THE EFFECT OF COUNTERION ON ALKALI ION-CROWN COMPLEX FORMATION: A NEAR-PARADOX IN DISSOCIATING SOLVENTS*

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Contrary to the widespread belief that counterion influences stability of charged complexes only in poorly solvating media, a dramatic effect of anion was discovered, ebulliometrically, in 0·6 molal M^+X^-—C_2H_5OH (M = K, Na, Li; X = SCN, OC_2H_5) and in 0·6 molal M^+X^-—H_2O (M = K; X = SCN, OH) solution upon complexing with 18-crown-6,15-crown-5 and 12-crown-4. Out of the nine crown–MSCN combinations examined in the ethanolic solution, seven yielded 1 : 1 (18-crown-6–KSCN; 18-crown-6–NaSCN, 15-crown-5–NaSCN, 15-crown-5–LiSCN, 12-crown-4–KSCN) or 2 : 1 (15-crown-5–KSCN, 12-crown-4–NaSCN) complexes quantitatively, whereas the corresponding crown–MOC_2H_5 combinations did not complex at all or the complexation was very incomplete. An analogous situation was found in the aqueous solution, with KSCN complexing 18-crown-6 quantitatively or 15-crown-5 and 12-crown-4 partly, whereas KOH did not yield complexes with any of the three crowns. Evidence is presented that the observed effect of anion does not originate from ion-pairing.

Although complexation of alkali ions has been subject of immense interest[1-4] in the past decade, some important problems still await exploration. The effect of counterion is a prominent example, owing to its relevance to such fundamental processes as are ion-exchange[5,6] and ion-transport across membrane[7]. It is generally assumed that, in a homogeneous solution, the effect of counterion originates from ion-pairing. A pronounced operation of the effect is therefore predicted only in poorly solvating media. In highly solvating media, as are water or ethanol, no effect of counterion is expected[8].

At variance with the simple concept, we report in this paper evidence that stability of 18-crown-6–M^+X^-, 15-crown-5–M^+X^- and 12-crown-4–M^+X^- complexes in 0·6 molal ethanolic (M = K, Na, Li; X = SCN, OC_2H_5) as well as in 0·6 molal aqueous (M = K; X = SCN, OH) solution depends critically on the anion. At the same time we report evidence that the observed effect does not originate from ion-pairing.

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EXPERIMENTAL

Materials: The macrocyclic ligands 18-crown-6, 15-crown-5 and 12-crown-4 were prepared by standard procedure[9-11] and recrystallized from hexane (under dry-ice cooling) prior use.

Lithium thiocyanate: Ammonium thiocyanate (76·1 g; 1 mol) was dissolved in water (400 ml), treated with hydrated lithium hydroxide (42·9 g; 1 mol) under stirring and the mixture was taken to dryness on a rotatory evaporator. The residue was dissolved in ethanol, saturated with carbon dioxide and filtered through a short column of silica. The solvent was taken down in vacuo and the residue was dried by a repeated azeotropic distillation with benzene.

Ebulliometry: Performed in a quartz apparatus analogously, as we described in the preceding paper[12]. The ebulliometric constants (K_E) required for calculation of the theoretical (model system) traces were also available from the previous work.

RESULTS AND DISCUSSION

As we already pointed out in the preceding paper[12], ebulliometric titration provides a very convenient tool for investigation of alkali ion complexation with crowns, particularly in moderately concentrated (0·05 – 1·0 molal) solutions. The procedure consists of measuring changes in boiling point temperature (ΔT) induced by a gradual addition of the macrocyclic ligand to an appropriate alkali salt solution. Since ΔT is a colligative property depending only on the number of particles present in the solution, crown complex formation can be assessed simply from a comparison of the experimental ebulliometric curve with the theoretical (model system) traces calculated for various complexation modes.

Complexation of Alkali Thiocyanates and Ethoxides in Ethanol

Fig. 1 records the ebulliometric curves obtained upon addition of two equivalents of 18-crown-6 (18C6), 15-crown-5 (15C5) and 12-crown-4 (12C4) to 0·6 molal ethanolic solution of alkali thiocyanate (X = SCN), to 0·6 molal ethanolic solution of alkali ethoxide[12] ($X = OC_2H_5$), and to the neat ethanol. Together with the experimental curves are in Fig. 1 recorded the model system traces calculated for a crown dissolution (*1*) and for 1 : 1 (*2*) and 2 : 1 (*3*) complex formation.

Let us examine first the ebulliometric curves corresponding to the complexation of alkali thiocyanates. A perfect fit is found between the experimental curve and the theoretical trace *2* in 18C6–KSCN, 18C6–NaSCN and 15C5–LiSCN combinations indicating a quantitative 1 : 1 crown–alkali salt complex formation. Similarly, an excellent fit is found between the experimental curve and the theoretical trace *3* in the 15C5–KSCN and 12C4–NaSCN combinations indicating a quantitative 2 : 1 crown–alkali salt complex formation. In the 12C4–KSCN and 15C5–NaSCN combinations, the experimental curve lies between the theoretical traces *2* and *3*, suggesting a quantitative 1 : 1 complex formation, followed by an incomplete transformation into the 2 : 1 complex upon addition of the second equivalent of the crown. Thus, seven out of the total nine crown–alkali thiocyanate combinations in Fig. 1 yield either 1 : 1 or 2 : 1 complex quantitatively. An incomplete complexation is found only in the 18C6–LiSCN and 12C4–LiSCN combinations, the experimental curve being intermediate between the theoretical trace *1* and *2*.

An entirely different pattern of complexation follows from the examination of the ebulliometric curves corresponding to alkali ethoxides. A comparison with the theoretical traces *1*–*3* shows that none of the crown–alkali ethoxide combinations in Fig. 1 leads to a quantitative complex formation. Four combinations (15C5–KOC_2H_5, 12C4–KOC_2H_5, 15C5–$NaOC_2H_5$ and 12C4–$NaOC_2H_5$) yield a very incomplete complexation, whereas the remaining five indicate a complete absence of complexation, within limits of the ebulliometric detection.

A powerful effect of counterion on complexation of alkali salts is thus demonstrated in the ethanolic solution. In any of the crown-alkali salt combination examined in Fig. 1, a replacement of thiocyanate by ethoxide anion leads to a very marked weakening of the complexes. The most dramatic effect is found in the combinations that yield quantitatively 1 : 1 crown–alkali thiocyanate complexes (18C6–KX, 18C6–NaX, 15C5–LiX): in these, upon replacement of the thiocyanate by ethoxide counterion, complexation virtually disappears.

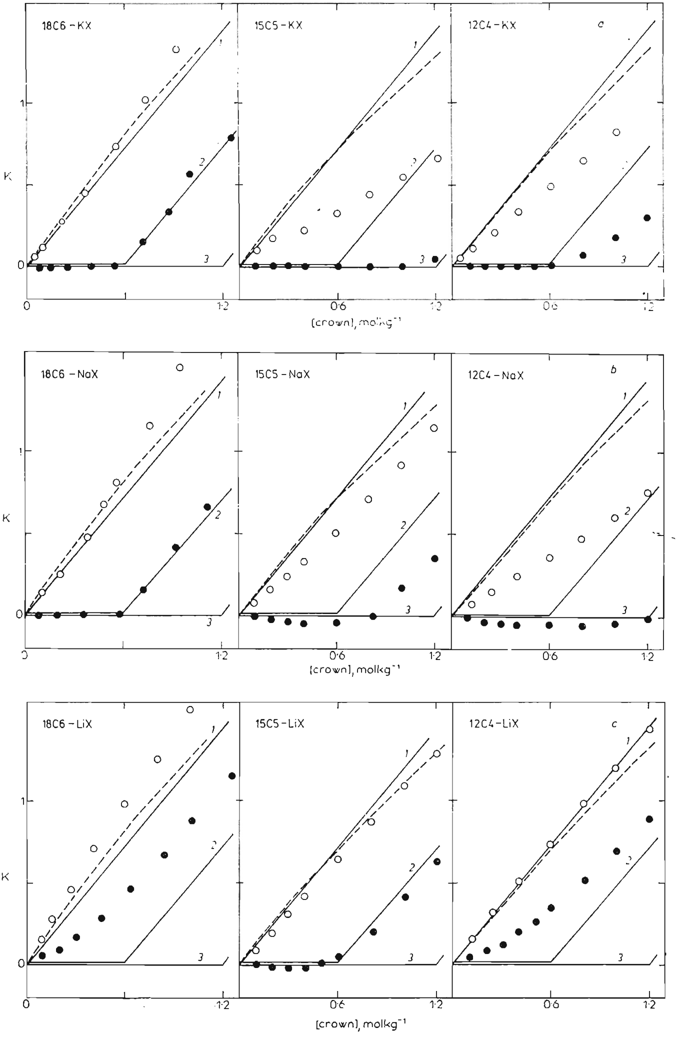
Complexation of Potassium Thiocyanate and Hydroxide in Water

Fig. 2 records the ebulliometric curves obtained upon addition of two equivalents of the macrocyclic ligand 18C6, 15C5, and 12C4 to 0·6 molal aqueous solution of potassium thiocyanate, to 0·6 molal aqueous solutions of potassium hydroxide, and to the neat water. Recorded are also the model system traces calculated for the crown dissolution (*1*) and for the 1 : 1 (*2*) and 2 : 1 (*3*) crown–alkali salt complex formation.

Examination of the ebulliometric curves in Fig. 2 shows again that complexation of the two compared salts is different. A practically complete complexation of 18C6 as well as the incomplete, but still significant, complexation of 15C5 and 12C4 crowns with potassium thiocyanate contrasts with the apparent absence of crown complexation with potassium hydroxide. It follows that a strong anion effect on crown complex stability operates also in the aqueous solution.

The Effect of Solvent on Stability and Structure of Crown Complexes

A cursory comparison between the results from Fig. 1 and Fig. 2 shows, in accord with earlier literature evidence[13,14], that crown complexes are more stable in the ethanolic than in the aqueous solutions. The difference reflects presumably the much stronger solvation of the alkali ions by water compared with ethanol, with which the macrocyclic ligand has to compete in the complex formation[13].


18C6 - KX
15C5 - KX
12C4 - KX
a
18C6 - NaX
15C5 - NaX
12C4 - NaX
b
18C6 - LiX
15C5 - LiX
12C4 - LiX
c
K
0
1
1
2
3
0·6
1·2
[crown], molkg⁻¹

A closer examination however suggests that not only the stability but also the structure of crown complexes may be affected by the solvent change. A very strong indication in this respect is provided by the comparison between the ebulliometric curve for 18C6–KSCN combination and the model system traces *2* and *3* suggesting that 1 : 1 complex has been formed in the ethanolic (Fig. 1) whereas 2 : 1 complex in the aqueous (Fig. 2) solution.

Such an eventuality does not appear entirely unreasonable when a possible operation of the hydrophobic effect is taken into account. We have noted already in the preceding paper[12] that apparent molecular weights of the ligands 18C6, 15C5 as well as 12C4 determined ebulliometrically in the aqueous solution are anomalously low (*cf.* the marked deviation between the experimental curve for the ligand dissolution and the theoretical trace *1* in Fig. 2). As an explanation we have proposed that the hydrophobic effect forces the molecules of the ligand to flock together. In this way, the hydrophobic effect might assist in the 2 : 1 (sandwich) complex formation.

However, as another alternative also hydrophobicity of the thiocyanate anion has to be taken into account. It was predicted by Lehn[8] that if anion is markedly hydrophobic, it may have a tendency, in aqueous solution, to associate with the complexed cation which is much more lipophilic than the free cation. A consideration of the model system traces which we calculated previously for such situations (*cf.* Fig. 4*b* in ref.[12]) shows that the association (yielding ion-paired 1 : 1 complex) might also account for the ebulliometric curve for 18C6–KSCN complexation in Fig. 2.

Does the Anion Effect on Complex Stability Originates from Ion-Pairing?

In order to assess the role of ion-pairing in the observed effect of anion, we have probed the state of ionic association of the alkali salts in ethanolic and aqueous solution, first in the absence and then also in the presence of the macrocyclic ligand. Pertinent evidence has been drawn from the ebulliometric curves obtained upon dissolving potassium salts in the pure solvents (Fig. 3) and in the corresponding solutions of 18C6 crown (Fig. 4).

FIG. 1

Changes in boiling point temperature, ΔT (K), induced in 0·6 molal KX–C_2H_5OH, 0·6 molal NaX–C_2H_5OH and 0·6 molal LiX–C_2H_5OH solution upon a gradual addition of two equivalents of crown (18C6, 15C5, 12C4): Experimental curves (●: X = SCN; ○: X = OC_2H_5; dashed line: dissolution of crown in the neat ethanol) and theoretical traces *1* for crown dissolution unattended by complex formation; *2* for 1 : 1 crown–alkali salt complex formation; *3* for 2 : 1 crown–alkali salt complex formation; calculated always under assumption that state of ionic association in the solution does not change upon addition of the ligand

Fig. 3*a* records the ebulliometric curves of dissolving potassium ethoxide and thiocyanate in ethanol, together with the theoretical traces calculated for a quantitative dissociation (*1*) and for a quantitative ion-pairing (*2*) of the dissolved salt in the solution. Corresponding data for dissolving potassium hydroxide and thiocyanate in water are recorded in Fig. 3*b*. In ethanol (Fig. 3*a*), the ebulliometric curve of the ethoxide as well as that of the thiocyanate lie approximately in the middle between the traces *1* and *2* suggesting that roughly same parts (halves) of both salts are free ions and ion-pairs. In water (Fig. 3*b*) the ebulliometric curve of the hydroxide as well as of the thiocyanate fits with the trace *1* suggesting a practically complete dissociation of both salts. Fig. 4*a* records the ebulliometric curves obtained on dissolving potassium ethoxide and thiocyanate in 1·2 molal ethanolic solution of 18C6 crown, together with the theoretical traces calculated for various complexation modes. Corresponding data for dissolving potassium hydroxide and thiocyanate in 1·2 molal aqueous solution of 18C6 crown are recorded in Fig. 4*b*. An excellent agreement is found between the experimental curve for potassium ethoxide and the trace *1* in Fig.

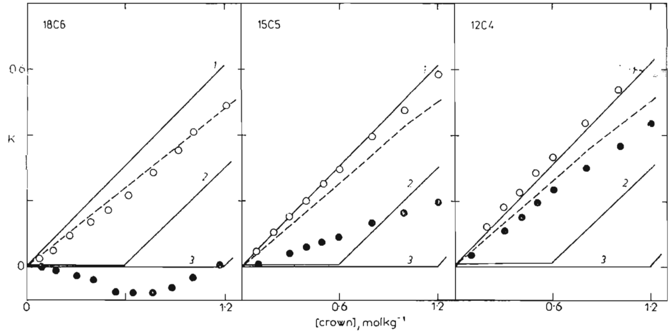


FIG. 2

Changes in boiling point temperature, ΔT (K), induced in 0·6 molal KX–H_2O solution upon a gradual addition of two equivalents of crown (18C6, 15C5, 12C4): Experimental curves (●: X = SCN; ○: X = OH, dashed line: dissolution of crown in the neat water) and theoretical traces *1* for crown dissolution unattended by complex formation, *2* for 1 : 1 crown–alkali salt complex formation and *3* for 2 : 1 crown–alkali salt complex formation calculated always under assumption that state of ionic association does not change in the solution upon addition of the ligand

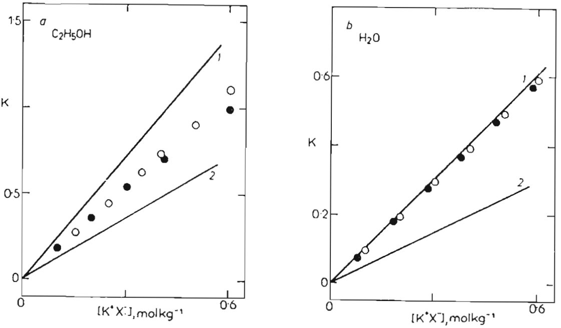


FIG. 3

Changes in boiling point temperature, ΔT (K), induced upon dissolving the potassium salt K^+X^- (*a*) in ethanol and (*b*) in water: Experimental curves (●: X = SCN; ○: X = OC_2H_5 in ethanol or OH in water) and theoretical traces calculated *1* for a complete dissociation; (slope = $= 2K_E$) and *2* for a complete ion-pairing (slope = K_E) of the salt

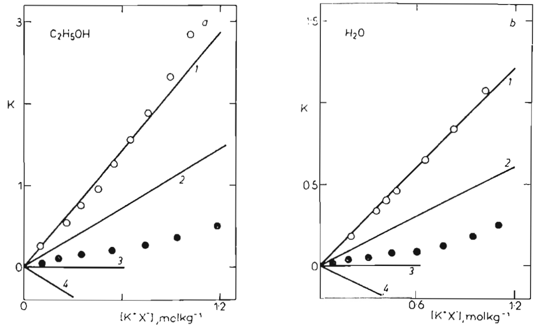


FIG. 4

Changes in boiling point temperature, ΔT (K), induced upon dissolving one equivalent of the potassium salt K^+X^- (*a*) in 1·2 molal solution of 18C6 in ethanol and (*b*) in water: Experimental curves (●: X = SCN; ○: X = OC_2H_5 in ethanol or X = OH in water) and theoretical model system traces calculated *1* for the formation of uncomplexed dissociated ions $[K^+; X^-]$; slope = $= 2K_E$, *2* for the formation of the dissociated 1 : 1 complex $[K^+(18C6); X^-]$; slope = K_E, *3* for the formation of the dissociated 2 : 1 complex $[K^+(18C6)_2; X^-]$ or for the formation of the ion-paired 1 : 1 complex $[K^+(18C6)\,X^-]$; slope = 0, *4* for the formation of the ion-paired 2 : 1 complex $[K^+(18C6)_2\,X^-]$; slope = $-K_E$

4a, and also between the experimental curve for potassium hydroxide and the trace *1* in Fig. *4b*. It allows a straightforward conclusion that the two salts in the 18C6 solutions exist prevalently as dissociated, uncomplexed, ions.

Interpretation of the corresponding ebulliometric curves of the complex-forming potassium thiocyanate from Fig. *4a* and *4b* presents a more difficult problem, for, as a consideration of the alternative model system traces *1* – *4* suggests, an unambiguous conclusion can be drawn only if stoichiometry of the prevailing complex species is known. In the ethanolic solution, an exclusive and quantitative formation of the 1 : 1 18C6–KSCN complex has been established by the ebulliometric evidence in Fig. 1. A correlation between the ebulliometric curve for potassium thiocyanate and the model system traces *2* and *3* allows us therefore to estimate that about two thirds of the complexed molecules are ion-pairs. In the aqueous solution, the situation is less certain owing to the possible participation of the 2 : 1 complexes. Accordingly, only lower and upper limits of ion-pairing in the solution may be reasonably assessed. If, as one extreme, the 2 : 1 complex were the main species, the extent of ion-pairing would be, as it follows from the correlation between the experimental and theoretical traces in Fig. *4b*, only slight. However, if, as the other extreme, the 1 : 1 complex were the main species, the extent of ion-pairing might approach that we found in ethanol (Fig. *4a*).

Summing up, the ebulliometric evidence shows that although ion-pairing may increase upon complexing with crown, a substantial part of the complexed salt still remains dissociated in the ethanolic as well as in the aqueous solutions. As a corollary it follows that ion-pairing cannot be the main factor which accounts for the observed effect of anion. Some other, stronger, interactions apparently have to be involved. Pertinency of the present findings to the theory of strong electrolytes and ion-exchangers is being examined.

REFERENCES

1. Poonia N. S., Bajaj A. V.: Chem. Rev. *79*, 389 (1979).
2. Melson G. A. (Ed.): *Coordination Chemistry of Macrocyclic Compounds*. Plenum Press, New York 1979.
3. Izatt R. M., Christensen J. J. (Eds): *Progress in Macrocyclic Chemistry*, Vol. 1. Wiley-Interscience, New York 1979.
4. Izatt R. M., Christensen J. J. (Eds): *Progress in Macrocyclic Chemistry*, Vol. 2. Wiley-Interscience, New York 1981.
5. Reichenberg D., Diamond R. M. in the book: *Ion Exchange and Solvent Extraction*, Vol. 1, (J. A. Marinski, I., Marcus, Eds), p. 249 and p. 277. Dekker, New York 1965.
6. Blasius E., Janzen K. P., Keller M., Lander H., Hguyen-Tien T., Scholten G.: Talanta *27*, 170 (1980).
7. Lamb J. D., Christensen J. J., Izatt S. R., Bedke K., Astin M. S., Izatt R. M.: J. Chem. Soc. *102*, 3399 (1980).
8. Lehn J. M.: Struct. Bond. *16*, 1 (1973).

9. Gokel G. W., Cram D. J., Liotta C. L., Harris H. P., Cook F. L.: Org. Syn. *57*, 30.
10. Greene R. N.: Tetrahedron Lett. *1972*, 1793.
11. Kuo P. L., Kawamura N., Miki M., Ohara M.: Bull. Chem. Soc. Jap. *53*, 1689 (1980).
12. Pechanec V., Kocián O., Závada J.: This Journal *48*, 1144 (1983).
13. Frensdorff H. K.: J. Amer. Soc. *93*, 600 (1971).
14. Agostiano A., Caselli M., Della Monica M.: J. Electroanal. Chem. Interfacial Electrochem. *74*, 95 (1976).

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