

INVESTIGATION OF THE INFLUENCE OF POLYVINYL PYRROLIDONE (PVP) ON HYDRATION PROCESSES IN ELECTROLYTES

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Abstract. The paper investigates the effect of polyvinylpyrrolidone (PVP) on the sum of the hydration numbers of anions and cations of salts KJ and K₂SO₄. The sum of hydration numbers was determined by the refractometric method. The data obtained show that the presence of the polymer in the electrolyte solution reduces the value of $h_1 + h_2$ which is associated with competition between polymer molecules and ions during the hydration process.

Keywords: polyvinylpyrrolidone (PVP), polyethylene glycol (PEG) hydration, hydration number.

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1. Introduction

Solvation or hydration (when the solvent is water) is one of the various processes that occur as a result of the interaction of solvent and solute molecules in solutions (Alkhayatt *et al.*, 2019; Masimov *et al.*, 2020; Bokii, 1971). As a result of hydration, solute particles (ions, atoms, molecules) and water molecules form hydrates, which are stable or unstable compounds. In this case, water molecules do not dissociate, i.e. a hydrogen ion (H⁺) and a hydroxyl ion (OH⁻) are not formed. The process of hydration during the dissolution of substances in water, during the formation of crystalline hydrates, the dissolution of substances in water in multiphase systems, etc. plays an important role. The particles of some substances hold water molecules weakly, others strongly. Since the hydration process generally characterizes all energetic and structural changes occurring in a solution, it is very important to determine the size of the hydration layer and the hydration number (Pissis & Kyritsis, 2013; Paez *et al.*, 2018; Mehrdad *et al.*, 2011; Sosa *et al.*, 2018; Bagirova, 2019).

In the paper the sum of the hydration number of ions in aqueous solutions is determined by the refractometric method and the influence of some PEG and PVP polymers on this parameter is also studied. The results of the study showed that with increasing molecular weight and concentration of polymers, the sum of hydration numbers of ions decreases.

As is known, hydration is the result of the interaction of solute molecules with water. When electrolytes are dissolved in water, due to the interaction of positive and negative particles of the compound with the dipole moments of water molecules, they dissociate

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and positive and negative ions appear in the solution. Thus, the compounds dissociate, the ions are hydrated, and the degree of hydration is characterized by the hydration number (Masimov *et al.*, 2023; Volkov *et al.*, 2020; Barmpalexis *et al.*, 2013).

Structural characteristics of water solutions of polymers is mainly described by the conformation, size, hydration, etc. of the polymer macromolecule. Since all biological processes take place in water, studying the hydration of macromolecules of biologically important polymers is one of the interesting and important issues (Sosa *et al.*, 2018; Mehrdad *et al.*, 2011). According to modern concepts, linearly sized dynamic macromolecules change to a wash form in solid polymer solutions.

According to modern concepts, linearly sized dynamic macromolecules change to a wash form in solid polymer solutions. Let's assume that the volume of the solution obtained when a polymer with a mass m_2 is dissolved in water with a volume of V_{su} was V_m . Let V_y , denotes the volume of each wash in water, and V_h denotes the volume of water remaining inside it (hydrated water). Assuming that the number of sinks in the water is N , we can write:

$$V_{su} + NV_y - V_m = NV_h \quad \Rightarrow \quad V_m - V_{su} = N(V_y - V_h) \quad (1)$$

We can replace the quantities V_{su} , V_m , N , V_y , V_h involved in expression (1) by the expressions

$$\begin{aligned} V_{su} &= \frac{m_1}{\rho_1} = \frac{v_1 M_1}{\rho_1}, & V_m &= \frac{m}{\rho} = \frac{vM}{\rho}, & N &= \frac{m_2}{M_2} N_A = v_2 N_A, \\ V_y &= \frac{m_y}{\rho_1} = \frac{M_2}{N_A \rho_1}, & V_h &= \frac{m_h}{\rho_1} = \frac{N_h m_{0su}}{\rho_1} = \frac{N_h M_1}{N_A \rho_1} \end{aligned} \quad (2)$$

Here m_1 is a mass of the water; m_2 is a mass of polymer and m is a mass of the solution. M_1 is a molar mass of water; M_2 is a molar mass of polymer; M is a molar mass of the solution; v_1 is a is the amount of substance in the solution of water; v_2 is the amount of substance in the solution of the polymer; v is the amount of substance in the solution; ρ_1 is a is the density of water; ρ is the density of the solution; m_h is a mass of hydrat water; m_{0su} is a mass of water molecule; N_h is the number of water molecules remaining inside the wash (hydration number); N_A is the Avagadro number. Note that since the balls float in the solvent, we can take their average density equal to the density of the solvent. Now let's define the expression to evaluate the hydration number. If we consider expressions

(2) in (1) and simplify the resulting equation taking $x_1 = \frac{v_1}{v}$, $x_2 = \frac{v_2}{v}$, $M = x_1 M_1 + x_2 M_2$ we get:

$$N_h = \left(\frac{x_1}{x_2} + \frac{M_2}{M_1} \right) \left(1 - \frac{\rho_1}{\rho} \right) \quad (3)$$

Here, x_1 is the molar fraction of water, x_2 is the molar fraction of polymer. If we take into account $x_1 = 1 - x$, $x_2 = x$ in expression (3), we get

$$N_h = \left(\frac{1-x}{x} + \frac{M_2}{M_1} \right) \left(1 - \frac{\rho_1}{\rho} \right) \quad (4)$$

In three-component systems, i.e. water-polymer-A system, x is the molar fraction of the polymer, M_1 is the molar mass of the solvent (water-A), M_2 is the molar mass of the

polymer, ρ_1 is the density of the solvent (water-A), and ρ is the density of the solution. Here, A is the third component that can be a salt, alkali, alcohol, etc.

The idea of ionic hydration was an essential step for the correct understanding of the processes occurring in aqueous solutions and thereby determining all further development of the theory of electrolyte solutions. It is also interesting to note that the first paper by N.S. Kurnakov, published in 1894, was devoted to the issues of hydration of ions in solutions, which is closely related to the structure of aqueous solutions of electrolytes. This connection was first explored in a classic study by Bernal and Fowler. A significant contribution to the study of ion hydration in solutions was described by O.Ya. Samoilov. Samoilov's approach to studying the hydration of ions in solutions is that hydration is considered not as the binding of one or another number of water molecules in a solution by ions, but as the effect of ions on the translational movement of nearby water molecules.

There are many methods for determining hydration numbers and, naturally, the values of hydration numbers obtained by the methods obtained do not always coincide (Shahbazova, & Masimov, 2007; Campbell, 1975).

Considering the fact that the refraction of solutions in many cases contains information about the structures and processes of hydration. In the work to obtain an analytical formula for the sum of the hydration numbers of a refractometer, the authors proceeded from the fact that at optical frequencies of the electric field, dipoles and ions cannot follow the direction of the field in the processes of polarization of the medium, only electrons play the main role. In this case, the polarization is described by the Lorentz-Lorentz equation

$$\frac{n^2-1}{n^2+2} = \frac{N_{H_2O}\alpha_{H_2O}}{3} + \frac{N_{K^+j}\alpha_{K^+j}^*}{3} + \frac{N_{A^-i}\alpha_{A^-i}^*}{3} + \frac{N_{K_iA_j}\alpha_{K_iA_j}}{3}. \quad (5)$$

Here n is the refractive index of the solution, α_{H_2O} , $\alpha_{K^+j}^*$, $\alpha_{A^-i}^*$, and $\alpha_{K_iA_j}$ are the polarization coefficients of water molecules, K^+ and A^- , K_i and A_j are the ions of molecules of the solute, respectively.

On the right side, the terms of equation (1) relate the first term to free water molecules, the second term to potassium ions (K^+), the third to an anion (A^-), and the fourth term to non-dissociated neutral molecules (K^+ , A^-).

In Masimov and Abbasov (2012), after some mathematical transformations for the sum of hydration numbers of dissociated ions, the following expression was obtained:

$$h_1 + h_2 = \frac{3Mtg\Phi}{\rho N_A \alpha_{H_2O}} - i \left(\frac{r_{K^+j}}{r_{H_2O}} \right)^3 - j \left(\frac{r_{A^-i}}{r_{H_2O}} \right)^3 \quad (6)$$

Here M is the molecular mass of the molecule of the dissolved substance, N_A is the Avagadro's number, α_{H_2O} is the polarization coefficient of water molecules, r_{H_2O} is the radius of a water molecule, r_{K^+j} and r_{A^-i} radius of the cation and anion, respectively, j is the valence of the ions and $tg\Phi$ is the tangent of the dependence angle.

2. Experimental part

In the preparation of the solutions used in the experiment, bidistilled water was taken as a solvent. An electronic scale with an accuracy of 0.001g was used in the preparation of the solutions. To prepare the solutions expressed by weight concentration, the soluble

substance was weighed in the required amount on an electronic scale and mixed until it was completely dissolved by adding the required amount of bidistilled water. The refractive index of the solutions was determined using a refractometer. For this purpose the Abbe refractometer (model RMT 95% Brix, 0-70) was used.

3. Results and discussion

Fig.1 shows the dependence $\frac{n^2-1}{n^2+2} - c$ for the salts KBr and K_2SO_4 in the concentration range $1 \leq c\% \leq 5$. To calculate the value (h_1+h_2) according to formula (6), we used the values of $\text{tg}\Phi$ and the values of other parameters from the literature ($a_{H_2O} = 1.45 \cdot 10^{-30} \text{m}^3$, $r_{H_2O} = 140 \text{ pm}$, $r_K = 138 \text{ pm}$ etc.).

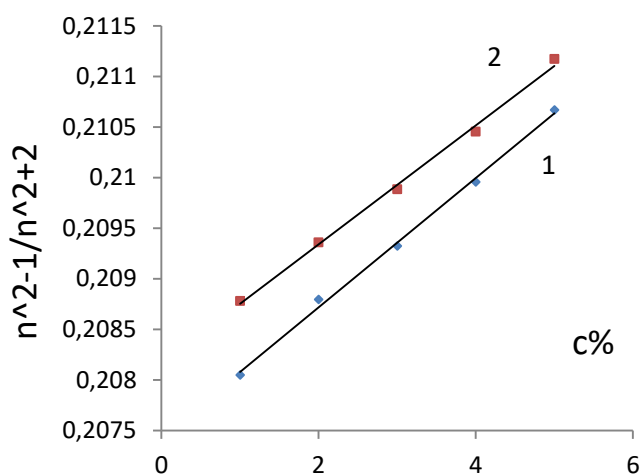


Fig. 1. Dependence of the value (n^2-1/n^2+2) on the concentration (c%) of an aqueous solution of KBr(1) and KBr+polymer (PVP)(2)

The work also studied the effect of PEG and PVP polymers on the value of the hydration number (h_1+h_2) . The obtained data are given in Tables 1-3.

Table 1. Effect of PEQ on hydration processes in aqueous solution of KBr salt

Solutions	h_1+h_2
KBr+H ₂ O	24,2
KBr+PEQ(6000)+ H ₂ O- 0,3ml	16,7
KBr+PEQ(6000)+ H ₂ O-0,5ml	12,6

Table 2. Effect of different fractions of PVP on hydration processes in aqueous solution of KBr salt

Solutions	h_1+h_2
KBr+H ₂ O	18,4
KBr+ PVP (12000) 1 ml	13,5
KBr+ PVP (12000) 2 ml	12,2
KBr+ PVP (25000) 1 ml	12,1
KBr+ PVP (25000) 2 ml	10,8
KBr+ PVP (45000) 1 ml	10,9
KBr+ PVP (45000) 2 ml	8,4

Table 3. Effect of different fractions of PVP on hydration processes in aqueous solution of K_2SO_4 salt

Solutions	h_1+h_2
$K_2SO_4+H_2O$	18,6
$K_2SO_4+ PVP (12000) 1 ml$	11,9
$K_2SO_4+ PVP (12000) 2 ml$	8,6
$K_2SO_4+ PVP (25000) 1 ml$	16,3
$K_2SO_4+ PVP (25000) 2 ml$	6,3
$K_2SO_4+ PVP (45000) 1 ml$	10,0
$K_2SO_4+ PVP (45000) 2 ml$	6,8

Hydration numbers (N_h) of PEQs of the considered molecular mass in the studied temperature and concentration range were determined. Calculations show that the hydration number almost does not depend on the concentration of PEQ. We suppose that N_h can be taken not depending on the concentration of solutions. The average values of the hydration numbers at the given temperatures are taken according to the considered concentrations. The values of N_h for the Du-PEQ system are given in Table 4.

Table 4. Temperature dependence of the hydration number of PEQ in water-PEQ systems

T, K	PEQ (1000)	PEQ (1500)	PEQ (3000)	PEQ (4000)	PEQ (6000)
293.15	8.6	11.6	14.9	20.7	56.7
298.15	8.3	11.2	14.4	20.1	56.3
303.15	7.9	10.8	14.1	19.6	56.0
308.15	7.4	10.3	13.6	19.2	55.8
313.15	7.0	9.8	13.2	18.7	55.4
318.15	6.7	9.5	12.6	18.2	54.9
323.15	6.2	9.2	12.4	18.0	54.8

As follows from the tables the polymers added to the solution reduce the amount of hydration number, which indicates the interaction of hydrophilic oxygen atoms of polymers with water molecules.

4. Conclusion

As can be seen in Table 4, the hydration number of the macromolecule increases with the increase of the molecular mass (M) of PEQ, and decreases with the increase of temperature (T). The variation of N_h as a function of M and T can be explained as follows. With the increase in molecular mass, the volume of PEQ macromolecule increases and the spaces inside the molecular shell increase, and the number of oxygen atoms in PEQ monomer that form hydrogen bonds with water molecules also increases, and as a result, N_h increases. As the average kinetic energy of thermal movement of molecules increases with temperature increase, hydrogen bonds cannot keep water molecules in hydrated macromolecular wash, and as a result, N_h decreases, and the number of free water molecules increases. It should be noted that during the hydration process, water molecules compete with each other to create hydrogen bonds with polymer macromolecules. This process is characterized by the maximum hydration energy of polymer macromolecules, which makes the resulting conformation more likely than other possible conformations.

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