On Excess Energies and Ion Activities of Aqueous Alkali—Metal Halide Solutions

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A previous interpretation of excess energy data for alkali—metal halide solutions is tested and used in an approach to single-ion activities. The result largely accords with convenient single-ion activity data and supports that a Born-charging describable deviation from ideal ion—water interactions (excess hydration energy) largely dominates the activity relations between the ions. This may not apply to cesium iodide, but apparently applies better the lighter the alkali—metal halide is.

It has long been known and recently been emphasized[1] that the mol-fraction bare-ion excess energy of aqueous single-salt solutions of alkali—metal halides at medium to high concentration essentially obeys a two-term equation equivalent to eqns. (1)—(3), where A and B are salt-specific constants,

$$G^{ex} = G^{el} + G^{re} \tag{1}$$

$$G^{el} = -nAc^{1/3}RT \tag{2}$$

$$G^{re} = nBmRT \tag{3}$$

c and m are the salt molarity and molality of the solution, and n is mol salt in the solution portion considered. The two terms (2) and (3) have been interpreted[1] as reflecting a quasi-lattice type of electrostatic ion-ion interaction and a Born-charging describable deviation from ideal ion—water interactions (excess hydration energy), respectively. In the present work, these interpretations are tested more thoroughly.

A convenient scale for single-ion activities has recently been described[2] and applied to alkali-metal chlorides,[2] bromides[3] and iodides[4] in aqueous single-salt solutions. Although these determinations

involve estimations of liquid-junction potential differences, they essentially represent an experimental approach to single-ion activities. In the present work, a more theoretical approach to the same goal is pursued through excess energy considerations. A crucial question in this connection is how to separate the excess energy of a dissolved salt into terms for its individual ions. The result is tested against those of the experimental approach[2-4] noted.

EXCESS CHEMICAL POTENTIALS

Using $\partial G/\partial n = 2\mu_\pm$ for $z{:}z$ salts[5] and ignoring volume changes ($dc/dm = c/m$), one obtains from (1)—(3) the empirical expressions (4)—(6); for the

$$\mu_\pm^{ex} = \mu_\pm^{el} + \mu_\pm^{re} \tag{4}$$

$$\mu_\pm^{el} = -(2/3)Ac^{1/3}RT \tag{5}$$

$$\mu_\pm^{re} = BmRT \tag{6}$$

(mol-fraction bare-ion) excess mean-ion chemical potential (and its two terms) of alkali—metal halides in aqueous single-salt solutions.

The interpretations[1] to be tested give the two-term equation (4) with the expressions (7) and (8)

$$\mu_\pm^{el} = -Ne^2(8\pi\varepsilon_o\varepsilon r)^{-1}A' \tag{7}$$

$$\mu_\pm^{re} = Ne^2(16\pi\varepsilon_o)^{-1}(r_+^{-1} + r_-^{-1})(\varepsilon^{-1} - \varepsilon_\omega^{-1}) \tag{8}$$

for the two terms; N is the Avogadro number, e is the proton charge, A' is a quasi-Madelung constant, r is the shortest anion—cation distance of the

solution quasi-lattice, r_+ and r_- are the effective radii of the dissolved cations and anions, and ε_o, ε_ω, and ε are the permittivity of free space and the relative permittivities of pure water and the solution, respectively. These equations are a Guntelberg-charging expression (7) and a Born-charging expression (8) for the energies considered.[6] To the author's knowledge, (8) represents a novel application of Born-charging considerations.

From equivalence of (5) with (7) and of (6) with (8), the theoretical expressions (9) and (10) are obtained for the empirical parameters A and B;

$$A = 3e^2(16\pi\varepsilon_o \varepsilon c^{1/3} rkT)^{-1} A' \qquad (9)$$

$$B = e^2(16\pi\varepsilon_o \varepsilon_\omega \varepsilon mkT)^{-1}(r_+^{-1} + r_-^{-1})c\delta \qquad (10)$$

k is the Boltzmann constant, and δ is the molar dielectric decrement defined by $\varepsilon = \varepsilon_\omega - \delta c$. These expressions give little concentration dependence to A and B (mainly the one concealed in ε). They further make A weakly and B strongly dependent on the salt identity. These expectations accord with observations.[1] A more quantitative test can be made by using (9) and (10) to determine values of $A'c^{-1/3}r^{-1}$ and of $r_+^{-1} + r_-^{-1}$ from dielectric[7] and density[8] data and experimental values[1] for A and B, and comparing the outcome (Table 1) with other estimates of the same parameters.

Any regular ionic lattice has a characteristic value of $A'c^{-1/3}r^{-1}$ representative of its geometrical arrangement and independent of the particular ions involved. Some such values in 10^7 mol$^{-1/3}$ are 20.2 (zinc blende lattice), 18.6 (sodium chloride lattice) and 17.3 (cesium chloride lattice). These lattices have 4:4, 6:6 and 8:8 coordination, respectively. It is satisfying that $A'c^{-1/3}r^{-1}$ shows a nearly characteristic value also for alkali−metal halide

solutions (Table 1) and that this is lower than for the solid-salt lattices mentioned.

For anion−cation pairs of alkali−metal and halide ions, the sum of reciprocal Pauling radii spans the range $10-22$ nm^{-1} (from CsI to LiCl). Expanding the radii by the diameter of the water molecule, the range shifts to $4-5$ nm^{-1}. It is satisfying that $r_+^{-1} + r_-^{-1}$ for alkali−metal halide solutions (Table 1) mostly comes in between these two extreme ranges and that it mostly shows a directionally correct trend from lithium to cesium. However, its span appears rather wide and the trend from chloride to iodide is partly inverted.

ACTIVITY COEFFICIENTS

The mol-fraction activity coefficient (f_i) of an ionic species (i) is connected to the mol-fraction excess chemical potential (μ_i^{ex}) by eqn. (11).

$$\log f_i = \mu_i^{ex}/(2.303RT) \qquad (11)$$

This basically applies both to individual ions and to hypothetical mean-ions,[5,6] but it is a question of how to separate an experimentally determinable excess mean-ion chemical potential into its single-ion terms. By the above excess-energy considerations, however, a way of doing this almost suggests itself, and this shall here be pursued.

All crystal lattices for 1:1 salts are internally symmetric in cation and anion arrangement. Assuming this to apply also to the quasi-lattice of such a salt in aqueous solution, one obtains eqn. (12)

$$\mu_+^{el} = \mu_-^{el} = \mu_\pm^{el} \qquad (12)$$

for the electrostatic ion−ion interaction part of the excess chemical potential of the ions involved.

Table 1. Parameter values for aqueous alkali−metal halide solutions. Obtained from (9) and (10) with experimental A and B values[1] and dielectric[7] and density[8] data for 1 M solutions. 25 °C.

	Li	Na	K	Rb	Cs
$A'c^{-1/3}r^{-1}/(10^7 \text{mol}^{-1/3})$					
Cl	13.6	14.2	14.6	15.2	17.0
Br	13.4	14.0	14.4	15.2	17.0
I	12.2	13.2	14.4	15.0	16.4
$(r_+^{-1} + r_-^{-1})/(\text{nm})^{-1}$					
Cl	9.9	6.6	4.6	4.6	5.0
Br	10.6	7.3	5.2	3.9	4.2
I	11.6	8.2	6.7	3.4	(2.3)

Actually, (7) implies this, and (8) implies eqns. (13)

$$\mu_+^{re} = Ne^2(8\pi\varepsilon_o)^{-1}(\varepsilon^{-1} - \varepsilon_\omega^{-1})r_+^{-1} \qquad (13)$$

$$\mu_-^{re} = Ne^2(8\pi\varepsilon_o)^{-1}(\varepsilon^{-1} - \varepsilon_\omega^{-1})r_-^{-1} \qquad (14)$$

and (14) for the remaining part of the excess chemical potential of the individual ions involved.

For a 1:1 salt, the molal bare-ion activity-coefficient ratio (γ_+/γ_-) is equal to the corresponding mol-fraction based ratio (f_+/f_-).[5] With (11)–(14), this yields eqn. (15) when use is made of

$$\log(\gamma_+/\gamma_-) = e^2(18.42\pi\varepsilon_o\varepsilon_\omega\varepsilon kT)^{-1}(r_+^{-1} - r_-^{-1})$$
$$(c/m)\delta m \qquad (15)$$

$\varepsilon = \varepsilon - \delta c$. A nearly linear $\log(\gamma_+/\gamma_-)/m$ relationship with slope decreasing regularly from lithium to cesium halides is hence expected. This accords with the convenient single-ion activity data.[2-4] A more quantitative test can be made by using (15) to determine $r_+^{-1} - r_-^{-1}$ from experimental $\log(\gamma_+/\gamma_-)/m$ slopes[2-4] and dielectric[7] and density[8] data, and comparing the outcome (Table 2) with other estimates of the same difference.

For anion–cation pairs of alkali–metal and halide ions, the difference $r_+^{-1} - r_-^{-1}$ will span the range from 0.4 to 12 nm^{-1} if Pauling radii be used. Expanding such radii for the cations by 0.085 nm (often recommended to obtain effective radii in hydration energy considerations[5,6,9]), the span will be from -1.6 to 2.4 nm^{-1}. It is satisfying that the values presently obtained for $r_+^{-1} - r_-^{-1}$ (Table 2) compare well with this, and that they show the expected trend from lithium to cesium. However, the trend from chloride to iodide mostly is inverse to expectation.

COMBINATION

A combined test can be made of the radius results of Tables 1 and 2 by combining them into separate results for the individual ions. Such combination yields as average values of r_+/nm:

$$0.14, \ 0.22, \ 0.39 \ \text{and} \ 0.56 \qquad (16)$$

for Li, Na, K and Cs, respectively, and of r_-/nm:

$$0.39, \ 0.34 \ \text{and} \ 0.28 \qquad (17)$$

Table 2. Values of $(r_+^{-1} - r_-^{-1})/(\text{nm})^{-1}$ for alkali–metal halides in aqueous solution. Obtained from (15) with experimental $\log(\gamma_+/\gamma_-)/m$ slopes[2-4] and dielectric[7] and density[8] data for 1 M solutions. 25 °C.

	Li	Na	K	Cs
Cl	4.6	1.7	0	−0.6
Br	3.9	1.6	−0.3	−1.5
I	3.8	1.8	−0.6	(−4.5)

for Cl, Br and I, respectively. Except for Cs, the effective radius thus obtained satisfactorily exceeds the Pauling radius by less than the diameter of the water molecule. It satisfactorily also increases from Li to Cs (although rather steeply), but it suspiciously decreases from Cl to I.

The results for CsI in Tables 1 and 2 deny combination into single-ion radii. For this salt, therefore, the above treatment may not apply. Perhaps presently unconsidered interactions here become too strongly co-determining for the excess-energy parameter B and the $\log(\gamma_+/\gamma_-)/m$ slope.

DISCUSSION

The present testing of the theoretical expressions (9) and (10) for the empirical constants A and B of the two-term equation (1)–(3) for the excess energy of aqueous alkali–metal halide solutions largely is positive. This conclusion is based on the parameter values emerging from this testing (Table 1) largely being acceptable. The partly inverted trend in $r_+^{-1} + r_-^{-1}$ from chloride to iodide, however, may indicate that (10) covers only the main contribution to the empirical constant B. There are several other possible contributions to this constant.[1] The present testing results may give some guidance for sorting out the most important of these.

The theoretical expression (15) for the molal bare-ion activity coefficient ratio (γ_+/γ_-) clearly carries the main features found for this ratio in convenient single-ion activity studies.[2-4] Even the present more quantitative testing of it largely is positive, since it gives largely acceptable values for $r_+^{-1} - r_-^{-1}$ (Table 2). The partly inverted trend in this difference from chloride to iodide, however, may indicate that (15) covers only the main contribution to the activity coefficient ratio. This explanation basically is the same as for $r_+^{-1} + r_-^{-1}$

above. Both mean that (8), (13) and (14) cover only the main contributions to the excess chemical potential terms concerned. This may cause also the inverted trend in the anion radius sequence (17).

In closing this discussion, it may be concluded that the simple electrostatic expressions (7) and (8) in sum largely cover the mean-ion excess chemical potential of alkali — metal halides in aqueous single-salt solutions, and that the self-suggested separation of this sum into single-ion terms largely yields by (11) the single-ion activities in such solutions. This may not apply to cesium iodide, but apparently applies better the lighter the alkali-metal halide is. Some uncertainty exists, however, in how to define and decide the effective radii needed in making this judgement.

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