the Zwanzig theory[34] of limiting ionic mobility. The large dibenzo- and dicyclohexano-substituted crown ether complexes are regarded as being spherical. The interionic distance, a_i, (center to center) in the solvent and ligand separated ion pair $M^+L \cdot$ solvent $\cdot X^-$ is the sum $r_i + r_{x^-}$. The resulting value of a_i is then introduced into the Bjerrum electrostatic model[35] (equation (2)) to calculate K_A at 25°C.

$$K_A = 3.92 \times 10^6 Q(b)/D^3. \tag{2}$$

In equation (2) $Q(b)$ is a function of a_i and D is the dielectric constant. In AC $\lambda_0(DCC30C10K^+) = 61.1$ (c.f. Table II) and $\lambda_0(DB24C8K^+) = 55.6$,[13] yielding $r_i = 6.55$ and 7.17 Å respectively. A value of $\lambda_0(Br^-) = 115.9$[36] was used. Taking r_x of unsolvated Br^-, 1.96 Å[29] and employing the Bjerrum treatment, $K_A(LKBr) = 140$ and 125, respectively, as compared to the experimental values of 97 and 125.[13] This agreement probably is fortuitous. In AN $K_A(DB30C10KBr)$ is abnormally large,[13] suggesting a close approach of the partially entrapped Na^+ to Br^-.

CONCLUSIONS

The profile of $\log K^f(LM^+)$ vs. ring size of 3m-crown-m in acetonitrile resembles that in methanol, with the exception of greater affinity of

15-crown-5 for Na^+ over K^+. The effect of cyclohexyl- or benzo-substituents on large crown ethers on $K^f(LM^+)$ in AN is small. The large values of $K^f(DCC30C10K^+)$ in i-propanol and n-butanol suggest the presence of a "wrap around" complex. From the ionic mobilities of potassium complexes of the larger crown ethers in acetone it is shown that the association constant of the ion pair $LM^+ \cdot$ solvent $\cdot X^-$ can be approximated using the simple Bjerrum model.

Acknowledgments

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