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

Tanganov B.B.
East Siberia State University of Technology and Menegement, Ulan-Ude, e-mail: tanganov@rambler.ru

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⁺, Mg²⁺, Ca²⁺, Cl⁻, SO₄²⁻) 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 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

<table>
<thead>
<tr>
<th>Author</th>
<th>Method</th>
<th>Hydration numbers</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Na⁺</td>
</tr>
<tr>
<td>I</td>
<td>a</td>
<td>–</td>
</tr>
<tr>
<td>II</td>
<td>b</td>
<td>8,4</td>
</tr>
<tr>
<td>III</td>
<td>b</td>
<td>–</td>
</tr>
<tr>
<td>IV</td>
<td>b</td>
<td>16,9</td>
</tr>
<tr>
<td>V</td>
<td>c</td>
<td>3</td>
</tr>
<tr>
<td>VI</td>
<td>d</td>
<td>3,5</td>
</tr>
<tr>
<td>VII</td>
<td>e</td>
<td>4,03</td>
</tr>
</tbody>
</table>


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:

$$\varphi_i = z_i e / \varepsilon R_s$$

where $\varepsilon$ 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 $\varphi_d$ of solvent molecule (by the number of $n_i$):

$$\varphi_i - n_i \varphi_d = \varphi_p$$

(2)

where $\varphi_p$ 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 $5k_BT/2$, in the form of evident condition $\nu_p = 5k_BT/2$, 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 $5k_BT/2$:

$$z_i e^2 / \nu_p - n_s e \nu_p / \nu_p = 5k_BT / 2.$$  

(3)

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

$$n_s = z_i e R_i^2 / r_p - 5k_B T e R_i^2 / 2 \nu_p,$$  

(4)

where $z_i$ and $r_p$ 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:

$$\omega = \omega_L \left(1 + (3/2) - k r_p^2\right).$$  

(6)

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

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

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

$$\omega = 5/2 \omega_L \left(5/2 \left(4\pi z_i e^2 n_o / m\right)^{1/2}.\right.$$  

(7)

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

$$r_s = \left(25 z_s e \hbar^2 / 3 m k_B T^2\right)^{1/2}.$$  

(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**

<table>
<thead>
<tr>
<th>Ion</th>
<th>Ion radius, $r_s$, nm</th>
<th>Hydrate number, $n_s$</th>
<th>The radius of hydrated ion, $r_{\nu_p}$, nm [4]</th>
<th>The radius of hydrated ion, $r_{\nu_p}$, nm [6]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$</td>
<td>0,098</td>
<td>4,03</td>
<td>0,360</td>
<td>0,330; 0,386</td>
</tr>
<tr>
<td>K$^+$</td>
<td>0,133</td>
<td>2,69</td>
<td>0,315</td>
<td>0,301</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>0,078</td>
<td>5,33</td>
<td>0,395</td>
<td>–</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>0,106</td>
<td>3,64</td>
<td>0,348</td>
<td>–</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>0,181</td>
<td>1,70</td>
<td>0,270</td>
<td>0,291</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>0,147</td>
<td>2,34</td>
<td>0,300</td>
<td>–</td>
</tr>
</tbody>
</table>

### References


