VISCOSYMETRIC AND DENSYTOMETRIC STUDY IN WATER - PEG-KCl SYSTEMS

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In this work, the dynamic viscosity and density of water-PEG-KCl was measured in the temperature range 293.15-323.15K and 0-0.001 mole fraction of PEG. PEG fractions with a molar mass 1000, 1500, 3000, 4000, 6000 were investigated and the concentration of KCl was considered to be 0.01-mole fraction. Using the results of the experiment, the activation parameters of the viscous flow and the partial molar volumes of PEG were calculated. It has been established that, with increasing concentration and the molecular mass, the solution becomes more structured.

Keywords: water solution, PEG, KCl, activation parameters of viscous flow, partial molar volume.
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1. INTRODUCTION

Polyethylene glycol (PEG) is one of the most studied polymers, as it is widely used in many industries (pharmacology, cosmetology, biotechnology etc.) [1-9]. One reason for the extensive use of PEG is that it has many molecular mass fractions. The PEG does not adversely affect the organism's immune system, it does not have toxic properties and is quickly cleansed from the body [1]. The PEG's large molecular mass fractions are heat-resistant and it is resistant to atmospheric moisture. PEG - all the molecular mass fractions are well soluble in water. It is supposed that (OH) groups in the PEG macromolecule to form hydrogen bonds with the water molecule of $-O-$ and $-H$ atoms. CH_2 groups in the PEG macromolecule create the hydrophobic effect [10]. Most of the PEG functions occur in the water environment. Therefore, studying the structural properties of water-PEG systems and the study of structural changes in the solution by adding the third component has great scientific and practical significance.

Here the structural features of the system of water-PEG-KCl at temperature 293.15-323.15 K and 0-0.001 partial molar concentration of PEG was investigated by means of methods viscosimetry and pycnometer. The dynamic viscosity and density of aqueous solutions were measured at observed temperature and concentration intervals. Based on experimental results dependence of activation Gibbs energy of viscous flow ($\Delta G_\eta^{\neq}$), activation enthalpy of viscous flow ($\Delta H_\eta^{\neq}$), activation entropy of viscous flow ($\Delta S_\eta^{\neq}$) and the partial molar volume of PEG ($\tilde{V}$) in solution of studied systems on the concentration of PEG were analyzed.

2. EXPERIMENTAL AND THEORETICAL PART

Objects of study: water-PEG-KCl was used as our objects of research. PEG fractions with a molar mass 1000, 1500, 3000, 4000, 6000 were investigated and the concentration of KCl was considered to be 0.01 mole fraction. Used PEG and KCl are chemical pure. Bidistilled water was used in the preparation of the solutions. The viscosity was measured by capillary viscosimeter and density was measured by pycnometer.

Due to activation Gibbs energy of viscous flow ($\Delta G_\eta^{\neq}$) according to Frenkel and Eyring theory [10] of liquid viscous flow

$$\Delta G_\eta^{\neq} = RT \ln \frac{\eta}{\eta_0} \qquad (1)$$

is defined by this expression. Due to Eyring theory [10] $\eta_0 = \frac{N_A h \rho}{M}$. Here is R- universal gas constant, N_A - is the Avogadro number, h-is the Planck's constant, and M-is the molecular weight of solution, determined according to equation $M = \sum_{i=1}^{N} x_i M_i$. Here x_i and M_i are the molar fraction and molar weight of the i-th component, respectively. Dynamic viscosity (η) and density (ρ) of the solution at different temperatures were determined experimentally.

The activation enthalpy of viscous flow ($\Delta H_\eta^{\neq}$) was determined by the equation [10-12]

$$\Delta H_\eta^{\neq} = R \frac{\partial \ln \cdot (\eta / \eta_0)}{\partial (1/T)} \qquad (2)$$

Thus, $\Delta G_\eta^{\neq}$ and $\Delta H_\eta^{\neq}$ were calculated by (1) and (2). The $\Delta G_\eta^{\neq}$ and $\Delta H_\eta^{\neq}$ values were used for determining the activation entropy of viscous flow ($\Delta S_\eta^{\neq}$) by the known thermodynamic equation [10]

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

The partial molar volume ($\tilde{V}$) of the solute in solution was determined by the equation [10, 13]

$$\tilde{V} = V_m + (1-x) \cdot \left(\frac{\partial V_m}{\partial x} \right)_{p,T} \qquad (4)$$

where V_m is the molar volume of the solution:

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$$V_m = \frac{M}{\rho} = \frac{1}{\rho}\sum_{i=1}^{N} x_i M_i \,.$$

3. RESULTS AND DISCUSSION

The system of water-PEG-KCl at the temperature 293,15 K dependence of the activation Gibbs energy of viscous flow ($\Delta G_\eta^{\neq}$), the activation enthalpy of viscous flow ($\Delta H_\eta^{\neq}$) on the PEG's concentration is shown in table 1 and 2, dependence activation entropy of viscous flow ($\Delta S_\eta^{\neq}$) on the PEG concentration (x) is shown in fig. 1.

It seems in table 1, table 2 and fig. 1, $\Delta G_\eta^{\neq}$, $\Delta H_\eta^{\neq}$ and $\Delta S_\eta^{\neq}$ the parameters are increased by increasing the concentration at the given temperature and increasing with the increased molar mass at the given temperature and concentration.

It should be noted that, $\Delta G_\eta^{\neq}$ is the energy used for activation 1 *mole* molecule, $\Delta H_\eta^{\neq}$ represents the changes in the solution in terms of energy and $\Delta S_\eta^{\neq}$ characterized the changes in solution in terms of structure. Thus, increased $\Delta G_\eta^{\neq}$ with the growth of concentration indicates that more energy can be consumed for overcoming the potential of molecule, while increase in $\Delta H_\eta^{\neq}$ indicates the system has steadier structure, increase in $\Delta S_\eta^{\neq}$ determines the system is becoming more structured [8-12]. Due to dependence of viscous flow parameters on concentration (table 1, table 2 and fig. 1) it is possible to tell that, in process of increase in concentration of PEG in solution has a stronger structure and more structured.

Structural properties of aqueous solutions are also characterized by the partial molar volume of components of solution. It is known that the partial molar volume of *i*-th component is equivalent to a change of volume at the addition of 1 *mol* from this component [10, 13]. The dependence of partial molar volume ($\tilde{V}$) of PEG on concentration (x) of PEG in system water-PEG-KCl for PEG's various molar mass at 293.15 K is shown in table 3.

Table 3 shows that partial molar volume of PEG in solution decreases with increase in concentration at the given temperature and the partial molar volume of PEG increase with increasing molecular mass at the given temperature and concentration. Calculation shows that partial molar volume $\left(\frac{\tilde{V}}{n}\right)_{av}$ of PEG in one monomer at given temperature and concentration practically doesn't depend on the molecular mass of PEG. In fig. 2 the dependence of PEG of various molar mass of average value of partial molar volume in a monomer on concentration at temperature 293.15 *K* is shown. We can describe this dependence with the equation

$$\left(\frac{\tilde{V}}{n}\right)_{av} = 1907623{,}2x^2 - 5694{,}2x + 38{,}3$$

It is possible to assume that the volume portion of big sizes associations in space, the fractional share of its separate parts is less than the sum of volume portion of and vice versa. According to model of the two-structured water [10, 14, 15], water consists of clusters of the different size and clusters of molecules of free liquid which are attached to hydrogen binding. Due to dependence of partial molar volume on concentration it is possible to assume that the molecules of PEG are connected first of all by hydrogen binding with free molecules of water. It leads to reduction of partial molar volume of PEG due to increasing in concentration in solution. This indicates that the solution has become more structured due to increase in PEG concentration.

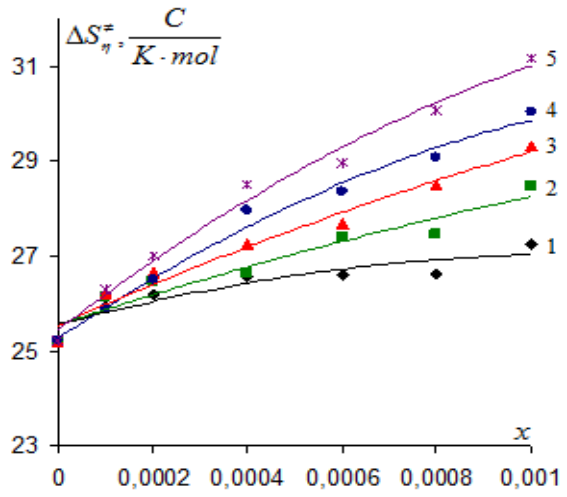

Fig. 1. Dependence activation entropy of viscous flow of water-PEG-KCl system on PEG concentration ($x_{KCl} = 0.01$, $T = 293.15K$).1-PEG(1000), 2-PEG (1500), 3 -PEG (3000), 4-PEG (4000), 5 -PEG (6000)

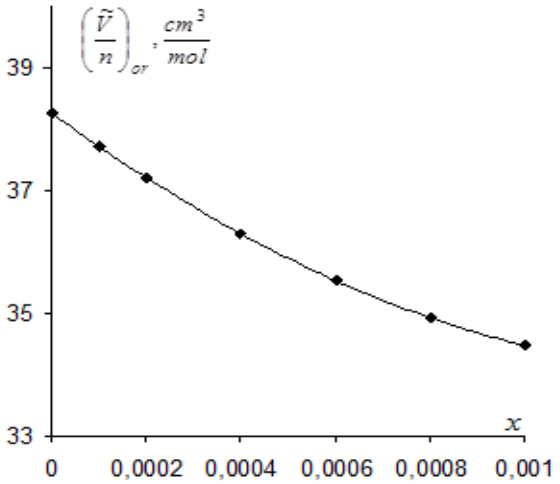

Fig. 2. Dependence of the average value of the partial molar volume of the PEG per monomer on concentration of PEG in system water-PEG-KCl ($x_{KCl} = 0.01$ $T = 293.15K$)

Table 1

Dependence activation Gibbs energy of viscous flow ($\Delta G_{\eta}^{\neq}, J/mol$) of water-PEG-KCl system on PEG concentration (x) ($x_{KCl} = 0.01$, $T = 293.15K$)

x	$M_{PEG} = 1000$	$M_{PEG} = 1500$	$M_{PEG} = 3000$	$M_{PEG} = 4000$	$M_{PEG} = 6000$
0	9274	9274	9274	9274	9274
0.0001	9353	9444	9543	9592	10504
0.0002	9487	9585	9847	10177	11346
0.0004	9544	10009	10580	10909	13427
0.0006	9749	10297	10999	11502	15248
0.0008	9803	10883	11409	12371	16164
0.001	10051	11146	12061	13016	17572

Table 2

Dependence activation entalphy of viscous flow ($\Delta H_{\eta}^{\neq}, J/mol$) of water-PEG-KOH system on PEG concentration (x) ($x_{KCl} = 0.01$, $T = 293.15K$)

x	$M_{PEG} = 1000$	$M_{PEG} = 1500$	$M_{PEG} = 3000$	$M_{PEG} = 4000$	$M_{PEG} = 6000$
0	16665	16665	16665	16665	16665
0.0001	17007	17110	17230	17180	18214
0.0002	17156	17340	17660	17948	19266
0.0004	17339	17814	18568	19106	21784
0.0006	17546	18331	19113	19818	23736
0.0008	17599	18932	19767	20893	24981
0.001	18041	19489	20657	21818	26712

Table 3

The dependence of the partial molar volume ($\tilde{V}, cm^3/mol$) of PEG in water-PEG-KCl systems on PEG concentration (x) ($x_{KCl} = 0.01$, $T = 293.15K$)

x	$M_{PEG} = 1000$	$M_{PEG} = 1500$	$M_{PEG} = 3000$	$M_{PEG} = 4000$	$M_{PEG} = 6000$
0	848	1310	2670	3602	5017
0.0001	837	1284	2632	3535	4983
0.0002	827	1261	2597	3471	4950
0.0004	811	1221	2534	3356	4889
0.0006	797	1189	2480	3258	4833
0.0008	788	1167	2436	3175	4782
0.001	781	1153	2403	3108	4736

4. CONCLUSION

Apparently, the dependence of both the activation entropy of viscous flow and the concentration of partial molar volume of the PEG in solution indicates that concentration as for both fractional PEGs taken at this temperature and for increase in molecular mass for the concentrated and various fractioned PEGs, the solutions becomes more structured. It is possible to assume that, in the studied system, around PEG's molecules water molecules are collected (first of all free molecules of water) by means of hydrogen bindings and certain size aggregates are formed. With increasing both concentration and molecular mass of PEG the number of such aggregates increases and their size increase, that leads to more structured solution. Indeed, since the K^+ and Cl^- ions are hydrated in the water-PEG-KCl system, the structure will be different from the structure of the water-PEG system.

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