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INFLUENCE OF A NUMBER OF ALKALIS AND SALTS ON THE HYDRATION NUMBER OF POLYETHYLENE GLYCOL

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Abstract. Here a new expression is given for the determination of the hydration number of polymers. With this expression, the hydration numbers of PEG is determined on the basis of experimental estimates of the density of water-PEG, water-PEG-alkaline and water-PEG-salt systems at different temperatures and concentrations and the effect of a number of alkalis (LiOH, NaOH, KOH) and salts (KCl, KBr, KI) on the hydration number of PEG was investigated. It has been determined that the hydration of PEG decreases with increasing numerical temperature, increases with increasing molecular weight of PEG, decreases according to the sequence of LiOH, NaOH, KOH under the influence of alkalis, under the influence of salts in the order corresponding to the order of KCl, KBr, KI.

Keywords: *Water, polyethylene glycol, macromolecule, hydration number*.

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1. Introduction

Polyethylene glycol (PEG), unlike its neighboring homologues polymethylene oxide (PMO) and polypropylene oxide (PPO) polyesters, dissolves well in water at room temperature over a wide range of polymerization rates (Kashmola & Estabraq, 2014; Sung *et al*, 2007; Chakraborty *et al*., 2020). It is believed that PEG is well soluble in water due to the fact that its ether oxygen atoms form hydrogen bonds with water molecules (Chen *et al*, 2005; Almasy *et al*, 2022). As a result of such interactions, gel-like aggregates, super molecular structures, associations, clusters are formed in PEG aqueous solution (Shikata *et al*, 2006). PEG ensures the sterile stability of solid particles by encapsulating them, retains surfactants and reduces friction in various processes (Chen *et al*, 2005; Sagawa & Shikata, 2013). Recently in the literature the study of systems consisting of polymer-water inorganic compounds has become widespread (Shulyak & Grushova, 2013; Masimov *et al*, 2020, 2021). Such systems are widely used in pharmacology and medicine. Most of the functions of PEG are mainly related to the aquatic environment. Therefore, the study of the hydration process in water-PEG systems, including the study of changes in the hydration process of PEG with the addition of a third component is of great importance both practically and scientifically.

Different processes take place in solutions as a result of the interactions between the molecules of the solvent and the solute. One such process is solvation or hydration

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(when the solvent is water) (Fonzo *et al.*, 2019). In the process of hydration, water molecules form stable or unstable compounds (hydrates) with the particles (ions, atoms, molecules) of the solute. In this process, water molecules do not dissociate, that is, no hydrogen ions (H^+) or hydroxyl ions (OH^-) are formed. Hydration process in the solubility of substances in water, in the distribution of substances in multi-component, multi-phase systems, in the formation of crystalline hydrates, etc. plays an important role. Particles of some substances keep water molecules strong, while others keep them weak. The process of hydration generally characterizes all the energy and structural changes that occur in the solution (Nishimura *et al.*, 2020; Pissis & Kyritsis, 2013). Therefore, it is very important to determine the hydrations number.

In the presented work, the process of hydration of PEG in water-PEG, water-PEG-alkaline (LiOH, NaOH, KOH) and water-PEG-salt (KCl, KBr, KI) systems was studied. In this study, the fractions of PEG with molecular weights of 1000, 1500, 3000, 4000 and 6000 *g/mol* were considered, and the concentration of alkalis and salts in all solutions was 0.01 molar fraction ($x_{\mathrm{LiOH}} = x_{\mathrm{NaOH}} = x_{\mathrm{KOH}} = 0.01$ and $x_{\mathrm{KCl}} = x_{\mathrm{KBr}} = x_{KI} = 0.01$). For this purpose, studied aqueous solutions was determined the density of PEG experimentally in the range of 0-0.001 molar fraction concentration and temperature of 20-50°C. Using the experimental results, the hydration number of PEG at the considered temperatures was calculated for the obtained fractional PEGs.

2. Method of calculation

The structural characteristics of aqueous solutions of polymers are mainly described by the conformation, size, hydration of the polymer macromolecule, etc. Since all biological processes take place in water, the study of hydration of macromolecules of biologically important polymers is an interesting and important issue (Pissis & Kyritsis, 2013; Abbasov, 2014). According to modern ideas, in liquid polymer solutions, linearly sized mobile macromolecules take the form of cluster. Suppose that in water the polymer with a volume of V_{wt} and m_2 mass when resolved the volume of solution obtained was V_s. Let us denote the volume of each cluster in water by V_w, and the volume of water remaining in it (hydrated water) by V_h. Assuming that the number cluster in the water is N, we can write:

$$V_{wt} + NV_w - V_s = NV_h \Rightarrow V_s - V_{wt} = N(V_w - V_h) \tag{1}$$

Quantities V_{wt}, V_s, N, V_w, V_h included in (1)

$$V_{wt} = \frac{m_1}{\rho_1} = \frac{\nu_1 M_1}{\rho_1}, \qquad V_s = \frac{m}{\rho} = \frac{\nu M}{\rho}, \qquad N = \frac{m_2}{M_2} N_A = \nu_2 N_A,$$
$$V_w = \frac{m_w}{\rho_1} = \frac{M_2}{N_A \rho_1}, \qquad V_h = \frac{m_h}{\rho_1} = \frac{N_h m_{0wt}}{\rho_1} = \frac{N_h M_1}{N_A \rho_1} \tag{2}$$

can replace with expressions. Here m_1 is the mass of water, m_2 is the mass of the polymer, m is the mass of the solution; M_1 is the molar mass of water, M_2 is the molar mass of the polymer, M is the molar mass of the solution; ν_1 is amount of water, ν_2 is the amount of polymer, ν is the amount of solution; ρ_1 is the density of water, ρ is the density of the solution; m_h is the mass of hydrated water, m_0 is the mass of water-water molecule, N_h is the number of water molecules left inside the mass (hydration number); N_A is the Avogadro number. Note that since the washes float in the solvent, we can take their average density equal to the density of the solvent. Now let's define the expression to estimate the number of hydrations. Considering the expressions (2) in (1) and simplifying the obtained

equation by $x_1 = \nu_1/\nu$, $x_2 = \nu_2/\nu$, $M = x_1M_1 + x_2M_2$ we obtain:

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

Here x_1 is the molar part of water and x_2 is the molar part of the polymer. Given that $x_1 = 1 - x$, $x_2 = x$ in expression (3), we obtain:

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

In three-component systems, that is, in the water-polymer-A system, x will be the molar part of the polymer, M_1 will be molar mass of solvent (water-A), M_2 will be molar mass of the polymer, ρ_1 will be density of solvent (water-A), ρ will be density of the solution. A third component here can be salt, alkali, alcohol and etc. Calculations show that hydration number is almost independent of the polymer concentration. In the presented work hydration number was determined based on the expression (4).

3. Experimental

Object of study and methods. As objects of study, aqueous solutions of different concentrations consisting of water-PEG, water-PEG-alkaline (LiOH, NaOH, KOH) and water-PEG-salt (KCl, KBr, KI) systems were taken. Used PEG, LiOH, NaOH, KOH, KCl, KBr, KI are chemically pure substances. Measurements were made at normal atmospheric pressure. The solutions were prepared by gravimetric method. Bidistilled water was used to prepare the solutions. During the preparation of the samples, an analytical scale manufactured by "KERN 770" was used and the measurements were taken with an accuracy of 0.0001 g. In this study, the density of liquids was determined by changing the volume with a thin long-necked (throat-graded) glass pycnometer with a volume of 15 cm^3. Density values relative to the reference fluid has been identified. Bidistilled water was used as the reference liquid, and water density values were taken from (Wagner & Pruß, 2002). A pycnometer was placed in the thermostat to determine the density of the solutions at different temperatures (20 °C, 25 °C, 30 °C, 35 °C, 40 °C, 45 °C and 50 °C). The temperature was measured with an accuracy of ± 0.05 K. The maximum relative error of the experiment during the determination of density was 0.30%.

4. Results and discussions

Calculations show that the hydrations number of PEG (N_h) for the studied systems is almost independent of the concentration of PEG. We assume that this result is acceptable in the form of pure solutions. Therefore, we can assume that N_h in liquid solutions does not depend on the concentration. The average values of the hydration numbers at the given temperatures were taken according to the considered concentrations of PEG. The values of N_h for the water-PEG system are given in Table 1.

As can be seen from Table 1, the hydration number of PEG increases with increasing molecular weight, decreases with increasing temperature. The change in the hydration number of PEG depending on the molecular weight and temperature can be explained as follows. As the molecular weight increases, the volume of the PEG macromolecule increases and the gaps inside the molecular mass increase. The number of oxygen atoms in the PEG monomer, which form hydrogen bonds with water molecules, also increases, resulting in an increase in N_h. As the average kinetic energy of the thermal motion of the

molecules increases with increasing temperature, the hydrogen bond cannot keep the water molecules in a hydrated macromolecular cluster and as a result, N_h decreases and the number of free water molecules increases. Note that, during the hydration process, water molecules do not simply combine with polymer macromolecules, there is also competition for water molecules to form hydrogen bonds with polymer macromolecules (Bang *et al*, 2016). This process is characterized by the maximum hydration energy of the polymer macromolecules, which makes the resulting conformation more likely than other conformations that may occur (Cao & Bowie, 2014).

Table 1. Temperature dependence of the hydration numbers of PEG in water-PEG systems

T, °C	PEG (1000)	PEG (1500)	PEG (3000)	PEG (4000)	PEG (6000)
20	8.6	11.6	14.9	20.7	56.7
25	8.3	11.2	14.4	20.1	56.3
30	7.9	10.8	14.1	19.6	56.0
35	7.4	10.3	13.6	19.2	55.8
40	7.0	9.8	13.2	18.7	55.4
45	6.7	9.5	12.6	18.2	54.9
50	6.2	9.2	12.4	18.0	54.8

To study the effect of a number of alkalis (LiOH, NaOH, KOH) and salts (KCl, KBr, KI) on the hydration number of PEG, we also determined the hydration number of PEG in water-PEG-alkaline and water-PEG-salt systems. In water-PEG, water-PEG-alkaline and water-PEG-salt systems, for all molecular weight solutions of PEG under consideration, the hydration of PEG changes with the same regularity depending on the numerical temperature we will give graphs of solutions corresponding only to the fraction of PEG with a molecular weight of 3000 *g/mol*. However, the explanations given here also apply to other molecular weight fractions of PEG studied (1000, 1500, 4000, 6000 *g/mole*). The temperature dependence of the hydration numbers (N_h) of PEGs of different molecular weights in water-PEG, water-PEG-alkaline and water-PEG-salt systems is given in Figure 1 and 2.

As can be seen from Figure 1 and Figure 2, when adding alkali (x_{alkali} = 0.01) or salt (x_{salt} = 0.01) of the same concentration separately to the water-PEG (3000) system the hydration numbers of PEG in the obtained solutions is relatively reduced. We assume that this is due to the hydration of alkaline or salt ions in the solution. Thus, while only PEG macromolecules are hydrated in water-PEG systems, both PEG macromolecules and alkaline (salt) ions are hydrated in water-PEG-alkaline (water-PEG-salt) systems. Note that, because electrostatic forces have the property of affecting long distances, the process of hydration in solutions containing both polymers and ions will be somewhat different from the process of hydration in solutions containing only polymers (non-ions). When studying the process of hydration in aqueous solutions consisting of polymers and ions, it is necessary to take into account the additional interactions caused by the presence of ions.

As can be seen from Figure 1 and Figure 2, the hydration number of PEG under the influence of alkalis and salts decrease the order of LiOH, NaOH, KOH for alkalis, for salts decrease according to the order KCl, KBr, KI. The process of hydration of the polymer in water-PEG-alkaline and water-PEG-salt systems can be described by the following model. When adding x_{alkali}= 0.01 concentration alkali (LiOH, NaOH, KOH) or x_{salt} =

0.01 concentration salt (KCl, KBr, KI) to the water-PEG system separately, since the maximum concentration of PEG is $x_{PEG} = 0.001$ ($x_{PEG} / x_{PEG} = N_{PEG} / N_{PEG}$ or $x_{salt} / x_{PEG} = N_{salt} / N_{PEG}$, where N_{alkali}, N_{salt}, and N_{PEG} are the number of alkali molecules, salt molecules, and PEG macromolecules in solution, respectively) always the number of ions in the solution (Li^+ and OH^-; Na^+ and OH^-; K^+ and OH^-; K^+ and Cl^-; K^+ and Br^-; K^+ and I^-) is much higher than the number of PEG macromolecules.

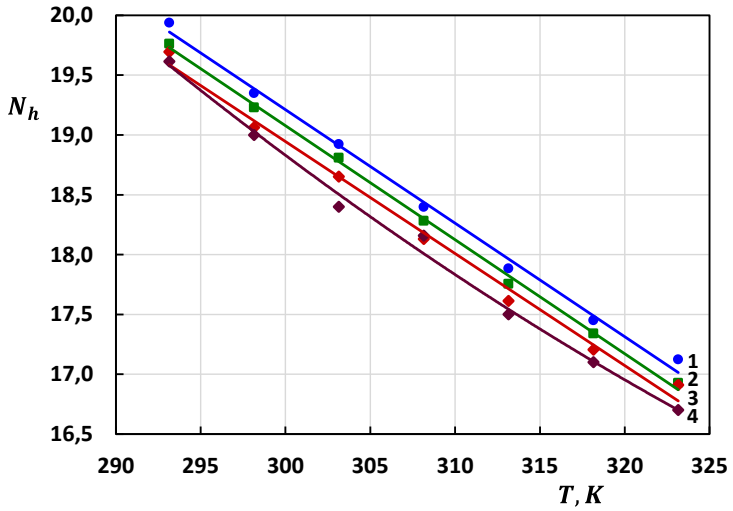

Fig. 1. Temperature dependence of hydration number of PEG in water-PEG (1), water-PEG-LiOH (2), water-PEG-NaOH (3), water-PEG-KOH (4) systems (M_{PEG}=3000 *g/mol*, x_{LiOH}=x_{NaOH}=x_{KOH}=0.01)

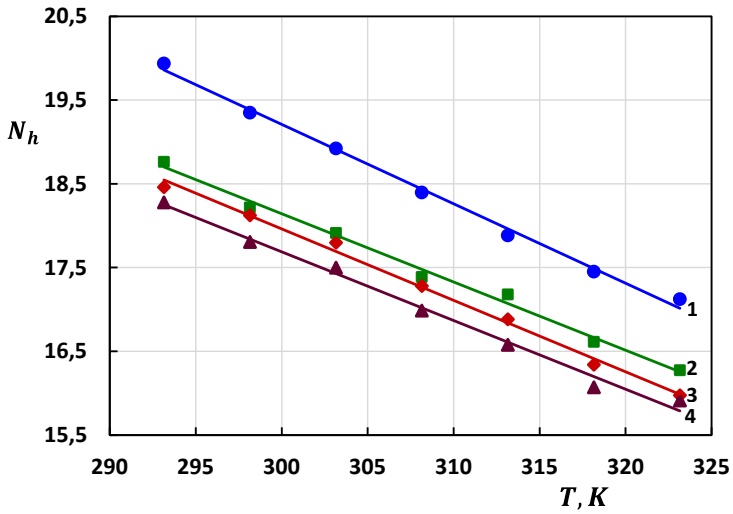

Fig. 2. Temperature dependence of hydration number of PEG in water-PEG (1), water-PEG-KCl (2), water-PEG-KBr (3), water-PEG-Kl (4) systems (M_{PEG} = 3000 g/mol, x_{KCl} = x_{KBr} = x_{KI} = 0.01)

Given that the effective radii of the ions of the studied alkalis are quite small than the size of the PEG macromolecule it can be assumed that the PEG macromolecular cluster also contains hydrated ions (Li^+ and OH^-; Na^+ and OH^-; K^+ and OH^-; K^+ and Cl^-; K^+ and Br^-; K^+ and I^-, respectively). Of course, the number of hydrated ions in the macromolecular cluster, which has a larger molecular weight, will be higher. Then we can assume that the hydrated water molecules around the ion inside the molecular mass are ion-dipole with

the ions, and some of them interact with the hydrogen bond with the PEG macromolecule. We believe that hydrated ions try to reduce the volume of water molecules to a certain extent by ion-dipole interaction, water molecules, on the other hand, interact with the PEG macromolecule by hydrogen bonding tries to reduce the volume to a certain extent. The validity of this assumption is reflected in the value of both the partial molar volume ($\tilde{V}$) of PEG in solution and the hydration numbers of PEG in the solution. Therefore, it will be $\tilde{V}$ (water-PEG) > $\tilde{V}$ (water-PEG-alkaline) and $\tilde{V}$ (water-PEG) > $\tilde{V}$ (water-PEG-salt) (Masimov *et al*, 2019), as well as N_h (water-PEG) > N_h (water-PEG-alkaline) and N_h (water-PEG) > N_h (water-PEG-salt). We assume that Na^+ is more hydrated than the K^+ ion and Li^+ is more hydrated than the Na^+ ion (Samoilov, 1965) N_h (water-PEG-LiOH) > N_h (water-PEG-NaOH) > N_h (water-PEG-KOH), and because Br^- has a stronger hydration than the I^- ion, and Cl^- has a stronger hydration than the Br^- ion it will happen like that (Samoilov, 1965) N_h (water-PEG-KCl) > N_h (water-PEG-KBr) > N_h (water-PEG-KI).

5. Conclusion

Here is given a new expression for the determination of the hydration number of polymers. With this expression, the hydration numbers of PEG in water-PEG, water-PEG-alkaline and water-PEG-salt systems was determined. It was found that the hydration number of PEG decreases with increasing temperature, increases with increasing molecular weight of PEG, alkalis (LiOH, NaOH, KOH) and salts (KCl, KBr, KI) to the hydration number of the PEG macromolecule for the considered systems affect the sequence according to the order

$$N_h \text{ (water-PEG)} > N_h \text{ (water-PEG-LiOH)} > N_h \text{ (water-PEG-NaOH)} > N_h \text{ (water-PEG-KOH)},$$

$$N_h \text{ (water-PEG)} > N_h \text{ (water-PEG-KCl)} > N_h \text{ (water-PEG-KBr)} > N_h \text{ (water-PEG-KI)}.$$

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