THE COEXTRACTION OF WATER INTO NITROBENZENE WITH ALKALINE
EARTH METAL 2,2',4,4',6,6'-HEXANITRODIPHENYLAMINATES
IN THE PRESENCE OF CROWN ETHERS

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The number of water molecules attached to alkaline earth metal
cations (M^{2+}: Ca^{2+}, Sr^{2+}, and Ba^{2+}), some crown ethers (L), and the
1:1 metal-crown complexes (ML^{2+}) extracted into nitrobenzene with
hexanitrodiphenylamine was determined by the Karl-Fischer method.
Ca^{2+}, Sr^{2+}, and Ba^{2+} have 13.0, 12.1, and 10.5 water molecules in
nitrobenzene respectively, and 6 to 8 water molecules are released
on complexation with the crown ethers.

In previous papers[1,2] it was shown that when alkali and alkaline earth metal
2,2',4,4',6,6'-hexanitrodiphenylaminates in aqueous solution are extracted into
nitrobenzene, the water molecules associated with them are transferred to the
organic phase, and the number of water molecules associated with the alkali metal
aminates in the organic phase is decreased by the equimolar addition of dibenzo-
18-crown-6. Crown ethers are known to combine stoichiometrically with a number
of cations forming primarily 1:1 metal-crown complexes, in which the metal ion
is located in the cavity of the polyether ring. However, depending on the
relative size of the cavity and the metal ion, the 1:2 and 2:3 complexes are
formed. The 'metal in the hole' picture of the 1:1 complexes suggests that the
number of water molecules associated with the cation is directly affected by
crown parameters such as cavity size, donor atom number and type, and ring sub-
stituent. The crowns used in this investigation were 15-crown-5 (15C5), 18-crown-
6 (18C6), dibenzo-18-crown-6 (DB18C6), cyclic diamine (CDA) as
shown in Fig. 1, and dibenzo-24-crown-8 (DB24C8).

15C5, 18C6, and DB24C8 were obtained from Nisso Co.,
Ltd. The first two crowns were used without further
purification. The DB24C8 was recrystallized repeatedly
from chloroform and then ethanol. DB18C6 was synthe-
sized and purified by the method of Pedersen.[3]   CDA
was obtained from 3,6-dioxa-1,8-octanediamine and
4,5-benzo-3,6-dioxaoct-4-ene-dioyl dichloride by the
method of Dietrich et al.[4]; the product obtained was
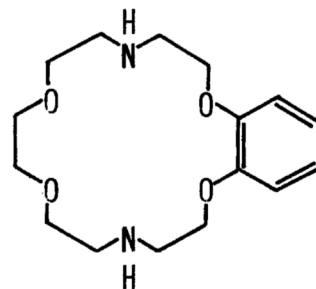recrystallized from 4-methyl-2-pentanone. The CDA was

Fig. 1.   CDA.

found to be monohydrate by measuring the weight loss on heating.   Alkaline earth
metal hexanitrodiphenylaminates (MA_2: $CaA_2 \cdot 11H_2O$, $SrA_2 \cdot 4H_2O$, and $BaA_2 \cdot 4H_2O$) were
prepared from commercial hexanitrodiphenylamine.

A nitrobenzene solution containing any one of MA_2 (5×10^{-3} M[*]) and of L
(up to 1.5×10^{-2} M) was shaken with an equal volume (20 cm^3) of an aqueous alka-
line earth metal solution (pH = 12; ionic strength I = 0.1 with MCl_2 and $M(OH)_2$)
for an hour at $(25 \pm 0.01)°C$ in a water bath incubator.   The water content in
the organic phase was determined by use of a Mitsubishi Kasei CA-1 Karl-Fischer
titrator.   The total concentration of the alkaline earth metal in the organic
phase, $[M(t)]_o$, was calculated from the aminate concentration in the aqueous
phase (the molar absorption coefficient, ε, of the aminate: $\varepsilon = 26500$ $M^{-1}cm^{-1}$ at
425 nm).   The total concentration of the crown in the organic phase, $[L(t)]_o$, was
determined as follows.   To the aqueous phase separated, a large excess of KCl and
an excess of potassium hexanitrodiphenylaminate were added.   The resulting
potassium complex with L was then extracted into nitrobenzene completely; the
absorbance of the extract was measured at 410 nm ($\varepsilon = 28300$ $M^{-1}cm^{-1}$).   For the
case of 15C5, 1,2-dichlorobenzene was used in place of benzene ($\varepsilon = 31000$ $M^{-1}cm^{-1}$
at 415 nm), the aqueous solution to be shaken with 1,2-dichlorobenzene being
adjusted to pH = 12 and I = 0.1 with NaOH and NaCl.

Nitrobenzene dissolves 0.178 M water at 25°C.   The water content in the
organic phase increases when MA_2 or L, or both are present.   The water increment,
Δs, due to L is plotted as a function of the crown concentration in the organic
phase, $[L]_o$, in Fig. 2.   Since the quantity of ML^{2+} extracted into the organic
phase in the absence of the aminate is
found to be negligibly small compared
with that of the uncomplexed crown, the
number of water molecules associated
with a molecule of L, $h(L)$, can be
calculated from the slope of the linear
plot.   The data obtained, together
with the values of the hole diameter
and the distribution coefficients for
L between nitrobenzene and water, D(L),
are summarized in Table 1.

Table 1 shows that all the crowns
exist in the slightly hydrated from in
the organic phase.   The presence of the
benzene ring seems to decrease $h(L)$,
while it increases markedly D(L).   The
pK values of CDA indicate that the acid
dissociation of CDA can be neglected at
pH = 12.

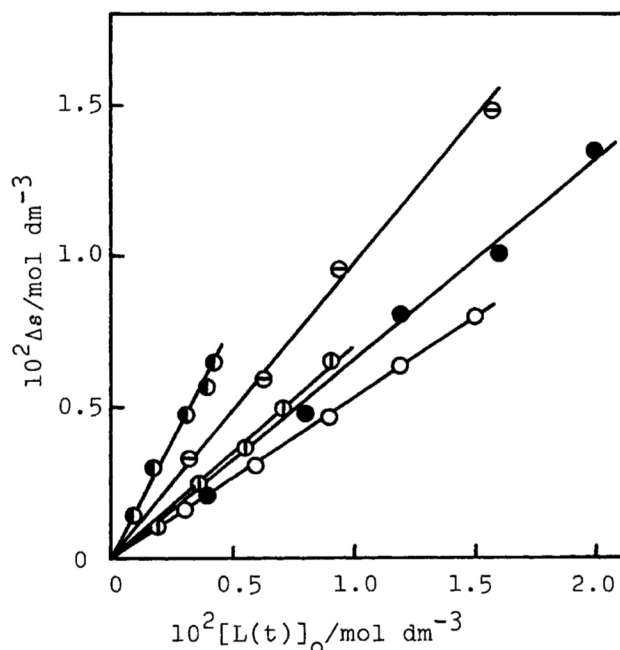Fig. 2.   Coextraction of water.
    ◐: 15C5,   ◑: 18C6,   ●: DB18C6
    ⊖: CDA,   ○: DB24C8.

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[*] 1 M = 1 mol dm^{-3}

The $\Delta s/[M(t)]_o$ values at $[L(t)]_o/[M(t)]_o = 0$ in Fig. 3 are identical with the number of water molecules associated with MA_2. Assuming that the aminate ion (A^-) is unhydrated in the organic phase, we obtained the hydration numbers for the cations in Table 2. The first decreasing-portions of the curves in Fig. 3 indicate that the quantity of ML^{2+} carrying less water molecules than M^{2+} is increased by the addition of L. When one equivalent of L is added to the extraction system, the complexation between L and M^{2+} proceeds quantitatively: $M^{2+} + L \rightleftharpoons ML^{2+}$. The completion of the reaction can be ascertained by the fact that the aqueous phase becomes colorless at the equivalence point. The second line-portions ($1 < [L(t)]_o/[M(t)]_o < 2$) indicate that ML^{2+} undergoes further complexation: $ML^{2+} + L \rightleftharpoons ML_2^{2+}$. On the other hand, when MA in nitrobenzene (5×10^{-3} M) is titrated with L in nitrobenzene (1.5×10^{-2} M), the conductivity of the resulting solution as measured by specific conductance, κ, decreases with an increase in the crown concentration as shown in Fig. 4. The slope of each line in Fig. 4 changes sharply at the first equivalence point except the case for Ba^{2+}- 15C5, while it does less sharply at the second equivalence point. It is clear from this finding that ML_2^{2+} is less stable than ML^{2+}. The fact that the slopes of the third line-portions in Fig. 3 are virtually the same as those obtained with the uncomplexed crowns (Fig. 2) indicates that no ML_2^{2+} undergoes further complexation. The absence of a knickpoint at the third equivalence point in Fig. 4 leads to the same conclusion.

Table 2 shows that the hydration numbers for the uncomplexed cations, $h(M^{2+})$, are 10.5 to 13.0 and more than one-half of the water molecules are released on complexation. The $h(M^{2+})$ values decrease in going from Ca^{2+} to Ba^{2+}.

Table 1.   Hydration numbers of crowns, $h(L)$

Crown	Hole diameter[a] (nm)	$h(L)$	$D(L)$
15C5	0.17 − 0.22	0.7	0.22
18C6		1.6	0.10
DB18C6	0.26 − 0.32	0.6[b]	2.3×10^4
CDA[c]		1.0	7
DB24C8	>0.4	0.5	$\sim 10^4$

a) From ref. 5.   b) From ref. 2.   c) $pK_1 = 7.9$, $pK_2 = 8.7$ (pH measurements).
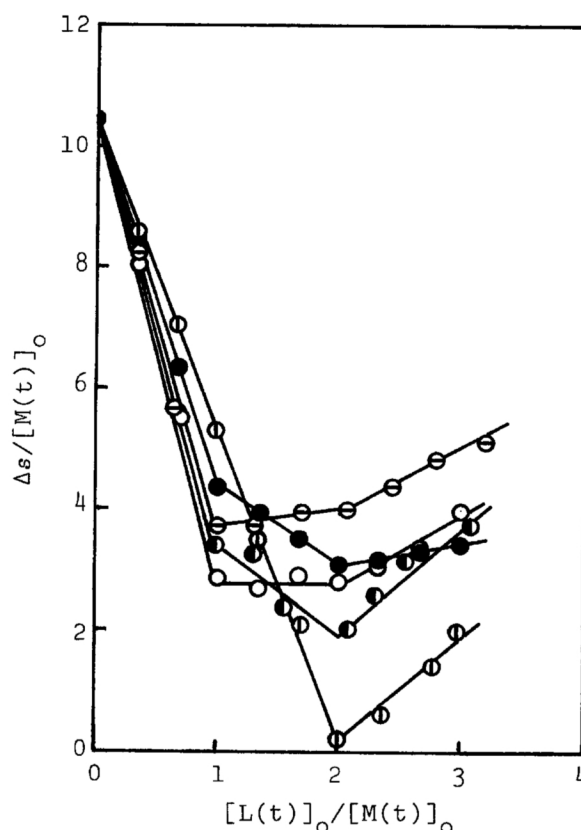

Fig. 3.   Effect of L on the coextraction of water. For indications, see Fig. 2.

Table 2. Hydration numbers of ML^{2+}, $h(ML^{2+})$

Crown	Cation		
	Ca^{2+} 0.198[a]	Sr^{2+} 0.226[a]	Ba^{2+} 0.270[a]
None	13.0	12.1	10.5
15C5	5.3	0.4[b]	0.2[b]
18C6	4.7	4.6	3.4
DB18C6	5.1	4.9	4.4
CDA	4.8	4.3	3.7
DB24C8	5.3	4.1	2.9

a) Ionic diameter (nm). b) Values of 1:2 metal-crown complexes.

This sequence is not altered by the equimolar addition of L. 15C5 does not appear to form the 1:1 complexes with Sr^{2+} and Ba^{2+}. A primary reason for this is that these cations are too large to fit into the molecular hole of 15C5 and hence for these complexes

Fig. 4. Conductometric titration. For indications, see Fig. 2.

a sandwich-type structure,[5] in which the metal ion is located between two crowns, is more stable than a 'metal in the hole' structure. It is noted that the number of released water molecules, which is given by the difference between $h(M^{2+})$ and $h(ML^{2+})$ or $h(ML_2^{2+})$, is almost equal to the number of the donor atoms of the crown used, as can be seen from the cases with $Ca(DB24C8)^{2+}$, $Sr(DB24C8)^{2+}$, $Ba(DB24C8)^{2+}$, $Ba(DB18C6)^{2+}$, and $Ba(15C5)_2^{2+}$. In the other cases, one or two additional water molecules are released on complexation.
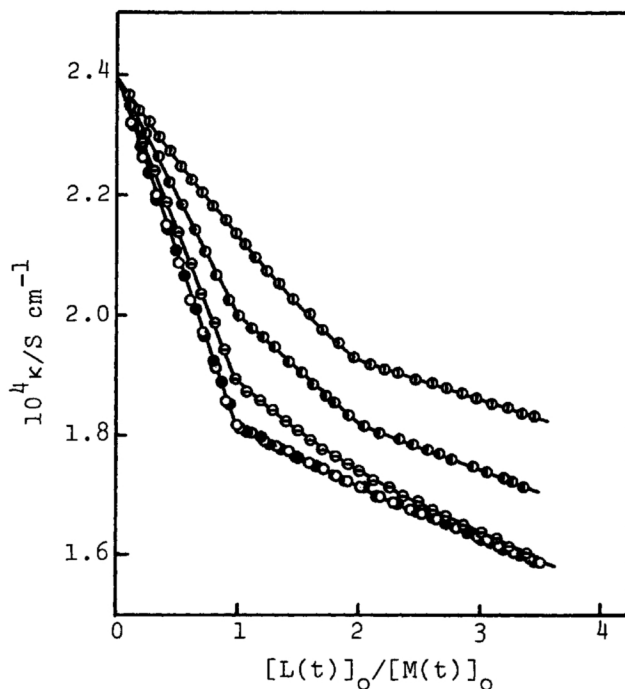
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