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Densities of Aqueous Electrolyte Solutions. A Model for a Data Bank

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A model is proposed for establishing a data bank of densities of aqueous electrolyte solutions. The model, based on the concept of the apparent molar volume, involves separation of the molar volume of the salt and of a parameter accounting for deviation of a system from additivity into cationic and anionic contributions. The model has been tested on a model set of aqueous solutions of alkali metal and ammonium halides (with the exception of fluorides) and nitrates at 25 °C over maximum concentration ranges. All the unknown parameters are obtained simultaneously by a regression method applied to all the experimental data involved. In this way, literature data for a set of 24 systems have been described by means of just 10 parameter pairs, which provide density values correct to three decimal places.

Introduction

A rigorous way of expressing the density, d , of a binary system is in terms of the molar volume V

$$V = (M_1x_1 + M_2x_2)/d \quad (1)$$

where M_1 and M_2 are the molecular weights of the two components and x_1 and x_2 are their mole fractions. With the concentration dependence of density transformed into the concentration dependence of the molar volumes of the components, we can take up the question of additivity of the molar volumes

$$V = V_1x_1 + V_2x_2 = V_sx + V_w(1-x) \quad (2)$$

where V_1 and V_2 are the molar volumes of pure components at the same temperature. For most binary systems, including the systems water-salt which are the subject of the present paper, deviations from additivity occur:

$$\Delta V^E = V - V_1x_1 - V_2x_2 \quad (3)$$

There are several approaches to accounting for these deviations. The classical thermodynamic approach operates with partial molar volumes of components, which are each a function of composition. Of more practical importance, however, is the semiempirical concept of the apparent molar volume (1-3). It was not the aim of present paper to provide an accurate description of densities of dilute solutions. Such data have been included in the set treated, but they overlap with somewhat less accurate results for the region of higher concentrations. For statistical reasons, therefore, the effects consistent with the Debye-Hückel theory are not demonstrable.

Model for the Dependence of Molar Volume on Composition

In this paper we adhere to the concept of the apparent molar volume of water, which is more logical than the concept of the apparent molal volume of the salt (2) and is capable of describing the deviations from additivity over the whole concentration range. In deriving a relation for the molar volume of a system, we start from the quasi-lattice model of solution, with water distributed between the cationic and anionic sublattices in the ratio of the stoichiometric coefficients of salt M_pX_q , i.e., $p:q$. Now, the probability of finding a water molecule in the immediate neighborhood of an ion is proportional to

Table I. Parameters for the Description of Molar Volumes and Densities of Individual Systems^a

salt	<i>x</i> range	A (eq 2)			B (eq 4)			
		V_S^{0b}	s_V	s_d	V_S^{0b}	a^b	s_V	s_d
LiCl	0.2647	20.81 (0.04)	0.0450	0.0027	23.57 (0.15)	-4.10 (0.23)	0.0215	0.0013
LiBr	0.2665	26.42 (0.05)	0.0307	0.0024	25.81 (0.38)	0.93 (0.56)	0.0296	0.0023
LiJ	0.1792	36.64 (0.06)	0.0187	0.0013	34.59 (0.44)	2.68 (0.58)	0.0134	0.0009
LiNO ₃	0.3021	31.44 (0.05)	0.0404	0.0025	34.13 (0.17)	-3.96 (0.25)	0.0202	0.0013
NaCl	0.1005	20.80 (0.06)	0.0341	0.0021	36.43 (0.34)	-18.18 (0.40)	0.0080	0.0005
NaBr	0.1421	27.62 (0.12)	0.0378	0.0025	34.84 (1.21)	-8.83 (1.47)	0.0259	0.0018
NaJ	0.1809	38.44 (0.07)	0.0324	0.0023	42.62 (0.56)	-5.45 (0.73)	0.0210	0.0015
NaNO ₃	0.1625	33.41 (0.17)	0.0693	0.0043	44.96 (0.67)	-14.20 (0.82)	0.0224	0.0014
KCl	0.0800	30.70 (0.06)	0.0287	0.0017	49.03 (0.60)	-20.73 (0.68)	0.0095	0.0006
KBr	0.0942	37.40 (0.06)	0.0247	0.0016	50.70 (0.47)	-15.32 (0.54)	0.0081	0.0005
KJ	0.1391	49.00 (0.07)	0.0397	0.0027	55.45 (0.74)	-7.98 (0.92)	0.0282	0.0020
KNO ₃	0.0639	41.81 (0.11)	0.0206	0.0012	54.76 (3.23)	-14.24 (3.55)	0.0168	0.0010
RbCl	0.1247	36.54 (0.15)	0.0503	0.0033	51.21 (0.93)	-17.60 (1.12)	0.0177	0.0012
RbBr	0.1077	43.27 (0.27)	0.0301	0.0018	57.34 (0.40)	-17.33 (0.49)	0.0017	0.0001
RbJ	0.0592	53.81 (0.23)	0.0247	0.0016	59.21 (9.16)	-5.98 (10.14)	0.0242	0.0016
RbNO ₃	0.0419	46.08 (0.18)	0.0126	0.0007	73.53 (3.88)	-29.24 (4.13)	0.0057	0.0003
CsCl	0.1707	44.16 (0.12)	0.0600	0.0044	53.63 (0.37)	-11.92 (0.46)	0.0149	0.0011
CsBr	0.0874	49.85 (0.22)	0.0246	0.0017	63.69 (0.78)	-16.06 (0.90)	0.0034	0.0002
CsJ	0.0597	60.02 (0.09)	0.0071	0.0005	73.80 (1.00)	-15.08 (1.09)	0.0028	0.0002
CsNO ₃	0.0151	52.46 (0.07)	0.0017	0.0001	94.45 (4.73)	-42.97 (4.85)	0.0008	0.0000
NH ₄ Cl	0.1174	39.14 (0.09)	0.0284	0.0015	47.72 (0.60)	-10.24 (0.72)	0.0095	0.0005
NH ₄ Br	0.1110	44.77 (0.24)	0.0542	0.0031	53.80 (3.79)	-10.70 (4.48)	0.0469	0.0027
NH ₄ J	0.1489	55.50 (0.07)	0.0145	0.0009	56.49 (1.27)	-1.30 (1.66)	0.0132	0.0009
NH ₄ NO ₃	0.3285	50.93 (0.06)	0.0749	0.0039	54.18 (0.12)	-5.24 (0.19)	0.0251	0.0013
total			0.0419	0.0026			0.0189	0.0012

^aA, additivity of volumes of salt and water is assumed; B, dependence of the volume of water on concentration is assumed. ^bValues in parentheses are standard deviations.

$(1-x)/(1-x+px+qx)$. For $p=q=1$, we can derive the relation

$$V = V_S^0 x + (1-x)[V_W^0 + ax/(1+x)] \quad (4)$$

where the parameter a accounts for the change of water volume in the neighborhood of an ion (and therefore includes the coordination number).

Additivity of Ionic Volumes

If the above relation were to be used to store experimental density data, the number of parameter pairs would be identical with the number of systems. It may however be recalled that the principle of the additivity of ionic properties has been profitably applied to a number of cases, for example, to ionic radii, conductivities at infinite dilution, and the B parameters in the Jones-Dole viscosity equation. After all, even the apparent molar volume of salt at infinite dilution, Φ^0 , has been treated as the sum of the so-called conventional ionic volumes (2). This work is an attempt to describe density data over the whole

concentration range by applying the additivity principle.

If we split the parameters V_S^0 and a in eq 4 into single ion contributions, we obtain

$$V = (V_C^0 + V_A^0)x + (1-x)[V_W^0 + (a_C + a_A)x/(1+x)] \quad (5)$$

The use of this equation to represent density data would involve a much smaller number of parameters. As an illustration, let us consider n cations and m anions, for which there are theoretically nm possible salts of $n+m$ different ions. If we confine ourselves to simple inorganic ions, we find an order-of-magnitude number $n=m=40$. In this particular case, we have $40 \times 40 = 1600$ salts in contrast to 80 ions, and thus the salts require 20 times more parameters. This aspect may be of great importance in building future data banks.

Model Set of Systems

Aqueous solutions of alkali metal halides at 25 °C were chosen as a model set for verifying our idea. Fluorides were

Table II. Parameters for the Description of Molar Volumes and Densities on the Basis of Ionic Additivity (Eq 5, $a_C = a_A = 0$)^a

	V_C^{0b}	V_A^{0b}			
		Cl	Br	J	NO ₃
		20.54 (0.04)	26.45 (0.06)	37.64 (0.08)	31.79 (0.05)
Li	0.00 (0.00)	0.0546 ^c 0.0035 ^c	0.0309 0.0025	0.0717 0.0058	0.0507 0.0031
Na	0.82 (0.07)	0.0434 0.0026	0.0423 0.0030	0.0325 0.0023	0.0881 0.0058
K	10.88 (0.07)	0.0419 0.0024	0.0248 0.0016	0.0513 0.0038	0.0358 0.0021
Rb	16.03 (0.14)	0.0503 0.0033	0.0527 0.0040	0.0252 0.0016	0.0361 0.0022
Cs	23.58 (8.11)	0.0601 0.0044	0.0259 0.0018	0.0180 0.0012	0.0135 0.0008
NH ₄	19.06 (0.06)	0.0402 0.0022	0.0677 0.0039	0.1431 0.0093	0.0756 0.0039

^aTotal $s_V = 0.0504$; $s_d = 0.0032$. ^bValues in parentheses are standard deviations. ^cAll upper values are s_V and all lower values are s_d .

Table III. Parameters for the Description of Molar Volume and Densities on the Basis of Ionic Additivity (Eq 5, $a_C = a_A = a$)^a

	V_C^{0b}	V_A^{0b}			
		Cl	Br	J	NO ₃
		24.25 (0.11)	30.14 (0.11)	41.19 (0.11)	35.25 (0.11)
Li	0.00 (0.00)	0.0317 ^c 0.0020 ^c	0.0652 0.0054	0.0521 0.0042	0.0281 0.0019
Na	1.60 (0.05)	0.0324 0.0019	0.0317 0.0022	0.0272 0.0020	0.0777 0.0051
K	11.81 (0.06)	0.0340 0.0020	0.0178 0.0011	0.0376 0.0027	0.0223 0.0013
Rb	16.85 (0.10)	0.0375 0.0025	0.0408 0.0031	0.0325 0.0022	0.0221 0.0013
Cs	24.17 (0.07)	0.0353 0.0025	0.0183 0.0014	0.0079 0.0005	0.0081 0.0005
NH ₄	19.02 (0.04)	0.0282 0.0015	0.0494 0.0029	0.0758 0.0050	0.0252 0.0013

^a $a = -5.367$, std dev. = 0.155. Total $s_V = 0.0349$; $s_d = 0.0024$. ^bValues in parentheses are standard deviations. ^cAll upper values are s_V and all lower values are s_d .

omitted from the treatment because no literature data were available for some of them. On the other hand, the set was extended to include nitrate and ammonium salts on account of their analogy to alkali metal halides. The final set comprised 24 systems composed of 6 cations and 4 anions.

The sources of data were monographs by Timmermans (4) and by Lobo (5, 6). After all the available density data were

fed to the memory of a computer and were converted to the mole fraction scale, some "sorting" of the data was necessary. First, conspicuous outliers were either adjusted by correcting a significant figure or rejected. When the entire data set from a source was aberrant, the error was sought in the concentration units stated. Only exceptionally was an entire data set eliminated. The treatment covered a total of 1101 density data from 143 different sources. The densities were converted to molar volumes by using eq 1.

Evaluation of Densities When Each System Is Considered Separately

For comparison purposes, the data were first evaluated in the classical way, each system being treated separately. Two relations were tested, one for the additivity of molar volumes of components and the other involving a term allowing for deviations from the additivity. The values of the parameters are summarized in Table I, along with standard deviations of molar volumes s_V and of densities s_d calculated from eq 1. The first column of the table gives results obtained from eq 4 and $a = 0$ while the second relates to eq 4 for $a \neq 0$. The figures below the parameter values are their standard deviations. The last row of the table gives the overall standard deviations relating to the description of the whole set by 24 parameters (or parameter pairs), obtained by summing the individual sums of the squares of the deviations and converting the resulting sums to standard deviations. The standard deviations in the second column of Table I may be considered as limiting values consistent with the scatter of the experimental data. Introduction of a further term to account for deviations from additivity (3) did not lead to any significant improvement of the fit.

Evaluation of Densities on the Basis of the Additivity Principle

All computations were performed on a HP 9830A desk calculator (16 kB) by using a regression algorithm described in ref 7.

$a_C = a_A = 0$. The first approach was to use eq 5 with $a_C = a_A = 0$. Since the ionic volumes are interdependent, the number of independent volumes is smaller by one, so that we have nine parameters. For the present model set, the volume of Li⁺ ion was, by convention, set equal to zero. In establishing an actual data bank, it would be more convenient to choose the volume of another ion, for example H⁺, as the zero reference base. A certain ambiguity arising from the convention of taking the volume of an ion as zero vanishes when the volumes of cations and anions are added together to give the salt volumes. Results of the evaluation are given in Table II, where standard

Table IV. Parameters for the Description of Molar Volumes and Densities on the Basis of Ionic Additivity (Eq 5, $a_C \neq a_A$)^a

	V_C^0	a_C^b	Cl,	Br,	J,	NO ₃ ,
			$V_A^0 = 24.03$, SD ^a = 0.13, $a_A = -2.45$, SD = 0.24	$V_A^0 = 26.86$, SD = 0.19, $a_A = 1.61$, SD = 0.30	$V_A^0 = 31.84$, SD = 0.40, $a_A = 8.46$, SD = 0.52	$V_A^0 = 33.15$, SD = 0.16, $a_A = 0.00$, SD = 0.00
Li	0.00 (0.00)	-2.36 (0.23)	0.0227 ^c 0.0014 ^c	0.0339 0.0027	0.0234 0.0017	0.0263 0.0016
Na	10.90 (0.39)	-13.82 (0.48)	0.0111 0.0007	0.0293 0.0021	0.0255 0.0019	0.0470 0.0030
K	24.47 (0.48)	-17.59 (0.56)	0.0101 0.0006	0.0085 0.0005	0.0287 0.0021	0.0181 0.0011
Rb	26.36 (1.00)	-14.07 (1.19)	0.0184 0.0012	0.0126 0.0009	0.0339 0.0023	0.0092 0.0005
Cs	29.96 (0.54)	-9.94 (0.69)	0.0151 0.0011	0.0153 0.0012	0.0089 0.0006	0.0045 0.0003
NH ₄	20.83 (0.18)	-4.88 (0.15)	0.0288 0.0015	0.0513 0.0029	0.0280 0.0018	0.0257 0.0013

^aTotal $s_V = 0.0227$; $s_d = 0.0015$. ^bValues in parentheses are standard deviations. ^cAll upper values are s_V and all lower values are s_d .

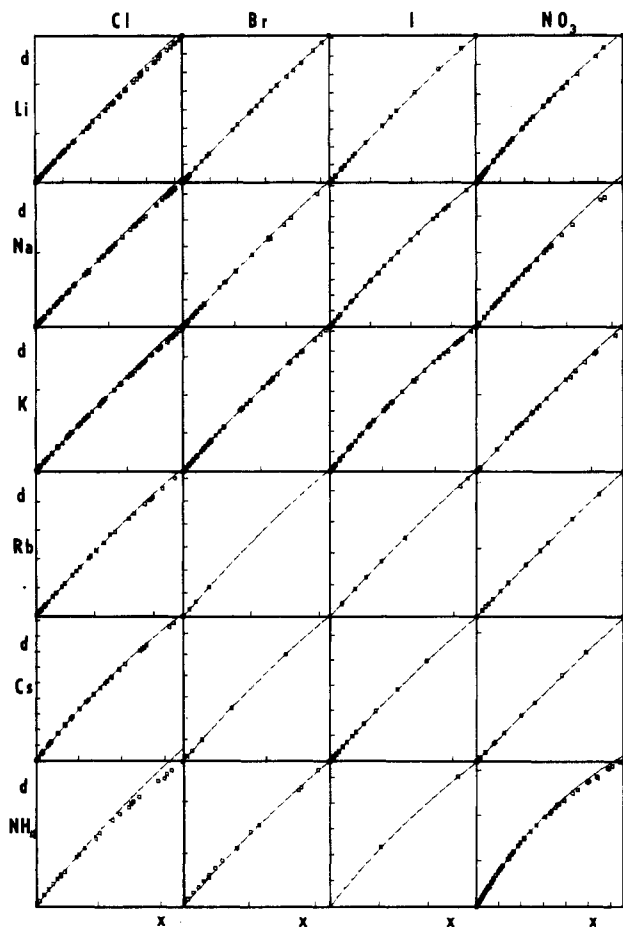


Figure 1. Comparison of experimental data for the density as a function of concentration with the fit of eq 5 based on ionic additivity principle (eq 5, $a_C \neq a_A$). (Tic marks are in steps of 0.05 for x and 0.1 for d .)

deviations of volume and density are listed for each cation-anion combination. The overall standard deviations quoted at the bottom of the table are only slightly higher than those in the first column of Table I.

$a_C = a_A = a$. In the next trial, the deviations from additivity were assumed to be nonzero and equal for all the components, i.e., $a_C = a_A = a$. From results given in Table III it is seen that introduction of this parameter leads to a significant improvement of the fit over that for the classical treatment requiring 24 parameters (Table I, column 1).

$a_C \neq a_A$. Finally, Table IV gives results obtained by using eq 5 in its full form. Again, the parameters a_C and a_A are

interdependent and so one of them, $a_{NO_3^-}$, was set equal to zero. Standard deviations for the description involving 18 independent parameters are only slightly higher than those for the classical treatment using 48 parameters (Table I, column 2).

Discussion

The goodness of fit may be judged from Figure 1, where experimental points for density as a function of concentration, as well as lines obtained by fitting the data to eq 5, are shown for all the systems treated. The tic marks along the axes are in steps of 0.05 for x and 0.1 for d .

Comparison of salt volumes obtained by summing the ionic contributions ($V_S = V_C + V_A$) with the molar volumes of the salts in the crystalline state shows that the two volumes are of the same order of magnitude but, with the exception of lithium salts, the former are about 15% smaller than the latter. Thus, the calculated volumes are characteristic of the behavior of the ions in solution.

As far as the temperature dependence of density is concerned, a possible approach would be to split each parameter into a minimum of two terms and in this way treat it as a linear function of temperature.

In conclusion, it should be pointed out that the classical evaluation of salt volumes (i.e., when each system is treated separately) and their subsequent treatment on the basis of the principle of additivity is unavailing! A cursory examination of the V_S^0 values in Table II shows how scattered they are. It is necessary that the unknown parameters for all the systems involved be evaluated simultaneously by a regression method. Admittedly, using such an approach in building a future data bank would entail a rather large volume of computation even at the present stage of computer development.

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