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Original article

Hydrogen Bonding and Local Electrostatic Interactions in a Non-Empiric Analytical Model of Ion Hydration Shell

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Abstract. As well-known, a confusion related to the volume of the ion hydration shell is more imaginary and artificial than real because the experimental hydration number determined for any ion generally depends upon the method of measurement. The currently existing theoretical models do not possess the required universality and do not allow one to do without empirical parameters. In the proposed study, being an attempt to prevent improper data, a new model of the hydration shell of the ion, based on its topological, electrostatic, and hydrophilic properties, is developed. A serious difficulty in developing a nonempirical modeling approach for describing the solvation phenomenon is to know how the dielectric permittivity depends on the distance from the central ion at the site of the hydration shell formation. In the author's recent papers, a useful non-empiric expression for the dielectric permittivity dependence on the distance was analytically derived. The hydration energy is described by taking into account not only the local dielectric permittivity, but also the type of interaction between ions and water molecules and the shape of the multilayer hydration shell. Geometric representation of the first hydration layer of a spherical ion in the form of Platonic solids is proposed. So, an icosahedron relates to "structure-making" ions, and a dodecahedron – to "structure-breaking" ones. It is shown, how the ion hydration number depends on the ionic radius, charge, and ability of the ion to hydrogen bonding. The calculations related to series of cations and anions are made.
Keywords: ion solvation; hydration number; hydration shell modeling; hydrogen bonds; local dielectric permittivity.
Acknowledgments: the work was carried out within the framework of the state task.
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ОРИГИНАЛЬНЫЕ СТАТЬИ

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Водородное связывание и локальные электростатические взаимодействия в неэмпирической аналитической модели гидратной оболочки ионов

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Аннотация. Как известно, путаница, связанная с объемом гидратной оболочки иона, является скорее мнимой и искусственной, чем реальной, поскольку экспериментальное число гидратации, определенное для любого иона, в общем случае зависит от метода измерения. Существующие в настоящее время теоретические модели не обладают необходимой универсальностью и не способны обойтись без эмпирических параметров. В предлагаемом исследовании, в качестве попытки предотвратить получение неправильных данных, разрабатывается новая модель гидратной оболочки иона, основанная на его топо-

логических, электростатических и гидрофильных свойствах. Серьезной трудностью в разработке неэмпирического подхода к моделированию для описания явления сольватации является знание того, как диэлектрическая проницаемость зависит от расстояния от центрального иона в месте образования гидратной оболочки. В недавних работах автора аналитически получено полезное неэмпирическое выражение для зависимости диэлектрической проницаемости от расстояния. Энергия гидратации описывается с учетом не только локальной диэлектрической проницаемости, но и типа взаимодействия между ионами и молекулами воды и формы многослойной гидратной оболочки. Предложено геометрическое представление первого гидратного слоя сферического иона в виде Платоновых тел. Так, икосаэдр относится к «структурообразующим» ионам, а додекаэдр – к «структуроразрушающим». Показано, как число гидратации иона зависит от ионного радиуса, заряда и способности иона к образованию водородных связей. Проведены расчеты, относящиеся к рядам катионов и анионов.

Ключевые слова: сольватация ионов; гидратное число, моделирование гидратной оболочки, водородные связи, локальная диэлектрическая проницаемость/

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Introduction

The solvation phenomenon governs the properties of electrolyte solutions and this is of great interest in various fields, including thermodynamics, electrochemistry, chemical analysis, etc. In this regard, it is more than surprising that the most important parameter of aqueous solutions, the ion hydration number, still has no ~~a~~ reliable measurement method, as well as a consistent theoretical interpretation. This was vividly demonstrated by Hinton and Amis in 1971 [1]. In recent years, experimental methods have been greatly improved and calculation algorithms based on the formalism of molecular dynamics created, but the determination of the hydration number has not become any clearer [2-5].

A real breakthrough in establishing order in the description of the hydration phenomenon came from the work of Marcus [6]. He proposed an empirical model and a method enabling the calculation of the hydration number from the thermodynamic data for a large number of electrolyte solutions. However, the developed model is not free of disadvantages not only because of the complexity of calculations but also the need to use the fitting parameters. On the other hand, the available non-empirical models are usually limited to the case of electrostatic forces described by assuming that the local permittivity remains constant, like in the bulk of aqueous medium [7]. In addition, without the consideration of hydrogen bonds, any description of aqueous solutions falls far from being completed.

From numerous studies of the hydration shell structure (see, for example, [8-10]), it follows that depending on the chemical nature of ions, the central hydrogen bonds may either create or destroy. This ability affects the structure and capacity of the ion hydration shell, which should also be considered in modeling.

Another difficulty in developing a non-empirical modeling approach for describing the solvation phenomenon is the need to know how the dielectric permittivity (DP) depends on the distance from the central ion at the site of the hydration shell formation. The local magnitude of DP is known to vary on the atomic scale from 1 to the bulk constant ε_b. This dependence can only be neglected at a sufficiently large distance from the charge (~1 nm) [16].

Considering ions of atomic sizes (~0.1 nm), we should take into account the variability of the local DP. The discreteness of the liquid assumes that the interaction energy of a molecule with an ion is averaged over the segment equal to the thickness of the monolayer. In the case of aqueous solutions, some

authors use the estimates of a discrete dependence specific for crystalline systems (containing one intermediate value between 1 and ε_b), ranging from 2 to 5 [11-13]. However, in an amorphous medium, the distribution of intermolecular distances is continuous, and such estimates turn out to be inaccurate. In the above-mentioned work [6], a continuous approximation is considered, but the use of fitting parameters reduces its significance. Other approximations of the continuous dependence are also not sufficiently universal [14-18]. In the author's recent paper [19], a useful non-empiric expression for the DP dependence on the distance was analytically derived:

$$\varepsilon = \varepsilon_b^{1-(r_0/r)^2},\ r \geq r_0 \qquad (1)$$

Nowadays, there are a number of articles using a semi-empirical approach to the energy description; they evaluate various patterns of ion-water clusters and choose some of them with a local or global minimum energy [20-22]. One of the positive features of those works is the suggestion of a dodecahedral structure of the first hydration shell of metal ions. The coordination number formed by hydrogen bonds for a molecule of such a shell is equal to 3. However, such approaches have a number of disadvantages affecting the results: (1) for the electrostatic field, the dependence of dielectric permittivity on the distance from an ion is not introduced; (2) hydrogen bonds are replaced by Coulomb forces; (3) such a replacement leads to inclusion of non-existent hydrogen bonds between the ion and water molecules.

The proposed study is devoted to the asymptotic description of the hydration shell of an ion by taking into account local electrostatics and the structure of hydrogen bonds without the use of empirical or fitting parameters.

Theory

Energy of hydration shell. The potential energy of an interaction between a point charge ez and a point-like dipole μ decreases as the inverse square of the distance: $\frac{ez\mu}{4\pi\varepsilon_0\varepsilon_b}r^{-2}$ (ε_0 is the vacuum constant; for simplicity, here and below, the charge and potential values are taken by modulus). Therefore, concentric monomolecular layers filled by dipoles of the number proportional to the area $4\pi r^2$, have the equal energy of interaction with the ion. We refer to a hydration shell as a set of all hydration monomolecular layers (where clarification is not required, we leave the accepted terminology, e.g. "first hydration shell", etc.). Consequently, the potential energy of the hydration shell is proportional to its effective thickness l. Neglecting the weak interaction of the dipoles with each other, and suggesting the DP is constant, we can write:

$$W_0 = \int_R^{R+l} \frac{ze\mu}{4\pi\varepsilon_0\varepsilon_b r^2} \times 4\pi r^2 c dr \approx \frac{ze\mu c_b}{\varepsilon_0\varepsilon_b} \times l, \qquad (2)$$

where c and c_b are the concentration of molecules in the spherical monolayer with the coordinate r and its average value for bulk, respectively; approximation $c \approx c_b$ is assumed; $R = r_I + r_0$ is the sum of the ion radius r_I and the molecule radius $r_0 = d/2$, where d is the diameter of the spherical molecule of the liquid (here, d=2.7 Å is the diameter of water molecule).

There exist such large ions for which the surface electrostatic potential is too low to hold the solvation shell. We denote as r_h the minimal radius of such non-solvated ions, having no solvation shell. Then,

$$l = r_h - r_I.$$

It follows from the definition of r_h, that the solvation shell forms only under the condition $r_I < r_h$.

Taking into account the variability of the local DP, the potential energy of the entire system of water layers around the ion can be expressed as an integral:

$$W = \frac{ze\mu}{\varepsilon_0}\int_R^{R+l}\frac{cdr}{\varepsilon} \equiv \frac{\Delta L}{l}\cdot W_0, \qquad (3)$$

where $R = r_I + r_0$. The integral term may be calculated analytically as a difference of functions:

$$\Delta L \equiv L(r_h + r_0) - L(r_I + r_0),\ L(x) \approx \varepsilon_b \int \frac{dx}{\varepsilon}.$$

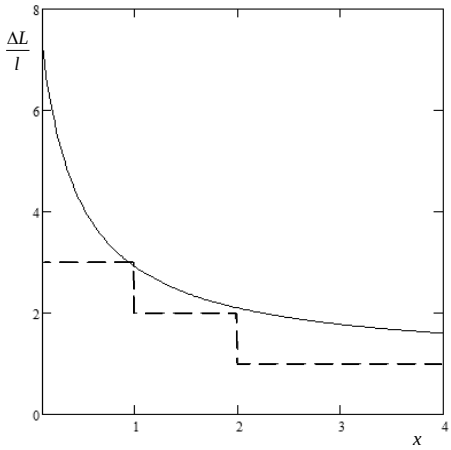

Fig. 1. Dependence of the coefficient in formula (3) on the coordinate of hydration shell. Upper boundary of the dependence, $I(x)$ (solid), and its approximation by the step function $I_a(x)$ (dashed)
Рис. 1. Зависимость коэффициента в формуле (3) от координаты гидратного слоя. Верхняя граница зависимости, (сплошная линия), и ее аппроксимация ступенчатой функцией (пунктир)

Substituting here Eq. (1), it is easy to calculate $L(x)$. The integral in Eq. (3) is the function of two variables:

$$\frac{\Delta L}{l} = f(R,l) \approx \frac{\varepsilon_b}{l}\int_R^{R+l}\frac{dr}{\varepsilon} \to \frac{\varepsilon_b}{d}\int_R^{R+d}\frac{dr}{\varepsilon} \approx f(R,d), \qquad (4)$$

where the arrow indicates the transition to a fixed parameter - the monolayer thickness, $l = d$. Note that from the energy point of view, by neglecting the change in entropy, the concept of "ion radius" (r_I) might be defined as a value up to an integer number of diameters of medium molecules. For example, the second hydration layer can be represented as the first layer of an ion with the radius increased by *d*. In this regard, the quantity *R* acquires the simple meaning of radial coordinate.

It is convenient to introduce a variable *x*, whose integer values enumerate the number of filled hydration layers, and the corresponding function:

$$I(x) = f(R,d)\,, \qquad x = d^{-1}(R - R_0), \qquad (5)$$

where $R_0 = min\, R$ is the minimal distance between the centers of the ion and the molecule of the first hydration layer, which cannot amount less than the sum of the Bohr radius a_0 and the radius of the water molecule r_0, i.e. $R_0 = a_0 + r_0$. Due to the minimum of R_0, function $I(x)$ limits the area of coefficients from above $\frac{\Delta L}{l}$. The value of the function for the first hydration layer up to its filling is equal to $I(0) = f(R_0, d) = 2.91$.

The discreteness of the molecular system of a hydrated ion is most clearly manifested in the first few layers. In the frame of the model approximation, the coefficient $\frac{\Delta L}{l}$ has the form of a step function of the layer number (Fig. 1):

$$I_a(x) = \begin{cases} 3{,}0 \le x < 1 \\ 2{,}1 \le x < 2 \\ 1, x \ge 2 \end{cases} \qquad (6)$$

Function (6) satisfies to the boundary conditions $I_a(x) \approx I(x)$ for $x = 0{,}1, \infty$.

It follows from the above analysis that the interaction energy of the filled first hydration layer is approximately 1.5 times greater than the energy of the filled second layer and 3 times greater than the energy of the third and subsequent layers.

According to the study [23], in the case of singly charged ions, the hydration shell contains only the first layer. The proposed model assumed a constant DP value, which, as shown here, should be 1/3 of ε_b, i.e. $\varepsilon = 27$ for aquatic environment at the normal temperature. This value was implicitly used in the cited article in accordance with the results of our previous work [24]. Thus, agreeing with the results of the article [23] on the parameters of the first hydration shell of the ion, the present study extends the action of

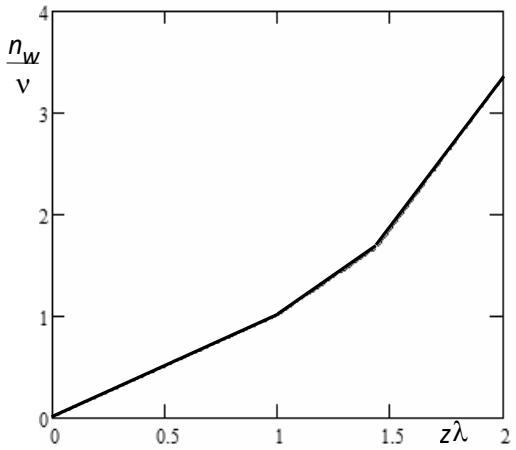

Fig. 2. Universal dependence (9) for the degree of population of the hydration shell $\frac{n_w}{\nu}$ on the ion parameters $z\lambda$.

Рис. 2. Универсальная зависимость (9) для степени заселенности гидратной оболочки $\frac{n_w}{\nu}$ от параметров иона $z\lambda$.

the model to the description of a multilayer hydration shell.

Filling degree of hydration shell. In the case of multiply charged ions, the first layer may overflow, and then it will be necessary to take into account the presence of the next layers.

In a monomolecular layer, the energy is related to the number of molecules, filling it, according to the Gibbs-Helmholtz thermodynamic equation $a_w dn = dW - TdS$, where a_w is the chemical potential. To estimate the maximum population of the shell, the entropy term should be omitted:

$$n^0 \equiv \frac{W}{a_w} = \nu_0 z \left(d^{-1} \int_R^{R+l} \frac{\varepsilon_b}{\varepsilon} dr \right) \quad (7)$$

Entropy correction to the hydration number in the form of $\frac{5}{2}\frac{kTr_0^2}{e\mu}\varepsilon$ (k is the Boltzmann's constant) at temperature $T = 293K$ has order of 0.01ε.

Without specifying the expression for the chemical potential, we note that the coefficient ν_0 introduced here has the meaning of the limiting population of the hydrate shell with the thickness $l = d$ of a singly charged ion ($z = 1$) at the absence of local dielectric inhomogeneity ($\frac{\varepsilon_b}{\varepsilon} = 1$), i.e. at $R \to \infty$. The term in parentheses in Eq. (7) within the framework of the model approximation is represented by a step function (6). For the first hydration layer, taking into account the coefficient 3, we find:

$$n^0 = 3\nu_0 z d^{-1}(r_h - r_I) \quad (8a)$$

Obviously, when the inequality $n^0 \le 3\nu_0$ is fulfilled, the entire hydration shell is placed in the first hydration layer. Otherwise, when the capacity of the first layer is filled up, other layers will be filled in the proportion corresponding to the ratio of the DEP values in the layers:

$$n^1 = 1.5(n^0 - 3\nu_0)\ 0 < n^1 \le 2\nu_0 \quad (8b)$$

$$n^2 = 2(n^1 - 2\nu_0) \qquad n^2 > 0 \quad (8c)$$

Opening the recurrence relations (8), we find the total number of molecules of the hydration shell (hydration number) $n_w = n^0 + n^1 + n^2$:

$$n_w = \begin{cases} \nu z\lambda \ , & 0 < z\lambda \le 1 \\ \frac{\nu}{2}(3z\lambda - 1)\ , & 1 < z\lambda \le \frac{13}{9} \\ \frac{\nu}{3}(9z\lambda - 8)\ , & z\lambda > \frac{13}{9} \end{cases} \quad (9)$$

where the designations $\lambda = d^{-1}(r_h - r_I)$, $\nu = 3\nu_0$ are introduced.

Fig. 2 demonstrates the graph of dependence of $\frac{n_w}{\nu}\frac{n_w}{\nu}$ ratio on $z\lambda$ in accordance with expressions (9).

The parameters (ν and r_h) of an ion hydration shell can be found in its geometric model. Note, since the energy of interaction between an ion and a water molecule de-

creases by an order of magnitude when passing from the first monolayer to the second one, the first layer geometry mainly determines the properties of the entire hydration shell.

Types of hydration shell structure. When an electric charge is placed in the aqueous phase, a hydration shell forms around it an isotropic structure. The obvious characteristics of the hydration shell around an ion include the size and charge of the ion, which determine the electrostatic interaction of the ion with the shell molecules. However, additional interaction is possible in water by the mechanism of hydrogen bond formation. Obviously, the difference between ions containing atoms of hydrogen, oxygen, and some other elements capable of participating in hydrogen bonds, and other ions, such as metal ions that do not have this ability, is reflected in the properties of the hydration shell.

We refer to "structure-making" ions that can form hydrogen bonds as W-ions (water-like), and "structure-breaking" ions that cannot form hydrogen bonds as M-ions (metal-like). The structure of the hydration layer with its almost spherical symmetry can be represented as a regular polyhedron with water molecules at its vertices. Determined by hydrogen bonds of water molecules, the coordination number (CN) of a molecule is equal to 4 for the structure of ice. In the aqueous phase, remaining the same on average (approximately 3.8 at the normal conditions [8]), and being an integer locally, the CN varies from 3 to 5. Due to the destruction of ice-like structures, the state with CN=4 is implemented in no more than 43% of cases – according to the percolation theory [25, 26]. It is easy to estimate for an aqueous phase that the three states of water molecules with CN 3, 4, or 5 are in approximate ratios of 2:2:1. The degree of binding of molecules in the hydration shell depends on the chemical type of the ion: CN 3 corresponds to type M, which destroys the network of hydrogen bonds, and CN 5 corresponds to type W, which creates new hydrogen bonds. We assume that there is no intermediate type of ions, which do not disturb the quasicrystalline structure of water with CN 4. This assumption is confirmed by the existence of the phenomenon of salting out when water freezes.

Such the types refer to both cations and anions. Therefore, three classes can be differentiated for ionic compounds, i.e., MM, MW, and WW.

Capacity of the first layer of hydration shells. An ion of M-type, when placed in an aqueous medium, destroys the network of the nearest hydrogen bonds in the radial direction. Such a process is characterized by decreasing CN (formed by hydrogen bonds) of water molecules. The destruction of radial bonds that stabilize the ice-like structure, which is less dense than water in equilibrium with ice, leads to system instability accompanied by its transfer into a denser state. In the process of destruction of a regular configuration, which has identical mutually attracting bodies located at the vertices, the system tends to transfer into the nearest local minimum of potential energy, corresponding to the movement of bodies to the centers of the faces. The original polyhedron is transformed into a dual regular configuration with a higher density at a lower thermodynamic potential. Among Platonic solids, two pairs are presented by the mutually dual polyhedra, one is a cube and an octahedron, and the other – is a dodecahedron and an icosahedron. The second pair of polyhedra has the required variants of CN. Thus, depending on the degree of binding of water molecules by hydrogen bonds, the capacity of the first hydration shell is equal to the number of vertices of a regular dodecahedron with 20 vertices with CN 3 (the case of an ion of the M type), or of its dual regular icosahedron with 12 vertices with CN 5 (the case of an ion of the type W). Both configurations are stationary states of the ion hydrate shell. The difference in the potential of these states of water molecule can be estimated by the Boltzmann law, relating the population of a level to its potential and the temperature. The differ-

ence in levels for the aforementioned configurations is equal to $kT\left|ln\frac{\nu_2}{\nu_1}\right| = kT\,ln\frac{5}{3} \approx 0.5kT$, which is ten times less than the energy of intermolecular interaction in water.

Energetic relations of structural model. Thus, the potential of a water molecule from the dodecahedral configuration is slightly lower than one from the icosahedral configuration. Judging from the postulate of structural chemistry that all the actual energy of a figure is contained in its bonds, when the task is to equalize (in the first approximation) the potential energy per a molecule of hydration layer, it is required that 5 bonds of the icosahedron have the energy of 3 bonds of the dodecahedron. This scenario is possible because the energy of point dipoles in the field of electric charge is inversely proportional to the square of distance. Therefore, the configuration with CN 5 should have longer sides than the configuration with CN 3, namely, the squares of intermolecular distances should be related as 5 to 3.

In the process of disjunction of the neighboring molecules located in the dense medium of a concentrating field of an ion, the freedom of rotation of molecules to the energetically correct position appears. Therefore, in the case of longer bonds, the arrangement of water molecules is such that the hydrogen atom is located on the segment between neighboring oxygen atoms following the nature of hydrogen bonds. The center of the dipole of the water molecule is located near the boundary of the oxygen atom. Therefore, the average distance between the centers of freely rotating water dipoles is approximately equal to the distance between the oxygen nuclei minus the atomic radius of oxygen. The well-known uncertainty in the size of an atom in a molecule makes it necessary to consider the distance between dipoles approximately equal to the length of the hydrogen bond between the proton and the oxygen nucleus of neighboring molecules. It was shown previously [27, 28] that the energy of a hydrogen bond at the boundary of the region of its existence, as well as the interaction between a charge and a dipole, obeys the inverse-square distance law. Therefore, assuming the approximate equality of the potentials of the configuration variants of the first hydrated layer, we obtain the following ratio between the lengths of the edges:

$$\left(\frac{x}{y-0.96}\right)^2 = \chi \cong \frac{3}{5}, \qquad (10)$$

where *x* and *y* are the edges (in Å) of the dodecahedron and icosahedron, respectively (in the denominator, the length of OH covalent bond, 0.96 Å, is subtracted).

In fact, as noted above, the potential energy of the hydrate layer molecule in the dodecahedron configuration is lower than that in the icosahedron. After correcting for the Boltzmann factor, we obtain an estimate for the relative difference in the potential energy of a water molecule in different configurations: $\delta \equiv \frac{\Delta E}{E} = \frac{kT}{E} ln\frac{5}{3} \approx 0.085$, where the normal temperature and energy of one H-bond of water are introduced. Accordingly, in the second approximation, the value χ is corrected:

$$\chi = \frac{\frac{3}{2}E+\delta\cdot E}{\frac{5}{2}E} = \frac{3+2\delta}{5} = 0.634.$$

The corrected equation (10) has the form:

$$\left(\frac{x}{y-0.96}\right)^2 = 0.634 \qquad (11)$$

Minimal radius of non-hydrated ion. The hydration shell undergoes transitions between dodecahedral and icosahedral structures, which involve the formation or breaking of hydrogen bonds. When the hydrogen bonds in the icosahedron are broken, a dodecahedron-shaped dual structure of the shell is formed. Figure 3 shows how this dodecahedron is achieved by repositioning water molecules from the vertices to the centers of the faces of the icosahedron.

Thus, there is a geometric condition for two possible configurations of the first hydration layer: the radius of the inscribed sphere for the icosahedron must be equal to the radius of the circumscribed sphere for the dodecahedron:

$$R_s^{'} = r_s \equiv \kappa R_s \qquad (12)$$

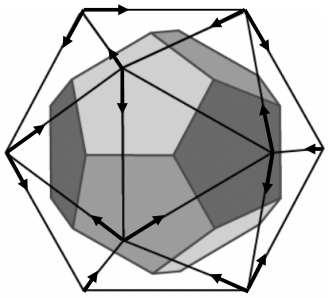

Fig. 3. Geometric model of the first hydration layer of an ion: regular icosahedron - for ions of type W, and regular dodecahedron inscribed in it - for ions of type M. Oxygen atoms are located at the vertices. The ends of the arrows indicate the arrangement of hydrogen atoms

Рис. 3. Геометрическая модель первого гидратного слоя иона: правильный икосаэдр - для ионов типа W, вписанный в него правильный додекаэдр – для ионов типа M. В вершинах расположены атомы кислорода. Концы стрелок обозначают вариант расположения атомов водорода

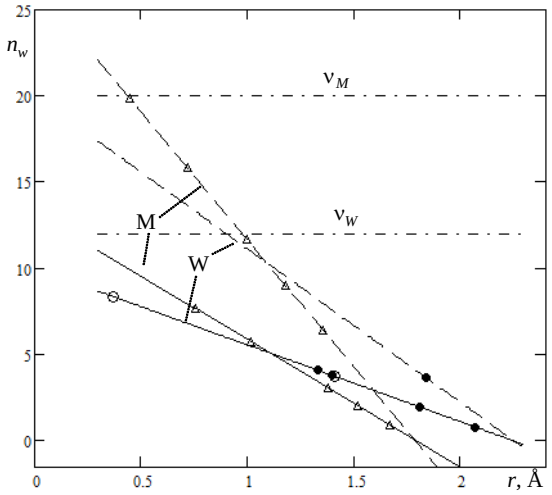

Fig. 4. Theoretical dependences (15) of hydration numbers on ionic radii for single charged (solid lines) and double charged (dashed lines) ions of two types: W – water-like; M - metal-like. Dots represent the values of the hydration number of ions, taken from Table 1: empty icons indicate cations, filled icons - anions.

Рис. 4. Теоретические зависимости (15) гидратных чисел от ионных радиусов для однозарядных (сплошные линии) и двухзарядных (штриховые линии) ионов двух типов: W – водоподобных; M – металлоподобных. Точками представлены значения гидратного числа ионов, взятые из таблицы 1: пустыми значками обозначены катионы, закрашенными - анионы

Here, the following designations are introduced: $\kappa \equiv \frac{r_s}{R_s} = \frac{r_s^{'}}{R_s^{'}} = 0.795$; r_s, R_s are the radii of inscribed and circumscribed spheres of the icosahedron ($R_s = 0.9510y$; $r_s = 0.7557y$); $r_s^{'}, R_s^{'}$ are the radii of inscribed and circumscribed spheres of the dodecahedron ($R_s^{'} = 1.401x; r_s^{'} = 1.114x$). Accordingly to Eq. (12) we obtain: $x = 0.5394y$. Substitution of this relation into Eq. (11), allows for determining the sides of the polyhedra:

$$y = \frac{0.96\sqrt{\chi}}{\sqrt{\chi} - 0.5394} = 2.98\text{Å}, \; x = 1.60\text{Å}.$$

Note that, in full accordance with the assumption about the nature of the bond in the icosahedron, its edge is equal to the distance between the oxygen atoms in the water dimer. The distance x=1.60Å between oxygens in the dodecahedron is related to a strongly compressed state. However, x significantly exceeds the length of the peroxide

Table 1. Theoretical values of the hydration numbers of ions obtained by substituting parameters (14) into formulas (9)

Таблица 1. Теоретические значения чисел гидратации ионов, полученные путем подстановки параметров (14) в формулу (9)

Ion	Type	Charge/*e*	Radius/Å [30, 31]	$z\lambda$	Hydration number		
					theory (9),(14)	[6]/[29]	[23]
H^+	W	1	0.37	0.692	8.3	2.7*/12	8
Li^+	M	1	0.76	0.38	7.6	5.2	8
Na^+	M	1	1.02	0.285	5.7	3.5	6
NH_4^+	W	1	1.40	0.308	3.7	2.4	4
K^+	M	1	1.38	0.15	3.0	2.6	3
Rb^+	M	1	1.52	0.1	2.0	2.4	2
Cs^+	M	1	1.67	0.044	0.89	2.1	0
Be^{2+}	M	2	0.45	0.99	19.8	16.0/18.0	-
Mg^{2+}	M	2	0.72	0.79	15.8	10.0	-
Ca^{2+}	M	2	1.00	0.585	11.7	7.2	-
Sr^{2+}	M	2	1.18	0.45	9.0	6.4	-
Ba^{2+}	M	2	1.36	0.32	6.4	5.3	-
Al^{3+}	M	3	0.54	1.39	31.7	20.4	-
OH^-	W	1	1.40	0.317	3.8	2.7	-
F^-	W	1	1.33	0.342	4.1	2.7	-
Cl^-	W	1	1.81	0.167	2.0	2.0	-
HS^-	W	1	2.07	0.067	0.80	1.7	-
S^{2-}	W	2	1.84	0.3	3.6	3.9	-
P^{3-}	M	3	2.12	-0.37	0	-	-

*H_3O^+

covalent bond (1.47 Å). The estimates obtained are in qualitative agreement with the results of Mancinelli et al. [10].

The maximum radius of a spherical ion that can be placed in the polyhedron, which simulates the first hydration layer, is equal to the radius of the inscribed sphere. The ion of this size is devoid of hydration water due to a lack of space. Therefore, the minimum size of unhydrated ion (r_h), which serves as the parameter of Eq. (9), is equal to the radius of the inscribed sphere. Radii of inscribed spheres of the polyhedra are: $r_h(M) = r_s^{'} = 1.79$Å, $r_h(W) = r_s = 2.25$Å, i.e.

$$\frac{r_h}{d} = \begin{cases} 0.663, \text{"M"} \\ 0.833, \text{"W"} \end{cases} \quad (13)$$

Results and discussion

Substitution of the following parameters of the considered configurations

$$\nu_M = 20, \lambda_M = 0.663 - \frac{r_I}{d};$$
$$\nu_W = 12, \lambda_W = 0.833 - \frac{r_I}{d} \quad (14)$$

(respectively, dodecahedral and icosahedral) into expressions (9) leads to expressions for the variants of populations of the hydration shell. In the important case $0 < z\lambda \leq 1$, we have:

$$n_w = \begin{cases} 20z\left(0.663 - \frac{r_I}{d}\right), \text{"M"} \\ 12z\left(0.833 - \frac{r_I}{d}\right), \text{"W"} \end{cases}, \quad (15)$$

Obviously, $n_w = 0$ at $\lambda \leq 0$. Plots of the functions (15) are presented in Figure 4.

Fig. 4. Theoretical dependences (15) of hydration numbers on ionic radii for single charged (solid lines) and double charged (dashed lines) ions of two types: W – water-like; M - metal-like. Dots represent the values of the hydration number of ions, taken from Table 1: empty icons indicate cations, filled icons - anions.

According to the graph, the filling of the first hydration layer for a single charged ion of type M does not exceed half of the capacity. Therefore, the hydrate molecules will

not be subject to deformation, because the distance between neighboring molecules will be established at least $\sqrt{3}x = 2.77$Å. For multiply charged ions of type M, saturation of the first hydration layer is possible. In this case, the attraction energy of hydrate molecules greatly increases and becomes comparable to the energy of a weak covalent bond. This ensures their compressed state, in which the distance between neighboring molecules decreases to 1.6 Å.

Thus, formulas (9) and (14) contain the result of the approach under development. In Table 1, the theoretical values of the hydration numbers of some ions are compared with the literature data obtained from the analysis of experimental studies [6, 23, 29]. For instance, the data of the study [23] were obtained from the ion exchange constants in the ion chromatography experiment. It should be underlined that our calculations correspond to extrapolation of the hydration number to a temperature of 0 K and does not take into account the contribution of entropy, which at normal conditions reduces the result by about $0.01\varepsilon = 0.3 \div 0.8$.

Almost all the ions presented in the table obey the condition $z\lambda \leq 1$. For beryllium, equality is achieved ($z\lambda = 1$). Only for aluminum we have $z\lambda = 1.39 > 1$ and, according to the model, it has the first hydration layer filled up, and the second layer approaches the complete filling. Smith et al. [9] studied the effect of anions on the structure of the surrounding water. They proved that halides and hydroxyl ion do not destroy the structure of water and can be classified as W-type entities. Schulz and Hartke [20] applied CN=3 to water molecules surrounding alkali metal ions, confirming our conclusion that such ions are M-type. Regarding lithium and calcium ions, Gonzalez et al. [21] obtained the hydration numbers of 4 and 8, respectively; however, a similar work [22] resulted in 10 for the water cluster of the lithium-ion.

Conclusions

The proposed model of the ion hydration shell is based on the description of the network of hydrogen bonds and features of the electrostatic field on the atomic scale. It is shown that the first hydration shell makes the main contribution to the hydration energy. We have shown that the properties of the hydration shell are mainly determined by its geometry, which is represented by Platonic bodies such as dodecahedron and icosahedron. Depending on the ability of ions to form hydrogen bonds, the variants of the structure of the first hydrate shell are defined as metal-like and water-like. The threshold values of radii of the ions for which there is no hydration are found. The capacity values of hydration monolayers are determined. Expressions are derived for the hydration number of ions of different sizes, charges, and different abilities to form hydrogen bonds. The estimates made for the hydration number of various cations and anions successfully correspond to the experimental values within the limits of the discrepancy in their interpretation.

The present theory has been developed for simple spherical ions; however, it can be further improved to describe more complex cases of irregularly shaped ions.

Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work presented in this paper.

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