

CALCULATION OF THE DENSITY OF AQUEOUS SOLUTIONS OF STRONG ELECTROLYTES FROM INDIVIDUAL IONIC PARAMETERS

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Based on a hypothesis verified earlier, according to which the concentration dependence of apparent molar volumes of ions in aqueous solutions is caused by their dehydration due to the decrease of the volume concentration of water, a method for the calculation of the density of concentrated aqueous electrolytes from individual ionic constants is proposed. The theory is verified by comparing with experimental data from the literature (420 solutions of 57 electrolytes).

Seeking a way how to calculate the densities of solutions from a minimum number of starting data led to the concept of the apparent molar volume of the solute, Φ , given by the equation

$$\Phi = M/d_0 + (1 - d/d_0)/c. \quad (1)$$

This quantity involves all volume changes due to dissolving the solute in a given solvent. If its value at a given temperature and concentration is known, the solution density can be calculated from Eq. (1) as

$$d = d_0 + (M - \Phi d_0) c, \quad (2)$$

where the term in parentheses is a molar parameter characterizing the solute at a given concentration, temperature, and solvent.

In aqueous solutions of strong electrolytes, the apparent volumes change strongly with the concentration; this dependence is well described by Masson's empirical square-root rule¹

$$\Phi = \Phi^0 + kc^{1/2}, \quad (3)$$

which has been verified with many highly soluble salts up to saturation²⁻⁴.

The volume Φ^0 extrapolated to infinite dilution can be divided into the contributions of the ions involved. These contributions are characteristic constants for each ion independent of the counter ions in the electrolyte. If the coefficients k in Eq. (3)

could be decomposed in an analogous way to additive constants, it would be possible to calculate from Eqs (2) and (3) the densities of aqueous electrolytes at any concentrations with the use of a limited set of individual ion constants. This was attempted by Geffcken², but without success.

According to our previous work^{5,6}, the apparent molar volumes of aqueous electrolytes are determined not solely by their concentration but rather by the volume concentration of the solvent. Hence, we concluded that the concentration dependence of the apparent molar volumes of ions is not due to electrostatic interactions among them^{7,8} but to a shift of their hydration equilibria with increasing occupation of the solution by apparent ion volumes, c/c' , where c' represents the concentration at which the volume fraction of the solvent would be equal to zero. This conclusion was substantiated independently by studies of electrolyte mixtures⁹.

We shall denote Φ' the apparent volume of electrolyte extrapolated to this concentration according to Eq. (3). Then

$$c'\Phi' = 1. \quad (4)$$

On introducing the ratio c/c' into Eq. (3) instead of c and using Eq. (4) we obtain¹⁰

$$\Phi = \Phi^0 + (\Phi' - \Phi^0)(c\Phi')^{1/2}. \quad (5)$$

The value of Φ' can be determined graphically^{5,6} from the intersection of the straight line $\Phi = \Phi^0 + kc^{1/2}$ drawn through the experimental points Φ with the hyperbola $\Phi - 1/c$.

If the considered ion forms an aquocomplex with n water molecules (which does not take part in dehydration equilibria giving rise to the dependence (3)), it is necessary to subtract the volume of the water bound in the complex from the volume of total water in solution, *i.e.*, to subtract the term cnM_0/d_0 . The apparent volume of this ion then comes out higher by this correction; this is manifested in the mentioned extrapolation by a shift of the intersection to lower c' values. (The number of bound water molecules, n , is found⁶ by comparing the values of Φ' found in this way for a given electrolyte and different values of n with those obtained from its crystallographic parameters. Alternatively, if the solution densities at various temperatures are known, from the condition of the temperature invariance of Φ' , derived theoretically from the dehydration model⁶.)

It turned out⁶ that the extrapolated values of Φ' corresponding to the "water-free" state of the system (disregarding the water bound in the aquocomplexes) show within the limits of accuracy of the extrapolation the same additivity of the individual ion contributions as is known in the case of the Φ^0 values. This leads to a new possibility how to solve the problem of the densities of aqueous strong electrolytes in the region of medium and high concentrations. The present work follows this line.

THEORETICAL

If the additivity of the ion contributions applies only to the values of Φ corresponding to the same degree of filling of the solution^{5,6,9,10} expressed by the ratio of c/c' , it is necessary to substitute the expression (5) for Φ in Eq. (2) for the solution density. On the assumption of additivity of both the quantities Φ' and Φ^0 Eq. (2) can then be written in the form

$$d = d_0 + c \sum_i v_i (M_i - d_0 \Phi_i^0) - c^{3/2} \sum_i v_i d_0 (\Phi_i' - \Phi_i^0) (\sum_i v_i \Phi_i')^{1/2}, \quad (6)$$

where the summation involves all ions occurring in the formula of the electrolyte with the stoichiometric coefficients v_i . It is convenient to introduce characteristic ionic constants

$$a_i = M_i - d_0 \Phi_i^0, \quad (7)$$

$$b_i = d_0 (\Phi_i' - \Phi_i^0). \quad (8)$$

The third ionic parameter is Φ_i' , whose temperature invariance was derived theoretically and verified experimentally in a wide range of temperatures⁶. To calculate the constants a_i and b_i , the values of M_i , Φ_i^0 and Φ_i' in Eqs (7) and (8) must correspond to that form of ions which is present in the solution in the considered concentration range. Thus, Eq. (7) involves molar masses equal to $M_{i,n=0} + nM_0$ and apparent volumes equal to $\Phi_{i,n=0} + n\Phi_0$ or $\Phi_{i,n=0}^0 + nM_0/d_0$, where the subscript zero refers to pure water at the considered temperature. The water terms are cancelled in the expression for a_i leading to the same values of a_i as for nonhydrated ions:

$$a_i = M_{i,n=0} - d_0 \Phi_{i,n=0}^0. \quad (9)$$

In contrast, the parameters b_i and Φ_i' are characteristic for the aquo complex.

In further treatment of the discussed problem, it has to be observed that mass concentrations are used in technological practice rather than molarities (compare the tabulated densities^{11,12}). Also thermodynamic calculations involve concentrations in mol per kg H₂O (molalities), which are related to mass percent p as $m = p/(100 - p)M$. However, Masson's square root rule involves molar concentrations and does not hold if the concentration is expressed otherwise. Therefore, it is necessary to express the "volume" concentration c in Eq. (6) as

$$c = dp/100M. \quad (10)$$

Since the tabulated values of p are referred to anhydrous electrolyte, the molar mass of the electrolyte M must be set equal to $\sum v_i M_i$, where M_i denotes molar mass of anhydrous ion species i .

The mentioned substitutions transform Eq. (6) into a semicubic equation for d

$$\left\{ \left[(dp/100)^{1/2} \left(\sum v_i \Phi'_i / \sum v_i M_i \right)^{1/2} \sum v_i b_i / \sum v_i M_i - \sum v_i a_i / \sum v_i M_i \right] p/100 + 1 \right\} d = d_0. \quad (11)$$

The coefficients involving the sums represent numerical constants at the given temperature, which can be evaluated from the tabulated ionic parameters a_i , b_i , Φ'_i , M_i , and v_i . The mass percent concentration p is the independent variable. The second term in brackets represents the contribution to the solution density in the hypothetical case where the apparent volume Φ of the electrolyte would be independent of its concentration and equal to the value Φ^0 corresponding to infinitely diluted solution.

The first term in brackets in Eq. (11) takes into account the change of the apparent ionic volumes with the concentration. If we neglect it, we obtain the first approximation of the density, d_1 , in the form

$$d_1 = d_0 \left[1 - \sum v_i a_i / \sum v_i M_i \right] p/100 \Big]^{-1}. \quad (12)$$

If we substitute d_1 for d in Eq. (11), its left-hand side will obviously be larger than d_0 ; this difference multiplied with d_1 and divided with d_0 is subtracted from d_1 to give the second approximation d_{II} , this in turn is used in further iteration and so on. The convergence of the successive approximation is rapid; results accurate to the third decimal place are obtained after three or four iterations even for most concentrated solutions, where the semicubic term attains highest values. The difference between d_1 and the exact value of d gives the value of the semicubic term in Eq. (6), from which we can see the contribution of the concentration dependence of the apparent molar volumes of ions to the solution density.

RESULTS AND DISCUSSION

We first attempt to divide into ionic increments the values of k in Eq. (3). We evaluated the apparent volumes at 18°C for all tabulated concentrations of strong electrolytes¹¹⁻¹³ using Eqs (1) and (10). After converting the mass percent p to molar concentrations c , we calculated the values of k by linear regression in the coordinates Φ , $c^{1/2}$ for a set of highly soluble electrolytes with common ions. Some data calculated earlier were also used^{5,6}. (Electrolytes with low solubility were omitted since exact determination of the value of k in a limited concentration region is difficult.) The results are given in Table I.

The differences of $k(\text{MeX}) - k(\text{MeI})$ for various cations Me and anions X (referred to one equivalent of electrolyte) are given in Table II. This gives some idea about the limits of validity of the additivity of ionic k values. It is seen that the values of these differences for the same anion and different cations are appreciably different, which results in variations of the apparent ionic volumes Φ amounting to thousandths of dm^3/mol . This means that the solution densities according to Eq. (2) at concentrations around $5 \text{ mol}/\text{dm}^3$ are subject to errors affecting the second decimal place. The differences between the densities of aqueous electrolytes and that of water attain never $1 \text{ kg}/\text{dm}^3$ and are mostly rather small. Hence, the deviations from the additivity of the values of k have to be considered as important, *i.e.*, the additivity is unsatisfactory.

TABLE I

Slopes k_i of the lines $\phi_i = \phi_i^0 + k_i c_i^{1/2}$ evaluated from the densities of single electrolyte solutions⁶, $10^{-3} \text{ dm}^{9/2} \text{ mol}^{-3/2}$, 18°C

Ions	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺	NH ₄ ⁺
I ⁻	0.98	1.81	1.97	1.81	1.55	1.31
Br ⁻	1.11	2.10	2.12	1.97	2.17	1.32
Cl ⁻	1.30	2.28	2.36	2.32	2.10	1.56
NO ₃ ⁻	1.38	2.75	2.67	2.77	2.53	1.33
F ⁻	—	3.10	2.95	3.14	—	3.05
OH ⁻	3.31	4.56	4.32	—	—	—
$\frac{1}{2}\text{SO}_4^{2-}$	5.23	6.84	6.66	—	—	5.79

TABLE II

Additivity test of ionic k_i -values by differences of molar k_i from Table I for different cations and the same pair of anions

Me ⁺	$k(\text{Br-I})$	$k(\text{Cl-I})$	$k(\text{NO}_3\text{-I})$	$k(\text{F-I})$	$k(\text{OH-I})$	$k(\frac{1}{2}\text{SO}_4\text{-I})$
Li ⁺	0.13	0.32	0.41	—	2.33	4.25
Na ⁺	0.29	0.47	0.94	1.29	2.75	5.03
K ⁺	0.15	0.39	0.70	0.98	2.35	4.69
Rb ⁺	0.16	0.51	0.96	1.33	—	—
Cs ⁺	0.32	0.55	0.98	—	—	—
NH ₄ ⁺	0.01	0.25	0.02	1.74	—	4.48

This difficulty can be explained on the basis of the described model of ionic solutions using the concept of filling up the space with ions. The apparent volume of each of the ions under consideration is a function of the degree of filling the solution with all of them. Therefore, it is natural that the dependence of its molar volume on the concentration is determined not only by its own ionic properties but also by the volume parameters of the other participating ions. A voluminous participating ion fills up the space more effectively than one with a small volume Φ , so that the slope k for a given ion is larger in the case of a voluminous participating ion than in the case of a small one. Therefore, it is not possible to find a definite ionic increment which would be involved in the values of k for all salts of a given ion. Accordingly, the additive ion contributions in the $c^{3/2}$ -term in Eq. (6) are multiplied with a term depending on the electrolyte composition.

The data in Table II are in support of this explanation. The differences $k(X-I) = k(\text{MeX}) - k(\text{MeI})$ increase with the volume of the cation Me, but there is a discontinuity between the Na^+ and K^+ ions. This is in accord with the finding^{6,9} that Li^+ and Na^+ ions form in aqueous solutions voluminous mono aquo complexes, whereas large cations NH_4^+ , K^+ , Rb^+ , and Cs^+ have only electrostatically bound hydration spheres, which are gradually splitted off with increasing concentration. It is apparent that the experimental values of k are in support of the model of filling the space with apparent volumes of ions as a factor determining their concentration dependence.

To test this model, we used the same experimental data¹¹⁻¹³ as in the preceding case. Tabulated experimental values of the solution densities d at 18°C were compared with those calculated from Eq. (11) with the use of ionic parameters n_i , Φ_i^0 and Φ_i' taken from the literature^{5,6,10,14,15} (with small corrections to minimize the mean quadratic deviation from tabulated data). The underlying constants are given in Table III; they were checked by calculating the solution densities for heavy alkali metal halides (Table IV, the first three columns). To judge the importance of the concentration dependence of the apparent ionic volumes Φ_i for the solution densities, the values of $\Delta d = d_{\text{calc}} - d_{\text{tab}}$ and of the semicubic term $y = d_1 - d_{\text{calc}}$ are given in Tables IV and following. All calculations were carried out to five decimal places.

As can be seen from Table IV, the described model of aqueous solutions of strong electrolytes makes it possible to find a set of individual ionic parameters which lead to the determination of the solution densities for any combinations of ions in the whole realizable concentration range with a good accuracy. The semicubic term corrects the results at concentrations around 30% with an accuracy to within 1–4% of its own value, *i.e.*, by one order of magnitude better than the corrections calculated on the assumption of additivity of the k values, evidence for the adequacy of the model used. When the difference of $d_{\text{calc}} - d_{\text{tab}}$ exceeds 10^{-4} kg/dm³ at highest concentrations, we have apparently to deal with deviations from the Masson's rule

TABLE III
Experimental ionic parameters in equations (7) and (8), 18°C

Ion (+n H ₂ O)	M 10 ⁻³ kg mol ⁻¹	ϕ^0 10 ⁻³ dm ³ mol ⁻¹	ϕ' 10 ⁻³ dm ³ mol ⁻¹	a 10 ⁻³ kg mol ⁻¹	b 10 ⁻³ kg mol ⁻¹
Li ⁺ (+1 H ₂ O)	6.94	- 3.5	15.0	10.3	0.5
Na ⁺ (+1 H ₂ O)	22.99	- 4.4	18.1	27.4	4.5
K ⁺	39.10	5.8	11.6	33.3	5.8
Rb ⁺	85.47	11.0	15.9	74.5	4.9
Cs ⁺	132.91	18.2	22.7	114.7	4.5
NH ₄ ⁺	18.04	15.3	16.4	2.7	1.0
Mg ²⁺ (+6 H ₂ O)	24.31	-26.4	85.8	50.7	4.2
Ca ²⁺ (+6 H ₂ O)	40.08	-23.2	90.0	63.3	5.2
Ba ²⁺ (+4 H ₂ O)	137.34	-15.0	62.0	152.4	5.0
Al ³⁺ (+9 H ₂ O)	26.98	-48.8	116.0	75.8	3.0
Cr ³⁺ (+6, viol.)	52.00	-45.6	71.0	97.6	8.6
F ⁻	19.00	0.8	13.3	18.2	12.5
Cl ⁻	35.45	20.0	26.7	15.5	6.7
Br ⁻	79.90	27.0	31.9	52.9	4.9
I ⁻	126.90	48.4	40.8	88.5	2.4
SCN ⁻	58.06	42.1	45.9	16.0	3.8
OH ⁻	17.01	- 3.1	16.2	20.1	19.3
NO ₃ ⁻ (+1 H ₂ O)	62.01	31.1	54.3	30.9	5.1
HCO ₃ ⁻ (+1 H ₂ O)	61.02	26.1	53.1	34.9	9.0
CO ₃ ²⁻ (+1 H ₂ O)	60.01	- 1.0	51.6	61.0	34.6
SO ₄ ²⁻	96.06	17.5	54.4	78.6	36.9

TABLE IV

Densities of aqueous solutions of heavy alkali metal salts, d (18°C); calculated from Eq. (11) with the use of individual ionic constants taken from Table III; γ is the semi-cubic correction term, Δd is the deviation from the tabulated experimental^{1,12} data, both in units 10^{-4} kg dm⁻³

p	d_{calc}	$-\gamma$	Δd	d_{calc}	$-\gamma$	Δd	d_{calc}	$-\gamma$	Δd	d_{calc}	$-\gamma$	Δd	d_{calc}	$-\gamma$	Δd
	CsI			CsBr			CsCl			CsNO ₃			Cs ₂ SO ₄		
1	1.0065	0	0	1.0065	0	0	1.0064	0	0	1.0061	0	0	1.0071	1	+ 6
2	1.0145	0	0	1.0145	1	0	1.0142	1	0	1.0137	1	-1	1.0157	2	+ 8
4	1.0308	1	0	1.0309	2	0	1.0302	3	0	1.0291	3	0	1.0332	6	+ 11
6	1.0476	2	0	1.0478	4	-1	1.0466	6	0	1.0450	5	0	1.0513	11	+ 14
10	1.0829	5	0	1.0832	8	-1	1.0809	14	0	1.0781	12	0	1.0889	26	+ 13
20	1.1820	18	+ 2	1.1824	30	0	1.1765	49	-1	1.1131	21	-1	1.1941	94	+ 22
30	1.3006	42	+ 2	1.3007	69	0	1.2890	113	-1				1.2636 ^a	162	+ 12
40	1.4449	84	+ 1	1.4441	138	+ 2	1.4235	224	-1						
50	1.6242	158	-1	1.6213	260	+ 2	1.5867	415	-4						
60							1.7884	747	-18						
	RbI			RbBr			RbCl			RbNO ₃			Rb ₂ SO ₄		
1	1.0063	0	0	1.0063	0	0	1.0061	1	0	1.0058	1	-1	1.0071	1	+ 1
2	1.0141	1	0	1.0142	1	0	1.0136	2	0	1.0130	1	0	1.0157	3	+ 2
4	1.0301	2	0	1.0301	3	0	1.0288	5	+ 1	1.0276	4	-1	1.0330	9	+ 3
6	1.0465	3	0	1.0465	5	-1	1.0444	9	0	1.0426	8	-2	1.0508	17	+ 4
10	1.0810	7	0	1.0808	12	-1	1.0768	22	+ 1	1.0737	18	0	1.0878	39	+ 8
20	1.1773	24	0	1.1762	43	-1	1.1657	75	+ 3	1.1591	61	+3	1.1900	139	+ 28
30	1.2918	56	+ 2	1.2888	100	0	1.2685	172	+ 7				1.3089	329	+ 52
40	1.4300	111	+ 7	1.4236	198	+ 1	1.3884	336	+ 13						
50	1.5999	206	+ 15	1.5876	367	-3	1.5299	629	+ 17						
	KI			KBr			KCl			KNO ₃			K ₂ SO ₄		
1	1.0060	1	0	1.0059	1	0	1.0051	1	0	1.0049	1	0	1.0068	2	+ 1
2	1.0134	1	0	1.0131	2	0	1.0115	4	0	1.0112	3	0	1.0150	6	0
4	1.0286	2	0	1.0280	5	0	1.0245	10	0	1.0239	7	-1	1.0314	16	- 1
6	1.0442	5	0	1.0431	9	0	1.0375	20	+ 1	1.0368	14	+5	1.0481	31	- 2
10	1.0766	11	-1	1.0745	21	-1	1.0641	45	+ 2	1.0631	32	-3	1.0822	72	- 2
20	1.1667	37	-1	1.1607	71	-2	1.1341	149	+ 5	1.1335	108	-4			
30	1.2721	84	-1	1.2598	161	-5									
40	1.3971	164	-1	1.3748	312	-10									
50	1.5474	298	+ 2												

^a 26% Cs₂SO₄.

and from the additivity of extrapolated "nonaqueous" volumes Φ' . The reasons for this can be the limited validity of this functional dependence, ion association effects, decomposition of aquo complexes, *etc.*, which may be seen from the non-linear course of the dependence of experimental values of Φ on $c^{1/2}$ in such cases^{5,6}.

The parameters of K^+ , Rb^+ , Cs^+ , Cl^- , Br^- , and I^- ions, found from their combinations by the described method, were used in calculating the densities of nitrate and sulphate solutions (the last two columns in Table IV) and of ammonium and light alkali metal salts, existing in aqueous solutions as monoquo complexes^{6,9} (Table V). The agreement between the calculated and tabulated densities interpolated from experimental data is similar to the preceding case. The deviations are irregularly distributed around zero, evidence for experimental errors and errors due to different interpolation methods of different authors. Negative deviations in the case of Li salts at highest concentrations are due to a deviation of the curve of apparent volumes toward lower values, which is caused by a change of the structure of the hydration sphere^{5,6}. Positive deviations in the case of Rb and Cs sulphates are obviously due to their association causing an increase of apparent volumes by partial splitting off of their hydration spheres; this leads to a decrease of the solution density with respect to values valid for fully dissociated salts⁶.

A similar comparison is made in Table VI for thiocyanates, salts with a large, little hydrated anion, whose apparent volume changes very little with the concentration, and further for salts of small anions F^- and OH^- and of divalent anions CO_3^{2-} , strongly hydrated, whose apparent volumes are strongly dependent on the concentration (owing to splitting off of the hydration sphere with increasing c). In the first case, the agreement between the theoretical and experimental data is as good as in the preceding one. Larger irregular deviations are also here an evidence for experimental and interpolation inaccuracies in the tabulated data. In the second case, systematic positive deviations at higher concentrations of NH_4F , RbF , $NaOH$, and KOH are observed, which affect the third or even the second decimal place and can be attributed to ion association. With the hydroxides, these deviations do not exceed 2–3% of the semicubic correction term. Negative deviations for $LiOH$, $RtOH$, and for the highest concentration of KOH can be attributed to a reorganization of the hydration sphere of OH^- ions. In the region of a large decrease of the water concentration, the voluminous clusters bound with hydrogen bonds change to a normal, closely packed structure of an electrostatically bound hydration sphere. This effect is in the case of $LiOH$ combined with an analogous reorganization of the hydration sphere of Li^+ ion, whereas with $RbOH$ an KOH it overcompensates the opposed effect of ion association.

The results obtained with the same parameters of Cl^- , Br^- , I^- , NO_3^- , and SO_4^{2-} ions combined with polyvalent cations are given in Table VII. Systematic positive deviations in the case of $MgCl_2$ are obviously due to ion association (formation of chloro complexes), which is known to take place at rather low concentrations

of this salt. Considerably positive deviations for BaBr_2 do not fit in the sequence chloride-bromide-iodide. With CaI_2 (as with BaBr_2), the deviations at lower concentrations exceed the value of the semicubic term, so that they cannot be eliminated

TABLE V
Ammonium and light alkali metal salts

ρ	d_{calc}	$-y$	Δd	d_{calc}	$-y$	Δd	d_{calc}	$-y$	Δd	d_{calc}	$-y$	Δd	d_{calc}	$-y$	Δd
	NH_4I			NH_4Br			NH_4Cl			NH_4NO_3			$(\text{NH}_4)_2\text{SO}_4$		
1	1.0049	0	-1	1.0043	0	0	1.0020	0	+3	1.0028	1	+1	1.0048	2	+3
2	1.0113	0	-1	1.0100	1	0	1.0051	4	+2	1.0069	2	0	1.0108	7	+2
4	1.0243	1	-1	1.0215	4	0	1.0113	11	+1	1.0151	6	-1	1.0227	20	+2
6	1.0376	2	-1	1.0332	7	0	1.0175	20	+2	1.0233	11	-3	1.0344	38	+1
10	1.0651	6	-1	1.0572	15	0	1.0294	44	+2	1.0399	25	-5	1.0576	88	-4
20	1.1406	18	-2	1.1215	51	0	1.0581	135	-8	1.0823	79	-14	1.1152	289	-9
30	1.2269	41	+4	1.1927	109	0				1.1264	161	-23	1.1723	616	-6
40	1.3269	76	+5							1.1725	276	-40	1.2287	1105	+2
50										1.2206	432	-65	1.2837	1802	+4
	NaI			NaBr			NaCl			NaNO_3			Na_2SO_4		
1	1.0064	0	0	1.0064	1	0	1.0058	2	+1	1.0054	1	+1	1.0078	3	+1
2	1.0142	1	0	1.0143	2	0	1.0130	5	+1	1.0122	3	0	1.0170	8	+1
4	1.0303	3	-1	1.0303	6	-1	1.0274	14	0	1.0259	9	0	1.0353	23	-1
6	1.0467	5	-1	1.0466	11	-2	1.0419	27	0	1.0398	17	0	1.0539	54	-3
10	1.0812	11	-2	1.0807	25	-3	1.0714	64	0	1.0683	39	+2	1.0919	103	-6
20	1.1774	39	-4	1.1747	86	+3	1.1488	217	+1	1.1442	132	+2	1.1926	370	+1
30	1.2912	91	-7	1.2840	199	-13	1.1985 ^a	361	-1	1.2280	293	+10			
40	1.4278	180	-9	1.4125	393	-28				1.3210	552	+19			
50	1.5946	389	-14												
	LiI			LiBr			LiCl			LiNO_3			Li_2SO_4		
1	1.0060	0	0	1.0059	0	0	1.0046	2	+1	1.0045	1	0	1.0074	3	+2
2	1.0136	0	0	1.0132	1	0	1.0104	5	+1	1.0105	2	0	1.0161	9	+1
4	1.0289	1	0	1.0282	4	0	1.0221	14	+2	1.0224	7	-1	1.0334	26	0
6	1.0447	2	0	1.0435	8	+1	1.0338	27	+3	1.0345	13	-3	1.0507	65	-3
10	1.0777	5	0	1.0753	17	+12	1.0572	62	+7	1.0591	30	-6	1.0858	119	-11
20	1.1697	19	+2	1.1627	60	+4	1.1167	203	+11	1.1243	99	+20	1.1765	421	-31
30	1.2784	43	+2	1.2639	137	+1	1.1788	433	+14	1.1954	213	-45			
40	1.4087	84	-4	1.3822	265	-24									
50	1.5675	154	-32												

^a 26% NaCl.

TABLE VI
 Hydroxides, fluorides, rhodanides, carbonates

<i>p</i>	<i>d</i> _{calc}	− <i>y</i>	Δ <i>d</i>	<i>d</i> _{calc}	− <i>y</i>	Δ <i>d</i>	<i>s</i> _{calc}	− <i>y</i>	Δ <i>d</i>	<i>d</i> _{calc}	− <i>y</i>	Δ <i>d</i>
	RbOH			KOH			NaOH			LiOH		
1	1-0078	1	− 2	1-0327 ^a	24	− 3	1-0101	6	0	1-0105	10	− 1
2	1-0170	4	− 4	1-0697 ^b	81	0	1-0213	17	0	1-0218	28	− 3
4	1-0358	12	− 11	1-0931 ^c	130	+ 1	1-0435	49	0	1-0436	85	− 6
6	1-0550	22	− 19	1-1974 ^d	344	+ 4	1-0656	95	+ 1	1-0645	165	− 10
10	1-0949	53	− 38	1-2415 ^e	727	+ 10	1-1101	231	+ 3	1-1042	397	− 39
20	1-2055	192	− 97	1-2992 ^f	1 124	+ 12	1-2223	874	+ 21	1-0093 ⁱ	3	+ 2
30	1-3072	395	− 148	1-4516 ^g	2 864	+ 46	1-3345	2 168	+ 54	1-0198 ⁱ	9	+ 3
40				1-5295 ^h	4 353	− 5	1-4423	4 599	+ 109	1-0409 ⁱ	29	+ 5
50							1-5409	9 572	+ 141	1-0622 ⁱ	58	+ 9
	RbF			KF			NaF			NH ₄ F		
1	1-0075	1	+ 1	1-0073	2	+ 1	1-0092 ^j	4	0	1-0040	3	+ 6
2	1-0164	3	+ 1	1-0160	6	+ 1	1-0198 ^k	11	− 1	1-0091	10	+ 6
4	1-0346	8	+ 1	1-0335	18	+ 1	1-0303 ^l	20	− 1	1-0189	28	+ 11
6	1-0533	15	+ 1	1-0513	35	+ 1	1-0409 ^m	31	0	1-0284	52	+ 19
10	1-0924	35	+ 2	1-0876	81	− 1	1-0515 ⁿ	45	0	1-0466	117	+ 46
14	—	—	—	1-1254	147	0				1-0639	204	+ 92
20	1-2015	126	+ 15	1-1849	289	+ 2						
30	1-3306	303	+ 47									
	K ₂ CO ₃			KCNS			NaCNS			NH ₄ CNS		
1	1-0077	2	+ 1	1-0036	1	+ 1	1-0039	1	+ 1	1-0010	1	+ 1
2	1-0167	6	− 1	1-0086	2	+ 1	1-0092	3	+ 2	1-0034	2	+ 2
4	1-0375	19	− 3	1-0187	6	+ 1	1-0197	8	+ 1	1-0081	5	+ 3
6	1-0530	37	− 5	1-0288	12	0	1-0303	14	0	1-0127	9	+ 3
10	1-0904	90	− 7	1-0493	27	− 2	1-0518	33	− 2	1-0219	19	+ 3
20	1-1895	331	− 12	1-1027	88	− 13	1-1078	106	− 3	1-0445	57	− 3
30	1-2979	791	− 10	1-1595	184	− 23	1-1673	225	− 4	1-0669	112	− 14
40	1-4159	1 602	+ 7	1-2204	325	+ 4	1-2308	400	+ 28	1-0893	182	+ 30
50	1-5430	3 074	+ 14	1-2856	525	+ 7	1-2642	514	− 8	—	—	—
60				1-3556	801	+ 2	(45% NaCNS)			1-1227	320	+ 14
70				1-4306	1 181	− 1				(55% NH ₄ CNS)		

^a 3-71%; ^b 7-72%; ^c 10-21%; ^d 20-90%; ^e 25-24%; ^f 30-74; ^g 44-70%; ^h 51-67%; ⁱ Na₂CO₃; ^j 1% NaF; ^k 2% NaF; ^l 3% NaF; ^m 4% NaF; ⁿ 5% NaF.

TABLE VII
Salts of polyvalent metals, 18°C

<i>p</i>	<i>d</i> _{calc}	- <i>y</i>	Δ <i>d</i>	<i>d</i> _{calc}	- <i>y</i>	Δ <i>d</i>	<i>d</i> _{calc}	- <i>y</i>	Δ <i>d</i>	<i>d</i> _{calc}	- <i>y</i>	Δ <i>d</i>	
BaI ₂ BaBr ₂ BaCl ₂ Ba(NO ₃) ₂													
2	1.0157	0	-1	1.0162	1	+	2	1.0163	3	0	1.0068 ^a	0	-4
4	1.0333	1	-3	1.0343	3	+	3	1.0345	6	-1	1.0151 ^b	1	0
6	1.0515	3	-3	1.0530	5	+	6	1.0532	11	-1	1.0321 ^c	4	+1
10	1.0899	6	-3	1.0924	13	+	11	1.0925	26	-2	1.0495 ^d	8	+1
20	1.1988	21	-5	1.2040	46	+	26	1.2027	94	-12	1.0674 ^e	13	0
30	1.3311	51	+11	1.3396	112	+	60				1.0859 ^f	18	-1
40	1.4953	106	+33	1.5074	233	+	135						
50	1.7043	206	+43										
60	1.9789	397	+59										
CaI ₂ CaBr ₂ CaCl ₂ Ca(NO ₃) ₂													
2	1.0152	1	-3	1.0156	2		0	1.0153	6	0	1.0138	3	+1
4	1.0322	2	-6	1.0330	6	-	1	1.0321	17	0	1.0291	9	0
6	1.0497	4	-8	1.0509	11	-	1	1.0491	32	0	1.0448	17	0
10	1.0865	10	-14	1.0883	26		0	1.0839	74	-2	1.0771	40	0
20	1.1903	36	-34	1.1928	92	+	1	1.1769	262	-14	1.1636	137	+10
30	1.3147	85	-58	1.3164	219	+	28	1.2795	608	-31	1.2635	312	+35
40	1.4666	174	-81	1.4648	446	+	68	1.3928	1200	-41			
MgSO ₄ — MgCl ₂ Mg(NO ₃) ₂													
2	1.0194	11	+3					1.0154	7	+4	1.0137	3	0
4	1.0402	33	+5					1.0322	20	+6	1.0289	10	-1
6	1.0611	63	+4					1.0491	37	+8	1.0444	18	-3
10	1.1037	152	-3					1.0836	87	+14	1.0763	43	-6
20	1.2156	563	-49					1.1748	308	+36	1.1625	147	-14
30								1.2737	712	+42			
CrCl ₃ (viol.) CrBr ₃ (viol.) AlCl ₃ Al(NO ₃) ₃													
1	1.0076	2	0	1.0074	1		0	1.0077	2	+2	1.0065	1	0
2	1.0166	5	0	1.0163	2	+	1	1.0167	6	+3	1.0144	3	-1
4	1.0348	15	-1	1.0345	5	+	1	1.0348	18	+4	1.0303	10	-2
6	1.0534	29	-1	1.0532	10		0	1.0533	35	+7	1.0465	19	-4
10	1.0917	69	0	1.0924	24	-	2	1.0911	83	+11	1.0801	43	-10
20	—	—	—	1.2029	86	-	2	1.1510 ^g	195	+19	1.1712	152	-33
30	—	—	—	1.3353	208	-	2	—	—	—	1.2745	349	-60

^a 1%; ^b 2%; ^c 4%; ^d 6%; ^e 8%; ^f 10%; ^g 16%.

by a change of the model but only by abandoning the additivity of the apparent ionic volumes Φ^0 in infinitely diluted solutions; this is, however, well founded both theoretically and experimentally. Hence, the mentioned deviations must be attributed to differences in experimental techniques, interpolation methods, *etc.*, among different authors on whose data the international tables are based. Similar discrepancies occur in the densities of solutions of aluminum salts, whether they are calculated for hexahydrate or enneahydrate of the Al^{3+} ion⁶, whereas the tabulated densities of solutions of violet Cr(III) salts (with the hexaquo complex of Cr^{3+}) are in a good agreement with the calculated ones.

These findings could constitute an argument in favour of the conclusion that in the case of discrepancies contradicting the homologous sequence of ions in the periodic system (and hence the association sequence), the densities calculated from Eq. (11) with the use of parameters evaluated from noncontradicting sets of experimental densities should be preferred; and this especially if the dubious data contradict the theoretically founded additivity of apparent ionic volumes in the region of low concentrations. This is also a reason why the densities theoretically calculated are here presented in full. The parameters for other temperatures and other ions can easily be calculated from the published experimental data by the proposed method.

LIST OF SYMBOLS

c	molar concentration (mol dm^{-3})
c'	molar concentration extrapolated to zero content of the solvent (mol dm^{-3})
d	solution density (kg dm^{-3})
d_0	density of the solvent (kg dm^{-3})
k	empirical constant in Eq. (3) ($\text{mol}^{-3/2} \text{dm}^{9/2}$)
m	molal concentration (mol kg^{-1})
M	molar mass of solute (kg mol^{-1})
M_0	molar mass of solvent (kg mol^{-1})
n	number of water molecules in an aquo complex
p	mass percent concentration (%)
Φ	apparent molar volume of solute ($\text{dm}^3 \text{mol}^{-1}$)
Φ^0	apparent molar volume of solute at infinite dilution ($\text{dm}^3 \text{mol}^{-1}$)
Φ'	apparent molar volume of solute extrapolated to zero content of the solvent ($\text{dm}^3 \text{mol}^{-1}$)
ν	stoichiometric coefficient

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