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R. MISZTAL, K. SANGWAL

Pedagogical University of Czestochowa, Technical University of Lublin, Poland

## **Analysis of the Concentration and Temperature Dependence of Densities of Aqueous Alkali Halide Solutions: a New Power-Law Approach**

The literature data on the concentration and temperature dependence of densities of aqueous solutions of alkali halides are analysed using a new power-law approach. Theoretical models based on additivity rule for densities and polarization of solvent around electrolyte ions are proposed and the origin of the power-law expression is discussed. The results suggest that the latter model qualitatively relates the parameters of the power-law expression with the physical processes occurring in solutions.

Keywords: alkali halides, densities of aqueous solutions, power-law approach, solution structure

### **1. Introduction**

Investigation of the physical properties and structure of solutions is of practical and theoretical importance. Data on some of the physical properties, such as density and refractive index, are frequently used to monitor supersaturation in crystal growth experiments while knowledge of the structure and distribution of entities present in supersaturated solutions is necessary to obtain information on the atomic level about the species entering into growth sites and the operative crystal growth mechanisms. Physical properties of electrolyte solutions strongly depend on solution concentration and temperature (HORVATH). These dependencies are usually described by second- or third-order empirical expressions. The constants of these expressions for different compounds as functions of solution concentration and temperature also show increasing or decreasing trends (SZEWCZYK, SANGWAL; FREJ et al.). However, in the case of most of the physical properties of solutions the physical significance of the constants of the expressions and the causes of increasing or decreasing trends still remain unclear.

Among the various physical properties, reliable experimental data on the densities of aqueous solutions of electrolyte solutions are abundantly available in the literature as functions of solution concentration and temperature (SÖHNEL, NOVOTNÝ). These data are usually represented by empirical polynomials (HORVATH). Unfortunately, in contrast to the abundantly available data on concentration and temperature dependence of density, for concentrated solutions which are involved in crystal growth, still there is no theory describing the above dependencies in terms of physical processes involved in solutions and their structure.

The present paper reports the results of an analysis of the supersaturation and temperature dependence of density of aqueous solutions of alkali halides (i.e. lithium, sodium, potassium, rubidium and cesium halides) using a new power-law approach. For the analysis the experimental data of densities of solutions up to their saturation concentrations at temperatures between 20 and 60°C collected in the handbook (SÖHNEL, NOVOTNÝ) and of

water from the compilation (LIDE) were taken. In order to discuss origin of the power-law expression theoretical models based on additivity rule for densities and polarization of solvent around electrolyte ions are proposed.

## 2. Experimental Results

Our analysis of the concentration dependence of the density of aqueous solutions of various alkali halides at different temperatures revealed that the data may also be satisfactorily represented by the power law:

$$d = d_0 + A c^m, \quad \text{constant } T, \quad (1)$$

where  $d_0$  is the density of water at the given temperature  $T$  (in Kelvins),  $c$  is the solute concentration in mole fraction, and  $A$  and  $m$  are constants characteristic of a salt. Some typical examples of the data plotted according to eq. (1) are illustrated in Figures 1a-c.

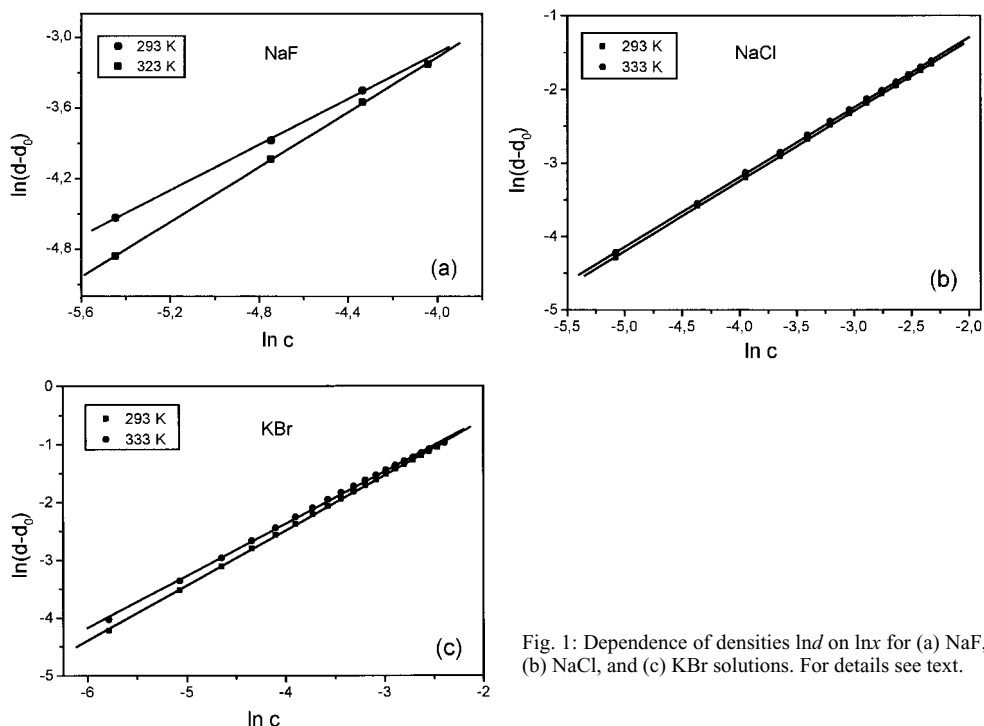


Fig. 1: Dependence of densities  $\ln d$  on  $\ln x$  for (a) NaF, (b) NaCl, and (c) KBr solutions. For details see text.

The above plots show examples when  $m$  decreases (Figures 1a, 1c) and remains constant (Figure 1b) with increasing temperature. For the sake of clarity the data are presented only for two temperatures in these figures. However, we found that in the entire range of temperature the constant  $m$  is practically temperature independent for a majority of the salts (LiCl, NaCl, NaBr, NaI, KI, CsF, CsCl) while in some cases with increasing temperature  $m$  either showed a slight systematically decreasing (LiBr, KF, KCl, KBr, RbBr and CsI) or increasing trend (LiF, NaF, RbF and RbI). Except in the case of NaF which showed a maximum deviation of 16% from the average value, for most of the salts the maximum

deviation in  $m$  was less than 1%. The exact causes of these deviations are not understood but it appears that they are due to errors involved in obtaining the experimental data of solution densities. The average values of  $m$  for different salts are listed in Table 1.

The constant  $A$  of eq. (1) depends on temperature and follows an Arrhenius-type relationship:

$$A = A_0 \exp(-E/kT), \quad (2)$$

where  $A_0$  is a constant characteristic of the electrolyte and  $E$  is the apparent activation energy for density change. Some typical examples of the dependences of  $A$  on  $T$  are illustrated in Figure 2. The values of  $A_0$  and  $E$  are also collected in Table 1.

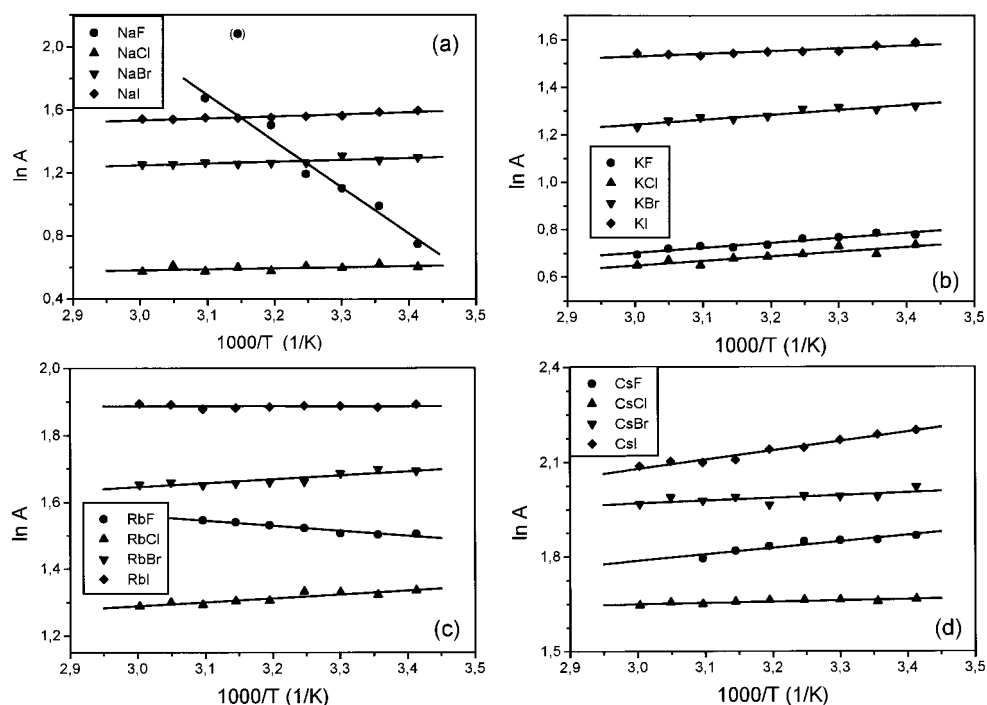


Fig. 2: Plots of  $\ln A$  against  $1/T$  for solutions of (a) sodium, (b) potassium, (c) rubidium and (d) cesium. For NaF the point in the brackets was excluded from the analysis.

### 3. Some General Features

Figure 2 show that, except for NaF which exhibits an anomalous behaviour, in the temperature range of measurements  $A$  changes in the order:  $\text{Cl}^- < \text{F}^- < \text{Br}^- < \text{I}^-$ . This trend also indicates that  $\text{F}^-$  behaves erratically.

Table 1 reveals that, except for NaF solutions,  $m < 1$  for all alkali halides. In the case of NaF we found  $m = 0.9707$  at  $T = 293$  K and an unusually high (anomalous) value of  $m = 1.3002$  at 318 K in comparison with  $m = 1.1911$  at 333 K. From these observations it seems that  $m$  is close to unity for NaF and that the deviations and anomalies are associated with the procuring of the experimental densities.

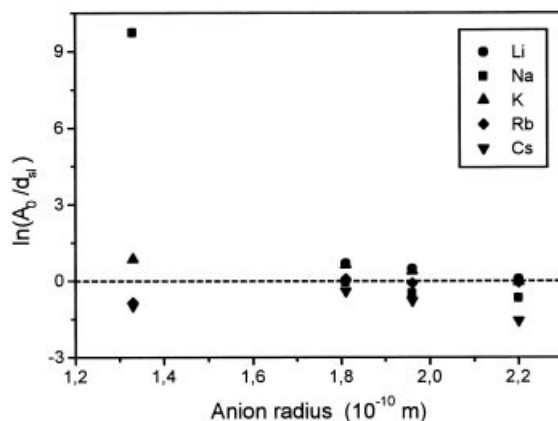
Cat-ion	$m$				$A_0 (10^3 \text{ kg/m}^3)$				$E (\text{kJ/mol})$			
	F <sup>-</sup>	Cl <sup>-</sup>	Br <sup>-</sup>	I <sup>-</sup>	F <sup>-</sup>	Cl <sup>-</sup>	Br <sup>-</sup>	I <sup>-</sup>	F <sup>-</sup>	Cl <sup>-</sup>	Br <sup>-</sup>	I <sup>-</sup>
Li <sup>+</sup>	-	0.9535	0.9681	0.9556	-	1.025	2.148	3.750	-	-0.13	-0.81	-0.39
Na <sup>+</sup>	1.1151	0.9555	0.9592	0.9403	2.85	2.271	5.198	7.159	24.34	-0.58	-0.98	-1.07
				$\times 10^3$								
K <sup>+</sup>	0.9390	0.9471	0.9108	0.9297	1.067	1.061	1.862	3.274	-1.77	-1.64	-1.73	-0.95
Rb <sup>+</sup>	0.9748	0.9437	0.9445	0.9414	7.489	2.551	3.657	6.615	1.26	-0.98	-0.97	0.01
Cs <sup>+</sup>	0.9764	0.9356	0.9571	0.9495	12.315	5.945	9.575	21.534	-1.70	-0.33	-0.72	-2.43

Table 1: Values of constants  $m$ ,  $A_0$  and  $E$  of eqs (1) and (2) for various halides

From Table 1 it may be seen that for all salts  $m_{\text{F}^-} > m_{\text{Br}^-}$ , and the positions of  $m_{\text{Cl}^-}$  and  $m_{\text{I}^-}$  are not fixed. This anomalous behaviour is clearly seen for potassium halides. Similarly, except for the chlorides the  $m$  values show a minimum with increasing radius of the cation.

Comparison of the values of  $A_0$  from Table 1 with the density  $d_{\text{sl}}$  of different halides in the crystalline phase revealed that it can be smaller or greater than the density  $d_{\text{sl}}$  of a salt. This feature is shown in Figure 3 which presents a plot of the ratio  $\ln(A_0/d_{\text{sl}})$  against the radii of anions.

Table 1 shows that the value of  $E$  is very low and can be both positive and negative. For chlorides and bromides of all alkali metals the values of  $E$  are negative but for fluorides and iodides  $E$  can be both positive as well as negative. Moreover, for all chlorides and bromides, with increasing cation radius the value of  $E$  first decreases and then increases exhibiting a minimum value for potassium. However, no such trend may be seen for fluorides and iodides. These observations suggest that there is no simple relationship between  $E$  and the size of ions.

Fig. 3: Plot of the ratio  $\ln(A_0/d_{\text{sl}})$  against the radii of anions. The dashed line indicates the boundary when  $A_0 = d_{\text{sl}}$ . Note that  $A_0$  can be both smaller and greater than the density  $d_{\text{sl}}$  of a salt.

#### 4. Discussion

The trends of changes of  $m$  with the radii of cations and anions, coupled with small differences in their values lying in the range of changes caused by measurement errors, indicate that it is difficult to establish a definite relationship between the constant  $m$  and the ionic radius. However, as suggested by the high solvation ability of Li<sup>+</sup> and F<sup>-</sup> ions (ROBINSON, STOKES; IZMAILOV) the salts of which give relatively high values of  $m$ , the constant  $m$  is related with the ability of solvation of ions.

From Figure 3 it may be seen that, if the fluorides are excluded, the ratio  $A_0/d_{\text{sl}}$  decreases with increasing size of the anion. Moreover, then for different salts the values of  $A_0/d_{\text{sl}}$

decrease in the order:  $\text{Li}^+ > \text{K}^+ > \text{Rb}^+ > \text{Na}^+ > \text{Cs}^+$ . These trends also suggest that the value of  $A_0$  is determined by the solvation characteristics of ions of the salts.

In order to discuss the above features of the parameters  $m$ ,  $A_0$  and  $E$ , from eqs (1) and (2) we write a general expression of the dependence of density of a solution as a function of temperature  $T$  and solute concentration  $c$  in the form:

$$d - d_0 = A_0 c^m \exp(-E/RT). \quad (3)$$

This equation may be obtained in two ways as given below.

#### 4.1. Additivity rule considerations

According to the conventional additivity rule, the density of a solution may be expressed by

$$d = (1 - x) d_0 + x d_{\text{sl}} = d_0 + Ax \quad (4)$$

where  $A = (d_{\text{sl}} - d_0)$ ,  $d_0$  and  $d_{\text{sl}}$  are the densities of solvent and solute, respectively, and the concentration is denoted in mole fraction  $x$ . According to eq. (4) the density difference  $(d - d_0)$  linearly changes with solute concentration  $x$ . However, as observed in the present study, this ideal additivity rule rarely holds in real solutions.

One of the possible causes of the deviation of the ideal additivity rule for densities is the concentration dependence of solvation of ions. In order to include these solvation effects we assume that the additivity rule holds in the modified form (called here modified additivity rule):

$$d = (1 - x)^m d_0 + x^m d_{\text{sl}}, \quad (5)$$

where the exponent  $m$  is a measure of deviations from the ideal solvation characteristics of solute molecules. Eq. (5) simplifies to the ideal additivity rule for  $m = 1$  while a solution exhibits a deviation from the ideal behaviour when  $m < 1$ .

For small values of  $x$  and  $m$  close to 1, eq. (5) may be approximated as

$$d = (1 - x^m) d_0 + x^m d_{\text{sl}} = d_0 + A x^m, \quad (6)$$

where, as in eq. (4),  $A = (d_{\text{sl}} - d_0)$ . It was found analytically that in alkali halides this approximation gives a maximum deviation of about 4% for  $x < 0.4$  and  $0.8 > m > 1$ . Eq. (6) is the same as the power-law expression (3).

It is well known that  $d_{\text{sl}}$  is practically temperature independent, especially in the interval of temperatures used for measurements of densities of solutions, and the solvent density  $d_0$  decreases with temperature following an Arrhenius-type relation. Therefore, the constant  $A = (d_{\text{sl}} - d_0)$  may be given by

$$A = d_{\text{sl}} - d_0^0 \exp(E_1/kT) = d_{\text{sl}} \exp(-E_2/kT), \quad (7)$$

where  $d_0^0$  is the extrapolated density of solvent when  $E_1/kT = 0$ ,  $E_1$  is the activation energy for density decrease and  $E_2 = (d_0^0/d_{\text{sl}})(kT + E_1)$ . Eq. (7) is of the same form as eq. (1) and is derived on the assumption that the approximation  $\exp i = 1 + i$  is valid (i.e.  $E_1 = kT$ ).

Eq. (7) shows that the solute density  $d_{\text{sl}}$  is equal to the pre-exponential factor  $A_0$  of eq. (1) and that the activation energy  $E_2 < kT$  since usually  $d_0^0 < d_{\text{sl}}$ . These conclusions are qualitatively in agreement with the experimental observations presented in Table 1 and Figure 3.

#### 4.2. Solvent polarization model

The additivity rule does not provide insight into the physical processes responsible for changes in the parameters  $m$ ,  $A_0$  and  $E$ . The ideal additivity rule indeed considers solute ions dispersed in a solvent. This model is similar to the molecular interaction model reported earlier (POLAK, SANGWAL 1995, 1996) to describe the distribution of solute clusters in solutions.

According to the molecular interaction model (POLAK, SANGWAL 1995, 1996), a solution is a continuum medium of dielectric constant  $\epsilon$ , in which ions and clusters of the solute are dispersed. Therefore, ion-ion and ion-cluster interactions are different from those in the vacuum. For the estimation of the size distribution of clusters in an electrolyte solution the above authors calculated the free energy change associated with the formation of clusters using contributions due to Coulomb energy of ions, cohesion energy of solvent molecules in contact with solute ions, and adsorption energy of water molecules on the surface of single ions. One of the main conclusions of the calculations was that for different alkali halides in undersaturated solutions the adsorption energy  $G_{\text{lads}}$  per water molecule on free ions of an alkali halide molecule lies between 10 and 50 kJ/mol (POLAK; POLAK, SANGWAL 1996).

Comparison of the values of  $G_{\text{lads}}$  with the activation energy  $E$  listed in Table 1 shows that  $E$  is much lower than  $G_{\text{lads}}$ . Since the molecular interaction model does not include entropy contributions, it is possible that some of the disagreement in the values of  $E$  and  $G_{\text{lads}}$  is due to entropy contributions. Moreover, it is not clear why  $E$  is negative as well as positive.

To describe the discrepancy between the values of  $A_0$  and  $d_{\text{si}}$  and the positive and negative values of  $E$  one may equally consider a model similar to that of the formation of vacancies in an ionic lattice. We assume that the solvent molecules form a lattice-like structure with an average distance  $a$  and the cations and anions of the electrolyte occupy the "lattice" sites of the solvent. If  $n$  is the number of pairs of cations and anions distributed over a total of  $(N+n)$  sites, one may write (see DEKKER)

$$n = (N+n) \exp(\Delta S_{\text{th}}/2k) \exp(-E/2kT), \quad (8)$$

where  $\Delta S_{\text{th}}$  is the increase in the thermal entropy of the system due to the occupation of the lattice by a cation-anion pair, and  $E$  is the energy required to occupy a cation-anion pair. The increase in thermal entropy may be expressed by (DEKKER)

$$\Delta S_{\text{th}} = 3kz \ln(v/v'), \quad (9)$$

where  $z$  is the number of nearest neighbours surrounding an ion, and  $v$  and  $v'$  are the frequencies of vibration of solvent molecule and solute ions, respectively, in the solution, such as  $v > v'$ . The energy required to accommodate a cation-anion pair in the solution may be given by (DEKKER)

$$E = E_s - P_+ - P_- = E_s - \frac{1}{2}e^2 \left(1 - \frac{1}{\epsilon}\right) \left(\frac{1}{R_+} + \frac{1}{R_-}\right), \quad (10)$$

where  $E_s$  is the evaporation energy of the solvent,  $e$  is the ionic charge,  $P_+$  and  $P_-$  are the polarization energies due to a cation and anion, respectively, and  $R_+$  and  $R_-$  are the corresponding radii in the solvent of dielectric constant  $\epsilon$ .

In eq. (8) the term  $(\Delta S_{\text{th}}/3kz) \geq 1$  (cf. eq. (9)) while, depending on the relative contributions of  $P_+$  and  $P_-$ ,  $E$  can take positive as well negative values. Estimates show that  $E$  is only a fraction of  $E_s$  (DEKKER).

In eq. (8) the number  $n$  of cation–anion pairs is connected with a change  $(d-d_0)$  in the solution density and  $(N+n)$  with solution density  $d$ . Then, this equation transforms to eq. (3) if

$$d \exp(\Delta S_{\text{th}}/k) = A_0 c^{1-m}. \quad (11)$$

This relationship shows that, as demonstrated in Figure 3, the constant  $A_0$  of eq. (3) is not directly related with the solute density. The values of  $A_0$  are determined by solution density, solute concentration  $c$  (through the parameter  $m$ ) and thermal entropy of the solution.

## 5. Conclusions

The following conclusions can be drawn from this study:

- (1) The power-law approach satisfactorily describes the experimental data of the concentration and temperature dependence of densities of aqueous alkali halide solutions.
- (2) The power-law expression relating solution density with their concentration and temperature can be derived from a modified additivity rule for densities and a model based on polarization of solvent molecules around electrolyte ions.
- (3) The additivity rule is essentially empirical but the model of polarization of solvent molecules relates the parameters of the power-law expression with the physical processes occurring in solutions.

## References

- DEKKER, A.J.: Solid State Physics, McMillan, London, 1952  
FREJ, H., JAKUBCZYK, M., SANGWAL, K.: J. Chem. Eng. Data **43** (1998) 158  
HORVATH, A.: Handbook of Aqueous Electrolyte Solutions, Ellis Horwood, Chichester, 1985  
IZMAILOV, N.A.: Elektrokhimiya Rostvorov (Electrochemistry of Solutions), 3rd edition, Khimiya, Moscow, 1976  
LIDE, D.R. (Editor): CRC Handbook of Chemistry and Physics, 77th edition, CRC Press, Boca Raton (1996/1997)  
POLAK, W.: Ph.D. thesis, M. Curie-Skłodowska University, Poland (1997)  
POLAK, W., SANGWAL, K.: J. Cryst. Growth **152** (1995) 182  
POLAK, W., SANGWAL, K.: J. Cryst. Growth **160** (1996) 154  
ROBINSON, R., STOKES, R.H.: Electrolyte Solutions, 2nd edition, Butterworths, London, 1959  
SÖHNEL, O., NOVOTNÝ, P.: Densities of Aqueous Solutions of Inorganic Substances, Academia, Prague, 1985  
SZEWCZYK, J., SANGWAL, K.: J. Chem. Eng. Data **33** (1988) 418

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### *Authors' addresses:*

mgr R. MISZTAL  
Institute of Chemistry, Pedagogical University of Czestochowa  
Al. Armii Krajowej 13/15, 42-200 Czestochowa, Poland

Prof. dr hab. K. SANGWAL\*  
Institute of Physics, Technical University of Lublin  
ul. Nadbystrzycka 38, 20-618 Lublin, Poland

\*Corresponding author

Fax: ++48 81 525 93 85; E-mail: sangwal@antenor.pol.lublin.pl