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The Ion Activity Function

An Approach to the Study of Electrolyte Behavior in Concentrated Solutions III. Formal Species in the Systems LiCl-H_2O and LiBr-H_2O

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Employing a method developed by Högfeldt for the estimation of ionic hydration numbers from activity and H_0-data, the systems $LiCl-H_2O$ and $LiBr-H_2O$ from dilute up to saturated solution can be described by the following equilibria:

$LiCl-H_2O$

$$Li^+ + 5H_2O \rightleftharpoons Li(H_2O)_5^+$$

$$\log [Li(H_2O)_5^+] = -0.33 + \log \phi_0\{Li^+\} + 5 \log \{H_2O\}$$

$$Li^+ + 3H_2O \rightleftharpoons Li(H_2O)_3^+$$

$$\log [Li(H_2O)_3^+] = -1.02 + \log \phi_0\{Li^+\} + 3 \log \{H_2O\}$$

$$Cl^- + 4H_2O \rightleftharpoons Cl(H_2O)_4^-$$

$$\log [Cl(H_2O)_4^-] = 0.34 + \log \phi_0^{-1}\{Cl^-\} + 4 \log \{H_2O\}$$

$$\log [Cl^-]_{free} = -0.20 + \log \phi_0^{-1}\{Cl^-\}$$

$$Li^+ + Cl^- + H_2O = Li(H_2O)Cl$$

$$\log [Li(H_2O)Cl] = -4.87 + \log \{Li^+\}\{Cl^-\} + \log \{H_2O\}$$

$LiBr-H_2O$

$$Li^+ + 5H_2O \rightleftharpoons Li(H_2O)_5^+$$

$$\log [Li(H_2O)_5^+] = -0.22 + \log \phi_0\{Li^+\} + 5 \log \{H_2O\}$$

$$Li^+ + 3H_2O \rightleftharpoons Li(H_2O)_3^+$$

$$\log [Li(H_2O)_3^+] = -1.36 + \log \phi_0\{Li^+\} + 3 \log \{H_2O\}$$

$$Br^- + 5H_2O \rightleftharpoons Br(H_2O)_5^-$$

$$\log [Br(H_2O)_5^-] = 0.31 + \log \phi_0^{-1}\{Br^-\} + 5 \log \{H_2O\}$$

$$\log [Br^-]_{free} = -0.53 + \log \phi_0^{-1}\{Br^-\}$$

$$Li^+ + Br^- + H_2O \rightleftharpoons Li(H_2O)Br$$

$$\log [Li(H_2O)Br] = -6.22 + \log \{Li^+\}\{Br^-\} + \log \{H_2O\}$$

In the literature activities and activity coefficients of electrolytes in water are referred to the completely dissociated, unhydrated ions. For systems where the mean activity coefficient shows a large increase with a corresponding decrease in water activity when approaching saturation, it is obvious that ion-solvent interactions are responsible for a large part of the observed variation in excess free energy. Examples of such systems are mixtures of strong acids and water, where proton hydration is extensive, and the lithium salts, where the small Li^+ can be expected to interact strongly with water, *e.g.* for LiBr at 20 m (molal) $\gamma_\pm = 485$, which indicates that the choice of the species Li^+, Br^- and H_2O is a very poor one indeed.

Some time ago, the ion activity function concept, developed for mixtures of strong acids and water, was applied to the systems $LiCl - H_2O$ and $LiBr - H_2O$.[1] This application is based on the following assumption: the ion activity function of a given anion is the same in both acid and salt solutions, when compared at the same water activity. This assumption is made by analogy to the behavior of the proton activity function, which has been found to be the same at the same water activity for several strong acids.[2] Ojeda and Wyatt [3] found that the Hammett acidity function (or proton activity function) also is a unique function of water activity in salt-acid mixtures, at least in dilute solutions.

Both for LiCl and LiBr we have found [1] that the anion activity coefficient functions are the same at the same water activity in acid as well as salt solutions. Moreover, we found that the lithium ion seems to carry a substantial amount of water of hydration even at 20 m, while the anion seems to be practically unhydrated in 8 – 10 m solutions.

In this paper we describe the two systems in terms of differently hydrated species, as has been done for several strong acids.[4–6]

The ion activity and activity coefficient functions. In order to construct functions mainly dependent on the behavior of a single ion, the following approach has been adopted. First consider the Hammett acidity function, H_0. This function is determined by studying the protonation of a series of uncharged bases, mostly substituted nitroanilines. These indicators participate in the following reaction

$$BH^+ \rightleftharpoons B + H^+ \tag{1}$$

Application of the law of mass action to (1) gives

$$\{B\}\{H^+\}/\{BH^+\} = K_{BH^+} \tag{2}$$

By taking the logarithm of (2) and rearranging the terms we get

$$pK_{BH^+} + \log([B]/[BH^+]) = -\log \phi_0\{H^+\} = H_0 \tag{3}$$

where

$$pK_{BH^+} = -\log K_{BH^+} \tag{4a,b}$$

$$\phi_0 = y_B/y_{BH^+}$$

The left hand side of (3) shows how H_0 is obtained experimentally by determination of the ratio $[B]/[BH^+]$ spectrophotometrically, when K_{BH^+} is known. In dilute solutions K_{BH^+} is obtained by extrapolating the stoichio-

metric equilibrium constant to infinite dilution. At high concentrations of acid K_{BH^+} is obtained in the range of overlap between two indicators. If H_0 is known (determined with another indicator) and the ratio $[B]/[BH^+]$ determined spectrophotometrically pK_{BH^+} can be computed from (3). The right hand side of eqn. (3) shows the physical meaning of H_0, being the product of the activity coefficient ratio ϕ_0 and the proton activity $\{H^+\}$.

In reaction (1) hydration of the indicator base and acid forms should be taken into account and the reaction formulated

$$BH(H_2O)_m^+ \rightleftharpoons B(H_2O)_n + H^+ + (m-n)H_2O \quad (5)$$

According to (5) only apparent hydration numbers can be obtained for the proton if the acid and base forms of the indicator are hydrated. The value $m-n$ should be added to the value estimated from the expression

$$\bar{n}_{H^+}' = -(\Delta \log \phi_0 y_{H^+})/(\Delta \log \{H_2O\}) \quad (6)$$

where $\phi_0 y_{H^+}$ is the proton activity coefficient function evaluated from

$$\log (\phi\{H^+\}/[H^+]_{tot}) = \log \phi_0 y_{H^+} \quad (7)$$

and $[H^+]_{tot}$ is the total molarity of all hydrated protons present in solution. Functions analogous to (6) can be written for anions as well as for cations other than H^+.

Since m can be expected to be larger than n, $\bar{n}_{H^+}'$ represents a lower limit for the hydration of the proton. In order to obtain information on m and n Essig and Marinsky [7] determined the activity coefficient of unprotonated base form of Hammett indicators as well as the protonated form using a reasonable extra thermodynamic assumption. From these data Högfeldt *et al.*[8] estimated m and n. It was found that $m-n$ is surprisingly small in concentrated solutions. This is the main reason why the method outlined above has so far given surprisingly reasonable numbers. For this reason we neglect $m-n$ in the following treatment.

Reaction (5) implies that K_{BH^+} refers to the state of hydration that B and BH^+ have in the acidity range where B is transformed to BH^+ rather than to the state of infinite dilution in water as suggested by Hammett.[9]

In recent years various other acidity functions have appeared among them H_R introduced by Deno *et al.*,[10,11] Boyds relative acidity function,[12] and the function H_A of Yates *et al.*[13] *etc.* They have been discussed by Rochester,[14] and from this discussion it is evident that H_0 still is a most useful acidity function.

However, a comparison of various acidity functions with respect to the possibility of constructing a more useful set of ion activity functions certainly merits further consideration and we plan to do this in the near future. In the meantime a consistent formalism can be developed based on H_0. This function has some useful properties which may not be shared by all other acidity functions. Besides being a unique function of water activity for several strong acids as first shown by Wyatt [15] and later confirmed by Högfeldt for H_0[2] but not for H_R,[16] it has been found that the anion activity coefficient function sometimes stays constant over a considerable concentration range as found for NO_3^- in HNO_3-H_2O[5] and for Br^- in $LiBr-H_2O$.[1] These observations are

interpreted in terms of formally unhydrated NO_3^- and Br^- in the concentration range under consideration.

According to (3) we can identify the proton activity function with H_0, *i.e.*

$$\log \phi_0\{H^+\} = -H_0$$

From the activity product $\{H^+\}\{A^-\}$, which can be obtained from the stoichiometric activity coefficient of HA, tabulated in the literature, and the proton activity function an anion activity function is obtained from

$$\log \phi_0^{-1}\{A^-\} = H_0 + \log \{H^+\}\{A^-\} \quad (8)$$

For a two-proton acid like H_2SO_4, similar but slightly more complicated expressions are obtained.[2]

Similarly to (7) an anion activity coefficient function can be evaluated from

$$\log \phi_0^{-1}\{A^-\}/[A^-]_{tot} = \log \phi_0^{-1} y_{A^-} \quad (9)$$

where $[A^-]_{tot}$ is the stoichiometric molarity of A^- in the solution.

With the aid of the ion activity and ion activity coefficient functions we can estimate the minimum number of ion-water complexes necessary to fit the experimental data. We shall start with the anions, then consider the possibility of ion-pair formation and finally consider cation hydration.

Anion hydration. In Fig. 1 $\log \phi_0^{-1} y_{A^-}$ is plotted against $\log \{H_2O\}$ for Cl^- and Br^- in the two lithium salts employing the assumption that the anion activity functions are the same at the same water activity in both acid and salt. The rising part of the curves in Fig. 1 can be interpreted as due to formation of hydrates, the horizontal portion by unhydrated anion and the decreasing part by formation of ion-pairs.

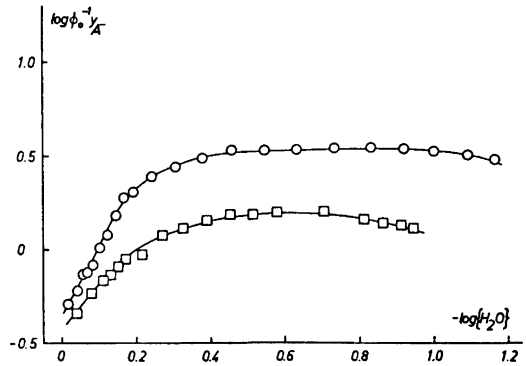

Fig. 1. The function $\log \phi_0^{-1} y_{A^-}$ plotted against $-\log \{H_2O\}$ for the systems (○) LiBr–H_2O and (□) LiCl–H_2O.

In order to find the minimum number of anionic species necessary to describe the experimental data we consider the following equilibrium

$$A^- + pH_2O \rightleftharpoons A(H_2O)_p^- \quad (10)$$

Application of the law of mass action to (10) gives

$$\{A(H_2O)_p^-\} = k\{A^-\}\{H_2O\}^p \tag{11}$$

We include the activity coefficient of $A(H_2O)_p^-$ in the equilibrium constant, use (8) for $\{A^-\}$ and get

$$[A(H_2O)_p^-] = k'10^{H_0}\{H^+\}\{A^-\}\{H_2O\}^p \tag{12}$$

where

$$k' = k\phi_0/y_{A(H_2O)_p^-} = k\frac{y_B}{y_{BH^+}y_{A(H_2O)_p^-}} \tag{13}$$

For the total concentration of A^- the following expression is obtained

$$[A^-]_{tot} = 10^{H_0}\{H^+\}\{A^-\}\sum_0^p k_i'\{H_2O\}^i = \phi_0^{-1}\{A^-\}\sum k_i'\{H_2O\}^i \tag{14}$$

In the range where the unhydrated anion predominates eqn. (14) gives

$$[A^-]_{tot} = [A^-]_{free} = \phi_0^{-1}\{A^-\}k_0' \tag{15a}$$

or

$$\log [A^-]_{tot} = \log [A^-]_{free} = \log k_0' + \log \phi^{-1}\{A^-\} \tag{15b}$$

and

$$\log \phi_0^{-1}y_{A^-} = -\log k_0' \tag{16}$$

According to (16) the horizontal asymptotes in Fig. 1 will give the values for k_0' and we find

$$\begin{aligned}\log [Cl^-]_{free} &= -0.20 + \log \phi_0^{-1}\{Cl^-\} = -0.20 + H_0 + \log \{H^+\}\{Cl^-\}\\ \log [Br^-]_{free} &= -0.53 + \log \phi_0^{-1}\{Br^-\} = -0.53 + H_0 + \log \{H^+\}\{Br^-\}\end{aligned} \tag{17a,b}$$

The concentration of unhydrated Cl^- and Br^- can be computed from eqns. (17a,b). By subtracting this amount from the total concentration the amount of hydrated anion is obtained.

In Fig. 2 $[\log ([A^-]_{tot} - [A^-]_{free})]/\phi_0^{-1}\{A^-\}$ is plotted against $-\log \{H_2O\}$. From Fig. 2 it is seen that two straight lines can be fitted to the data with slopes close to 4 for Cl^- and 5 for Br^-. This indicates that one hydrate alone is sufficient to describe the data. If only one complex predominates over an extended concentration range we get from (14)

$$\log [A(H_2O)_p^-] = \log [A^-]_{tot} = \log k_p' + \log \phi_0^{-1}\{A^-\} + p \log \{H_2O\} \tag{18}$$

or

$$\log \frac{[A^-]_{tot}}{\phi_0^{-1}\{A^-\}} = -\log \phi_0^{-1}y_{A^-} = \log k_p' + p \log \{H_2O\} \tag{19}$$

which is the equation of a straight line with a slope equal to p. According to (19) the data for dilute solutions are consistent with $Cl(H_2O)_4^-$ and $Br(H_2O)_5^-$.

The constants k_4' and k_5' were computed from (18) with $p = 4$ for Cl^- and $p = 5$ for Br^- and an acceptable fit was obtained with the following relations

$$\begin{aligned}\log [Cl(H_2O)_4^-] &= 0.34 + \log \phi_0^{-1}\{Cl^-\} + 4 \log \{H_2O\}\\ \log [Br(H_2O)_5^-] &= 0.31 + \log \phi_0^{-1}\{Br^-\} + 5 \log \{H_2O\}\end{aligned} \tag{20a,b}$$

If the indicators are hydrated one must subtract the unknown quantity $(m-n)$ from the hydration numbers evaluated above. This indicates that in the range where formally unhydrated ions predominate either the indicators are practically unhydrated or the variation in hydration is cancelled by other effects, such as electrostatic interactions. In the latter case it would be surprising if these effects effectively cancel over a large range of water activity.

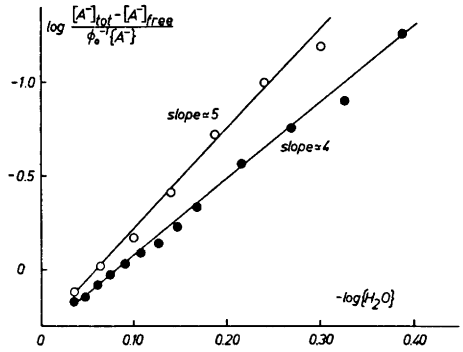

Fig. 2. $[\log([A^-]_{tot}-[A^-]_{free})]/(\phi^{-1}\{A^-\})$ plotted against $-\log\{H_2O\}$ for the systems (○) Br^- in $LiBr-H_2O$ and (●) Cl^- in $LiCl-H_2O$.

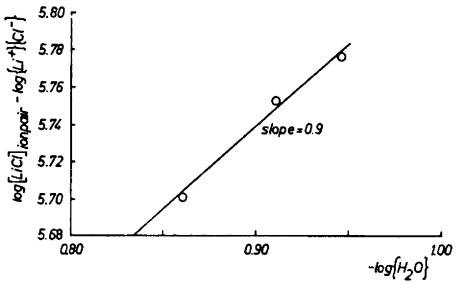

Fig. 3. $\log[LiCl(H_2O)_n]-\log\{Li^+\}\{Cl^-\}$ plotted against $-\log[H_2O]$ for the system: $LiCl-H_2O$. A straight line with a slope close to unity can be fitted to the data.

Ion-pair formation. The decreasing part of the curve in Fig. 1 was previously supposed to be due to formation of ion-pairs at high concentrations.[1] In the present paper the difference between the total concentration and the other two species is taken to be due to an ion-pair *i.e.*,

$$[LiA(H_2O)_q]=[A]_{tot}-[A]_{free}-[A(H_2O)_q^-] \tag{21}$$

This fits the data well for Br^- and satisfactorily for Cl^-. The concentration of the ion-pair is obtained from the α-values computed from the expressions

$$\log \alpha_{I,iBr}=\log \phi_0^{-1}y_{Br^-}-0.53$$
$$\log \alpha_{I,iCl}=\log \phi_0^{-1}y_{Cl^-}-0.20 \tag{22a,b}$$

derived previously,[1] which can be taken as a consistency test for the two methods of estimating the concentration of the ion-pair.

As indicated in (21) the ion-pair may be hydrated. In order to evaluate the hydration of the ion-pair, consider the following reaction

$$Li^+ + A^- + qH_2O \rightleftharpoons LiA(H_2O)_q \tag{23}$$

Assuming the activity coefficient of the hydrated ion-pair to be practically constant it is included in the equilibrium constant and the equilibrium law applied to (23) then gives

$$\log [LiA(H_2O)_q] = \log k_q + \log \{Li^+\}\{A^-\} + q \log \{H_2O\} \tag{24}$$

In Fig. 3 $\log [LiA(H_2O)_n] - \log \{Li^+\}\{Cl^-\}$ with the first term computed from (21) is plotted against $\log \{H_2O\}$ for the system $LiCl - H_2O$. A straight line with a slope close to unity can be fitted to the data indicating that the predominant species might be $LiCl.H_2O$. Similarly for $LiBr - H_2O$ the ion-pair $LiBr.H_2O$ seemed to fit the data best. For reaction (24) with $n = 1$ the following constants are obtained

$$\log [LiCl.H_2O] = -4.87 + \log \{Li^+\}\{Cl^-\}\{H_2O\}$$
$$\log [LiBr.H_2O] = -6.22 + \log \{Li^+\}\{Br^-\}\{H_2O\} \quad (25a,b)$$

Cation hydration. From the activity product $\{Li^+\}\{A^-\}$ and $\phi_0^{-1}\{A^-\}$ we get the cation activity and activity coefficient functions according to the relations:

$$\log \phi_0\{Li^+\} = \log \{Li^+\}\{A^-\} - \log \phi_0^{-1}\{A^-\} \quad (26)$$

$$\log \phi_0 y_{Li^+} = \log \phi_0\{Li^+\} - \log[Li^+]_{tot} \quad (27)$$

Knowing the equilibrium constant for the formation of the ion-pair we can correct for the amount of lithium that participates in the ion-pair formation and evaluate the corrected ion activity coefficient function according to the relation

$$\log \phi_0 y_{Li^+corr} = \log \phi_0\{Li^+\}/\{Li^+\}_{corr} \quad (28)$$

In Fig. 4 $\log \phi_0 y_{Li^+corr}$ is plotted against $-\log \{H_2O\}$ for the two systems. From Fig. 4 it is seen that to begin with the two curves coincide to about $\{H_2O\} = 10^{-0.5}$ where they start to deviate, although the limiting slopes of the curves in both cases approach a value of about 3 indicating a formal hydration number of 3 for Li^+, even close to saturation.

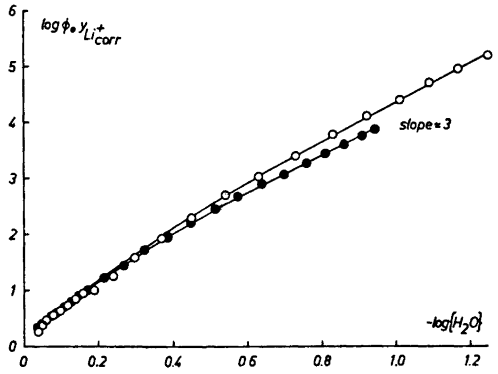

Fig. 4. $\log \phi_0 y_{Li}{}^+{}_{corr}$ plotted against $-\log \{H_2O\}$ for the systems (○) $LiBr - H_2O$ and (●) $LiCl - H_2O$.

For the equilibrium

$$Li^+ + 3\ H_2O \rightleftharpoons Li(H_2O)_3{}^+ \quad (29)$$

we find

$$\text{LiCl}-\text{H}_2\text{O}:\ \log [\text{Li}(\text{H}_2\text{O})_3^+] = -1.02 + \log \phi_0\{\text{Li}^+\} + 3 \log \{\text{H}_2\text{O}\}$$
$$\text{LiBr}-\text{H}_2\text{O}:\ \log [\text{Li}(\text{H}_2\text{O})_3^+] = -1.36 + \log \phi_0\{\text{Li}^+\} + 3 \log \{\text{H}_2\text{O}\} \quad (30a,b)$$

Computing the amount of the trihydrato complex from (30) and subtracting it from the total lithium concentration we obtain

$$D = [\text{Li}^+]_{\text{tot}} - [\text{LiH}_2\text{OA}] - [\text{Li}(\text{H}_2\text{O})_3^+] \quad (31)$$

In Fig. 5 $\log D - \log \phi_0\{\text{Li}^+\}$ is plotted against $-\log \{\text{H}_2\text{O}\}$ for the system $\text{LiBr}-\text{H}_2\text{O}$. A straight line with a slope of 5 can be fitted to the data indicating that we have a formal hydrate $\text{Li}(\text{H}_2\text{O})_5^+$. Two lines with slopes of 4 and 6 are also indicated in Fig. 5, showing that 5 is the best choice. Similarly for $\text{LiCl}-\text{H}_2\text{O}$ the data can be fitted with a pentahydrate, although the spread is larger and the conclusion not so well-established as for the system $\text{LiBr}-\text{H}_2\text{O}$.

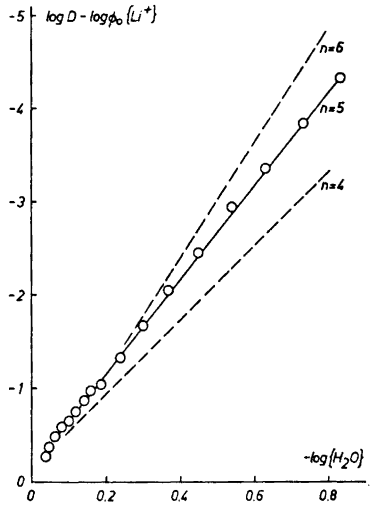

Fig. 5. $\log D - \log \phi_0\{\text{Li}^+\}$ plotted against $-\log \{\text{H}_2\text{O}\}$ for the system: $\text{LiBr}-\text{H}_2\text{O}$. A straight line with a slope of 5 has been fitted to the data. Two other straight lines with slopes 4 and 6 are also indicated.

For the equilibrium

$$\text{Li}^+ + 5\text{H}_2\text{O} \rightleftharpoons \text{Li}(\text{H}_2\text{O})_5^+ \quad (32)$$

we get

$$\text{LiCl}-\text{H}_2\text{O}:\ \log [\text{Li}(\text{H}_2\text{O})_5^+] = -0.33 + \log \phi_0\{\text{Li}^+\} + 5 \log \{\text{H}_2\text{O}\}$$
$$\text{LiBr}-\text{H}_2\text{O}:\ \log [\text{Li}(\text{H}_2\text{O})_5^+] = -0.20 + \log \phi_0\{\text{Li}^+\} + 5 \log \{\text{H}_2\text{O}\} \quad (33a,b)$$

The uncertainty in the various constants is about ± 0.03. In Figs. 6–9 the various anionic and cationic species present in the two systems are indicated and their sum compared with the total anion and cation concentration. As seen a reasonably good fit is obtained over the entire concentration range.

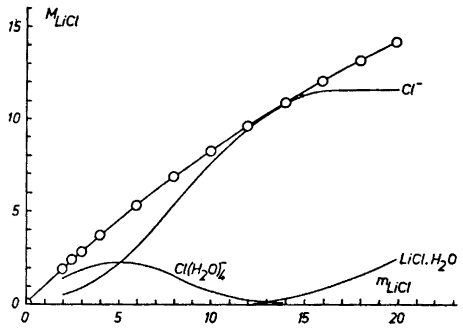

Fig 6. The stoichiometric molarity M plotted against the stoichiometric molality m for the system: $LiCl-H_2O$. The two anionic species and the ion-pair assumed to be present are indicated by the full-drawn curves and their sum compared with the stoichiometric molarity. (———) Stoic hiometric molarity and (O) computed sum for the three species present.

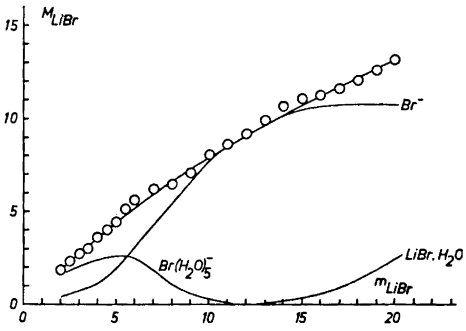

Fig. 7. The stoichiometric molarity M plotted against the stoichiometric molality m for the system: $LiBr-H_2O$. The two anionic species and the ion-pair assumed to be present are indicated by the full-drawn curves and their sum compared with the stoichiometric molarity. (———) Stoichiometric molarity and (O) computed sum for the three species present.

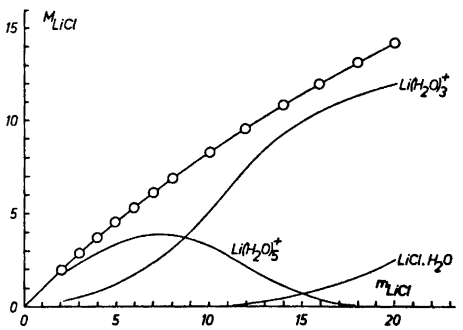

Fig. 8. The stoichiometric molarity M plotted against the stoichiometric molality m for the system: $LiCl-H_2O$. The two cationic species and the ion-pair assumed to be present are indicated by the full-drawn curves and their sum compared with the stoichiometric molarity. (———) Stoichiometric molarity and (O) computed sum for the three species present.

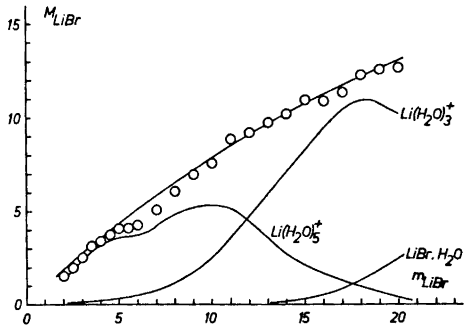

Fig. 9. The stoichiometric molarity M plotted against the stoichiometric molality m for the system. $LiBr-H_2O$. The two cationic species and the ion-pair assumed to be present are indicated by the full-drawn curves and their sum compared with the stoichiometric molarity. (———) Stoichiometric molarity and (O) computed sum for the three species present.

DISCUSSION

The formal hydration numbers obtained in this approach differ from earlier estimates by being assigned to given complexes, and not being overall averages. Hitherto very few investigations have dealt with the variation of hydration

number with composition. As mentioned elsewhere,[1] the overall averages obtained from equations similar to (6) for cation and anion hydration compare favorably with other estimates of primary hydration. Further support can be adduced from the compilations of Bockris and his coworkers [17,18] and of Desnoyers and Jolicoeur,[19] in which a coordination number close to 5 ± 1 is given for Li^+. An investigation covering the whole accessible concentration range has been made by Pottel.[20] From dielectric constant measurements he estimated the overall number of water molecules hindered from rotation. This overall value decreases from nine to two when going from dilute to concentrated LiCl solutions, which is surprisingly close to the overall hydration number obtained by us.[1] Although this coincidence might be fortuitous it is encouraging. Estimates from NMR measurements have been made by Crechmore and Reilly [21] from a study of the temperature dependent proton chemical shift. Although only 3 – 4 m solutions were studied they obtained rather low values $\bar{n}(=3.4$ at 3.08 m and $\bar{n}=3.2$ at 4.62 m). They rationalized their results by assigning an hydration number of four to Li^+ and practically zero for Cl^-. Although not in exact agreement with our description their results give the same general picture with strong cation hydration and very little anion hydration.

That water is strongly attached to the lithium ion as illustrated by the results of Munson and Tyndall [22] who find about 6 H_2O per Li^+ in noble gas atmosphere, which upon extrapolation of the ratio field strength/gas pressure seems to suggest 3 – 4 H_2O per Li^+. Although a gas phase is a considerably different environment from a concentrated aqueous solution, their results support ours in showing that water is strongly bound to the lithium ion.

For the anions our results are in qualitative agreement with those obtained by Robinson and Stokes [23] in their attempt to account for hydration in electrolyte solutions. On the other hand the very scanty information given by Bockris and Reddy [18] indicates roughly the same hydration by Cl^- and Br^- and *i.e.* 2 ± 1. If we compare the average hydration numbers for these anions as defined by the relation analogous to eqn. (6) we find that for $m_{LiCl} > 4$ they are practically the same. Only in more dilute solutions does the difference become appreciable, and at these low concentrations the assumption that most of the change in excess free energy is due to changes in energy of hydration becomes a poor one.

The formation of solvent-separated ion-pairs may be given as a simple explanation for the decreasing part of the curves in Fig. 1. As mentioned elsewhere,[1] through the formation of such ion-pairs enough water is released to provide three water molecules for the formation of $Li(H_2O)_3^+$ even above 18 m, where less water than $3H_2O$/LiCl is present. However, these ion-pairs as well as the various hydrates suggested can at present only be regarded as formal entities permitting a very simple description of the two systems LiCl – H_2O and LiBr – H_2O. It is most encouraging, however, that the present approach gives a rather simple description of the system, with only two cationic and two anionic species together with an hydrated ion-pair, all the way up to saturated solutions.

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