

ON CHEMICAL FORM OF H^+ ION IN AQUEOUS SOLUTIONS

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Using the method of the addition of another salt worked out and verified in the previous work, it has been concluded from experimental densities of aqueous NaCl + HCl solutions that even in highly diluted solutions, H^+ ion exists as integral H_3O^+ species which is bonded to the "ice-like" structure of surrounding water only by relatively weak hydrogen bonds. This bonding does not prevent the outer hydration sheath from fully participating in hydration equilibria of other ions present in solution. The hypothesis about the stable $H_9O_4^+$ complex could not be maintained.

In view of the importance of the knowledge of structural incorporation of hydrogen ion in solution for the biochemistry and physical chemistry of aqueous electrolyte solutions, the present work attempts at contributing with the use of the so far not applied method to the solution of the question whether excess proton in water is bonded to the bulkier hydrate cluster $O(H-OH_2)_3^+$, *i.e.* $H_4O_9^+$, as concluded from X-ray and IR evidence of the "ice-like" structure of the liquid water¹⁻⁵ by a number of authors⁶⁻¹¹ and further supported by Grahn¹² on the basis of quantum mechanical calculation of the energy of $H-OH_2$ bonds in the complex (which was two times greater than the average energies of the electrostatic bond between water molecules and univalent ions^{13,14}), or whether proton is strongly bound to only one H_2O molecule to form H_3O^+ particle, from which any of the three protons can jump (*via* tunneling effect¹⁵) to the adjacent molecule, thus forming the basis for the known high molar conductance of hydrogen ion in aqueous solutions.

Confrontation¹⁶ of the hydration numbers of H^+ ion in solution determined by statical methods with the measured¹⁷⁻²² electrolytic transport of water on H^+ ion allows to conclude that in intervals between proton jumps, the H^+ ion migrates in dilute solutions in the outer electrostatic field as a stokesian particle of molar conductance $30 \pm 5 \text{ S cm}^2 \text{ mol}^{-1}$ (25°C) dragging $12 \pm 2 \text{ H}_2\text{O}$ molecules (including the water contained in the electrostatically bound hydration sheath). When compared to the hydrates of other univalent ions²³, the radius of this particle is 0.44 nm. This corresponds to the loosely packed structure, which was confirmed also on the basis of the apparent²⁴ molar volume Φ of strong acids in aqueous solutions and of the low slope of their massonian $\Phi - c^{1/2}$ straight line²⁵. At high concentrations (5 mol .

. dm^{-3} and higher), this structure transforms into the more packed one, in consistency with the assumption about transformation of the cluster into the radially close-packed hydration sheath electrostatically bound to the discrete H_3O^+ particle which was detected in this region by IR spectra²⁶. The same conclusion has been drawn also from measurements of apparent (resp. partial) molar volumes of strong acids in highly concentrated aqueous solutions of salts²⁷. The problem represent dilute solutions for which the known methods do not provide detailed information about bonding within the cluster. This problem is dealt with in the present work.

THEORETICAL

The method is based on the assumption²⁸ that the known increase in the apparent volume of strong electrolytes Φ with increasing concentration of their aqueous solutions c is predominantly (and at concentrations higher than 1 mol dm^{-3} essentially completely) caused by the continuous reduction of electrostatically bound hydration sheaths of ions (which from this aspect can be included in the content of "mobile" water). From this it was concluded²⁹ that when some ionic species is bonding water by short-range forces to form the aquocomplex, the ligands which are thus excluded from the "mobile" water content participating in electrostatic hydration equilibria, the apparent volume of a second strong electrolyte added will increase with increasing concentration at a faster rate than if all the water were available for hydration of the ions. For this electrostatic hydration, and thus also for the apparent volume of the ionic species present in solution, one common functional dependence on the total volume fraction of the "mobile" water in solution has been accepted (irrespective of the composition of the latter), with density taken as equal to that of free liquid water at a given temperature, along with the already proved³⁰ additivity of apparent molar volumes of ions measured in thus defined corresponding states. As far as the shape of this function is concerned, the linear dependence of Φ ($\text{dm}^3 \cdot \text{mol}^{-1}$) on the square root of concentration c (mol dm^{-3}) was accepted for the free (non-associated) ions. This dependence found empirically by Masson²⁵ to hold for strong electrolytes was theoretically supported for the low concentration region³¹⁻³³ by using Debye-Hückel model of ion atmospheres and its validity was experimentally verified³⁴⁻³⁶ up to the highest concentrations realizable, even though here the Debye-Hückel model is no more valid.

The dehydration model of the concentration increase of Φ , along with the above mentioned linear dependence on $c^{1/2}$ made it possible to introduce^{24,37-39} — in addition to the apparent molar volume Φ^0 extrapolated to $c = 0$ — also the concept of "anhydrous" volume Φ' extrapolated to the hypothetical state in which the volume fraction of the "mobile" water equals to zero and the whole volume of the solution is filled with ions (including their stable aquocomplexes which do not undergo dehydration according to Masson's square-root rule), *i.e.* to concentrations c'

defined by the condition $c'\Phi' = 1$. By introducing parameters A (kg mol^{-1}) and B ($\text{kg mol}^{-3/2} \text{ dm}^{3/2}$), the values of which for each electrolyte are determined by empirical adjustment from densities of aqueous solutions of a given electrolyte (using minimalization of the sum of squared deviations) according to the relation

$$\varrho = \varrho_0 + Ac - Bc^{3/2} \quad (1)$$

derived from the Masson's rule, and using further the parameters φ^0 (kg mol^{-1}) = $\varrho_0\Phi^0$ and $\varphi' = \varrho_0\Phi'$ (ϱ_0 is the density of the pure liquid water at a given temperature), the values of which are determined from experimental values of parameters A and B according to the relations

$$A = M - \varphi^0 \quad (2)$$

$$B = (\varphi' - \varphi^0)(\varphi'/\varrho_0)^{1/2}, \quad (3)$$

the following expression is obtained²⁹ for the density of mixed solution of two strong electrolytes (1, 2)

$$\varrho = \varrho_0 + A_1c_1 + A_2c_2 - (B_1c_1 + B_2c_2q^{-1/2})(c_1 + c_2q)^{1/2}, \quad (4)$$

where $q = \varphi'_2/\varphi'_1$. If any of two electrolytes forms aquocomplexes with n molecules of water which do not participate in hydration equilibria of ions, its molar mass M in Eq. (2) should be increased by adding n -multiple of molar mass of water. This changes its parameter q , *i.e.* the whole semicubic term in Eq. (4), for which the symbol y has been introduced²⁹. Comparison of densities $\varrho(\text{exp})$ determined for mixed solutions with the ϱ values calculated for the same solutions from Eq. (4) by substituting alternative values of the parameter q makes it possible to decide between different aquocomplexes considered for the electrolyte under study, providing that the value of n for the other one (*i.e.* the added "indicator" electrolyte) is known. As shown in the previous work²⁹, the sensitivity of the semicubic term y to the differences in the values of parameter q is proportional to the product c_1c_2 , which confirms that the described method requires the simultaneous presence of both electrolytes.

EXPERIMENTAL

For determining the form of H^+ ions in aqueous solutions by the above method, Wirth's data³³ on densities of mixed $\text{HCl} + \text{NaCl}$ solutions at 25°C obtained (similarly as those for $\text{KCl} + \text{NaCl}$ solutions³² used in the previous work²⁹) by magnetic float method with the temperature stabilized to $\pm 0.001^\circ\text{C}$ (ensuring the measurement of densities on sixth decimal) have been used. Because of the aggressive medium, silver-coated flasks were replaced by pyrex flasks, and the solutions

were prepared as earlier, using the water of maximum available purity (density $\rho_0 = 0.997074 \text{ kg} \cdot \text{dm}^{-3}$). The preparation of solutions, the determination of c_1 and c_2 and the procedure used in the measurements were described in detail elsewhere^{32,33}.

RESULTS AND DISCUSSION

As the described method is based on the determination of the existence of aquo-complexes of a given electrolyte from the volume changes of the added salt as "indicator" due to competitive dehydration, one has to know whether and what aquo-complexes are formed by the indicator. In the case of H⁺ ions in aqueous solutions, the only accurate data available so far are those for mixed HCl + NaCl solutions. The state of Na⁺ ions in its aqueous solution was determined in the previous work²⁹ from densities of aqueous solutions of potassium and sodium salts, assuming that K⁺ ions do not form stable aquo-complexes. There are no direct physical methods to verify this assumption.

With respect to the importance of this question in connection with the conclusive evidence based on the results of the present work, we attempted at finding the solution by an indirect method by comparing the Φ' values for potassium salts obtained by extrapolation of Φ to the "anhydrous" state with the corresponding crystallographic parameters. On the basis of the independence of Φ' values on temperature, found experimentally for potassium halides²⁸, data for 18°C reported in preceding work²⁸ were used for Φ'_K . In treating these data we have presumed that on decreasing volume fraction of water in the solution, the ions with opposite charge agglomerate, their arrangement resembling the cubic NaCl lattice (Glueckauf's as well as Frank-Thompson's "quasi-lattice" structure⁴⁰ – irrespective of the lattice which a given salt forms in the solid state). In dividing the molar volume of salts Φ' to the ionic volumes Φ'_i , we took as a guidance the ratio of cubes of the mean tabulated values of crystallographic radii r_i in CsCl as the salt with the bulkiest (of the aquo-complex formation least capable) and in the size least different anions and cations. The other ionic volumes were calculated by subtracting successively Φ'_{Cl^-} or Φ'_{Cs^+} , respectively (and then the so obtained individual volumes of other cations) from the extrapolated experimental values of the molar volumes Φ' of the other halides.

By this way, the following values of Φ'_- ($\text{cm}^3 \text{ mol}^{-1}$) and r_- (pm) were determined for halogenide ions, compared to the crystallographic radii r_i (cryst.) reported⁴¹:

$\Phi'_{\text{Cl}^-} = 27.1$	$r_{\text{Cl}^-} = 178$	$r_{\text{Cl}^-} (\text{cryst.}) = 181$
$\Phi'_{\text{Br}^-} = 33.3$	$r_{\text{Br}^-} = 191$	$r_{\text{Br}^-} (\text{cryst.}) = 195-196$
$\Phi'_I = 43.0$	$r_{I^-} = 208$	$r_{I^-} (\text{cryst.}) = 216-220$

which can be taken as a good agreement. The low negative deviation of r_- can be regarded as insignificant in view of the approximative character of the model.

The result confirms the well known fact that Cl^- , Br^- , and I^- ions do not form aquocomplexes in aqueous solutions and speaks also for the adequacy of the extrapolation model used.

The values of Φ'_+ and r_+ which, along with previous data, were obtained for Group IA cations, are presented in Table I. It is evident that the extrapolated volumes of Cs^+ , Rb^+ , and K^+ ions correspond to crystallographic radii of these ions as such^{41,42} *i.e.* without formation of aquocomplexes, while for all three small ions, Na^+ , Li^+ , and H^+ , there are significant negative differences that exceed markedly the deviations found for halogenide ions and attain even negative values of Φ'_+ . This indicates that up to the highest realizable concentrations these ions exist in aqueous solutions as aquocomplexes. (Formulas in parentheses at Φ'_+ and r_+ denote the electrolyte, solution of which was used to obtain data).

The confirmation of the hypothesis about non-existence of K^+ ion in the form of aquocomplex in aqueous solutions provides additional support for the conclusions concerning the formation of the monoaquocomplex of Na^+ ions, arrived at in the previous work²⁹ from densities of mixed aqueous solutions of potassium and sodium salts. This makes also the results of the present work more reliable and justifies the conclusions about H^+ ions drawn from the densities of mixed $\text{NaCl} + \text{HCl}$ solutions, Na^+ ion being taken as the monoaquocomplex. The important conclusion is that the previous method based on comparison of the extrapolated values of Φ' in solution of only one electrolyte with its crystallographic data does not depend on the present method of mixed solutions that is based on the dehydration competition of the components, irrespective of their crystallographic parameters – even though both methods start from experimental densities of aqueous solutions.

Using Eq. (4) (Na^+ taken as $\text{Na}(\text{H}_2\text{O})^+$ complex), the following theoretical densities of mixed aqueous $\text{NaCl} + \text{HCl}$ solutions were calculated:

TABLE I

Apparent volumes of IA group cations extrapolated to $c_{\text{H}_2\text{O}} = 0$, $\Phi'_+(\text{cm}^3 \text{mol}^{-1}$, ref.²⁸) and the evaluated radii r_+ (pm), compared with the crystallographic ionic radi $r_{+, \text{cryst}}$, (refs^{41,42})

Ion M^+	$\Phi'_+(\text{MCl})$	$\Phi'_+(\text{MBr})$	$\Phi'_+(\text{MI})$	$r_+(\text{MCl})$	$r_+(\text{MBr})$	$r_+(\text{MI})$	$r_{+, \text{cryst}}$
Cs^+	20.9	20.9	20.9	163	163	163	161–169
Rb^+	15.2	13.7	14.0	147	142	143	140–148
K^+	10.9	9.3	9.7	131	125	126	122–133
Na^+	2.2	0.7	–0.4	77	53	–	94–100
Li^+	–2.2	–3.3	–3.3	–	–	–	65–70
H^+	–3.1	–2.1	–2.4	–	–	–	–

(1) $\varrho(HCl)$ for the case where on increasing concentration of the solution, the dehydration of H^+ ion leads from the very beginning to anhydrous HCl molecules, *i.e.* all the water bound to H^+ ion participates in distribution hydration equilibria of present ions,

(2) $\varrho(H_3O \cdot Cl)$ for the case where H^+ ion exists in aqueous solutions (at least in the concentration region studied) as the stable monohydrate, exchanging protons with surrounding water molecules but not allowing the water molecule to which the proton is bound at a given moment to participate in hydration equilibria of the other ions, and

(3) $\varrho(H_9O_4 \cdot Cl)$ for the case where H^+ ion exists as the stable tetrahydrate^{6,7,12}.

In order to eliminate the interfering effect of ion association, data only up to concentrations at which the solutions of each single component attain density of around 1.036 kg dm^{-3} , *i.e.* up to 1 mol dm^{-3} for NaCl and c. 2 mol dm^{-3} for HCl, were used. The parameters of the components obtained by adjustment to the experimental densities of the solutions of each component separately, using Eqs. (1) to (3) (in units given above), were as follows: for NaCl. H_2O $A = 0.041934$, $B = 0.001914$, $\varphi_1^0 = 0.03454$, $\varphi_1' = 0.04368$ (in the previous work²⁹ 0.041920 , 0.001914 , 0.03454 , and 0.04373 , respectively) and for HCl: $A = 0.018410$, $B = 0.000870$, $\varphi_0^0 = 0.018055$, $\varphi_1^0 = 0.036073$, $\varphi_2^0 = 0.090119$, $\varphi_3^0 = 0.02370$, $\varphi_1' = 0.04040$, and $\varphi_4' = 0.09297$, giving $q_0 = 0.5426$, $q_1 = 0.9249$, and $q_4 = 2.1284$ (*i.e.* $Bq^{-1/2}$ for model (1) 0.00118 , for model (2) 0.000905 , and for model (3) 0.000596).

The inaccuracy of experimental determination of densities which (as judged from the differences between two parallel measurements) amounts to several units of sixth decimal in the cited work (at maximum one unit of fifth decimal), results in a certain range of the values of adjusted parameters A , B , corresponding to these experimental errors. This is documented by the value of A (NaCl) calculated (by the method of minimalization of the sum of squared deviations) earlier²⁹ from data reported in work³² and now from those reported in work³³. As a result, in the mean of the concentration range studied (around 0.5 mol dm^{-3} NaCl), the difference in the results is 7 units and at the upper limit (1 mol dm^{-3}) 14 units of sixth decimal, which corresponds to the differences between parallel experiments reported in each work separately. The same uncertainty occurs also with the densities of mixed solutions calculated theoretically from Eq. (4). The present method of mixed solutions makes it possible to differentiate only between such models and in such concentration ranges for which Eq. (4) gives differences which are significantly greater than the above uncertainty, *i.e.* greater than several units of sixth decimal at both c_1 and c_2 around the mean one, for which case the highest sensitivity of the method is attained.

The results are summarized in Table II (for increasing NaCl concentration at constant HCl concentrations) and in Table III (for increasing HCl concentration at constant NaCl concentrations). Experimental data for the whole region investigated

TABLE II
Results of the calculation for constant HCl concentrations

c_{NaCl} mol dm^{-3}	c_{HCl} mol dm^{-3}	$\varrho_{\text{exper.}}$ kg dm^{-3}	$\Delta(1, e)$ $\cdot 10^6$	$-\gamma_1$ $\cdot 10^6$	$\Delta(0, 1)$ $\cdot 10^6$	$\Delta(4, 1)$ $\cdot 10^6$	c_{NaCl} mol dm^{-3}	c_{HCl} mol dm^{-3}	$\varrho_{\text{exper.}}$ kg dm^{-3}	$\Delta(1, e)$ $\cdot 10^6$	$-\gamma_1$ $\cdot 10^6$	$\Delta(0, 1)$ $\cdot 10^6$	$\Delta(4, 1)$ $\cdot 10^6$
0	0.04007	0.997805	0	7	0	0	0	0.35964	1.003506	0	188	0	0
0	0.04023	0.997809	-1	7	0	0	0.12872	0.35880	1.008694	-3	388	7	-48
0	0.04154	0.997832	0	7	0	0	0.12945	0.35880	1.008721	-1	389	7	-48
0.04967	0.04151	0.999879	3	39	0	-6	0.27626	0.35783	1.014591	-12	665	13	-91
0.04996	0.04151	0.999888	3	40	1	-5	0.27714	0.35782	1.014625	-8	666	12	-91
0.11484	0.04146	1.002549	3	101	1	-9	0.62650	0.35544	1.028415	-12	1 487	22	-172
0.11539	0.04146	1.002570	3	102	2	-9	1.04760	0.35248	1.044756	13	2 724	29	-224
0.31397	0.04131	1.010621	1	379	3	-18	0	0.98757	1.014385	16	854	0	0
0.63098	0.04107	1.023280	-8	1 018	4	-26	0	0.98910	1.014416	11	856	0	0
0	0.15516	0.999880	-3	53	0	0	0.20685	0.98522	1.022527	-3	1 362	20	-131
0	0.15582	0.999885	4	54	0	0	0.20790	0.98520	1.022569	-4	1 365	20	-131
0	0.15651	0.999904	-2	54	0	0	0.42686	0.98102	1.031077	-11	1 969	35	-255
0.08872	0.15558	1.003502	6	150	3	-20	0.42951	0.98096	1.031183	-16	1 977	35	-256
0.08916	0.15557	1.003520	5	151	3	-20	0.92398	0.97125	1.050122	6	3 573	63	-487
0.19720	0.15527	1.007891	9	302	6	-38	0	2.2449	1.035467	10	2 926	0	0
0.19929	0.15527	1.007978	6	306	6	-39	0	2.2578	1.035680	9	2 951	0	0
0.47057	0.15448	1.018834	2	815	9	-73	0.29725	2.1659	1.045580	-3	3 836	44	-286
0.82688	0.15343	1.032880	-1	1 695	12	-103	0.29790	2.1659	1.045605	-3	3 838	44	-286
0	0.34870	1.003312	2	179	0	0	0.63318	2.1510	1.058117	-7	5 116	84	-579
0	0.35898	1.003495	1	187	0	0	0.63521	2.1509	1.058192	-7	5 123	84	-581

TABLE III
Results of the calculation for constant NaCl concentrations

c_{NaCl}^{-3} mol dm ⁻³	c_{HCl}^{-3} mol dm ⁻³	$\rho_{\text{exper.}}^{-3}$ kg dm ⁻³	$\Delta(1, e) \cdot 10^6$	$-\gamma_1 \cdot 10^6$	$\Delta(0, 1) \cdot 10^6$	$\Delta(4, 1) \cdot 10^6$	c_{NaCl}^{-3} mol dm ⁻³	c_{HCl}^{-3} mol dm ⁻³	$\rho_{\text{exper.}}^{-3}$ kg dm ⁻³	$\Delta(1, e) \cdot 10^6$	$-\gamma_1 \cdot 10^6$	$\Delta(0, 1) \cdot 10^6$	$\Delta(4, 1) \cdot 10^6$
0.039860	0	0.998729	0	16	0	0	0.35673	0	1.011626	0	408	0	0
0.03982	0.04999	0.999628	0	36	1	-5	0.35587	0.12580	1.013768	0	546	6	-51
0.03982	0.05052	0.999636	2	36	1	-5	0.35581	0.13454	1.013916	0	556	6	-54
0.03977	0.11791	1.000841	1	71	2	-8	0.35486	0.27855	1.016358	-4	729	12	-94
0.03977	0.12175	1.000913	-3	73	2	-8	0.35477	0.28539	1.016470	-1	737	13	-96
0.03964	0.29836	1.004034	1	194	3	-15	0.35243	0.62265	1.022129	-6	1193	22	-162
0.03964	0.29921	1.004049	0	195	3	-14	0.35239	0.62819	1.022225	-9	1201	22	-163
0.03941	0.59643	1.009233	5	473	4	-19	0.34941	1.05390	1.029271	-10	1868	33	-221
0.15911	0	1.003621	4	121	0	0	0.039861	0	0.998728	1	16	0	0
0.15884	0.08781	1.005163	1	188	3	-21	0.97918	0	1.036277	2	1854	0	0
0.15883	0.09293	1.005253	1	192	3	-22	0.97920	0	1.036279	2	1855	0	0
0.15849	0.19603	1.007050	-1	280	5	-39	0.97546	0.19075	1.039293	9	2189	16	-140
0.15849	0.19932	1.007109	-3	283	5	-39	0.97484	0.22262	1.039799	6	2246	19	-160
0.15763	0.47235	1.011819	-1	562	9	-68	0.97088	0.42460	1.042973	13	2618	33	-273
0.15763	0.48263	1.011998	-3	574	10	-68	0.97081	0.42911	1.043050	7	2627	34	-275
0.15653	0.84330	1.018113	21	1029	14	-93	0.96106	0.92486	1.050782	12	3607	63	-485

lie close to the densities calculated for the monohydrate. The deviations $\Delta(1, e) = \rho(\text{H}_3\text{OCl}) - \rho(\text{exp})$ are in the region of sixth decimal (only seldom they exceed one unit of fifth decimal), *i.e.* at limits of the accuracy of the method, and are randomly scattered to positive and negative values. This indicates that they originate from experimental errors and not from the inadequacy of model 2. Therefore, Eq. (4) with the parameter q corresponding to the monoaquocomplex of H^+ can be taken as a correlation equation in which accidental errors in experimental data are eliminated. Hence, the differences in theoretical values of ρ of the other two models can be calculated from this correlation curve, to ascertain whether the mutual deviations $\Delta(0, 1) = \rho(\text{HCl}) - \rho(\text{H}_3\text{OCl})$ and $\Delta(4, 1) = \rho(\text{H}_9\text{O}_4\text{Cl}) - \rho(\text{H}_3\text{OCl})$ significantly exceed experimental errors.

For estimating to what extent the real situation is described by assuming the apparent ionic volume being the square-root function of the filling of the solution by the proper ionic volumes, resp. of the volume fraction of the "mobile" water, in addition to the deviations $\Delta(1, e)$, in Tables II and III are also presented the corresponding values of the semicubic term y_1 by which this concentration dependence is incorporated in the theoretically calculated values of $\rho(\text{H}_3\text{OCl})$ and on which in the present work the differentiation between aquocomplexes is based. As it is seen, the semicubic term corrects the theoretical density in the case of the monohydrate to fifth and sixth decimal even if itself attains the values higher by three orders of magnitude. With models 1 and 3, starting already from the low concentrations of both components of mixed solutions (of magnitude $10^{-1} \text{ mol dm}^{-3}$), theoretical densities calculated from models 1 and 3 deviate significantly from experimental ones. The described test based on the density of mixed solutions thus excludes without any doubt the existence of the stable complex $\text{O}(\text{H}-\text{OH}_2)_3^+$ proposed by Higgins and Grahn, having the high energies of hydrogen bonding between the central H_3O^+ particle and three OH_2 ligands bonded to it. It proves that H^+ – similarly to Li^+ (ref.²⁸) and Na^+ (refs.^{28,29}) ions – exists in aqueous solutions (in contradistinction to the bulky K^+ , Rb^+ , Cs^+ (ref.²⁸), and NH_4^+ (refs.^{43,44}) ions) as the stable monoaquocomplex MH_2O^+ which in dilute solution is incorporated *via* hydrogen bonding to the "ice-like" structure of the liquid water to form larger clusters. These additional water molecules are however bound so weakly that they are not prevented from participating in equilibrium distribution of water between electrostatically bound hydration sheaths of all the present ions. By the independent way, an additional support is thus provided for the conclusion that small H^+ , Li^+ , and Na^+ ions from the upper left-hand corner of the Periodic system form homological series^{24,28,29,45}, as far as their chemical structure in aqueous solution is concerned. This series differs from the sequence of the other univalent Group IA cations (K^+ , Rb^+ , Cs^+ , and Fr^+) as a result of the predominant energy of the covalent bond in the monoaquocomplex (which increases steeply with decreasing ionic radius) over the energy of the electrostatic ion-dipole interaction. This may be cause why

there is the steep jump in the properties of ions in aqueous solutions on going from the first to the second group: of the jump from the low stokesian molar conductances (H⁺ around 30 (ref.¹⁶), Li⁺ 38, and Na⁺ 50 S cm² mol⁻¹ at 25°C) to the values close to 80 S cm² mol⁻¹ as well as the jump in the formation of crystallo-hydrates and in the hygroscopicity of ion combinations with such anions as SO₄²⁻, NO₃⁻, etc. This can also explain the high solubility of the combinations with bulky anions (ClO₄⁻, PtCl₆⁻) as compared to KClO₄ or K₂PtCl₆, and especially the strikingly different functions of H⁺ and Na⁺ ions compared to K⁺ ions in biological systems, particularly in cell membranes. In this jump from the aquocomplexes to the ions with hydration sheaths bound purely electrostatically, which occurs in Group IA between Na⁺ and K⁺ ions, one could perhaps find the "chemical" theoretical basis for the generally accepted empirical classification of ions in aqueous solutions as "structure-formers" and "structure-breakers".

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