

**ANION EFFECT ON ALKALI ION-CROWN COMPLEX FORMATION  
IN A MODERATELY CONCENTRATED SOLUTIONS: A SENSITIVE  
PROBE OF HIDDEN INTERIONIC INTERACTIONS OPERATING  
IN DISSOCIATING PROTIC SOLVENTS\***

Jiří ZÁVADA, Václav PECHANEC and Oldřich KOCIÁN

*Institute of Organic Chemistry and Biochemistry,  
Czechoslovak Academy of Sciences, 166 10 Prague 6*

Received August 23, 1989

Accepted September 22, 1989

A powerful anion effect destabilizing alkali ion-crown complex formation has been found to operate in moderately concentrated protic ( $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_5\text{OH}$ ) solution, following the order  $\text{HO}^- > \text{AcO}^- > \text{Cl}^- > \text{Br}^- > \text{NO}_3^- > \text{I}^- > \text{NCS}^-$ . Evidence is provided that the observed effect does not originate from ion-pairing. A simple explanation is provided in terms of concordant hydrogen bond bridges of exalted stability between the gegenions,  $\text{M}^+ \cdots \text{OR}-\text{H} \cdots (\text{OR}-\text{H})_n \cdots \text{OR}-\text{H} \cdots \text{A}^-$ . It is proposed that encapsulation of alkali ion by the macrocyclic ligand leads to a dissipation of the cation charge density destroying its ability to participate in the hydrogen bond bridge. An opposition against the alkali ion-crown complex formation arises accordingly in the solution in dependence on strength of the hydrogen bridge; for a given cation, the hydrogen bond strength increases with increasing anion charge density from  $\text{NCS}^-$  to  $\text{HO}^-$  ( $\text{RO}^-$ ). It is pointed out, at the same time, that the observed anion effect does not correlate with the known values of activity coefficients of the individual alkali salts which are almost insensitive to anion variation under the investigated conditions. As a resolution of the apparent paradoxon it is proposed that, in absence of the macrocyclic ligand, the stabilizing (concordant) bonding between the gegenions is nearly balanced by a destabilizing (discordant) hydrogen bonding between the ions of same charge (co-ions). Intrinsic differences among the individual salts are thus submerged in protic solvents and become apparent only when the concordant bonding is suppressed in the alkali ion-crown complex formation.

Of the multifarious factors that may influence metal ion-crown complex formation<sup>1-4</sup>, the role of counterion was given only a sparse attention, in spite of the available evidence suggesting that in related situations<sup>5-14</sup> counterion effects are sometimes very strong.

In particular, surprisingly little is known about the counterion effect in a homogeneous solution<sup>15</sup>, a possible explanation being that so far the effect has been viewed more as an obstacle in the metal ion-crown complex stability determination than as a problem of a considerable interest on its own right.

\* Part X in the series Chemistry of Multidentate Ligands; Part IX: Collect. Czech. Chem. Commun. 54, 1043 (1989).

In a customary analysis, anion effect on cation–crown complex stability is assumed to arise from ion pairing. It is assumed accordingly that suppression of ion pairing in solution – which may be attained by a judicious choice of solvent – will suppress also the counterion effect from operation in the complex-forming reaction. Such an assumption has been concisely expressed by Lehn<sup>16</sup> in the well-known dictum: “In water and other highly solvating media, the charged complex and the anion are separately solvated, and no anion effect on complex stability is expected”.

In a striking discord with the expectation, we have recently discovered<sup>17,18</sup> a powerful anion effect on alkali ion–crown complex formation operating in the most dissociating protic solvents. Analysis of the “illegitimate” effect is the subject of the present study.

## EXPERIMENTAL

*Materials:* 18-crown-6 ether was prepared by a described procedure<sup>19</sup> and recrystallized from hexane prior use. Alkali salts employed in the study were analytical grade (Lachema).

*Ebullioscopy:* Performed in a quartz apparatus analogously as it was described in previous papers<sup>20–22</sup>. Theoretical (model system) traces employed in the discussion were calculated from the equation

$$\Delta T = K_E \sum m_i, \quad (1)$$

where  $\Delta T$  is the expected change in boiling point temperature (in K),  $K_E$  is ebullioscopic constant characteristic for a given solvent (cf. ref.<sup>21</sup>) and  $\sum m_i$  is a sum of concentration of the individual ionic and/or non-ionic species present in the solution (in mol kg<sup>-1</sup>).

## RESULTS AND DISCUSSION

### *Survey of the Ebullioscopic Evidence Demonstrating Anion Effect in Metal Ion–Crown Complex Formation*

As we pointed out in the preceding papers<sup>17,22</sup>, ebulliometric titration may serve as a very convenient tool for investigation of alkali ion complexation with crowns in moderately concentrated (0.05–1.2 mol kg<sup>-1</sup>) solutions. The procedure consists of measuring changes of boiling point temperature ( $\Delta T$ ) induced by a gradual addition of the macrocyclic ligand to an appropriate alkali salt solution (or vice versa). Since  $\Delta T$  is a colligative parameter depending, in the first approximation, only on quantity, not on quality of particles present in the investigated solution (cf. Eq. (1)), crown complex formation can be assessed simply from a comparison of the experimental ebulliometric curve with theoretical (model system) traces calculated for alternative complexation modes.

With the ebullioscopic procedure we accomplished an extensive study of potassium, sodium and lithium ion complex formation with 18-crown-6, 15-crown-5

and 12-crown-4 ethers in three hydroxylic solvents differing greatly in ion-separating ability (ROH; R = C<sub>2</sub>H<sub>5</sub>, CH<sub>3</sub> and H). Replacing in the investigated series, at random, the alkali salt counterion (MX; X = RO<sup>-</sup> and SCN<sup>-</sup>, respectively) we have found<sup>17</sup>, unexpectedly, a very pronounced effect of anion. Figure 1 exemplifies the situation by the results we obtained in the ebulliometric titration of the two alternative potassium salts with 18-crown-6 ether. On basis of crown cavity size–metal ion diameter correlation the combination is particularly suitable for a 1 : 1 complex formation.

In all the three hydroxylic solvents shown in Fig. 1 the thiocyanate salt (KSCN) exhibits a practically complete complexation, which appears “normal” both from the standpoint of the crown cavity–ion diameter correlation, as well as in respect of the complex stability data reported earlier in literature<sup>15,23,24</sup>. In a contrast, however, the alkoxide or hydroxide (ROK) indicates an almost complete absence of complex formation, which is clearly anomalous. Entirely analogous differences have been found<sup>17</sup> between the corresponding sodium salts (NaSCN and RONA, respectively).

A question posed itself, on basis of the experimental evidence, whether the anomalous effect is specific only for the solvent-conjugated (alkoxide or hydroxide) anion. Therefore we have subjected a wider series of potassium salts to the ebulliometric titration with 18-crown-6 ether. A broad spectrum of ebulliometric curves has been obtained in aqueous solution (Fig. 2) ranging widely between the theoretical limits calculated for a quantitative and for none complex formation, the observed

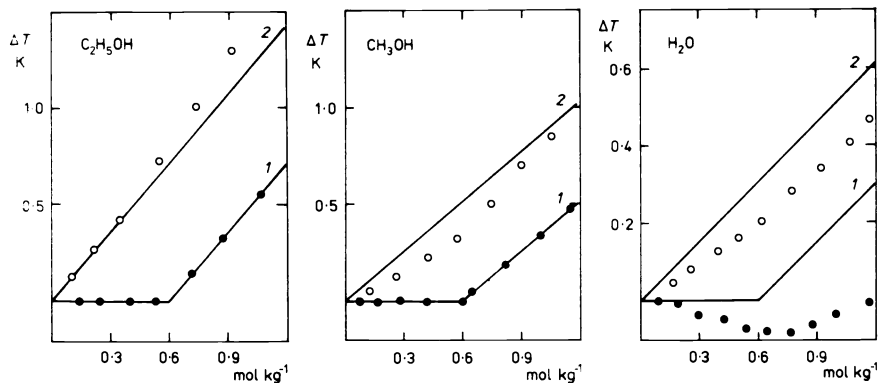


FIG. 1

Changes of boiling point temperature,  $\Delta T(K)$ , induced in a  $0.6 \text{ mol kg}^{-1}$  KX solution in a protic solvent (ROH) upon a gradual addition of two equivalents of 18-crown-6 ether. Experimental curves (● X = SCN; ○ X = OR) and theoretical traces calculated 1 for a quantitative (1 : 1) and 2 for none complex formation (crown ether dissolution)

order of anion proclivity to support complex formation being  $\text{NCS}^- > \text{I}^- > \text{NO}_3^- > \text{Br}^- > \text{Cl}^- > \text{AcO}^- > \text{HO}^-$ . It may be seen accordingly that the two anions involved in the former study (Fig. 1), thiocyanate and hydroxide, approach, incidentally, most closely the extremes, whereas the others occupy intermediate positions. In this way it follows that the observed anion effect does not represent an exceptional but rather a "normal" feature in crown complex formation, at least under the investigated ebullioscopic conditions.

Seeking explanation for the observations, we must first consider possible flaws in the ebullioscopic evidence. As we pointed out already in the preceding papers<sup>17,22</sup>, interpretation of the experimental data from ebulliometric titration rests on a comparison with the theoretical model (Fig. 3a) assuming that ionic association does not change upon addition of the macrocyclic ligand to the investigated solution. That the assumption is of a crucial importance becomes apparent from examination of an alternative theoretical model (Fig. 3b) in which addition of crown ether changes ion association in the solution.

Let us examine first, in the alternative model, a hypothetical situation that a dissociated alkali salt gives rise to an ion-paired complex (1 : 1) upon addition of the crown. Such a process would lead to an overall decrease in the number of solute particles — two free ions being always replaced by a single ion-pair — and a boiling point depression would be accordingly observed (trace 1 in Fig. 3b). A comparison with the experimental data from Figs 1 and 2 will however immediately show that such a complication, albeit not perhaps entirely absent (due to hydrophobic interactions<sup>25</sup>) in the aqueous solution (Fig. 2; experimental curves for KSCN, KI and  $\text{KNO}_3$ ) it cannot be the main factor responsible for the anion effect observed in the ebulliometric titration.

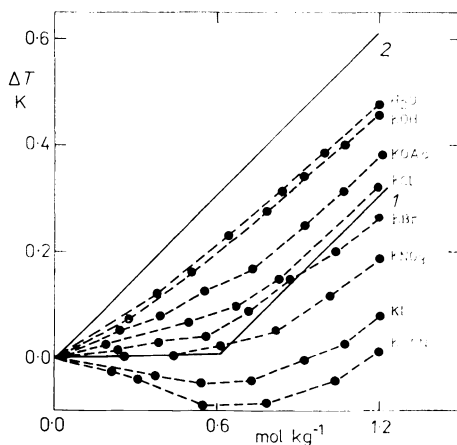


FIG. 2  
Changes of boiling point temperature,  $\Delta T(\text{K})$ , induced in a  $0.6 \text{ mol kg}^{-1}$  aqueous solution of a potassium salt ( $\text{KX}$ ) upon a gradual addition of two equivalents of 18-crown-6 ether. Experimental curves (dashed lines;  $\text{H}_2\text{O}$  a dissolution of 18-crown-6 ether in a neat water) and theoretical traces (full lines) calculated 1 for a quantitative (1 : 1) and 2 for none complex formation (crown ether dissolution)

Let us examine next an exactly opposite situation in which alkali salt is initially ion-paired but gives rise to a dissociated complex consisting of a crown-encapsulated cation and a free anion. Such a process would apparently double the overall number of solute particles and a boiling point elevation would be accordingly observed (trace 2 in Fig. 3b).

The latter eventuality must be very carefully considered, because it might provide a very simple explanation for the different ebullioscopic behaviour of the individual salts. The sole prerequisite for such a scenario would be that in absence of the crown one extreme salt (hydroxide or alkoxide) is ion-paired whereas the other (thiocyanate) is dissociated, but that both the two salts yield a dissociated 1 : 1 complex upon addition of the macrocyclic ligand.

In order to probe this eventuality, we have investigated ebullioscopically degree of ionic association of the two alkali salts in the absence of crown in the solution.

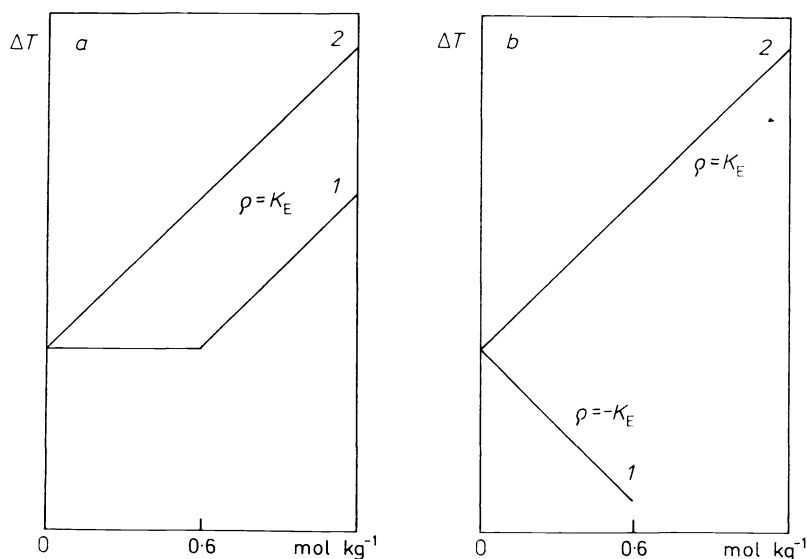


FIG. 3

Alternative model systems in ebullioscopic titration. Theoretical traces for different modes of complexation in  $0.6 \text{ mol kg}^{-1}$   $\text{KX}$  solution upon addition of two equivalents of 18-crown-6 ether calculated *a* under the assumption that ionic association of the dissolved alkali salt does not change upon addition of the macrocyclic ligand (1 a quantitative 1 : 1 complex formation; 2 none complex formation) and *b* under the assumption that ionic association of the dissolved salt changes upon addition of the macrocyclic ligand (1 a quantitative formation of an ion-paired 1 : 1 complex from a dissociated salt; 2 a quantitative formation of a dissociated 1 : 1 metal ion-crown ether complex from an ion-paired salt)

As inspection of Fig. 4 summarizing the ebulliometric curves obtained on dissolving potassium hydroxide (alkoxide) and thiocyanate shows, the experimental curves for the two different salts are almost identical in any of the investigated three solvents indicating that the relative extent of ionic association is practically unaffected by anion. Moreover, in the aqueous and methanolic solutions, the experimental lines lay very closely to the theoretical trace calculated for a complete dissociation of the investigated salt. It hardly allows any other explanation than that ion-pairing is practically absent in the solution. Independent evidence in this respect is available e.g. from conductometric measurements<sup>26</sup>.

In this way it follows that different ion-pairing of individual alkali salt cannot explain the observed effect of anion. Some other, stronger, interaction has apparently to be taken into account.

### Some Related Results

So far we have dealt exclusively with ebullioscopic evidence. A question may be raised accordingly whether the anion effect can be detected also by other techniques. In 1970 Frensdorff<sup>15</sup> employing potentiometric titration with sodium selective electrode, investigated sodium ion-dicyclohexyl-18-crown-6 complex formation from two different sodium salts (NaOH and NaCl) in aqueous solution. No difference between the two salts was found. A small but significant effect of salt concentration was how-

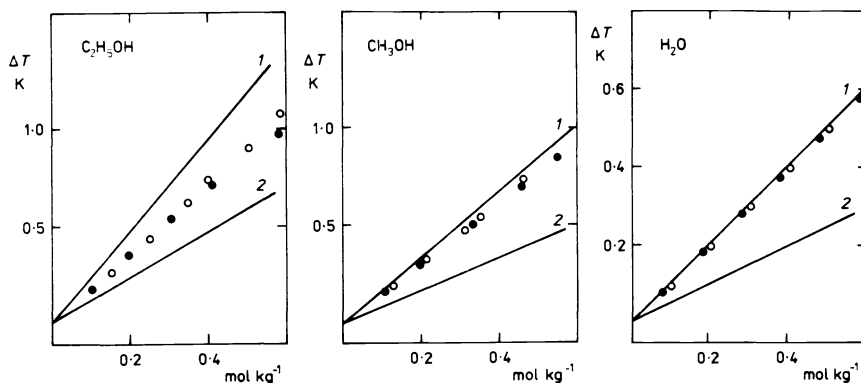


FIG. 4

Changes of boiling point temperature,  $\Delta T(K)$ , induced upon dissolving potassium salt ( $KX$ ) in a protic solvent ( $ROH$ ). Experimental curves (X: ● SCN; ○ OR) and theoretical traces calculated 1 for a complete dissociation (slope equals  $2K_E$ ) and 2 for a complete ion-pairing (slope equals  $K_E$ ) of the salt

ever noted in the crown complex stability measurement, and it was attributed to "an unidentified equilibrium" taking part in the complex-forming reaction.

Since the Frensdorff study was performed at much lower salt concentration than our ebullioscopic measurements, we have accomplished subsequently an analogous potentiometric study of 18-crown-6 complex formation with three different sodium salts (NaOH, NaCl, NaSCN) covering a range of higher salt concentrations in the aqueous solution. A small but significant anion effect has been found already at the lowest investigated concentration ( $0.01 \text{ mol l}^{-1}$ ), the value of the ratio of stability constants obtained for the two extreme salts,  $K(\text{NaSCN})/K(\text{NaOH})$  being about 1.5. On going to more concentrated solution magnitude of the effect gradually increases; in  $1.0 \text{ mol l}^{-1}$  solution the  $K(\text{NaSCN})/K(\text{NaOH})$  ratio already approaches the value of about 20 (Table I). A quite analogous but even more pronounced effect has been found in methanol<sup>18</sup>. It follows that the anion effect we now have under study is concentration dependent.

The thermodynamic stability constant,  $K_{\text{th}}$ , for a 1 : 1 metal ion–ligand complex formation



is defined by

$$K_{\text{th}} = \frac{a_{\text{ML}^+}}{a_{\text{M}^+} a_{\text{L}}} = \frac{[\text{ML}^+] \gamma_{\text{ML}^+}}{[\text{M}^+] [\text{L}] \gamma_{\text{M}^+} \gamma_{\text{L}}} \quad (3)$$

Because values of activity coefficients  $\gamma_{\text{ML}^+}$  and  $\gamma_{\text{L}}$  are unknown, it is a common practice (also in potentiometric measurements) to replace the thermodynamic constant by the concentration constant (pseudoconstant),  $K_{\text{c}}$ , defined by

$$K_{\text{c}} = K_{\text{th}} \frac{\gamma_{\text{M}^+} \gamma_{\text{L}}}{\gamma_{\text{ML}^+}} \quad (4)$$

TABLE I

Potentiometric stability constant,  $K_{\text{c}}$  (taken from ref.<sup>18</sup>), for sodium ion–18-crown-6 ether complex formation determined in aqueous solution: The effect of anion and salt concentration

[NAX] mol l <sup>-1</sup>	X		
	<OH>	<Cl>	<SCN>
0.01	19.1	23.8	27.6
0.1	6.0	7.9	10.3
0.5	1.9	4.8	9.7
1.0	0.5	2.5	9.7

In this way, anion effect on crown complex stability can be attributed to the variation of  $\gamma_{M^+}\gamma_L/\gamma_{ML^+}$  term.

From literature it is known that mean activity coefficients of potassium and sodium salts in water vary<sup>26</sup> with salt concentration as well as with identity of anion\*. However, the actual differences found in the investigated region (Table II) are too small for explanation of the pronounced effects found\*\* in Figs 1 and 2 as well as in Table I.

As it concerns  $\gamma_L$  variation, it is known that strong electrolytes may affect<sup>23,29,30</sup> activity coefficients of neutral solutes in a manner depending on the salt concentration as well as on identity of the anion (cf. e.g. Hofmeister lyotropic series)<sup>29</sup>. A closer examination of literature data however again reveals that the reported variation is too small to account for the present results. Typically, activity coefficient of benzene in aqueous solution of sodium salts ranges<sup>30</sup> as follows:

$$1.80 (1M\text{-NaOH}) > 1.57 (1M\text{-NaCl}) > 1.31 (1M\text{-NaNO}_3).$$

Apparently, differences at least one order of magnitude greater would be required for explanation of the present results.

No direct evidence is available concerning variation of the metal ion-crown complex activity coefficient,  $\gamma_{ML^+}$ , with anion.\*\*\* Significant is however our observation that ebulliometric curves obtained for 18-crown-6 ether-potassium iodide

TABLE II

Activity coefficients of alkali salts (MX) in  $0.6 \text{ mol l}^{-1}$  aqueous solution (data taken from ref.<sup>28</sup>)

M <sup>+</sup>	X						
	<OH>	<OAc>	<Cl>	 	<I>	<NO <sub>3</sub> >	<SCN>
K <sup>+</sup>	0.733	0.754	0.637	0.646	0.667	0.519	0.633
Na <sup>+</sup>	0.685	0.736	0.673	0.692	0.723	0.599	0.712

\* It must be stressed that mean activity coefficients,  $\gamma_{\pm}$ , from Table II are not necessarily identical with single ion activity coefficients,  $\gamma_{M^+}$ , in Eqs (3) and (4). A number of arbitrary non-thermodynamic formulations and conventions has been devised for dividing the mean activity coefficients into their ionic components<sup>31,32</sup>. For univalent electrolytes the simplest convention of this type is  $\gamma_+ = \gamma_- = \gamma_{\pm}$ .

\*\* Concerning relationships between mean activity coefficients and ebullioscopic behaviour of alkali salts see, e.g. ref.<sup>27</sup>.

\*\*\* Concerning a subtle variation of  $\gamma_{M^+}\gamma_L/\gamma_{ML^+}$  with salt concentration see ref.<sup>36</sup>



complex formation are almost identical in a neat water and in  $0.6 \text{ mol kg}^{-1}$  KOH solution (Fig. 5).

#### *On the Origin of the Anion Effect on Alkali Ion–Crown Complex Formation*

With the evidence provided in the preceding paragraphs, origin of the anion effect now gets on the agenda of our discussion. Apparently, involvement of ion pairing which is customarily assumed to be the responsible factor can now be dismissed from a further consideration, a simple argument being that ion pairs, of Bjerrum as well as of Fuoss type<sup>26,33–35</sup>, are unimportant under the investigated conditions. Also small specific effects of individual salts (ions) known from earlier studies of strong electrolytes<sup>25,26,30,37–39</sup> do not offer any reasonable explanation. Operation of some other factor which so far escaped notice or which becomes apparent only in the presence of crowns must be therefore considered.

A clue to the elusive factor may be deduced from Fig. 2. The decreasing propensity of the individual potassium salts to alkali metal ion–18-crown-6 ether complex formation following the order  $\text{NCS}^- > \text{I}^- > \text{NO}_3^- > \text{Br}^- > \text{Cl}^- > \text{AcO}^- > \text{HO}^-$  correlates well with the increasing anion charge density<sup>37</sup>, which in turn correlates with increasing energy of anion solvation<sup>40</sup> (hydration):  $\text{NCS}^- (69.9 \text{ kcal mol}^{-1}) < \text{Br}^- (72.5 \text{ kcal mol}^{-1}) < \text{Cl}^- (75.8 \text{ kcal mol}^{-1}) < \text{HO}^- (90.6 \text{ kcal mol}^{-1})$ .\*

Ample evidence is available in literature that anion solvation energies strongly affect behaviour of salts in phase-transfer<sup>11–13</sup>, ion-exchange<sup>14,41</sup>, ion-transport<sup>6,7</sup> and ion-separation processes<sup>8–10</sup>. In explaining anion effects in such processes it is invariably assumed that a (partial) desolvation of ions takes place on going from

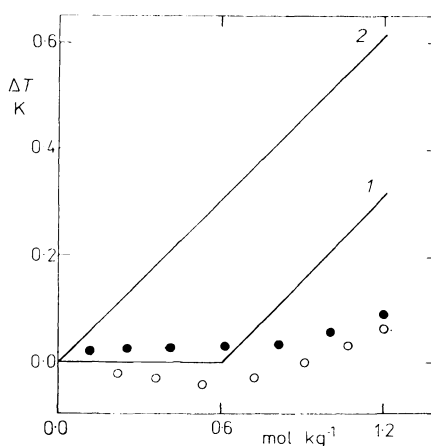


FIG. 5

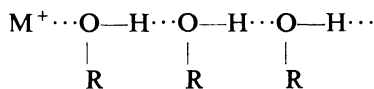
Changes of boiling point temperature,  $\Delta T(\text{K})$ , induced upon a gradual addition of two equivalents of 18-crown-6 ether to a  $0.6 \text{ mol kg}^{-1}$  solution of potassium iodide in a neat water (○) and in  $0.6 \text{ mol kg}^{-1}$  aqueous potassium hydroxide (●). Theoretical traces for a quantitative (1:1) and for none complex formation (crown ether dissolution) are included for a comparison (lines 1 and 2, respectively)

\*  $1 \text{ kcal mol}^{-1} = 4.184 \text{ kJ mol}^{-1}$ .

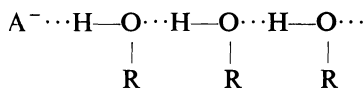
aqueous to organic medium. The energy differential resulting from the desolvation is assumed to give rise to the effect of anion. However, no such anion desolvation can be reasonably conceived either in the ebullioscopic or in the potentiometric studies that, in contradistinction of the aforementioned processes, take place in a homogeneous solution. Superficially, therefore, there is no apparent reason why a correlation between anion solvation energy and alkali ion-crown complex stability should exist in the present study.

Let us however consider more closely the relationship between ion solvation and hydrogen bonding. In protic solvents, such as alcohols and water, interaction of anionic centers with the solvent is a hydrogen bonding phenomenon. Oxyanions are well-known hydrogen-bonding acceptors. Also halide ions are known to engage as many as five or six halide...hydrogen bond in crystals<sup>42,43</sup>. Large shifts,  $\Delta\nu$ , are displayed in the order  $\text{Cl}^- > \text{Br}^- > \text{I}^-$  in inert solvents<sup>44,45</sup>. Identification of  $\Delta\nu$  is difficult in aqueous or alcoholic solutions but a qualitative order is  $\text{HO}^- > \text{Cl}^- > > \text{NCS}^-$ , i.e. it parallels the order of anion hydration energies<sup>46</sup>.

Significantly, also cation solvation in protic solvents involves hydrogen bonding. Coordination of water (alcohol) molecules in the inner-solvation sphere of a cation leads to an increase in the solvent hydrogen atom acidity<sup>35,47</sup>. The enhanced positive charge of the first solvation shell enhances hydrogen bond strength to the second-nearest neighbour waters (alcohols) and the cycle may repeat itself, giving thus rise to hydrogen bond chains<sup>48</sup>.



Entirely analogous hydrogen bond chains, but with opposite charge orientation, may be visualized to take place with anions, the enhancement of the hydrogen bond strength being again the more effective, the higher charge density of the solvated anion.

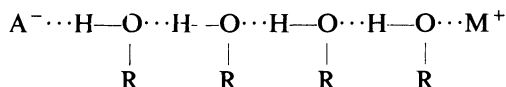


According to semiempirical MO calculations, the enhanced hydrogen bonding disappears only after about six intervening water molecules in the model, for high-charge density ions at least<sup>46,48</sup>.

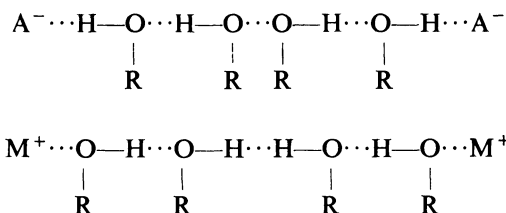
Assumedly, it may have important consequences for the hydrogen bonding model of moderately concentrated salt solution. Since the number of intervening waters between anion and cation is on average about eight in a  $0.1 \text{ mol l}^{-1}$  solution of 1 : 1 electrolyte, it is likely that "living ends" of the hydrogen bond chains of the

opposing ions meet each other at this and at higher concentration, the obvious result of the partial charge relay being an exalted stability of the hydrogen bond.

As it was proposed by Gordon<sup>49</sup>, such hydrogen-bonding potentialities between gegenions may be called concordant. The exalted stability of the concordant bridges should increase with increasing charge density of the participating ions as well as with the decreasing length of the solvent chain, e.i. with increasing concentration.



Such concordant bonding is not possible between ions possessing same charges, i.e. co-ions. Any sequence of waters (alcohols) between the same charge ions cannot be continuously bonded; the orientation of poles proceeding from each ion is identical and hence discordant.



In this way, the hydrogen-bonding relationship may provide a very simple explanation for the concentration-dependent anion effect on alkali ion-crown complex formation we have found in the dissociating protic solvents. Encapsulation of alkali ion by the macrocyclic ligand presumably leads to a pronounced dissipation of ion charge density, destabilizing or perhaps completely destroying the cation capability to participate in the concordant hydrogen bridges. It, obviously, may lead to a destabilization of the alkali ion-crown ether complex in a protic solution. The opposition against the complex formation may be assumed to be the stronger, the greater is stability of the concordant hydrogen bond bridge; for a given cation, the destabilization will increase with increasing anion charge density (from  $NCS^-$  to  $HO^-$ ) as well as with increasing salt concentration, in accordance with our observations.

It may be asked why the differences in the concordant hydrogen bonding which we have now invoked for explanation of the anion effect in the metal ion-crown complex formation are not apparent (Table II) also in the values of activity coefficients of the individual alkali salts.

As an explanation, we are inclined to assume that, in absence of the macrocyclic ligand, the stabilizing concordant hydrogen bonding between the opposite ions –

gegenions — is nearly balanced\* by the destabilizing discordant hydrogen bonding between the co-ions. The intrinsic differences among the individual salts are thus submerged and become apparent only when the concordant bonding is suppressed by the alkali ion–crown complex formation.

It follows, as a corollary, that crown ethers may serve as an invaluable probe for investigation of hidden interionic interactions operating in protic solutions. Consideration of the elusive effect of anion, of which we have now given account, leaves us with an impression that some dark corners still remain in the theory of strong electrolytes that await explanation.

### 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. Izaat R. M., Christensen J. J. (Eds): *Progress in Macrocyclic Chemistry*, Vols 1 and 2. Wiley, New York 1979 and 1981, respectively.
4. Izaat R. M., Christensen J. J. (Eds): *Synthetic Multidentate Macrocyclic Compounds*. Academic Press, New York 1978.
5. Poonia N. S.: Ref.<sup>3</sup>, Vol. 1, Chap. 3, p. 131.
6. Christensen J. J., Lamb J. D., Izatt S. R., Starr S. E., Weed G. C., Astin M. S., Stitt B. D., Izatt R. M.: *J. Am. Chem. Soc.* **100**, 3220 (1978).
7. Lamb J. D., Christensen J. J., Izatt S. R., Bedke K., Astin M. S., Izatt R. M.: *J. Am. Chem. Soc.* **102**, 3399 (1980).
8. Cox B. G., Buncel E., Shin H. S., Bannard R. A. B., Purdon J. G., *Can. J. Chem.* **64**, 920 (1986).
9. Buncel E., Shin H. S., Bannard R. A. B., Purdon J. G.: *Can. J. Chem.* **62**, 926 (1984).
10. Marcus Y., Asher L. E.: *J. Phys. Chem.* **82**, 1246 (1978).
11. Montanari F., Landini D., Rolla F.: *Top. Curr. Chem.* **101**, 147 (1982).
12. Landini D., Maia A., Podda G.: *J. Org. Chem.* **47**, 2264 (1982).
13. Landini D., Maia A., Montanari F.: *J. Am. Chem. Soc.* **106**, 2917 (1984).
14. Blasius E., Janzen K. P., Keller M., Lander H., Huyen-Tien T., Scholten G.: *Talanta* **27**, 170 (1980).
15. Frensdorff H. K.: *J. Am. Chem. Soc.* **93**, 600 (1971).
16. Lehn J.-M.: *Struct. Bond.* **16**, 1 (1973).
17. Závada J., Pechanec V., Kocián O.: *Collect. Czech. Chem. Commun.* **48**, 2509 (1983).
18. Závada J., Pechanec V., Zajíček J., Stibor I., Vitek A.: *Collect. Czech. Chem. Commun.* **50**, 1184 (1985).
19. Gokel G. W., Cram D. J., Liotta C. L., Harris H. P., Cook F. L.: *Org. Synth.* **57**, 30 (1977).
20. Pechanec V., Kocián O., Halaška V., Pánková M., Závada J.: *Collect. Czech. Chem. Commun.* **46**, 2166 (1981).
21. Pechanec V., Kocián O., Závada J.: *Collect. Czech. Chem. Commun.* **47**, 3405 (1982).

\* A residual concordant bonding can be deduced on scrutinizing mean activity coefficients of alkali salts with highest charge density; cf. Robinson–Harned theory of localized hydrolysis of alkali salts (refs<sup>38,39</sup>).

22. Pechanec V., Kocián O., Závada J.: *Collect. Czech. Chem. Commun.* **48**, 1144 (1983).
23. Agostiano A., Caselli M., Della Monica M.: *J. Electroanal. Chem. Interfacial Electrochem.* **74**, 95 (1976).
24. Izatt R. M., Bradshaw J. S., Nielsen S. A., Lamb J. D., Christensen J. J.: *Chem. Rev.* **85**, 271 (1985).
25. Jencks W. P.: *Catalysis in Chemistry and Enzymology*. McGraw-Hill, New York 1969.
26. Robinson R. A., Stokes R. H.: *Electrolyte Solutions*. Butterworth, London 1970.
27. Smith R. P.: *J. Am. Chem. Soc.* **61**, 500 (1939).
28. Weast R. C. (Ed.): *Handbook of Chemistry and Physics*, 48th ed. CRC Press, Cleveland, Ohio 1964.
29. Robinson D. R., Jencks W. P.: *J. Am. Chem. Soc.* **87**, 2467 (1965).
30. Long F. A., McDevit W. F.: *Chem. Rev.* **51**, 119 (1952).
31. Bates R. G., Alfenara M. in: *Ion Selective Electrodes* (R. A. Durst, Ed.), Nat. Bur. Stand. (US) Spec. Publ. 314. U.S. Government Printing Office, Washington, D.C. 1969.
32. Bates R. G., Staples B. R., Robinson R. A.: *Anal. Chem.* **42**, 867 (1970).
33. Conway B. E.: *Ionic Hydration in Chemistry and Biophysics*. Elsevier, New York 1981.
34. Szwartz M.: *Ions and Ion Pairs in Organic Reactions*. Wiley, New York 1972.
35. Gutmann V.: *Chimia* **31**, 1 (1977).
36. Smetana A. J., Popov A. I.: *J. Chem. Thermodyn.* **11**, 1145 (1979).
37. Arnett E. M., Chawla B., Hornung N. J.: *J. Solution Chem.* **6**, 781 (1977).
38. Robinson R. A., Harned H. S.: *Chem. Rev.* **28**, 419 (1941).
39. Diamond R. M.: *J. Am. Chem. Soc.* **80**, 4808 (1958).
40. Friedman H. L., Krishnan C. V. in: *Water, a Comprehensive Treatise* (F. Franks, Ed.), Vol. 3. Plenum Press, New York 1973.
41. Reichenberg J. D., Duamond R. M.: in: *Ion Exchange and Solvent Extraction* (J. A. Marinski and I. Marcus, Eds), Vol. 1, p. 249 and 277. Dekker, New York 1965.
42. Lundgram J.-O., Olofson I.: *J. Chem. Phys.* **49**, 1068 (1968).
43. Beurskens G., Jeffrey G. A.: *J. Chem. Phys.* **41**, 917 (1964).
44. Dwivedi P. C., Rao C. N. R.: *Spectrochim. Acta A* **26**, 1535 (1970).
45. Mohr S. C., Wilk W. D., Barrow G. M.: *J. Am. Chem. Soc.* **87**, 3048 (1965).
46. Hartman K. A.: *J. Phys. Chem.* **70**, 270 (1966).
47. Burton R. E., Daly J.: *Trans. Faraday Soc.* **66**, 1281 (1970).
48. Burton R. E., Daly J.: *Trans. Faraday Soc.* **67**, 1219 (1971).
49. Gordon J. E.: *The Organic Chemistry of Electrolyte Solutions*. Wiley, New York 1975.

Translated by the author (J.Z.).