

ON THEORY OF IONIC VOLUMES IN DILUTE AQUEOUS SOLUTIONS OF ELECTROLYTES

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For purposes of calculation of densities of aqueous solutions of strong electrolytes and of their mixtures, theoretical substantiation of the formerly outlined empirical model of apparent molar ionic volumes Φ in solution is presented. According to the model, the hydration sheaths of ions consisting of radially close-packed H_2O molecules having effective molar volume V'_w , the same for all ions, are on their contact with the adjacent structure of liquid water surrounded by a layer of excess voids. This layer can be substituted in the model by a continuous "gap" of width d_0 , which again is common to all the ions and is temperature-independent. Using experimental Φ values of twenty-seven strong electrolytes together with the data on electrolytic transport of water on ions, $V'_w = 12 \text{ cm}^3 \text{ mol}^{-1}$ and $d^0 = (40 \pm 2) \text{ pm}$ were found for mono- and divalent ions in 1 mol dm^{-3} solutions, independently of ionic charges and crystallographic radii. The exception are small ions Li^+ and Na^+ , the volumes of which — if interpreted on the basis of the model — correspond to hydration sheaths formed by a cluster of voluminous ice-like structure. An anomaly in this respect has been encountered also in the case of NH_4^+ ion.

In previous works^{1,2} the model of apparent molar volumes Φ_i of ions in aqueous solutions was outlined. Its applicability to theoretical calculation of densities of solutions of strong electrolytes was demonstrated not only for one electrolyte³ but also for the mixture of electrolytes⁴. On the other hand, the model turned out to be applicable for determining chemical constitution of these solutions (formation of aqua^{2,4-7} and acido complexes⁵⁻⁷), particularly in high concentration range where the other methods fail. The present work attempts at forming theoretical basis for substantiation of model relations introduced. Experimental data needed for this purpose were taken from the literature⁸⁻¹².

Starting from the definition of the apparent molar volume Φ ($\text{dm}^3 \text{ mol}^{-1}$) of a solute in solution, we get for the density of its aqueous solution, ρ :

$$\rho = \rho_0 + (M - \rho_0 \Phi) c, \quad (1)$$

where ρ_0 (kg dm^{-3}) is the density of the free liquid water at the given temperature, M (kg mol^{-1}) is the molar mass of the solute (electrolyte), and c (mol dm^{-3}) is solute concentration. Using this relation, the apparent volumes of electrolytes can

be calculated from experimental densities of solutions:

$$\Phi = -[(\rho/\rho_0) - 1]/c + M/\rho_0. \quad (2)$$

In the theory of apparent molar ion volumes in aqueous solutions, there are two basic concepts. One (in various modifications) is based on Born model¹³ of a continuous increase of compression ("electrostriction") of water with decreasing distance from the electric centre of the ion due to its coulombic action on liquid water taken as a polarizable structureless continuum. The second theory, on the other hand, is based on Stokes and Robinson hypothesis¹⁴⁻¹⁶ that the assembly of water molecules closest to the ion is bound to the ion by ion-dipole forces to give a unit structurally different from the surrounding structure of liquid water. (For details see ref.¹⁷).

The large positive deviations of experimental Φ values from the above models were attempted to explain by the authors by introducing independent supplementary hypotheses. The attempt based on the idea of an expansion of ions on their passage from crystal to solution¹⁸⁻²⁰, however, has been disproved by X-ray diffraction measurements of the ion-H₂O distances in solution²¹⁻²³ as well as by calculations of the inner pressure in crystals²⁴. On the other hand, the argument against the hypothesis about existence of additional contact voids at the ion-water contact^{14-16, 25-29}, supported by the results of macroscopic experiments with jarring balls^{20,28} (strongly influenced by their mutual friction) are the high values of volume difference: Mukerjee³⁰ reports 80 per cent of the proper crystallographic volume of ions, Hepler²⁰ gives the values 85% for cations and up to 110% for anions, Couture and Laidler^{28,29} found the reverse difference between cations and anions by about one order of magnitude. The most acceptable seem to be those concepts which localize the above volume difference to greater distances from the centre of the ion, i.e. in the outer layer of its hydration sheath, assuming either an "arching" (Auswölbung in original paper³¹) of this layer or a formation of a "fuzzy", unordered transition zone of H₂O molecules between the close-packed structure of the hydration sheaths of ions and the surrounding voluminous structure of liquid water³². Both these hypotheses, however, are only qualitative.

THEORETICAL

The model proposed in the present work takes into account the following facts: 1) Taking plausible coefficient of the internal field (within layers of the radially oriented H₂O dipoles with fully suppressed orientation polarization, only little smaller than 1, e.g. 0.7 up to 0.8), the coulombic orientation energy of H₂O dipoles in ion sheaths exceeds the bonding energy of H₂O molecules in the structure of liquid water (which amounts^{33,34} to c. 40 kJ mol⁻¹) already at the distance of 300 up to 350 pm from

the electric centres for univalent ions, 420 up to 480 pm for divalent ones and from 520 up to 600 pm for trivalent ions at ambient temperatures of aqueous solutions. 2) Already small change in the distance within these values – by one order of magnitude smaller than is van der Waals radius of H_2O molecule – is enough to cause (at the known rigid structure of liquid water³⁴) a discontinual structural transformation. Hence, we have introduced the concept of a sharp interface between the radially close-packed structure, in which water has the same molar volume V'_w in the hydration sheaths of all ions, and the structure of surrounding liquid water with the molar volume V_w^0 . Taking into account the rigidity and incompatibility of both structures, one should suppose – for purely geometrical (temperature-independent) reasons – the existence of contact voids, which are additional to those already present in the interior. The volume contribution of these voids can be substituted in the model by a continuous gap of width d_0 which can be expected to be the same for all ions. In case of full rigidity of both structures and their inability to fit into each other, the limit of d_0 would amount to the radius of the given particles, i.e. 140 pm for water. At partial flexibility of one of them (here of the voluminous structure of surrounding liquid water common to all ions), this value would be smaller but again the same value can be taken for all ions, independently of concentration c . As the gap mentioned is localized in greater distance from the centre of the ion than its “hard-body” radius r_i , the observed volume differences between experiment and theory can be explained by using much smaller, from the physical point of view quite acceptable d_0 value as compared to that which results from localization of voids on the proper “surface” of the ions.

From definition of volume Φ_i as the molar volume left for ions in solution after subtracting all the water bound in their hydration sheaths taken as the free liquid component, $-n_i V_w^0$, from the volume effectively occupied by the ions together with their hydration sheaths in solution, $V'_i(\text{eff})$, it follows that

$$V'_i(\text{eff}) = \Phi_i + n_i V_w^0 \quad (3)$$

(n_i is the number of water molecules bound to the ion). In a similar way, the following expression is obtained for the molar “hard-body” volume of ions together with the above hydration sheaths, V'_i , with no additional contact voids included:

$$V'_i = V_i + n_i V'_w, \quad (4)$$

where $V_i = (4/3)\pi N r_i^3$ is the volume of “naked” ion, the proper crystallographic (respectively van-der-waalsian, for polyatomic ions) radius of which is r_i . Supposing that the electrostatic field of the given ion has a spherical symmetry, the radius of the whole hydrate inclusive additional contact voids, i.e. $r'_i(\text{eff})$, would – according to Eq. (4) – be equal to $(3/4\pi N)^{1/3} (V_i + n_i V'_w)^{1/3} + d_0$, whence we have, for the

effective volumes of ions in aqueous solution:

$$V_i'(\text{eff}) = [(V_i + n_i V_w')^{1/3} + (4\pi N/3)^{1/3} d_0]^3 \quad (5)$$

so that one obtains from Eq. (3) for the apparent volume of electrolyte Φ (Φ and V in $\text{dm}^3 \text{mol}^{-1}$ and d_0 in nm):

$$\Phi = \sum_i [(V_i + n_i V_w')^{1/3} + 1.36 d_0]^3 - \sum_i n_i V_w^0, \quad (6)$$

where the summation relates to all free ions in electrolyte formula in the given state of its dissociation in solution. (In the case of incomplete dissociation, for n_i and V_i the values corresponding to the dissociation degree should be taken.)

On increasing concentration c , the volume fraction of water in solution decreases and thus, according to MGW, also n_i values decrease. This according to Eq. (6) means that at $V_w' < V_w^0$ (as corresponds to the model) and constant d_0 , the apparent volume Φ increases. This finding can be, at least qualitatively, used to account for Masson empirical rule³⁵ of linear increase of Φ of strong electrolytes in aqueous solutions with $c^{1/2}$, which was experimentally proved to be valid up to the highest concentrations possible^{12,36,37}:

$$\Phi = \Phi^0 + kc^{1/2} \quad (7)$$

from which, by putting into Eq. (1), one obtains

$$\rho = \rho_0 + Ac - Bc^{3/2}, \quad (8)$$

which is Root equation³⁷ with the coefficients

$$A = M - \rho_0 \Phi^0 \quad (9)$$

$$B = k\rho_0 \quad (10)$$

the values of which can be determined experimentally from densities ρ measured at different concentrations c in using two-parameter adjustment to Eq. (8). From the so obtained coefficient A and Eq. (9), one can calculate the apparent volume of electrolyte Φ^0 extrapolated to $c = 0$.

If in aqueous solution the electrolyte forms stable aqua complexes with n_{aq} H_2O ligands bonded with significantly higher energies than those of water molecules in the electrostatically bound sheath, the present model allows us to conclude that the effective molar volume $V_w^{(e)}$ of these ligands will involve voids at contact with the sheath to give (since we deal here with two spherically close-packed structures)

the same value V'_w as has water in this sheath. Hence, in Eq. (6) total experimental values of n_i can be used, without separating n_{aq} and without distinguishing between $V_w^{(c)}$ and V'_w , up to the limit where the splitting-off of hydration sheaths on increasing concentration starts to expose the coordination sphere of the aqua complex to direct contacts with the adjacent structure of free water, i.e. only in extrapolation to $c = 0$ (or, in approximation, up to $c = 1 \text{ mol dm}^{-3}$).

RESULTS AND DISCUSSION

If in the interface between the hydration sheaths of ions and the structure of surrounding water there exists a zone of additional voids, this will be the weakest point in which the most frequent shifts of H_2O molecules bound in the hydration sheaths of ions against the molecules in the adjacent structure of liquid water will take place during migration of ions in the given solution. This makes it possible to determine experimentally n_i from electrolytic transport of water on ions. Experiments thus performed on non-selective diaphragms³⁸⁻⁴⁸ gave (after the reduction of results to $c = 1 \text{ mol dm}^{-3}$) n_i values summarized in Tables I and II for univalent and divalent ions, respectively.

The concept of the spherically close-packed hydration sheaths allows us to test independently these results. Assuming negligibly small compressibility as well as orientation polarizability of these hydration sheaths as compared to free liquid water, the total hydration number 7 was obtained from compressibility measurements on KCl solutions (1 mol dm^{-3})⁴⁹⁻⁵¹ and 6 from dielectric permittivity measurements^{52,53}; similar values resulted from entropy measurements on ions in solution⁵⁴. As an absolute rigidity of the sheaths cannot be expected in our model, the above hydration numbers of KCl thus represent rather the lower limit. On the other hand, the numbers obtained from the salting-out of non-electrolytes caused by the expulsion of their less polarizable molecules from the vicinity of ions by polar H_2O molecules (the action radius of which necessarily lies outside of the close-packed sheaths) will approach n_i values "from above". Salting-out data obtained from solubility⁵⁵ and cryoscopic⁵⁶ measurements yield for the number of moles of water inaccessible for molecules of N_2O (ref.⁵⁵) and pyrocatechol⁵⁶ in aqueous solution of KCl (1 mol dm^{-3}) the value of 8.7 and 8.6, respectively. The approximate mean value between both limits agrees well with Remy³⁸⁻⁴⁰ and Baborovský⁴¹⁻⁴⁸ sums of cationic and anionic water transport numbers for KCl (1 mol dm^{-3}) being 7 up to 9 at 20°C. In this electrolytic method of experimental determination of n_i , the results are affected to a different extent by electroosmotic entraining of water (depending on the method, especially on the membrane used) which grows with increasing dilution of the solution. However, the literature data on concentration limits under which this effect begins to play a significant role differ from each other by order of magnitude. On non-selective diaphragms⁵⁷, electroosmotic entraining

of water ceases to interfere only above $c = 1 \text{ mol dm}^{-3}$. The results reported by Rutgers and Hendriks⁵⁸ for selective ion exchange membranes and obtained with the use of heavy water detection at $c = 0.3 \text{ mol dm}^{-3}$ are markedly higher but preserve the proportionality to data reported by both previously mentioned authors³⁸⁻⁴⁸. For univalent ions, these data can be reduced to the 1 mol dm^{-3} level by using the coefficient 0.6 (see Table I). (It is worth mentioning that individual n_i values of ions undergo incessant statistical fluctuations; experimental data in Tables I and II thus represent statistical quantities).

TABLE I

Crystallographic radii r_i (pm), molar hard-sphere volumes V_i ($\text{cm}^3 \text{ mol}^{-1}$) and hydration numbers n_i of monoatomic univalent ions determined from water transport ($c_i = 1 \text{ mol dm}^{-3}$, 20°C)

Ion	r_i		V_i	n_i^b	n_i^c	n_i^d	$0.6n_i^e$	aver.
	limits ^a	aver.						
Li ⁺	60–70	65	0.7	12.6	13.0	13.5	—	13.0
Na ⁺	(90)–100	96	2.2	8.4	8.6	8.5	—	8.5
K ⁺	(122)–133	131	5.7	4.0	4.2	5.0	4.2	4.6
Rb ⁺	(140)–148	146	7.9	—	4.0	—	—	4.0
Cs ⁺	(161)–169	166	11.5	—	3.5	—	3.6	3.5
Cl ⁻	181–181	181	14.9	3.0	3.0	4.0	3.0	3.3
Br ⁻	195–196	196	19.0	2.2	2.0	3.0	3.0	2.5
I ⁻	216–220	218	26.1	3.7	3.5	2.0	—	(2.5)

^a Refs^{59,60}; ^b ref.³⁹; ^c ref.⁴⁰; ^d refs⁴¹⁻⁴⁸ (aver.); ^e ref.⁵⁸.

TABLE II

Crystallographic radii r_i (pm), molar hard-sphere volumes V_i ($\text{cm}^3 \text{ mol}^{-1}$), and hydration numbers n_i of monoatomic divalent ions determined from water transport ($c_i = 1 \text{ mol dm}^{-3}$, 20°C)

Ion	r_i^a (aver.)	V_i	n_i^b	$0.7n_i^c$	$0.4n_i^d$	aver.
Mg ²⁺	69	0.8	14	14	14	14
Ca ²⁺	100	2.5	12	12	12	12
Sr ²⁺	115	3.8	(8)	11	12	11.5
Ba ²⁺	136	6.4	(4)	(8)	11	11

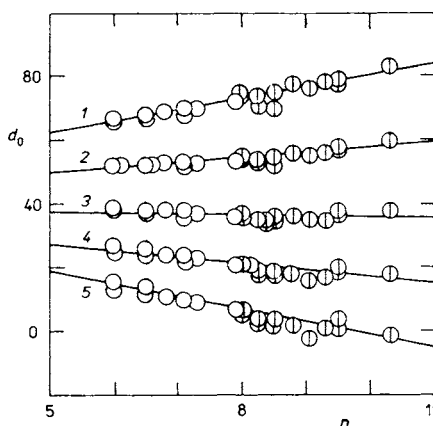
^a Ref.⁵⁹; ^b ref.⁴⁰; ^c refs⁴¹⁻⁴⁸ (averaged); ^d ref.⁵⁸.

In the case of divalent ions with rare-gas electron configuration (Table II), measurements with non-selective membranes are influenced by the effect of ion pairing, which increases with increasing ionic radii. These associates, too, penetrate through diaphragms and are markedly less hydrated compared to free M^{2+} ions. Results which are evidently affected by this effect (as judged from their comparison with other data) are given in Table II in brackets. Measurements by Baborovský⁴⁴⁻⁴⁸ made at concentration 0.5 mol dm^{-3} of the ion in question are affected by this association much less, but they are on the other hand influenced by electroosmosis. Comparison with non-associating Mg^{2+} and Ca^{2+} ions shows that to eliminate this effect, the use of the coefficient 0.7 appears as adequate. Measurements on selective membranes⁵⁸ at $c(M^{2+}) = 0.15 \text{ mol dm}^{-3}$ are obviously not affected by such association effects but the reduction coefficient 0.4 is required to eliminate the strong participation of the interfering accessory phenomena.

The average values of all results thus obtained (the last column of Table II) are in agreement with the sequence of crystallographic radii of ions (the left side of Table II). The uncertainty of ± 0.5 unit in determination of n_i (which according to Tables I and II seems to be roughly the true estimate) causes in Eq. (6) the error in calculated d_0 values of $\pm 1.5 \text{ pm}$, which is on the level of accuracy of the experimental determination of Φ at $c = 1 \text{ mol dm}^{-3}$. The present test of the model is valid within these limits. The d_0 values (pm) calculated according to Eq. (6) (using n_i and V_i from Tables I and II) from the apparent volumes $\Phi^{(1)}$ of strong electrolytes (taken – for purposes of consistence with experimental n_i values – for densities of solutions at $c = 1 \text{ mol dm}^{-3}$, 20°C) are represented graphically in Fig. 1. The volumes $\Phi^{(1)}$ were both interpolated from the Φ values calculated from solution densities (ref⁸⁻¹⁰, 20°C) for different c according to Eq. (2) and evaluated from

FIG. 1

Effective width d_0 (pm) of the layer of additional contact voids on the surface of hydration sheaths of ions, calculated from the apparent molar volumes $\Phi^{(1)}$ ($1.0 \text{ mol} \cdot \text{dm}^{-3}$, 20°C) of salts for different molar volumes of water, V'_w , in these hydration sheaths: 1 7.5; 2 10.0; 3 12.5; 4 15.0; 5 $17.5 \text{ cm}^3 \text{ mol}^{-1}$, in dependence on their experimental hydration numbers n_i ; ○ 1,1-valent electrolytes, ⊙ 2,1-valent electrolytes



coefficients A and B adjusted¹² to these densities by using regression function (8) together with Eqs (7) and (10), according to which

$$\Phi^{(1)} = \Phi^0 + B/\rho_0 = (M - A + B)/\rho_0, \quad (11)$$

where the term $(M - A)/\rho_0$ was substituted for Φ^0 . Calculation of d_0 from Eq. (6) was made with the use of the averages of both values thus obtained.

As it is seen from Fig. 1, within experimental errors, one can find one common value of $V'_w = 12 \text{ cm}^3 \text{ mol}^{-1}$, for which the contact void width d_0 is the same for all strong electrolytes investigated, independently of their hydration number, valence type and their ionic radii. This value agrees fairly well with the effective molar volume calculated for spherical particles having radius r_w around 140 pm and close-packed in "pole-to-pole" layers, where for $V'_w = 4Nr_w^3\sqrt{3}$ one obtains $11.4 \text{ cm}^3 \cdot \text{mol}^{-1}$. Deviations of the d_0 values calculated from experimental $\Phi^{(1)}$ and n_i data

TABLE III

The width d_0 (pm) of the contact "gap" between the hydration sheaths of ions and the adjacent structure of liquid water evaluated from Eq. (6) in using experimental $\Phi^{(1)}$ ($\text{cm}^3 \text{ mol}^{-1}$) volumes of salts and n_i values of ions ($c_i = 1 \text{ mol dm}^{-3}$, 20°C , $V'_w = 12 \text{ cm}^3 \text{ mol}^{-1}$)

Salt	$\sum n_i$	$\Phi^{(1)}$			d_0	Salt	$\sum n_i$	$\Phi^{(1)}$			d_0
		a	b	aver.				a	b	aver.	
CsI	6.0	58.7	58.7	58.7	42	BaI ₂	16.0	65.5	66.2	65.9	40
CsBr	6.0	47.5	47.5	47.5	41	BaBr ₂	16.0	47.5	48.0	47.8	41
CsCl	6.8	40.8	40.5	40.7	41	BaCl ₂	17.6	34.0	30.3	32.2	40
RbI	6.5	51.5	50.9	51.2	41	SrI ₂	16.5	58.0	57.0	57.5	39
RbBr	6.5	40.4	40.2	40.3	40	SrBr ₂	16.5	39.5	39.7	39.6	39
RbCl	7.3	33.6	33.2	33.4	40	SrCl ₂	18.1	24.0	22.6	23.3	39
KI	7.1	46.4	46.1	46.3	41	CaI ₂	17.0	55.5	54.5	55.0	38
KBr	7.1	35.2	34.7	35.0	39	CaBr ₂	17.0	37.5	37.1	37.3	40
KCl	7.9	28.5	28.4	28.5	40	CaCl ₂	18.6	24.0	20.3	22.2	39
NaI	11.0	35.9	35.7	35.8	(44)	MgI ₂	19.0	53.0	52.3	52.7	41
NaBr	11.0	24.8	24.6	24.7	(43)	MgBr ₂	19.0	32.5	31.8	32.2	41
NaCl	11.8	18.2	17.8	18.0	(44)	MgCl ₂	20.6	20.1	20.3	20.2	41
LiI	15.5	35.9	36.5	36.2	(53)	1,1-electrolytes, average					40.3
LiBr	15.5	25.8	26.7	26.3	(52)	2,1-electrolytes, average					39.9
LiCl	16.3	19.1	19.4	19.3	(53)						

^a Volumes interpolated to $c = 1 \text{ mol dm}^{-3}$ from volumes Φ evaluated from experimental densities⁸⁻¹¹, Eq. (2), for different concentrations at 20°C ; ^b values obtained from coefficients A , B (20°C , ref.¹²), using Eq. (11).

for $V'_w = 12 \text{ cm}^3 \text{ mol}^{-1}$ (Table III) from the mean $d_0 = 40 \text{ pm}$ lie within experimental errors. The higher values of the parameter d_0 for sodium and lithium salts speak for a more voluminous structure of their hydration sheaths in the sense of Frank and Wen³² "iceberg" clusters. For that reason, lithium and sodium salts have not been included in Fig. 1. If for the contact gap width d_0 of these ions the value $d_0 = 0$ is accepted (as corresponds to a coalescence of the cluster with the structure of surrounding free water), then from experimental $\Phi^{(1)}$ one obtains the molar volume of water V'_w of Li^+ ions close to the lower limit of $18 \text{ cm}^3 \text{ mol}^{-1}$ for H_2O molecules randomly bonded by hydrogen bonds. It seems likely that for both ions there is an equilibrium in solution between clusters and close-packed sheaths which is shifted from the former to the latter ones on increasing concentration (as indicated by deviations from Masson straight line toward lower Φ values, quite striking in the case of lithium salts at high concentrations¹).

TABLE IV

Ionic hydration numbers n_i ($c = 1 \text{ mol dm}^{-3}$, 20°C) evaluated from experimental volumes $\Phi_i^{(1)}$ ($\text{cm}^3 \text{ mol}^{-1}$) according to Eq. (5) and (3) with $V'_w = 12 \text{ cm}^3 \text{ mol}^{-1}$ and $d_0 = 40 \text{ pm}$, and the so obtained effective molar volumes $V'_i(\text{eff})$ ($\text{cm}^3 \text{ mol}^{-1}$), Eq. (3), together with the effective radii $r'_i(\text{eff})$ (pm) in confrontation with limiting ionic conductances λ_i^0 ($\text{S cm}^{-1} \text{ mol}^{-1}$, 18°C)

Ion	V_i	$\Phi_i^{(1)}$			n_i		$V'_i(\text{eff})$	$r'_i(\text{eff})$	λ_i^0/z_i
		a	b	aver.	calc.	exp.			
I^-	26.1	38 ^c	40 ^c	39	2.3	2.0–3.5	81.0	318	66.9
Br^-	19.0		29.3 ^d		2.5 ^d	2.0–3.0	74.3 ^e	309 ^e	68.3
Cl^-	14.9		22.1 ^d		3.3 ^d	3.0–4.0	81.5 ^e	319 ^e	66.3
Cs^+	11.5	18.2	18.6	18.4	3.0	3.5–3.6	72.4	307	66.8
Rb^+	7.9	11.0	11.3	11.2	4.1	4.0	84.1	322	66.3
K^+	5.7	5.7	6.4	6.1	5.0	4.0–5.0	95.5	336	63.7
NH_4^+	8.2	14.5	14.9	14.7	2.6	—	61.5	290	63.6
F^-	6.2	0 ^c	4 ^c	2 ^c	6.7	—	122.6	365	47.6
Na^+	2.2	-4.6	-4.1	-4.3	8.5 ^e	8.4–8.6	148.7 ^e	390 ^e	42.6
Li^+	0.7	-3.0	-2.8	-2.9	13 ^e	12.6–13.5	231.1 ^e	451 ^e	32.6
Ba^{2+}	6.4	-10.8	-12.0	-11.4	11.1	11	188.2	421	27.2
Sr^{2+}	3.8	-19.0	-20.9	-19.9	12.6	11–12	206.9	435	25.3
Ca^{2+}	2.5	-21.3	-22.0	-21.6	12.7	12	206.9	435	25.2
Mg^{2+}	0.8	-26.4	-24.0	-25.2	13.1	14	210.6	438	22.3

^a Evaluated from experimental $\Phi^{(1)}$ (MBr), Table III; ^b evaluated from $\Phi^{(1)}$ (MCl) values; ^c evaluated from experimental $\Phi^{(1)}$ (MX), using cationic $\Phi_i^{(1)}$ values; ^d evaluated from experimental n_i values Table I, using Eq. (6); ^e evaluated from experimental n_i values ($c = 1 \text{ mol dm}^{-3}$, 20°C), using Eq. (3).

The above d_0 and V_w' values make it possible to calculate for ions for which experimental n_i values are known with minimal uncertainty (e.g. Cl^- and Br^- anions) their individual apparent molar volumes Φ_i in solution on the basis of Eqs (3) and (5), and by subtracting these values from experimental Φ data to obtain thus the Φ_i values for counter-ions. By using the latter data the hydration numbers n_i of these counter-ions can be calculated backwards from Eqs (3) and (5) again. The so obtained results for $c = 1 \text{ mol dm}^{-3}$ are presented in Table IV, along with the calculated $V_i'(\text{eff})$ and $r_i'(\text{eff})$. A condition for such a calculation is that at the given concentration, deviations from the additivity of Φ_i of ions (which exactly holds only for Φ_i^0 in infinite dilution) do not yet play a significant role. This additivity test is shown in Table V. The standard deviation of $\pm 0.6 \text{ cm}^3 \text{ mol}^{-1}$ is fully within the accuracy of measurements and the individual differences are randomly distributed. The so

TABLE V

Additivity test of ionic $\Phi_i^{(1)}$ from Table IV ($\text{cm}^3 \text{ mol}^{-1}$). Upper numbers: sums of cationic and anionic $\Phi_i^{(1)}$ values, lower numbers: mean experimental $\Phi_i^{(1)}$ values of electrolytes from Table III (1 mol dm^{-3} , 20°C)

Ion	I^- 39.0	Δ	Br^- 29.3	Δ	Cl^- 22.1	Δ
Cs^+	57.4		47.7		40.5	
18.4	58.7	+1.3	47.5	-0.2	40.7	+0.2
Rb^+	50.2		40.5		33.3	
11.2	51.2	+1.0	40.3	-0.2	33.4	+0.1
K^+	45.1		35.4		28.2	
6.1	46.3	+1.2	35.0	-0.4	28.5	+0.3
Na^+	34.7		25.0		17.8	
-4.3	35.8	+1.1	24.7	-0.3	18.0	+0.2
Li^+	36.1		26.4		19.2	
-2.9	36.2	+0.1	26.3	-0.1	19.3	+0.1
Ba^{2+}	66.4		47.0		32.6	
-11.6	65.9	-0.5	47.8	+0.8	32.2	-0.4
Sr^{2+}	58.1		38.7		24.3	
-19.9	57.5	-0.6	39.6	+0.9	23.3	-1.0
Ca^{2+}	56.4		37.0		22.6	
-21.6	55.0	-1.4	37.3	+0.3	22.2	-0.4
Mg^{2+}	52.8		33.4		19.0	
-25.2	52.7	-0.1	32.2	-1.2	20.2	+1.2

obtained $r'_i(\text{eff})$ data correlate well with the limit molar ion conductances. λ_i^0 (18°C), reduced to the same tractive force in the external electrostatic field, i.e. to λ_i^0/z_i , in agreement with Stokes law. We have intentionally chosen the correlation of $r'_i(\text{eff})$ at $c = 1 \text{ mol dm}^{-3}$ with λ_i^0 at $c = 0$ and not the correlations of both quantities at the same concentration, since – as already mentioned – below $c = 1 \text{ mol dm}^{-3}$ the electroosmotically conditioned uncertainty in experimental transport n_i and thus also $r'_i(\text{eff})$ steeply increases (and other methods are here inapplicable because of their low sensitivity) and, at the same time, the molar conductance fastly decreases on going from $c = 0$ to $c = 1 \text{ mol dm}^{-3}$ (for 1,1-valent electrolytes by 30 up to 40 per cent, for polyvalent ions by one-half or even more) as the result of retarding effect of neighbouring counter-ions which has nothing in common with the Stokes radii of their hydration sheaths. The decrease of the number of H_2O molecules in these sheaths between $c = 0$ and $c = 1 \text{ mol dm}^{-3}$ can exert significant effect only for 1,2-valent electrolytes, judging from the high slope of their Masson straight lines². This would explain relatively low conductances of divalent cations (Table IV) as the result of the significant increase of their hydration radii $r'_i(\text{eff})$ between $c = 1 \text{ mol dm}^{-3}$, where their hydration numbers n_i were measured, and infinitely diluted solutions, to which the λ_i^0 values are extrapolated.

Of the fair degree of correlation of conductances λ_i^0 with radii $r'_i(\text{eff})$ of the spherical domains which ions effectively occupy in aqueous solution according to our model, NH_4^+ ion represents a significant deviation. Using the value $r_i = 148 \text{ pm}$ (ref.⁵⁹) we obtain, with $d_0 = 40 \text{ pm}$ and $V'_w = 12 \text{ cm}^3 \text{ mol}^{-1}$, a too low n_i value (2.6) and the effective radius too small (290 pm), i.e. by 15 per cent smaller than found for K^+ ion (336 pm) with which NH_4^+ ion has approximately the same molar conductance. This might indicate that in dilute solutions the hydration sheath of NH_4^+ ion is more voluminous and contains more H_2O molecules than are obtained from its experimental $\Phi_i^{(1)}$ in using Eqs (3) and (5) with the same d_0 and V'_w as for the other ions. One might suggest here the existence of weak hydrogen bonding to four H_2O molecules in tetrahedral configuration, similarly to the structure of liquid water, with the molar volume corresponding to this state. With $\Phi_i^{(1)} = 14.7 \text{ cm}^3 \cdot \text{mol}^{-1}$ (Table IV) and $n_i = 4$, from Eq. (3) one obtains for NH_4^+ ion the effective volume of the hydrate $V'_i(\text{eff}) = 87 \text{ cm}^3 \text{ mol}^{-1}$ and the radius $r'_i(\text{eff}) = 326 \text{ pm}$, only by 3 per cent lower than that of K^+ ion, with the contact gap on the interface with surrounding water reduced according to Eq. (6) to $d_0 = 8$ up to 10 pm, which is the difference between van der Waals radii of NH_4^+ ions and H_2O molecules, in accordance with the "electron isostery" of both these particles. This seems to be a similar case as with Na^+ and Li^+ ions, however, with the reserve that the nature of the bonds between the tetrahydrate of NH_4^+ and the adjacent water structure (as well as the hence arising answer to increased concentrations) might be different – as the result of much lower energies of the $\text{NH}\cdots\text{OH}_2$ hydrogen bonds.

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