

The Ion Activity Function — An Approach to the Study of Electrolyte Behavior in Concentrated Solutions I.

The Systems LiCl-H₂O and LiBr-H₂O

ERIK HÖGFELDT and LESLIE LEIFER

Department of Inorganic Chemistry, Royal Institute of Technology, Stockholm 70, Sweden and Department of Chemistry and Laboratory for Nuclear Science, Massachusetts Institute of Technology, Cambridge 39, Massachusetts, U.S.A.

An approach to behavior in concentrated electrolytes is presented. Utilizing the fact that a unique ion activity function was obtained for H₃O⁺ in several strong acids we have been able to calculate ion activity and ion activity coefficient functions for the ions in the systems LiCl-H₂O and LiBr-H₂O over a wide composition range. Our results indicate that free Li⁺ carries about three water molecules even in the most concentrated solutions and Cl⁻ and Br⁻ are unhydrated in the region 12 m to saturation.

We have interpreted the decrease in $\varphi_o^{-1}y_{Cl^-}$ and $\varphi_o^{-1}y_{Br^-}$ (seen in the highest concentrations of the salt solutions) as due to ion-pair formation. We assume that the ion activity coefficient function of Cl⁻ and Br⁻ would be constant in the high salt concentration if no ion-pairing occurred and deviations allow us to calculate approximate values for the degree of dissociation, α , of the ion pair.

In a recent investigation of ion activities in mixtures of strong acids and water functions were constructed whose properties depend mainly on those of a single ion¹. These so-called ion activity functions are obtained by combination of activity data with the Hammett acidity function. For example the H₃O⁺ and Cl⁻ ion activity functions are constructed in the following manner:

$$\log \varphi_o a_{H_3O^+} = -H_o + \log a_{H_2O} \quad (1)$$

$$\log \varphi_o^{-1} a_{Cl^-} = H_o + \log a_H + \alpha a_{Cl^-} \quad (2)$$

In eqns. (1) and (2) φ_o equals y_B/y_{BH^+} , the molarity activity coefficient ratio of basic to acid forms of the indicators used in the experimental determination of H_o , the Hammett acidity function. The activity products given above are on a molar scale. It was found that a single curve was obtained when the logarithm of the ion activity function of the hydronium ion ($\log \varphi_o a_{H_3O^+}$) was

plotted against $\log a_{\text{H}_2\text{O}}$ for the acids: H_2SO_4 , HClO_4 , HNO_3 , HCl and HBr . However, the ion activity functions of the various anions in these acids all behaved differently, although ClO_4^- and HSO_4^- gave similar curves.

These functions have given some information about ionic behavior in strong acids and it would be very interesting if utilization of ion activity functions in salt solutions would yield information regarding the species present as well as interactions in concentrated electrolyte solutions.

In attempting to construct such functions in salt solutions one is faced with many arbitrary possibilities. The possibility of working directly with a cation function is eliminated because no measurement analogous to H_0 in strong acids is possible for salt solutions. Thus we have made 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 imposes a certain spread in the calculated cation activity functions but our results indicate that this is not serious, and it does provide at least a first approximation to ionic behavior in concentrated electrolytes.

We have been able to evaluate the ion activity and ion activity coefficient functions in the systems $\text{LiCl}-\text{H}_2\text{O}$ and $\text{LiBr}-\text{H}_2\text{O}$, in the region 2–20 m. Data have been taken from Ref.^{3c} and Ref.⁹ For other lithium salts the necessary activity data are not known at sufficiently low values of the water activity for this treatment to be applied. Knowing $\varphi_0^{-1}a_{\text{Cl}^-}$ and $\varphi_0^{-1}a_{\text{Br}^-}$ as func-

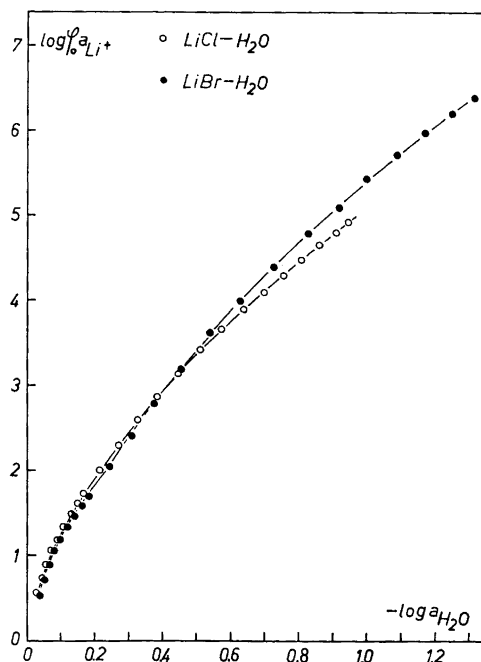


Fig. 1. $\log \varphi_0 a_{\text{Li}^+}$ plotted against $-\log a_{\text{H}_2\text{O}}$ for the systems \circ $\text{LiCl}-\text{H}_2\text{O}$; \bullet $\text{LiBr}-\text{H}_2\text{O}$.

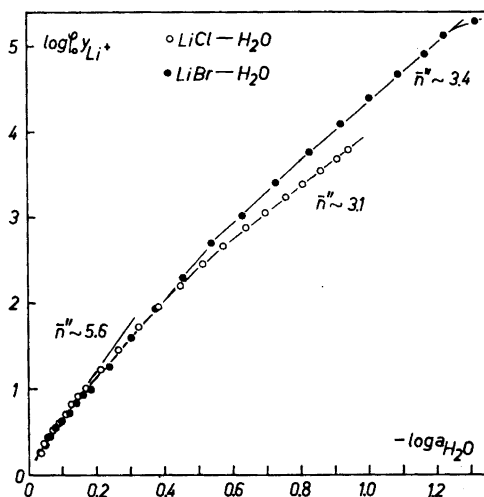


Fig. 2. $\log \varphi_0 y_{\text{Li}^+}$ plotted against $-\log a_{\text{H}_2\text{O}}$ for the systems: \circ LiCl-H₂O; \bullet LiBr-H₂O.

tions of the water activity in HCl and HBr solutions and using the assumption given above the values of the lithium ion activity function at the corresponding water activities were obtained from eqns. (3) and (4) below.

$$\log \varphi_0 a_{\text{Li}^+} = \log a_{\text{Li}^+} + a_{\text{Cl}^-} - \log \varphi_0^{-1} a_{\text{Cl}^-} \quad (3)$$

$$\log \varphi_0 a_{\text{Li}^+} = \log a_{\text{Li}^+} + a_{\text{Br}^-} - \log \varphi_0^{-1} a_{\text{Br}^-} \quad (4)$$

In Fig. 1 $\log \varphi_0 a_{\text{Li}^+}$ is plotted against $-\log a_{\text{H}_2\text{O}}$ for the two lithium salts. At low values of the water activity the curves deviate, this deviation being due to the departure from unity of the activity ratio $a_{\text{Li}^+} + a_{\text{Br}^-} / a_{\text{H}^+} + a_{\text{Br}^-}$; the ratio $a_{\text{Li}^+} + a_{\text{Cl}^-} / a_{\text{H}^+} + a_{\text{Cl}^-}$ being essentially unity.

Using the ion activity functions for the species present we calculate the corresponding ion activity coefficient functions by means of the expressions:

$$\log \varphi_0 y_{\text{Li}^+} = \log \varphi_0 a_{\text{Li}^+} - \log C \quad (5)$$

and

$$\log \varphi_0^{-1} y_{\text{A}^-} = \log \varphi_0^{-1} a_{\text{A}^-} - \log C \quad (6)$$

where C = the stoichiometric molarity of LiA ($A = \text{Cl}^-$, Br^-) and y = the activity coefficient on the molar scale.

In Fig. 2 $\log \varphi_0 y_{\text{Li}^+}$ is plotted against $-\log a_{\text{H}_2\text{O}}$ for the two lithium salts. The curves coincide down to water activities of $10^{-0.45}$ but deviate from each other at lower water activities. However, the deviation in the limiting slopes of these curves is small and will be discussed further in the section on ionic hydration.

Now let us look at the ion activity coefficient functions for the anions Cl^- and Br^- . According to our hypothesis the function $\varphi_0^{-1} a_{\text{A}^-}$ in eqn. (6) should

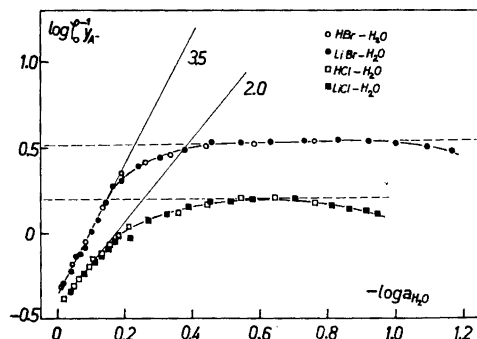


Fig. 3. $\log \varphi_0^{-1} y_{A^-}$ plotted against $-\log a_{H_2O}$ for the systems: \circ HBr-H₂O; \bullet LiBr-H₂O; \square HCl-H₂O; \blacksquare LiCl-H₂O.

be the same in HA-H₂O and LiA-H₂O at the same water activity, and the values for these functions obtained from the acids have been used in the evaluation of $\varphi_0^{-1} y_{A^-}$. In order to compare $\varphi_0^{-1} y_{A^-}$ for the salt solutions with the corresponding function in the acids, eqn. (6) was used to evaluate $\varphi_0^{-1} y_{A^-}$ using C as the stoichiometric concentration of the acid. In Fig. 3 the values of $\log \varphi_0^{-1} y_{Cl^-}$ and $\log \varphi_0^{-1} y_{Br^-}$ are plotted against $-\log a_{H_2O}$ in the four systems: HCl-H₂O, LiCl-H₂O, HBr-H₂O, and LiBr-H₂O. It is seen that the values for the ion activity coefficient functions of Cl⁻ in HCl-H₂O and LiCl-H₂O and of Br⁻ in HBr-H₂O and LiBr-H₂O coincide in the range of overlap. This coincidence is a consequence of the assumption that the anion activity functions are the same in salt and acid as well as the fact that the stoichiometric concentration of salt and acid is the same at the same water activity.

In the concentrated solutions under consideration the variation in excess free energy depends mainly on two effects: ion-solvent interactions and ion-ion interactions. We consider first ion-solvent interactions which we evaluate in terms of ionic hydration numbers.

THE AVERAGE DEGREE OF HYDRATION

In a preceding paper¹ it was shown how a function, \bar{n}_X^z , approximating the average degree of hydration of an ionic constituent X^z, can be obtained from the slope of a plot of $\log \varphi_0^z y_X$ vs. $\log a_{H_2O}$, i.e.

$$\bar{n}_X^z = - \frac{d \log (\varphi_0^z y_X)}{d \log a_{H_2O}} \quad (7)$$

From the slopes of the curves shown in Fig. 2 we obtain a value of 5.6 for the primary hydration of the lithium ion ($\bar{n}_{Li^+}^z$) in dilute aqueous LiCl and LiBr solutions, a value of 3.4 in concentrated LiBr solutions and a value of 3.1 in concentrated LiCl solutions. For the anions we note that the slopes of the curves shown in Fig. 3 tend toward zero with increasing concentration,

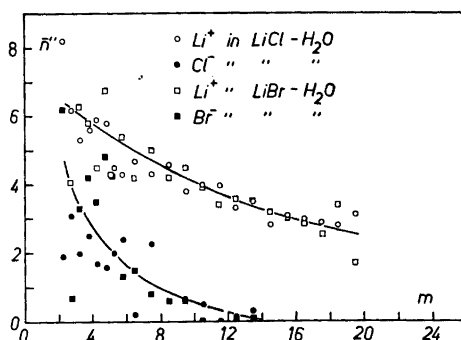


Fig. 4. Ion hydration number, \bar{n}'' , plotted against molality of salt for the ions: \circ Li^+ in $\text{LiCl}-\text{H}_2\text{O}$; \bullet Cl^- in $\text{LiCl}-\text{H}_2\text{O}$; \square Li^+ in $\text{LiBr}-\text{H}_2\text{O}$; \blacksquare Br^- in $\text{LiBr}-\text{H}_2\text{O}$.

indicating that in very concentrated solutions Br^- and Cl^- are unhydrated. In dilute solutions we obtain \bar{n}'' -values of 3.5 for Br^- and 2.0 for Cl^- . The slight decrease in $\log \varphi_0^{-1} y_{\text{A}^-}$ values at the highest concentrations are incompatible with a variation in degree of hydration, however they may be correlated with ion-ion interaction in terms of ion-pair formation. This is discussed further in the next section. In Table 1 we have compared our results with the various values reported in the literature. Glueckauf² estimated ionic hydration from activity data and Robinson and Stokes^{3a} have assembled data on hydration of salts obtained by different methods. The hydration number for the salt \bar{n}' is obtained by addition of the \bar{n}'' values of the two ions. The average of our hydration values for the salts in dilute and concentrated solutions compares favorably with the data given by Robinson and Stokes. Since the primary hydration of salts certainly changes with composition as shown in Fig. 4 the tabulation of hydration numbers without specifying the composition is of questionable value.

The values given by Glueckauf are seen to approach the hydration numbers we find in concentrated solutions, the value for Li^+ being practically the same and those of the anions somewhat higher. The agreement between our estimates and the literature implies that the approximations involved in the derivation of eqn. (7) are not more severe than those of the other methods. However, our method has the advantage of great simplicity and the ability of making the distinction not only between dilute and concentrated solutions but also between anionic and cationic hydration.

It is interesting to note from Fig. 3 that

$$\log \varphi_0^{-1} y_{\text{Br}^-} = \log \frac{(y_{\text{BH}^+} \cdot y_{\text{Br}^-})}{y_{\text{B}}} \sim 0.53 \quad (8)$$

for $-1 < \log a_{\text{H}_2\text{O}} < -0.5$

This implies that variations in the electrostatic free energy are negligible and that BH^+ and Br^- are practically unhydrated below $a_{\text{H}_2\text{O}} = 10^{-0.5}$. The other possibility, that the variations in electrostatic and hydration energy

Table 1. Ionic hydration in LiCl-H₂O and LiBr-H₂O.

System	Li ⁺		Cl ⁻		Br ⁻		\bar{n} Aver- age	\bar{n}_{Lit} Ref. ^{3a}
	Dil. soln	Conc. soln	Dil soln	Conc. soln	Dil. soln	Conc. soln		
LiCl-H ₂ O	5.6	3.1	2.0	0	—	—	5.4	7.1, 6.3, 6
LiBr-H ₂ O	5.6	3.4	—	—	3.5	0	6.3	7.6, 5.6, 5-6
Glueckauf (Ref. ²)	3.4		0.9		0.9		4.3	

should cancel seems unlikely in view of the broad concentration range over which eqn. (8) is valid. The hydration numbers given in Table 1 for concentrated solutions may thus be close to the true ones.

That BH⁺ may be unhydrated for $a_{H_2O} < 10^{-0.5}$ differs from a suggestion by Taft⁴, who by comparing H_o with H_R would ascribe part of the difference between the two acidity functions as due to BH⁺ being hydrated and containing 2-3 H₂O-molecules while the large triphenyl cations used in the evaluation of H_R should be regarded as unhydrated. However, it has recently been shown⁵ that H_R cannot be used for defining a unique hydronium ion activity function as can be done with H_o . This is likely to be due to individual variations in the activity coefficients of the indicators used in the evaluation of H_R . This effect may invalidate Taft's argument. More has to be learned about activity coefficients in these systems before valid conclusions can be drawn. A step in that direction has recently been taken by Deno and coworkers^{6,7}, although much remains to be done before a consistent picture can be obtained.

ION-PAIR FORMATION

The slight decrease in the curves $\log \phi_o^{-1} y_{Cl^-}$ and $\log \phi_o^{-1} y_{Br^-}$ vs. $-\log a_{H_2O}$ in very concentrated LiBr and LiCl solutions will be treated in terms of ion-ion interactions giving rise to the formation of ion-pairs. This would lower the free energy in accordance with this observation. We assume that in the range of interest Cl⁻ and Br⁻ are unhydrated and the functions $\phi_o^{-1} y_{Cl^-}$ and $\phi_o^{-1} y_{Br^-}$ would be constant if no ion pairing occurred. By applying a reasoning analogous to that used by Robinson and Stokes^{3b} for the activity coefficients of partly dissociated weak acids we find:

$$\log \alpha_{LiBr} = \log \phi_o^{-1} y_{Br^-} - 0.53 \quad (9a,b)$$

$$\log \alpha_{LiCl} = \log \phi_o^{-1} y_{Cl^-} - 0.20$$

where 0.53 and 0.20 (the dashed horizontal lines in Fig. 3) are the assumed constant values of $\log \phi_o^{-1} y_{Br^-}$ and $\log \phi_o^{-1} y_{Cl^-}$ if no ion-pair formation occurred. α is the degree of dissociation of the ion pair. Using eqn. (9) and the data in

Fig. 3 α -values varying from 1 to 0.8 in 15–20 m LiCl(LiBr) are obtained. That ion-pair formation is more extensive in LiCl than in LiBr is due to the smaller size and higher charge density of the chloride ion compared to the bromide ion. The activity coefficient function of Li^+ is of course also influenced by the formation of ion pairs. This certainly accounts for part of the decrease in the slope of $\log \varphi_0 y_{\text{Li}^+}$ and is in accord with the observation that the limiting hydration number for Li^+ is smaller in LiCl than in LiBr. Formation of ion-pairs containing little or no water releases enough water to provide the free lithium ions with 3 or 4 water molecules even above 18 m where the total water present is less than three moles per mole of salt. Thus the limiting slopes in Fig. 2 extend above 18 m instead of showing a sharp decrease at the highest salt concentrations. The solid phases precipitating out at about 20 m have the composition $\text{LiCl}\cdot\text{H}_2\text{O}$ and $\text{LiBr}\cdot 2\text{H}_2\text{O}$ ⁸. In the case of lithium chloride the dihydrate is the stable phase below about 19°C. It is extremely difficult and somewhat hazardous to predict the nature of the solid phase from solution data. Nevertheless it is perhaps interesting to speculate on the possibility of the "ion-pair" being a precursor to the phase precipitating out.

Selection of experimental data. Densities of LiCl and LiBr solutions necessary for the transformation from the molality to the molarity scale were taken from the *International Critical Tables*⁹. Activity and osmotic coefficients were taken from the isopiestic measurements of Robinson and Stokes^{3c}.

Note added in proof: Since this paper was written evidence has accumulated in favor of a picture, in which mixtures of strong acids and water behave almost ideally if complex formation between water and the other species (acids, protons and anions) is taken into account (Erik Högfeldt, *Svensk Kem. Tidskr.* **75** (1963) 63). In the near future we want to apply this approach to the systems considered above.

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