ON THEORY OF APPARENT MOLAR VOLUMES IN CONCENTRATED AQUEOUS SOLUTIONS OF STRONG ELECTROLYTES

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On the basis of the method reported in the previous work, according to which close-packed hydration sheaths of ions are surrounded by excess voids which in the above model were replaced by contact gap of width d_0 independent of temperature and concentration, it is inferred in the present study that on extrapolating the apparent volumes of strong electrolytes to zero volume fraction of water in solution, temperature-independent "water-free" ion volumes Φ_i' are obtained. These volumes correspond to the state in which the contact gap is shifted up to the very surface of ions, without changing its width $d_0 = 39 \pm 2$ pm. The volumes Φ_i' show additivity and acquire thus the properties of parameters which are applicable to calculation of the density of aqueous solutions of strong electrolytes as well as of their mixtures up to the highest possible concentrations. With Li^+ and Na^+ ions, the condition of temperature invariance of Φ_i' results in that the hydrate nucleus is not "naked" cation but a species MH_2O^+ analogous to H_3O^+ ion. This explains likely the different function of Na^+ and K^+ ions in biological systems (especially concerning their permeation through membranes). In the case of Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} ions, the "hard-body" centre of their hydrates is formed by hexaaqua-complexes.

In the previous work[1], on the basis of experimental data we have verified the model of hydration of ions in aqueous solutions which was based on two structurally different regions in contact: the radially packed sheath of H_2O molecules with the effective molar volume V_w' common to all the ions, and the region of surrounding free liquid water of molar volume V_w^0. In their contact surface, a zone of additional contact voids is formed, the volume contribution of which can be included into calculation as a contact gap of the effective width d_0. This width is determined exclusively by the configurational incompatibility of both structures and by the rigidity of both the former and the latter one[2-5], and thus, within the generally obtained accuracy, independent of concentration and temperature. According to this concept, the extrapolation of apparent molar volumes of strong electrolytes Φ to the hypothetical limit Φ' where the volume fraction of water in solution is $p_w = 0$, i.e. to the concentration c' defined by the expression $c'\Phi' = 1$, would lead to the temperature-independent values corresponding to the state in which contact gaps are shifted to the very surface of ions without changing the width d_0. Verification of this conclusion is presented in this work.

THEORETICAL

Based on the already reported model for the ions with spherical (or isometric quasi-spherical) symmetry of electrostatic field, the apparent volume of electrolyte extrapolated to a hypothetical "water-free" state in solution can be expressed by the relation

$$\Phi' = \sum_i \tfrac{4}{3}\pi N(r_i + d_0)^3 = \sum_i (V_i^{1/3} + 1.36d_0)^3 \tag{1}$$

(Φ', V_i in dm^3 mol^{-1}, d_0 in nm) where summation relates to all free ions in the electrolyte formula, $V_i = (4/3)\,\pi N r_i^3$ stands for the molar "hard-sphere" volumes of ions, r_i are their "hard-body" radii and N is Avogadro constant. If for the extrapolation just mentioned, Masson's[6] empirical linear dependence of Φ vs $\sqrt{c}$ is accepted for the whole concentration region, the condition that for $c = c'$, where $p_w = 0$, there has to be $c'\Phi' = 1$ and $\Phi = \Phi'$, allows to write Masson's equation in the following way:

$$\Phi = \Phi^0 + \left(\Phi' - \Phi^\circ\right)\left(\Phi'c\right)^{1/2} . \tag{2}$$

(Physical substantiation of the assumption about the validity of Masson's equation in the whole region of concentrations up to hypothetical "water-free" state is not object of this work). By inserting the expression (2) into the definition equation of the apparent molar volumes of the solute in solution[1]

$$\varrho = \varrho_0 + \left(M - \varrho_0\Phi\right)c \tag{3}$$

one obtains the expression for the density of solutions which is formally identical with the Root equation[7]

$$\varrho = \varrho_0 + Ac - Bc^{3/2} \tag{4}$$

with coefficients

$$A = M - \varrho_0\Phi^0 \tag{5}$$

$$B = \varrho_0(\Phi' - \Phi^0)\sqrt{\Phi'} \tag{6}$$

(ϱ, ϱ_0 in kg dm^{-3}, Φ in dm^3 mol^{-1}, c in mol dm^{-3}, the molar mass of the solute in kg mol^{-1}). Then, from A and B adjusted according to Eq. (4) to the experimental densities of solutions, the parameters Φ^0 and Φ' can be evaluated. As follows from Eq. (1), thus extrapolated "water-free" volumes of electrolytes should fulfil the condition of additivity of ionic Φ_i''s analogous to that long known and theoretically substantiated for the volumes Φ^0 extrapolated to $c = 0$.

The values of Φ_i' calculated with the use of Eq. (1) from r_i (resp. V_i) of monoatomic ions (and NH$_4^+$, ref.[8]) with several selected d_0's in the region around 40 pm (found[1]

independently as the average from data for diluted solutions) are presented in Table I. From the just described model it follows that these "water-free" volumes should change only little with temperature, essentially on the level of temperature dependence of crystallographic ionic radii or (taking into account also polyatomic ions and complexes) on the level of thermal expansion of solid substances, i.e. by one order of magnitude lower than is the expansion of voluminous structure of liquid water. Hence, Masson's lines should intersect at different temperatures in one point (in accordance to Eq. (1)) with coordinates c' and Φ' and located on the hyperbola $c\Phi = 1$.

If in aqueous solutions the ions of electrolyte form stable aqua-complexes with $n_{i,aq}$ H_2O ligands bonded to the central ion so firmly that they do not split on

TABLE I

Theoretical "water-free" volumes Φ'_i (cm^3 mol^{-1}) of ions, radii r_i (pm) and molar "hard-sphere" volumes V_i (cm_0 mol^{-1}) calculated for widths d_0 of the contact "gap" between 36 and 44 pm

Ion	$r_i{}^a$	V_i	Φ'_i for d_0(pm)				
			36	38	40	42	44
I^-	218	26·1	41·2	42·2	43·2	44·2	45·2
Br^-	196	19·0	31·4	32·2	33·1	33·9	34·8
Cl^-	181	14·9	25·7	26·4	27·1	27·9	28·6
F^-	134	6·2	12·4	12·8	13·3	13·7	14·2
NH_4^+	148	8·2	15·7	16·2	16·7	17·3	17·8
Cs^+	166	11·5	20·7	21·4	22·0	22·6	23·3
Rb^+	146	7·9	15·2	15·7	16·2	16·7	17·2
K^+	131	5·7	11·7	12·1	12·6	13·0	13·5
Na^+	96	2·2	5·8	6·1	6·3	6·6	6·9
Li^+	65	0·7	2·6	2·8	2·9	3·1	3·2
Ba^{2+}	136	6·4	12·8	13·3	13·7	14·2	14·7
Sr^{2+}	115	3·8	8·7	9·0	9·4	9·7	10·1
Ca^{2+}	100	2·5	6·3	6·6	6·9	7·2	7·5
Mg^{2+}	69	0·8	2·9	3·1	3·3	3·4	3·6
NaH_2O^+	152^b	8·8	16·7	17·2	17·8	18·3	18·9
LiH_2O^+	143^b	7·3	14·3	14·8	15·3	15·8	16·3
$Ba(H_2O)_6^{2+}$	293^b	63·4	89·6	91·2	92·9	94·6	96·2
$Sr(H_2O)_6^{2+}$	289^b	60·8	86·7	88·3	90·0	91·6	93·3
$Ca(H_2O)_6^{2+}$	287^b	59·5	84·8	86·4	88·0	89·6	91·2
$Mg(H_2O)_6^{2+}$	284^b	57·8	82·4	84·0	85·5	87·1	88·6

[a] Ref.[8]; [b] calculated from molar V_i values obtained as the sum of molar volumes of the centra ion and the ligands H_2O.

increasing concentration together with electrostatically bonded sheaths, the extrapolation from the region of low and medium concentrations (where aqua-complexes still maintain their structure) would be directed to the volume Φ' corresponding to the aqua-complexes, of course without regarding the water contained in these complexes, which is here considered as free according to Eq. (3), i.e. reduced by $n_{i,aq}V_w^0$. In order to obtain true Φ' of the electrolyte with aqua-complexes, on calculating the apparent volumes from the density of solutions according to Eq. (3), one has either to add the $n_{i,aq}$ multiple of molar mass of water M_w to M of the given electrolyte or — which is equivalent — to add the value of $n_{i,aq}M_w/\varrho_0 = n_{i,aq}V_w^0$ to the molar volumes calculated from Eq. (3) without the above correction.

The point of intersection of Masson's lines with the hyperbola of the "water-free" state $c\Phi = 1$ is thus shifted to the region of higher Φ's and lower concentrations c'. Similarly, the conclusion about the temperature invariance of Φ', too, is valid only for such concentrations c' at which the thermal dilatation of the aqua-complex itself as well as its thermal dissociation do not become significant. According to the results obtained, this assumption holds in most cases for temperatures up to $50-60°C$ and can serve there for determining $n_{i,aq}$. (As far as the calculation of densities of solutions from Eqs (4) to (6) is concerned, the deviations of $\Phi'_{i,aq}$ of aqua-complexes even above this temperature limits are so small that they do not affect the accuracy of values of ϱ which is frequently required in practice). Starting from Eq. (1), one gets for the so obtained $\Phi'_{i,aq}$'s

$$\Phi'_{i,aq} = [(V_i + n_{i,aq}V_w^{(c)})^{1/3} + 1\cdot36d_0]^3 , \tag{7}$$

where V_i is the molar crystallographic "hard-sphere" volume of the central ion and $V_w^{(c)}$ is the effective molar volume of H_2O ligands in the aqua-complex (both in dm^3 . mol^{-1}, d_0 in nm).

RESULTS

Conclusions were tested on the values of Φ' extrapolated from experimental densities of aqueous solutions either directly from the apparent molar volumes of electrolytes calculated by means of Eq. (3) from tabulated densities[9-15] for different concentrations, or with the use of Eqs (5) and (6) from the values of parameters A and B in the function (4) evaluated[15] from experimental densities at 20°C. Here we have disregarded such cases in which the calculated values of Φ^0 from Eq. (5) for $c = 0$ did not fit the already well verified and generally accepted condition of the additivity of ionic contributions. Tables II and III show that both extrapolation procedures lead to the same results within accuracy limits, i.e. with $\Delta\Phi'$ c. $\pm1\ cm^3\ mol^{-1}$ for 1,1-valent electrolytes and about ±2 to $3\ cm^3\ mol^{-1}$ for 2,1-valent ones (due to the several times higher slopes of their massonian lines). This results in both cases

in the uncertainty in determination of d_0 from Eq. (1) of c. ± 1 to 2 pm. With salts with bulky univalent ions (with r_i similar to van der Waals radius of H_2O molecule and higher), the calculated d_0's agree well within above accuracy limits with the mean value of d_0 equal to 40 pm which was found at $c = 1 \, mol \, dm^{-3}$ from the water transport on ions in dilute solutions[1]. This supports the assumption that the effective width d_0 of the layer of contact voids remains unchanged for all ions during the process of destruction of their electrostatically bonded sheaths on increasing concentration.

Significant differences, by far exceeding the limits of extrapolation inaccuracy, appear in d_0 values for the salts with small univalent ion Li^+ and Na^+ and with divalent cations Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}. If the same d_0 value (40 pm) resulting in average from the extrapolated "water-free" volumes of salts with bulky univalent cations is taken for the anions, the volume differences left-over for these cations become smaller than are their proper molar crystallographic volumes V_i; in most cases these volumes are even negative (Table IV). This can be explained by formation of the aqua-complexes that are so stable that they preserve the character of an

TABLE II

Width of the contact "gap", d_0 (pm), evaluated from experimental volumes Φ'_{20} ($cm^3 \, mol^{-1}$) extrapolated to $p_w = 0$, 20°C, 1,1-valent electrolytes

Salt	Φ'_{20}			d_0	Salt	Φ'_{20}			d_0
	a	b	aver.			a	b	aver.	
CsI	63·8	62·6	63·2	38	NaI	42·6	41·9	42·3	(28)
CsBr	54·5	54·2	54·4	39	NaBr	34·0	33·6	33·8	(29)
CsCl	48·5	49·2	48·9	40	NaCl	29·3	29·9	29·6	(32)
CsF	—	36·1	36·1	42	LiI	39·7	—[c]	39·7	(28)
RbI	57·0	59·8	58·4	39	LiBr	30·0	—[c]	30·0	(27)
RbBr	47·5	48·3	47·9	38	LiCl	24·9	—[c]	24·9	(28)
RbCl	42·9	43·7	43·3	40	Na(H₂O)I	59·2	58·7	59·0	38
RbF	30·0	(34)	30·0	41	Na(H₂O)Br	49·8	49·6	49·7	39
KI	52·6	52·9	52·8	36	Na(H₂O)Cl	44·5	45·1	44·8	40
KBr	43·1	45·8	44·5	38	Li(H₂O)I	56·9	—[c]	56·9	38
KCl	38·4	38·0	38·2	37	Li(H₂O)Br	47·0	—[c]	47·0	39
KF	25·2	26·3	25·8	40	Li(H₂O)Cl	41·0	—[c]	41·0	38
NH₄I	60·3	(54)	60·3	41	Salts with "naked" ions, aver.				38·9
NH₄Br	48·3	47·5	47·9	37	Salts with aqua-ions, aver.				38·7
NH₄Cl	43·7	43·4	43·6	40	2,1-electrolytes, Table III				39·8

[a] Extrapolated from Φ_{20} values of salts obtained from experimental densities, refs[9,10], using Eq. (3); [b] evaluated from A_{20}, B_{20}, ref.[15], using Eqs (5) and (6); [c] non-linear Φ–$c^{1/2}$ dependence, method b inapplicable.

integral particle up to the highest stages of destruction of the electrostatically bonded hydration sheath practically realizable by increasing the concentration.

The model just discussed makes it possible to solve this question on the basis of the hence deduced independent condition of temperature invariance of Φ', which is the most significant criterion of the adequacy of the model. This question was analyzed by using the values Φ' found for different temperatures again with the aid of both above-mentioned procedures. Examples of the application of the first procedure to electrolytes containing large univalent ions are shown in Fig. 1 for KI and in Fig. 2 for KCl. As seen, Masson's lines intersect within accuracy limits at different temperatures in one point which is located on the curve of the hypothetical "water--free" state of the solution. The same result has been obtained also for other similar salts. This condition is not, however, fulfilled by those salts which in the previous test based on crystallographic data, when no account was taken of the formation of aqua-complexes, yielded d_0 values far exceeding the limits of experimental inaccuracy. Extrapolation to the "water-free" state, as shown for NaCl in Fig. 2 (B),

TABLE III
Width of the contact "gap", d_0 (pm), evaluated from experimental volumes Φ'_{20} (cm^3 mol^{-1}) extrapolated to $p_w = 0$, 20°C, 2,1-valent electrolytes. Left: Cations taken as existing in solution without firmly bonded H_2O ligands; right: cations taken as aqua-complexes referred to in Table I

| Salt | $\Phi'_{20}{}^a$ | d_0 | Salt | Φ'_{20} | | | d_0 |
				a	b	aver.	
BaI_2	80·0	(23)	$Ba(H_2O)_6I_2$	181·0	180·3	180·7	41
$BaBr_2$	62·7	(23)	$Ba(H_2O)_6Br_2$	162·2	(156)	162·2	42
$BaCl_2$	50·0	(20)	$Ba(H_2O)_6Cl_2$	147·7	146·9	147·3	40
SrI_2	72·0	(18)	$Sr(H_2O)_6I_2$	174·0	173·4	173·7	39
$SrBr_2$	57·0	(20)	$Sr(H_2O)_6Br_2$	156·0	159·0	157·5	41
$SrCl_2$	48·0	(21)	$Sr(H_2O)_6Cl_2$	144·0	(157)	144·0	40
CaI_2	68·3	(16)	$Ca(H_2O)_6I_2$	169·7	174·7	172·2	39
$CaBr_2$	54·5	(20)	$Ca(H_2O)_6Br_2$	153·1	156·0	154·6	40
$CaCl_2$	45·3	(20)	$Ca(H_2O)_6Cl_2$	141·3	144·0^c	142·7	40
MgI_2	63·0	(12)	$Mg(H_2O)_6I_2$	165·2	166·8	166·0	37
$MgBr_2$	51·1	(18)	$Mg(H_2O)_6Br_2$	150·0	153·0	151·5	40
$MgCl_2$	42·0	(19)	$Mg(H_2O)_6Cl_2$	138·2	138·0	138·1	39

^{a} Extrapolated from Φ_{20} values (obtained from experimental densities) of salts refs[9,10], using Eq. (3); ^{b} evaluated from A_{20}, B_{20}, ref.[15], using Eqs (5) and (6); rem. to the left section of the Table: The extrapolation using constants A, B to very high concentrations necessary in method b in the case of cations taken as "naked" is rather unreliable here; ^{c} evaluated by method a from data Lyons P.A., Riley J. F.: J. Am. Chem. Soc. 76, 5216 (1954), quoted by ref.[14]; the A, B parameters from ref.[15] yield 153 cm^3 mol^{-1}, giving strongly deviating d_0.

for $MgCl_2$ in Fig. 3 (A), and for $CaCl_2$ in Fig. 4 (A), leads here at different temperatures to markedly different Φ values, the differences exceeding substantially the inaccuracy of extrapolation.

At the same time, Masson's lines for each of these salts intersect in one point which, however, is not situated on the hyperbola of "water-free" state. To shift this point to the hyperbola, in calculating Φ from Eq. (3) one needs for all temperatures to add one molar volume of free water $V_w^0 = M_w/\varrho_0$ (C in Fig. 2) to the results for Na^+ (and also Li^+) salts, and to add sixfold molar volume in the case of Mg^{2+} and Ca^{2+} (and also Sr^{2+} and Ba^{2+}) salts (B in Figs 3 and 4), i.e. to shift all experimental points along with the interpolated lines to Φ's increased by this difference. The value of Φ' read from the points of intersection of the straight lines with the curve of "water-free" state gives after this shifting the same d_0 as was found for the

TABLE IV

Extrapolated cationic volumes Φ'_+ ($cm^3 mol^{-1}$) calculated from the difference $\Phi'_{salt} - \Phi'_-$ ($cm^3 mol^{-1}$) with experimental values Φ'_{salt} from Tables II and III and with Φ'_- from Table I; Φ'_+ (theor.) are values calculated from "hard-sphere" volumes V_i of cations (Table I), using Eq. (7) with $d_0 = 40$ pm. Left section: Cations taken as existing in solution without firmly bonded H_2O ligands. Right section: Cations taken as aqua-complexes referred to in Table I

Salt	"Naked" ions		Aqua-complexes			
	Φ'_{salt}	Φ'_+	Φ'_{salt}	Φ'_+	Φ'_+(aver.)	Φ'_+(theor.)
NaI	42·3	−0·3	59·0	16		
NaBr	33·8	+0·7	49·7	17		
NaCl	29·6	+2·5	44·8	18	17	18
LiI	39·7	−3·5	56·9	14		
LiBr	30·0	−3·1	47·0	14		
LiCl	24·9	−2·2	41·0	14	14	15
BaI$_2$	80·0	−6·4	180·7	94		
BaBr$_2$	62·7	−3·5	162·2	96		
BaCl$_2$	50·0	−4·2	147·3	93	94	93
SrI$_2$	72·0	−14·4	173·7	87		
SrBr$_2$	57·0	−9·2	157·5	91		
SrCl$_2$	48·0	−6·2	144·0	90	90	90
CaI$_2$	68·3	−18·1	172·2	86		
CaBr$_2$	54·5	−11·7	154·6	88		
CaCl$_2$	45·3	−8·9	142·7	89	88	88
MgI$_2$	63·0	−23·4	166·0	80		
MgBr$_2$	51·1	−15·1	151·5	85		
MgCl$_2$	42·0	−12·2	138·1	84	83	85

other salts and acquires thus the temperature invariance corresponding to the proposed model. This demonstrates that with Li^+ and Na^+ ions we deal here with the stable monoaqua-complexes which are analogous to H^+ ion, whereas in the case of Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} ions we deal with hexaaqua-complexes, as already established for these ions from the crystallohydrates of their salts.

On the basis of these facts one can estimate the proper "hard-body" volumes of the complexes. LiH_2O^+ and NaH_2O^+ ions can be regarded as analogical to H_3O^+ ion, i.e. as the species, the centre of which is formed by the oxygen atom of van der Waals radius[8] (including both hydrogens) of around 138 pm (which gives $V_w^{(c)} = 6.6$ cm^3 mol^{-1}), the free electron pair of which is involved in bonding Li^+ ion with $V_i = 0.7$ cm^3 mol^{-1} resp. Na^+ ion with $V_i = 2.2$ cm^3 mol^{-1}. Therefore, the "hard-body" volume of the complex without contact voids between itself and the adjacent water is equal to 7.3 in the former case and to 8.8 cm^3 mol^{-1} in the latter. $M(H_2O)_6^{2+}$ complexes consist of the central M^{2+} ion surrounded symmetrically by six H_2O ligands, the effective coordination volume of which, $V_w^{(c)}$, (including contact voids on the contact of the central atom with these ligands) — based on data of
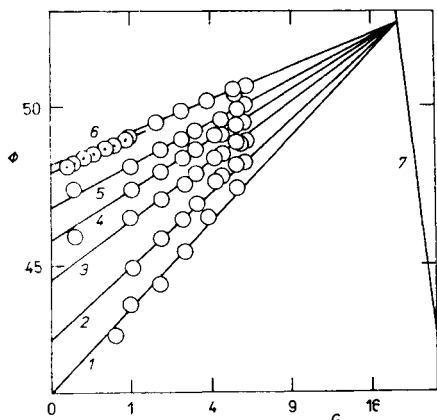

FIG. 1

Apparent molar volumes Φ (cm^3 mol^{-1}) of KI in dependence on concentration c (mol dm^{-3}) at temperatures 1 0, 2 10, 3 20, 4 30, 5 40, 6 55°C; calculated from Eq. (3), densities taken from refs[11,15] (o) and ref.[12] (⊙); 7 curve $c\Phi = 1\ 000$
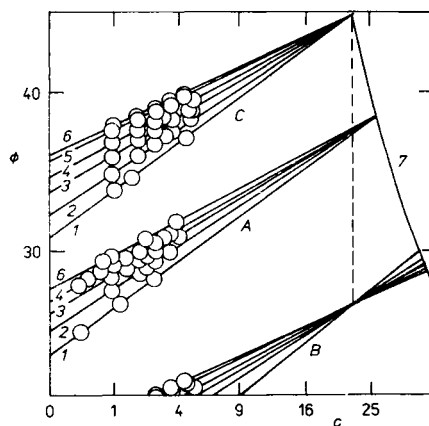
FIG. 2

Apparent molar volumes Φ (cm^3 mol^{-1}) in dependence on concentration c (mol dm^{-3}) at temperatures 1 0, 2 10, 3 20, 4 30, 5 45, 6 55°C; A KCl, B NaCl (part) with "naked" Na^+ ion, C NaCl with monoaqua-complex NaH_2O^+; system C identical with B, compared to which it is linearly shifted by $V_w^0 = 18$ cm^3 mol^{-1}; calculated according to Eq. (3), densities taken from refs[9-13,15]; curve 7 $c\Phi = 1\ 000$

different authors[8] — has the value of $9.5 \text{ cm}^3 \text{ mol}^{-1}$. In Tables II and III are presented d_0 values obtained with these volumes according to Eq. (1) from the volumes Φ' extrapolated from experimental data for the given aqua-complexes. As it is seen, the d_0 values are in average the same (in contradistinction to the d_0's calculated without allowance for H_2O ligands) as those for the electrolytes not forming stable aqua-complexes.

Besides of that, the right hand side of Table IV shows that the inclusion of H_2O ligands to the proper "hard-body" volume of cations leads to the disappearance of the strong dependence of their Φ_+'s on the anion, yielding the additivity of ion Φ_i''s which is only influenced by random scatter corresponding to the extrapolation inaccuracy. The average values of Φ'_+ of cations thus obtained agree within these limits with the values calculated theoretically on the basis of the model from "hard-body" volumes V_i of ions in Table I for $d_0 = 40 \text{ pm}$.

DISCUSSION

The conclusion about the existence of stable monoaqua-complexes of Na^+ is in agreement with the evidence of the presence of these stable monohydrates given
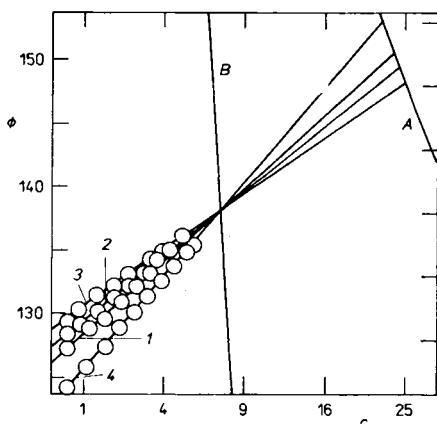

FIG. 3

Apparent molar volumes Φ $(\text{cm}^3 \text{ mol}^{-1})$ of $MgCl_2$ in dependence on concentration c (mol dm^{-3}) at temperatures *1* 0, *2* 10, *3* 40, *4* 100°C; curves $c\Phi = 1\,000$: A (scale at right hand side) Mg^{2+} ions do not form aqua-complexes, B they form stable hexa-aqua-complexes; calculated from Eq. (3), densities taken from ref.[15]
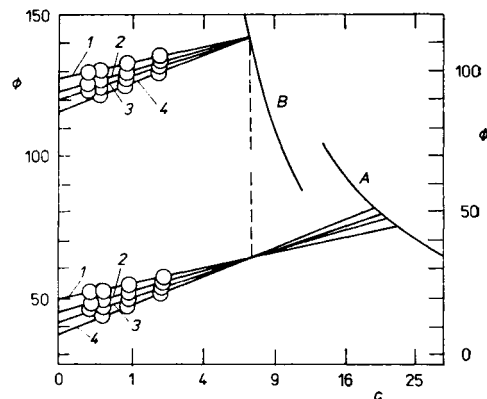
FIG. 4

Apparent molar volumes Φ $(\text{cm}^3 \text{ mol}^{-1})$ of $CaCl_2$ in dependence on concentration c (mol dm^{-3}) at temperature *1* 40, *2* 100, *3* 120, *4* 140°C; A, B as in Fig. 3; calculated from Eq. (3), densities taken from ref.[9]

in previous works[16] based on experimental densities of mixed solutions of two salts, starting from the assumption of hydration competition of both components (where the result is independent of both crystallographic data and the condition of temperature invariance of Φ' and can be thus taken as the independent argument).

The results demonstrate that the temperature invariance of Φ' in the case of aqua--complexes is not affected by thermal dilatation only in the region in which also thermal changes of the molar volume V_w^0 of free liquid water remain by far below the limits of extrapolation inaccuracies. It is the region where the values of Φ at low concentrations for all strong electrolytes increase with temperature (evidently due to the destruction of close-packed electrostatically bonded sheaths). At higher temperatures, this increase is overlapped by the fast decrease of ϱ_0, which according to Eq. (3) causes that the Φ volumes begin to decrease after attaining maximum (mostly around 50 to 80°C). For the aqua-complexes in this region, the invariance of extrapolated Φ''s becomes to be distrubed, their values begin to increase with increasing temperature, and the aqua-complexes undergo dilatation which is comparable to the thermal dilatation of liquid water. This effect can be compensated (thus maintaining the temperature invariance of Φ' of the aqua-complexes also at higher temperatures) by adding at all temperatures the term $n_{i,aq}V_w^0$ with one and the same value of V_w^0 taken from the region of lower temperatures to Φ calculated from Eq. (3). This is made in Figs 2 to 4 by using the average value of $V_w^0 = 18.1$ cm^3 . . mol^{-1} which is valid for the temperature interval from 0 up to 40°C. Even with the high number of added H_2O ligands, the so corrected values of the aqua-complexes maintain their temperature invariance up to 100°C (see the line **4** in Fig. 3) or even at higher temperatures, in which case the apparent volumes were calculated from densities of solutions which were determined under increased pressure (Fig. 4).

The existence of stable monoaqua-complexes of Li^+ and Na^+ (and also H^+, ref.[17]) ions explains why these ions — in contradistinction to the bulkier univalent cations and anions — are surrounded in solution by voluminous clusters of ice-like structure of water[1], obviously due to short-range forces, namely hydrogen bonds between H_2O ligands in the aqua-complex and the surrounding structure of liquid water. At small radii r_i these forces prevail (due to their higher power-type dependence on ionic radii) over electrostatic ion–dipole forces (which orient H_2O molecules to the radially close-packed ion hydration sheaths). As inferred from apparent volumes at $c = 1$ mol dm^{-3} (ref.[1]) and from conductance λ_i^0, the aqua-complexes of divalent cations with rare-gas configuration do not form such clusters and seem thus to be surrounded by normal close-packed, electrostatically bonded hydration sheaths. This can most likely be explained by that the directional effect of their twice higher charge on the H_2O dipoles prevails over the above-mentioned short--range effect of their H_2O ligands on the surrounding water.

The triad H^+, Li^+, and Na^+ represents thus in aqueous solutions a unique specific case in the whole periodic system which differentiates from the heavier

homologues of IA group by the marked limit of solubility of their salts (e.g. (H_3O). $.ClO_4 + NaClO_4$ vs $KClO_4$, or $(H_3O)_2PtCl_6 + Na_2PtCl_6$ vs K_2PtCl_6), by the ability of formation of well crystallizing alums, by formation of crystallohydrates ($NaOH.H_2O$ vs KOH, $Na_2CO_3.10\ H_2O$ vs K_2CO_3 or $Na_2SO_4.10\ H_2O$ vs K_2SO_4), by hygroscopy ($NaNO_3$ vs KNO_3) and — as mentioned earlier[16,17] — especially by their transport through cell membranes.

That Li^+ and Na^+ ions are capable of short-distance chemical bond formation with H_2O molecule (in contradistinction to K^+, Rb^+, and Cs^+ ions) is evidenced also by Shcherba and Sukhotin study[18] of IR spectra of water traces in dilute aceto-

TABLE V

Additivity test of the cationic and anionic "waterless" volumes Φ_i' ($cm^3\ mol^{-1}$) given together with the hence obtained d_0 values (pm), in brackets. Upper numbers: sums of the cationic and anionic Φ_i''s, lower numbers: extrapolated Φ'''s of salts obtained from experimental densities of aqueous solutions (Tables II and III)

Ion	I^- 42·0 (38)	Br^- 32·3 (38)	Cl^- 27·1 (40)	F^- 14·2 (44)
Cs^+	63·7	54·0	48·8	35·9
21·7(39)	63·2	54·4	48·9	36·1
Rb^+	58·0	48·3	43·1	30·2
16·0(39)	58·4	47·9	43·3	30·0
K^+	53·4	43·7	38·5	25·6
11·4(34)	52·8	44·5	38·2	25·8
NH_4^+	58·8	49·1	43·9	31·0
16·8(40)	60·3	47·9	43·6	—
$Na(H_2O)^+$	59·4	49·7	44·5	31·9
17·3(38)	59·0	49·7	44·8	—
$Li(H_2O)^+$	56·5	46·8	41·6	28·5
14·5(37)	56·9	47·0	41·0	—
$Ba(H_2O)_6^{2+}$	179·8	160·4	150·0	—
95·8(43)	180·7	162·2	147·3	
$Sr(H_2O)_6^{2+}$	174·8	155·4	144·9	—
90·8(41)	173·7	157·5	144·0	
$Ca(H_2O)_6^{2+}$	172·9	153·5	143·1	—
88·9(41)	172·2	154·6	142·7	
$Mg(H_2O)_6^{2+}$	168·3	148·9	138·5	—
84·3(38)	166·0	151·5	138·1	

nitrile solutions of lithium and sodium salts, where in addition to common v_1 and v_3 bands of non-associated water molecules, there are also bands at 3 483 cm^{-1} for Li$^+$ salts and at 3 443 cm^{-1} for Na$^+$ salts which are not present in the spectra of salts with bulkier univalent cations. The similarity of Li$^+$ with H$^+$ ion is documented also by the finding[19] of formation of relatively firm lithium bridges — C— O—L:— —O—C— in the alcoholates and similar organic compounds, detectable by vibrational spectroscopy, in analogy to hydrogen bonding in these systems. The reason is obviously the ability (documented at present from densities of solutions) of small univalent cations Li$^+$ and Na$^+$ (in analogy to H$^+$) to add free electron pair of the oxygen atom bonded in H$_2$O molecule or in other polar molecules, which ability is not displayed by the somewhat bulkier K$^+$ cations. Here may be the hidden roots of concepts such as Samoilov's assumption[20,21] about positive and negative hydration of ions in aqueous solutions or of the now widely accepted differentiation of ions according to their behavior in aqueous solution to "structure formers" and "structure breakers"[21−24].

Volumes Φ' are read at markedly different concentrations c' even in the case of the salts with the same cation or anion (cf. e.g. 15·9, 19·0, 26·3, and 39·7 mol dm^{-3} for K$^+$ in KHSO$_4$, KI, K$_2$SO$_4$, and KF at 18°C, resp.). Despite of this fact they show ionic additivity as corresponds to Eq. (1) and as was confirmed also in Table IV. This is illustrated also in Table V presenting Φ'_i values corrected by the method of minimation of sums of squared deviations. These are presented at ion symbols in the upper and left side of the table, along with the d_0 values calculated from them according to Eq. (7). The mean value of d_0 is 39 pm, and deviations from $d_0 = 40$ pm found from transport of water on ions[1] in dilute solutions lay within experimental errors and extrapolation inaccuracy. (The lower d_0 for K$^+$ ion can be explained from previous results by assuming that also in this case the ion occurs together with a small admixture of the aqua-complex in the concentration range from which volumes Φ' are extrapolated. As shown in Table IV, neglection of this admixture leads to smaller d_0 values. The presence of this admixture is indicated also by the sligthly decreased conductivity[1] of K$^+$ ion, 63·7 vs the average 66·9 S cm^{-1} mol^{-1} for Cs$^+$, Rb$^+$, Cl$^-$, Br$^-$, and I$^-$ ions. However, this circumstance does not affect the chemical and biochemical properties of K$^+$ ion).

The additivity of "water-free" volumes Φ'_i provides (along with the known additivity of the volumes Φ_i^0 extrapolated to $c = 0$) the possibility to replace the extensive set of molar volumes of salts at different concentrations used in calculation of the densities of aqueous solutions of electrolytes and their mixtures by the substantially smaller set of ion constants Φ_i^0 and Φ'_i, which on empirical basis was already shown in previous works[16,17]. It should be noted that both Masson's empirical rule on which the extrapolation of the volumes to "water-free" state is based and the experimentally found dependence of Φ^0 on temperature in infinitely diluted solutions are

not still physically substantiated. This is, however, a separate problem, which we have not intended to solve in the present work.

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