ABOUT SIZES OF THE HYDRATED
SALT IONS – THE COMPONENTS OF SEA WATER

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Facing severe and increasing shortage of fresh water on the planet that can even lead to local conflicts, methods of seawater desalination for industrial and municipal purposes become urgent. The article gives a model of estimation of the size of hydrated ions, the components of seawater.

Keywords: seawater desalination, hydrated ions, size of hydrated ions

Distillation desalination method leads to huge electricity consumption and therefore alternative, less expensive ways are being searched for. Construction and operation methods of desalination with the help of various membranes (e.g., the method of reverse osmosis) involve large energy and economic costs. In particular, for desalination of 1 cubic meter seawater not less than 400 kilowatts of electricity and the pressure to 6,5 MPa (65 atm) are required. When the mesh size has a radius of 0,1 nm, the costs are much more than the production of the membrane with a radius of 0,2 nm. Since the radii of hydrated ions are significantly (almost twice) larger than the radius of a water molecule (0,138 nm) passed through the membrane, then the estimation of the size of hydrated ions, the components of sea water

(mainly: Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}) for the manufacture of membranes with optimal size becomes meaningful because of lowering operating pressures and reducing costs of manufacturing devices for desalination.

As a rule available information on individual n_S ions, benchmarks for assessing the size of hydrated ions, determined by Russian and foreign researchers differ by several units. For example, the hydration number of K^+ ion is 16 by Remy and 1,9 – by Robinson-Stokes equations. The high value of the hydrated potassium ion by Remy can be explained by the fact that the model of ionic hydration involving all water molecules in the formation of hydration shells, which, of course, could not be possible.

For some ions these numbers are given in table 1.

Table 1

Values of ions hydration according to various authors

Author	Method	Hydration numbers					
		Na$^+$	K$^+$	Mg^{2+}	Ca^{2+}	Cl$^-$	SO$_4^{2-}$
I	a	–	16	–	–	–	–
II	b	8,4	5,4	–	–	–	–
III	b	–	22	–	–	–	–
IV	b	16.9	9.6	–	–	–	–
V	c	3	4	–	–	–	–
VI	d	3,5	1,9	–	–	–	–
VII	e	4,03	2,69	5,33	3,64	1,70	2,34

N o t e s : I – Remy; II – Washbourne; III – Rosenfeld; IV – Smith; V – Brinttsmiger; VI – Robinson and Stokes; VII – Baldanov and Tanganov. Methods: *a* – ion mobility; *b* – coefficient of diffusion; *c* – speed of diffusion through the membrane; *d* – dependence of activity coefficients on concentration; *e* – plasma-like theory of electrolyte solutions.

A non-empirical method for calculating hydration numbers of ions in solutions [1, 2] is elaborated, according to which the ion charge $q_i = z_i e$ in liquid, incompressible polar dielectric is screened by the nearest environment of solvent molecules forming the hydration shell.

The interaction of ion is dipole. The relevant potentials are equal:

$$\varphi_i = z_i e/\varepsilon r_i; \quad \varphi_d = p / \varepsilon R_s^2, \qquad (1)$$

where ε is dielectric constant, R_s is radius of the solvent molecule.

The potential of the central ion in a dielectric medium is neutralized by the dipole potentials φ_d of solvent molecule (by the number of n_s):

$$\varphi_i - n_s \varphi_d = \varphi_p, \qquad (2)$$

where φ_p is the resulting potential.

If equation (1) transform into the finite-difference equation of ion-dipole energy, then from the obtained equation (2), the boundary

of the hydrated complex is cut by energy of thermal motion $5k_Б T/2$, in the form of evident condition $e\varphi_p = 5k_Б T/2$, which means that the obtained difference between the energies of ions and water molecules is compensated at the boundary of the thermal energy of the medium itself $5k_Б T/2$:

$$z_i e^2 / \varepsilon r_i - n_s pe / \varepsilon R_s^2 = 5k_Б T / 2. \qquad (3)$$

Here n_s is the number of solvent molecules in the hydration complex and $k_Б$ is Boltzmann constant. Thus, the hydration number n_s will be determined by the relation:

$$n_s = z_i e R_s^2 / r_i p - 5k_Б T \varepsilon R_s^2 / 2pe, \qquad (4)$$

where z_i and r_i are charge and ionic radius.

Now let's consider the size of nanoparticles, the radii of hydrated ions. According to our concept [3, 4, 5], they can be calculated basically on the model of oscillating with a plasma-like frequency of particles in electrolyte solutions using the dispersion of the Vlasov's equation:

$$\omega = \omega_L \cdot (1 + (3/2) \cdot k^2 r_D^2). \qquad (6)$$

Here $\omega_L = (4\pi z_i z_D e^2 n_o / m)$ – Langmuir's plasma frequency; $z_i e, z_D e$ are ion charge and dipole of the solvent; $n_o = n_s / V = n_s / (4/3) \cdot \pi r_s^3$ is – density of charges, in this case the number of solvent molecules in the hydrate complex, n_s is hydration number, M is mass of the solvent molecules, r_s is the radius of hydrated ion.

The dipole charge is $z_D e = p/l$, where p is the dipole moment and l is dipole distance for the solvent.

Damping parameter kr_D, where k is a wave number, r_D is Debye radius, has limits of changing $0 \le kr_D \le 1$. In considering the ions of electrolyte in the solution as a system of charges, $kr_D = 1$ takes place, i.e. spatial dispersion is at maximum, oscillations are damping, but they are maintained at a frequency of external perturbation.

$$\omega = 5/2\omega_L = (5/2) \cdot (4\pi z_i z_D e^2 n_0 / m)^{1/2}. \qquad (7)$$

If you multiply the expression (7) on the Planck constant $\hbar$, and bear in mind that the total energy $\hbar\omega$ is $(3/2)k_Б T$ (for spherically – symmetric distribution all three degrees of freedom are taken into account), then we obtain formula (8), in which values n_o и $z_D e$, given earlier, are introduced:

$$r_s = \left(25 z_i p e n_s \hbar^2 / 3mlk_Б^2 T^2 \right)^{1/2}. \qquad (8)$$

The values of the radii of solvated ions in water, calculated according to equation (8), are also listed in table 2.

As it seen from table 1 and 2, the estimated hydration numbers and the radii of hydrated ions (the size of nanoparticles) are in satisfactory agreement with scientific literature data. The given model estimates the size of hydrated ions of seawater and the obtained values r_s can be recommended for the development of more energy-and resource-saving technologies of seawater desalination not only for the regions with a harsh shortage of drinking water.

Table 2

Characteristics of hydrated ions

Ion	Ion radius, r_i, nm	Hydrate number, n_s	The radius of hydrated ion, r_s, nm [4]	The radius of hydrated ion, r_s, nm [6]
Na^+	0,098	4,03	0,360	0,330; 0,386
K^+	0,133	2,69	0,315	0,301
Mg^{2+}	0,078	5,33	0,395	–
Ca^{2+}	0,106	3,64	0,348	–
Cl^-	0,181	1,70	0,270	0,291
SO_4^{2-}	0,147	2,34	0,300	–

References

1. Munko Baldanov, Boris Tanganov To the problem of solvation numbers and masses of solvated ions in alcohol solutions // Journal of Physical Chemistry. – 1992. – Vol. 66, no. 4. – P. 1084–1088.

2. Munko Baldanov, Boris Tanganov Calculation of solvation numbers of ions in nonaqueous media // Journal of General Chemistry. – 1992. – Vol. 63, no. 8. – P. 1710–1712.

3. Munko Baldanov, Boris Tanganov Vlasov's dispersion equation and the radii of solvated ions in methanol // Journal of General Chemistry. – 1994. – Vol. 64, no.1. – P. 32–34.

4. Munko Baldanov, Darima Baldanova, Seseg Zhigzhitova, Boris Tanganov To the problem of the radii of hydrated ions // Reports of the Russian High School Academy of Science. – 2006. – Vol. 2. – P. 32–34.

5. Tanganov B., Baldanova D., Baldanov M. Characteristics of hydrated nanoparticles (hydration numbers, mass and size) // in proceedings of the Fifteenth International Scientific and Practical Conference «Natural and intellectual resources of Siberia» (SIBRESURS-15-2009). – Irkutsk, 2009. – P. 95–98.

6. Melvin-Hughes E.Y., Physical Chemistry (Book II). – M.: Foreign literature Press, 1962.