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ESTIMATION OF SOLVATE SPHERE SIZES OF CATION AQUACOMPLEXES IN SALT SOLUTION

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The problem of determination of sizes of supermolecular formation (a cluster) consisting of the molecules of water coordinated around a central ion has been analytically solved. The obtained values of the cation aquacomplex point out the possibility of exciting their drift by applying asymmetric electric field with frequency in the range from hundreds of Hz to units of kHz on aqueous salt solution. Drift parameters are determined by inertial properties of aquacomplexes that allows dividing them.

Introduction

On solution of salts the complex formation takes place as a result of which solvated complexes (in aqueous solutions – hydrated complexes) are formed [1]. Formation of cation aquacomplexes is explained by donor-acceptor interaction of a cation with water molecule, but that of anion complexes is due to hydrogen bond. These interactions are the basis of the process of primary hydration. Aquacomplexes, in their turn, are also hydrated. I.e. around each of them water molecules are coordinated owing to hydrogen bond. Orientation and positioning of water molecules on this stage is the base of rehydration process. Solvation sphere is formed by the definite quantity of water which is equal to the number of hydration [2]. Each molecule of water presents an element of solvation sphere, the state of which is defined by the position with respect to cation. Hereafter water molecule forming the sphere is referred to as solvation group. Many physical properties of solutions are defined by the size of aquacomplexes which, in their turn, are connected with cation parameters.

In the experiments on electric field influence of high frequencies on aqueous salt solutions of rare-earth and alkali metals a stable effect consisting in the following has been found. Unexcited aquacomplex, the solvation sphere of which is not deformed, is neutral. The sphere performs the function of screen which prevents from the action of constant constituent of high frequency electric field. Here the constituent forming the conical form of Fourier series expansion of periodic signal of any form is meant [3]. Deformation of solvation sphere and, therefore, formation of polarization charge in aquacomplex provides the conditions for action of constant constituent of the field and excitement of directed aquacomplex drift [4, 5]. The purpose of the given work is to define the sizes of solvation sphere of cation aquacomplexes on the basis of the main statements of electrodynamics of continuum and, hence, their properties which appear under the action of high frequency electric fields.

According to the basic statements of quantum mechanics, for linear system of rigidly bounded particles frequency ν_p , corresponding to the basic rotational state is defined by the relation [6]:

$$\nu_p = \frac{h}{4\pi^2 I}, \quad (1)$$

where $I = \frac{m_1 \cdot m_2}{m_1 + m_2} \cdot r_0^2$ – moment of inertia of the system; m_1 и m_2 – masses of the particles; r_0 – distance between

them; h – Planck's constant. It is seen from the relation that the determining influence on the value ν_p is exerted by the value of the distance between the particles forming oscillating system.

In the very first approximation to determine the order of the magnitude ν_p as a calculation analogue for solvated cation a two-particle system with similar properties will be used. One of the particle of the system is cation, the second one is solvation sphere formed by solvation groups. Even in such rough consideration there appear three complex questions dealing with the structure of aquacomplex.

The first question is what is the value of sphere radius formed by water molecules which are structured in the electrical field of the cation?

If one assumes that it is equal to the radius of solvation sphere, then there appears the next question – what solvation sphere: as a result of primary or secondary hydration?

The second question is what is the number of solvation groups within the sphere equal to, i.e. what is the mass of aquacomplex equal to? If one assumes that the field affects the solvation sphere formed by the primary hydration, then the number of solvation group is to correspond to the coordination number of cation. If the field affects the sphere formed by the secondary hydration, then the additional suppositions are necessary.

The third question is could we restrict our consideration to the secondary hydration? At present the mechanism of ion-molecular interaction remains unclear. There are some experimental data [7] that testify that the size of solvation spheres in aqueous electrolytes amounts several tens of water molecular diameter. According to [8] the energy of ion-dipole interaction becomes quickly weaker and cannot provide structuring of water polar molecules in the electric field of the central cation at the distances of more than 100 of water molecule diameters. Thus, the radius of the aquacomplex amounts to not less than ten diameters of water molecule. Within the sphere of such radius not less than 10^5 of solvation groups are situated. Thus, if the radius of aquacomplex is 100 diameters of water molecule (about $1,93 \cdot 10^{-6}$ sm), then in the volume of the sphere formed by this radius there must be nearly $9 \cdot 10^5$ solvation group. There are also experimental data testifying that the introduction of bulk charge into a low conductive liquid is accompanied by forming the supermolecular formation. From the

estimation of associated mass of water structured around each ion it follows that the radius of such supermolecular formation – «cluster» – amounts about 1 mkm. In the sphere of the volume equal to such cluster there must be more than 10^{10} molecules of water.

To determine the value ν_p it is necessary to choose the approximation according to which the value r_0 – the distance between cation and solvated sphere associated into one particle at quantum-mechanic description is set. Suppose that r_0 is equal to the distance at which the cation electric field does not result in structuring polar molecules of water.

The value r_0 , determined for the solvation sphere at the primary hydration of La^{3+} cation amounts 2,74 Å for $n=9$. Consider the system formed by cation and solvation OH_2 groups, which are associated in supermolecular formation – in cluster. Suppose that rotary (directed perpendicular to bond line) motion of cluster with respect to cation. In this case the value of r_0 amounts not less than ten diameters of water molecule, but the mass of the structured water in the sphere is equal to the order of 100 masses of water molecule. The estimations made by the relation (1) show that in these assumptions the value ν_p corresponds to about 32 MHz and about 21 MHz for Y and La aquacomplexes correspondingly. In the table the hypothetic (expected) values ν_p of obtained at different assumptions relatively to efficient (real) value of r_0 and efficient (real) mass of the associated solvation group are presented.

The estimations shows that the quantity of solvation OH_2 groups structured around the ion within the solvation sphere do not significantly influence the value of frequency. The size of Solvation sphere is conditioning, to be more precise – supermolecular formation consisting of solvation groups.

Table. The hypothetic frequencies of excitement of rotation motion of solvation groups in aquacomplex, ν_p , Hz

Ion	Y^{3+}	La^{3+}
$r_0=50d_{\text{H}_2\text{O}}$ $m_2=10^3m_{\text{H}_2\text{O}}$	$1,2 \cdot 10^6$	$7,8 \cdot 10^5$
$r_0=100d_{\text{H}_2\text{O}}$ $m_2=4 \cdot 10^3m_{\text{H}_2\text{O}}$	$3,0 \cdot 10^5$	$1,9 \cdot 10^5$
$r_0=0,5$ mkm (cluster) $m_2=10^3m_{\text{H}_2\text{O}}$	452,4	290,4

In the previous experiments [4] the induced, directed drift and accumulation of solvated cations of lithium near isolated potential grid placed in the aqueous salt solution of LiCl was observed. The asymmetric electric voltage of high frequency was applied to the grid. The field appeared between the potential and grounded grid which was also in the solution. The field geometry is homeotropic. The effect had a stable character at the frequency of the external field in the range of 5...50 kHz, the amplitude of field intensity 1...20 W/sm and the symmetry coefficient 1...0. In this connection the experiments were made in which the water solution of MgCl_2 and CaCl_2 salts was affected by asymmetric electric field with the frequency in the range of 2...10 kHz. Chelatometric titration of the solution probes exposed to the field showed the presence of the effect of selective drift of Mg^{2+} and Ca^{2+} cations.

The frequency intervals stated in the experiments permit to estimate the value of the efficient (real) magnitude r_0 in the approximations mentioned above. It amounts several hundreds of «diameters» of water molecule [9].

The sizes of supermolecular formation – «cluster»

According to Debye-Huckel's theory [2], the basic characteristics determining the size of supermolecular formation – «cluster» is electric potential and its distribution around the ion (cation or anion) located in the continuum formed by polar molecules of water.

Suppose that Poisson's equation connecting charge density with potential is applicable to the distribution of charge:

$$\nabla^2\psi(r) = -4\pi\rho(r)/\varepsilon, \quad (2)$$

where ∇^2 – Laplace operator; ψ – potential; ρ – charge density in point r , for which the potential is calculated; ε – dielectric permittivity.

Charge density ρ in Poisson's equation (2) is a difference between the number of positive and negative charges in a volume unit located at a distance from the central ion. The potential at this distance is equal to ψ .

For salt concentration in aqueous solutions providing the condition $n_i \ll n_{\text{H}_2\text{O}}$, where $n_{\text{H}_2\text{O}}$ – quantity of water molecule in a unit of volume, n_i – that for the quantity of ions, one can assume that: *the potential becomes negligibly small at the distances less than the distance between the nearest ions.*

Then the charge density ρ is nothing else but density of the polarised charge formed by polarization of water molecules. In formalism, used in continuum electrostatics, one does not need the consideration of each point charge. Polarised charge is considered to be continuous, that is the result of the statistic averaging [2].

Polarization of water molecule can result in attaining both positive and negative polarised charge. If consider a cation, its field deforms the generalized electron shell of water molecule and cause the formation of positive polarised charge at a distant end of dipole from cation. If anion, it cause that of negative one.

In any case the quantity of polarized water molecules having the potential ψ is defined by Boltzmann equation

$$n_{\text{pol}} = \bar{n} \cdot \exp\left(-\frac{U}{kT}\right),$$

where \bar{n} – average number of water molecules in a unit of volume of solution, U – Their energy corresponding to the potential ψ , T – temperature, k – Boltzmann's constant.

The energy of polarized water molecules having the potential ψ is defined by the expression:

$$U = q_{\text{H}_2\text{O}}\psi,$$

where где $q_{\text{H}_2\text{O}}$ – polarized charge of the molecule. The polarized charge resulted from displacement of electron distribution induces an additional dipole moment.

Thus,

$$n_{\text{pol}} = \bar{n} \cdot \exp\left(-\frac{q_{\text{H}_2\text{O}}\psi}{kT}\right).$$

The polarized charge of the molecule (dipole) is proportional to the ion charge (cation or anion) [10]. Its value is also defined by the quantity of water molecules which are «arranged» in lines connecting ion and the molecule involved, and screens the ion field [11]. Thus, the polarized charge is inversely proportional to the quantity of water molecule which is between the ion and the molecule involved. This quantity is directly proportional to the volume of sphere formed by these «screening» molecules, i.e. to the cube of the distance between the ion and the molecule. In this connection one might write down:

$$q_{\text{H}_2\text{O}} \sim \frac{Cq}{r^3},$$

where $C = \text{const}$ – coefficient of proportionality, q – ion charge, r – distance between the ion and the molecule for which the polarized charge is defined.

Thus, the density of polarised charge is defined by the relation:

$$\rho = q_{\text{H}_2\text{O}} n_{\text{noi}} = \bar{n} \frac{Cq}{r^3} \cdot \exp\left(-\frac{Cq\psi}{r^3 kT}\right). \quad (3)$$

The expression defining the value of the constant C can hardly be obtained from general physical factors. But one can state that the equation defining the distribution of potential around ion has the view:

$$\nabla^2 \psi = -\text{const} \cdot q f(T) \frac{1}{r^3}. \quad (4)$$

The sense is to define the relation describing the distribution of the potential around the ion placed in the dielectric medium from electrostatic equations.

The density of polarized charge is defined by the relation:

$$\rho_{\text{noi}} = -\nabla \vec{P}, \quad (5)$$

where vector of polarisation \vec{P} is linearly connected with vector of electric field \vec{E} intensity provided by ion:

$$\vec{P} = \chi \varepsilon_0 \vec{E},$$

where χ – dielectric sensitivity of the dielectric, ε_0 – electric constant of vacuum.

The ion having the charge q creates the field in dielectric medium the distribution of which is described by the relation:

$$\vec{E} = \frac{q \cdot \vec{r}}{4\pi \varepsilon_0 \aleph r^3},$$

where $\aleph = 1 + \chi$ – relative electric permittivity, \vec{r} – position vector the beginning of which coincides with the geometric centre of ion.

The relation (5) describes the distribution of the resultant charge in the dielectric provided by heterogeneous polarization.

Taking into account that radial component if the vector of electric field intensity $E_r = \frac{q}{4\pi \varepsilon_0 \aleph r^2}$, but the field of the central ion is spherically symmetrical, it is easy to obtain the relation:

$$\rho_{\text{noi}} = \chi \frac{q}{2\pi \aleph} \cdot \frac{1}{r^3}.$$

As in the previously obtained relation (3), the density of polarized charge is inversely proportional to the third degree of the distance counted from ion centre.

At the absence of electric field some molecules of water are oriented in different directions by chance; therefore, the total dipole moment in a unit of volume equals to zero [10].

In the electric field of the central ion (cation or anion) the two processes take place at once: firstly, additional dipole moment is induced due to the forces acting on electrons (electron polarizability); secondly, electric field tends to arrange separate molecules creating the resultant, different from zero moment in a unit of volume. The molecule collisions do not permit them to follow the strictly fixed direction at their chaotic Brownian motion, but the formation of supermolecular structure (cluster) does take place [8].

Taking into account that dipole energy in the electric field $U = -\vec{p}_0 \cdot \vec{E}$ (\vec{p}_0 – dipole moment of the molecule) and that in the state of thermodynamic equilibrium (according to Boltzmann's statistics) the number of the molecules with potential energy U is proportional to $\exp\left(-\frac{U}{kT}\right)$, one can easily obtain the relation:

$$\chi = \aleph - 1 = \frac{\bar{p}}{\varepsilon_0 \vec{E}} = \frac{\bar{n} p_0^2}{3\varepsilon_0 kT}.$$

Thus:

$$\rho_{\text{noi}} = \frac{\bar{n} p_0^2}{3\varepsilon_0 kT} \cdot \frac{q}{2\pi \aleph} \cdot \frac{1}{r^3},$$

but Poisson equation is written down in the form:

$$\nabla^2 \psi = -\frac{2}{3} \cdot \frac{\bar{n} p_0^2 q}{(\varepsilon_0 \aleph)^2 kT} \cdot \frac{1}{r^3}, \quad (6)$$

which is in agreement with the expression (4), obtained in the range of Debye-Huckel approximation.

The equation (6) is suitable to rewrite in the form:

$$\frac{d^2 \psi}{dr^2} + \frac{2}{r} \cdot \frac{d\psi}{dr} = \frac{a}{r^3}, \quad (7)$$

where $a = -\frac{2}{3} \cdot \frac{\bar{n} p_0^2 q}{(\varepsilon_0 \aleph)^2 kT}$.

Boundary conditions for Poisson's equation applicable to the case involved are written down in the view:

$$\psi(r=r_0) = \psi_0; \quad \psi(r \rightarrow \infty) = 0, \quad (8)$$

where r_0 – ion radius, ψ_0 – ion potential. The equality of potential to zero in infinite moving off from the point charge follows from the basic statements of electrostatics and electrodynamics of continuum [11]. Ion potential is defined as a potential of uniformly discharged sphere (charge q) with radius r_0 [12].

The equation (7) is a linear heterogeneous equation of the second order with variable coefficients. Its solution has the view:

$$\psi(r) = -\frac{1}{r} (\ln \frac{C_1}{r^a} - a) + C_2,$$

where C_1 and C_2 – constants defined by boundary conditions (8). It is seen that according to the second bound-

dary condition $C_2=0$, but the use of the first one provides the possibility to define:

$$C_1 = r_0^a \cdot \exp(r_0 \psi(r_0) + a).$$

For example, in ISU system, the value C_1 amounts 1 for ions Y^{3+} and Ce^{3+} . Value a in ISU system amounts $-1,951 \cdot 10^{-10}$ for $T=298$ K and $q=3|\bar{e}|$, where \bar{e} – electron charge.

Electric field intensity like function r in the spheric coordinate frame in the case of central symmetry is defined by the relation:

$$E_r(r) = -\frac{d\psi}{dr} = -\frac{1}{r^2} \cdot \ln \frac{C_1}{r^a}.$$

Theoretical and experimental investigation of the processes of nanometric functional structure formation [13] shows that due to dipole-dipole interaction of water molecule it is possible to build bridges in the inelectrode gap. In this case there is a critical electric field E_{kp} to form molecular bridges:

$$E_{kp} = \frac{1}{\alpha} \cdot [(p_0^2 + 2\alpha kT)^{1/2} - p_0],$$

where α – polarizability of water molecule.

In figure the view of the function $E_r(r)$ is presented for cation Y^{3+} at $r=0,2\dots 1,0$ mkm.

At $E > E_{kp}$ polarized molecules are connected by dipole-dipole interaction and oriented in the direction to the field of central ion. At $E < E_{kp}$ heat motion of molecules is to break bridges. Radius of cluster can be estimated from the condition $|E|=|E_{kp}|$ that is from the relation:

$$\frac{1}{r_{kc}^2} \ln \frac{C_1}{r_{kc}^a} \approx \frac{1}{\alpha} [(p_0^2 + 2\alpha kT)^{1/2} - p_0]. \quad (9)$$

The given condition means that at $r=r_{kc}$ the field of central ion gets «balanced» by the oppositely directed field of «the bridge» of the arranged dipoles. That is, hydrated shell of arranged dipoles screens the central ion.

Solution of transcendental equation (9) at $T=298$ K permits to define the cluster radius formed by structured

water molecules around cation Y^{3+} . Its value amounts about 0,276 mkm.

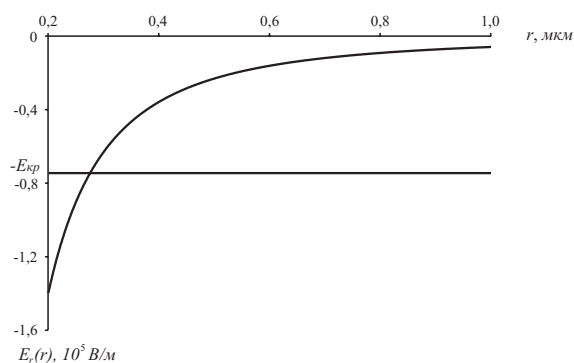


Figure. Distribution of electric field $E_r(r)$ intensity of cation Y^{3+} placed in water under normal conditions (spheric coordinate frame, central symmetry)

Conclusion

Thus, the investigation carried out points out that the sizes of supermolecular formations (clusters), which are formed by polarized molecules of water around point ion of metal amounts from 0,5 to 1,0 mkm. Radius of cluster is defined by the solution of self-consistent problem of distribution description of polarised charge in the dielectric medium, where a «sample» point charge is placed. Within each cluster there are from $1,75 \cdot 10^{10}$ to $1,4 \cdot 10^{11}$ molecules of water. Values of characteristic frequencies of excitement of revolute-translational motion of cation aquacomplexes (units – tens kHz) indicate that one must not restrict by considering only secondary hydration examining complex formation in aqueous salt solution. In this case a more concrete thing is to use the term «close» and «far» hydration introduced by O.Ya. Samoylov [14].

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