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DEPENDENCE OF DENSITIES OF ALKALI HALIDE AQUEOUS SOLUTIONS ON THEIR CONCENTRATION AND TEMPERATURE: A NEW POWER-LAW APPROACH

Abstract: The experimental data of relative change in solution density are analyzed as functions of solution concentration and temperature, using a new power-law approach for the former and an Arrhenius-type relation for the latter. A new theoretical equation relating relative change in solution density with temperature, increase in thermal entropy produced by the introduction of a cation-anion pair into the solvent and the activation energy required for this process is then proposed. Assuming that the solvent is composed of ionized species forming a lattice-like structure, this equation is derived considering the polarization of solvent around electrolyte ions. The theoretical expression of the model is compared with the final expression relating the experimental relative change in solution density as functions of solution concentration and temperature. The results revealed that the activation energy E for density change is practically zero for all alkali halides. The condition that $E = 0$ gives the radii of ions in aqueous solutions, which agree well with the optimized radii reported by Li et al. [Fluid Phase Equilibria 145, 1 (1998)]. It is also found that the constants of the final equation of the solution density are related with the crystal density.

1. Introduction

Data on the temperature and concentration dependence of the physical properties of solutions are frequently used in various fields. Consequently, there is a voluminous literature reporting data on the subject for a variety of inorganic compounds [1]. It is also well known that the physical properties of electrolyte solutions strongly depend on their concentration and temperature [1,2]. 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], we analyzed the concentration and temperature dependence of the density of aqueous solutions of some alkali halides. The main conclusion of our work was that the traditional expressions reported in the literature do not give information on the solution structure. Recently, Li et al. [4] considered the electrolyte aqueous solution as a mixture of ionic hard spheres and compressible water situated in the field of an external pressure, and proposed a generalized method for predicting the density of single- and binary-electrolyte aqueous solutions from ionic radii and osmotic pressure. These authors found that, for the single-electrolyte solutions, the average absolute relative deviation between the experimental and predicted densities as a function of solute concentration was the lowest (0.88%) when the optimized radii were used to estimate the intrinsic volume.

Despite its success in predicting the concentration dependence of density of electrolyte aqueous solutions, at least two questions remain unaswered in the approach of Li et al. [4]:

(1) Although the electrolyte solution is considered as a mixture of ionic hard spheres and compressible water in the field of an external pressure, the model provides no information about the nature of the mixture and the processes involved in its formation.

(2) The optimized radii of ions reproduce the experimental densities of electrolyte solutions most satisfactorily but their significance in relation with the nature of the solution (mixture) remains unexplained.

The aim of the paper is two-fold: (1) to describe the concentration dependence of density of aqueous solutions of alkali halides on solution concentration and temperature using a power-law, and (2) to analyze the power-law relation from the standpoint of a model based on a lattice-like distribution of solute ions and solvent molecules.

2. Analysis of the experimental data

The data on the densities d of aqueous solutions of various concentrations of different alkali halides were first analyzed using the expression:

$$(d - d_0)/d = Ax^{\lambda}, \quad (\text{const.} T) \qquad (1)$$

where d_0 is the density of water at a particular temperature T, x is the solute concentration in mole fraction and A and λ are constants characteristic of a salt. A typical example of the plot of the dependence of $(d-d_0)/d$ on solute concentration x is illustrated in Fig. 1. The values of the exponent λ are listed in Table 1.

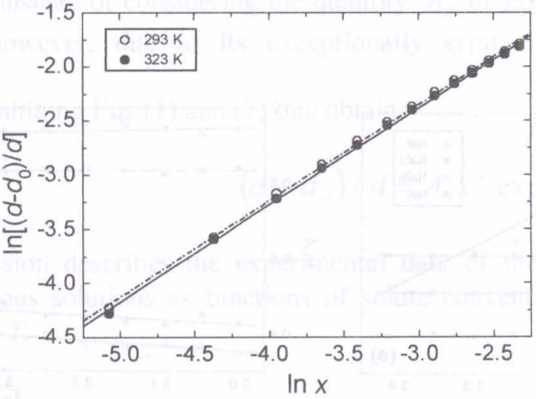

Fig. 1. Typical example of the dependence of $(d - d_0)/d$ on $\ln x$ for NaCl

Table 1

Values of constants λ, E and A for various halides

Cation	Constants	Anion			
		F^-	Cl^-	Br^-	I^-
Li^+	λ	-	0.86	0.85	0.83
	$10^3 E$ (kJ/mol)	-	-0.2	0.5	-0.2
	$\ln A$	-	-0.269	0.534	0.871
Na^+	λ	1.01	0.89	0.82	0.82
	$10^3 E$ (kJ/mol)	-52	0.2	-0.1	0
	$\ln A$	1.2	0.31	0.66	0.96
K^+	λ	0.86	0.90	0.89	0.78
	$10^3 E$ (kJ/mol)	1.2	1.8	-0.8	-0.2
	$\ln A$	0.38	0.45	0.94	0.83
Rb^+	λ	0.88	0.82	0.82	0.81
	$10^3 E$ (kJ/mol)	-3.0	-0.1	0.1	-0.6
	$\ln A$	1.03	0.72	1.02	1.21
Cs^+	λ	0.89	0.82	0.81	0.81
	$10^3 E$ (kJ/mol)	1.3	-0.2	0	2.4
	$\ln A$	1.35	1.03	1.23	1.39

It was observed that the temperature dependence of the constant A may be represented by an Arrhenius-type relationship:

$$A = A_0 \exp(-E/kT) \tag{2}$$

where A is a constant characteristic of a salt and E is the apparent activation energy for the density change. Some typical plots of the dependence of $\ln A$ on $1/T$ are shown in Fig. 2.

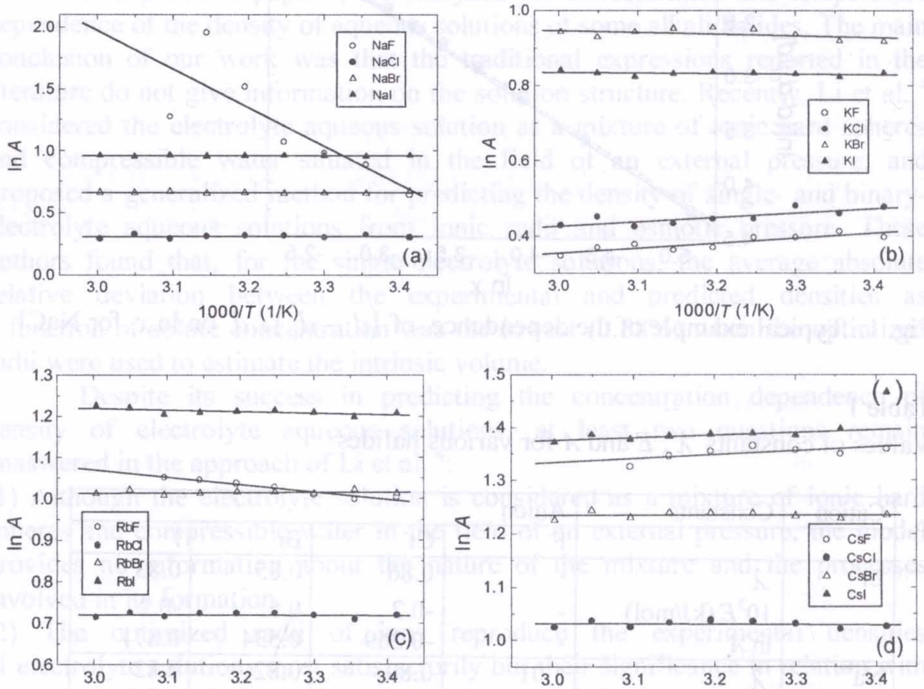

Fig. 2. Dependence of $\ln A$ on $1/T$ for aqueous solutions of halides of: (a) sodium, (b) potassium, (c) rubidium and (d) cesium. The point contained in brackets in (d) was omitted in the analysis. Note an erratic dependence for NaF.

The values of E are collected in Table 1. From the table it may be noted that in most of the cases the value of the activation energy E for density change is practically zero. The usual exceptions are fluorides mainly due to experimental errors involved in the preparation of solutions and the measurement of density. Among the fluorides, NaF solutions exhibit exceptionally erratic temperature dependence of A. In view of the result that the value of E is practically zero, for different salts the average values of A, given in Table 1, instead of considering the quantity A_0 of Eq. (2), were used in the analysis. However, due to its exceptionally erratic behaviour, NaF was excluded.

Combining Eqs (1) and (2) one obtains

$$\left(d-d_0\right)/\,d=A_0 x^{\lambda}\,\exp\!\left(-E\,/\,kT\right) \qquad (3)$$

This expression describes the experimental data of the densities d of alkali halide aqueous solutions as functions of solute concentration x and solution temperature T.

3. The model

The concentration dependence of activity coefficients of electrolyte solutions reveals that the Debye-Hückel ionic-cloud model holds only up to low electrolyte concentrations (about 0.001 M for 1:1 electrolytes) due to the existence of long-range Coulombic interactions. At such concentrations the short-range noncoulombic interactions are less important. However, with increasing concentration the long-range interactions are overwhelmed by short-range interactions, thereby introducing a short-range order indicative of a quasi-lattice structure. A quasi-lattice is composed of a regular lattice of the parent ionic crystal from which 10 to 30% of the ions are removed to give vacancies [6].

In our quasi-lattice approach, we consider a solution to be a homogeneous mixture in which solvent molecules, and cations and anions of the electrolyte occupy the normal lattice sites. To derive a theoretical expression relating the densities d of solutions of binary electrolytes with solute concentration x and solution temperature T, we follow an analogy with the model of formation of vacancies in a perfect ionic crystal of composition A^+B^-.

In the model of lattice vacancies, we consider that N ions of one type and the corresponding n ion vacancies are distributed over a total of $(N+n)$ available sites. Then the number n of pairs of cation-anion vacancies distributed over a total of $(N+n)$ pairs of cation-anion sites may be given by [7].

$$n/(N+n)=\exp(\Delta S_{th}/2k)\exp(-\phi/2kT) \qquad (4)$$

where ΔS_{th} is the increase in thermal entropy caused by the formation of a pair of cation-anion vacancies, ϕ is the energy required to produce the pair of vacancies, k is the Boltzmann constant and T is the temperature in Kelvin. The entropy increase ΔS_{th} is given by [7].

$$\Delta S_{th}=3z\ln\left(\nu_0/\nu^{'}\right) \qquad (5)$$

where ν_0 and $\nu^{'}$ 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 [7]

$$\phi=U_L-P_+-P_-=\alpha_M\frac{e^2}{a_0}\left(1-\frac{1}{\eta}\right)-\frac{e^2}{2}\left(1-\frac{1}{\varepsilon}\right)\left(\frac{1}{R_+}+\frac{1}{R_-}\right) \qquad (6)$$

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.

Now we assume that the N lattice sites occupied by cations or anions are replaced by N water molecules while the n cation or anion vancancies by cations or anions of the 1:1 electrolyte. Then the situation is exactly the same as in the case of formation of vacancies in a perfect lattice, and the expressions (4)-(6) are still valid. For solutions however, one has to assume that the water molecules form a lattice similar to that of the electrolyte. Then, R_+ and R_- are the radii of a cation and an anion in solution, respectively, and ε is the dielectric constant of water.

Dividing the numbers n and $(N+n)$ of cation-anion pairs by volume, one can express them as concentrations (i.e. number/volume) and describe any physical property of a solution where the lattice-like structure composed of a mixture of solute and solvent species is valid. For example, if the numbers are replaced by masses, at a particular temperature T the density d of a solution of a particular concentration x and the density d_0 of solvent may be expressed by

$$d = \left(Nm_{solv} + nm_{solute}\right) / V, \qquad d_0 = Nm_{solv} / V \tag{7}$$

where m_{solv} and m_{solute} are the masses of a solvent and solute molecule, respectively, and V is the total volume of the solution. Then one may write Eq. (4) as

$$(d - d_0) / d = \exp(\Delta S_{th} / 2k) \exp(-\phi / 2kT) \tag{8}$$

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 quantities ΔS_{th} and ϕ are given by Eqs (5) and (6), respectively.

4. Comparison of theoretical and experimental equations

4.1. Ionic radii in solutions and the thermal entropy

It is interesting to note that Eqs. (3) and (8) are very similar. Comparison of these two expressions gives

$$\ln\left(A_0 x^{\lambda}\right) = 3z \ln\left(\nu_0 / \nu'\right) \tag{9}$$

and $\phi / 2 = E$ Physically, Eq. (9) means that $\left(\nu_0 / \nu'\right) = 1$ when $x = 0$. However, from this equation it is difficult to estimate the parameter z for infinite dilution. An indirect way to estimate z is to obtain the value of $\left(\nu_0 / \nu'\right)$ from Eq. (9) for very low concentrations. Thus, for solutions of $x = 0.01$ one obtains $z > 100$. From this value of z it can easily be seen that the solvated ions in aqueous solutions have radii of about 1 nm, indicating that the interactions involved during the solvation of cations and anions of alkali halides extend up to 4-5 water molecules surrounding them. Obviously, an increase in the thermal entropy resulting from the introduction of an ion into the solvent causes a disorder around it and the disorder around the ion extends far beyond its first solvation shell.

As noted above, $\phi / 2 = E$. Therefore, $\phi = 0$, and from Eq. (6) one obtains

$$\frac{\alpha_M}{a_0}\left(1-\frac{1}{\eta}\right)=\frac{1}{2}\left(1-\frac{1}{\varepsilon}\right)\left(\frac{1}{R_+}+\frac{1}{R_-}\right) \tag{10}$$

Using the values of α_M and a_0 for different salts from Ref. [7] and that of ε = 81, one obtains the values of $(1/R_+ + 1/R_-)$ for different salts. From these values of $(1/R_+ + 1/R_-)$, the ionic radii R_+ and R_- were calculated by selecting arbitrarily the value of the radius of one anion. The average calculated values of R_+ and R_- are given in Table 2 for R_{Br^-} = 2.004 Å [4] and $R_{Cl^-} = R_{K^+}$ = 1.737 Å. For comparison, the values of the optimized radii given by Li et al. [4] and the Pauling radii r_+ and r_- of the unhydrated cations and anions are also given in Table 2.

Table 2

Values of Pauling radii r_P, optimized radii R_{LPKL} of Li et al., bromine-based radii R_{Br^-} and KCl-based radii R_{KCl}

Ion	r_P (Å)	R_{LPKL} (Å)	R_{Br^-} (Å)	R_{KCl} (Å)
Li^+	0.60	1.270	1.293 ± 0.037	1.349 ± 0.037
Na^+	0.95	1.428	1.422 ± 0.021	1.490 ± 0.025
K^+	1.33	1.574	1.652 ± 0.018	1.744 ± 0.024
Rb^+	1.48	1.781	1.758 ± 0.042	1.862 ± 0.048
Cs^+	1.69	1.959	1.968 ± 0.046	2.099 ± 0.048
F^-	1.36	1.360	1.390 ± 0.044	1.336 ± 0.034
Cl^-	1.81	1.810	1.827 ± 0.021	1.697 ± 0.129
Br^-	1.95	2.004	2.004	1.898 ± 0.027
I^-	2.16	2.214	2.250 ± 0.054	2.118 ± 0.060

It is interesting to note from Table 2 that the values of the radii calculated on the basis of selection of R_{Br^-} are comparable with those reported by Li et al. [4] while those calculated with reference to $R_{Cl^-} = R_{K^+}$ differ from the former ones by less than 10%. The radii R_+ of cations calculated with reference to R_{Br^-} are always greater than the Pauling radii r_+ of bare cations but the radii $R_- \approx r_-$ for anions. However, when it is assumed that $R_{Cl^-} = R_{K^+}$, $R_+ > r_+$ while $R_- < r_-$. Since the Pauling radii correspond to nonsolvated ions, it may be concluded that the assumption $R_{Cl^-} = R_{K^+}$ is not justified because the radii R of solvated ions must always be greater than or equal to the radii r of their nonsolvated counterparts. This inference also provides a physical significance for the optimized radii used by Li et al.[4]

It should be noted that in the calculation of the ionic radii R in solution from Eq. (10) it was assumed that a_0 is equal to the lattice constant of a salt. Probably this assumption is a consequence of the presence of short-range order in solutions.

The observation $\phi = 0$ means that the ionized water molecules surrounding a cation and an anion become polarized. The polarization consists of the formation of dipoles induced by the Coulomb field of the introduced ion and a slight displacement of ionized water molecules composing the liquid lattice. Experiments and molecular orbital calculations show[8,9] that HO^- and H^+ ions of water are hydrated but their higher hydrated species exhibit a gradual decrease in the hydrogen-bond energy. This means that the most common hydrated species existing in water are $H_3O_2^-$ and H_3O^+ ions and that liquid water may be considered as an equilibrium mixture of species like HO^-, H^+, $H_3O_2^-$ and H_3O^+. However, if the water species are to exist in the lattice-like structure, the average distance a between water species should be greater than twice the radius r_{H_2O} of a H_2O molecule. This condition enables to know the possible water species present in the solution. Assuming a halide-type lattice structure of solutions, the average distance between water species may be given by

$$a_{\alpha H_2O} = \left(\alpha\, m_{H_2O} / 8 d_0\right)^{1/3} \tag{11}$$

where α is the average number of water molecules in neighboring species in the liquid lattice, d_0 is the density of water and m_{H_2O} is the mass of a water molecule. It may be seen that $a_{\alpha H_2O}$ is equal to 2.46 Å for HO^- and H^+ (i.e. $\alpha = 1$), 3.10 Å for HO^- and H_3O^- (i.e. $\alpha = 2$), and 3.55 Å for $H_3O_2^-$ and H_3O^+ (i.e. $\alpha = 3$). Since the radius of a water molecule is 1.38 Å (i.e. $2r_{H_2O} = 2.78$ Å), obviously the possible species forming the liquid lattice structure are HO^- and H_3O^+ (i.e. $\alpha = 2$).

Assuming the presence of HO^- and H_3O^+ ions in aqueous solution, the effect of polarization by a cation and an anion is schematically illustrated in Fig. 3. The figure represents the polarization in the case of a two-dimensional lattice. It may be seen easily that, for the halide-type lattice, a cation will attract six HO^- species and will displace eight H_3O^+ species, thus ensuring a relatively strong first solvation shell composed of six water molecules due to two oxygen atoms involved in the species. Similarly, an anion will attract six H_3O^+ species and displace eight HO^- species. Adsorption of water molecules onto an ion is determined by attractive forces between the oxygen and hydrogen atoms of the former. Therefore, in comparison with the interaction of an anion with several hydrogen atoms of a water molecule, the interaction of a cation involves a smaller number of oxygen atoms. Consequently, a cation is always more solvated than an anion. Obviously, from this argument also it follows that the radius R of a solvated ion cannot be smaller than the radii r of the bare ion. This general picture of hydration is consistent with the hydration number of water molecules in the first solvation shell of ions [6]. However, in our approach we have considered suitably oriented charged water species rather than isolated dipoles of neutral water molecules forming the solvation shell around an ion.

In Fig. 3 the displacement of ionized water species is shown only up to the first and second nearest neighbors. However, the rearrangement of ionized water species around an ion spreads over several interionic distances due to the long range of Coulomb forces. This feature is evident from the increase in the thermal entropy of anion-cation pairs but does not follow from the values of radii R_+ and R_- of cations and anions, estimated on the basis that $\phi = 0$. This discrepancy is due to the simplified model [7] used in the derivation of Eq. (6). However, the fact that $\phi = 0$ indicates that the free energy change involved during the introduction of ions into a solvent is essentially associated with an increase in the thermal entropy in solution due to the introduction of anion-cation pairs (cf. Eq. (4)).

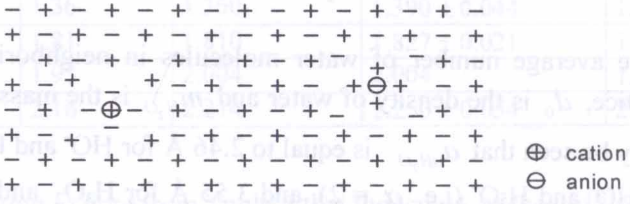

Fig. 3. Schematic illustration of the polarization of solvent surrounding a cation and an anion. The lattice-like structure is considered to be two-dimensional and is composed of HO^- and H_3O^+ species. The oppositely charged species are displaced towards an ion while the similarly charged species are displaced outward. The figure shows the displacement of only first- and second-nearest neighbors but in reality the displacement extends up to several interionic distances.

4.2. Relationship between A, λ, and crystal density d_{CS}

Like the constant A, the exponent λ is practically temperature independent for a salt and essentially lies between 0.8 and 1 for different salts. The constants A and λ are related by the empirical relation

$$\ln A = B - C\lambda, \tag{12}$$

where B and C are new constants. The dependence of ln A on λ is shown in Fig. 4. From the figure it may be seen that the $\ln A(\lambda)$ data for most of the salts may be described by one linear plot (curve 2), while the data for the remaining salts like NaCl, KCl, KBr, CsF and RbI by another linear plot (curve 1). The values of constants B and C are given in Table 3. The table shows that $B \approx$ C for both plots. The inverse relationship between A and λ is a consequence of compensation law. This follows from Eq. (1) since at a given concentration x the quantity $\ln[(d - d_0)/d_0]$ is practically a constant.

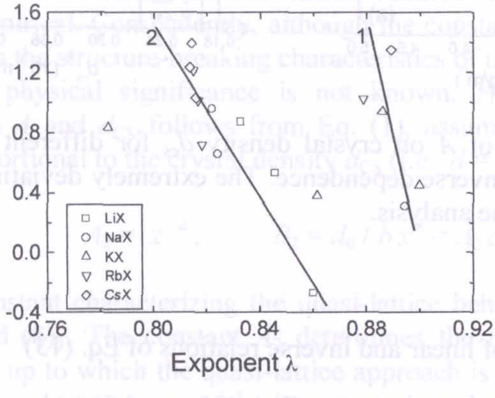

Fig. 4. Dependence of ln A on exponent λ for alkali halide solutions. The extremely deviating points for KF and KI from curve 2 were omitted in the analysis.

Table 3

Values of constants B and C of Eq. (12) of ln $A(\lambda)$ relation

Plot	B	C	CC*
1	32.1	35.2	0.660
2	12.8	14.6	0.711

CC* denotes correlation coefficient

The constant A for an alkali halide is related with the density d_{CS} in the solid state. The following equations were used to establish a relation between the constant A and the density d_{CS}:

$$A = A_1 + B_1 d_{CS} \qquad \text{Linear relation} \qquad (13)$$
$$A = A_2 - B_2 d_{CS} \qquad \text{Inverse relation}$$

where A' and B' are constants. The plots of the dependences predicted by these relations are illustrated in Fig. 5, while the values of the constants are listed in Table 4. The deviations in the estimated values were found to be between 10 and 15%.

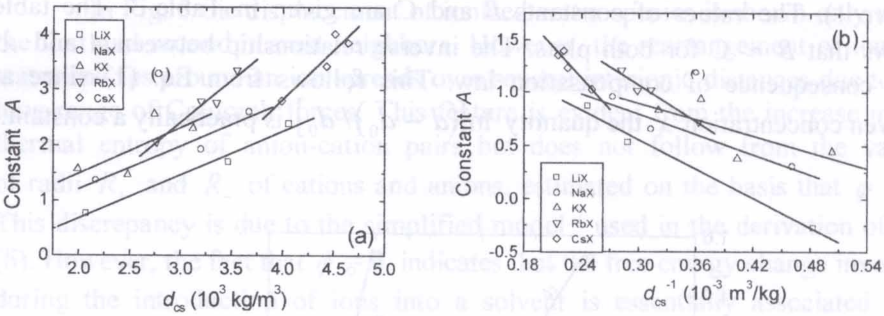

Fig. 5. Dependence of A on crystal density d_{cs} for different salts: (a) linear dependence and (b) inverse dependence. The extremely deviating point for NaF was excluded from the analysis.

Table 4
Values of constants of linear and inverse relations of Eq. (13)

Salts	Linear relation			Inverse relation			
	$-A_1$	$10^3 B_1$ (kg/m^3)	CC*	A_2	$10^{-3} B_2$ (kg/m^3)	CC*	b
LiX	0.91	0.79	0.999	1.94	4.60	0.992	0.42
NaX	0.39	0.78	0.966	1.74	3.14	0.962	0.55
KX	0.16	0.83	0.730	1.66	2.54	0.716	0.65
RbX	2.22	1.54	0.970	2.78	5.70	0.975	0.49
CsX	4.37	1.80	0.930	3.52	9.94	0.945	0.35

Table 4 shows that, for structure-making cations like Li^+, Na^+ and K^+, the slope B_1 of the plots of linear relation between A and d_{CS} is practically constant while the value of the constant A_1 decreases with increasing structure-making capability of a cation, i.e.with decreasing ionic radius. The constant A_1 is practically zero for K^+ because its radius is close to that of a water molecule. It is expected that the slope $B_1 \approx 1$ for such a cation. In fact the positive slope indicates the structure-breaking behavior of anions. However, for large structure-breaking cations like Rb^+ and Cs^+, A_1 decreases while B_1 increases with increasing ionic radius. Thus, it may be concluded that the value of the slope $B_1 > 1$ of the plot of A against d_{CS} indicates the structure-breaking nature of Rb^+ and Cs^+ and the decreasing trend of A_1 with increasing cation radius a consequence of the interdependence of A_1 and B_1.

The values of constants A_2 and B_2 of the inverse relation reveal that, for structure-making cations like Li^+, Na^+ and K^+, the constant A_2 is practically constant while the value of the slope B_2 decreases with increasing structure-making capability of a cation, i.e. with decreasing ionic radius (see Table 4). In contrast, for large structure-breaking cations like Rb^+ and Cs^+, A_2 is also practically constant but it is about twice the value observed for the former cations. The slope B_2 increases with increasing ionic radius.

It should be noted that the linear relation between A and d_{CS} is essentially empirical. Consequently, although the constants A_1 and B_2 appear to be related with the structure-breaking characteristics of the cations in aqueous solutions, their physical significance is not known. However, the inverse relation between A and d_{CS} follows from Eq. (1), assuming that the solution density d is proportional to the crystal density d_{CS} (i.e. $d = b\, d_{CS}$). Then

$$A_2 = x^{-\lambda}, \qquad B_2 = d_0 / b x^{\lambda} = A_2 d_0 / b, \tag{14}$$

where b is a constant characterizing the quasi-lattice behavior of the solution [cf. Eqs. (3) and (8)]. The constant A_2 determines the upper limit of solute concentration x up to which the quasi-lattice approach is valid. From Eq. (14) one obtains $b = d_0(A_2/B_2) \approx 10^{-3} A_2/B_2$, assuming that the water density $d_0 = 1000$ kg/m^3. The calculated values of the constant b are listed in Table 4.

It may be seen from Table 4 that the constant b lies between 0.35 and 0.65, and its value strongly depends on the radii of cations. As expected $b < 1$. It seems that the values of b are associated with the solvation characteristics of ions composing the solution.

5. Concluding remarks

Analysis of the experimental data of the densities of alkali halide aqueous solutions as functions of solute concentration (mole fraction) and solution temperature reveals that they may be described by an empirical power-law relation (Eq. (3)) and that for all alkali halides the value of the activation energy E is practically zero, suggesting that the quantity A of Eq. (3) is a temperature independent quantity. The power-law relation is then analyzed from the standpoint of a model based on a lattice-like distribution of solute ions and solvent molecules.

The experimental fact that $E = 0$, allows to obtain the values of radii of ions in solutions, which are comparable with the optimized radii reported by Li et al.[4] The values of radii of ions suggest that anions in aqueous solutions are practically nonsolvated while cations are solvated.

Finally, it should be mentioned that the idea of lattice-like model of electrolyte solutions is more than eighty years old but has been revived from time to time to explain their different properties (see Ref. [11] for the literature). In these works from a consideration of charge-charge and charge-solvent interactions some theoretical expression has been derived and confronted with the experimental data. In the present paper however, the constants A and λ of Eq. (3) representing these interactions have been obtained from the experimental data of density of alkali halide aqueous solutions. The constants A and λ are related with the radii and solvation characteristics of ions. The relationship between A, ionic radii and solution entropy will be reported elsewhere[12].

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Zależność gęstości wodnych roztworów halogenków metali alkalicznych od ich stężenia i temperatury: nowe podejście prawa potęgowego

Streszczenie: Przeanalizowano doświadczalne dane względnych zmian gęstości roztworów w funkcji stężenia i temperatury stosując nowe podejście prawa potęgowego i równania typu Arrheniusa. Następnie zaproponowano nowe teoretyczne równanie opisujące względne zmiany w gęstości roztworu ze zmianą stężenia i temperatury, wzrost entropii cieplnej spowodowany przez wprowadzanie do rozpuszczalnika pary kation-anion oraz energię aktywacji potrzebną w procesie. Zakładając, że rozpuszczalnik składa się ze zjonizowanych jednostek tworzących strukturę quasi-sieciową, równanie to wyprowadzono uwzględniając polaryzację rozpuszczalnika w otoczeniu jonów elektrolitów. Teoretyczne równanie modelu porównano z końcowym wyrażeniem otrzymanym na podstawie względnych zmian w doświadczalnych gęstościach roztworów w funkcji ich stężenia i temperatury roztworu. Wyniki porównania wykazały, że energia aktywacji E dla zmian gęstości jest praktycznie równa zero dla wszystkich halogenków alkalicznych. Warunek, że $E = 0$ umożliwia otrzymanie wartości promieni jonowych w wodnych roztworach. Wartości tych promieni jonowych wykazują dobrą zgodność z optymalnymi promieniami podawanymi przez Li i in. [Fluid Phase Equilibria 1998, **145**, 1]. Stwierdzono również, że wartości stałych z końcowego równania dla gęstości roztworu są związane z gęstością kryształu.