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ABSTRACT

of the dissertation for the degree of Doctor of Science

**INFLUENCE OF A NUMBER OF LOW-MOLECULAR
COMPOUNDS ON THE STRUCTURE OF AN AQUEOUS
SOLUTION OF POLYETHYLENE GLYCOL WITH
DIFFERENT FRACTIONS**

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GENERAL CHARACTERISTICS OF WORK

Relevance and currency of the research topic. Different solutions are used in nature due to their importance and properties. The properties of the solution depend on its structure, and the structure depends on the size of the particles that make it up and the interactions between the particles. Aqueous solutions are of particular importance because water is the basis of all living things and is the most universal solvent in nature. It is possible to affirm without exaggeration that the originality and diversity of the physical and biological world are determined by the specific characteristics of the physical, chemical, and physicochemical properties of water. It is no coincidence that nature has chosen water namely, as an environment in which multifaceted and complex activities of living organisms take place. Water is a direct participant in all processes taking place in the living world and has a profound effect on the course of these processes. Active conformations of macromolecules with biological function are formed in the aquatic environment, the transportation of various substances in living organisms is carried out through the water, water takes an active part in the process enzymatic reactions, the water protects the body from mechanical impacts and incisive temperature changes in the environment. Water can absorb, scatter and disperse high-energy rays. Although water resembles, at first sight, a simple substance, a study of its physical and chemical properties shows that it is a very complex substance. Almost all physical and chemical properties of water are anomalous. These mysterious properties of water are associated with a structure that is formed by the presence of hydrogen bonds as a result of the specific distribution of the electron cloud in its molecule and with its unusual properties. Changes in the structure or thermodynamic state of water for various reasons are reflected in all biochemical processes in living organisms.

It is known that the importance of aqueous solutions depends on the importance of its other components, it is also directly related to its effect on the structure of water. Recently, the usage of polymers in all areas of industry have become widespread. One such

practical and biologically important polymer is polyethylene glycol (PEG). Because PEG does not have toxic properties, does not adversely affect the immune system, and is rapidly eliminated from the body, it is widely used in the food industry, medicine, pharmacology, cosmetology, biotechnology, etc. PEG has the properties of ensuring the sterile stability of solid particles by encapsulating them, retaining surfactants, and reducing friction in various processes. There are many molecular weight fractions of PEG, and all of these fractions are well soluble in water. This increases the opportunities for the wider use of PEG in industry. Aqueous solutions of PEG are biocompatible, used in tissue regeneration and organ protection. In some cases, PEG affects the processes in living organisms, and the study of the molecular mechanism of this effect makes it necessary to further study the physical and chemical properties of aqueous solutions of PEG.

We should note that in biological systems, the main activity of both polymers and individual ions occurs in the aquatic environment. There is no environment that can be compared to water in which both different polymers (including PEG) and a number of ions (Li^+ , Na^+ , K^+ , Mg^{2+} , Fe^{3+} , Cl^- , Br^- , I^- and etc.) perform the same important function as in water. Therefore, the study of the structural properties of biological systems and the study of the effects of various substances on this structure is of great importance in modern molecular physics, physical chemistry, biophysics, molecular biology. The structural properties of water-polymer-electrolyte systems are determined by the interactions between the molecules of the components of the system, and it is very difficult to explain the mechanism of change of this structure. Different interactions cause different structural changes in the system. This leads to the formation of complexes and associations. In some cases, these structures are incompatible. Although there is a lot of research in this area, there is a great need for new research. Aqueous solutions of PEG have been intensively studied for many years. However, there are some gaps and shortcomings in this direction. The most common scientific work on water-PEG systems in the literature is related to the study of two-phase systems. The effects of various substances on the structure of

water-PEG systems, and conformation, size, hydration of PEG macromolecule in solution, etc. come upon rarely. An analysis of the scientific literature shows that there is a need for such research in a purposeful and systematic manner. The presented dissertation work is devoted to the topical problem of studying the structural features of water-PEG-electrolyte in biological systems.

Research objects and subjects. The objects of the study were aqueous solutions of PEGs of different fractions (1000, 1500, 3000, 4000, 6000), a number of alkalis (LiOH, NaOH, KOH) and salts (KCl, KBr, KI). As the subject of research studied structural features occurring in the aqueous solutions under study the structural features of the aqueous solutions were studied as the subject of the study.

Aims and purpose of the research: The purpose of the dissertation is to study the structural features of water-PEG-alkaline and water-PEG-salt systems in accordance with different fractions of PEGs with a wide range of applications, to study the effect of a number of alkalis and salts on the structure of aqueous solutions of PEGs, to study the molecular mechanism of these effects and to achieve purposeful changes in the properties in accordance with the areas of application of the solution.

To achieve this goal, the following issues were raised and resolved in the dissertation:

- experimental determination of aqueous solutions consisting of water-alkaline, water-salt, water-PEG, water-PEG-alkaline and water-PEG-salt systems at different temperatures and concentrations viscosity, density, electrical conductivity and frequency of valence oscillations of OH groups belonging to water molecules in the absorption spectra in the IR region;

- to determine the parameters of the viscous flow of aqueous solutions of a number of alkalis and salts at different temperatures and concentrations, the partial molar volumes of alkalis and salts in solution and to determine the concentration dependence of these quantities at a given temperature;

- to determine at different temperatures and concentrations of water-PEG, water-PEG-alkaline and water-PEG-salt systems corresponding to different fractional PEGs the parameters of viscous

flow activation, the partial molar volume of PEG in solution, including the partial molar volume of PEG per monome ring and determine the dependence of these quantities on the concentration at a given temperature;

- to determine the energy and length of hydrogen bonds between water molecules in solution based on the frequency of valence oscillations of OH groups belonging to water molecules in the IR region of a number of studied solutions and to determine the concentration dependence of these quantities at a given temperature;

- to determine the electrical conductivity, effective radii, hydration numbers and activation parameters of ionic conductivity of ions at different temperatures in water-alkaline, water-salt, water-PEG-alkaline and water-PEG-salt systems;

- to determine the hydration number of the PEG macromolecule at different temperatures in water-PEG, water-PEG-alkaline and water-PEG-salt systems in accordance with all fractions of PEG studied, to determine the effect of alkalis and salts on the hydration number;

- comparative study of the effect of alkalis, salts and PEGs on the structure of water, as well as the structure of alkalis and salts on the structure of water-PEG systems by different methods and the study of the molecular mechanism of structural changes in the system;

- to determine the structural characteristics (intrinsic viscosity, Huggins constant, parameter α included in the Mark-Kuhn-Houwink formula, swelling coefficient, average square distance between the ends of the macromolecular chain, length of the Kuhn segment) of the PEG macromolecule in liquid solutions consisting of water-PEG, water-PEG-alkaline and water-PEG-salt systems and to determine the variation of these quantities depending on various external (temperature, concentration, molecular weight of the polymer) factors;

- to determine the structural characteristics (characteristic viscosity, average square distance between the ends of a macromolecular chain, length of the Kuhn segment) of the unexcited PEG macromolecule in the θ -solvent and to determine the variation

of these quantities depending on various external factors (temperature, concentration, molecular weight of the polymer);

- determination of the effect of alkalis and salts on the conformation and size of the PEG macromolecule and analysis of the molecular mechanism of changes.

Research methods. Viscosimetry, densitometry, conductometry and IR spectroscopy were used as research methods in the dissertation. With these experimental research methods the rheological, volume, electrical conductivity and spectroscopic properties of the aqueous solutions studied were studied.

Basic provisions for defense.

1. The molecule involved in the viscous flow process in liquids must go through two stages in order to pass from one state to another due to the additional energy it receives. In the first stage, part of the extra energy is used to separate (tearing off) the molecule from the other molecules around it. In the second stage, the rest of the extra energy (the free part) is spent on the movement of the molecule (converted into kinetic energy).

2. With increasing concentration of alkalis (LiOH, NaOH, KOH) in aqueous solutions the activation entropy of the viscous flow of the solution decreases, and the partial molar volumes of alkalis in the solution increase. They became like that $\Delta S_{\eta}^{\ddagger}(\text{water-LiOH}) > \Delta S_{\eta}^{\ddagger}(\text{water-NaOH}) > \Delta S_{\eta}^{\ddagger}(\text{water-KOH})$ and $\tilde{V}(\text{water-LiOH}) < \tilde{V}(\text{water-NaOH}) < \tilde{V}(\text{water-KOH})$.

3. With increasing concentration in aqueous solutions of salts (KCl, KBr, KI), the activation entropy of the viscous flow of the solution decreases, the partial molar volumes of salts in the solution increase, and the energy of hydrogen bonding between water molecules decreases. They became like that $\Delta S_{\eta}^{\ddagger}(\text{water-KCl}) > \Delta S_{\eta}^{\ddagger}(\text{water-KBr}) > \Delta S_{\eta}^{\ddagger}(\text{water-KI})$, $\tilde{V}(\text{water-KCl}) < \tilde{V}(\text{water-KBr}) < \tilde{V}(\text{water-KI})$, $E_H(\text{water-KCl}) > E_H(\text{water-KBr}) > E_H(\text{water-KI})$.

4. With increasing concentration of alkalis (LiOH, NaOH, KOH) and salts (KCl, KBr, KI) have a destructive effect on the structure of water and water-PEG system. This destructive effect is amplified according to the order of LiOH, NaOH, KOH for alkalis,

and to the order for KCl, KBr, KI for salts.

5. With increasing concentration in aqueous solutions of PEGs of different fractions the viscous flow activation parameters of the solution increase, the partial molar volumes of PEG in the solution decrease, and the energy of the hydrogen bond between the water molecules increases. Depending PEG on both concentration and molecular weight has a structural effect on water.

6. At a given temperature and concentration in water-PEG, water-PEG-alkaline and water-PEG-salt systems, the partial molar volume of PEGs of different molecular weights per unit monomer ring does not depend on the molecular weight of PEGs.

7. Hydration number of PEG macromolecule decreases with increasing temperature, increases with increasing molecular weight of PEG decreases under the influence of alkalis in the order of LiOH, NaOH, KOH, and under the influence of salts in the order of KCl, KBr, KI.

8. Compared to water, the electrical conductivity and hydration numbers of Li^+ , Na^+ , K^+ , OH^- , Cl^- , Br^- , Γ ions in the water-PEG system decrease, effective radii decrease, the activation entropy of ionic electrical conductivity increases. That is like that $N_h(\text{Li}^+) > N_h(\text{Na}^+) > N_h(\text{K}^+)$, $\Delta S_\lambda^\ddagger(\text{Li}^+) > \Delta S_\lambda^\ddagger(\text{Na}^+) > \Delta S_\lambda^\ddagger(\text{K}^+)$ and $N_h(\text{Cl}^-) > N_h(\text{Br}^-) > N_h(\Gamma)$, $\Delta S_\lambda^\ddagger(\text{Cl}^-) > \Delta S_\lambda^\ddagger(\text{Br}^-) > \Delta S_\lambda^\ddagger(\Gamma)$.

9. As the temperature increases, the value of the Haggins constant in the water-PEG system, the average square distance between the ends of the PEG macromolecule chain, and the length of the Kuhn segment decrease.

10. PEG macromolecule in water, water-alkaline and water-salt systems got the shape a ball of yarn and partially swollen, which is able to penetrate of surrounding fluid. It is like that $\alpha(\text{water-PEG-LiOH}) < \alpha(\text{water-PEG-NaOH}) < \alpha(\text{water-PEG-KOH})$, $\alpha(\text{water-PEG-KCl}) < \alpha(\text{water-PEG-KBr}) < \alpha(\text{water-PEG-KI})$.

11. As the concentration of alkalis and salts increases, the value of the Haggins constant for water-PEG-alkaline and water-PEG-salt systems increases. It is $K_H(\text{water-PEG-LiOH}) > K_H(\text{water-PEG-NaOH}) > K_H(\text{water-PEG-KOH})$ and $K_H(\text{water-PEG-KCl}) >$

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

12. As the concentration of alkalis and salts increases, the average square distance between the ends of the PEG macromolecule chain in the solution and the length of the Kuhn segment decrease. That is $\langle h \rangle(\text{water-PEG-LiOH}) < \langle h \rangle(\text{water-PEG-NaOH}) < \langle h \rangle(\text{water-PEG-KOH})$, $A(\text{water-PEG-LiOH}) < A(\text{water-PEG-NaOH}) < A(\text{water-PEG-KOH})$ and $\langle h \rangle(\text{water-PEG-KCl}) < \langle h \rangle(\text{water-PEG-KBr}) < \langle h \rangle(\text{water-PEG-KI})$, $A(\text{water-PEG-KCl}) < A(\text{water-PEG-KBr}) < A(\text{water-PEG-KI})$.

13. In the θ -solvent, the mean square distance between the ends of the PEG macromolecule chain and the length of the Kuhn segment increase as the alkali concentration increases, as the concentration of salts increases, it decreases. It is $\langle h_\theta \rangle(\text{water-PEG-LiOH}) > \langle h_\theta \rangle(\text{water-PEG-NaOH}) > \langle h_\theta \rangle(\text{water-PEG-KOH})$, $A_\theta(\text{water-PEG-LiOH}) > A_\theta(\text{water-PEG-NaOH}) > A_\theta(\text{water-PEG-KOH})$ and $\langle h_\theta \rangle(\text{water-PEG-KCl}) > \langle h_\theta \rangle(\text{water-PEG-KBr}) > \langle h_\theta \rangle(\text{water-PEG-KI})$, $A_\theta(\text{water-PEG-KCl}) > A_\theta(\text{water-PEG-KBr}) > A_\theta(\text{water-PEG-KI})$.

Scientific innovations.

1. Due to the process of viscous flow in liquids a new approach has been proposed.

2. The structural properties of water-alkaline and water-salt systems have been studied comparatively by using different methods, the effect of alkalis and salts on the structure of water has been studied.

3. The structural properties of PEGs with different molecular weights in aqueous solutions were studied comparatively by different methods and the effect of PEGs on the structure of water was studied.

4. A new method was given to determine the hydration number of the polymer macromolecule in the solution and a new expression for the determination of the hydration number was obtained. With this expression, the hydration number of the PEG macromolecule in water-PEG, water-PEG-alkaline and water-PEG-salt systems was determined.

5. For the first time, the structural properties of water-PEG-

alkaline and water-PEG-salt systems were studied comparatively by different methods, the effect of alkalis and salts on the structure of water-PEG systems was studied.

6. In water-PEG, water-PEG-alkaline and water-PEG-salt systems, the partial molar volumes of PEGs of different molecular masses per unit monomer ring have been determined and expressions were obtained describing the concentration dependence of the average value of the partial molar volume per monomer.

7. Activation parameters of electrical conductivity, effective radii and hydration numbers of alkali and salt ions in water and water-PEG system have been determined.

8. For the first time in water, water-PEG-alkaline and water-PEG-salt systems, the dimensions of the PEG macromolecule were evaluated and its conformation was determined and the effect of temperature, alkalis, salts on the size and conformation of the PEG macromolecule were studied.

9. For the first time in θ -solvents selected according to water-PEG, water-PEG-alkali and water-PEG-salt systems the dimensions of the unexcited PEG macromolecule were evaluated and its mobility was determined, the effect of temperature, alkalis, salts to the size and mobility of the unexcited PEG macromolecule was studied.

Theoretical and practical significance of the research. Exact experimental results in biological systems (especially density and viscosity measurements), determination of the conformation of polymer macromolecules, evaluation of their size and hydration are extremely important in molecular-dynamic modeling for the formation of different cells. Also, the ability to purposefully change the structure of water under the influence of various substances in biological systems can play an important role in the formation of active conformations of macromolecules with biological functions. Therefore, the research conducted in the dissertation (both experimental results and calculated quantities) has both theoretical and some practical significance from the physical, physico-chemical, biophysical and medical-biological point of view.

Approbation and application. The main provisions and results of the dissertation were discussed at the following

conferences and published in their materials: 1) XVII International Conference Chemical Thermodynamics in Russia, June 29 - July 3 2009, Kazan, Russia; 2) VI Международная научная конференция, Кинетика и механизм кристаллизации, Самоорганизация при фазообразовании, 21-24 сентября 2010, Иваново, Россия; 3) XI Международная научная конференция, Проблемы сольватации и комплексообразования в растворах, 10-14 октября 2011, Иваново, Россия; 4) VII Международная научная конференция, Кинетика и механизм кристаллизации, 25-28 сентября 2012, Иваново, Россия; 5) Fizikanın aktual problemləri respublika elmi konfransı, 17 dekabr 2015, BDU, Bakı, Azərbaycan; 6) BDU-nun Fizika Problemləri İnstitutunun yaradılmasının 10 illiyinə həsr olunmuş beynəlxalq konfrans, Opto, nanoelektronika, kondensə olunmuş mühit və yüksək enerjilər fizikası, 25-26 dekabr 2015, BDU, Bakı, Azərbaycan; 7) II International Scientific Conference of Young Researchers, 27-28 April 2018, BEU, Baku, Azerbaijan; 8) Fizika və astronomiya problemləri beynəlxalq elmi konfransı, 24-25 may 2018, BDU, Bakı, Azərbaycan; 9) Conference Proceedings, Modern Trends In Physics, 01-03 May, 2019, BSU, Baku, Azerbaijan.

The materials of the dissertation were published in 33 articles (13 of them in journals indexed in the Web of Science) and 8 theses in local and foreign journals. 1 monograph and 1 textbook on the topic and materials of the dissertation were also published.

Name of the organization where the dissertation work is executed. The dissertation work was accomplished at the departments of "Optics and Molecular Physics" and "Matter Structure" of Baku State University.

Structure, volume and main content of dissertation work. Dissertation work is posted on 341 pages as a whole. It consists of an introduction, including 75 figures, 73 tables, 6 chapters, a conclusion, a list of 357 references titles, a list of abbreviations and symbols. The volume of the dissertation (with the exception of gaps and pictures in the text, tables, graphs, appendices and list of reference) - 373816 characters (introduction - 22186, Chapter I - 95728, Chapter II - 62027, Chapter III - 43692, Chapter IV - 26655, Chapter V - 58013, Chapter VI - 58980, result - 6535 characters).

CONTENT OF THE DISSERTATION WORK

The introduction is justified the relevance of the topic of the dissertation, The purpose of the work and the main provisions of the defense were given, research objects, research methods, approbation and publication of dissertation materials were indicated, scientific novelty and practical significance were explained.

The first chapter is devoted to the analysis of scientific literature. In the review mainly was analyzed the literature data of recent years structure and properties of water, interactions in polymer solutions and structural features, hydration processes in biological systems and on the physical and chemical properties of water-PEG systems modern ideas have been interpreted. In this chapter modern and comprehensive information gives about the structure of water molecules, hydrogen bonds in water, physical properties of water, structural models of water, interactions and structural properties of polymer solutions, rheology of polymer solutions, conformation of polymer macromolecules in water, two-phase polymer systems, hydration process (ionic polymer macromole , including hydration of proteins), Hofmeister series, application of PEG and study of physical and chemical properties of water-PEG systems by various methods, etc.

The second chapter is devoted to the experimental determination of a number of quantities and the interpretation of methods for calculating various quantities in connection with the study of structural properties in aqueous solutions. This chapter covers research objects, research methods and reasons for their selection, sample preparation, devices used in research, calculation of viscous flow activation parameters, calculation of partial molar volume, determination of hydration number of polymer macromolecule, determination of polymer macromolecule conformation and size, effective ionization radius and determination of hydration numbers, calculation of activation parameters of ionic electrical conductivity, determination of energy and length of hydrogen bond between water molecules by IR spectroscopy method are explained in detail.

Activation of the viscous flow of liquids is determined by the expression Gibbs energy according to Frenkel's and Eyring's theories¹.

$$\Delta G_{\eta}^{\ddagger} = RT \ln \left(\frac{\eta}{\eta_0} \right) \quad (1)$$

According to Eyring's theory, $\eta_0 = N_A h \rho / M$ is calculated. Here R -universal gas constant, N_A -Avogadro number, h -Planck constant, T -absolute temperature, η -dynamic viscosity, ρ -density, M -molar mass (calculated in terms of solutions $M = \sum_{i=1}^N x_i M_i$). Viscous flow activation enthalpy

$$\Delta H_{\eta}^{\ddagger} = R \frac{d \ln(\eta / \eta_0)}{d(1/T)} \quad (2)$$

is defined by the expression¹. Known from thermodynamics because viscous flow occurs at constant pressure and temperature

$$\Delta G_{\eta}^{\ddagger} = \Delta H_{\eta}^{\ddagger} - T \Delta S_{\eta}^{\ddagger} \quad (3)$$

the expression for the activation entropy of the viscous flow ($\Delta S_{\eta}^{\ddagger}$) is calculated¹.

If the molar part of the solvent in the solution is x_1 , the molar mass is M_1 and the molar part of the solute is x_2 , and the molar mass is M_2 , the partial molar volumes of the solvent (\tilde{V}_1) and the solute (\tilde{V}_2)

$$\tilde{V}_1 = V_m - x_2 \left(\frac{\partial V_m}{\partial x_2} \right)_{p,T}, \quad \tilde{V}_2 = V_m - x_1 \left(\frac{\partial V_m}{\partial x_1} \right)_{p,T} \quad (4)$$

is defined by the expressions ($x_1 + x_2 = 1$, $V_m = (x_1 M_1 + x_2 M_2) / \rho$)¹.

If the molar part of the solvent in the solution is x_1 , the molar mass is M_1 and the molar part of the polymer is x_2 , and the molar mass is M_2 , the hydration number of the polymer macromolecule (N_h)

$$N_h = \left(\frac{x_1}{x_2} + \frac{M_2}{M_1} \right) \left(1 - \frac{\rho_1}{\rho} \right) \quad (5)$$

is defined by the expression ($x_1 + x_2 = 1$). Here ρ_1 - is the density of

¹ Məsimov E.Ə., Həsənov H.Ş., Paşayev B.G. Mayelərin özlülüyü. Dərs vəsaiti. / – Bakı: Ləman Nəşriyyat Poliqrafiya, – 2016, – 285 s.

water and ρ - is the density of the solution.

Reduced viscosity (η_g) based on the kinematic viscosities of the solvent (ν_h) and the solution (ν_m) in liquid polymer solutions

$$\eta_g = \frac{\nu_m - \nu_h}{\nu_h c} \quad (6)$$

is expressed in terms of¹. c - is the concentration of the polymer in the solution. From the Haggins equation

$$\eta_g = [\eta] + K_H [\eta]^2 c \quad (7)$$

intrinsic viscosity ($[\eta] = \lim_{c \rightarrow 0} (\eta_g)$) and Haggins constant (K_H) are determined. The relationship between the intrinsic viscosity ($[\eta]$) and the molecular weight (M) of the polymer

$$[\eta] = KM^\alpha \quad (8)$$

it is described by the Mark-Kuhn-Houwink formula¹. Here K - is a quantity that does not depend on the molecular weight of the polymer, α - is a quantity that does not depend on the conformation of the polymer macromolecule. The value of the intrinsic viscosity ($[\eta]_\theta$) in the θ -solvent is used to determine the size of the unexcited polymer macromolecule. Intrinsic viscosity in θ -solvent according to Flory's theory

$$[\eta]_\theta = K_\theta M^{1/2} \quad (9)$$

is expressed in terms of¹. Here it is called K_θ - θ -constant. Stokmayer-Fixman formula, the relationship between $[\eta]$ and K_θ is as follows:

$$\frac{[\eta]}{\sqrt{M}} = K_\theta + 0,51B\Phi\sqrt{M} \quad (10)$$

B - is called the remote effect parameter. $[\eta]_\theta$ is calculated from expressions (9) and (10). In an arbitrary solvent ($\langle\langle h \rangle\rangle$) and θ -solvent ($\langle\langle h_\theta \rangle\rangle$) we can find the standard deviation between the ends of the chain of the macromolecule in the Flory-Fox equation¹:

$$[\eta] = \Phi \frac{\langle h \rangle^3}{M}, \quad [\eta]_\theta = \Phi \frac{\langle h_\theta \rangle^3}{M} \quad (11)$$

Here $\Phi = 2.1 \cdot 10^{23} \text{ mol}^{-1}$ is the Flory coefficient. Swelling coefficient of macromolecule in solution (β)

$$\beta = \left(\frac{[\eta]}{[\eta]_{\theta}} \right)^{1/3} = \frac{\langle h \rangle}{\langle h_{\theta} \rangle} \quad (12)$$

is expressed in terms of¹. In arbitrary solvent (A) and θ -solvent (A_{θ}) the length of the Kuhn segment, respectively

$$A = \frac{\langle h \rangle^2}{L} = \frac{\langle h \rangle^2}{nl_0}, \quad A_{\theta} = \frac{\langle h_{\theta} \rangle^2}{L} = \frac{\langle h_{\theta} \rangle^2}{nl_0} \quad (13)$$

is determined by the expressions. Here L - is the full length of the macromolecule chain, n - is the degree of polymerization, and l_0 - is the contour length of the repeating monomer ring.

Stokes radius (r_s) of ions according to the limit values of molar electrical conductivity of ions (λ_{\pm}^0)

$$r_s = \frac{|z_{\pm}|F^2}{6\pi N_A \eta \lambda_{\pm}^0} \quad (14)$$

calculated by the expression². η - is the dynamic viscosity of the solvent, F - is the Faraday number. The effective radius (r_{ef}) of ions

$$r_{ef} = r_s + 0.0103\varepsilon + r_y \quad (15)$$

determined from the empirical equation². Here ε - is the dielectric constant of water. For solvents with high dielectric constant (for example, water), $r_y = 1.13 \text{ \AA}$. The number of hydrations of ions

$$N_h = \frac{r_{ef}^3 - r_i^3}{r_{su}^3} \quad (16)$$

we can determine the expression. Here r_i - is the crystallographic or ionic radius of the ion, $r_w = 1.38 \text{ \AA}$ is the radius of the water molecule.

Activation Gibbs energy of ionic electrical conductivity

$$\Delta G_{\lambda}^{\ddagger} = -RT \ln \left(\frac{\lambda_{\pm}^0}{\lambda_0} \right) \quad (17)$$

is expressed in terms of³. According to Eyring's theory

$$\lambda_0 = \frac{|z_{\pm}|eF}{6h} \left(\frac{M}{\rho N_A} \right)^{\frac{2}{3}} \quad (18)$$

calculated by the expression³. Here $|z_{\pm}|$ - is the valence of the ion, e - is the charge of the electron, ρ - is the density of the solvent, and M -

is the molar mass of the solvent. Activation enthalpy of ionic conductivity

$$\Delta H_{\lambda}^{\neq} = -R \frac{d \ln(\lambda_{\pm}^0 / \lambda_0)}{d(1/T)} \quad (19)$$

is determined by the expression³ and after the appointment $\Delta G_{\lambda}^{\neq}$ and $\Delta H_{\lambda}^{\neq}$

$$\Delta G_{\lambda}^{\neq} = \Delta H_{\lambda}^{\neq} - T\Delta S_{\lambda}^{\neq} \quad (20)$$

the activation entropy (ΔS_{η}^{\neq}) of ionic electrical conductivity is calculated by the expression³.

IR - in the area based on the frequency of the OH valence oscillations of water molecules to determine the energy and length of the hydrogen bond between water molecule by Johansen

$$-E_H = \frac{18\Delta\nu}{720 + \Delta\nu}, \quad R_H = 2.44 \cdot (-E_H)^{-0.2} \quad (21)$$

statements are given¹. Here, $\Delta\nu = \nu_0 - \nu$, ν - is the oscillation frequency of the bound OH valence bond, and ν_0 - is the oscillation frequency of the isolated OH valence bond. Note that for water is equal to $\nu_0 = 7062 \text{ cm}^{-1}$. The unit of energy and length of the hydrogen bond determined by (21) corresponds to *kcal/mol* and Å , respectively¹.

The third chapter is devoted to the analysis of structural features in water-alkaline and water-salt systems. In this chapter, the effects of a number of alkalis (LiOH, NaOH, KOH) and salts (KCl, KBr, KI) on the structure of water are compared by different methods. Dynamic viscosity and density of the aqueous solutions of the studied alkalis and salts in the range of 283.15-333.15 K and 0-0.07 molar fraction, electrical conductivity in the range of 283.15-333.15 K temperature and 0.001-0.01 *mol/l* molar concentration were measured. IR spectra of different concentrations of aqueous solutions

² Влаев Л.Т., Николова М.М., Господинов Г.Г. Электротранспортные свойства ионов в водных растворах H_2SeO_4 и Na_2SeO_4 // Журнал структурной химии, – 2005, том 46, № 4, – с. 655-662.

³ Məsimov E.Ə., Nəsonov H.Ş., Paşayev B.G. Maye məhlulların elektrik keçiriciliyi. Monoqrafiya. / – Bakı: AzTU-nun mətbəəsi, – 2011. – 84 s.

of salts were drawn, and based on these spectra, the frequency of OH valence oscillations of water molecules in the IR region was determined. Concentration dependence of viscosity flow activation parameters of solutions determined on the basis of experimental values, partial molar volume of solute in solution, energy and length of hydrogen bond between water molecules in solution, activation parameters of ionic electrical conductivity in water, ions (Li^+ , Na^+ , K^+ , OH^- , Cl^- , Br^- , I^-) and a comparative analysis of the temperature dependence of the hydration numbers and effective radii.

To study the structural properties of aqueous solutions, it is necessary to determine the activation parameters of the viscous flow and the partial molar volume. For aqueous solutions of the studied alkalis, the Gibbs energy of viscous flow activation increases with increasing temperature concentration, the enthalpy of activation of viscous flux increases for LiOH and NaOH solutions, decreases for KOH solution, and the entropy of viscous flow activation decreases, as well as $\Delta G_{\eta}^{\ddagger}(\text{water-LiOH}) > \Delta G_{\eta}^{\ddagger}(\text{water-NaOH}) > \Delta G_{\eta}^{\ddagger}(\text{water-KOH})$, $\Delta H_{\eta}^{\ddagger}(\text{water-LiOH}) > \Delta H_{\eta}^{\ddagger}(\text{water-NaOH}) > \Delta H_{\eta}^{\ddagger}(\text{water-KOH})$, $\Delta S_{\eta}^{\ddagger}(\text{water-LiOH}) > \Delta S_{\eta}^{\ddagger}(\text{water-NaOH}) > \Delta S_{\eta}^{\ddagger}(\text{water-KOH})$. The partial molar volumes of the alkalis studied in solution at a given temperature increase with increasing concentration, as well as $\tilde{V}(\text{water-LiOH}) < \tilde{V}(\text{water-NaOH}) < \tilde{V}(\text{water-KOH})$. At a temperature of 293.15 K, the partial molar volume of LiOH is negative in solution up to $x \approx 0.03$ and NaOH is negative up to $x \approx 0.02$. An electric field is created around each ion in the water, and the intensity of this field decreases sharply with increasing distance. In such a heterogeneous field, water molecules orient around the ion. As a result, the volume occupied by water molecules around the ion is smaller than the volume they occupy in the water phase. This compression effect is called electrostriction, and all ions form electrostriction in aqueous solutions. We assume that the electrostrictive effect of Li^+ and Na^+ ions is so great that at low concentrations the ions themselves compensate for the increase in volume at their own expense. Note that in most cases, the increase in volume due to the ions themselves is greater than the decrease in

volume due to the effect of electrostriction. Therefore, the partial molar volume is positive, with a few exceptions, such as liquid solutions of LiOH and NaOH. Summarizing this, based on the analysis of the viscous flow and volume properties of water-alkaline systems in the studied temperature and concentration range, we can say that as the concentration of alkalis in solution increases, the structure of water collapses. Also, NaOH has a more destructive effect on the structure of water than LiOH, and KOH has a stronger destructive effect than NaOH.

As the concentration increases at the temperature taken for the aqueous solution of the salts under study, the Gibbs energy of activation of the viscous flux first decreases (this decrease continues to $x \approx 0.01$ molar for KCl and $x \approx 0.03$ molar for KBr and KI), then increases, the activation enthalpy of viscous flux and the entropy only decreases. Also $\Delta G_{\eta}^{\ddagger}(\text{water-KCl}) > \Delta G_{\eta}^{\ddagger}(\text{water-KBr}) > \Delta G_{\eta}^{\ddagger}(\text{water-KI})$, $\Delta H_{\eta}^{\ddagger}(\text{water-KCl}) > \Delta H_{\eta}^{\ddagger}(\text{water-KBr}) > \Delta H_{\eta}^{\ddagger}(\text{water-KI})$, $\Delta S_{\eta}^{\ddagger}(\text{water-KCl}) > \Delta S_{\eta}^{\ddagger}(\text{water-KBr}) > \Delta S_{\eta}^{\ddagger}(\text{water-KI})$. The partial molar volumes of the salts studied in solution at a given temperature increase with increasing concentration, and also become $\tilde{V}(\text{water-KCl}) < \tilde{V}(\text{water-KBr}) < \tilde{V}(\text{water-KI})$. The study of absorption spectra of solutions in the IR region is of great importance for the quantitative characterization of hydrogen bonds. Absorption spectra of aqueous solutions of KCl, KBr and KI salts at different concentrations in the IR region were plotted. Based on the study of the IR spectra of aqueous solutions of salts, the energy and length of the hydrogen bond between water molecules at the considered concentrations were calculated (Table 1). It was found that as the concentration of KCl, KBr and KI increases, the energy of the hydrogen bond between the water molecules in the solution decreases and the length increases. At a given temperature and concentration, the energy of the hydrogen bond between water molecules in aqueous solutions of KCl, KBr and KI is $E_{\text{H}}(\text{water-KCl}) < E_{\text{H}}(\text{water-KBr}) < E_{\text{H}}(\text{water-KI})$. Thus, the analysis of viscous flow and volume properties of water-KCl, water-KBr and water-KI systems in the studied temperature and concentration range, as well

as absorption spectra in the IR region allows us to say that as the concentration of KCl, KBr and KI in solution increases, the structure of the water disintegrates. Also, KI salt has a stronger destructive effect on the structure of water than KBr, and KBr salt has a stronger destructive effect than KCl.

Table 1. KCl, KBr and KI in different concentrations in aqueous solutions the frequency (ν) of valence oscillations of OH groups of water molecules in the IR region, energy (E_H) and length (R_H) of hydrogen bonds between water molecules

p, %	x	ν , cm^{-1}	E_H , kJ/mol	R_H , Å
water-KCl				
0	0	6862.00	16.4	1.86
10	0.0261	6893.17	14.3	1.91
20	0.0570	6907.23	13.3	1.94
25	0.0745	6926.65	11.9	1.98
water-KBr				
10	0.0165	6911.78	13.0	1.94
20	0.0365	6939.91	10.9	2.01
30	0.0609	6947.25	10.4	2.04
35	0.0754	6948.16	10.3	2.04
water-KI				
10	0.0119	6903.23	13.6	1.93
20	0.0264	6935.71	11.3	2.00
30	0.0444	6950.56	10.1	2.05
40	0.0675	6956.07	9.7	2.06
45	0.0816	6959.69	9.4	2.08

The study of electrical conductivity in aqueous solutions of electrolytes is of great importance for the study of the processes of hydration and migration of ions in solution. Calculations show that as the temperature increases, the electrical conductivity of the ions under study increases, the effective radii and hydration numbers decrease slightly for Li^+ , Na^+ , OH^- ions, and almost do not change for K^+ , Cl^- , Br^- , I^- ions. Also $r_{ef}(\text{Li}^+) > r_{ef}(\text{Na}^+) > r_{ef}(\text{K}^+)$, $N_h(\text{Li}^+) > N_h(\text{Na}^+) > N_h(\text{K}^+)$, $r_{ef}(\text{Cl}^-) \approx r_{ef}(\text{Br}^-) \approx r_{ef}(\text{I}^-)$, $N_h(\text{Cl}^-) > N_h(\text{Br}^-) >$

$N_h(I)$. The increase in the electrical conductivity of ions in water with increasing temperature can be explained by a decrease in the viscosity of water and an increase in the mobility of ions. To characterize the process of ion migration in aqueous solutions of alkalis and salts, let's make a comparative analysis of the temperature dependence of the activation parameters of ionic conductivity and the values of these quantities for each ion. The activation parameters of the electrical conductivity of the studied ions (Li^+ , Na^+ , K^+ , OH^- , Cl^- , Br^- , I^-) in the considered temperature range decrease with increasing temperature. This can be caused by the following: a decrease in the viscosity of the solution, an increase in the thermal energy of water molecules and ions, a weakening of the interaction of water molecules with each other and with ions, the formation of vacancies, a decrease in the effective ionic radius, a decrease in hydration, a decrease in hydration energy, whether the ion has positive or negative hydration. We assume that all of these cases contribute to the dependence on $\Delta G_\lambda^\ddagger(T)$, $\Delta H_\lambda^\ddagger(T)$, and $\Delta S_\lambda^\ddagger(T)$. As a result, as the temperature increases, $\Delta G_\lambda^\ddagger$ decreases as the migration of ions in the solution becomes easier, $\Delta H_\lambda^\ddagger$ decreases as all interactions weaken, and $\Delta S_\lambda^\ddagger$ decreases as chaoticity increases.

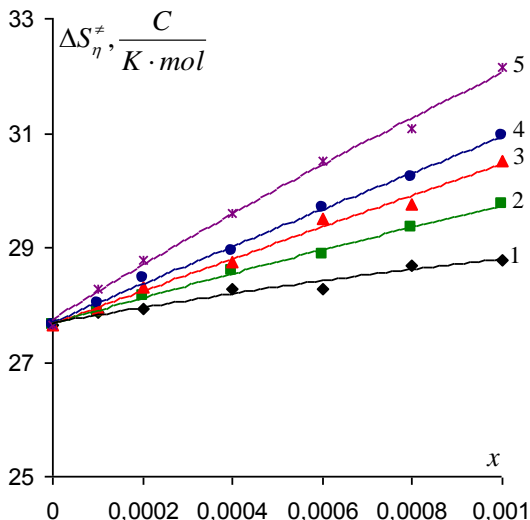
The fourth chapter is devoted to the analysis of structural features in water-PEG systems. In this chapter, the effect of PEGs of different molecular weights on the structure of water is studied, as well as the effect of temperature on the conformation and size of the PEG macromolecule in water-PEG systems and θ -solvents selected according to these systems. Dynamic viscosity and density of aqueous solutions of PEGs of different fractions (1000, 1500, 3000, 4000, 6000) in the range of 293.15-323.15 K temperature and 0-0.001 molar fraction, kinematic in the range of 293.15-323.15 K temperature and 0-5 g/dl concentration. The viscosity was measured, IR spectra were drawn at different concentrations, and based on these spectra, the frequency of OH valence oscillations of water molecules in the IR region was determined. Concentration dependence of the activation parameters of the viscous flow of solutions determined on the basis of experimental values, the partial molar volume of PEG in

the solution, the energy and length of the hydrogen bond between water molecules in the solution, the number of hydration of the PEG macromolecule, the intrinsic viscosity of the solution A comparative analysis of the temperature dependence of the α parameter, the swelling coefficient of the macromolecule, the mean square distance between the ends of the chain of the excited PEG macromolecule in water and not excited in the θ -solvent, and the length of the Kuhn segment.

The PEG macromolecule ($\text{HO}-(\text{--CH}_2\text{--CH}_2\text{--O--})_n\text{--H}$) has both hydrophobic (CH_2) and hydrophilic (OH) groups. The OH group of PEG, the --O-- and --H atoms, can form hydrogen bonds with the water molecule, while the CH_2 groups create a hydrophobic effect. It can be expected that the presence of a hydrophobic effect in PEG will enhance the formation of hydrogen bonds between hydrophilic groups of PEG and water molecules. It was found that the activation parameters of the viscous flow of aqueous solutions of PEGs of different fractions increase with increasing molecular weight and concentration of PEG (Figure 1), and the partial molar volume of PEG in solution increases with increasing molecular weight of PEG, decreases with increasing concentration. Calculations show that at a given temperature and concentration, the partial molar volume of PEG per unit monomer ring does not depend on the molecular weight of PEG. We can describe the concentration dependence of the average value of the partial molar volume of PEGs of different molecular masses per unit monomer ring at a temperature of 293.15 K (\tilde{V}/n)_{av}=1906007.0x²-5854.9x+39.6.

Polymer macromolecules are hydrated due to hydrogen and other interactions between water molecules and polymer macromolecules. Quantitative study of the process of hydration of polymer macromolecules and analysis of the obtained results are of great importance in the study of structural features of the system. The hydration numbers of the considered molecular weight PEGs in the studied temperature and concentration range were determined. Calculations show that the number of hydrations is almost independent of the concentration of PEG. Here are the hydration numbers at the given temperatures average values were taken

according to the concentrations under consideration (Table 2). As can be seen from Table 2, the hydration number of the macromolecule increases with increasing molecular weight of PEG and decreases with increasing temperature.



**Figure 1. Dependence of viscous flow activation entropy on concentration in water-PEG systems (T=293.15 K).
1-PEG (1000), 2-PEG (1500), 3-PEG (3000),
4-PEG (4000), 5-PEG (6000)**

Table 2. PEG in water-PEG system temperature dependence of the hydrations number

T, K	PEG(1000)	PEG(1500)	PEG(3000)	PEG(4000)	PEG(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

Absorption spectra of aqueous solutions of PEGs with molecular weights of 1000, 4000 and 6000 in the IR region were plotted. The energy and length of the hydrogen bond between water molecules at different concentrations were calculated based on the frequency of the valence oscillations of the OH groups of water molecules in the IR spectrum of solutions. The results show that as both the molecular weight and the concentration of PEG increase, the energy of the hydrogen bond between the water molecules in the solution increases and the length decreases, as well as $E_H(\text{water-PEG}(1000)) < E_H(\text{water-PEG}(4000)) < E_H(\text{water-PEG}(6000))$. Analysis of the viscous flow and volume properties of water-PEG systems in the studied temperature and concentration range, as well as the absorption spectra in the IR region, allows us to say that all molecular weight PEGs studied have a structural effect on water, and this effect is enhanced by an increase in the molecular weight and concentration of PEG. It can be assumed that in the studied systems, aggregates of certain sizes are formed as a result of the accumulation of water molecules (primarily free water molecules) around the PEG macromolecules by hydrogen bonding. As the concentration of PEG increases, the number of such aggregates increases, the size increases with increasing molecular weight, and as a result, the solution becomes more structured.

The structural properties of polymer solutions are mainly described by the conformation, size, hydration, etc. of the polymer macromolecule. The conformation and size of the PEG macromolecule in the solution depend on the properties of the solvent and the PEG, temperature, etc. depends. The study of the conformation and size of the PEG macromolecule in an aqueous medium is an interesting and important issue. Calculations show that the value of the intrinsic viscosity increases with increasing molecular weight of PEG at a given temperature, and for a given molecular mass of PEG decreases slightly with increasing temperature. The intrinsic viscosity of a solution is the additional viscosity formed by the rotation of polymer macromolecules in the solvent medium. The intrinsic viscosity is directly proportional to the size of the macromolecule. Increasing the size of the PEG

macromolecule with increasing molecular weight, increasing polarity, also, as it interacts with more water molecules, it becomes more difficult to rotate in the environment, and therefore its intrinsic viscosity increases. We assume that the temperature-dependent decrease in the intrinsic viscosity for the obtained molecular weight PEG is due to the decrease in the viscosity of the medium with increasing temperature and the decrease in the volume of the PEG macromolecule.

It was found that the value of the Haggins constant decreases with increasing molecular weight of PEG at a given temperature, and for a given molecular mass of PEG decreases slightly with increasing temperature. Haggins characterizes the intensity of interactions between particles in a fixed system. The worse the solvent for a given polymer, the higher the value of the Haggins constant. The decrease in the value of the Haggins constant with increasing molecular weight at a given temperature indicates that water is a better solvent for relatively large molecular weight PEGs. This can be explained by the hydration of the PEG macromolecule. Decrease in the value of the Haggins constant with increasing temperature for the obtained molecular weight PEG shows that solubility of PEG in water with increasing temperature is getting better. This is probably due to the increase in the number of free water molecules as a result of the collapse of the structure of water with increasing temperature.

The parameter α , which is included in the Mark-Kuhn-Houwink formula, is a quantity that allows to determine the shape of the polymer macromolecule in solution, and any interaction that changes the shape of the polymer molecule changes the value of α . Our research shows that the parameter α takes values in the temperature range (0.7-0.8) we are considering, and increases partially with increasing temperature. This indicates that the PEG macromolecule is in the form of a wash that can be penetrated by the surrounding fluid in the aquatic environment, and this macromolecular wash is partially opened as the temperature increases. In non-ideal solvents, the size of the polymer wash is β times larger than in θ -solvents due to its swelling in the solvent. The swelling coefficient of the PEG macromolecule in water increases

slightly with increasing molecular weight and temperature of the PEG, and in all cases becomes $\beta > 1$. It is likely that the increase in β with increasing molecular weight is due to the hydration of PEG and the increase in temperature is due to the weakening of the interaction between PEG and water molecules, the decrease in the viscosity of the medium and the conformation of the macromolecule.

The mean square distance between the ends of a chain of PEG macromolecules excited in solution and not excited in θ -solvent calculated. Calculations show that the mean square distance between the ends of the chain of both excited and unexcited PEG macromolecules increases with increasing molecular weight of PEG and decreases with increasing temperature. We assume that the increase in the quantities $\langle h \rangle$ and $\langle h_{\theta} \rangle$ with increasing molecular weight is accompanied by an increase in the volume of the molecular mass, and a decrease with increasing temperature is associated with a decrease in the number of hydrations of PEG and due to the reduction of the volume of the macromolecular mass.

Polymer macromolecules are in the form of long chains and their internal parts tend to heat action. As a result, the macromolecule has a large number of conformational states. The set of conformations can also be taken as a measure of the mobility of a polymer chain. The most important parameter that characterizes the mobility of a macromolecule chain is the length of the Kuhn segment. For water-PEG systems, the values of the length of the Kuhn segment at different temperatures were determined for the PEG macromolecule excited in solution and not excited in θ -solvent. Calculations show that the length of the Kuhn segment of the excited PEG macromolecule in water-PEG systems increases with increasing molecular weight of PEG and decreases with increasing temperature. The length of the Kuhn segment of the unexcited PEG macromolecule in the θ -solvent does not depend on the molecular weight of the PEG and decreases with increasing temperature. The length of the Kuhn segment depends on the interactions between the polymer and the solvent molecules. The stronger these interactions, the more difficult it is for the bonds in the macromolecule to rotate in space, that is, the conformational transformation of the

macromolecule becomes difficult, and as a result the length of the Kuhn segment becomes larger. As the molecular weight of PEG increases, the activation enthalpy of viscous flow in the water-PEG system increases, indicating that the interaction between water and PEG molecules increases. Most likely, this is why the length of the Kuhn segment increases with increasing molecular weight in water. Since the interaction energy between the polymer and the solvent molecules in the θ -solvent does not change and the macromolecule is not excited, the length of the Kuhn segment does not depend on the molecular weight of the PEG. As the temperature increases and the intermolecular interactions weaken, a conformation transformation occurs in the PEG macromolecule (α , β , A changes), and due to the decrease in the values of $\langle h \rangle$ and $\langle h_\theta \rangle$, polarity decreases. As a result, the macromolecule changes from a more polar conformation to a less polar conformation. We assume that due to the increase in temperature and the increase in the kinetic energy of heat transfer, the weakening of the interactions between the solvent and PEG molecules, as well as the decrease in the polarity of the PEG macromolecule the mobility of the PEG macromolecule in the water-PEG and θ -solvent increases, ie A and A_θ decrease.

The fifth chapter is devoted to the analysis of structural properties of water-PEG-alkaline (LiOH, NaOH, KOH) systems. This chapter analyzes the effect of alkalis on the structure of water-PEG systems corresponding to PEGs of different molecular weights (1000, 1500, 3000, 4000, 6000), as well as on the conformation and size of PEG macromolecule in solution and θ -solvent. In the studied water-PEG-alkaline systems dynamic viscosity and density of 293.15-323.15 K temperature and PEG in the range of 0-0.001 molar fraction (with $x_{\text{LiOH}}=0.01$, $x_{\text{NaOH}}=0.01$, $x_{\text{KOH}}=0.01$), kinematic viscosity of alkali at a temperature of 293.15 K in the range of 0-0.05 molar fraction and PEG concentration 0-5 g/dl, 283.15-333.15 K temperature and in the range of 0.001-0.01 mol/l molar concentration of alkalis ($M_{\text{PEG}} = 4000 \text{ g/mol}$, $x_{\text{PEG}} = 0.0002$) electrical conductivity was measured. The parameters of the activation of the viscous flow of solutions determined on the basis of experimental values, the partial molar volume of PEG in the solution, the intrinsic viscosity of

the solution, the Huggins constant, the α parameter included in the Mark-Kuhn-Houwink formula, the swollen coefficient and the average square distance between the ends of the chain of the excited PEG macromolecule in the θ -solvent and the length of the Kuhn segment from the concentration of alkalis, the number of hydrations of the PEG macromolecule in solution, the activation parameters of ionic conductivity in the water-PEG system, ions (Li^+ , Na^+ , K^+ , OH^-) comparative analysis of the temperature dependence of the radii is given.

The study of structural changes in the solution with the introduction of a third component in water-PEG systems is of great scientific and practical importance. It was found that the activation parameters of the viscous flow of water-PEG-alkaline systems increase with increasing molecular weight and concentration of PEG. Determination of the partial molar volumes of the components of the solution allows to clarify the molecular interactions in the solution. The results show that the partial molar volume of PEG in solution decreases with increasing concentration of PEG, and as in water-PEG systems, the partial molar volume of PEG per unit monomer ring in water-PEG-alkaline systems does not depend on the molecular weight of PEG. In water-PEG-LiOH, water-PEG-NaOH and water-PEG-KOH systems at 293.15 K, the average values of the partial molar volume of PEG per unit monomer ring depend on the concentration of $(\tilde{V}/n)_{\text{av}}=1511612.1x^2-5440.5x+38.9$, $(\tilde{V}/n)_{\text{av}}=2106749.5x^2-5922.9x+38.7$, $(\tilde{V}/n)_{\text{av}}=2193496.5x^2-6804.1x+38.6$ can be described by these expressions. We have studied the process of hydration of PEG to characterize the interactions between PEG macromolecules, alkaline ions and water molecules in water-PEG-alkaline systems. It was determined that the hydration number of PEG increases with increasing molecular weight, partially decreases with increasing temperature. It should be noted that due to the effect of electrostatic forces on long distances, the process of hydration in solutions containing both polymers and ions, will be somewhat different from the hydration process in solutions containing only polymers (without ions). Our results show that as both the molecular weight and the concentration of PEG in the solution increase, the

solution acquires a stronger structure and becomes more structured. Of course, in addition to water-PEG-alkaline systems the structure of the ions (Li^+ and OH^- , Na^+ and OH^- , K^+ and OH^-) will be different from the structure of the water-PEG system. This is shown by the comparison of the values of the parameters ΔG_η^\ddagger , ΔH_η^\ddagger , ΔS_η^\ddagger , \check{V} and N_h set for water-PEG and water-PEG-alkaline systems.

When PEG is soluble in water, both the structure of the water and the conformation and size of the macromolecule change due to the interactions between PEG macromolecules and water molecules. Our results show that in water-PEG-alkaline systems, the intrinsic viscosity of solutions corresponding to PEGs of different molecular masses increases with increasing molecular weight of PEG, and decreases with increasing concentration of alkalis. We assume that the decrease in $[\eta]$ depending on the concentration of alkalis for the obtained molecular weight PEG is due to the decrease in the volume of the PEG macromolecule with increasing concentration. Thus, despite the increase in the viscosity of the solution with increasing concentration of alkalis, the volume of the PEG macromolecule decreases, resulting in easier rotation of the macromolecule in the environment. For water-PEG-alkaline systems, it has been determined that the Huggins constant decreases with increasing molecular weight of PEG, increasing with increasing concentration of alkalis. This indicates that the solubility of PEG in alkaline systems deteriorates with increasing concentration of alkalis for the obtained molecular weight PEG. This is probably due to the hydration of alkaline ions in the solution. Thus, while only PEG macromolecules are hydrated in water-PEG systems, both PEG macromolecules and Li^+ and OH^- , Na^+ and OH^- , K^+ and OH^- ions are hydrated in water-PEG-alkaline systems.

To determine the shape of the PEG macromolecule in water-PEG-alkaline systems and to study the effect of alkalis on this form, the value of the parameter α included in the Mark-Kuhn-Houwink formula was determined for solutions studied at 293.15 K and different concentrations of alkalis (Figure 2). It was determined that the α parameter is at a temperature of 293.15 K and in the concentration range of the alkalis we are considering for the water-

PEG-LiOH system (0.58 - 0.72), for the water-PEG-NaOH system (0.62 - 0.72) and for the water-PEG-KOH system (0.68 - 0.72). gets prices. This price range indicates that the PEG macromolecule has a swollen wash chain with a mobile chain in an aqueous-alkaline environment, in a good solvent. The α parameter decreases in part with increasing alkali concentration. This indicates that as the concentration of alkalis in the solution increases, at least this macromolecular washout accumulates. In all cases considered for water-PEG-alkaline systems, $\alpha > 0.5$, $\beta > 1$, and the coefficient of swelling of the PEG macromolecule in the water-alkaline system increases with increasing molecular weight of PEG, decreasing with increasing concentration of alkalis in solution. The decrease in β with an increase in the concentration of alkalis in the solution is most likely due to the hydration of the alkali ions in the solution, the increase in the viscosity of the medium, and the conformational transformation of the macromolecule (the value of α decreases). Indeed, $N_h(\text{water-PEG-alkali}) < N_h(\text{water-PEG})$.

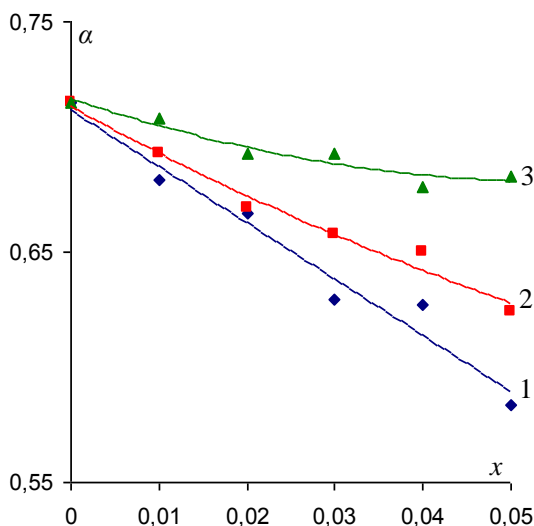


Figure 2. In water-PEG-alkaline systems dependence of the parameter α included in the Mark- Kuhn-Houwink formula on the concentration of alkalis (T = 293.15 K). 1 - water-PEG-LiOH, 2 - water-PEG-NaOH, 3 - water-PEG-KOH

The results obtained for water-PEG-alkaline systems show that the average square distance between the ends of the chain of excited PEG macromolecule at 293.15 K increases with increasing molecular weight of PEG, decreases with increasing concentration of alkalis in solution. However, the standard deviation between the ends of the chain of the unexcited PEG macromolecule increases with increasing molecular weight of the PEG and the concentration of alkalis in the solution. We assume that a decrease in $\langle h \rangle$ with an increase in the concentration of alkalis is associated with a decrease in the number of hydrations of PEG and a decrease in the volume of the molecular mass, and an increase in $\langle h_0 \rangle$ is associated with an increase in the volume of the molecular mass ($[\eta]_\theta$ decreases). The mobility of the polymer chain is one of the most important characteristics that characterize polymers and determine their basic macroscopic properties. The mobility of a polymer chain is called the ability of the manga to change its shape under the influence of thermal action and the external field. It was found that the length of the Kuhn segment of the excited PEG macromolecule in water-PEG-alkaline systems increases with increasing molecular weight of PEG and decreases with increasing concentration of alkalis in solution. The length of the Kuhn segment of the unexcited PEG macromolecule in the θ -solvent does not depend on the molecular weight of the PEG and increases with increasing alkali concentration. Based on the values of the Kuhn segment, PEG can be considered a mobile polymer in all cases considered for water-PEG-alkaline systems. Note that since most polymer chains have many conformations, these conformational transitions are entropy in nature. Hence, mobility is a property of the polymer chain that characterizes the entropic nature of the conformational transitions. When alkali is added to the Water-PEG system, the alkaline ions (Li^+ and OH^- , Na^+ and OH^- , K^+ and OH^- , respectively) are hydrated, the hydration number of the PEG macromolecule is reduced and the size is reduced as a result, the interactions between water and PEG molecules are weakened. When alkali is added to the θ -solvent, the size of the PEG macromolecule increases and the polarity increases, as a result, the interactions between θ -solvent and PEG molecules are relatively strong. We

assume that for these reasons the motility of the PEG macromolecule increases in water-PEG-alkaline systems with increasing concentration of alkalis decreases in the θ -solvent. For visibility for water-PEG-LiOH systems, the values of the quantities $[\eta]$, K_H , β , $\langle h \rangle$ and A at different concentrations of LiOH are given in Table 3.

Table 3. In water-PEG-LiOH systems dependence of intrinsic viscosity ($[\eta]$), Haggins constant (K_H), swelling coefficient (β), mean square distance between the ends of the PEG macromolecule chain ($\langle h \rangle$) and length of the Kuhn segment (A) on LiOH concentration (x) (T=293.15 K).

x	PEG(1000)	PEG(1500)	PEG(3000)	PEG(4000)	PEG(6000)
$[\eta], dl/q$					
0	0.0341	0.0471	0.0675	0.0837	0.1343
0.01	0.0318	0.0443	0.0623	0.0770	0.1167
0.02	0.0304	0.0429	0.0602	0.0746	0.1077
0.03	0.0298	0.0388	0.0564	0.0698	0.0945
0.04	0.0286	0.0367	0.0519	0.0674	0.0899
0.05	0.0271	0.0347	0.0502	0.0623	0.0771
K_H					
0	5.269	3.627	1.998	1.433	1.117
0.01	5.770	3.834	2.279	1.633	1.371
0.02	5.633	3.742	2.209	1.578	1.285
0.03	6.468	4.557	2.397	1.724	1.403
0.04	6.284	5.083	2.766	1.618	1.370
0.05	6.840	5.035	2.699	1.920	1.698
β					
0	1.173	1.220	1.226	1.255	1.373
0.01	1.120	1.170	1.167	1.194	1.282
0.02	1.096	1.149	1.146	1.173	1.240
0.03	1.073	1.096	1.106	1.132	1.170
0.04	1.078	1.095	1.095	1.139	1.171
0.05	1.037	1.053	1.061	1.087	1.091

Table 3 (continued)

x	PEG(1000)	PEG(1500)	PEG(3000)	PEG(4000)	PEG(6000)
$\langle h \rangle, \text{Å}$					
0	25.33	32.28	45.86	54.21	72.67
0.01	24.74	31.63	44.65	52.74	69.34
0.02	24.37	31.30	44.13	52.18	67.52
0.03	24.21	30.27	43.20	51.05	64.64
0.04	23.88	29.72	42.02	50.46	63.56
0.05	23.45	29.16	41.54	49.15	60.40
$A, \text{Å}$					
0	11.96	12.95	13.07	13.70	16.41
0.01	11.41	12.44	12.39	12.97	14.94
0.02	11.07	12.18	12.10	12.69	14.17
0.03	10.93	11.39	11.60	12.15	12.98
0.04	10.63	10.98	10.97	11.87	12.55
0.05	10.26	10.57	10.73	11.26	11.33

When alkali is added to the water-PEG system, the alkaline ions formed as a result of dissociation interact with the PEG and water molecules, and a new structure of the solution is formed. In the study of such structural changes, along with the rheological and volumetric properties of solutions, it is necessary to study the electrical conductivity properties. The results show that with increasing temperature in the water-PEG-alkaline system, the electrical conductivity of the ions under consideration (Li^+ , Na^+ , K^+ , OH^-) increases, the effective radii, hydration numbers and activation parameters of the electrical conductivity decrease, as well as in water the water-PEG medium also contains $r_{ef}(\text{Li}^+) > r_{ef}(\text{Na}^+) > r_{ef}(\text{K}^+)$, $N_h(\text{Li}^+) > N_h(\text{Na}^+) > N_h(\text{K}^+)$. The above sequence of r_{eff} and N_h quantities for Li^+ , Na^+ , K^+ ions can be explained by the hydration of the ions. Based on our results, we can say that the electrical conductivity, effective radii and hydration numbers of alkali ions are smaller in the water-PEG system than in water. At a given temperature, the migration of ions in the water-PEG environment is slower than in water, because the viscosity of the aqueous solution of

the molecular weight and concentration of PEG considered is greater than the viscosity of water. Therefore, $\lambda_+^0(\text{water-PEG-ion}) < \lambda_+^0(\text{water-ion})$ becomes. It is known that although only ions are hydrated in alkaline systems, along with ions in water-PEG-alkaline systems PEG macromolecules are also hydrated. Therefore, $r_{ef}(\text{water-PEG-ion}) < r_{ef}(\text{water-ion})$, $N_h(\text{water-PEG-ion}) < N_h(\text{water-ion})$. In comparison, we see that the activation parameters of ionic electrical conductivity are higher in water-PEG-alkaline systems than in water-alkaline systems. That is, $\Delta G_\lambda^\ddagger(\text{water-PEG-ion}) > \Delta G_\lambda^\ddagger(\text{water-ion})$, $\Delta H_\lambda^\ddagger(\text{water-PEG-ion}) > \Delta H_\lambda^\ddagger(\text{water-ion})$, $\Delta S_\lambda^\ddagger(\text{water-PEG-ion}) > \Delta S_\lambda^\ddagger(\text{water-ion})$. Note that, this result is the same as the results obtained based on the viscous flow activation parameters. We believe that these results are due to the structural effect of PEG on the water-alkaline system.

Let's investigate the effects of LiOH, NaOH and KOH on the structure of Water-PEG systems. Summarizing the results, we can write that $\Delta G_\eta^\ddagger(\text{water-PEG-LiOH}) > \Delta G_\eta^\ddagger(\text{water-PEG-NaOH}) > \Delta G_\eta^\ddagger(\text{water-PEG-KOH}) > \Delta G_\eta^\ddagger(\text{water-PEG})$, $\Delta H_\eta^\ddagger(\text{water-PEG-LiOH}) > \Delta H_\eta^\ddagger(\text{water-PEG-NaOH}) > \Delta H_\eta^\ddagger(\text{water-PEG}) > \Delta H_\eta^\ddagger(\text{water-PEG-KOH})$, $\Delta S_\eta^\ddagger(\text{water-PEG}) > \Delta S_\eta^\ddagger(\text{water-PEG-LiOH}) > \Delta S_\eta^\ddagger(\text{water-PEG-NaOH}) > \Delta S_\eta^\ddagger(\text{water-PEG-KOH})$. In water-PEG-alkaline systems compared to water-PEG systems in addition, the hydrated Li^+ and OH^- , Na^+ and OH^- , K^+ and OH^- ions will be activated. Therefore, compared to the water-PEG system in the water-PEG-alkaline system, the value of ΔG_η^\ddagger increases to some extent. Because the Na^+ ion has less hydration than the Li^+ ion and the K^+ ion has less hydration than the Na^+ ion for ΔG_η^\ddagger the above sequence is formed. We assume that since Li^+ and Na^+ are positively hydrated ions and K^+ is negatively hydrated, the value of ΔH_η^\ddagger is higher in the water-PEG-LiOH and water-PEG-NaOH systems than in the water-PEG system and smaller than in the water-PEG-KOH

system. Our results show that when LiOH, NaOH or KOH of the same concentration are added to the water-PEG system separately, the activation entropy of the viscous flow of the solution at a given temperature and concentration and the partial molar volume of PEG in the solution decrease in the corresponding sequence, also, as the concentration of LiOH, NaOH, or KOH increases, their partial molar volumes in solution increase. Based on this fact, we can say that when LiOH, NaOH, KOH is added to the water-PEG system, the partial molar volume of PEG decreases, while the partial molar volume of LiOH, NaOH and KOH separately will increase as in water. The results show that when LiOH or NaOH or KOH is added to the water-PEG system, the water-structuring effect of PEG is weakened in the corresponding sequence. This shows that LiOH, NaOH and KOH have a more destructive effect in the sequence corresponding to the structure of the water-PEG system.

When the same concentration of alkali is added to the water-PEG system, the hydration number of PEG in the obtained solutions decreases in the order corresponding to the sequence LiOH, NaOH, KOH. Occurring in water-PEG-alkaline systems structural features and microscopic view of the solution can be described by the following model. When adding LiOH, NaOH or KOH with a concentration of $x_{\text{alkali}} = 0.01$ separately to the water-PEG system since the maximum concentration of PEG in the case under consideration is $x_{\text{PEG}} = 0.001$ ($x_{\text{alkali}} / x_{\text{PEG}} = N_{\text{alkali}} / N_{\text{PEG}}$ becomes, here N_{alkali} and N_{PEG} are the number of alkali molecules and PEG macromolecules in solution) always the number of ions in solution (Li^+ , OH^- or Na^+ , OH^- or K^+ , OH^-) is more than the number of PEG macromolecules. Given that the effective radii of the ions of the alkalis under study are quite small compared to the size of the PEG macromolecule, it can be assumed that the PEG macromolecular mass also contains hydrated Li^+ , Na^+ , K^+ , OH^- ions, respectively. Of course, the number of hydrated ions in the macromolecular mass, which has a relatively large 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 assume that hydrated ions try to reduce the volume of the macromolecular mass by interacting with water-molecules through ion-dipole interactions, and water molecules by hydrogen bonding to the PEG macromolecule. The validity of this assumption is reflected in the estimate of the partial molar volume and hydration number of PEG in solution. Probably because Na^+ is more hydrated than the K^+ ion and Li^+ is more hydrated than the Na^+ ion $\tilde{V}(\text{water-PEG}) > \tilde{V}(\text{water-PEG-LiOH}) > \tilde{V}(\text{water-PEG-NaOH}) > \tilde{V}(\text{water-PEG-KOH})$ and $N_h(\text{water-PEG}) > N_h(\text{water-PEG-LiOH}) > N_h(\text{water-PEG-NaOH}) > N_h(\text{water-PEG-KOH})$. Viscous flow activation parameters in water-PEG, water-PEG-LiOH, water-PEG-NaOH and water-PEG-KOH systems, based on the study of the partial molar volume and hydration number of PEG in solution we can say that the addition of LiOH, NaOH or KOH to the water-PEG system weakens the structural effect of PEG in the appropriate sequence. This is due to the destructive effect of LiOH, NaOH and KOH on the structure of the solution in the appropriate sequence.

Let us now examine the effect of alkalis on the conformation and size of the PEG macromolecule in water-PEG-alkaline systems. The determined values of the intrinsic viscosity for water-PEG-alkaline systems show that $[\eta](\text{water-PEG-LiOH}) < [\eta](\text{water-PEG-NaOH}) < [\eta](\text{water-PEG-KOH})$. It can be considered that the specified sequence of intrinsic viscosity in water-PEG-alkaline systems is related to the size of PEG macromolecules in solution. That is, as the size of the macromolecule decreases intrinsic viscosity takes smaller values. For water-PEG-alkaline systems, the determined values of the Huggins constant are $K_H(\text{water-PEG-LiOH}) > K_H(\text{water-PEG-NaOH}) > K_H(\text{water-PEG-KOH})$. This series shows that the water-LiOH system is worse solvent for PEG than the water-NaOH system, and the water-NaOH system is worse than the water-KOH system. We assume that this is due to the hydration of cations (Li^+ , Na^+ , K^+) in the solution. Thus, in both water-alkaline systems and water-PEG-alkaline systems, the Li^+ ion has a higher hydration number than Na^+ , and the Na^+ ion has a higher hydration number than K^+ .

A comparison of the values of the parameter α included in the

Mark-Kuhn-Houwink formula shows that $\alpha(\text{water-PEG-LiOH}) < \alpha(\text{water-PEG-NaOH}) < \alpha(\text{water-PEG-KOH})$ (Figure 2). That is, the PEG macromolecule accumulates more in the water-LiOH system than in the water-NaOH system, and more in the water-NaOH system than in the water-KOH system. A comparison of the values of the swelling coefficient shows that $\beta(\text{water-PEG-LiOH}) < \beta(\text{water-PEG-NaOH}) < \beta(\text{water-PEG-KOH})$. This allows us to say that the PEG macromolecule swells more in the water-KOH system than in the water-NaOH system, and in the water-NaOH system more than in the water-LiOH system. In water-PEG-alkaline systems, based on the determined values of the mean square distance between the ends of the PEG macromolecule chain and the length of the Kuhn segment $\langle h \rangle$ ($\langle h \rangle(\text{water-PEG-LiOH}) < \langle h \rangle(\text{water-PEG-NaOH}) < \langle h \rangle(\text{water-PEG-KOH})$) and $A(\text{water-PEG-LiOH}) < A(\text{water-PEG-NaOH}) < A(\text{water-PEG-KOH})$. This indicates that the mean square distance between the ends of the PEG macromolecule chain is smaller than that of water-PEG-NaOH in the water-PEG-LiOH system and less than that of water-PEG-KOH in the water-PEG-NaOH system also, the mobility of the PEG macromolecule chain is higher in the water-PEG-LiOH system than in the water-PEG-NaOH, and in the water-PEG-NaOH system than in the water-PEG-KOH. Note that this sequence is reversed in θ -solvents.

In water-PEG-alkaline systems regularities obtained in the change of quantities $[\eta]$, K_H , α , β , $\langle h \rangle$, A under the influence of alkalis we can explain based on the model we have described above. Probably because water molecules interact with alkaline ions ion-dipole the energy of the hydrogen bond formed by the PEG macromolecule decreases. We assume that the main reason for this is a change in the energy and length of the hydrogen bond between water and PEG molecules as a result of a change in the orientation of water molecules under the influence of the electrostatic field of the ion. Undoubtedly, as the hydrogen bond between water molecules and PEG monomers weakens the mobility of the PEG macromolecule chain will increase accordingly and vice versa. Summarizing the above, we can come to the following conclusion: when KOH, NaOH, LiOH are added to the Water-PEG

system separately, the size (volume) of the PEG macromolecular mass is further reduced in the sequence corresponding to their effect macromolecular mass accumulates more, the solubility of PEG worsens, the PEG macromolecule swells less and the mobility of the PEG macromolecule chain increases further. In the θ -solvent, the standard deviation between the ends of the chain of the PEG macromolecule decreases according to the sequence of LiOH, NaOH and KOH, and the mobility of the macromolecule increases.

The sixth chapter is devoted to the analysis of structural properties of water-PEG-salt (KCl, KBr, KI) systems. This chapter analyzes the effect of salts on the structure of water-PEG systems corresponding to PEGs of different fractions (1000, 1500, 3000, 4000, 6000), as well as on the conformation and size of PEG macromolecule in solution and θ -solvent. The temperature of the studied water-PEG-salt systems was 293.15-323.15 K and in the range of 0-0.001 molar part of PEG ($x_{\text{KCl}}=0.01$, $x_{\text{KBr}}=0.01$, $x_{\text{KI}}=0.01$) dynamic viscosity and density, kinematic viscosity of 0-0.05 molar fraction of salts at a temperature of 293.15 K and PEG in the concentration range 0-5 g/dl, in the range of 283.15-333.15 K temperature and molar concentration of salts 0.001-0.01 mol/l ($M_{\text{PEG}} = 4000 \text{ g/mol}$, $x_{\text{PEG}} = 0.0002$ electrical conductivity was measured. The parameters of the activation of the viscous flow of solutions determined on the basis of experimental values, the partial molar volume of PEG in the solution, the intrinsic viscosity of the solution, the Huggins constant, the Mark-Kuhn-Houwink formula α , the swelling coefficient of the macromolecule and the average square distance between the ends of the chain of the unexcited PEG macromolecule in the θ -solvent and the length of the Kuhn segment from the salt concentration, the hydration number of the PEG macromolecule in solution, the activation parameters of ionic conductivity in the water-PEG system, hydration ions (K^+ , Cl^- , Br^- , I^-) a comparative analysis of the temperature dependence of the radii is given.

The structural properties of polymers in aqueous solutions depend on various heterogeneous interactions (hydrophilic and hydrophobic) that occur around the macromolecule. Hydrophilic and

hydrophobic interactions are key processes in the physicochemistry of solutions. The competition of these interactions with each other leads to structural features under certain conditions and structural destructive features under certain conditions. PEG is an interesting polymer in terms of the presence of both hydrophilic and hydrophobic groups in the macromolecule. It was found that the activation parameters of viscous flow for water-PEG-salt systems increase with increasing both molecular weight and molar fraction of PEG and $\Delta H_{\eta}^{\ddagger}(\text{water-PEG}) > \Delta H_{\eta}^{\ddagger}(\text{water-PEG-KCl}) > \Delta H_{\eta}^{\ddagger}(\text{water-PEG-KBr}) > \Delta H_{\eta}^{\ddagger}(\text{water-PEG-KI})$, $\Delta S_{\eta}^{\ddagger}(\text{water-PEG}) > \Delta S_{\eta}^{\ddagger}(\text{water-PEG-KCl}) > \Delta S_{\eta}^{\ddagger}(\text{water-PEG-KBr}) > \Delta S_{\eta}^{\ddagger}(\text{water-PEG-KI})$. In this case, the difference between the values of $\Delta G_{\eta}^{\ddagger}$ and the effect of salts is not comparable. Water-PEG-salt systems also contain additional hydrated K^+ and Cl^- , K^+ and Br^- , K^+ and I^- ions compared to water-PEG systems. Since K^+ , Cl^- , Br^- , I^- ions are negatively hydrated ions and their hydration is weakened according to the order Cl^- , Br^- , I^- , the energy of the solution consisting of these ions also weakens in the same sequence. Therefore, for the effect of KCl, KBr and KI on the water-PEG system, the above order is obtained. When KCl, KBr or KI salts with the same concentrations are introduced into the Water-PEG system separately, the value of $\Delta S_{\eta}^{\ddagger}$ decreases in the corresponding sequence (Figure 3). Thus, when KCl or KBr or KI is added to a water-PEG system, the structural effect of PEG on water is relatively reduced in the appropriate sequence. This indicates that the salts KCl, KBr and KI have a more destructive effect on the structure of the water-PEG system in the appropriate sequence. We can explain this based on the process of hydration between water molecules, PEG macromolecules and ions (K^+ , Cl^- , Br^- , I^-). We assume that since the I^- ion is less hydrated than the Br^- ion and the Br^- ion is less hydrated than the Cl^- ion, the destructive effect of the KBr salt on the KCl salt and the KI salt on the structure of the water-PEG system is greater than that of the KBr salt.

In water-PEG-salt systems, the partial molar volume of PEG decreases with increasing concentration of PEG. Calculations show

that at a given temperature and concentration, the partial molar volume of PEG per unit monomer ring in water-PEG-salt systems does not depend on the molecular weight of PEG. In the studied systems different molecular weights of PEGs the dependence of the average value of the partial molar volume per unit monomer ring at a temperature of 293.15 K on the molar part of PEG for water-PEG-KCl, water-PEG-KBr and water-PEG-KI systems respectively $(\tilde{V}/n)_{av}=1907623.2x^2-5694.2x+38.3$, $(\tilde{V}/n)_{av}=2004774.7x^2-5644.4x+37.3$, $(\tilde{V}/n)_{av}=2145252.6x^2-5795.6x+36.5$ can be described by expressions. When KCl, KBr or KI salts with the same concentrations are added to the Water-PEG system separately, as the concentration of salts increases, their partial molar volumes in solution increase as in water. The results show that PEG has a structural effect on water-salt systems, and salts have a destructive effect on the structure of water-PEG system (KCl, KBr, KI sequence).

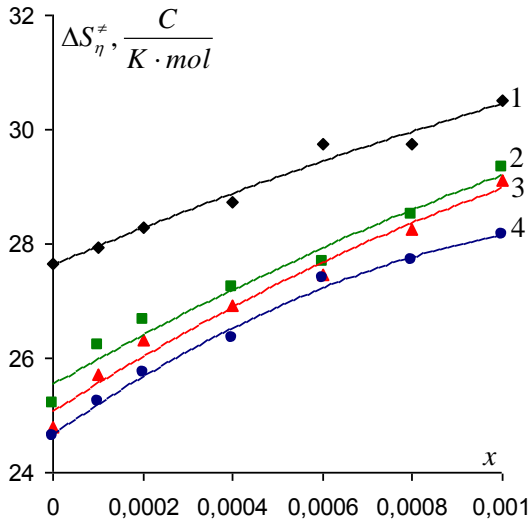


Figure 3. Dependence of viscous flow activation entropy on PEG concentration in water-PEG (1), water-PEG-KCl (2), water-PEG-KBr (3), water-PEG-KI (4) systems ($M_{PEG}=3000$ g/mol, $T=293.15$ K, $x_{KCl}=x_{KBr}=x_{KI}=0.01$).

To describe the interactions between the solute (PEG) and the solvent (water-salt system) molecules and to clarify the overall physical picture of the system, the hydration numbers in the temperature and concentration range of the fractional PEGs examined in the aqueous-salt medium were determined. It was determined that PEG with a relatively large molecular weight is more hydrated, and depending on the temperature, the number of hydrations of PEG decreases, and this decrease increases relative to the order of KCl, KBr, KI (Figure 4).

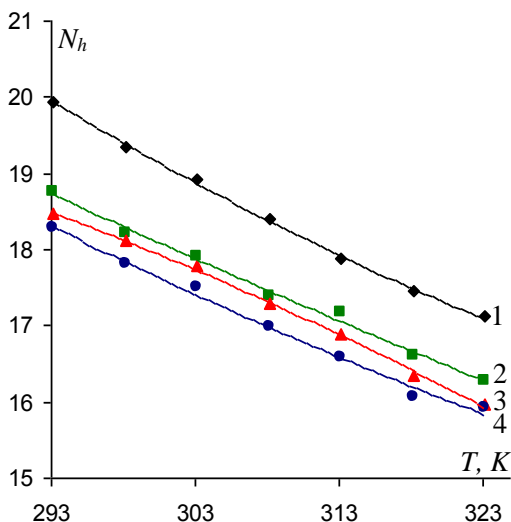


Figure 4. Dependence of the temperature on the hydration number of PEG in water-PEG (1), water-PEG-KCl (2), water-PEG-KBr (3), water-PEG-KI (4) system ($M_{\text{PEG}}=3000$ g/mol, $x_{\text{KCl}}=x_{\text{KBr}}=x_{\text{KI}}=0.01$).

Of course, the hydration processes of the PEG macromolecule in water and water-PEG-salt systems will differ to some extent. This is due to the presence of additional electrostatic interaction forces in water-PEG-salt systems due to the presence of ions (K^+ and Cl^- , K^+ and Br^- , K^+ and I^- , respectively). It should be noted that during the hydration process, the area, structure, configuration of the macromolecule's surface contact with water and its ability to form

hydrogen bonds play an important role. The dependences $\Delta G_{\eta}^{\ddagger}(x)$, $\Delta H_{\eta}^{\ddagger}(x)$, $\Delta S_{\eta}^{\ddagger}(x)$, $\tilde{V}(x)$ in water-PEG-salt systems for PEGs of different fractions and the results obtained for Nh show that PEG has a structural effect on both water and water-KCl, water-KBr and water-KI systems, but the addition of KCl, KBr or KI to the water-PEG system reduces the structural effect of PEG in the appropriate sequence. This is due to the destructive effect of KCl, KBr and KI salts on the structure of the solution in the appropriate sequence. Based on the results, we can say that the effect of salts (KCl, KBr, KI) on the structure of water-PEG systems is similar to the effect on the structure of pure water.

By studying the electrical conductivity of ions, it is possible to calculate a number of quantities that give an idea of the structural properties of aqueous solutions. Calculations show that in water-PEG-salt systems, the electrical conductivity of the ions of the salts under consideration (K^+ , Cl^- , Br^- , Γ) increases with increasing temperature, while the effective radii and hydration numbers decrease slightly as in water, the water-PEG medium contains $r_{ef}(Cl^-) > r_{ef}(\Gamma) \geq r_{ef}(Br^-)$, $N_h(Cl^-) > N_h(Br^-) > N_h(\Gamma)$. For Cl^- , Br^- , Γ ions, the arrangement of λ_-^0 , r_{ef} and N_h quantities in the above sequence can be explained by the hydration process of the ions. It was found that the activation parameters of the electrical conductivity of the ions studied in the considered temperature range decrease with increasing temperature. Our results show that the electrical conductivity, effective radii, and hydration numbers of salt ions are smaller in a water-PEG solution than in water. At a given temperature, the viscosity of an aqueous solution of PEG with a molar fraction $x_{PEG} = 0.0002$ and a molecular weight of 4000 g/mol (at $20^{\circ}C$ $\eta = 1.375 \text{ mPa}\cdot\text{s}$) is greater than the viscosity of water (at $20^{\circ}C$ $\eta = 1.0020 \text{ mPa}\cdot\text{s}$). Therefore, the migration of ions in the water-PEG environment slows down to a certain extent compared to being in the water. Therefore, becomes $\lambda_-^0(\text{water-PEG-ion}) < \lambda_-^0(\text{water-ion})$. Note that while only ions are hydrated in water-salt systems, both ions and PEG macromolecules are hydrated in water-PEG-salt systems. For this reason $r_{ef}(\text{water-PEG-ion}) < r_{ef}(\text{water-ion})$,

$N_h(\text{water-PEG-ion}) < N_h(\text{water-ion})$. We also believe that the interactions between PEG macromolecules and salt ions also contribute to this relationship. Our results show that the parameters $\Delta G_\lambda^\ddagger$, $\Delta H_\lambda^\ddagger$ and $\Delta S_\lambda^\ddagger$ are greater in water-PEG-salt systems than in water-salt systems. We think that this is due to the structural effect of PEG on the water-salt system.

Very hard chain polymer washes have similar shapes and sizes in liquid solutions of various solvents. The intrinsic viscosities of solutions of such polymers in different solvents and Huggins constants are almost the same. Mobile chain polymers have different shapes and sizes in different solvents also the values of the intrinsic viscosities and the Huggins constants differ significantly from each other. Therefore, the study of the intrinsic viscosity of solutions and the Huggins constant is very important in the study of physical and chemical properties of polymer solutions. It was found that the intrinsic viscosity in water-PEG-salt systems increases with increasing molecular weight of PEG, decreases with increasing concentration of salts, while the Huggins constant, on the contrary, decreases with increasing molecular weight of PEG, and increases with increasing salt concentration. Also under the influence of $[\eta](\text{water-PEG-KCl}) < [\eta](\text{water-PEG-KBr}) < [\eta](\text{water-PEG-KI})$ and $K_H(\text{water-PEG-KCl}) > K_H(\text{water-PEG-KBr}) > K_H(\text{water-PEG-KI})$. We assume that the decrease in the intrinsic viscosity of the solution for the considered fractional PEG depending on the concentration of salts is due to the decrease in the volume of the PEG macromolecule and the decrease in the viscosity of the solution with increasing concentration. The sequence of intrinsic viscosities is mainly related to the volume of PEG macromolecules in solution. Thus, as the volume of a macromolecule decreases, it becomes easier to rotate in the environment and as a result the value of the intrinsic viscosity decreases. For a given fractional PEG, an increase in the value of the Huggins constant as the concentration of salts increases indicates that the solubility of PEG in water-salt systems deteriorates depending on the concentration. This is most likely due to the hydration of the salt ions in the solution. Thus, if in water-PEG systems only PEG macromolecules are hydrated, in water-PEG-salt

systems, along with PEG macromolecules, K^+ and Cl^- , K^+ and Br^- , K^+ and I^- ions are also hydrated, respectively. The above order of the Huggins constant under the influence of salts shows that the water-KCl system is worse solvent for PEG than the water-KBr system, and the water-KBr system is worse than the water-KI system. Most likely, this is due to the hydration of anions (Cl^- , Br^- , I^-) in the solution. Thus, in both water-salt systems and water-PEG-salt systems, the Cl^- ion has a greater number of hydrations than Br^- , and the Br^- ion has a greater hydration number than I^- .

From the determined values of the parameter α included in the Mark-Kuhn-Houwink formula, it can be seen that at a temperature of 293.15K and α in the concentration range of the salts we are considering, for the water-PEG-KCl system (0.71-0.74), for the water-PEG-KBr system (0.71-0.77), and for the water-PEG-KI system (0.71-0.78) got value in the range. This indicates that the PEG macromolecule is in the form of a wash that can be penetrated by the surrounding fluid in a water-salt medium. The α parameter increases to some extent with increasing salt concentration. This means that as the concentration of salts in the solution increases, indicates a slight opening of the PEG macromolecular mass. A comparison of the values of the parameter α included in the Mark-Kuhn-Houwink formula in water-PEG-salt systems shows that α (water-PEG-KCl) < α (water-PEG-KBr) < α (water-PEG-KI). That is, the PEG macromolecule is more open in the water-KI system than in the water-KBr system, and more open in the water-KBr system than in the water-KCl system.

Because polymers are composed of molecules of large size and elastic chains, the properties of their solutions differ sharply from the properties of solutions of small molecular weight compounds. The dissolved polymer macromolecules are reminiscent of an irregularly assembled mass that contains a large amount of solvent molecules. The volume of such a lump is tens of times larger than the specific volume of the macromolecule. One of the important parameters determining the characteristics of the macromolecule in solution is the swelling coefficient. It was determined that, for water-PEG-salt systems, the concentration in question is always $\alpha > 0.5$. This

indicates that the size of the excited PEG macromolecule in non-ideal solvents (water-PEG-salt solution) is larger than the size of the unexcited PEG macromolecule in ideal solvents (θ -solvent). For water-PEG-salt systems the swelling coefficient is $\beta > 1$ in all considered cases and the swelling coefficient of the PEG macromolecule in water-salt systems and increases with increasing concentration of salts in the solution. As the molar fraction of salts in the solution increases, β increases it is likely that the ions of the salts in the solution (K^+ and Cl^- , K^+ and Br^- , K^+ and I^- , respectively) have a negative hydration, probably it is related to reduction of the viscosity of the medium and conformational transformation of the macromolecule (the value of α increases). A comparison of the values of the swelling coefficient shows that $\beta(\text{water-PEG-KCl}) < \beta(\text{water-PEG-KBr}) < \beta(\text{water-PEG-KI})$. The results show that the PEG macromolecule swells more in the water-KI system than in the water-KBr system, and more in the water-KBr system than in the water-KCl system.

In water-PEG-salt systems excited and in a θ -solvent according to selected these systems the values of the dimensions of the unexcited PEG macromolecules show that in both water-PEG-salt systems and in the θ -solvent selected according to this system, the standard deviation between the ends of the chain of unexcited PEG macromolecule increases with increasing molecular weight of PEG and decreases with increasing concentration of salts in solution. It is likely that the decrease in $\langle h \rangle$ and $\langle h_\theta \rangle$ parameters as the concentration of salts increases is due to a decrease in the number of hydrations of PEG and a decrease in the volume of the macromolecular mass. The mean square distance between the ends of the PEG macromolecule chain is determined by the effect of salts $\langle h \rangle(\text{water-PEG-KCl}) < \langle h \rangle(\text{water-PEG-KBr}) < \langle h \rangle(\text{water-PEG-KI})$ and $\langle h_\theta \rangle(\text{water-PEG-KCl}) > \langle h_\theta \rangle(\text{water-PEG-KBr}) > \langle h_\theta \rangle(\text{water-PEG-KI})$. This shows that the mean square distance between the ends of the PEG macromolecule chain is smaller than that of water-PEG-KBr in the water-PEG-KCl system and less than that of water-PEG-KI in the water-PEG-KBr system. The opposite case is true of θ -solvents.

The mobility of the polymer chain has a very strong effect on the properties of the polymers (for example, solubility). Mobile macromolecules, which are easily separated from each other, diffuse rapidly between the solvent molecules. In water-PEG-salt systems in an excited θ -solvent selected according to these systems based on the calculated values of the length of the Kuhn segment of the unexcited PEG macromolecule, it was determined that the length of the Kuhn segment of the excited PEG macromolecule in water-PEG-salt systems increases with increasing molecular weight of PEG and decreases with increasing salt concentration. In the θ -solvent, the length of the Kuhn segment for the unexcited PEG macromolecule does not depend on the molecular weight of the PEG and decreases as the salt concentration increases. Based on the estimates we obtain for the length of the Kuhn segment, we can say that in water-PEG-salt systems, as in water, PEG is a mobile polymer. When KCl, KBr and KI are added to the water-PEG system separately, the K^+ and Cl^- , K^+ and Br^- , K^+ and I^- ions are hydrated, respectively the hydration number of the PEG macromolecule decreases and the size decreases as a result, the interactions between water and PEG molecules are weakened. We believe that for these reasons, as the concentration of salts in the water-PEG-salt system and θ -solvent increases, the mobility of the PEG macromolecule increases, ie A and A_θ decrease. Salts $A(\text{water-PEG-KCl}) < A(\text{water-PEG-KBr}) < A(\text{water-PEG-KI})$ and $A_\theta(\text{water-PEG-KCl}) > A_\theta(\text{water-PEG-KBr}) > A_\theta(\text{water-PEG-KI})$ affect according to the order. This shows that the mobility of the PEG macromolecule chain is higher in the water-PEG-KCl system than in the water-PEG-KBr, and in the water-PEG-KBr system than in the water-PEG-KI. The opposite is true for θ -solvents selected according to these systems.

In water-PEG-salt systems quantities characterizing the size and conformation of the PEG macromolecule regularities observed in the change of salts can be explained based on such a model. When adding KCl, KBr or KI separately to the water-PEG system due to changes in the concentration of salts (0-0.05 molar fraction) and the concentration of PEG (0-5 g/dl) in the case under consideration the number of ions in the solution is much higher than the number of

PEG macromolecules. Given that the effective radii of the ions of the salts under study are sufficiently smaller than the size of the PEG macromolecule, we can assume that the PEG macromolecular mass may also contain K^+ , Cl^- , Br^- , I^- ions, respectively. Then we assume that the water molecules around the hydrated ion inside the molecular mass are formed by the interaction of the ion with the ion-dipole some water molecules also interact with the PEG macromolecule by hydrogen bonding. We assume that hydrated ions try to reduce the volume of water molecules by ion-dipole interactions, and water molecules, in turn, try to reduce its volume by acting on the PEG macromolecule with hydrogen bonds. The validity of this assertion is expressed in the values of $[\eta]$ and $\langle h \rangle$. Thus, in all cases considered, $[\eta](\text{water-PEG}) > [\eta](\text{water-PEG-salt})$ and $\langle h \rangle(\text{water-PEG}) > \langle h \rangle(\text{water-PEG-salt})$. Undoubtedly, K^+ ions also contribute to the resulting inequality. We assume that Br^- has less hydration than Cl^- and I^- has less hydration than Br^- ion the value of $[\eta]$ and $\langle h \rangle$ is lower in the water-PEG-KCl system than in the water-PEG-KBr, and in the water-PEG-KBr system than in the water-PEG-KI. Note that this model is based on the partial molar volume of salts, PEG in solution ($\tilde{V}(\text{water-PEG}) > \tilde{V}(\text{water-PEG-KCl}) > \tilde{V}(\text{water-PEG-KBr}) > \tilde{V}(\text{water-PEG-KI})$) and successfully explains the effect of hydration on the number ($N_h(\text{water-PEG}) > N_h(\text{water-PEG-KCl}) > N_h(\text{water-PEG-KBr}) > N_h(\text{water-PEG-KI})$).

MAIN RESULTS

1. A new approach to the viscous flow process in liquids has been proposed: A molecule involved in the viscous flow process must go through two stages in order to pass from one state to another due to the additional energy it receives. In the first stage, part of the extra energy is used to break the bonds (release of the molecule) that exist with other molecules around the molecule. In the second stage, the remaining part of the additional energy (free part), is spent on the work for the transformation of a molecule into another in the form of kinetic energy.

2. Activation parameters of viscous flow and partial molar

volumes of alkalis in solution were determined on the basis of experimental values of dynamic viscosity and density of aqueous solutions of alkalis (LiOH, NaOH, KOH) in the range of 283.15-333.15 K temperature and 0-0.07 molar particle concentration. The obtained results show that at a temperature of 293.15 K the partial molar volume of LiOH is negative up to the value of concentration $x \approx 0.03$ in the solution, up to $x \approx 0.02$ the partial molar volume of NaOH is negative, while the partial molar volume of KOH is positive in all cases. It was determined that with an increase in all three alkaline concentrations have a destructive effect on the structure of water and this effect is enhanced by a sequence corresponding to the sequence of LiOH, NaOH, KOH.

3. Activation parameters of viscous flow and partial molar volumes of salts in solution were determined on the basis of experimental values of dynamic viscosity and density of aqueous solutions of salts (KCl, KBr, KI) in the studied temperature and concentration range. Also, based on the study of the absorption spectra of aqueous solutions of KCl, KBr and KI in the IR region, the values of the energy and length of the hydrogen bond between water molecules in the solution at different concentrations were calculated. It was determined that, with increasing in the concentration of all three salts have a destructive effect on the structure of water and this effect is amplified according to the KCl, KBr, KI sequence.

4. A new method was given to determine the hydration number of the polymer macromolecule in the solution, a new expression for the determination of the hydration number was obtained. For the first time, hydration number of the PEG macromolecule in water-PEG, water-PEG-alkaline and water-PEG-salt systems was determined by this expression. It was determined that in all cases under consideration the hydration of the macromolecule decreases with increasing numerical temperature, increasing with increasing molecular weight of PEG. For the systems under consideration, the hydration number of the PEG macromolecule decreases according to the following sequence:

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

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

5. Based on experimental values of dynamic viscosity and density of aqueous solutions of PEGs of different molecular weights in the range of temperature 293.15-323.15 K and concentration of 0-0.001 molars, the parameters of viscous flow activation and partial molar volumes of PEG in solution were determined. Also, based on the study of the absorption spectra of aqueous solutions of PEGs of different molecular weights in the IR region, the values of the energy and length of the hydrogen bond between water molecules in the solution at different concentrations were calculated. It was found that PEG has a structural effect on water, which is enhanced by increasing concentration and molecular weight.

6. Activation parameters of viscous flow and partial molar volumes of PEG in solution were determined on the basis of experimental values of dynamic viscosity and density in the studied temperature and concentration range of water-PEG-alkaline (LiOH, NaOH, KOH) and water-PEG-salt (KCl, KBr, KI) systems. It was determined that the effect of alkalis and salts on the structure of water-PEG systems is related with their effect on the structure of water.

7. It was determined that in water-PEG, water-PEG-alkali (LiOH, NaOH, KOH) and water-PEG-salt (KCl, KBr, KI) systems partial molar volume per unit monomer ring of PEGs with different molecular weights at a given temperature and concentration does not depend on molecular weight. For each system studied, expressions describing dependence of the average value of the partial molar volume of PEG per unit monomer ring on the concentration at a temperature of 293.15 K were obtained.

8. Activation parameters, effective radii and hydration numbers of ions (Li^+ , Na^+ , K^+ , OH^- , Cl^- , Br^- , I^-) were determined on the basis of experimental values of specific electrical conductivity in the range of 283.15 - 333.15 K temperature and 0.001 - 0.01 mol/l molar concentration in solutions of alkalis, salts in water and water-PEG systems. It was found that compared to water the effective radii of the ions studied in water-PEG systems are reduced, hydration numbers decrease and the activation entropy of electrical conduction

increases. The hydration numbers of the ions and the activation entropy of the electrical conductivity decrease in the order corresponding to the sequence Li^+ , Na^+ , K^+ for cations, and for the anions Cl^- , Br^- , I^- .

9. Intrinsic viscosity, Haggins constant, parameter α included in the Mark-Kuhn-Houwink formula, swelling coefficient, average square distance between the ends of the macromolecular chain in water and θ -solvent, length of Kuhn segment in water and θ -solvent were determined in water and θ -solvent on the basis of experimental values of kinematic viscosity of aqueous solutions of PEGs of different molecular weights in the range of 293.15-323.15 K temperature and 0-5 g/dl concentration. It was determined that, PEG macromolecule in aqueous medium has the form of like mobile a swollen ball of yarn chain. As the temperature increases, the solubility of PEG in water is getting better, the average square distance is reduced between the ends of the PEG macromolecule chain, the mobility of the macromolecule increases.

10. Intrinsic viscosity, Haggins constant, parameter α included in the Mark-Kuhn-Houwink formula, swelling coefficient, average square distance between the ends of the macromolecular chain and length of the Kuhn segment were determined based on experimental values of kinematic viscosity of water-PEG-alkali (LiOH , NaOH , KOH) and water-PEG-salt (KCl , KBr , KI) systems at a temperature of 293.15 K and 0-0.05 molar fraction of alkali, and PEG concentration range 0-5 g/dl. It was found that the PEG macromolecule is in the form of like a mobile swollen ball of yarn chain in water-alkaline and water-salt environments, as well as in water, and in all cases β was $\beta > 1$.

11. It has been found that the solubility of PEG in solution deteriorates with increasing concentration of alkalis or salts. The mean square distance between the ends of the PEG macromolecule chain is reduced, the mobility of the macromolecule increases and these regularities are amplified in the order of KOH , NaOH , LiOH for alkalis, and KI , KBr , KCl for salts.

12. In the studied temperature and concentration range in θ -solvents selected according to water-PEG-alkaline and water-PEG-

salt systems intrinsic viscosity, the mean square distance between the ends of the unexcited macromolecule chain, and the length of the Kuhn segment were determined. It was determined that as the concentration of alkalis (salts) increases, the mean square distance between the ends of the PEG macromolecule chain in the θ -solvent increases (decreases), and the mobility of the macromolecule decreases (increases). According to the sequence of LiOH, NaOH, KOH for alkalis in θ -solvent, and KCl, KBr, KI for salts, the average square distance between the ends of the PEG macromolecule chain decreases, and the mobility of the macromolecule increases.

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