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ON THE ROLE OF WATER IN THE COMPLEXATION OF ALKYLAMMONIUM SALTS BY CROWN ETHERS

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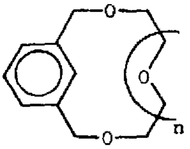
Recently, Cram and co-workers[1] reported a simple method to determine the association constants (K_a) between tert-butylammonium thiocyanate and a large number of crown ethers in deuteriochloroform. The K_a values were obtained from equilibration experiments between D_2O solutions of the salt and $CDCl_3$ solutions of the crown ethers.

Studying extractions from H_2O instead of D_2O solutions, we have found that under these conditions water plays an important role in the solubilization of tert-butylammonium hexafluorophosphate by crown ethers 1a-1f[2].



1a , n = 2　　1d , n = 5
1b , n = 3　　1e , n = 6
1c , n = 4　　1f , n = 7

First, we determined the solubilization of water by these crown ethers in the absence of salt. To this end, C_0 molar solutions of the crown ethers in $CDCl_3$ (1.0 ml) were equilibrated with water (2.0 ml) and the concentration of water in the organic phase relative to that of the crown ether ($R_w = [H_2O]/C_0$) was determined by PMR spectroscopy. Table I gives the equilibrium constants K_w and the amount of solubilized water per mole of crown ether ($R_w - \frac{S_w}{C_0}$, in which S_w stands for the solubility of water in neat chloroform) calculated[3] on the basis of eq. (1), in which CE stands for crown ether.

$$H_2O + CE \overset{K_w}{\rightleftarrows} CE.H_2O \qquad (1)$$

The results clearly show that the crown ethers are efficient agents for solubilizing water in chloroform, and that their complexing power increases with their ring size. For comparison, the non-cyclic counterpart of 1c has been included as well in Table I and it is seen to be only

TABLE I

Complexation of water by crown ethers in $CDCl_3$ at 22 ± 1 °C[3]

Crown ether	K_w (a)	$R_w - \frac{S_w}{C_0}$	Compound	K_w (a)	$R_w - \frac{S_w}{C_0}$
1a	8	0.27	1e	23	51
1b	14	0.38	1f	47	68
1c	14	0.39	$[\phi(CH_2OCH_2)_3]_2$	7	24
1d	20	0.47			

(a) estimated accuracy: 10 %

slightly less effective. Hence it must be concluded that the complexing power towards water is mainly determined by the number of ethylene-oxy units, the size of the cavity being less important[4].

Next, we determined the simultaneous complexation of water and tert-butylammonium hexafluorophosphate by equilibrating a C_0 molar crown ether solution in $CDCl_3$ (1.0 ml) with successive portions (2.0 ml) of a 0.4 M solution of $t\text{-}BuNH_3.PF_6$ in water[5] until the salt concentration in $CDCl_3$ was constant. The relative concentrations of salt ($R_a = [t\text{-}BuNH_3.PF_6]/C_0$) and water ($R_w = [H_2O]/C_0$) were calculated from 90-MHz PMR spectra.

TABLE II

Complexation of water and $t\text{-}BuNH_3.PF_6$ in $CDCl_3$ at 22 ± 1 °C

	$100 \times R_a$			$R_w - S_w/C_0$		
Crown ether \ C_0	0.01	0.10	0.50	0.10	0.25	0.50
1a	<0.1	<0.1	0.4	0.18	0.16	0.16
1b	88	90	92	0.20	0.22	0.22
1c	10	19	41	0.40	0.48	0.50
1d	13	42	76	0.40	0.72	1.63
1e	10	27	52	0.35	0.70	0.82
1f	10	19	46	0.50	0.68	1.01

If the complexation of salt and water would occur independently, it could simply be described by equilibria (1) and (2). In this case R_a and (R_w-S_w/C_0) should both be independent

$$\underline{t}\text{-BuNH}_3.\text{PF}_6 + \text{CE} \overset{K_a}{\rightleftharpoons} \underline{t}\text{-BuNH}_3^{\oplus}.\text{CE}.\text{PF}_6^{\ominus} \qquad (2)$$

of the crown ether concentration[6]. From Table II it is seen that only the data obtained for crown ether 1b are in agreement with the behaviour predicted by equilibria (1) and (2). For the compounds containing larger rings (1c-1f) both R_a and (R_w-S_w/C_0) increase with increasing crown ether concentration, the apparent K_a values, as calculated on the basis of eqs. (1) and (2), becoming proportional to $(C_0)^{\frac{1}{2}}$ at high crown ether concentrations.

These observations can be most simply rationalized by a scheme involving the formation of hydrated dimers (eq. (3)):

$$2n\,\text{H}_2\text{O} + 2\,\underline{t}\text{-BuNH}_3^{\oplus}.\text{CE}.\text{PF}_6^{\ominus} \overset{K_d}{\rightleftharpoons} \left[\underline{t}\text{-BuNH}_3^{\oplus}.\text{CE}.\text{PF}_6^{\ominus}.(\text{H}_2\text{O})_n\right]_2 \qquad (3)$$

The equilibria (1) (H_2O complexation), (2) (1 : 1 salt complex formation) and (3) were found to describe the extraction process quantitatively for crown ether concentrations from 0.01 M to 0.5 M. The calculated[7] equilibrium constants, compiled in Table III, nicely demonstrate the validity of the proposed mechanism for alkylammomium complexation. At low concentration 1 : 1 complexes are formed; the relative complexing abilities for this type of complex (Table III) are in accord with those obtained under anhydrous conditions[8]. At higher concentrations the crown ethers containing cavities that are too large to give stable 1 : 1 complexes (1c-1f) form dimers in which water molecules serve as additional and indispensable building blocks[9].

TABLE III

Calculated relative complexing abilities[7] for 1 : 1 (K_a) and 2 : 2 (K_d) complexes

Crown ether	$(K_a)_{rel.}$	$(K_d)_{rel.}$	Crown ether	$(K_a)_{rel.}$	$(K_d)_{rel.}$
1a	<0.08	-	1d	0.9	$100^{(b)}$
1b	$100^{(a)}$	0.01	1e	1.3	14
1c	1.3	0.4	1f	1.3	14

(a) $K_a\,.S_s = 11.9$;

(b) $K_d[H_2O]^{2n} = 2500$

REFERENCES AND FOOTNOTES

(1) J.M. Timko, R.C. Helgeson, M. Newcomb, G.W. Gokel, and D.J. Cram, J. Amer. Chem. Soc., **96**, 7097 (1974).

(2) D.N. Reinhoudt and R.T. Gray, Tetrahedron Letters, 2105 (1975).

(3) K_w is obtained from the relation $R_w.C_0 = S_w + C_0\,[K_w S_w/(1+K_w S_w)]$. The value of S_w was found to be 0.045 ± 0.005 M at 22 ± 1 °C.

(4) Related compounds, e.g. polyoxyethylene nonylphenyl ethers, have also been found to solubilize water, although in these cases solubilization takes place through micelle formation; see K. Kon-no and A. Kitahara, J. Colloid. Interface Sci. **34**, 221 (1970).

(5) Prepared from equal volumes of 0.8 M t-$BuNH_3.Cl$ and 0.8 M $LiPF_6$ solutions.

(6) Note 7, $r = 0$

(7) R_a follows from the expression $R_a/(1-R_a) = [q-1-p+\{(1+p+q)^2+8(rC_0)\}^{\frac{1}{2}}]/2(1+p)$, in which $q = K_a S_s$; $p = K_w S_w$; $r = K_d[H_2O]^{2n}q^2$ and S_s is the amount of salt extracted from 0.4 M salt solutions by chloroform only. Since S_s is very small ($\leq 10^{-4}$ mol/l), the amount of solubilized salt, $R_a - \frac{S_s}{C_0}$, equals R_a under these conditions.

(8) F. de Jong, D.N. Reinhoudt and C.J. Smit, Tetrahedron Letters, following paper.

(9) The amount of water involved in eq. (3) was $n = 1.5 \pm 0.5$ for crown ethers **1c**-**1f**.