THE COEXTRACTION OF WATER INTO NITROBENZENE WITH ALKALI METAL SALTS OF HEXANITRODIPHENYLAMINE IN THE PRESENCE OF DIBENZO-18-CROWN-6

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The hydration numbers of alkali metal cations and their complex cations with dibenzo-18-crown-6 in water-saturated nitrobenzene were determined. The complexation causes a clear decrease in hydration number, indicating that the water molecules hydrated have partly been replaced by the six oxygen atoms of dibenzo-18-crown-6.

In a previous paper[1] it has been demonstrated that when ion-pairs of alkali metal cations with some bulky organic anions are extracted into nitrobenzene, the water molecules strongly hydrated to the cations are transferred to the organic phase. It is known that macrocyclic polyethers complex cations and in the resulting complexes the metal cations are situated in the center of the inwardly oriented oxygen atoms.[2,3] This 'metal in the hole' picture suggests that the hydration number of the cations, that is, the quantity of the water coextracted into nitrobenzene is much affected by the complexation. The present paper deals with the quantitative effect of dibenzo-18-crown-6 (L) on the coextraction of water.

Nitrobenzene solutions of alkali metal and ammonium 2,2',4,4',6,6'-hexanitro-diphenylaminates (MA) (0 - 0.02 M), L (0 - 0.03 M), and MA plus L (mole ratio of L to MA, 0 - 3) were shaken separately with an equal volume of an aqueous solution for an hour at 25 $\pm$ 0.05°C in a thermostated water bath, all the aqueous solutions being adjusted at pH = 11.7 and ionic strength I = 0.1 with either the corresponding alkali metal chloride and hydroxide or the corresponding sulfate and carbonate. The nitrobenzene solution of L was shaken with an aqueous solution prepared with potassium salts. The water content in the organic phase was determined by the Karl-Fischer method (Mitsubishi Kasei Co., Ltd., MCI Model CA - 1). The total aminate and L[4] concentrations in the aqueous phase were determined spectrophoto-metrically. Conductance measurements were carried out at 25 $\pm$ 0.005°C by the use of a universal bridge (Ando Electric Co., Ltd., LCR - 10) equipped with platinized platinum electrodes.

Figure 1 shows that the solubility of water in nitrobenzene, S (0.178 M), increases slightly when potassium aminate (KA) or L, or both, are present. The hydrolysis product of the aminate ion (A$^-$) was not detected. The concentrations

of the complex ion-pairs of L with alkali
metal chlorides or sulfates in the organic
phase were found to be negligibly small
compared with the concentrations, C, of the
solutes.   Thus, the number of molecules of
water associated with KA, L, and the complex
between them can be evaluated to be 1.3, 0.7,
and 0.1 respectively from the slope of the
linear plot as shown in Fig. 1.   Meloan's
data[5] reveal that the observed changes in
I and pH during the extraction have no sig-
nificant effect on S.   From the data on the
solubility of water in nitrobenzene[6] it can
be seen that the observed variation of the
temperature causes an error of less than
about 0.1 molecule of water.

In Fig. 2 the solubility increment
divided by the total concentrations of the
aminates in the organic phase, $\Delta S/c^A$, is
plotted as a function of the ratio of the
total concentrations of L to the aminates,
c^L/c^A.   The decreasing portion of the curve
indicates that the quantity of the complex
ion-pairs which carry less water than MA in-
creases with the concentration of L.   The
position of a minimum point in Fig. 2 shows
that all the resulting complex ion-pairs are
of a 1 : 1 stoichiometry.   The slope of the
linearly increasing portion of the curve is
identical with that of L in Fig. 1; this
finding suggests that the excess of L does
no longer participate in the formation of
such a complex as ML_2A.   It may be noted
that caesium shows a slightly different
behavior when L is added in excess.

The 1 : 1 stoichiometry of the complex
ion-pairs (MLA) was also confirmed by means
of conductometric titrations (Fig. 3).   From
the curvature at the equivalence point in Fig.
3 it can be seen that three times as much L
as M^+ is sufficient to complete the complexa-
tion: $M^+ + L = ML^+$, and hence the conductance
measurements for obtaining the dissociation
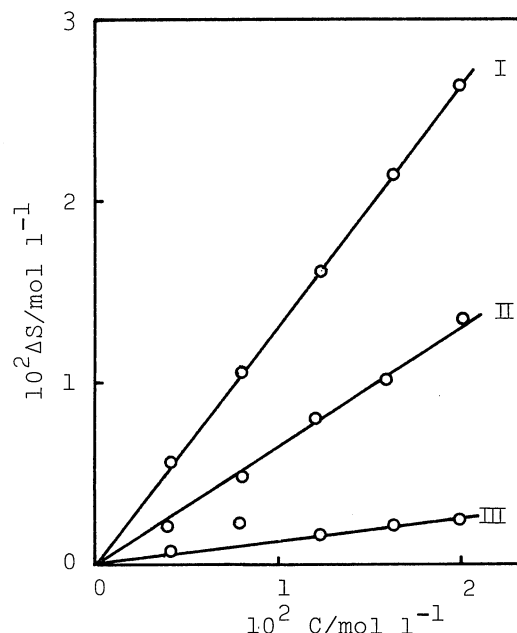constant, K_d, of MLA were carried out under

Fig. 1.   Coextraction of water.
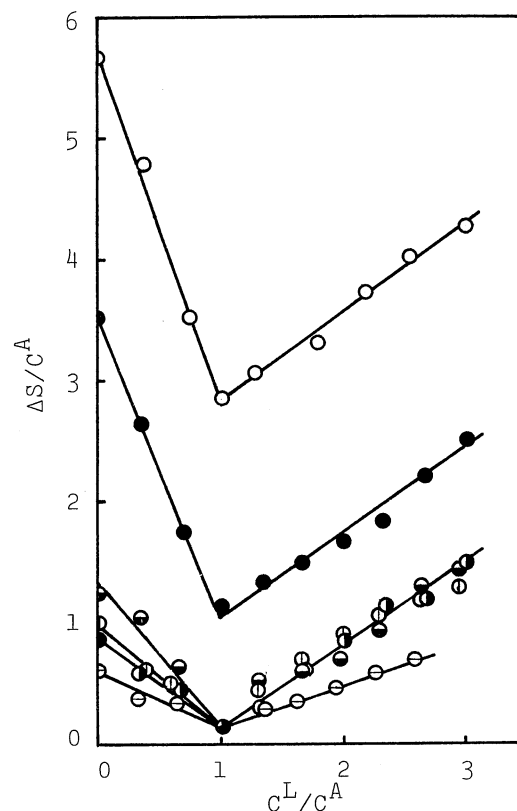I: KA, II : L, III: KA + equiv. L

Fig. 2.   Effect of L on the coex-
traction of water.
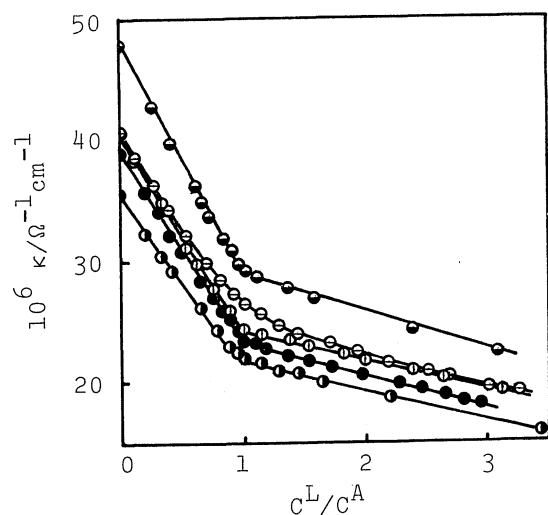O : LiA, ●: NaA, ◐ : KA, ◑ : RbA
◒ : CsA, ⊕: NH_4A

Fig. 3. Plot of specific conductance, κ, vs. c^L/c^A.
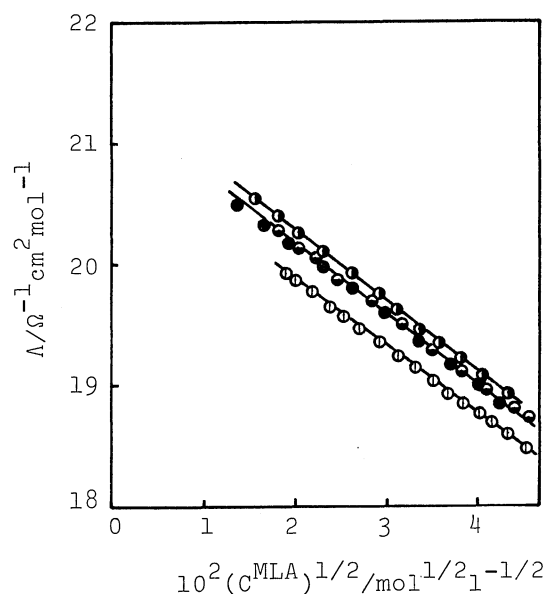For indications, see Fig. 2.

Fig. 4. Equivalent conductivity of MLA.
For indications, see Fig. 2.

the conditions as $c^L/c^A = 3$. A plot of equivalent conductivity, Λ, vs. the square root of the concentration of MLA gives a straight line in the concentration range about 4×10^{-4} to 20×10^{-4} M, as is shown in Fig. 4. The values of K_d calculated by the method of Shedlovsky[7] are shown in Table 1. The words 'dry' and 'wet' in Table 1 refer to nitrobenzene solutions containing water at concentrations of less than 300 and about 2000 μg/ml respectively. A difference in the ionic diameter of M^+ is scarcely reflected in the magnitude of the limiting equivalent conductivities, Λ°, of MLA in both the dry and wet solutions, indicating that the complex cations to be tested are almost equal in size, as can be expected from the above-mentioned structure of ML^+. The limiting equivalent conductivity of A^-, $\lambda^\circ(A^-)$, at 25°C in nitrobenzene can be computed as $\lambda^\circ_- = \Lambda^\circ - \lambda^\circ_+$ by using the data for Λ° for salts and λ°_+ for the constituent cations. Two pairs

Table 1. Dependence of the Hydration of MLA on Λ° and K_d

MLA	$\Lambda^\circ / \Omega^{-1} cm^2 mol^{-1}$		$K_d/mol\ l^{-1}$		waters per		h[a]
	dry	wet	dry	wet	MA	MLA	
Li^+					5.6	2.9	4.25
Na^+	21.4	21.9	10	14	3.5	1.2	2.9
K^+	21.4	21.7	7	8	1.3	0.1	1.2
Rb^+	21.5	21.8	8	7	0.9	0.1	0.5
Cs^+					0.6	0.1	0.1
NH_4^+	21.1	21.5	5	11	1.1	0.1	1.05

a) The hydration number of M^+ in aq. soln., Ref. 10.

of the data are available: $\Lambda°(KA) = 29.7$,[8] $\lambda°(K^+) = 17.8$[9] and $\Lambda°(NH_4A) = 30.1$, $\lambda°(NH_4^+) = 18.4$.[9] The $\lambda°(A^-)$ value thus obtained is on the average 11.8. The values of $\lambda°(ML^+)$ can then be calculated to be 9.3 - 9.7 from the corresponding $\Lambda°$ values listed in Table 1. The fact that the values of $\lambda°(ML^+)$ are much smaller than those of $\lambda°(M^+)$ shows that ML^+ is much bulkier than M^+ in nitrobenzene.

The K_d values of MA and MLA in Table 1 shows that they are almost fully dissociated in the organic phase regardless of the presence or obsence of water. Therefore, if A^- is assumed to be not hydrated, the number of water molecules associated with MA or MLA can be identical with the hydration number of M^+ or ML^+; the existence of hydrated M^+ in nitrobenzene has been confirmed by the shift of PMR spectra.[1] Cation hydration can also be seen from the fact that the dissociation of MA in nitrobenzene is greatly affected by the presence of water (e.g., $K_d(KA) = 32.65$[8] in the dry solution; $K_d(KA) = 10.32$[8] in the wet solution), while as shown in Table 1 those for MLA are not. It is noticeable that the hydration numbers of M^+ in the organic (the 6th column) and aqueous phases (the last column in Table 1) are similar in magnitude.[10]

As can be seen from the structure of L, the formation of ML^+ does not require stripping of entire hydration shell of M^+. Hence, water molecules attached to M^+ in the direction perpendicular to the plane of the ring of L may be left unstripped on complexation. It can be expected that the effect of the complexation on the change in hydration number is much obvious for highly hydrated cations such as lithium or sodium cations.

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