

On the Thermodynamics of Hydrated Protons Activities, Activity Coefficients and the Average Degree of Hydration

ERIK HÖGFELDT

Department of Inorganic Chemistry, Royal Institute of Technology, Stockholm 70, Sweden

Activities and activity coefficients for hydrated ions in mixtures of acids with water are derived and their properties investigated. It is shown that the activity product $a_{n+} \cdot a_{n-}$ of the ions $H^+(H_2O)_{n+}$ and $A^-(H_2O)_{n-}$ (A^- = anion of the strong acid HA) must have a maximum at $X = \frac{1}{1+n}$ where X is the stoichiometric mole fraction of HA and $n = n_+ + n_-$. The maximum is obtained independent of whether the ions in question predominate or even exist.

Various activity coefficients are studied and it is found that the molarity activity coefficient for $H^+(H_2O)_4$, ClO_4^- passes through a maximum near 8 M (moles · liter⁻¹) $HClO_4$ while the corresponding function for $H^+(H_2O)_4 \cdot NO_3^-$ is practically constant in the range 9–16 M HNO_3 . This difference in behavior can be primarily attributed to differences in dissociation of the two acids. Above 9.5 M $HClO_4$, there is not enough water present to keep all H^+ in the form $H^+(H_2O)_4$ while, on the other hand, there is sufficient water in the HNO_3 mixtures all the way up to 16 M.

By considering hydrated ions as mononuclear complexes, ordinary complex chemistry methods can be employed to derive a function \bar{n}' closely related to the "true" average degree of hydration. It is found that \bar{n}' is practically the same for H^+ , ClO_4^- and H^+ , HSO_4^- in a large part of the range of overlap while it is smaller for H^+ , NO_3^- thus implying a smaller degree of hydration for NO_3^- than for ClO_4^- and HSO_4^- . For the ion pair H^+ , HSO_4^- \bar{n}' tends towards unity upon approaching pure acid. It is also shown that a maximum ionic concentration will appear at $X = \frac{1}{1+\bar{n}'}$. For H_2SO_4 and $HClO_4$, the maximum is located in the range $X = 0.4-0.5$ while HNO_3 has its maximum at about $X = 0.2-0.3$ consistent with the view that HNO_3 forms a compound $HNO_3 \cdot H_2O$ before it starts to dissociate.

In dealing with electrolyte solutions, Bjerrum¹ and Scatchard^{2,3} made use of a simple model in which ions and molecules are considered to bind part of the solvent giving solvated species that are dissolved in the remaining free solvent. This distinction between two different kinds of water, free water and water bound as water of hydration, has been used in several instances

and recently by Stokes and Robinson^{4a} as well as Glueckauf⁵ and Miller⁶ in their attempts to evaluate hydration numbers. All these treatments were restricted to dilute solutions where the average degree of hydration can be imagined to stay practically constant. However, upon decreasing the water content in the system by increasing the ionic concentration, the amount of water considered as bound as water of hydration must decrease. In case of the proton, it has been suggested that $H^+(H_2O)_4$ should be an especially stable complex in dilute solutions^{5,7-10}. In concentrated solutions, most of this water is stripped off until H_3O^+ is finally obtained which seems to be the predominating proton species in these solutions^{11a} and so stable that it may be recovered in the crystalline state¹².

In the following, the properties of the activities and activity coefficients of hydrated ions are investigated. Since $H^+(H_2O)_4$ and H_3O^+ seem to be so stable as to be experimentally observable, the thermodynamic functions for these two compositions of the hydrated proton will be evaluated and used as examples. We shall then construct a function approximating the average degree of hydration and investigate its bearing on the maxima in ionic concentration found in mixtures of strong acids with water.

Some of the results below have been given in a preliminary note^{11b}.

LIST OF SYMBOLS

a_{H^+}, a_{A^-}, a_{HA}	Activities of H^+ , A^- , HA etc.
a_{n+}, a_{n-}	» » $H^+(H_2O)_{n+}$, $A^-(H_2O)_{n-}$
a_1, a_4	» » H_3O^+ and $H^+(H_2O)_4$
y_+, y_-	''True'' molarity activity coefficients of various hydrated ions
y_{n+}, y_{n-}	Stoichiometric molarity activity coefficients of $H^+(H_2O)_{n+}$ and $A^-(H_2O)_{n-}$
y_1, y_4	Stoichiometric molarity activity coefficients of H_3O^+ and $H^+(H_2O)_4$
$y = [y_{H^+} \cdot y_{A^-}]^{\frac{1}{2}}$	Stoichiometric molarity mean activity coefficient of H^+ , A^-
γ_{n+}, γ_{n-}	» molarity activity coefficients of $H^+(H_2O)_{n+}$ and $A^-(H_2O)_{n-}$
$\gamma = [\gamma_{H^+} \cdot \gamma_{A^-}]^{\frac{1}{2}}$	Stoichiometric molality mean activity coefficient of H^+ , A^-
f_{n+}, f_{n-}	» mole fraction activity coefficients of $H^+(H_2O)_{n+}$ and $A^-(H_2O)_{n-}$
$f = [f_{H^+} \cdot f_{A^-}]^{\frac{1}{2}}$	Stoichiometric mole fraction mean activity coefficient of H^+ , A^-
C_{H^+}, C_{A^-}	Molarities of H^+ , A^-
C	Stoichiometric molarity of acid
m_{H^+}, m_{A^-}	Molalities of H^+ , A^-
m	Stoichiometric molality of acid
X_{H^+}, X_{A^-}	Mole fraction of H^+ , A^-
X	Stoichiometric mole fraction of acid
K, K_n	Equilibrium constants
N_{H_2O}, N_{HA}	Number of moles of H_2O and HA mixed together

n	Number of water molecules attached to an ion
\bar{n}	Average degree of hydration
\bar{n}'	Function approximating \bar{n}
S^+ , S , S^-	$S = \sum K_n a_{\text{H}_2\text{O}}^n$ Function appearing in the treatment of complex equilibria
α	Degree of dissociation

SELECTION OF EXPERIMENTAL DATA

In the choice of experimental data for the computation of thermodynamic functions involving hydrated ions, the measurements that appear to be the most careful have been used wherever possible.

The data selected will now be discussed for each acid in turn.

a) *Hydrochloric acid*. Densities of HCl solutions at 25°C, necessary for the transformation from the molality to the molarity scale, were computed from the formulas given by Åkerlöf and Teare¹³. Stoichiometric mean activity coefficients were taken from Harned and Owen¹⁴ for dilute solutions and from Robinson and Stokes for concentrated solutions^{4b}. The activity coefficients of Harned and Owen are based on emf measurements by Harned and Ehlers¹⁵. The activities of Robinson and Stokes are calculated from their own isopiestic measurements^{16,17} and agree well with those of Åkerlöf and Teare¹⁸ obtained from emf measurements. Water activities were computed from osmotic coefficients given by Robinson and Stokes^{4c}.

b) *Perchloric acid*. Densities for HClO₄ solutions at 25°C have been taken from Markham¹⁹ and water activities together with stoichiometric mean activity coefficients from Robinson and Baker²⁰ who used the isopiestic method. These data seem to be accepted as being the best available at present²¹. For estimating the concentration of various species, the results from the NMR (nuclear magnetic resonance) measurements by Hood, Redlich and Reilly²¹ have been used, which values show a better consistency than the Raman measurements by Redlich, Holt and Bigeleisen²².

c) *Nitric acid*. Densities of HNO₃ solutions at 20°C have been taken from Landolt-Börnstein^{23a}. Concerning water and nitric acid activities at this temperature, the agreement between different investigations is not as good as could be desired^{23b, 24—26}. For this reason, it is difficult to make a choice between the various data. However, those by Potier²⁶ have been chosen because of the large concentration range studied and the reasonably good internal consistency.

The concentrations of the species present have been determined with the Raman technique by Redlich and Bigeleisen²⁷ and by Young and Krawetz^{28,29a}. Concentrations determined from NMR measurements by Redlich *et al*²¹, are said to agree well with the Raman measurements by Krawetz^{29a}. The precision of the NMR measurements is not quite so good as for the Raman method but the NMR data were the only data accessible to the present writer and they have been used in this paper.

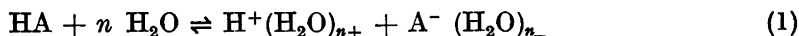
d) *Sulfuric acid*. Densities of H₂SO₄ solutions at 25°C have been taken from the International Critical Tables³⁰. When the present investigation

was begun, the best available thermodynamic data for sulfuric acid seemed to be the recent isopiestic measurements by Glueckauf and Kitt³¹ which agree well with the vapor pressure measurements of Shankman and Gordon³² and Hornung and Giaque³³. The measurements of Glueckauf and Kitt stop around 16 M (moles · liter⁻¹). Now Deno and Taft³⁴ have given water activities up to nearly pure H₂SO₄ using a simple empirical relation between the water activity and the Hammett acidity function, H_0 . Both sets of values agree well in the overlapping part of the range. The present writer has used Deno and Taft's water activities to compute the corresponding sulfuric acid activities by graphical integration with the aid of the Gibbs-Duhem equation. The value for pure sulfuric acid obtained by extrapolation, $\log a_{\text{H}^+}^2 \cdot a_{\text{SO}_4^{2-}} = 9.55$, differs considerably from the value 8.76 estimated by Abel³⁵ from literature data available at that time. However, thanks to the courtesy of Professor Giaque, a set of thermodynamic data, unpublished at that time, for sulfuric acid collected during the course of many years in Berkeley³⁶ were made available to the present writer. The value for pure sulfuric acid at 25°C is $\log a_{\text{H}^+}^2 \cdot a_{\text{SO}_4^{2-}} = 9.53$ which is so close to the value found from the data of Deno and Taft that their empirical method for correlating water activities with H_0 must be regarded as essentially correct. The water activity and the stoichiometric activity coefficient of H₂SO₄ obtained by Giaque *et al.* agree within a few per cent with those of Glueckauf and Kitt in the overlapping section of the range. This is such a good agreement that no recalculation using the data of Giaque *et al.* seemed necessary.

For the concentrations of the species present, Raman^{29a,37} and NMR³⁸ measurements are available. The Raman measurements reported by Young *et al.*^{29a} are believed to be more accurate than the early measurements reported by Young and Blatz^{37,39}. Since the evaluation of the NMR data depends upon the Raman measurements, no decisive information about the correctness of the Raman data can be obtained from them. In the following, the more recent Raman data^{29a} will be used.

ACTIVITIES

Definitions. In the Bjerrum treatment of solvation, ions are assumed to bind the solvent to form solvated ions. For the acid HA, we wish to consider the following reaction:



where

$$n = n_+ + n_- \quad (2)$$

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

$$a_{\text{H}^+(\text{H}_2\text{O})_{n+}} \cdot a_{\text{A}^-(\text{H}_2\text{O})_{n-}} = K_n \cdot a_{\text{HA}} \cdot a_{\text{H}_2\text{O}}^n \quad (3a)$$

For the sake of simplicity in notation, we write:

$$\begin{aligned} a_{n+} &= a_{\text{H}^+(\text{H}_2\text{O})_{n+}} \\ a_{n-} &= a_{\text{A}^-(\text{H}_2\text{O})_{n-}} \end{aligned} \quad (4a, b)$$

and thus

$$a_{n+} \cdot a_{n-} = K_n \cdot a_{\text{HA}} \cdot a_{\text{H}_2\text{O}}^n \quad (3b)$$

For the dissociation into unhydrated ions, we have

$$a_{\text{H}^+} \cdot a_{\text{A}^-} = K \cdot a_{\text{HA}} \quad (5)$$

where K is the thermodynamic dissociation constant of HA. The activities of H^+ and A^- are defined such that they approach the analytical concentrations of these ions in dilute solutions. From (3b) and (5) it is found:

$$a_{n^+} \cdot a_{n^-} = \frac{K_n}{K} \cdot a_{\text{H}^+} \cdot a_{\text{A}^-} \cdot a_{\text{H}_2\text{O}}^n$$

The simplest way of relating the activity scale of hydrated ions to that of the unhydrated ions is to define

$$K_n = K \quad n = 1, 2 \dots \quad (6)$$

for all possible values of n . We thus obtain:

$$a_{n^+} \cdot a_{n^-} = a_{\text{H}^+} \cdot a_{\text{A}^-} \cdot a_{\text{H}_2\text{O}}^n \quad (7)$$

Since $a_{\text{H}_2\text{O}} \rightarrow 1$ when approaching infinite dilution, the reference state of the hydrated ions is the same as for the unhydrated ions, *i.e.* the activity tends towards the analytical concentration upon dilution. Since the activity product $a_{\text{H}^+} \cdot a_{\text{A}^-}$ can be obtained from the stoichiometric activity coefficients and water activities which are either tabulated directly or can be computed from osmotic coefficients reported in the literature, the activity products given by (7) can be evaluated for several strong acids and often over considerable concentration ranges.

The maximum. From eqn. (7), it is seen that the activity product of the hydrated ions is composed of two terms, one containing the activity product of the unhydrated ions and the other the activity of water. Since the first term increases monotonically and tends towards a finite limit and the second, the water activity, decreases monotonically towards zero with increasing concentration of acid, there must be a maximum for the activity product of the hydrated ions. In order to investigate this, (5) is substituted in (7), *i.e.*

$$a_{n^+} \cdot a_{n^-} = K \cdot a_{\text{HA}} \cdot a_{\text{H}_2\text{O}}^n \quad (8)$$

Logarithmic differentiation of (8) gives:

$$\text{dln } a_{n^+} + \text{dln } a_{n^-} = \text{dln } a_{\text{HA}} + n \text{dln } a_{\text{H}_2\text{O}} \quad (9)$$

Application of the Gibbs-Duhem equation to this system gives:

$$N_{\text{HA}} \text{dln } a_{\text{HA}} = -N_{\text{H}_2\text{O}} \text{dln } a_{\text{H}_2\text{O}} \quad (10)$$

N_{HA} and $N_{\text{H}_2\text{O}}$ are the number of moles of HA and H_2O mixed together. By inserting (10) into (9) and using the condition that at the maximum

$\text{dln } a_{n^+} + \text{dln } a_{n^-} = 0$ we find:

$$\text{dln } a_{\text{H}_2\text{O}} \left(n - \frac{N_{\text{H}_2\text{O}}}{N_{\text{HA}}} \right) = 0$$

Since $\text{dln } a_{\text{H}_2\text{O}} \neq 0$, the maximum must be located at the stoichiometric mole fraction of acid given by:

$$X = \frac{1}{1+n} \quad (11)$$

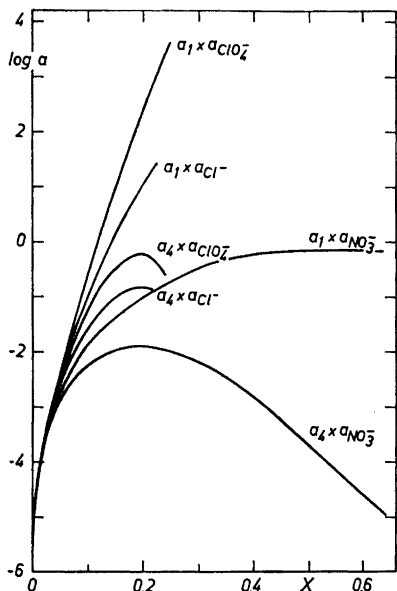


Fig. 1. The logarithms of the mole fraction activity products $a_1 \cdot a_{A^-}$ and $a_4 \cdot a_{A^-}$ plotted versus stoichiometric mole fraction, X , of acid for the three acids: HNO_3 , HCl and HClO_4 .

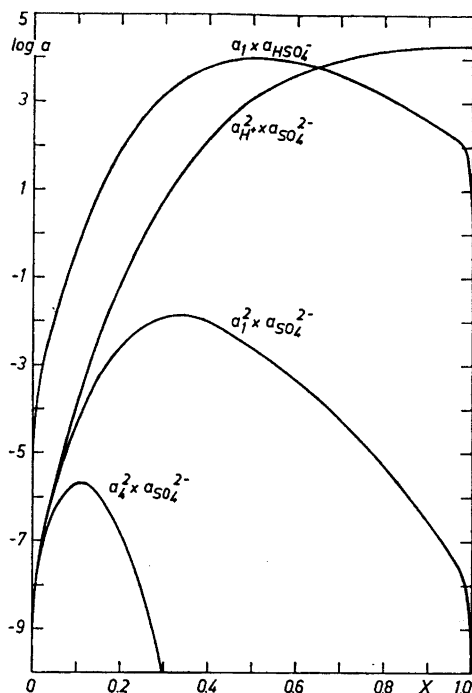
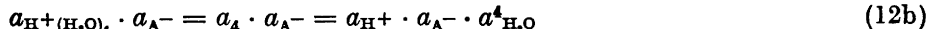


Fig. 2. The logarithms of the mole fraction activity products $(a_{\text{H}^+})^2 \cdot a_{\text{SO}_4^{2-}}$, $a_1 \cdot a_{\text{HSO}_4^-}$, $a_1^2 \cdot a_{\text{SO}_4^{2-}}$ and $a_4^2 \cdot a_{\text{SO}_4^{2-}}$ plotted versus X .

This maximum is a purely thermodynamic consequence and shows that the activity product $a_{n^+} \cdot a_{n^-}$ has a maximum when the solution has the corresponding composition HA , $n \text{ H}_2\text{O}$. The maximum is obtained independent of whether the ions in question exist or not.

Comparison of the activity products for two different n -values. Since many differently hydrated ions are possible, a large number of activity products $a_{n^+} \cdot a_{n^-}$ can be constructed. In order to study the properties of these activities, the following two special cases will be considered:



where a_1 and a_4 are convenient notations. In Fig. 1, the activity products (12) on the mole fraction scale for the two acids HNO_3 and HClO_4 are plotted versus the stoichiometric mole fraction of acid. As is seen, the maximum of $a_4 \cdot a_{\text{A}^-}$ appears, for both acids, at $X = 0.2$. For HNO_3 , the maximum for $a_1 \cdot a_{\text{A}^-}$ at $X = 0.5$ is hard to locate since the curve is very flat. For HClO_4 , data are not available up to $X = 0.5$.

The only strong acid which has been studied over the whole concentration range from pure water to pure acid is sulfuric acid. In Fig. 2, the mole fraction activity products, $(a_{\text{H}^+})^2 \cdot a_{\text{SO}_4^{2-}}$, $a_1 \cdot a_{\text{HSO}_4^-}$, $a_1^2 \cdot a_{\text{SO}_4^{2-}}$ and $a_4^2 \cdot a_{\text{SO}_4^{2-}}$, are plotted on a logarithmic scale against stoichiometric mole fraction of H_2SO_4 . The activity product $a_1 \cdot a_{\text{HSO}_4^-}$ can be computed from $(a_{\text{H}^+})^2 \cdot a_{\text{SO}_4^{2-}}$ and $a_{\text{H}_2\text{O}}$ with knowledge of the second dissociation constant of sulfuric acid. The value $\text{p}K_{\text{HSO}_4^-} = 2.00$ for 25°C recently suggested by Hamer^{29b} from considerations of available literature data has been accepted. This value agrees well with $\text{p}K_{\text{HSO}_4^-} = 2.01$ calculated by Kerker⁴⁰ from transference and conductance data. The activity product $a_1 \cdot a_{\text{HSO}_4^-}$ can now be computed from

$$\begin{aligned} \log a_1 \cdot a_{\text{HSO}_4^-} &= \log (a_{\text{H}^+})^2 \cdot a_{\text{SO}_4^{2-}} \cdot a_{\text{H}_2\text{O}} \cdot K^{-1}_{\text{HSO}_4^-} = \\ &= \log (a_{\text{H}^+})^2 \cdot a_{\text{SO}_4^{2-}} + \log a_{\text{H}_2\text{O}} + 2.00 \end{aligned} \quad (13)$$

As seen from Fig. 2, all functions have maxima as requested by (11). The function $(a_{\text{H}^+})^2 \cdot a_{\text{SO}_4^{2-}}$ can be considered as a special case with $n = 0$ for which (11) gives a maximum for the pure acid.

ACTIVITY COEFFICIENTS

For the acids, HClO_4 , HNO_3 and H_2SO_4 , Raman and NMR methods have been used to distinguish between the undissociated and dissociated parts of acids in concentrated solutions. It is thus possible to compute activity coefficients and study their properties.

a) *Definitions.* For the strong acid HA where the concentrations of the species present have been estimated using one of the methods mentioned above, the ionic activity coefficient products on the molarity scale for $\text{H}^+(\text{H}_2\text{O})_{n+}$, $\text{A}^-(\text{H}_2\text{O})_{n-}$ can be computed from

$$y_{n+} \cdot y_{n-} = \frac{a_{n+}^c \cdot a_{n-}^c}{(aC)^2} \quad (14a)$$

where the superscript c refers to the molarity scale, a is the degree of dissociation and C the stoichiometric molarity of HA.

The analogous expressions on the molality (m) and mole fraction (x) scales are:

$$\gamma_{n+} \cdot \gamma_{n-} = \frac{a_{n+}^m \cdot a_{n-}^m}{m_{\text{H}^+} \cdot m_{\text{A}^-}}; \quad f_{n+} \cdot f_{n-} = \frac{x_{n+} \cdot x_{n-}}{x_{\text{H}^+} \cdot x_{\text{A}^-}} \quad (14b, c)$$

The activity coefficients in (14) have the same reference state as ordinary activity coefficients, *i.e.* they approach unity at infinite dilution. In the evaluation of these activity coefficients, the total ionic concentration is used because of the difficulty of making a distinction between differently hydrated ions. They are thus stoichiometric activity coefficients which approach the true ones at those concentrations where the corresponding ionic species may predominate.

b) *Properties.* The stoichiometric activity coefficients of the hydrated ions are related to the ordinary stoichiometric activity coefficients in the following way:

$$\begin{aligned}
 y_{n+} \cdot y_{n-} &= \left(\frac{y}{a}\right)^2 \cdot a_{\text{H}_2\text{O}}^n \\
 \gamma_{n+} \cdot \gamma_{n-} &= \left(\frac{\gamma}{\alpha}\right)^2 \cdot a_{\text{H}_2\text{O}}^n [1 - \alpha n \cdot m \cdot (55.51)^{-1}]^2 \\
 f_{n+} \cdot f_{n-} &= \left(\frac{f}{\alpha}\right)^2 \cdot a_{\text{H}_2\text{O}}^n [1 - \alpha(n-1)X]^2
 \end{aligned}
 \tag{15a, b, c}$$

The term $(n-1)$ appearing in (15c) is due to the convention that, in the evaluation of the mole fractions, the ions of the dissociated acid are counted as separate entities. For $n = 0$, (15b) degenerates into the relation

$\gamma_{\text{H}^+} \cdot \gamma_{\text{A}^-} = \left(\frac{\gamma}{\alpha}\right)^2$ used by Robinson and Stokes⁴. From (15), it is seen that the activity coefficient product of the hydrated ions will always be smaller than that of the unhydrated ions because $a_{\text{H}_2\text{O}} \leq 1$.

It can be shown from (15) that the ratio of the activity coefficient product of any pair of hydrated ions to that of the unhydrated ions will in pure acid be the same for all three kinds of activity coefficients and equal to $a_{\text{H}_2\text{O}}^n$, where $a_{\text{H}_2\text{O}}$ refers to the activity of water in pure acid.

c) *Comparison of activity coefficient products for some different n-values.* For the two cases H_3O^+ , A^- and $\text{H}^+(\text{H}_2\text{O})_4$, A^- considered in the discussion of the activities, the activity coefficients on the molarity scale take the form:

$$y_1 \cdot y_{\text{A}^-} = \left(\frac{y}{\alpha}\right)^2 \cdot a_{\text{H}_2\text{O}} \tag{16a}$$

$$y_4 \cdot y_{\text{A}^-} = \left(\frac{y}{\alpha}\right)^2 \cdot a_{\text{H}_2\text{O}}^4 \tag{16b}$$

As seen from (15), the activity coefficients take the most simple form on the molarity scale because it is not necessary to distinguish between free and bound water when evaluating the molarities of the constituents present.

In Fig. 3, $\log y_1 \cdot y_{\text{A}^-}$ and $\log y_4 \cdot y_{\text{A}^-}$ are plotted against the stoichiometric molarity of the acid for HNO_3 and HClO_4 . It is not suitable to plot the activity

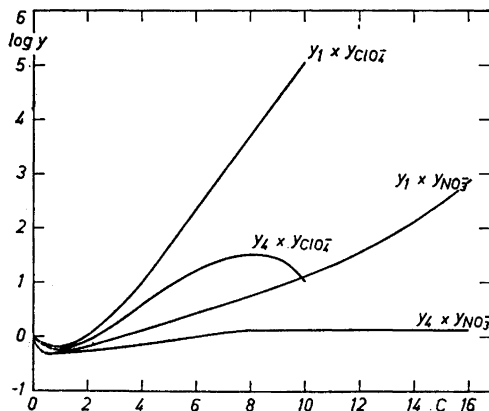


Fig. 3. The molarity activity coefficients $y_1 \cdot y_{\text{A}^-}$ and $y_4 \cdot y_{\text{A}^-}$ plotted on a logarithmic scale versus stoichiometric molarity of acid, C , for HNO_3 and HClO_4 .

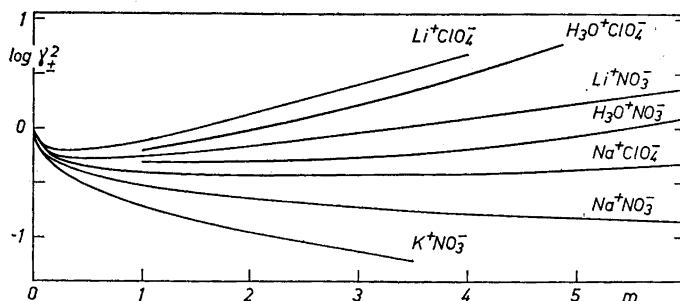


Fig. 4. The logarithms of the stoichiometric molality activity coefficients $\gamma_+ \cdot \gamma_-$ for LiClO_4 , LiNO_3 , NaClO_4 , NaNO_3 , KNO_3 , H_3O^+ , ClO_4^- , and H_3O^+ , NO_3^- plotted versus the stoichiometric molality m .

coefficients versus the ionic strength or the total ionic concentration since these quantities go through a maximum and do not lead to single-valued activity coefficient functions.

It should be noted that, while $y_4 \cdot y_{\text{ClO}_4^-}$ goes through a maximum near 8 M HClO_4 , $y_4 \cdot y_{\text{NO}_3^-}$ seems to be practically constant in the range 9–16 M HNO_3 . On the other hand, both curves $y_1 \cdot y_{\text{A}^-}$ rise steeply. The maximum of $y_4 \cdot y_{\text{ClO}_4^-}$ can be imagined to be due to overcompensation caused by assuming too high a hydration number. From the data of Redlich *et al.*²¹ near 9.5 M HClO_4 , it appears that the amount of water present has decreased to four times that of H^+ . Above this concentration, there is not enough water present to have all protons in the form of $\text{H}^+(\text{H}_2\text{O})_4$. This may be the main reason for the maximum in $y_4 \cdot y_{\text{ClO}_4^-}$.

For HNO_3 on the other hand, the data by Redlich *et al.*²¹ show that the amount of water present is at least six times that of H^+ even at 16 M HNO_3 . For this acid, there is sufficient water to have a considerable fraction of the

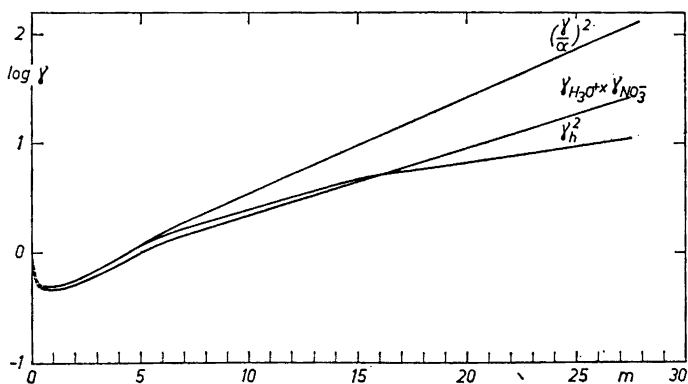


Fig. 5. $\log \gamma_{\text{H}_3\text{O}^+} \cdot \gamma_{\text{NO}_3^-}$ compared with $\log \left(\frac{\gamma}{a}\right)^2$ and $\log \gamma_{\text{H}^+}^2$.

protons as $\text{H}^+(\text{H}_2\text{O})_4$ or $\text{H}^+(\text{H}_2\text{O})_3$. The nearly constant value of $y_4 \cdot y_{\text{NO}_3^-}$ between 9 and 16 M might thus be due to a practically negligible displacement of the proton equilibria towards less hydrated protons over almost the whole range of dissociation of HNO_3 . On the other hand, for stronger acids like HClO_4 , there is a change from something like $\text{H}^+(\text{H}_2\text{O})_4$ in dilute solutions towards H_3O^+ in concentrated solutions.

Since free protons do not seem to exist in water solutions in measurable amounts, it is natural to consider H_3O^+ as the primary proton species which like any other ion upon dilution undergoes further hydration. Since H_3O^+ is a singly charged ion of a size comparable to K^+ , it might be of interest to compare the molality activity coefficient products of H_3O^+ , NO_3^- and H_3O^+ , ClO_4^- with those of some related 1:1 electrolytes. This has been done in Fig. 4 where $\log \gamma_{\text{X}^+} \cdot \gamma_{\text{A}^-}$ is plotted *versus* the stoichiometric molality for LiClO_4 , LiNO_3 , NaNO_4 , KNO_3 , N_3O^+ , ClO_4^- and H_3O^+ , NO_3^- . As seen, H_3O^+ falls between Li^+ and Na^+ for both NO_3^- and ClO_4^- . Upon considering only the size effect, one should have expected H_3O^+ to fall closer to K^+ . The order of decreasing activity coefficients suggests that the degree of hydration decreases in the order $\text{Li}^+ > \text{H}_3\text{O}^+ > \text{Na}^+ > \text{K}^+$ in qualitative agreement with recent estimates^{4a, 5, 6} although the different authors do not agree about the magnitude of the hydration numbers.

McKay⁴¹ has recently evaluated an activity coefficient for the ionized part of HNO_3 where the tries to account formally for the influence of undissociated acid on the ions. In Fig. 5, this activity coefficient, γ_h , is compared with those of H^+ , NO_3^- and H_3O^+ , NO_3^- . $\log \gamma_h^2$ was computed from

$$\log(\gamma_h)^2 = \log \left(\frac{\gamma}{a} \right)^2 - 0.048 (1-a) \cdot m$$

For the derivation of this expression, the reader is referred to the original paper. As seen in Fig. 5, γ_h^2 is close to $\left(\frac{\gamma}{a} \right)^2$ in dilute solutions while in concentrated solutions it falls below $\gamma_{\text{H}_3\text{O}^+} \cdot \gamma_{\text{NO}_3^-}$. Although the construction of γ_h contains an interesting attempt to correct for the influence of undissociated acid on the ionic activity coefficients, it suffers from the defect of referring to unhydrated protons and not to the actual species present.

A FUNCTION APPROXIMATING TO THE AVERAGE DEGREE OF HYDRATION

Considerations of only one kind of hydrated ionic species at a time must necessarily always be very crude. By considering the more realistic case of the simultaneous existence of several differently hydrated ionic constituents and by applying ordinary complex chemistry methods to the ion-water equilibria, a function closely related to the average degree of hydration can be derived as follows:

For the two types of reactions (n may have several values):



the law of mass action gives:

$$\left. \begin{aligned} C_{\text{H}^+(\text{aq})} &= \frac{K_n}{y_+} \cdot a_{\text{H}^+} \cdot a_{\text{H}_2\text{O}}^n \\ C_{\text{A}^-(\text{aq})} &= \frac{K_n}{y_-} a_{\text{A}^-} \cdot a_{\text{H}_2\text{O}}^n \end{aligned} \right\} \quad (18a, b)$$

We can now sum over all differently hydrated ionic constituents and get

$$\left. \begin{aligned} C_{\text{H}^+} &= \alpha C = \Sigma C_{\text{H}^+(\text{aq})} = \frac{a_{\text{H}^+}}{y_+} \Sigma K_{n^+} \cdot a_{\text{H}_2\text{O}}^n = \frac{a_{\text{H}^+}}{y_+} \cdot S^+ \\ C_{\text{A}^-} &= \alpha C = \Sigma C_{\text{A}^-(\text{aq})} = \frac{a_{\text{A}^-}}{y_-} \Sigma K_{n^-} a_{\text{H}_2\text{O}}^n = \frac{a_{\text{A}^-}}{y_-} \cdot S^- \end{aligned} \right\} \quad (19a, b)$$

In the derivation of (19), it is assumed that the activity coefficients of the differently hydrated protons are the same ($= y_+$) and can be placed outside the summation sign and analogously for the anions.

The sums S^+ and S^- are functions appearing in the mathematical treatment of complex equilibria. They have the property:

$$\frac{d \log S}{d \log a_{\text{H}_2\text{O}}} = \frac{\Sigma n K_n a_{\text{H}_2\text{O}}^n}{\Sigma K_n a_{\text{H}_2\text{O}}^n} = \bar{n} \quad (20)$$

where \bar{n} is the average number of water molecules attached to the ion under consideration.

By multiplying (19a) with (19b) and inserting the stoichiometric activity coefficient $y = \left[\frac{a_{\text{H}^+}^c \cdot a_{\text{H}^-}^c}{C_{\text{H}^+} \cdot C_{\text{A}^-}} \right]^{\frac{1}{2}} = (y_{\text{H}^+} \cdot y_{\text{A}^-})^{\frac{1}{2}}$ we get after differentiation and use of equation (20):

$$d \log(y_+ \cdot y_-) / d \log a_{\text{H}_2\text{O}} - d \log \left(\frac{y}{\alpha} \right)^2 / d \log a_{\text{H}_2\text{O}} = \bar{n}_+ + \bar{n}_- = \bar{n} \quad (21)$$

In (21), all quantities except $y_+ \cdot y_-$ are known from experimental measurements. Various attempts to estimate related activity coefficient products have been made in recent papers on ionic hydration ^{4a,5,6}. However, these treatments employ the Debye-Hückel expression which is likely to break down in concentrated solutions. Because of our lack of knowledge of how to correct for electrostatic interactions in concentrated solutions of electrolytes, (21) cannot be employed for computing absolute \bar{n} -values. It can be used, however, for the computation of relative hydration numbers. When comparing the two acids HÅ and HB at the same water activity, we get from (21)

$$d \log \left(\frac{y}{\alpha} \right)_{\text{HÅ}}^2 / d \log a_{\text{H}_2\text{O}} - d \log \left(\frac{y}{\alpha} \right)_{\text{HB}}^2 / d \log a_{\text{H}_2\text{O}} = \bar{n}_{\text{B}^-} - \bar{n}_{\text{A}^-} \quad (22)$$

if the assumption

$$\frac{d \log y_{\text{A}^-}}{d \log a_{\text{H}_2\text{O}}} = \frac{d \log y_{\text{B}^-}}{d \log a_{\text{H}_2\text{O}}} \quad (23)$$

is correct. Even if not strictly valid, (23) might be a good first approximation and thus eqn. (22) may give reasonably good relative hydration numbers.

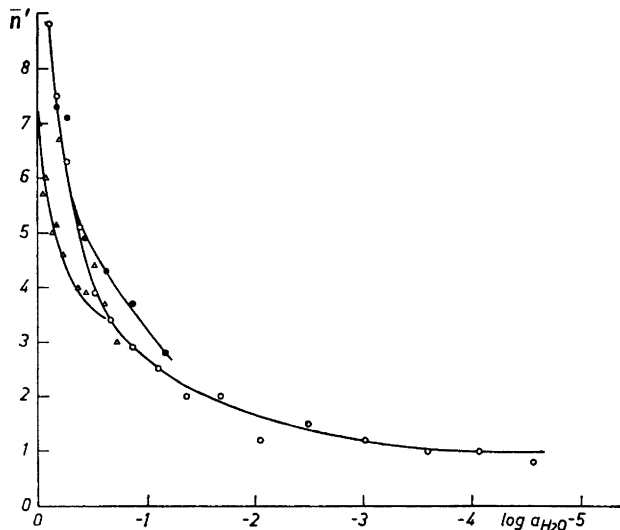


Fig. 6. The function \bar{n}' for various ion pairs plotted versus $\log a_{\text{H}_2\text{O}}$.

- H^+ , HSO_4^-
- H^+ , ClO_4^-
- △ H^+ , NO_3^-

We can also use (21) to define an approximation to \bar{n} . From (21) we get

$$\bar{n}' = -d \log \left(\frac{y}{a} \right)^2 / d \log a_{\text{H}_2\text{O}} = \bar{n} - d \log y_+ y_- / d \log a_{\text{H}_2\text{O}} \quad (24)$$

This approximation may be expected to be bad in dilute solutions because the activity coefficients vary very much while $a_{\text{H}_2\text{O}}$ varies rather little. In concentrated solutions, on the other hand, activity coefficients seem to vary relatively little while the variation of $a_{\text{H}_2\text{O}}$ is large and the function $d \log y_+ \cdot y_- / d \log a_{\text{H}_2\text{O}}$ therefore close to zero. One might thus expect \bar{n}' to approach \bar{n} in very concentrated solutions.

In order to study the behavior of \bar{n}' , this function, calculated according to (24), is plotted in Fig. 6 versus $\log a_{\text{H}_2\text{O}}$ for the three ion pairs:

H^+ , ClO_4^- , H^+ , NO_3^- and H^+ , HSO_4^- . As seen, the curves for H^+ , ClO_4^- and H^+ , HSO_4^- practically coincide at high water activities. On the other hand, the curve for H^+ , NO_3^- lies below the two others indicating a smaller degree of hydration for NO_3^- as compared with ClO_4^- and HSO_4^- . Unfortunately, there is a large scattering in the data for H^+ , NO_3^- — it seems however that, in dilute solutions, ClO_4^- and HSO_4^- contain 2–3 more H_2O in the hydration shell as compared with NO_3^- . In more concentrated solutions, this difference decreases to $\frac{1}{2}$ –1 around $\log a_{\text{H}_2\text{O}} = -0.5$. It should also be noted that, in the range $-0.3 > \log a_{\text{H}_2\text{O}} > -0.9$ corresponding to 9–16 M HMO_3^- \bar{n}' varies rather little in agreement with previous considerations of $y_4 \cdot y_{\text{NO}_3^-}$

in the same concentration range. For the pair H^+ , HSO_4^- , it is interesting to note that $\bar{n}' \rightarrow 1$ upon approaching pure H_2SO_4 . This result seems reasonable since $\text{H}^+(\text{H}_2\text{O})_n$ can be imagined to tend towards H_3O^+ and HSO_4^- to lose all its water of hydration with decreasing water activity. From the data presented here, it cannot be definitely concluded whether the remaining water molecule in the hydration shell belongs to H^+ or HSO_4^- . However, in a following paper, evidence is given that H^+ is likely to exist as H_3O^+ in concentrated solutions of H_2SO_4 ^{11a}. The fact that \bar{n}' tends towards a plausible limit lends support to the suggestion that $d \log y_+ \cdot y_- / d \log a_{\text{H}_2\text{O}} \approx 0$ in concentrated solutions and thus $\bar{n}' \approx \bar{n}$.

THE MAXIMUM IN IONIC CONCENTRATION

From Raman and NMR measurements in mixtures of strong acids with water, it has been found that each ionic constituent has a maximum concentration at a certain composition of the mixture. The location of this maximum can be correlated with the hydration of the ions in the following manner.

By multiplying (19a) and (19b) we get

$$C_{\text{H}^+} \cdot C_{\text{A}^-} = (C_{\text{A}^-})^2 = \frac{a_{\text{H}^+}^c \cdot a_{\text{A}^-}^c}{y_+ \cdot y_-} \cdot S^+ \cdot S^- = \frac{K \cdot a_{\text{HA}}}{y_+ \cdot y_-} \cdot S^+ \cdot S^- \quad (25)$$

Differentiating (25) logarithmically, using the definition of \bar{n}' given by (24) and the condition that at the maximum $d \log C_{\text{A}^-} = 0$ gives, after combining with the Gibbs-Duhem equation (10):

$$X = \frac{1}{1 + \bar{n}'} \quad (26)$$

Eqn. (26) is obviously an extension of (11). In order to estimate which \bar{n}' -values correspond to the maxima found experimentally, the locations of the maximum ionic concentration for NO_3^- , ClO_4^- and HSO_4^- are compared with equation (26) in Table 1.

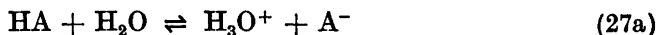
As seen from Table 1, the ions ClO_4^- and HSO_4^- have their maximum concentration in a range where $\bar{n}' \approx 1-2$ while NO_3^- has its maximum in a more

Table 1. Comparison of experimental material with eqn (26).

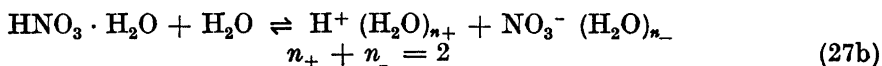
\bar{n}'	X Eqn. (26)	X		
		NO_3^-	Exptl. ClO_4^-	HSO_4^-
1	0.50			
2	0.33		(21) 0.40-0.50	(29a) 0.42
3	0.25	(28, 29a) * (21) 0.21-0.26		
4	0.20			

* Quoted from Ref⁴¹.

dilute solution where $\bar{n}' \approx 3-4$. This might be due to the weaker dissociation of HNO_3 . If we consider the reaction:



an infinitely strong acid will give one H_3O^+ and one A^- for every H_2O added. In such a case, the maximum will be at $X = 0.5$. Weaker acids on the other hand will have their maxima displaced towards lower concentrations. The maxima for HClO_4 and H_2SO_4 near $X = 0.5$ imply that these acids should be considered very strong and much stronger than HNO_3 . It is surprising that such a difference is not more emphasized in the values of the thermodynamic dissociation constants of HNO_3 (22)²¹ and HClO_4 (38)²¹. If, on the other hand, HNO_3 first reacts with water to form a compound like $\text{HNO}_3 \cdot \text{H}_2\text{O}$ before it dissociates, then the reaction might be:



and the maximum in ionic concentration would be located somewhere below $X = 0.33$. The dissociation constant could nevertheless be of the same order of magnitude as that of HClO_4 in spite of the lower dissociation. Actually there is evidence that HNO_3 forms hydrates before it dissociates and also the Raman measurements show that the dissociation starts near the composition $\text{HNO}_3 \cdot \text{H}_2\text{O}$. These results support the dissociation reaction (27b) rather than (27a) for HNO_3 .

For H_2SO_4 , $X = 0.42$ gives $\bar{n}' = 1.40$ which implies that at the maximum concentration of HSO_4^- practically all of the free water has become bound as water of hydration. Now, the Raman measurements by Young et al show that measurable amounts of H_2SO_4 start to appear at about the same concentration. It thus seems that molecules of H_2SO_4 cannot appear until nearly all of the free water has been tied up as water of hydration.

Acknowledgements. The author wants to express his sincere thanks to Professors L. G. Sillén and R. E. Connick for valuable discussions and helpful advice, to Professor T. F. Young for comments on equilibria in strong sulfuric acid and to Professor W. F. Giauque for providing access to previously unpublished data for the system $\text{H}_2\text{SO}_4 - \text{H}_2\text{O}$. Mr D. Gillam corrected the English text. The financial support of the *Swedish Atomic Energy Committee* and the *Swedish Natural Science Research Council* is gratefully acknowledged.

REFERENCES:

1. Bjerrum N. *Medd. Vetenskapsakad. Nobelinst.* 5 (1919) 1.
2. Scatchard G. *J. Am. Chem. Soc.* 43 (1921) 2406.
3. Scatchard G. *Ibid.* 47 (1925) 2098.
4. Robinson, R. A. and Stokes, R. H. *Electrolyte Solutions*, Butterworth, London 1955; a) p 239-253, b) 489, c) 468.
5. Glueckauf, E. *Trans. Faraday Soc.* 51 (1955) 1235.
6. Miller, D. G. *J. Phys. Chem.* 60 (1956) 1296.
7. *Discussions Faraday Soc.* 24 (1957)
 - a) Bascombe, R. N. and Bell, R. P. p. 158,
 - b) Wyatt, P. A. H. p. 162,
 - c) van Panthaleon van Eck, C. L., Mendel, H. and Boog, W. p. 200,
 - d) Redlich, O. and Hood, G. C. p. 87.

8. Glueckauf, E. and Kitt, G. P. *Proc. Roy. Soc. London A* **228** (1955) 322.
9. Wicke, E., Eigen, M. and Ackermann, Th. *Z. physik. Chem. NF* **1** (1954) 340.
10. Tuck, D. G. and Diamond, R. M. *Proc. Chem. Soc.* **1958** 236.
11. a) Högfeldt, E. *Acta Chem. Scand.*, **14** (1960) 1627.
b) Högfeldt, E. *Nature* **185** (1960) 760.
12. Volmer, M. *Ann.* **440** (1924) 200.
13. Åkerlöf, G. and Teare, J. *J. Am. Chem. Soc.* **60** (1938) 1226.
14. Harned, H. S. and Owen, B. B. *The Physical Chemistry of Electrolytic Solutions*, Third Ed., Reinhold, N. Y. 1958, p. 716.
15. Harned, H. S. and Ehlers, R. W. *J. Am. Chem. Soc.* **55** (1933) 2179.
16. Stokes, R. H. *Trans. Faraday Soc.* **44** (1948) 295.
17. Robinson, R. A. and Stokes, R. H. *Trans. Faraday Soc.* **45** (1959) 612.
18. Åkerlöf, G. and Teare, J. W. *J. Am. Chem. Soc.* **59** (1937) 1855.
19. Markham, A. E. *J. Am. Chem. Soc.* **63** (1941) 874.
20. Robinson, R. A. and Baker, O. J. *Trans. Proc. Roy. Soc. New Zealand* **76** (1946) 250, as reported in *Chem. Abstr.* **41** (1947) 5000 d.
21. Hood, G. C., Redlich, O. and Reilly, C. A. *J. Chem. Phys.* **22** (1954) 2067.
22. Redlich, O., Holt, E. K. and Bigeleisen, J. *J. Am. Chem. Soc.* **66** (1944) 13.
23. *Landolt-Börnstein Physikalisch-Chemische Tabellen*. Julius Springer, Berlin.
a) Eg II a, 1931, p. 254;
b) Eg III c, 1936, p. 2145.
24. Forsythe, W. R. and Giaque, W. F. *J. Am. Chem. Soc.* **64** (1942) 48.
25. Vandoni, M. R. and Laudy, M. *J. chim. phys.* **49** (1952) 99.
26. Potier, A. *Ann. fac. sci. univ. Toulouse* **20** (1956) 1.
27. Redlich, O. and Bigeleisen, J. *J. Am. Chem. Soc.* **65** (1943) 1883.
28. Krawetz, A. A. *Thesis*, University of Chicago 1955.
29. Hamer, W. J. *The Structure of Electrolytic Solutions*, John Wiley, New York 1959.
a) Young, T. F., Maranville, L. F. and Smith, M. M. p. 35,
b) Hamer, W. J., p. 236.
30. *International Critical Tables*, Vol 3, McGraw Hill, New York 1928 p. 56—57.
31. Glueckauf, E. and Kitt, G. *Trans. Faraday Soc.* **52** (1956) 1074.
32. Shankman, S. and Gordon, A. R. *J. Am. Chem. Soc.* **61** (1939) 2370.
33. Hornung, E. W. and Giaque, W. F. *J. Am. Chem. Soc.* **77** (1955) 2744.
34. Deno, N. C. and Taft, R. W. Jr. *J. Am. Chem. Soc.* **76** (1954) 244.
35. Abel, E. *J. Phys. Chem.* **52** (1948) 908.
36. Giaque, W. F., Hornung, E. W. Kunzler, J. E. and Rubin, T. R. *J. Am. Chem. Soc.* **82** (1960) 62.
37. Young, T. F. and Blatz, L. A. *Chem. Revs.* **44** (1949) 93.
38. Hood, G. C. and Reilly, C. A. *J. Chem. Phys.* **27** (1957) 1126.
39. Young, T. F. *Private communication*.
40. Kerker, W. *J. Am. Chem. Soc.* **79** (1957) 3664.
41. McKay, H. A. C. *Trans. Faraday Soc.* **52** (1956) 1568.

Received April 2, 1960.