Excess Energies and Interactions in Concentrated Aqueous Solutions of Alkali-metal Halides

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From osmotic and activity coefficient data together with density data, the excess energy of aqueous alkali-metal halide solutions at 25 °C is found largely to obey the two-term equation $G^{ex}/(nRT) = -Ac^{1/3} + Bm$ in the molality range $1-7$. Through the values obtained for the salt-specific constants A and B of this equation, some guidance is gained towards elucidating component interactions in concentrated aqueous electrolyte solutions. Emphasis is on $-Ac^{1/3}$ being a quasi-lattice electrostatic ion-ion interaction term and Bm an excess ion-water interaction term.

Much thermodynamic data on aqueous single-salt solutions is stored in tables for the mean molal bare-ion activity coefficient ($\gamma_\pm$) and the molal osmotic coefficient (ϕ).[1,2] Both these coefficients carry information on interactions between the solution components, and they combine to do so in the bare-ion excess energy of the solutions ($G^{ex} = G - G^{id}$). When referred to mol-fraction ideality, this excess energy is:[1−3]

$$G^{ex}/(nRT) = v[\ln \gamma_\pm - \phi + (1 + \frac{55.51}{vm}) \ln (1 + \frac{vm}{55.51})]$$

(1)

where n is moles of salt in the solution portion considered, v is mol of ions per mol of salt at complete dissociation, m is the salt molality, 55.51 is the water molality, and RT has its usual meaning. For dilute solutions, the last term of the three inside the brackets differs negligibly from unity.

The excess energy is the sum of an electrostatic ion-ion interaction term (G^{el}) and a remaining term (G^{re}) which mostly reflects ion-water interaction effects. In dilute solutions, G^{el} is the dominant excess term and is well-described by the extended Debye-Hückel theory.[1−4] This theory yields a limiting square-root concentration dependence for G^{el}/n at infinite dilution, but it is invalidated already at concentrations exceeding the order of 10^{-3} M. At higher concentrations, a quasi-lattice cube-root dependence ($G^{el}/(nRT) = -Ac^{1/3}$) appears to take over,[3−6] but modern statistical theories have not yet revealed this clearly. Our knowledge of G^{re} is poor, but there are a variety of possible reasons (solvation, cosphere overlap, heat of mixing, component size differences) to expect G^{re}/n to vary approximately linearly with the salt molality.[1,3,6,7] The relationship:

$$G^{ex}/(nRT) = -Ac^{1/3} + Bm$$

(2)

where A and B may be salt-dependent constants, is thus suggested for single-salt solutions at moderate to high concentrations.

In the present work, eqn. (1) is used to obtain excess energy data from molal activity and osmotic coefficient data[1] for aqueous solutions of alkali-metal halides at 25 °C. These energy data are then used together with c/m or density data[2,8] to test the applicability of eqn. (2). This is all done with a SIMULA program on a DEC-10 computer. The testing part of this program determines for each salt the value of A which best gives $((G^{el}/nRT) + Ac^{1/3})/m$ a constant value (B) over the molality range $1-6$ (with emphasis on the molality range $2-4$). A main aim is, through the values thus appearing for the constants A and B, to seek some guidance towards a better understanding of the interactions occurring in aqueous electrolyte solutions.
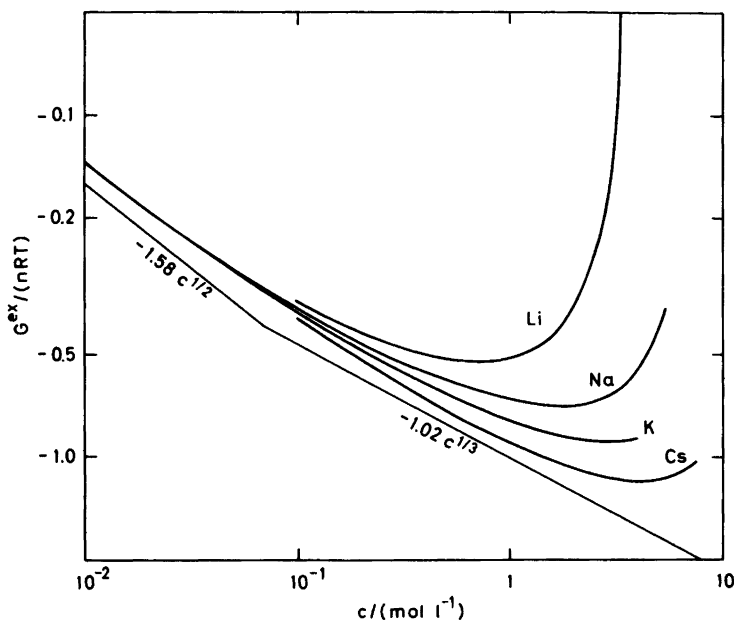
Fig. 1. Log-log plot of excess energy *vs.* molarity for aqueous solutions of alkali-metal chlorides at 25 °C. Straight lines represent the square-root Debye-Hückel limiting law ($-1.58\ c^{1/2}$) and a cube-root function presently used for cesium chloride ($-1.02\ c^{1/3}$).

THE EXCESS ENERGY (G^{ex})

Fig. 1 presents a log-log plot of the excess energy obtained for alkali-metal chloride solutions vs. their molarity (c). This presentation illustrates the change generally occurring from a square-root law at low concentration to some cube-root law mixed with an increasing contribution from a repulsive interaction term at higher concentrations. Analogous behaviour is observed for the alkali-metal bromides and iodides.

Figs. 2–4 present testings of eqn. (2) for the various alkali-metal halides with best fitting values for the constant A. For the molality range covered, these testings largely are positive, provided the values thus obtained for A are acceptable (see below). These values are presented in Table 1 together with those obtained for the constant B.

THE ELECTROSTATIC TERM (G^{el})

Since the average distance between neighbouring ions is proportional to $c^{-1/3}$, the above cube-root expression for the electrostatic interaction energy (G^{el}) is analogous to the Madelung expression for the electrostatic lattice energy of ionic crystals. Consequently, with the relevant Madelung constant, the relevant $r/c^{-1/3}$ relationship, and the relevant dielectric constant, one may easily calculate lattice-connected values for the constant A of the electrostatic energy term. For 1:1 salts in water ($\varepsilon=78$), some results are: 1.45 (zinc blende lattice), 1.34 (sodium chloride lattice), and 1.24 (cesium chloride lattice), all values in $(l/mol)^{1/3}$. These lattices have 4:4, 6:6 and 8:8 coordination, respectively. It is satisfying that the values obtained for A (Table 1) are lower than the lattice-connected ones.

By a mathematical approximation to statistical theories, Glueckauf[6] has developed a simple, unified equation for G^{el}. This equation follows statistically derived ones accurately at low concentrations and then turns smoothly into a cube-root function at higher concentrations. For 1:1 electrolytes in water at 25 °C, the latter function yields the following expression for the constant A of the electrostatic cube-root term:

$$A/(1\ mol^{-1})^{1/3} = 1.44(a/\text{Å})^{-1/3} \tag{3}$$

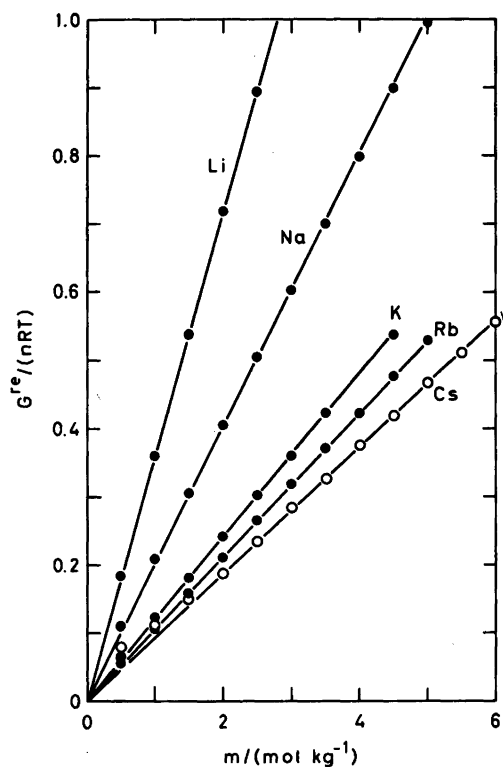where a is the ion-size parameter of the statistical

Fig. 2. The remaining term (G^{re}) *vs.* molality for aqueous solutions of alkali-metal chlorides at 25 °C. Determined from $G^{re} = G^{ex} + Ac^{1/3}nRT$ with A-values (Table 1) giving best fit to eqn. (2).
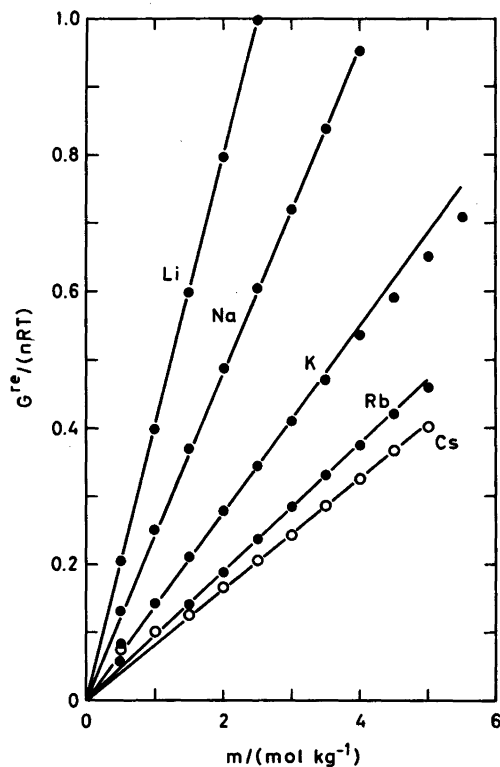
Fig. 3. For bromides as for chlorides in Fig. 2.

Table 1. The constants A and B of eqn. (2) for aqueous single-salt solutions of alkali-metal halides at 25 °C.

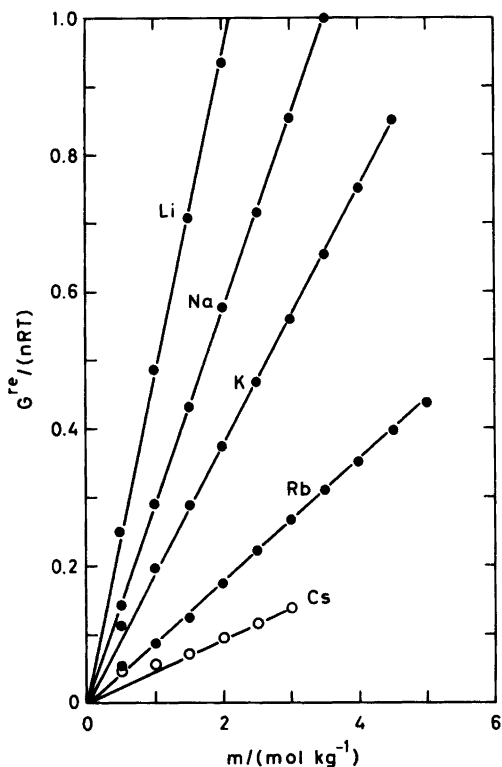|	Li	Na	K	Rb	Cs
$A/(1\ mol^{-1})^{1/3}$					
Cl	0.88	0.89	0.90	0.93	1.02
Br	0.88	0.89	0.90	0.93	1.02
I	0.81	0.86	0.90	0.93	0.99
$B/(kg\ mol^{-1})$					
Cl	0.36	0.20	0.12	0.106	0.094
Br	0.40	0.24	0.14	0.095	0.083
I	0.47	0.28	0.19	0.088	0.047

Fig. 4. For iodides as for chlorides in Fig. 2.

theories (the distance of closest approach of dissolved ions), and Å is the Ångström unit (10^{-8} cm).

With the values presently obtained for A (Table 1), eqn. (3) gives partly acceptable[1-3] a-values (ranging from 2.8 Å for CsCl to 5.6 Å for LiI). It may thus largely (but not completely) account for the observed dependence of A on the salt identity.

THE REMAINING TERM (G^{re})

As mentioned above, there are several possible contributions to the remaining excess energy term

(G^{re}). In the Robinson-Stokes hydrated-ion solution description,[1,9] this term is a purely statistical one, caused by ion hydration affecting the number of "free" water molecules in the solution. In the Gurney-Friedman hydration-cosphere model for ions in water,[7] the term comes from cosphere overlap. Let us briefly consider these two possible contributions.

The statistical ion-hydration energy term simply is the Kelvin temperature multiplied by the difference between the ideal entropies of mixing bare ions with all the water molecules and hydrated ions with the remaining "free" water molecules, respectively. Its full expression is long and cumbersome, but it is well approximated (at least at hm below about 15 mol kg^{-1}) by the simple equation:

$$G^{re}_{st}/(nRT) = (vh/55.51)m \qquad (4)$$

where h is mol of water per mol of salt in the hydrated ion species. If this be the main contribution to G^{re}, the constant B of eqn. (2) should mainly be $vh/55.51$. With the presently obtained B-values (Table 1), this yields the h-values presented in Table 2.

The h-values of Table 2 are higher than those originally obtained by Robinson and Stokes[1,9] using the extended Debye-Hückel expression for G^{el}, but they still suffer from the inadequacies already discussed by these authors. Except for the lithium halides, they compare better with h-values obtained from compressibilities (Appendix 6.2 of Ref. 3).

The possible contribution by cosphere overlap is presently less clear. However, a summary[7] of the main results of the first investigations on the matter suggests that this contribution be *negative* for all the alkali-metal halides except for those of lithium (the negative trend increases from Li to Cs and from Cl to I). If this be true, the cosphere-overlap contribution cannot be the leading one in G^{re}, since G^{re} is *positive* for all the alkali-metal

Table 2. The hydration parameter h of eqn. (4) for alkali-metal halides in water at 25 °C.

	Li[a]	Na	K	Rb	Cs
Cl	(10.0)	5.6	3.3	2.9	2.6
Br	(11.1)	6.7	3.9	2.6	2.3
I	(13.0)	7.8	5.3	2.4	1.3

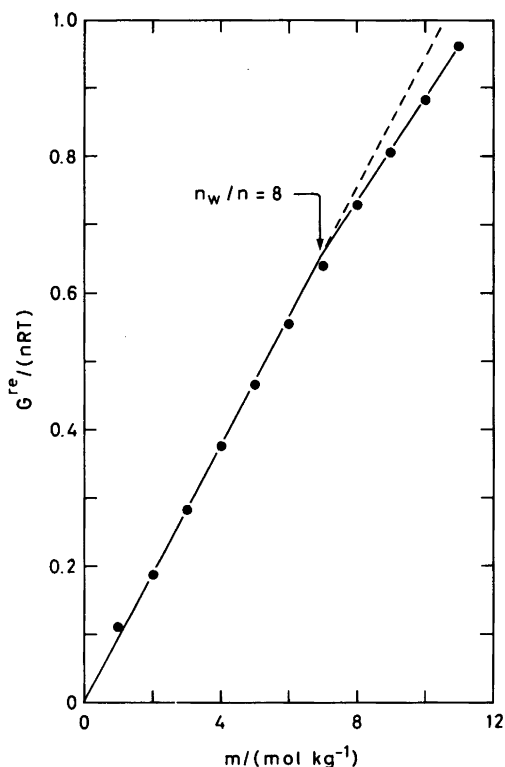[a] ( ), near applicability limit of eqn. (4) to present data.

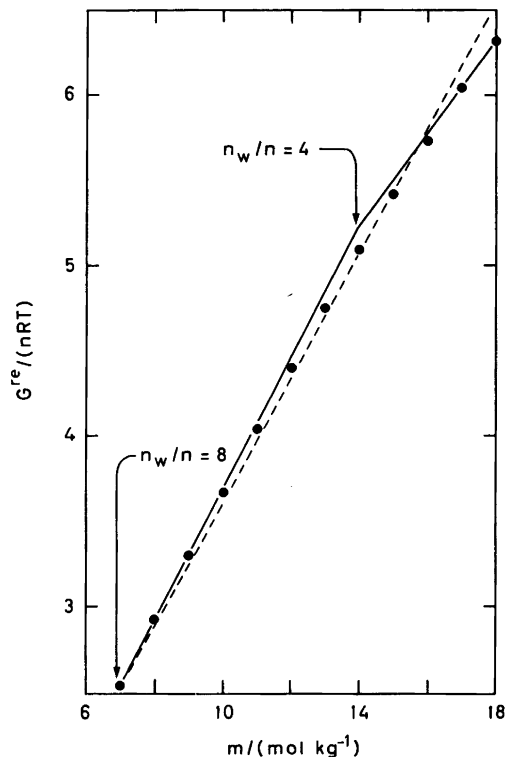Fig. 5. For cesium chloride as in Fig. 2, but extended to saturation.

Fig. 6. For lithium chloride as in Fig. 2, but at higher concentrations. The dashed line is an extrapolation of the one for lithium chloride in Fig. 2.

halides (Figs. 2–4). Correction for such a contribution, however, may improve the h-values of Table 2.

EXCESS HYDRATION ENERGY

A different approach to elucidating the remaining excess-energy term (G^{re}) simply is to consider it being an excess hydration energy of the dissolved salt. This may be pursued by combining the Born-charging equation for the hydration energy of ions[1–4] with the dielectric-decrement equation for aqueous solutions ($\varepsilon = \varepsilon_w - \delta m = \varepsilon_w - \delta_+ m_+ - \delta_- m_-$). For 1:1 electrolytes at $m \ll \varepsilon_w/\delta$, assuming the charging of an ion to occur in an environment mostly affected by ions of the opposite charge, one thus obtains for the constant B of eqn. (2):

$$B = e^2(8\pi\varepsilon_0\varepsilon_w^2 kT)^{-1}(\delta_- r_+^{-1} + \delta_+ r_-^{-1}) \qquad (5)$$

where ε_0 is the permittivity of vacuum, ε_w is the relative permittivity of liquid water, r_+ and r_- are the effective radii of the positive and negative ions of the salt in the solution and other symbols have their usual meaning.

Eqn. (5) is most safely applied to salts for which $r_+ = r_-$, since its last factor may then be replaced by δr_-^{-1} and the crystal radius used for r_-. For lithium chloride to rubidium chloride, δ goes[1] from 14 to 10 kg mol^{-1}, and r_- is about 1.8 Å. With δr_-^{-1} as replacement in eqn. (5), this gives B-values from 0.35 to 0.25 kg mol^{-1}. This compares well with the empirical B-values for the lighter alkali-metal chlorides (Table 1). For sodium chloride to sodium iodide, δ goes from 11 to 15 kg mol^{-1} and r_- from 1.8 to 2.2 Å, yielding (as above) B-values from 0.27 to 0.31 kg mol^{-1}. Also this is interesting and promising, not least by showing the same trend in B from chloride to iodide as is observed for the lighter alkali-metal halides (Table 1).

Whereas the constant B, according to the present treatment, depends directly on a dielectric decrement (δ), the constant A should depend inversely on a dielectric constant (ε). For $m \ll \varepsilon_w/\delta$, this gives negligible concentration dependence to A. At higher concentrations, however, the tendency should be for A to increase with the concentration. It may be that effects of such a happening possibly are absorbed by the remaining excess term of the present work. This should, in that case, make the empirical B-values (Table 1) be lower than those emerging from eqn. (5). The latter is what generally is found.

HIGH CONCENTRATIONS

For cesium chloride, lithium chloride and lithium bromide, suitable data exist for extending the above treatment to higher concentrations.[1,8] Figs. 5 and 6 present such extensions for the two chlorides mentioned. These results (which have been obtained by using the relevant A-values of Table 1 all through the concentration ranges covered) suggest that there are breaks in the G^{re}/m lines at about 8 and 4 mol of water per mol of salt (n_w/n). A break at n_w/n about 8 occurs for all three salts considered (downwards for CsCl, upwards for LiCl and LiBr). A break at n_w/n about 4 is clearly exhibited only by lithium chloride (LiBr does not show this break clearly and CsCl is not soluble enough to reach this concentration).

DISCUSSION

The present results support suggestions that the excess energy (1) of aqueous alkali-metal halide solutions in the molality range $1-7$ (n_w/n range $55-8$) at 25 °C largely obeys the two-term eqn. (2) with salt-specific constants A and B (Table 1). Below 1 m, the electrostatic ion-ion interaction term tends to change from its quasi-lattice cube-root law towards its ion-cloud square-root law. Above 7 m, the remaining term apparently breaks away from its original molality dependence ($G^{re}/nRT = Bm$). The latter, however, may also be due to possible unconsidered changes in the electrostatic term (e.g. changes in the dielectric constant involved).

The constant A of the electrostatic cube-root term satisfactorily is lower than lattice-connected values calculated for it (with no regard of possible

short-range repulsive forces). This constant and its dependence on the salt identity (Table 1) may have some explanation in the ion-size involving expression (3) deduced for it from a treatment by Glueckauf.[6] This treatment, however, is not more than a mathematical approximation. A basic theory is still lacking for a cube-root law of ion-ion interaction at medium to high concentrations. Such a theory must consider the salt specificity observed.

The remaining term (G^{re}) is essentially linear in molality dependence (better so than in molarity dependence). The constant B of this term (Table 1) is positive for all the alkali-metal halides, and it all the way through increases from Cs to Li (i.e. with decreasing bare-ion size). For the cesium and rubidium halides, it accordingly increases also from I to Cl. For the lighter alkali-metal halides, however, the latter trend is reversed. The remaining term may perhaps be explained by a combination of the Robinson-Stokes[1,9] hydrated-ion solution description (statistical effects) with the Gurney-Friedman[7] hydration-cosphere model for ions in water (cosphere-overlap effects). Such a combination may yield more consistent values for the hydration parameter h than those obtained from a hydrated-ion treatment alone (Table 2). However, a different approach to explaining the remaining term is the hydration-energy treatment of the present work. This approach appears promising and deserves further attention and refinement.

Some guidance is thus obtained from osmotic and mean-ion activity coefficient data together with density data towards elucidating interactions in concentrated electrolyte solutions. Further guidance may come from convenient single-ion activity data. Such data are available for the alkali-metal chlorides,[10] but ought to be determined also for the corresponding bromides and iodides before being seriously invoked.

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