

ON CHEMICAL FORM OF  $\text{Na}^+$  ION IN AQUEOUS SOLUTIONS

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*Dedicated to Professor J. Klikorka on the occasion of his 60th birthday.*

Experimental densities of mixed aqueous solutions of sodium and potassium salts have been compared with the densities calculated for various alternative models to show that  $\text{Na}^+$  ion (in contrast to bulkier cations  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ) is present as a  $\text{NaH}_2\text{O}^+$  particle analogous to hydroxonium ion  $\text{H}_3\text{O}^+$ . The experimental data also suggest that apparent molar volumes of ions in aqueous solutions depend on the degree of "filling" of the solution with the ion volumes, or otherwise, on volume fraction of the water left in the solution for formation of electrostatically bound hydration sheaths of the ions. The observed increase of apparent volumes of electrolytes with their concentration is due to degradation of these close-packed hydration sheaths with decreasing proportion of water in the system.

So far little is known about bonding interaction of alkali metal ions with water in aqueous solutions. X-Ray studies<sup>1-3</sup> of aqueous solutions of lithium and sodium salts showed diffraction lines which agreed well with the internuclear distances  $\text{Me}^+-\text{O}$  calculated as the sum of crystallographical radii of  $\text{Me}^+$  cations and water molecules (or the van der Waals radius 140 pm for bivalent oxygen atom), but therefrom it cannot be decided whether this is a simple ion-dipole electrostatic interaction with the dipoles of  $\text{H}_2\text{O}$  molecules oriented at radial direction in the field of the cation, or a chemical bond  $\text{Me}-\text{OH}_2$  with the metal cation sharing one of the two non-bonding orbitals of oxygen atom.

Out of the I. group ions only the  $\text{H}_3\text{O}^+$  cation could be proved (by the method of vibration spectra)<sup>4</sup> to involve such chemical bond in aqueous solutions. By means of hydrogen bonds with neighbouring water molecules, this particle is incorporated in structure of liquid water with formation of bulky clusters whose existence was also confirmed by molar volumes of strong acids in aqueous solutions<sup>5,6</sup>. Besides this case, vibration modes of  $\text{H}_2\text{O}-\text{Me}$  bonds were only found in Raman spectra of polyvalent ions with  $d^{10}$  electron configuration (cations of B metals according to Phillips-Williams classification), *e.g.* with Zn (ref.<sup>7</sup>) where the bond contains an appreciable covalent share thanks to dative participation of  $d$  orbitals of the central ion. However, the high degree of ionic character of the  $\text{H}_2\text{O}-\text{Me}^+$  bonds which must be expected with univalent cations possessing rare-gas electron configuration makes it impossible for the present experimental techniques (even with the use of laser sources) to prove similarly the chemical bond between water molecules and cations of alkali metals, even if such were present in solution.

Our earlier communication<sup>8</sup> showed that the necessary information can be obtained from the apparent molar volumes of electrolytes in solution,  $\Phi$ , defined as the volume left in the solution per 1 mol of the electrolyte after subtraction of volume of all the involved water taken as pure

liquid component. It was shown that the increase of apparent ion volumes with increasing concentration, described by the Masson empirical rule<sup>9</sup> (linear dependence on square root of concentration  $c$ ), depends on degree of space filling of the solution with the apparent ion volumes. On this basis the term was formulated of "anhydrous" apparent volume  $\Phi'$  by linear extrapolation (in the Masson's square-root coordinates) to hypothetical state with  $c\Phi = 1$  and the apparent volume identical with the real volume of ions occupied in the solution, because here the item of solvent contraction involved in the  $\Phi$  volumes decreases to zero.

The values  $\Phi'$  extrapolated in this way were shown<sup>8</sup> to exhibit (in solutions containing a single electrolyte) additivity of ionic increments similar to that found for the apparent volumes  $\Phi^0$  extrapolated to infinitely diluted solution. Moreover, the  $\Phi'$  volumes were shown to be simply related to crystallographical radii of the ions, being temperature independent within experimental error in a broad temperature range.

If, in addition to the usual outer electrostatically bound hydration sheath, the ion also has  $n$  water molecules bound in different way (these water molecules form with the ion a close unit and are exempted from the dehydration process which controls the electrostatically bound ion sheath within the concentration range of validity of the Masson rule, *i.e.* up to 5–10 mol dm<sup>-3</sup> when the solution still contains free water between the hydration sheaths), the obtained extrapolated  $\Phi'$  values are loaded with residual contraction corresponding to this bonding of water in aquo complex. This fact disturbs both the additivity of ionic increments in  $\Phi'$  and the temperature independence of the  $\Phi'$  volumes and their simple relation to crystallographic parameters of the ions. To restore validity of all these relations, the water volume subtracted from the solution volume when determining apparent volume of the electrolyte must be reduced by the term  $cnV_0$  corresponding to the water bound in aquo complex, and so the Masson's straight line of apparent molar volumes of the electrolyte is shifted upwards to a parallel position at the distance  $nV_0$ , whereby point of its intersection with the hyperbola of anhydrous state  $c\Phi = 1$  is shifted to lower  $c$  values; the solution is filled with the ion volumes sooner than it would happen in the absence of the aquo complexes.

On this basis the paper<sup>8</sup> investigates formation of stable hydrates of ions of alkali metals both according to the criterion of additivity of ionic increments and according to that of temperature invariance of  $\Phi'$  and, moreover, by confrontation of the  $\Phi'$  values with crystallographic parameters of the participating particles. All the three independent ways lead to the same conclusion that bulky univalent monatomic ions  $\text{I}^-$ ,  $\text{Br}^-$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{Cs}^+$ ,  $\text{Rb}^+$ ,  $\text{K}^+$  with radii above 0.1 nm only possess (in aqueous solutions of all concentrations) a degradable, electrostatically bound hydration sheath, whereas the small ions  $\text{Na}^+$  and  $\text{Li}^+$  exist here as firm monohydrates  $\text{Na}(\text{H}_2\text{O})^+$  and  $\text{Li}(\text{H}_2\text{O})^+$  resembling in composition (and, perhaps, in structure, too) the  $\text{H}_3\text{O}^+$  ion for whose analogues they can be considered. This water-ion bond also makes itself felt by diminished contraction in dilute solution which suggests that the hydration sheaths of these monoaquo complexes have not the close-packed radial structure similar to that of the said bulkier univalent ions with noble gas configuration, their water occupying greater molar volume due obviously to incorporation of the complex by hydrogen bonds into voluminous "ice-like" structure of the liquid water which is thereby stabilized and does not undergo destruction to such extent as in the field of other ions<sup>10</sup>.

All these findings, however, are restricted to one-electrolyte solutions. Our previous report<sup>11</sup> gives — on the described model basis — derivation of relations for calculation of density of solutions of electrolytes from the individual constants of the participating ions (their apparent volumes  $\Phi_i^0$ ,  $\Phi_i'$  and molar masses  $M_i$ ). Up to high concentrations (50% or even 60% w/w in the case of very soluble electrolytes), confrontation with experimental densities confirmed that apparent molar volumes of ions really depend on space filling of the solution with ions rather than on their

concentration  $c$  or ionic strength  $I$  of the solution, which was presumed by Rosenfeld and Redlich<sup>12</sup>, Wirtz<sup>13</sup> and others. The apparent volume of an ion increases with concentration  $c$  in combination with a bulky counter-ion (e.g.  $\Phi_i$  of cations in combination with  $I^-$  or  $ClO_4^-$  ions) much more steeply than that in the combination with a small counter-ion ( $Cl^-$ ). At a given concentration or ionic strength the apparent volume of the same ion combined with various counter-ions has various values, and, on the contrary, the same volumes are assumed in these cases at different concentrations and at different values of ionic strength which correspond — for different counter-ions — to the same degree of space filling with the ion volumes.

Thereby a way was opened to a further independent test of the mentioned findings on  $Na^+$  ion in aqueous solutions, much more conclusive than the previous ones — for detection of non-coulombic bond of water to  $Na^+$  ion from densities of aqueous mixed solutions containing a sodium salt in binary combinations with additions of other salts (of different proper molar volume, at various concentrations and at various mutual molar ratios). These problems are dealt with in the present communication.

### THEORETICAL

The method is based on the idea that, according to the model described, any salt will (in the case its ions form aquo complexes in the solution, and its apparent volume is limited — on filling the solution — by the value  $\Phi'$  corresponding to these bulky aquo complexes) fill the solution at a given concentration more than it would do, if volume of its ions were limited by the value  $\Phi'$  for anhydrous ions, and, therefore, it will increase apparent volume of the other added salt more strongly at the same concentrations of the two salts. This fact will make itself felt then in different values of density  $\rho$  calculated for such mixed solutions according to the two said cases. Experimental densities of the mixed solutions can differentiate between the two alternatives, and, at the same time, they can even more exactly differentiate between the described model of apparent ion volumes based on the idea of space "filling" of the solution and the models presuming dependence of the apparent ion volumes on total molar concentration of the solution or on its ionic strength. In the last cases, formation of aquo complexes should have no effect on density of the mixed solution, because it changes neither its concentration nor ionic strength; it only changes the space filling, especially so at higher concentrations, which, however, would have no effect — according to these models — on apparent volumes of the components and, hence, on the resulting density of the solution.

In our previous report<sup>11</sup> functional dependence of density  $\rho$  of a single-electrolyte solution on parameters of the involved ions was derived in the form:

$$\rho = \rho_0 + c \sum_i v_i a_i - c^{3/2} \sum_i v_i b_i \left( \sum_i v_i \Phi_i' \right)^{1/2}, \quad (1)$$

where constant ion parameters were introduced

$$a_i = M_i - \rho_0 \Phi_i^0 \quad (2)$$

$$b_i = \varrho_0(\Phi'_i - \Phi_i^0) \quad (3)$$

with the indexes  $i$  relating to the participating ionic species and index 0 for solvent (water) in the state of pure liquid at the given temperature.

Equation (1) conforms to semi-cubic correlation equation expressing relation between density of solutions of a single strong electrolyte and its concentration

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

which was derived by Root<sup>14</sup> from the Masson's rule. It gives physical interpretation of the parameters  $A$ ,  $B$  and also enables an easy transition to mixtures of electrolytes. The whole mixture can simply be considered to be a single electrolyte of an average composition and concentration  $c$  equal to sum of concentrations of the components, and the stoichiometric coefficients  $v_i$  will then express relative population of all participating ions in 1 mol of the mixture; this means that the products  $cv_i$  will give directly the concentrations  $c_i$  of each participating kind of ions. Equation (1) thus changes into the relation

$$\varrho = \varrho_0 + \sum_i c_i a_i - \sum_i c_i b_i (\sum_i c_i \Phi_i')^{1/2} \quad (5)$$

which applies generally to any mixed solution of strong electrolytes. (Of course, the condition is that additivity of apparent volumes of ions in the mixed solution must be maintained to the same extent as in each solution of the individual components; but as far as the ions form no associates or complexes, there is no theoretical reason to doubt fulfilment of this condition.)

If ions of each component are united in one group with molar concentrations  $c_i$  and parameters  $A_i = v_i^+ a_i^+ + v_i^- a_i^-$ ,  $\Phi_i' = v_i^+ \Phi_i'^+ + v_i^- \Phi_i'^-$ , and, hence,  $B_i = (v_i^+ b_i^+ + v_i^- b_i^-) \Phi_i'^{1/2}$ , Eq. (5) for the case of two strong electrolytes is transformed into

$$\varrho = \varrho_0 + A_1 c_1 + A_2 c_2 - (B_1 c_1 + B_2 c_2 q^{-1/2})(c_1 + c_2 q)^{1/2} \quad (6)$$

with the parameters  $A$ ,  $B$  determined from the correlation Eq. (4) by empirical adjusting to experimental densities of solutions of pure individual components and with a newly introduced parameter

$$q = \Phi_2'/\Phi_1' = \varphi_2'/\varphi_1', \quad (7)$$

where the constants  $\varphi$  ( $\text{kg mol}^{-1}$ ) replaced the products  $\varrho_0 \Phi$  in Eqs (2) and (3). For solutions of a single strong electrolyte the last equations change to Eqs (8) and (9)

after the above-given recalculation for the characteristic constants  $A$ ,  $B$  of the present electrolytes.

$$A_i = M_i - \varphi_i^0 \quad (8)$$

$$B_i = (\varphi'_i - \varphi_i^0)(\varphi'_i/\rho_0)^{1/2} \quad (9)$$

Equation (8) can be used to evaluate its parameter  $\varphi_i^0$  from the values of  $A_i$  parameters adjusted empirically to experimental densities of solutions of the individual components according to Eq (4); introduction of  $\varphi_i^0$  into Eq. (9) and subsequent iteration procedure allow to determine its  $\varphi'_i$  parameter values of each component from the empirically adjusted  $B_i$  parameter. In this way we obtain all the constants necessary for theoretical calculation of densities of mixed solutions of strong electrolytes by Eq. (6) with the parameter  $q$  calculated from Eq. (7) and on the condition that the apparent molar volumes of ions depend on degree of filling of the solution by apparent volumes of all the present ions.

In the case of existence of aquo complexes of one of the two components it is necessary to add mass of the bound water molecules to the respective molecular mass  $M_i$  in Eq. (8); the obtained increased  $\varphi_i^0$  value is then introduced into Eq. (9) for calculation of the  $\varphi'_i$  parameter whose value is thus changed, which (according to Eq. (7)) also means a change of the  $q$  parameter in Eq. (6) from  $q_\varphi$  to  $q_\varphi^*$ . The presumption that the apparent volumes of ions depend of volume filling of the solution results thus (in the case of formation of aquo complexes) in changed theoretical densities of mixed solution of strong electrolytes, which is independent of any model ideas about relation of the  $\varphi'_i$  constants to crystallographical parameters of the ions, their temperature dependence *etc.* In this respect the method differs from and is more conclusive than all the previous ones.

The presumption by Redlich<sup>12</sup> and Wirtz<sup>13</sup> that the apparent volumes of ions in aqueous solutions are a function of ionic strength  $I$  leads — by the same procedure — to an equation formally identical with Eq. (6), the difference being that the  $q$  parameter has the value

$$q_1 = w_2/w_1, \quad (10)$$

where the coefficients  $q = I/c = \frac{1}{2}(v_+z_+^2 + v_-z_-^2)$  represent a transformation factor between molar concentrations of components and their contributions to ionic strength  $I$  of the solution. As already stated, in this case formation of aquo complex should have no effect on the resulting density.

The  $q$  constant, respecting physical character of concentration dependence of apparent volumes of ions (within the range of validity of the Masson's rule), only affects — as shown by Eq. (6) — the semicubic term in density of mixed solutions of strong electrolytes. The linear members remain unaffected by  $q$  and express the

contribution to density of solution which would be brought by the dissolved components in the case their apparent volumes were not changed with concentration and maintained under all conditions the values  $\Phi_i^0$  which they exhibit in infinitely diluted solution. Thus the negative semicubic term corrects the result with respect to the changes of  $\Phi_i$  caused by changes in composition and concentration of the solution. Therefore, on the basis of values of this semicubic term only it is possible to decide the question of adequacy of the considered three models: (a) the apparent volumes of ions  $\Phi_i$  depend on ionic strength  $I$  of the solution ( $q = q_1$ ); (b)  $\Phi_i$  depend on volume filling of the solution, "anhydrous"  $\text{Na}^+$  ion, *i.e.* with only electrostatically bound hydration sheath ( $q = q_\Phi$ ); (c) the same as (b), but  $\text{Na}^+$  ion as mono-aquo complex as an integer central particle to which the electrostatically bound hydration sheath is connected ( $q = q_\Phi^*$ ). Thus resolving power of the method will depend on sensitivity of the semicubic term (denoted as  $y$ ) to changes of the  $q$  parameter. From Eq. (6) it follows

$$\partial y / \partial q = \frac{1}{2}(B_1 - B_2 q^{-3/2})(c_1 + c_2 q)^{-1/2} c_1 c_2, \quad (11)$$

where the factor  $c_1 c_2$  indicates that the resolving power depends on simultaneous presence of the both electrolytes. If concentration of any of them equals to zero, all the three models give the same results for the density  $\rho$  irrespective of the value  $q$ . Thus measured densities of solutions of a single component cannot differentiate between the models in this way.

According to Eq. (11) the highest sensitivity is reached about the state when each of the two components contributes with the same value to the semicubic term, which is fulfilled for electrolytes of the same valence type at  $c_1 = c_2 = c/2$  and for electrolytes of different valence types at about the state when total ionic strength  $I$  of the solution is distributed equally between the two components. In such case we get for the semicubic term the expression

$$y = (I/2)^{3/2} (B_1 w_1^{-3/2} + B_2 w_2^{-3/2} Q^{-1/2})(1 + Q)^{1/2}, \quad (12)$$

where the introduced parameter  $Q = q w_1 / w_2$  has the value of 1 according to Eq. (10) in the case of validity of the model (a), whereas it is generally different from 1 for the two other models.

Equation (12) makes it possible to assess the highest theoretically possible differences between the said three alternatives (a, b, c) for particular combinations of salt pairs whose  $B$  parameters have been determined by measurements of densities of solutions of the individual components (and the  $\Phi'$  parameters have been calculated from empirical values of the  $A$  and  $B$  parameters in the above-mentioned way), and therefrom to judge whether experimental accuracy of determination of densities of the mixed solutions will enable to decide between them.

## RESULTS AND DISCUSSION

Suitable for determination of chemical hydration of  $\text{Na}^+$  ion in aqueous solutions by the method described is combination of sodium and potassium salts with total concentration not too high (up to about  $1 \text{ mol dm}^{-3}$ ) which allows to presume with certainty that no direct interactions between ions (association *etc.*) occur to a distinct extent which would disturb additivity of their apparent volumes. Density of such mixed solutions was measured by Wirtz<sup>13</sup> who used the magnetic float method with calibration to water of the highest attainable purity ( $\rho_0 = 0.997074 \text{ kg dm}^{-3}$ ) with sensitivity for the 6. decimal at  $25^\circ \pm 0.001^\circ\text{C}$ , the combinations measured being sodium chloride with potassium chloride, bromide, and sulphate. Table I gives values of the  $A$ ,  $B$  parameters of Eq. (4) evaluated by adjusting to his data and the  $\varphi_i^0$  and  $\varphi_i'$  values obtained therefrom by Eqs (8) and (9), respectively.

Table II gives the therefrom calculated values of  $Q$  parameter of Eq. (12) according to Eqs (7) and (10) for various combinations of potassium salt (index 1) with sodium salt (index 2) and the respective values of semicubic term in  $10^{-6} \text{ kg} \cdot \text{dm}^{-3}$  units for  $I = 1$  at the ratio  $I_1 : I_2 = 1 : 1$  according to Eq. (12) for the three alternatives considered,  $a$ ,  $b$ ,  $c$  ( $q = q_1, q_\phi$ , and  $q_\phi^*$ , respectively). From the Table it can be seen that for  $\text{NaCl} + \text{KCl}$  combination the differences between the three models only vary at the 6. decimal even in the most favourable case. So this combination holds out no hope of their experimental differentiation, it can only serve for verification of additivity of the apparent molar volumes of ions in mixtures and, hence, also applicability of the procedure of theoretical calculation of density of mixed solutions based thereon irrespective of ideas about functional dependence of the apparent volumes on concentration of the components. For the  $\text{NaCl} + \text{KBr}$  combination the difference between the model ( $b$ ) and the other two models exceeds

TABLE I

Values of the parameters  $A$  ( $\text{kg mol}^{-1}$ ),  $B$  ( $\text{kg dm}^{3/2} \text{ mol}^{-3/2}$ ),  $\varphi^0$ , and  $\varphi'$  ( $\text{kg mol}^{-1}$ ) of salts evaluated from the data by Wirtz<sup>13</sup>,  $25^\circ\text{C}$

| Salt                    | $10^3 A$ | $10^3 B$ | $10^3 \varphi^0$ | $10^3 \varphi'$ |
|-------------------------|----------|----------|------------------|-----------------|
| KCl                     | 47.91    | 2.082    | 26.64            | 37.41           |
| KBr                     | 85.15    | 1.852    | 33.85            | 42.81           |
| $\text{K}_2\text{SO}_4$ | 142.30   | 12.670   | 31.95            | 77.50           |
| $\text{NaCl(I)}^a$      | 41.92    | 1.914    | 16.52            | 28.00           |
| $\text{NaCl(II)}^a$     | 41.92    | 1.914    | 34.54            | 43.73           |

<sup>a</sup> I and II denotes the anhydrous salt and the monohydrate, respectively.

already (in the considered optimum case) 3 units at the 5. decimal, which – with respect to the accuracy attained by Wirtz – could already be sufficient for their differentiation. But the models (a) and (c) cannot be differentiated here either. The NaCl + K<sub>2</sub>SO<sub>4</sub> combination, on the contrary, cannot tell model (b) from (a), but it differentiates distinctly model (c), the difference in  $Q$  values between (c) and the other models reaching almost to the 4. decimal. (When calculating the data of Table II we also tested the presumption that the extrapolated state corresponding to complete degradation of the electrostatically bound hydration sheaths of the ions according to the alternative (b) and (c) falls within a smaller degree of filling of the solution by the ion volumes than 100%; it was shown, however, that decrease of the critical limit of volume filling of the solution from 100% to 75% would cause changes in  $Q$  and  $y$  values smaller at least by one order of magnitude as compared with differences between the models (b) and (c), and even a lowering of the limit to 50% would not introduce relevant changes into the mutual relations, which means that the method is – on the whole – independent of arbitrary presumptions concerning critical degree of volume filling corresponding to physical dehydration of the ions.)

#### NaCl + KCl Solutions

Table III gives results for this combination of salts. In his measurements Wirtz chose combinations of a concentration set of one salt with the same concentration set of the other salt, the concentration differences corresponding to approximately equal intervals in the Masson's square-root scale. Of course, concentration of the

TABLE II

Values of the dimensionless parameter  $Q$  in Eq. (12) for different combinations of potassium salts with NaCl and the hence evaluated values of the semi-cubic term  $y$  ( $10^{-6}$  kg dm<sup>-3</sup>) for  $I_1 = I_2 = 0.5$  mol dm<sup>-3</sup>, 25°C

| System                                | Term | Model           |                 |                   |
|---------------------------------------|------|-----------------|-----------------|-------------------|
|                                       |      | a ( $q = q_1$ ) | b ( $q = q_0$ ) | c ( $q = q_0^*$ ) |
| NaCl + KCl                            | $Q$  | 1.00            | 0.75            | 1.17              |
|                                       | $y$  | -1.998          | -2.007          | -2.006            |
| NaCl + KBr                            | $Q$  | 1.00            | 0.65            | 1.02              |
|                                       | $y$  | -1.883          | -1.918          | -1.883            |
| NaCl + K <sub>2</sub> SO <sub>4</sub> | $Q$  | 1.00            | 1.08            | 1.69              |
|                                       | $y$  | -2.176          | -2.183          | -2.268            |



TABLE III

Absolute values of the linear and the (c)-model semi-cubic term  $y$  ( $10^{-6}$  kg dm $^{-3}$ ) in the calculated densities of mixed electrolyte solutions, Eq. (6), (line 1), and the deviations ( $10^{-6}$  kg dm $^{-3}$ ) of the models (a), (b), (c), respectively, from the experimental densities<sup>1,3</sup> of pairs of solutions of approximately equal composition (lines 2 and 3) for aqueous solutions of NaCl + KCl at 25°C;  $c_{\text{NaCl}}$  and  $c_{\text{KCl}}$  (mol dm $^{-3}$ ) are rounded-off mean values for each row or column

|       | $c_{\text{KCl}}$  |       |      | 0     |      |       | 0.04 |       |       | 0.16  |       |      | 0.36  |      |    | 0.64 |    |    | 1.00 |  |  |
|-------|-------------------|-------|------|-------|------|-------|------|-------|-------|-------|-------|------|-------|------|----|------|----|----|------|--|--|
|       | $c_{\text{NaCl}}$ | a     | b    | c     | a    | b     | c    | a     | b     | c     | a     | b    | c     | a    | b  | c    | a  | b  | c    |  |  |
| 0     | 1                 | 0     | 0    | 0     | 1901 | 17    | 7604 | 132   | 17175 | 447   | 30937 | 1080 | 47709 | 2069 |    |      |    |    |      |  |  |
|       | 2                 | 0     | 0    | 7     | 7    | 7     | 2    | 2     | 4     | 4     | 4     | 4    | 4     | 4    | 4  | 4    | 4  | 4  | 4    |  |  |
|       | 3                 | 5     | 5    | 5     | 5    | 5     | 6    | 6     | 6     | 3     | 3     | 3    | 3     | 3    | 3  | 3    | 3  | 3  | 3    |  |  |
| 0.038 | 1                 | 1626  | 15   | 3515  | 44   | 9230  | 180  | 18776 | 517   | 32126 | 1151  |      |       |      |    |      |    |    |      |  |  |
|       | 2                 | 1     | 1    | 4     | 4    | 4     | 3    | 3     | 3     | 6     | 6     | 6    | 6     | 6    | 6  | 6    | 6  | 6  | 6    |  |  |
|       | 3                 | 1     | 1    | 0     | 0    | 0     | 8    | 7     | 2     | 1     | 1     | 1    | 1     | 1    | 1  | 1    | 1  | 1  | 1    |  |  |
| 0.154 | 1                 | 6592  | 118  | 8385  | 167  | 14063 | 351  | 23460 | 740   | 37055 | 1450  |      |       |      |    |      |    |    |      |  |  |
|       | 2                 | 0     | 0    | 6     | 5    | 5     | -1   | -1    | 2     | -1    | -1    | -1   | -1    | -1   | -1 | -1   | -1 | -1 | -1   |  |  |
|       | 3                 | 0     | 0    | 2     | 2    | 2     | -1   | -2    | -2    | -2    | -5    | -5   | -5    | -5   | -5 | -5   | -5 | -5 | -5   |  |  |
| 0.345 | 1                 | 14611 | 394  | 16433 | 465  | 22137 | 709  | 31466 | 1175  | 44838 | 1966  |      |       |      |    |      |    |    |      |  |  |
|       | 2                 | -1    | -1   | 0     | 0    | 0     | -3   | -6    | -6    | -3    | -9    | -8   | 8     | -1   | 0  |      |    |    |      |  |  |
|       | 3                 | -1    | -1   | -9    | -10  | -10   | -2   | -5    | -4    | -2    | -8    | -7   | -7    | -7   | -7 | -7   | -7 | -7 | -7   |  |  |
| 0.617 | 1                 | 25919 | 931  | 27843 | 1029 | 33500 | 1336 | 42848 | 1898  |       |       |      |       |      |    |      |    |    |      |  |  |
|       | 2                 | 1     | 1    | 4     | 2    | 2     | 14   | 10    | 10    | 2     | 3     | 3    | 3     | 3    | 3  | 3    | 3  | 3  | 3    |  |  |
|       | 3                 | 4     | 4    | 4     | 3    | 3     | 5    | 1     | 1     | 1     | 1     | 1    | 1     | 1    | 1  | 1    | 1  | 1  | 1    |  |  |
| 0.97  | 1                 | 40736 | 1834 | 42592 | 1952 |       |      |       |       |       |       |      |       |      |    |      |    |    |      |  |  |
|       | 2                 | -2    | -2   | 2     | 0    | 0     |      |       |       |       |       |      |       |      |    |      |    |    |      |  |  |
|       | 3                 | -2    | -2   | 0     | -1   | -2    |      |       |       |       |       |      |       |      |    |      |    |    |      |  |  |

"constant" component in a given series slightly varies due to technical limitations to reproducibility. The Table gives in its heading and the left column rounded-off average values concerning the respective series of solutions. The numbers in the heading of each frame give the value of linear and semicubic term of Eq. (6) in  $10^{-6}$   $\text{kg dm}^{-3}$  units (the latter with opposite sign gives the result for the alternative (c), but relative differences from (a) and (b) are small). Each frame then gives differences of the calculated  $\rho$  values of the three models from the experimental value. The author<sup>13</sup> measured each concentration combination (except for the higher concentrations) using two solutions with practically the same composition (within technical possibilities) prepared independently, and he gives the composition with the accuracy  $10^{-4}$   $\text{mol dm}^{-3}$  (NaCl, KCl, KBr) and  $10^{-5}$   $\text{mol dm}^{-3}$  ( $\text{K}_2\text{SO}_4$ ). The upper line of differences in each frame corresponds to the solutions in which NaCl concentration resulting from preparation of the solutions in each of these pairs was slightly lower, the second line corresponds to the solutions with higher  $c_2$ . Comparison of these pair measurements allows an evaluation of magnitude of scattering of experimental data, because at such small concentration differences the choice of model plays no part, and the whole difference in the deviations of calculation from experiment is due to experimental error. It is seen to reach mostly several units of the 6. decimal, ten units at most, so reproducibility of the measurements can be guaranteed to the 5. decimal. The deviations of the calculated values from the measured ones vary roughly within these limits for all the three alternatives. (In accordance with the theoretically derived data of Table II, the choice of model has no detectable effect here.)

Thus we can accept it as confirmed that in mixed aqueous solutions of strong electrolytes the apparent volumes of components are additive within the investigated concentration range, if validity of the Masson's square-root rule is accepted for their dependence on the volume concentration  $c$  of the solution irrespective of the question whether the determining quantity is ionic strength of the solution or volume fraction of water.

#### NaCl + KBr Solutions

The data of Table II show that difference between the model (b) and the two other models lies far behind the limit of experimental error in this case at the most favourable component ratio and at  $I = 1$   $\text{mol dm}^{-3}$ , hence the models (a), (c) can be differentiated from (b). This fact is confirmed by Table IV. In the region of the upper concentration limit the measured densities approach quite clearly the values calculated for the (a), (c) models. This means that the model (b), i.e. anhydrous  $\text{Na}^+$  ion, can be excluded, the functional dependence being valid between  $\Phi_1$  and degree of filling of the solution by volumes of ions. Either the apparent volumes of ions depend on ionic strength  $I$  of the solution (model a) — then it is impossible to determine the hydration form of  $\text{Na}^+$  ions by the described way, or the functional

TABLE IV  
The same data as in Table III for the system  $H_2O-NaCl-KBr$  at 25°C

| $c_{NaCl}$ | 0 |        |       | 0.04   |       |        | 0.16  |        |       | 0.36   |       |        | 0.64  |    |    | 1.00 |   |   |
|------------|---|--------|-------|--------|-------|--------|-------|--------|-------|--------|-------|--------|-------|----|----|------|---|---|
|            | a | b      | c     | a      | b     | c      | a     | b      | c     | a      | b     | c      | a     | b  | c  | a    | b | c |
| 0          | 1 | 0      | 0     | 3 419  | 15    | 13 666 | 119   | 30 825 | 403   | 54 825 | 957   | 85 731 | 1 871 |    |    |      |   |   |
|            | 2 | 0      | 0     | 4      | 4     | 10     | 10    | 9      | 9     | 2      | 2     | 2      | 8     | 8  |    |      |   |   |
|            | 3 |        |       | 8      | 8     | -2     | -2    | -2     | -2    | -2     | -13   | -13    | -6    | -6 | -6 |      |   |   |
| 0.039      | 1 | 1 635  | 15    | 5 042  | 42    | 15 225 | 165   | 32 183 | 466   | 55 692 | 1 026 |        |       |    |    |      |   |   |
|            | 2 | 1      | 1     | 2      | 0     | -1     | -3    | -1     | 4     | 1      | 4     | -7     | -11   | -7 |    |      |   |   |
|            | 3 | 1      | 1     | 3      | 2     | -5     | -7    | -5     | -10   | -13    | -10   |        |       |    |    |      |   |   |
| 0.156      | 1 | 6 527  | 118   | 9 996  | 167   | 20 142 | 334   | 37 016 | 689   | 60 902 | 1 317 |        |       |    |    |      |   |   |
|            | 2 | 0      | 0     | 1      | -1    | -6     | -12   | -6     | -2    | -13    | -2    | -4     | -19   | -4 |    |      |   |   |
|            | 3 | -1     | -1    | 4      | 2     | 4      | -1    | -7     | -1    | -9     | -19   | -9     |       |    |    |      |   |   |
| 0.61       | 1 | 25 909 | 930   | 28 203 | 1 015 | 39 290 | 1 292 | 56 034 | 1 799 | 79 633 | 2 603 |        |       |    |    |      |   |   |
|            | 2 | 4      | 4     | 2      | -2    | 5      | -11   | 5      | -4    | -36    | -4    | 0      | -49   | 0  |    |      |   |   |
|            | 3 | 0      | 0     | -5     | -9    | -2     | -19   | -2     | -5    | -37    | -5    |        |       |    |    |      |   |   |
| 0.97       | 1 | 40 774 | 1 836 |        |       |        |       |        |       |        |       |        |       |    |    |      |   |   |
|            | 2 | 1      | 1     | 1      |       |        |       |        |       |        |       |        |       |    |    |      |   |   |
|            | 3 | -2     | -2    | -2     |       |        |       |        |       |        |       |        |       |    |    |      |   |   |

dependence on the volume filling of the solution is valid – and then the  $\text{Na}^+$  ion is present predominantly in the form of  $\text{NaH}_2\text{O}^+$  (model *c*). The decision was made possible by the results obtained in the third system measured.

#### $\text{NaCl} + \text{K}_2\text{SO}_4$ Solutions

The results are given in Table V. Within the limits of reproducibility of experimental data, the alternative (*c*) only agrees with the values measured in this case. The model based on dependence of  $\Phi_i$  on ionic strength *I* fails completely here. Thereby this alternative is excluded, and simultaneously it becomes clear that agreement between experimental data and this model in the case of  $\text{NaCl}$ – $\text{KCl}$  and  $\text{NaCl}$ – $\text{KBr}$  combinations (which was used by Wirtz<sup>13</sup> to support his opinion) is purely a result of the chance that parameters of Eq. (6), which was derived in this communication for calculation of density of mixed solutions, agree in the case of the model (*a*) by Wirtz and Redlich within experimental error with the parameters valid for the case of the dependence of  $\Phi_i$  on volume filling of the solution with simultaneous existence of  $\text{Na}^+$  ion in the monohydrate form (model *c*, see Table II). On the contrary, the discrepancy between the measured data and the presumed dependence of  $\Phi_i$  on ionic strength in the  $\text{NaCl}$ – $\text{K}_2\text{SO}_4$  system, which was considered non-explainable anomaly by Wirtz<sup>13</sup>, results simply from the fact that there is no accidental agreement between the two models in this case. The measured data fit the model (*c*) with the monohydrate  $\text{NaH}_2\text{O}^+$  which differs markedly from the model by Wirtz and Redlich in the theoretically calculated numerical values.

#### CONCLUSION

On the whole the results show (*i*) that the apparent volumes of ions in aqueous solutions are the Masson's function of filling of the solution with the apparent volumes of ions and (*ii*) that  $\text{Na}^+$  ion exists in aqueous solutions as the  $\text{NaH}_2\text{O}^+$  particle which is analogous to  $\text{H}_3\text{O}^+$ . Hence it can be considered proven (in a new, more conclusive way) that the same is true of the  $\text{Li}^+$  ion for which (similarly as for  $\text{Na}^+$  ion) this conclusion was derived in our previous paper<sup>8</sup> by three other independent ways.

The assumption readily occurs that by this binding to electronic system of water the said two ions – in contrast to big univalent monoatomic ions  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$  – acquire a possibility to incorporate themselves into the liquid water structure by means of hydrogen bonds (in analogy to the  $\text{H}_3\text{O}^+$  ion) and to form here bulky clusters, which could explain low equivalent conductivity of  $\text{Li}^+$  and  $\text{Na}^+$  ions (38 and 50  $\text{S cm}^2 \text{ mol}^{-1}$ , respectively, at  $c = 0$  at 25°C) as compared with the other above-mentioned ions (76 to 79  $\text{S cm}^2 \text{ mol}^{-1}$  under the same conditions). Hence cations of the elements H, Li, Na from the left upper corner of periodic table represent

TABLE V

The same data as in Table III for the system  $H_2O-NaCl-K_2SO_4$  at 25°C

| $c_{NaCl}$ | $c_{K_2SO_4}$ |       |      |       |     |      |       |     |      |       |     |      |       |     |      |       |     |      |
|------------|---------------|-------|------|-------|-----|------|-------|-----|------|-------|-----|------|-------|-----|------|-------|-----|------|
|            | 0             |       |      | 0.015 |     |      | 0.059 |     |      | 0.133 |     |      | 0.236 |     |      | 0.333 |     |      |
|            | a             | b     | c    | a     | b   | c    | a     | b   | c    | a     | b   | c    | a     | b   | c    | a     | b   | c    |
| 0          | 1             | 0     | 0    | 2     | 108 | 23   | 8     | 378 | 181  | 19    | 087 | 622  | 33    | 465 | 1445 | 47    | 372 | 2434 |
|            | 2             | 0     | 0    | 2     | 2   | 2    | 1     | 1   | 1    | 5     | 5   | 5    | -     | 9   | -    | 9     | 4   | 4    |
|            | 3             |       |      | -     | 1   | -    | 1     | 8   | 8    | 0     | 0   | 0    | -     | 11  | -    | 11    |     |      |
| 0.038      | 1             | 1623  | 15   | 3     | 717 | 55   | 10    | 044 | 242  | 20    | 466 | 698  | 35    | 090 | 1561 |       |     |      |
|            | 2             | 1     | 1    | 4     | 4   | 2    | 9     | 9   | 3    | 13    | 12  | 4    | 16    | 15  | 3    |       |     |      |
|            | 3             | 1     | 1    | 5     | 5   | 3    | 7     | 7   | 2    | 9     | 9   | 0    |       |     |      |       |     |      |
| 0.154      | 1             | 6475  | 116  | 8     | 562 | 185  | 14    | 910 | 438  | 25    | 379 | 974  | 39    | 958 | 1916 |       |     |      |
|            | 2             | -     | -    | 1     | 2   | -    | 3     | 18  | 17   | 0     | 27  | 25   | -     | 4   | 36   | 32    | -   | 9    |
|            | 3             | 0     | 0    | 6     | 6   | 1    | 17    | 16  | -    | 1     | 27  | 24   | -     | 5   |      |       |     |      |
| 0.350      | 1             | 14630 | 395  | 16    | 822 | 499  | 23    | 184 | 837  | 33    | 543 | 1478 | 48    | 392 | 2566 |       |     |      |
|            | 2             | 1     | 1    | 9     | 8   | 0    | 31    | 28  | 0    | 55    | 51  | -    | 4     | 88  | 82   | -     | 2   |      |
|            | 3             | -     | -    | 1     | 9   | 1    | 26    | 24  | -    | 5     | 58  | 54   | -     | 1   |      |       |     |      |
| 0.618      | 1             | 25963 | 933  | 28    | 080 | 1067 | 34    | 286 | 1482 | 44    | 774 | 2258 |       |     |      |       |     |      |
|            | 2             | 0     | 0    | 21    | 20  | 8    | 45    | 42  | 2    | 93    | 87  | 5    |       |     |      |       |     |      |
|            | 3             | 1     | 1    | 11    | 10  | -    | 50    | 47  | 6    | 88    | 82  | 0    |       |     |      |       |     |      |
| 0.97       | 1             | 40777 | 1836 | 42    | 915 | 2004 | 49    | 093 | 2509 |       |     |      |       |     |      |       |     |      |
|            | 2             | -     | -    | 2     | 20  | 19   | 4     | 64  | 59   | 8     |     |      |       |     |      |       |     |      |
|            | 3             | 1     | 1    | 18    | 19  | 4    | 67    | 62  | 11   |       |     |      |       |     |      |       |     |      |

an anomaly in aqueous solutions which has no analogy in the rest of the table<sup>15</sup>.

Here can be the reason of the well-known jump in solubilities when going from Na salts to K salts (*cf.*  $\text{NaClO}_4\text{-KClO}_4$  or  $\text{NaF-KF}$ ), in the formation of crystallohydrates (*cf.*  $\text{Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ ,  $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4$ , or even  $\text{NaOH-KOH}$ ) as well as the reason of different physiological action of  $\text{Na}^+$  and  $\text{K}^+$  ions in biological membranes ("Na-K pump") *etc.* This different behaviour of two ions, which are otherwise so close chemically and have analogous electronic noble-gas configuration, in aqueous solutions is obviously due to their different magnitudes; formation of the Me-OH<sub>2</sub> covalent bond resulting in tri-covalent oxygen atom predominates, in the case of these small particles  $\text{Na}^+$ ,  $\text{Li}^+$ , and  $\text{H}^+$ , in the competition with the ion-dipole interaction orienting the H<sub>2</sub>O dipoles radially in the coulombic field of the ion, the interaction energy of the last being increased with decreasing interatomic distances less steeply than the energy of covalent bonds.

#### { LIST OF SYMBOLS

- $a_i$  individual ionic constant in mixed solutions defined by Eq. (2), ( $\text{kg mol}^{-1}$ )  
 $A$  empirical linear-term constant in Eq. (4), ( $\text{kg mol}^{-1}$ )  
 $A_i$  linear-term constant of electrolytes in mixed solutions defined by Eq. (8), ( $\text{kg mol}^{-1}$ )  
 $b_i$  individual ionic constant in mixed solutions defined by Eq. (3), ( $\text{kg mol}^{-1}$ )  
 $B$  empirical semicubic-term constant in Eq. (4), ( $\text{kg dm}^{3/2} \text{mol}^{-3/2}$ )  
 $B_i$  semi-cubic term constant of a component in mixed solutions of strong electrolytes defined by Eq. (9), ( $\text{kg dm}^{3/2} \text{mol}^{-3/2}$ )  
 $c$  molar concentration ( $\text{mol dm}^{-3}$ )  
 $I$  ionic strength of the solution and of its components — index  $i$ , ( $\text{mol dm}^{-3}$ )  
 $M_i$  molar mass of the electrolyte, ( $\text{kg mol}^{-1}$ )  
 $M_0$  molar mass of solvent ( $\text{kg mol}^{-1}$ )  
 $n$  number of water molecules in an aquo complex  
 $q$  dimensionless parameter in Eq. (6)  
 $Q$  dimensionless parameter in Eq. (12),  $qw_1/w_2$   
 $V_0$  molar volume of free liquid water at the given temperature, ( $\text{dm}^3 \text{mol}^{-1}$ )  
 $w$  dimensionless coefficient for conversion of molar concentrations into ionic strengths,  
 $w = \frac{1}{2}(v_+z_+^2 + v_-z_-^2)$   
 $y$  semicubic term in the density functions, ( $10^{-6} \text{kg dm}^{-3}$ )  
 $z$  ionic charge (elementary charge unit multiples, dimensionless)  
 $\nu$  stoichiometric coefficient  
 $\rho$  density of the solution, ( $\text{kg dm}^{-3}$ )  
 $\rho_0$  density of pure liquid water at the given temperature, ( $\text{kg dm}^{-3}$ )  
 $\varphi = \Phi \rho_0$ , ( $\text{kg mol}^{-1}$ )  
 $\Phi$  apparent molar volume of the electrolyte, ( $\text{dm}^3 \text{mol}^{-1}$ )  
 $\Phi^0$  apparent molar volume of the electrolyte (or ion) at infinite dilution, ( $\text{dm}^3 \text{mol}^{-1}$ )  
 $\Phi'$  apparent molar volume of the electrolyte (or ion) extrapolated to zero content of water,  
( $\text{dm}^3 \text{mol}^{-1}$ )

## REFERENCES

1. Dorosh A. K., Skryshevskii A. F.: *Zh. Strukt. Khim.* 1, 5 (1964).
2. Skryshevskii A. F.: *Rentgenografiya Zhidkosti*. Izd. Kiievsk. Univ., Kiiiev 1966.
3. Shapovalov I. M., Radchenko I. V., Lesovtsikaya M. K.: *Zh. Strukt. Khim.* 10, 921 (1969); 13, 139 (1972).
4. Falk M., Giguère P. A.: *Can. J. Chem.* 35, 1195 (1957).
5. Čeleda J.: *Sci. Papers Instit. Chem. Technol. Prague FAT 1*, 467 (1958).
6. Čeleda J., Jedináková V.: *Sci. Papers Instit. Chem. Technol. Prague B-12*, 167 (1968).
7. Kermarrec Y.: *C. Rend.* 258, 5836 (1964).
8. Čeleda J.: *Sci. Papers Inst. Chem. Technol. Prague, Inorg. Technol.* 5, 17 (1964).
9. Masson O.: *Phil. Mag.* (7) 8, 218 (1929).
10. Čeleda J.: *Sci. Papers Inst. Chem. Technol. Prague FAT + FOT 3*, 15 (1959).
11. Čeleda J.: *This Journal* 48, 1538 (1983).
12. Redlich O., Rosenfeld P.: *Z. Phys. Chem. A* 155, 65 (1931).
13. Wirtz H. E.: *J. Amer. Chem. Soc.* 59, 2549 (1937).
14. Root C. W.: *J. Amer. Chem. Soc.* 55, 850 (1933).
15. Čeleda J.: *Sci. Papers Inst. Chem. Technol. B* 26, 51 (1981).

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