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New Application of Crown Ether. V.[1] The Effect of Crown Ethers on the Acid-Base Interaction between 2,4,4′,6-Tetranitrodiphenylamine and Primary Amines in Benzene

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The effect of crown ethers on the acid-base interaction of 2,4,4′,6-tetranitrodiphenylamine (HA, λ_{max} 380 nm, $pK_a=8.88$ in water) with primary amines (RNH_2) in benzene was investigated spectrophotometrically. Crown ethers assisted strongly the formation of association complexes, $R\overset{+}{N}H_3\cdot$crown ether$\cdot A^-$, which existed as a single chemical species (λ_{max} 478 nm) assignable to "crown ether-separated ion pair." The effect of the steric factors of various primary amines on the equilibrium to form the association complex was discussed on the basis of the equilibrium constants and thermodynamic parameters of the systems involving 18-crown-6 and benzo-18-crown-6.

Macrocyclic polyethers (crown ethers) form stable complexes with mono-alkylammonium salts as well as alkali and alkaline earth metal salts. Structural effect of crown ethers on the ion-association extraction of an alkylammonium salt as crown ether complexes was investigated in detail by Cram and his collaborators[2] for $t\text{-}Bu\overset{+}{N}H_3\cdot\overset{-}{SCN}$, but structural effect of alkylamine moiety has not yet been studied. It is known that the formation of the crown ether complexes is dependent not only on the structure of crown ether itself, but also on the nature of the anion involved in the association complexes extracted in a non-polar solvent. In the case of the alkylammonium complexes, steric interactions between the substituent on the alkylamines and the crown ethers are presumed to be an important factor to affect the extent of the formation of the association complexes.

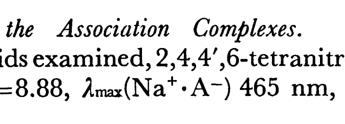
We recently showed that alkylamine–water–crown ether systems could be used as an effective hydroxide ion source in the reduction of unsaturated carbonyl compounds by hydridocarbonylferrate in a two-phase system (benzene–water).[3] The efficiency of the reduction was dependent not only on the nature of the crown ether added but also on the structure of the alkylamines.

The circumstances prompted us to study the association equilibrium between a weak acid and primary amines in a non-polar solvent (benzene) in the presence of crown ethers. Variation of the extent of the equilibrium (Eq. 1) with the structure of the amines and crown ethers (18-crown-6 and benzo-18-crown-6) is discussed in a quantitative manner in this paper.

$$\underset{\mathbf{1}}{HA} + RNH_2 + CR \overset{K}{\rightleftarrows} \underset{\mathbf{2}}{R\overset{+}{N}H_3\cdot CR\cdot A^-} \qquad (1)$$

CR: crown ether

HA:



Results and Discussion

Structure of the Association Complexes. Among several weak acids examined, 2,4,4′,6-tetranitrodiphenylamine (**1**; $pK_a=8.88$, $\lambda_{max}(Na^+\cdot A^-)$ 465 nm, ε_{max} 23800 in water[4]) was proved to be a suitable probe for spectroscopic study of the equilibrium. The acid (**1**) showed a strong absorption maximum at 380 nm in benzene. The reaction of **1** with RNH_2 to form $R\overset{+}{N}H_3\cdot A^-$ lies so far to the starting materials in a non-polar solvent such as benzene. Thus, the absorption spectra did not change even in the presence of excess amount of n-$BuNH_2$ (n-$BuNH_2$/**1**=10—500). When 18-crown-6 (18C6) was added to the benzene solution of **1** and n-$BuNH_2$ a strong bathochromic shift of the absorption maximum from 380 to 478 nm was observed (Fig. 1). The presence of an isosbestic point at 412.5 nm indicated that a single chemical species was formed by the addition of the crown ether. The increase in the intensity of the band at 478 nm ceased when the ratio of the crown ether to **1** reached around 1500 at 26.6 °C (150 at 6 °C) as shown in Fig. 1. Addition of an equimolar amount of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene, a strong organic base) to a benzene solution of **1** produced a bathochromic shift of the absorption (380 nm) to 455

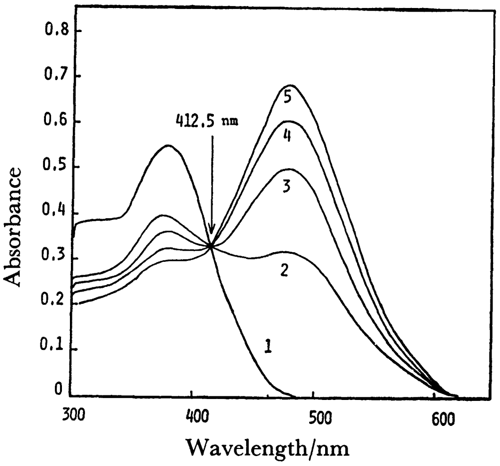


Fig. 1. UV spectra of $BuNH_2$–HA–18C6 system.

		A^-(mol %)
1	HA : 18C6 = 1 : 0	0
2	HA : 18C6 = 1 : 6.5	28
3	HA : 18C6 = 1 : 13	44
4	HA : 18C6 = 1 : 19	53
5	HA : 18C6 = 1 : 26	61

$HA=3.3\times10^{-5}$ mol/dm³, $BuNH_2=8.25\times10^{-4}$ mol/dm³, temp 26.6 °C.

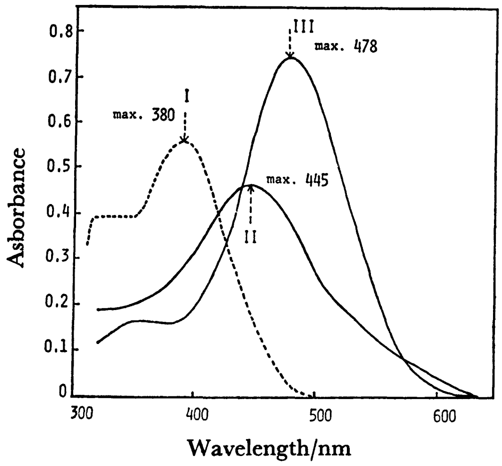


Fig. 2. UV spectra of crown ether complexes.
I: HA, II: Na^+A^--B15C5, III: $\overset{+}{RNH_3}$-A^--18C6.

Table 1. Efficiency of crown ethers for the formation of the ammonium ion complexes

Crown ether[b)]	Crown ether/HA[a)]		
	n-BuNH$_2$	s-BuNH$_2$	t-BuNH$_2$
18C6	4	13	18
DC18C6 (*cis-syn-cis*)	15	105	450
DC18C6 (*cis-anti-cis*)	105	635	1400
B15C5	4800[c)]	10000[c)]	14000[c)]
B18C6	170	306	194

a) The amount of crown ether (in molar ratio to HA) necessary to reach equal concentration of HA (380 nm) and A^- (478 nm). HA$=1.09\times10^{-4}$ mol/dm^3, RNH$_2=5.5\times10^{-3}$ mol/dm^3, Temp 27.3 °C.
b) C: crown, DC: perhydrodibenzo, B: benzo.
c) Those to reach [A]/[HA]$=1/9$.

nm in the absence of the crown ether, and the absorption maximum moved up to 478 nm by further addition of DBU ($\approx$100 fold excess). The latter bathochromic shift can be accounted for on the basis of the change in the structure of the resulting acid–base association complex, *i.e.* the change from a contact ion pair to a solvent-separated ion pair. It is to be noted that in n-BuNH$_2$–**1**–18C6 system, the position of the absorption maximum did not materially change with the variation of amine/**1** ratio from 10 to 500. The behavior of the crown ether complex of the alkylamine as well as that of the DBU-complex are noticeably compared with the observation that the absorption of $Na^+\cdot A^-$–benzo-15-crown-5 complex in benzene at 445 nm (Fig. 2) showed very little shift on further addition of B15C5 ($\approx$50 fold excess). From these observations, it could be reasonably concluded that the ionic species with the absorption at 445 nm (and 455 nm for the DBU–**1** system) and the one absorbing at 478 nm are assigned to the contact ion pair and the crown ether-separated ion pair (or solvent-separated ion pair), respectively. Other crown ethers included in Table 1 as well as a bis(benzocrown ether), 1,7-bis[3,4-(1,4,7,10,13-pentaoxatridecane-1,13-diyl)phenyl]-1,4,7-trioxaheptane,[5)] showed the behavior same as 18C6 forming complexes with an absorption maximum at 478 nm. It is to be added incidentally that in the absence of a crown ether the addition of a large amount of alkylamine (RNH$_2$/**1**$\approx$1000) to the benzene solution of **1** caused a slow displacement of p-nitroanilino group in **1** by the amine giving N-alkylpicrylamine, which was characterized by the appearance of new absorptions at 338 and 417 nm.

Effect of the Structures of Alkylamines and Crown Ethers. Table 1 shows a qualitative comparison of the extent of the formation of the butylammonium ion complexes (**2**), where the values represent the amounts of a crown ether (molar basis) being necessary to reach to [**2**]/[**1**]$=$ 1 (for B15C5 see footnote in the Table). In line with the previous results,[2)] 18C6 entered into the formation of the association complexes to a large extent, and B15C5 was much less efficient. With most of the crown ethers the increase in steric bulk of the alkyl group of

Table 2. Equilibrium constants in RNH$_2$–HA–crown ether system in benzene

Temp °C	RNH$_2$ R–	K (mol^{-2} dm^6)		
		18C6	B18C6	AB18C6[a)]
6.0	n-Bu	$(5.66\pm0.09)\times10^7$	$(2.28\pm0.09)\times10^6$	
	s-Bu	$(1.50\pm0.02)\times10^7$	$(1.28\pm0.01)\times10^6$	
	t-Bu	$(9.47\pm0.10)\times10^6$	$(1.92\pm0.02)\times10^6$	
26.6	n-Pr	$(2.29\pm0.07)\times10^6$	$(1.22\pm0.01)\times10^5$	
	i-Pr	$(1.64\pm0.05)\times10^6$	$(1.44\pm0.03)\times10^5$	
	n-Bu	$(2.31\pm0.10)\times10^6$	$(1.52\pm0.03)\times10^5$	$(6.16\pm0.20)\times10^4$
	s-Bu	$(7.01\pm0.13)\times10^5$	$(7.56\pm0.14)\times10^4$	$(3.56\pm0.07)\times10^4$
	t-Bu	$(4.59\pm0.14)\times10^5$	$(9.99\pm0.30)\times10^4$	$(4.74\pm0.25)\times10^4$
	Pentyl	$(2.30\pm0.06)\times10^6$	$(1.75\pm0.01)\times10^5$	
	1-Methylbutyl	$(8.09\pm0.19)\times10^5$	$(8.36\pm0.22)\times10^4$	
	1-Ethylpropyl	$(8.44\pm0.07)\times10^4$	$(9.65\pm0.60)\times10^3$	
	t-Pentyl	$(2.22\pm0.20)\times10^5$	$(4.54\pm0.61)\times10^4$	
35.0	n-Bu	$(9.76\pm0.08)\times10^5$	$(5.98\pm0.22)\times10^4$	
	s-Bu	$(3.06\pm0.04)\times10^5$	$(3.13\pm0.01)\times10^4$	
	t-Bu	$(1.99\pm0.04)\times10^5$	$(4.18\pm0.05)\times10^4$	

a) 4′-Acetylbenzo-18-crown-6.

TABLE 3. COMPARISON OF EQUILIBRIUM CONSTANTS (K/K_0) ON THE BASIS OF FRAMEWORK OF AMINES

Amine R–	K/K_0[a)]	
	18C6	B18C6
C–C–C–	0.99$_1$	0.052$_8$
C–C–C–C–	1.00	0.065$_8$
C–C–C–C–C–	0.99$_6$	0.075$_8$
C–C–C–	0.99$_1$	0.052$_8$
C–C–C– | C	0.30$_3$	0.032$_7$
C | C–C–C– | C	0.096$_1$	0.019$_7$
C–C–C– | C | C	0.036$_5$	0.004$_2$
C–C–C–	0.99$_1$	0.052$_8$
C–C– | C	0.71$_0$	0.062$_3$
C | C–C– | C	0.19$_9$	0.043$_2$

a) K_0 is the equilibrium constant of 18C6– *n*-BuNH$_2$ system at 26.6 °C.

the amines depressed the formation of the complex, but benzo-18-crown-6 (B18C6) showed an irregular order of the efficacy as *n*-BuNH$_2$>*t*-BuNH$_2$>*s*-BuNH$_2$. In order to inquire the factors which are related to the discrepancy, equilibrium constants for Eq. 1 were determined for various alkylamines with the use of 18C6 and B18C6, and the results are summarized in Table 2. Table 3 shows the relative ratios of the equilibrium constants at 26.6 °C which are derived by taking the 18C6–*n*-BuNH$_2$ system as a reference. The values for normal alkylamine–18C6 system were almost invariant with the chain length of the amines, while those in the B18C6 system showed some increase with the increase of the alkyl chain. A noticeable difference between the two systems was observed in the effect of α-alkyl substitution of the amines. The decrease of the ratio by the introduction of methyl group(s) was clearly smaller in the B18C6 system than in that of 18C6 as seen in the set involving *n*-PrNH$_2$, *i*-PrNH$_2$, and *t*-BuNH$_2$. The presence of α-ethyl group, however, caused larger steric effect in both systems, as is observed in the case of 3-aminopentane.

Thermodynamic parameters of the equilibrium in 18C6- and B18C6-*n*-BuNH$_2$ systems in benzene at 26.6 °C are shown in Table 4. The entropy change in the 18C6 system are almost constant ($\Delta S = -2.12$—-2.16×10^2 J/K mol), and the enthalpy term seems to mainly determine the extent of the complex formation decreasing in the order : *n*-BuNH$_2$>*s*-BuNH$_2$>*t*-BuNH$_2$. In the system of B18C6, however, the change of the two terms occurs in an opposite manner with the increase of the steric bulk of the amines to yield the orders, *t*-BuNH$_2$>*s*-BuNH$_2$>*n*-BuNH$_2$ for the enthalpy term and *n*-BuNH$_2$>*s*-BuNH$_2$>*t*-BuNH$_2$ for the entropy term, respectively. Thus, a subtle balance of the two terms would lead to the unexpected order of the stability among the alkylammonium complexes of B18C6 and also of 4′-acetylbenzo-18-crown-6, though the origin for the specificity of the B18C6 systems is not clear at present.

TABLE 4. THERMODYNAMIC PROPERTIES OF BUTYLAMINE–HA–CROWN SYSTEM[a)]

Crown	BuNH$_2$	$-\Delta G$ kJ/mol	$-\Delta H$ kJ/mol	$-\Delta S$ kJ/mol
18C6	*n*-	36.5	102	216
	s-	33.5	97.5	213
	t-	32.5	96.7	212
B18C6	*n*-	29.7	90.2	201
	s-	28.0	92.4	213
	t-	28.7	95.6	222

a) ΔG, ΔH, and ΔS at 26.6 °C.

Thermodynamic parameters for the complex-forming equilibria between crown ethers and various metal or ammonium salts have been reported mainly in a protic or a dipolar medium such as DMF. The entropy terms obtained[6)] vary widely depending on the nature of the salts and crown ethers as well as the medium, but scarcely exceed −20 e.u. for the systems utilizing the crown ethers bearing 15- or 18-ring. The large loss of entropy (around -2.1×10^2 J/K mol or −50 e.u.) in the present equilibrium system suggests that several molecules of the medium, excess alkylamine (and/or benzene), are interacting with the alkylammonium complexes, in view of the result[7)] that in the equilibrium of Eq. 2 in chloroform the entropy term much decreases from −23 to −40 e.u. by replacement of the crown ether with diglyme.

$$\text{HBr} + \text{Br}_2 + \text{di-Br-DBC} \rightleftarrows \text{H}^+\cdot(\text{di-Br-DBC})\cdot\text{Br}_3^- \quad (2)$$

di-Br-DBC: 4,4′-dibromodibenzo-18-crown-6

Experimental

Materials. All crown ethers used were prepared according to the conventional methods;[8)] 18C6: mp 39.9—40.2 °C, B18C6: mp 44.1—44.5 °C, 4′-acetylbenzo-18-crown-6: mp 77.9—78.2 °C,[5)] and B15C5: mp 80.8—81.7 °C.

2,4,4′,6-Tetranitrodiphenylamine (HA, **1**) was prepared by the reaction of picryl chloride and *p*-nitroaniline in ethanol in the presence of sodium carbonate, and then recrystallized from ethanol (three times); yellow needles, mp 222.8—224.2 °C (uncorrected) (lit, 219 °C,[9)] 220—220.6 °C[10)]), Found: C, 41.20; H, 2.03; N, 19.98%. Calcd for $C_{12}H_7N_5O_8$: C, 41.27; H, 2.02; N, 20.06%. 1-Methylbutylamine and 1-ethylpropylamine were prepared by the methods described in the literature,[11)] and other alkylamines (RNH$_2$) were of reagent grade. These amines were distilled over KOH and stored under nitrogen atmosphere prior to use. Benzene was dried over sodium metal and distilled under nitrogen atmosphere before use.

The complex of B15C5 with $\text{Na}^+\cdot\text{A}^-$ was prepared by the addition of a methanol solution of the crown ether to $\text{Na}^+\cdot\text{A}^-$ in methanol.

Absorption Spectra. The electronic spectra of the solutions were recorded on a Shimadzu UV-200 spectrophotometer over a temperature range from 6.0 to 35.0 °C (±0.1 °C).

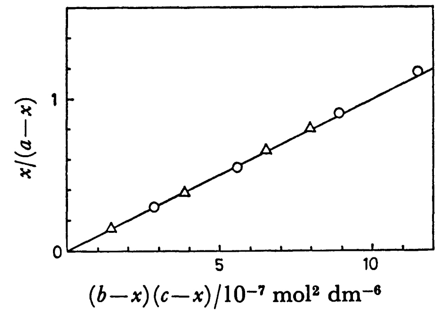


Fig. 3. Determination of formation constant according to Eq. 4.
○: [n-BuNH$_2$]/[HA]=25, [HA]=3×10^{-5} M (M=mol·dm^{-3}), [18C6]/[HA]=11—75 at 35.0 °C.
△: [18C6]/[HA]=1.8, [HA]=5×10^{-5} M, [n-BuNH$_2$]/[HA]=33—266 at 35.0 °C.
Both systems gave the same formation constant (K=(0.976±0.08)×10^4 M^{-2}) within the experimental error.

A quartz cell with a silicone rubber stopper was used in all determinations. A constant temperature of ±0.1 °C was maintained by circulating water from a thermostated bath. The temperature inside the cell compartment was monitored with a thermocouple. In benzene solution, the absorption maxima and absorption coefficients of **1** and $Na^+ \cdot A^-$–B15C5 were 380 nm (ε_{max}: 1.64×10^4) and 445 nm (ε_{max}: 1.72×10^4), respectively. The absorption maxima and absorption coefficient of crown separated ion pair, $R\overset{+}{N}H_3 \cdot CR \cdot A^-$, in benzene were obtained from the RNH$_2$–**1**–18C6 system containing such amount of the crown ether that the absorbance of the system did not increase by its further addition. Concentration change of **1** was corrected. The resulting absorption coefficient for n-BuNH$_2$– and n-pentylamine–**1**–18C6 (and B18C6) systems was the same value (λ_{max}: 478 nm, ε_{max}: 3.41×10^4). The conductance of these solutions was negligible.

Calculations. The formation constants of the complexes were calculated from the measured concentration of $R\overset{+}{N}H_3 \cdot CR \cdot A^-$ by considering the following equilibrium.

$$\underset{(a-x)}{HA} + \underset{(b-x)}{CR} + \underset{(c-x)}{RNH_2} \overset{K}{\rightleftharpoons} \underset{x}{R\overset{+}{N}H_3 \cdot CR \cdot A^-} \tag{3}$$

CR : A crown ether
a, b, and c : Initial concentrations of **1**, CR, and RNH$_2$, respectively.
K : Formation constant

The constant K may be represented by

$$K = x/(a-x)(b-x)(c-x) = \frac{d-d_{HA}}{d_A-d} \times \frac{1}{\left(b-\frac{d-d_{HA}}{\varepsilon_A-\varepsilon_{HA}}\right)\left(c-\frac{d-d_{HA}}{\varepsilon_A-\varepsilon_{HA}}\right)}, \tag{4}$$

where the symbols have the following significance, x: the fraction of ionized HA, ε_{HA}, and ε_A: the absorption coefficients of HA and $R\overset{+}{N}H_3 \cdot CR \cdot A^-$ at 478 nm, respectively; $d_{HA}=a \cdot \varepsilon_{HA}$ and $d_A=a \cdot \varepsilon_A$. On the basis of the absorbance at 478 nm (=d) concentrations of HA and $R\overset{+}{N}H_3 \cdot CR \cdot A^-$ are given by $x=(d-d_{HA})(\varepsilon_A-\varepsilon_{HA})^{-1}$ and $(a-x)=(d-d_A)(\varepsilon_{HA}-\varepsilon_A)^{-1}$. Substitution of the values of x and $(a-x)$ into Eq. 4 leads to Eq. 5.

$$\frac{d-d_{HA}}{d_A-d} = K \cdot \left(b-\frac{d-d_{HA}}{\varepsilon_A-\varepsilon_{HA}}\right) \cdot \left(c-\frac{d-d_{HA}}{\varepsilon_A-\varepsilon_{HA}}\right) \tag{5}$$

A plot of $(d-d_{HA})(d_A-d)^{-1}$ *vs.* $[b-(d-d_{HA})(\varepsilon_A-\varepsilon_{HA})^{-1}] \times [c-(d-d_{HA}) \times (\varepsilon_A-\varepsilon_{HA})^{-1}]$ gives a straight line, and hence K can be obtained from its slope. Figure 3 shows the validity of this method. Initial concentrations of HA and RNH$_2$ used were 3×10^{-5} and 7.5×10^{-4} mol/dm^3, respectively.

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