Activity of Ions in and Structure of Concentrated Solutions of Electrolytes*

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In a review of recent work done in the author's laboratory certain aspects of activity coefficients and of structure of concentrated solutions of electrolytes are discussed. The theses presented in the introductory part are corroborated by experimental results and thermodynamic interpretation.

In this report I would like to bring out some of the results of investigations on activity of ions and of the structure of concentrated electrolyte solutions done in our laboratory. There are four topics for discussion.

Firstly: In electrolyte solutions of high concentration ($m \geq 1$) it is (often) not possible to determine exactly the mean activity coefficient. $f_{\pm}$

Secondly: In such solutions there are large differences between the single ion activity coefficients of cation and anion: especially $f_{+} \gg f_{-}$, if the hydration of the cation is large.

Thirdly: The activity coefficients are essentially influenced by the interference ion-solvent (especially water) and the structure of the solvent in the electrolyte solution.

Fourthly: The quarternary cations NR_4^{+} destroy not only the structure of the water but also the hydration shell of the inorganic cations.

(i) At high concentrations $m_{\pm} < Q\, m_E = (\nu_+^{\nu_+} \nu_-^{\nu_-})^{1/\nu} m_E$, for ion pair formation and complexing diminish the number of ions, but the true value of $m_{\pm}$ cannot be determined exactly, therefore the true $f_{\pm} > \dfrac{a_{\pm}}{Q m_E}$

(ii) There are much different, not distinguishable, particle species, because not all ions are fully hydrated, the great number of ions compete for the water molecules. But the activity refers to an ideal diluted, fully hydrated solution.

Therefore it is extremely difficult, to give a quantitative theoretical interpretation for the thermodynamic behaviour of such concentrated solutions ($J > 1$).

In the last time many investigations of the mean activity coefficients in ternary solutions are made[1-3]. The Harned rule, which is valid for constant

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ionic strength, was extended and correlations between its coefficients and the entropy of the ions were found.

We have measured by potentiometric methods the activity of a much diluted electrolyte with constant concentration m_1 in dependence of the high increasing concentration of a second electrolyte ($m_2 \gg m_1$). In the most already published systems[4] we have found a similar equation as the Harned rule for $\lg f_{\pm_1}$ resp. $f_{\pm_1}^2$

$$\lg f_{\pm_1} = \lg (f_{\pm_1})_0 + K \cdot n_e \cdot m_2 \qquad (1)$$

when $J > 0.5$ Mol/kg, $(f_{\mp})_0$ refers to the ionic strength $\cong 0.5$. The gradient K is proportional to the reciprocal of the radius of the cation of electrolyte 2. These measurements were made with cells without transference for example

$$(Pt) H_2 / HCl (m_1) \text{ salt } (m_2) \text{ AgCl (s) / Ag} \qquad (a)$$
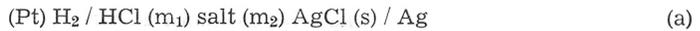
But if we measured with cells with transference

$$(Pt) H_2 / HCl (m_1) \text{ salt } (m_2) // \text{ sat. Cal. el.} \qquad (b)$$
$$Ed$$
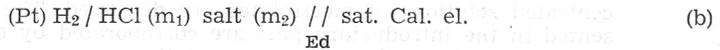
and calculated the activity coefficient of the cation (here hydrogen ion) neglecting the junction potential, we found the same dependence and the same gradient K. Fig. 1 is an example for many other systems not only with
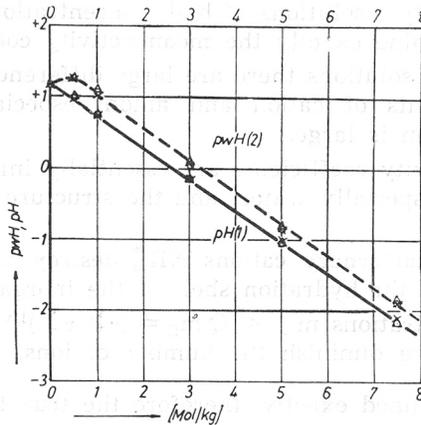
Fig. 1. pH- and pwH-shift in 0.1 M HCl by addition of Sr(ClO$_4$)$_2$.
(1) △ (Pt) H$_2$/0.1 M HCl, Sr(ClO$_4$)$_2$//NaCl$_{sat}$//KCl$_{sat}$, Hg$_2$Cl$_2$ $_{sat}$/Hg
(1) ... Hg/Hg$_2$Cl$_2$ $_{sat}$, KCl$_{sat}$//0.1 M HCl/glass/0.1 M HCl, Sr(ClO$_4$)$_2$//NaCl$_{sat}$//KCl$_{sat}$, Hg$_2$Cl$_{2sat}$/Hg
    ○ ... glass electrode made of alkali-proof high-temperature glass
    × ... glass electrode made of universal glass
(2) △ (Pt) H$_2$/0.1 M HCl, Sr(ClO$_4$)$_2$, AgCl/Ag
(2) ... Hg/Hg$_2$Cl$_2$ $_{sat}$, KCl$_{sat}$//0.1 M HCl/glass/0.1 M HCl, Sr(ClO$_4$)$_2$, AgCl$_{sat}$/Ag
    ○ ... glass electrode made of alkali-proof high-temperature glass
    × ... glass electrode made of universal glass.

hydrogen ions but also with Cd^{2+} and Na$^+$. But with Tl$^+$ we received[5] a decrease of the $\lg f_{Tl^+}$

$$\lg f_{Tl^+} = \lg f_{Tl^+}^0 - K \cdot n_e \cdot m_2 \qquad (2)$$

The small constant difference between $pH \cong - \lg m_{H^+} f_{H^+}$ and $pwH \equiv$ $\equiv - \lg m_{H^+} f_{H^+} f_{Cl^-}$ means that

$$\lg f_{Cl^-} = pH - pwH \tag{3}$$

and f_{Cl^-} is small and constant, on the contrary f_{H^+}, $f_{Cd^{2+}}$ rise exponentially with the ionic strength to values of more than thousand. This is only valid, when the junction potential is small and nearly constant. We have proved, that this is right in the following manner.

(i) We measured f_{Cl^-} with the cell with transference (c)

$$Ag / AgCl (s), HCl (m_1) \text{ salt } (m_2) // \text{ sat. Cal. el.} \tag{c}$$
$$\underset{Ed}{}$$
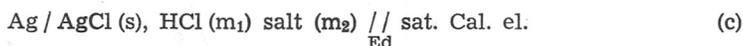
and received values corresponding to the values from equation (3). (Table I).

TABLE I

Activity Coefficient f_- of Cl-ions

	0.1 M HCl + M CaCl$_2$				
M CaCl$_2$	0.5	2	3	5	7
pH	0.92	0.33	—0.12	—1.06	—1.68
pwH	1.34	0.71	0.18	—0.75	—1.40
$f_{H^.}$	1.20	4.18	13.2	115	479
$f_{Cl^,}$ from pH—pwH	0.38	0.42	0.50	0.49	0.53
$f_{Cl^,}$ from cell (c)	0.39	0.45	0.54	0.56	0.59

Such correspondence was also found for the Br$^-$ ion.

(ii) We determined the activity of the hydrogen ion with spectrophotometric methods (Hammett function) and received within the measuring accuracy the same value as by potentiometric methods (Fig. 2). Many comparisons of this manner had the same result[6].
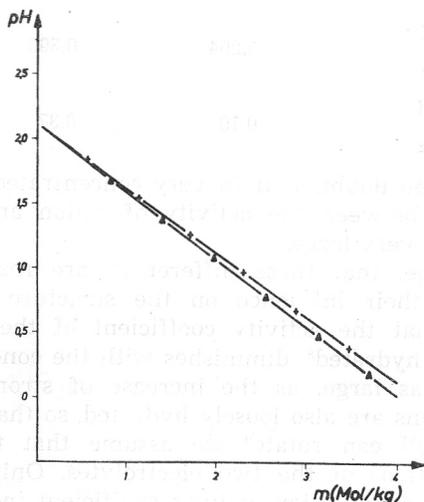
Fig. 2. pH-shift in 0.01 M HClO$_4$ by addition of Mg(ClO$_4$)$_2$.
— ▲ — determined by potentiometric method;
— ✕ — determined by spectrophotometric method.

(iii) We have measured the catalytic decomposition of diazoacetic ether[7]

$$N_2 = CH\text{---}COOC_2H_5 + H_2O \xrightarrow{\text{H}^+} CH_2OH\text{---}COOC_2H_5 + N_2 \qquad (4)$$

by 5×10^{-4} M $HClO_4$ in dependence of the concentration of $NaClO_4$ and $Ba(ClO_4)_2$ (Fig. 3). The gradient of $\lg K \sqrt{\dfrac{\Delta \lg K_r}{\Delta m_2}}$ was the same as $-\dfrac{\Delta pH}{\Delta m_2}$
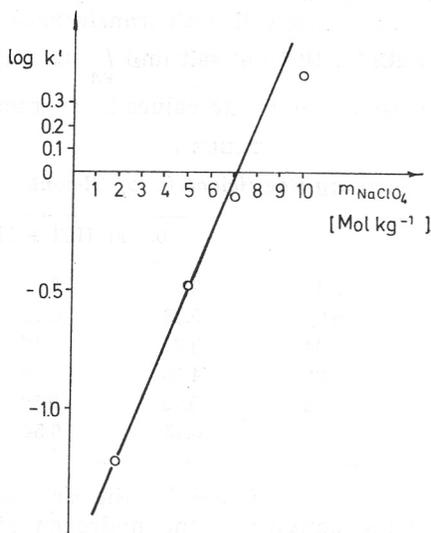
Fig. 3. Rate of decomposition of diazoacetic ether in dependence of the amount of added NaClO₄.

	NaClO₄	Ba (ClO₄)₂
$\dfrac{\Delta \lg K_r}{\Delta m_2}$	0.204	0.390
$-\dfrac{\Delta pH}{\Delta m_2}$	0.19	0.37

I think, there is no doubt, that in very concentrated solutions of electrolytes the differences between the activity of cation and anion at the same concentration may be very large.

Now we shall see, that these differences are result of the hydration of the ions and of their influence on the structure of the solution. We have already said, that the activity coefficient of the thallium ion, which is not or very loosely hydrated[8], diminishes with the concentration of salt two. The decrease is not as large, as the increase of strongly hydrated cations (H⁺ and Cd²⁺). As anions are also loosely hydrated, so that the water molecules in the hydration shell can rotate[9] we assume that the increase of $f_{\pm}$ is dependent on the cations of the two electrolytes. Only if both cations are strongly hydrated their single ion activity coefficient increases.

If the cation of the electrolyte 2 is hydrophobic as quarternary ammonium ions, then the activity coefficients f_{H^+} and $f_{\pm}^2$ decrease as is seen in the Fig. 4,
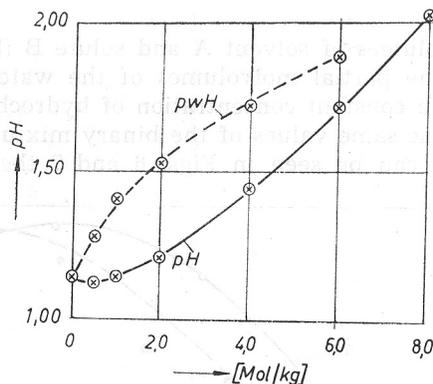
Fig. 4. pH- and pwH-shift in 0.1 M HCl by addition of TEACl.
— ○ — (Pt) H₂/0.1 M HCl, TEACl//KCl$_{sat}$, Hg₂Cl₂ $_{sat}$/Hg
-- ○ -- (Pt) H₂/0.1 M HCl, TEACl, Hg₂Cl₂ $_{sat}$/Hg
— × — Hg/Hg₂Cl₂ $_{sat}$, 0.1 M HCl/glass/0.1 M HCl, TEACl//KCl$_{sat}$, Hg₂Cl₂$_{sat}$/Hg
-- × -- Hg/Hg₂Cl₂ $_{sat}$, 0.1 M HCl/glass/0.1 M HCl, TEACl, Hg₂Cl₂ $_{sat}$/Hg

where is shown the pH and pwH in dependence of the concentration of tetraethylammoniumchloride. pH and pwH increase not linear with the concentration and the distance between the two values is not constant and larger than in Fig. 1. It is well known, that such cations destroy the structure of the water[10] and have a positive excess volume, (Fig. 5) whereas the excess volumes of
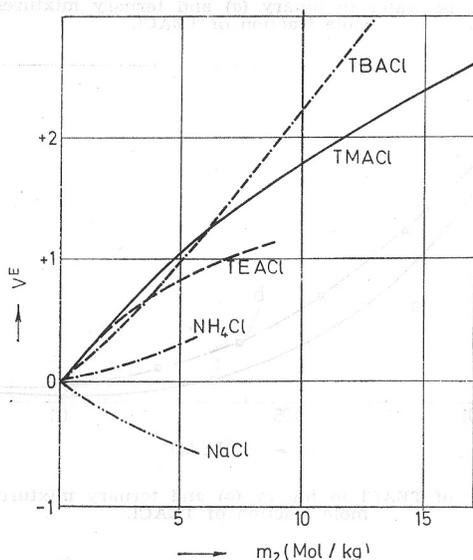
Fig. 5. Comparison of the excess volumes of some inorganic salts as a function of concentration.

$$V^E = V_m - x_A \cdot V_A^o - x_B \cdot V_B^o \tag{5}$$

the inorganic salts with strongly hydrated cations are negative. (V_m is the mean molvolume of the mixture $\dfrac{v}{n_A + n_B}$, x_A and x_B are the molfractions,

V_A^o and V_B^o the molvolumes of solvent A and solute B (here the electrolyte). In ternary mixtures the partial molvolumes of the water and of tetraethyl-ammoniumchloride at a constant concentration of hydrochloric acid (1 mol/kg) were compared with the same values of the binary mixture as function of the salt concentration. As can be seen in Figs. 6 and 7 the partial molvolumes
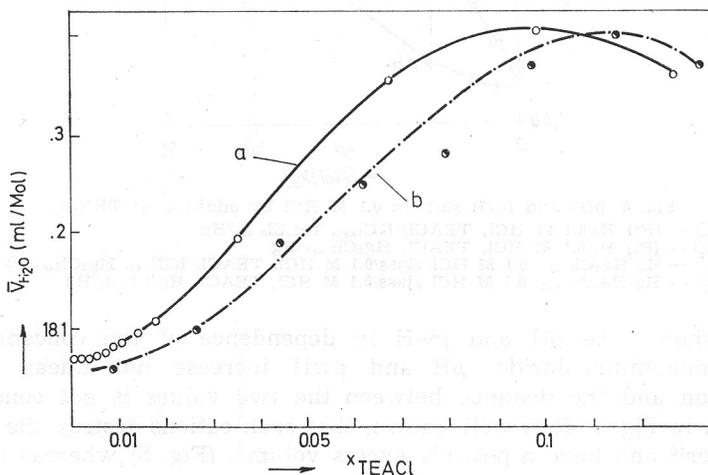
Fig. 6. Partial molvolume of water in binary (a) and ternary mixtures (b) as a function of mole fraction of TEACl.
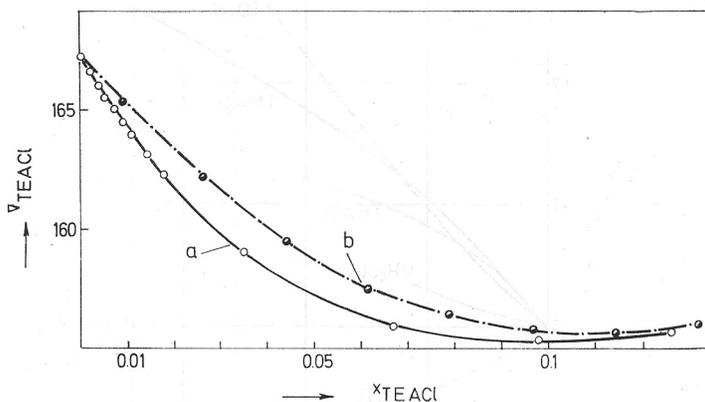
Fig. 7. Partial molvolume of TEACl in binary (a) and ternary mixtures (b) as a function of mole fraction of TEACl.

are not essentially influenced by the hydrochloric acid at all concentrations of the quarternary salt. That means, that the structure of the solution is formed by the quarternary salt even at low concentrations. The hydration shell of the hydrogen ion is almost without influence. At the other hand the partial molvolumes of hydrochloric acid and sodium chloride resp. influence each other not very much[11]. The partial molvolume of HCl increases in the binary mixture as well as with the concentration of sodium chloride.

The large effect of quarternary salts on the mobility of hydrogen ion in water as seen in Figs. 8 and 9 is another proof, that these cations change the
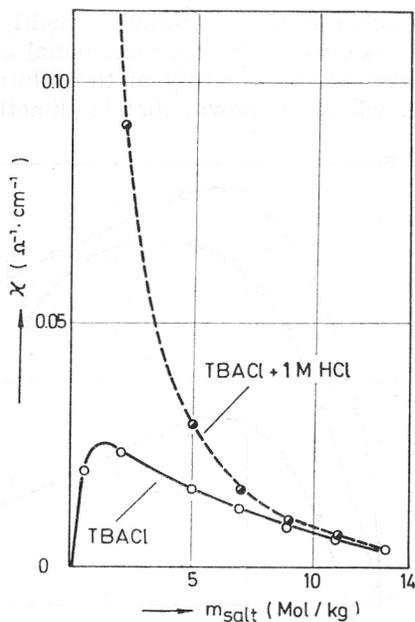
Fig. 8. Specific conductivity of TBACl- and (1 M HCl + TBACl)-solution as a function of TBACl-concentration.
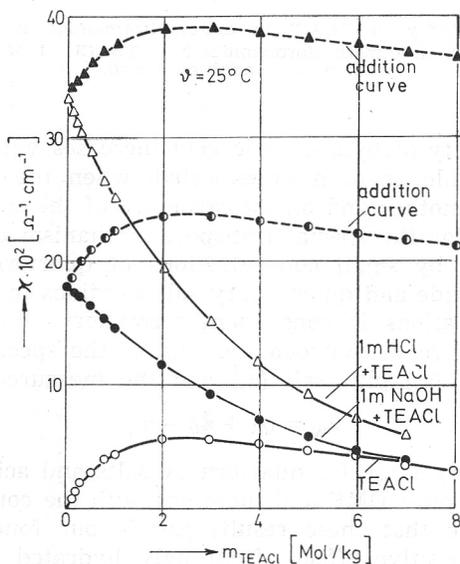
Fig. 9. Specific conductivity of TEACl —, (1 M HCl + TEACl) and (1 M NaOH + TEACl)-solution as a function of TEACl-concentration.

water structure completely. The spec. conductivity of acids and bases in water solutions is diminished if we add quarternary ammonium salts even at small concentrations.

If one molal hydrochloric acid contains 5 mol/l tetrabutylammonium-chloride its conductivity is $10^0/_0$ of the pure one molal acid. That this effect is not caused by an increase of the viscosity of the solution was proved and is also seen from Fig. 10, where is shown, that in dimethylformamide solution
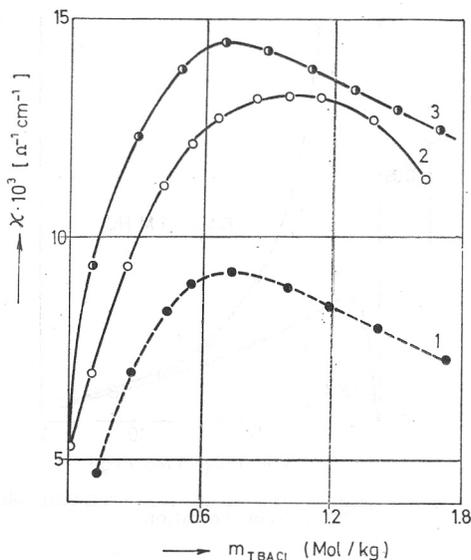
Fig. 10. Specific conductivity of TBACl in dimethylformamide in dependence of TBACl concentration: 1 — TBACl in dimethylformamide; 2 — TBACl + 1 M HCl in dimethylforma-mide; 3 — addition curve.

(DMF) the conductivity of hydrochloric acid increases with addition of tetra-butylammoniumchloride as to been expected, when the ions have no large influence one upon another and on the structure of the solution. In water the structure necessary for the special transport mechanism of the hydrogen ion is destroyed already by small concentrations of quarternary salts. In mixtures of sodium chloride and quarternary salt solutions in water the influence of the quarternary cations is consequently smaller[4g]. We have termed this influence by the difference between the sum of the specific conductivities of the acid (resp. base) ($\varkappa_1$) plus salt ($\varkappa_2$) and the measured spec. conductivity

$$\varkappa_W = (\varkappa_1 + \varkappa_2) - \varkappa_m \tag{6}$$

This difference is very large for quarternary salts and acids in water (Figs. 8 and 9), but small in pure DMF and increases with the concentration of water (Fig. 11). We believe that these results justify our fourth assumption and that therefore the positive effect of strongly hydrated cations on lg f$_+$ of other hydrated ions and on their own activity is mainly a consequence of the change in the structure.
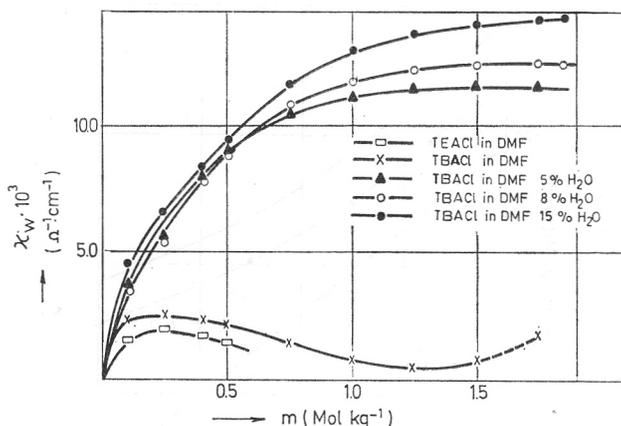
Fig. 11. $\varkappa_w$ as a function of TEACl- and TBACl-concentration in dimethylformamide and dimethylformamide-water mixtures.

The activity coefficient, measuring the free excess enthalpy can be influenced by a change of enthalpy ΔH^E and entropy ΔS^E

$$RT \ln f = \Delta H^E - T \Delta S^E \qquad (7)$$

$$\lg f = \frac{\Delta H^E}{2.3\ RT} - \frac{\Delta S^E}{2.3\ R} \qquad (7a)$$

When our assumption is right, then the increase of f_+ or $f_\pm$ must be mainly caused by a decrease of ΔS^E and a decrease of the activity coefficient by an increase of the entropy. Two strongly hydrated cations (H^+ and M^{++} f. a.) will compete for the water molecules, the minimum of entropy or the maximum of free excess enthalpy will be reached if all cations have the possible maximum of hydration in the concentrated solution.

The reaction entropy of the cell reaction in a cell of Type (a) is given by

$$\Delta S^o = S^o_{Ag} + \overline{S}^o_{HCl} - 1/2\ S^o_{H_2} - S^o_{AgCl} \qquad (8)$$

and can be calculated from the temperature gradient of the standard electromotive force E^o of the cell:

$$\left(\frac{\delta E^o}{\delta T} \right)_p = - \frac{\Delta S^o}{F} \qquad (9)$$

(F = Faraday constant, 23062 cal)
From (8) we find the partial molal entropy of hydrochloric acid and its change with the concentration of the salt (m_2). By equation (7) this change is connected with the mean activity coefficient of the hydrochloric acid. In Fig. 12 we see, that the partial molal entropy decreases indeed almost linearly with the concentration of sodium perchlorate for HCl, HBr and HI. If we assume, that the excess enthalpy ΔH^E does not depend on the concentration of the salt, the gradient of $\lg f_\pm$ should be

$$\frac{\partial \lg f_\pm}{\partial m_2} = - \frac{1}{4.57} \frac{\partial \Delta S^E}{\partial m_{NaClO_4}} \qquad (10)$$
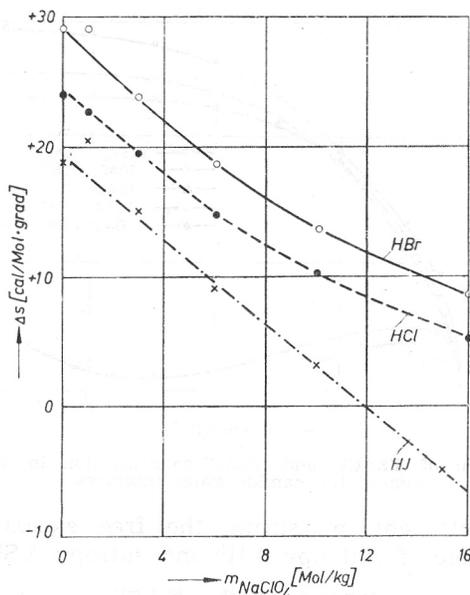
Fig. 12. Concentration dependence of ΔS for HCl, HBr and HI by addition of $NaClO_4$.

Really we find, that this gradient is smaller than the term $- \dfrac{1}{4.57} \dfrac{\partial \Delta S^E}{\partial m_{NaClO_4}}$

First calorimetric measurements have shown, that ΔH^E determined by the heat of mixing in the ternary system, decreases with salt concentration, therefore equation (10) is not fully justified.

Quarternary cations produce by their strong hydrophobic effect a dense, disordered structure with holes in their neighbourhood (Fig. 13) even if
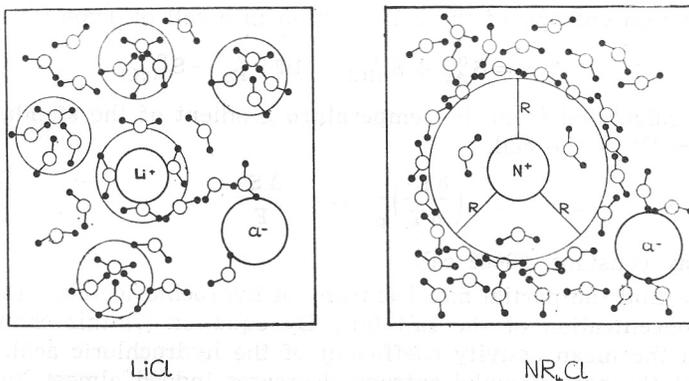
Fig. 13. Structure of aqueous solutions of LiCl and NR₄Cl.

strongly hydrated cations are present and therefore ΔS^E of the hydrated electrolyte increases or lg f decreases. The same is the matter with loosely hydrated ions (as Tl^+ or most anions) combined with strongly hydrated cations (as Li^+, Mg^{2+}, Al^{3+}, a. s. o.) The first named ions lose their hydration shell, that corresponds to an increase in entropy with respect to the un-

disturbed, soluted ion, this increase will be a function of the ion radius or the hydration number of the other cation, therefore we find the greatest decrease of the activity coefficient of Tl^+ by addition of the strongly hydrated Mg^{2+}.

A quantitative test of these assumptions will be very difficult from the reasons named at the beginning. But we hope, that further measuring investigations especially with high frequency sprectroscopy, dielectric and proton magnetic relaxation and so on in ternary systems can prove, if this assumption is justified or not. In every case it seems important, to gain new knowledge of the behaviour of ions in concentrated solutions so much used in the chemical industry. Then it influences not only the thermodynamics but also the kinetics in such solutions as we could show for instance with respect to the anodic dissolution of iron[12] or the cathodic reduction of benzaldehyde[4b].

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IZVOD

Aktivitet iona i struktura u koncentriranim otopinama elektrolita

K. Schwabe

U preglednom referatu o koncentriranim otopinama elektrolita sistematski se razmatraju četiri teme. Prvo: razlozi zašto je u koncentriranim elektrolitima često nemoguće odrediti srednji koeficijent aktiviteta, $f_\pm$. Drugo, u koncentriranim elektrolitima postoji velika razlika između koeficijenata aktiviteta kationa i aniona; ako je kation jako hidratiziran, $f_+ \gg f_-$. Treće, koeficijenti aktiviteta uvjetovani su interferencijom između iona i otapala (naročito to vrijedi za vodu) te strukturom otapala u elektrolitnoj otopini. Četvrto, kvarterni kationi tipa NR_4^+ razaraju ne samo strukturu vode, nego i hidratacionu ovojnicu anorganskih kationa. Termodinamičkim razmatranjima i eksperimentalnim podacima dokazuju se navedene tvrdnje.

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