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RELATIONSHIP BETWEEN IONIC RADII, SOLUTION ENTROPY AND CONSTANTS OF THE POWER-LAW APPROACH FOR THE DENSITIES OF ALKALI HALIDE AQUEOUS SOLUTIONS

Abstract: The relationship between the A parameter in the quasi-lattice-like model for the concentration and temperature dependence of the densities of solutions and the thermal entropy of solution is analyzed. It is shown that the A parameter is intimately connected with the thermal entropy of solution, and the entropy increase depends on the ratio of ionic radii as well as solution concentration.

The concentration and temperature dependences of most of the physical properties are described by empirical relations with parameters whose physical meanings often remain unclear ^{1,2}. In a previous paper ³, the authors described the concentration dependence of density of aqueous solutions of alkali halides on solution concentration and temperature using the power-law:

$$(d - d_0) / d = Ax^\lambda = A_0 x^\lambda \exp(-E / kT), \quad (1)$$

where d is the density of a solution of concentration x at a particular temperature T , d_0 is the corresponding density of water, the solute concentration x is in mole fraction, k is the Boltzmann constant, E is the activation energy for density decrease, and A , A_0 and λ are constants characteristic of a salt. It was shown

that Eq. (1) may be obtained from the standpoint of a model based on a lattice-like distribution of solute ions and solvent molecules.

Analysis of the experimental data of the density of alkali halides revealed that in most of the cases the value of the activation energy E for density change is practically zero, suggesting that for different salts the value of A is practically temperature independent. This implies that one should use the average values of A , instead of the quantity A_0 of Eq. (1), while exploring the physical basis of the model. The aim of the present paper is to analyze the relationship between the constant A , the radii and solution entropy.

According to our quasi-lattice approach the density d of a solution is related with its temperature by [3]

$$(d - d_0) / d = \exp(\Delta S_{th} / 2k) \exp(-\phi / 2kT) \quad (2)$$

where ΔS_{th} is the increase in the thermal entropy produced by the introduction of a cation-anion pair into the solvent and ϕ is the activation energy required in this process. The entropy increase is given by [4]

$$(\Delta S_{th} / 2k) = 3z \ln(\nu_0 / \nu') \quad (3)$$

where ν_0 and ν are the average frequencies of vibration of solvent molecule and solute ion, respectively, and z is the number of nearest neighbors surrounding an ion. The activation energy for the formation of a cation-anion vacancy pair may be given by [4]

$$\phi = U_L - P_+ - P_- = \alpha_M \frac{e^2}{a_0} \left(1 - \frac{1}{\eta}\right) - \frac{e^2}{2} \left(1 - \frac{1}{\varepsilon}\right) \left(\frac{1}{R_+} + \frac{1}{R_-}\right) \quad (4)$$

where U_L is the lattice energy, P_+ and P_- are the polarization energies resulting from the presence of cation and anion vacancies of radii R_+ and R_- , respectively, inside the medium of dielectric constant ε , α_M is the Madelung constant of the lattice, a_0 is the interionic distance, η is the repulsive exponent equal to about 8, and e is the ionic charge. Comparison of Eqs. (1) and (2) gives

$$\ln(A_0 x^\lambda) = (\Delta S_{th} / 2k) \quad (5)$$

and $\phi / 2 = E$. As found earlier³, $E = \phi / 2 \approx 0$. Therefore, A_0 in Eq. (5) should be replaced by average A .

From Eq. (5) it follows that the introduction of an ion into a solvent causes an increase in the thermal entropy associated with a disorder around the ion. It may be seen that the disorder around the ion extends far beyond its first solvation shell.

The A parameter for the alkali halide solutions is related with the Pauling radii r_+ and r_- and the optimized radii R_+ and R_- of their cations and anions (cf. Ref. ³). However, since the constant A is associated with solutions, the relationship between A and the Pauling radii was not taken into consideration in the analysis. The data of A of different alkali halides as a function of the ionic ratio R_-/R_+ are shown in Fig. 1. The analysis of the data was carried out in three steps. First the $A(R_-/R_+)$ data were analyzed for chlorides, bromides and iodides. Then a relation between the constant of the

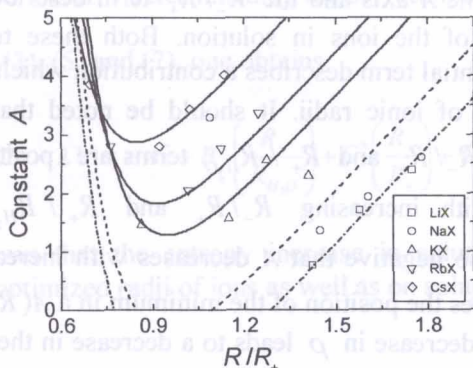


Fig. 1. Dependence of experimental A on the ratio (R_-/R_+) of "optimised radii" for different alkali halides. The radii were calculated on the assumption that $R_{Br} = 2.004 \text{ \AA}$. The curves are drawn by using Eq. (7). The point for NaF was omitted in the analysis.

plots and the ratio R was established. The following relation was used in these steps:

$$Y = Y_0 + ZX \quad (6)$$

where Y denotes A or $\ln A$, X denotes R_-/R_+ or R_+/R_{H_2O} and their logarithms, and Y_0 and Z are constants for a salt. Finally, to include the data for fluorides a correction term was added to the equation based on the previous two steps of the analysis. It was found that an exponential term is satisfactory for the correction. The final expression describing the $A(R_-/R_+)$ data most reliably was the following:

$$A = A^* + B^* \left(\frac{R_+}{R_{H_2O}} \right) + C^* \left(\frac{R_-}{R_+} \right) + D^* \exp \left(- \frac{(R_-/R_+)}{\rho} \right) \quad (7)$$

where the constants $A^* = -16.2$, $B^* = 9.7$, $C^* = 5.5$, $D^* = 1600$, and ρ is equal to 0.12 for LiX, NaX and KX salts, $\rho = 0.115$ for RbX salts, and $\rho = 0.105$ for CsX salts.

In Eq. (7) the R_+/R_{H_2O} term represents the relative displacement of the curves along the A -axis and the R_-/R_+ term describes the contribution of the relative size of the ions in solution. Both these terms are positive. However, the exponential term describes a contribution which is opposite to that of the ratio R_-/R_+ of ionic radii. It should be noted that all variables are dimensionless. The R_-/R_+ and R_+/R_{H_2O} terms are positive in such a way that A increases with increasing R_-/R_+ and R_+/R_{H_2O} . However, the exponential term is so negative that A decreases with increasing R_-/R_+ . The constant ρ determines the position of the minimum in a $A(R_-/R_+)$ plot as well as the value of A . A decrease in ρ leads to a decrease in the value of the ionic ratio R_-/R_+ corresponding to the minimum and to a decrease in A . At the minimum, the value of $(R_-/R_+)/\rho$ is a constant equal to 8 which yields the exponential term equal to 0.53 for all salts.

The $A(R_-/R_+)$ plots for the halides of an alkali metal by using Eq. (7) are shown in Fig. 1. These curves reveal that a minimum in the $A(R_-/R_+)$ plots is not attained in LiX and NaX salts due to a relatively low contribution of the R_+/R_{H_2O} term.

It is interesting to note that there is a similarity between Eq. (7) and the total lattice energy U_L of an ionic salt, expressed in the form [5]

$$U_L = N_A \left[-\frac{\alpha_M e^2}{R} + z\Lambda \exp\left(-\frac{R}{\rho_0}\right) \right] \quad (8)$$

where N_A is the Avagadro number, R is the distance between nearest ion neighbors, and Λ and ρ_0 are empirical constants of the Coulomb potential $\pm e^2 / R$ between ions in the lattice. However, it is possible to imagine a correspondence between Eqs. (7) and (8) if the dimensionless parameter A is expressed in terms of lattice energy by multiplying it by $N_A e^2 / R$. Here R_0 is the average distance between ions in the lattice-like solution such that $R_0 \neq (R_+ + R_-)$. In any case, without speculating further on the relationship between A and U_L , the similarity between their expressions strongly suggests an average lattice-like structure present in solutions. Since the radii R_+ and R_- are intimately connected with the solvation characteristics of ions in solutions, it may be concluded that A is determined by the solvation behavior of ions.

Using Eq. (3), (5) and (7), one obtains

$$3z \ln\left(v_0/v'\right) = \Delta S/2k = \lambda \ln x + A^* + B^* \left(\frac{R_+}{R_{H_2O}}\right) + C^* \left(\frac{R_-}{R_+}\right) + D^* \exp\left(-\frac{(R_-/R_+)}{\rho}\right) \quad (9)$$

This equation shows that the entropy increase in solutions depends on the relative values of optimized radii of ions as well as on solution concentration x .

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Współzależność między promieniami jonowymi, entropią roztworu a stałymi w nowym prawie potęgowym gęstości wodnych roztworów halogenków alkalicznych

Streszczenie: Przeanalizowano współzależność między parametrem A w modelu quasi-sieciowym proponowanym do wyjaśnienia zależności gęstości roztworów od stężenia i temperatury a entropią cieplną roztworów. Pokazano, że parametr A jest ściśle związany z entropią cieplną roztworu oraz, że wzrost entropii zależy od stosunku promieni jonowych i stężenia roztworu.

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