STRUCTURAL FEATURES IN SYSTEMS
WATER- POLYETHYLENEGLYCOL -KCl, KBr, KI

B.G. PASHAYEV

Baku State University, Physics Department, 23, Z. Khalilov, AZ1073, Baku, Azerbaijan
E-mail: p.g.bakhtiyar@gmail.com

In this work, the dynamic viscosity and density of the water-PEG systems, water-PEG-KCl, water-PEG-KBr, and water-PEG-KI were measured in the temperature range 293.15-323.15 *K* and 0-0.001 mole fraction of PEG. PEG fractions with a molar mass 1000, 1500, 3000, 4000, 6000 and the concentration of salts (KCl, KBr, KI) in the water-PEG-KCl, water-PEG-KBr, water-PEG-KI systems were 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, and the dependences of these parameters on the concentration of PEG in this temperature range and concentration of the studied systems were investigated. It was found that PEG has a structural effect on both water and water-KCl, water-KBr and water-KI systems, but the presence of KCl, KBr, KI consistently weakens the structural effect of PEG. This is due to the destructive effects on the structure of KCl, KBr, KI in the corresponding sequence.

1. INTRODUCTION

It is known that the water is actively involved in all biological, biochemical and biophysical processes occurring in living organisms. Water, as a solvent in these processes, plays an important role in the formation of active conformations of biological functions, all interaction in the body, fermentative reactions, and transportation of chemicals. The functional activity of biological objects is determined by the structure of the water and the physical properties of the aqueous solution depend heavily on the nature of its components. It should be noted that the physical and chemical properties of the aqueous solutions are related to the interaction between water molecules, soluble molecules and water-soluble molecules. Such molecular interaction formates the structure of the solution the expense of hydrogen, ion-dipole and other types of bonds [1]. Water soluble substances change its structure. It affects all the processes that take place. Therefore, the study of water structure, including the study of the effects of various substances to water is actual.

For its practical significance, polyethyleneglycol (PEG), KCl, KBr and KI have been the research object of researchers [2-15]. All the molecular mass fractions of polyethylene glycol are well soluble in water [4]. There are hydrophobic (CH$_2$) and hydrophilic (OH) groups in the PEG molecule (HO–[–CH$_2$–CH$_2$–O–]$_n$–H) [1]. The PEG (OH) group and –O– and –H atoms are able to form hydrogen bonds with the water molecule, CH$_2$ groups produce hydrophobic effect. PEGis widely used in medicine, pharmacology, cosmetology and the food industry because it does not have toxic properties [5]. PEG is able to capsulate solid particles to maintain their sterile stability, maintain surface active substances and reduce friction in different processes [6, 7]. Although PEG has a wide range of applications, the properties of aqueous solutions of its various molecular mass fractions and the volume properties are less investigated. Also, the

analysis of scientific literature shows that it is necessary to investigate structural properties of the water-PEG system and to study the effects of various salts on this system. For this reason, the study of structural properties of water–PEG–KCl, KBr, KI systems is of great importance.

Here the structural features of systems of water-PEG, water-PEG-KCl, water–PEG–KBr and water–PEG–KI at temperature 293.15-323.15 *K* and 0-0.001 partial molar concentration of PEG were investigated by means of methods viscosimetry and pycnometres. Polyethylene glycol molecules with a molecular weight of 1000, 1500, 3000, 4000 were investigated and the concentration of salts (KCl, KBr, KI) in the systems of water–PEG–KCl, water–PEG–KBr, water–PEG–KI were taken 0,01 molar fraction. The dynamic viscosity and density of aqueous solutions were measured observed temperature and concentration interval and based on experimental results dependence of activation Gibbs energy of viscous flow ($\Delta G_\eta^{\neq}$), activation entalpy 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 and the dependencies on concentration of PEG were analyzed.

2. EXPERIMENTAL AND THEORETICAL PART

PEG, KCl, KBr və KI were used as our objects of research with molecular weight 1000, 1500, 3000, 4000 and 6000. Used substances 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 pinometer.

Due to activation Gibb's energy of viscous flow ($\Delta G_\eta^{\neq}$) according to Frenkel and Eyring theory [1] 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 [1] $\eta_0 = \dfrac{N_A h \rho}{M}$. 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 $M = \displaystyle\sum_{i=1}^{N} x_i M_i$ [1]. 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 [1]:

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

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 [1, 16]

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

The partial molar volume ($\tilde{V}$) of the solute in solution was determined by the equation [1, 17]

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

where V_m is the molar volume of the solution:

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

3. RESULTS AND DISCUSSION

The systems of water-PEG, water-PEG-KCl, water-PEG-KBr and water-PEG-KI at the temperature 293,15 K dependence activation Gibb's 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 partial molar volume ($\tilde{V}$) of PEG in solution, the dependence on the PEG concentration (x) is shown in figures 1-4.

As can be seen from Table 1-4, for the studied systems the activation parameters of viscous flow ($\Delta G_{\eta}^{\neq}, \Delta H_{\eta}^{\neq}, \Delta S_{\eta}^{\neq}$) increase with increasing the concentration, while the parsial molar volume ($\tilde{V}$) of the PEG decreases. When fluid is calming (not running), the leakage of particles in all directions is the same. However, the number of particles leaps in the flow direction prevails over other destinations. $\Delta G_{\eta}^{\neq}$, $\Delta H_{\eta}^{\neq}$ and $\Delta S_{\eta}^{\neq}$ parameters are equivalent to the difference in the values of the corresponding parameters when activation 1 mole molecule: (G_b, H_b, S_b) to (G_a, H_a, S_a) [1]: $\Delta G_{\eta}^{\neq} = G_a - G_b$, $\Delta H_{\eta}^{\neq} = H_a - H_b$, $\Delta S_{\eta}^{\neq} = S_a - S_b$ $\Delta G_{\eta}^{\neq}$ 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 growth of concentration indicates that more energy can be consumed for overcoming 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 [10-13]. It is known that, the partial molar volume of i-th component is equivalent to change of volume at addition of 1 *mole* from this component [1, 10-13].

As can be seen from Table 1-4, the investigated solutions in accordance with every quantity $\Delta G_{\eta}^{\neq}(x)$, $\Delta H_{\eta}^{\neq}(x)$, $\Delta S_{\eta}^{\neq}(x)$ and $\tilde{V}(x)$ dependencies are identical. The $\Delta S_{\eta}^{\neq}(x)$ və $\tilde{V}(x)$ dependencies of PEG for fractional molars of $M_{PEG} = 1500$ molar mass are shown in fig. 1 and 2.

Table 3 and fig. 1 show that, when adding the same concentration ($x_{KCl} = x_{KBr} = x_{KI} = 0.01$) KCl, KBr and KI to the water-PEG system, given temperature and concentration, the value of the $\Delta S_{\eta}^{\neq}$ parameter decreases in the appropriate sequence. This shows that, when adding KCl, KBr and KI to the water-PEG system, the structure of the PEG solution is weak in sequence. This indicates that KCl, KBr and KI in sequence have a more destructive effect on water- PEG systems. To explain this result, we will based on the hydration process formed by electrostatic interaction between ions and water molecules. In the aqueous solution, the ions change the internal electrostatic field created by polar water molecules. This change is related to the surface current density of the ion. It is natural that small ions with large surface current density relative to large ions with small surface current density, will have a different impact on the water structure. Because of the intensity of the electric field around the ions the surface current density, these ions attract water molecules and create hydrate layer around them. The ion-dipole interaction effect in the ions in the low density of surfaces does not suffice for the formation of the hydrate layer. Note that Br⁻ ion compared to Cl⁻ ion, since I⁻ ion has relatively poor hydration compared to Br⁻ion [18], It seems that, KBr relative to KCl, KI compared to KBr has more destructive effect on water-PEGsystem in given temperature and concentration.

Table 1.

Dependence activation Gibbs energy viscous flow of water-PEG, water-PEG–KCl, Water–PEG–KBr and water–PEG–KI systems on PEG concentration (J/mol) $T = 293.15K$, $x_{KCl} = x_{KBr} = x_{KI} = 0.01$)

x	$M_{PEG} = 1000$			
	Water-PEG	Water-PEG-KCl	Water-PEG-KBr	Water-PEG-KI
0	9292	9274	9222	9180
0.0001	9373	9353	9299	9258
0.0002	9423	9487	9385	9343
0.0004	9610	9544	9596	9506
0.0006	9735	9749	9776	9583
0.0008	9920	9803	9862	9864
0.001	10064	10051	10009	9975
x	$M_{PEG} = 1500$			
	Water-PEG	Water-PEG-KCl	Water-PEG-KBr	Water-PEG-KI
0	9292	9274	9222	9180
0.0001	9463	9444	9395	9352
0.0002	9682	9585	9589	9550
0.0004	10023	10009	9908	9939
0.0006	10405	10297	10362	10437
0.0008	10735	10883	10870	10623
0.001	11149	11146	11117	11096
x	$M_{PEG} = 3000$			
	Water-PEG	Water-PEG-KCl	Water-PEG-KBr	Water-PEG-KI
0	9292	9274	9222	9180
0.0001	9561	9543	9495	9455
0.0002	9862	9847	9804	9768
0.0004	10435	10580	10389	10563
0.0006	10937	10999	10818	10946
0.0008	11552	11409	11522	11291
0.001	12062	12061	11876	12015
x	$M_{PEG} = 4000$			
	Water-PEG	Water-PEG-KCl	Water-PEG-KBr	Water-PEG-KI
0	9292	9274	9222	9180
0.0001	9711	9592	9649	9611
0.0002	10162	10177	10111	10079
0.0004	10978	10909	10832	11124
0.0006	11749	11502	11835	11502
0.0008	12449	12371	12296	12410
0.001	13081	13015	13063	13047
x	$M_{PEG} = 6000$			
	Water-PEG	Water-PEG-KCl	Water-PEG-KBr	Water-PEG-KI
0	9292	9274	9222	9180
0.0001	10525	10504	10485	10459
0.0002	11656	11346	11326	11618
0.0004	13417	13427	13411	12994
0.0006	14938	15248	14635	14527
0.0008	16154	16164	15949	16150
0.001	17261	17572	17256	16899

Table 2.
Dependence activation entalphy of viscous flow of water-PEG, water-PEG-KCl, Water–PEG–KBr and water–PEG–KI systems on PEG concentration (J/mol) ($T = 293.15K$, $x_{KCl} = x_{KBr} = x_{KI} = 0.01$)

x	$M_{PEG} = 1000$			
	Water-PEG	Water-PEG-KCl	Water-PEG-KBr	Water-PEG-KI
0	17397	16665	16489	16400
0.0001	17543	17007	16618	16586
0.0002	17643	17156	16936	16734
0.0004	17897	17339	17274	17015
0.0006	18059	17546	17457	17288
0.0008	18333	17599	17698	17549
0.001	18503	18041	17889	17663
x	$M_{PEG} = 1500$			
	Water-PEG	Water-PEG-KCl	Water-PEG-KBr	Water-PEG-KI
0	17397	16665	16489	16400
0.0001	17633	17110	16923	16712
0.0002	17908	17340	17221	17010
0.0004	18407	17814	17578	17709
0.0006	18870	18331	18294	18216
0.0008	19390	18932	18984	18590
0.001	19869	19489	19267	19212
x	$M_{PEG} = 3000$			
	Water-PEG	Water-PEG-KCl	Water-PEG-KBr	Water-PEG-KI
0	17397	16665	16489	16400
0.0001	17747	17230	17033	16489
0.0002	18158	17660	17516	17314
0.0004	18858	18568	18284	18286
0.0006	19654	19113	18867	18974
0.0008	20271	19767	19803	19414
0.001	21006	20657	20406	20272
x	$M_{PEG} = 4000$			
	Water-PEG	Water-PEG-KCl	Water-PEG-KBr	Water-PEG-KI
0	17397	16665	16489	16400
0.0001	17926	17180	17180	17026
0.0002	18508	17948	17827	17707
0.0004	19465	19106	18826	18969
0.0006	20452	19818	20094	19632
0.0008	21315	20893	20697	20715
0.001	22158	21817	21756	21585
x	$M_{PEG} = 6000$			
	Water-PEG	Water-PEG-KCl	Water-PEG-KBr	Water-PEG-KI
0	17397	16665	16489	16400
0.0001	18818	18214	18068	18050
0.0002	20093	19266	19165	19326
0.0004	22091	21784	21584	21089
0.0006	23880	23736	23180	22926
0.0008	25262	24981	24688	24896
0.001	26685	26712	26328	25721

Table 3.

Dependence activation entropy of viscous flow of water–PEG, water–PEG–KCl, Water–PEG–KBr and water –PEG–KI systems on PEG concentration (J/mol) ($T = 293.15K$, $x_{KCl} = x_{KBr} = x_{KI} = 0.01$)

x	$M_{PEG} = 1000$			
	Water-PEG	Water-PEG-KCl	Water-PEG-KBr	Water-PEG-KI
0	27,65	25,21	24,79	24,63
0.0001	27,87	26,11	24,97	25,00
0.0002	28,04	26,16	25,76	25,21
0.0004	28,27	26,59	26,19	25,61
0.0006	28,39	26,60	26,20	26,29
0.0008	28,70	26,59	26,73	26,21
0.001	28,79	27,25	26,88	26,23
x	$M_{PEG} = 1500$			
	Water-PEG	Water-PEG-KCl	Water-PEG-KBr	Water-PEG-KI
0	27,65	25,21	24,79	24,63
0.0001	27,87	26,15	25,68	25,11
0.0002	28,06	26,46	26,04	25,45
0.0004	28,60	26,63	26,17	26,51
0.0006	28,87	27,41	27,06	26,54
0.0008	29,52	27,46	27,68	27,18
0.001	29,75	28,46	27,80	27,68
x	$M_{PEG} = 3000$			
	Water-PEG	Water-PEG-KCl	Water-PEG-KBr	Water-PEG-KI
0	27,65	25,21	24,79	24,63
0.0001	27,93	26,22	25,72	25,22
0.0002	28,30	26,65	26,31	25,74
0.0004	28,73	27,25	26,93	26,35
0.0006	29,74	27,68	27,46	27,38
0.0008	29,74	28,51	28,25	27,71
0.001	30,51	29,32	29,10	28,17
x	$M_{PEG} = 4000$			
	Water-PEG	Water-PEG-KCl	Water-PEG-KBr	Water-PEG-KI
0	27,65	25,21	24,79	24,63
0.0001	28,02	25,88	25,69	25,29
0.0002	28,47	26,51	26,32	26,02
0.0004	28,95	27,96	27,27	26,76
0.0006	29,69	28,37	28,17	27,73
0.0008	30,24	29,07	28,66	28,33
0.001	30,96	30,03	29,65	29,13
x	$M_{PEG} = 6000$			
	Water-PEG	Water-PEG-KCl	Water-PEG-KBr	Water-PEG-KI
0	27,65	25,21	24,79	24,63
0.0001	28,29	26,30	25,87	28,89
0.0002	28,78	27,02	26,74	26,29
0.0004	29,59	28,51	27,88	27,61
0.0006	30,50	28,95	29,15	28,65
0.0008	31,07	30,08	29,81	29,84
0.001	32,15	31,18	30,94	30,09

Table 4.

Dependence of partial molar volume of PEG in water–PEG,water–PEG–KCl, Water–PEG–KBr systems and water–PEG–KI systems on PEG concentration (J/mol) ($T = 293.15K$, $x_{KCl} = x_{KBr} = x_{KI} = 0.01$)

| x	$M_{PEG} = 1000$			
	Water-PEG	Water-PEG-KCl	Water-PEG-KBr	Water-PEG-KI
0	865	848	827	804
0.0001	857	837	816	795
0.0002	849	827	807	787
0.0004	835	811	790	772
0.0006	823	797	778	760
0.0008	813	788	770	750
0.001	804	781	765	743
x	$M_{PEG} = 1500$			
	Water-PEG	Water-PEG-KCl	Water-PEG-KBr	Water-PEG-KI
0	1343	1310	1275	1247
0.0001	1319	1284	1251	1224
0.0002	1297	1261	1230	1203
0.0004	1257	1221	1192	1164
0.0006	1225	1189	1161	1131
0.0008	1199	1167	1137	1104
0.001	1180	1153	1120	1082
x	$M_{PEG} = 3000$			
	Water-PEG	Water-PEG-KCl	Water-PEG-KBr	Water-PEG-KI
0	2829	2670	2611	2558
0.0001	2782	2632	2572	2514
0.0002	2738	2597	2536	2474
0.0004	2663	2534	2472	2407
0.0006	2602	2480	2420	2357
0.0008	2557	2436	2380	2325
0.001	2527	2403	2351	2311
x	$M_{PEG} = 4000$			
	Water-PEG	Water-PEG-KCl	Water-PEG-KBr	Water-PEG-KI
0	3785	3602	3512	3444
0.0001	3710	3535	3449	3376
0.0002	3639	3471	3388	3312
0.0004	3513	3356	3278	3198
0.0006	3405	3258	3182	3102
0.0008	3316	3175	3100	3023
0.001	3246	3108	3032	2962
x	$M_{PEG} = 6000$			
	Water-PEG	Water-PEG-KCl	Water-PEG-KBr	Water-PEG-KI
0	5085	5017	4903	4799
0.0001	5050	4983	4864	4752
0.0002	5016	4950	4828	4711
0.0004	4955	4889	4765	4642
0.0006	4903	4833	4714	4592
0.0008	4859	4782	4676	4562
0.001	4824	4736	4649	4551
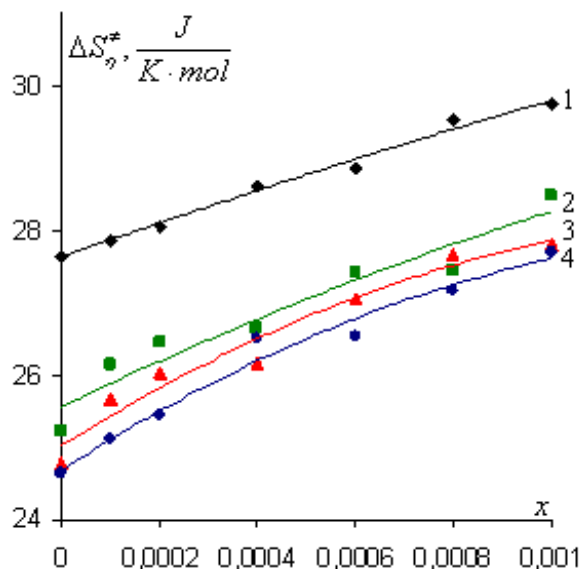
Fig.1. Dependence activation entropy of viscous flow of Water–PEG (1), water–PEG–KCl (2), water–PEG–KBr (3) and water–PEG–KI (4) systems on PEG concentration.
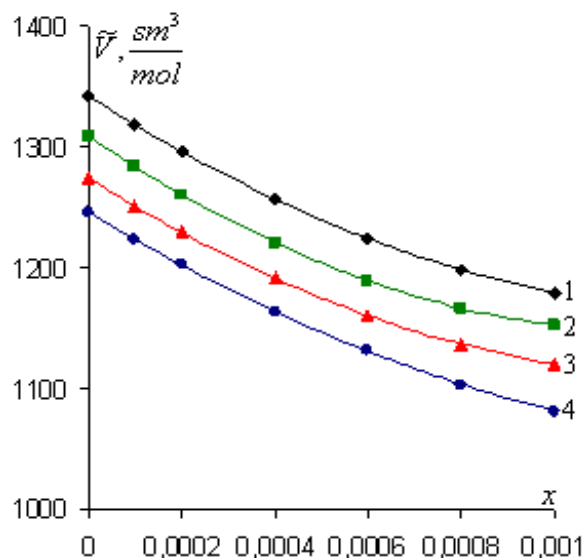

Fig.2. Dependence of partial molar volume of PEG in water PEG, water–PEG–KCl, water–PEG–KBr and water-KI systems on PEG concentration.

$$(M_{PEG} = 1500, \; T = 293.15K, \; x_{KCl} = x_{KBr} = x_{KI} = 0.01)$$

As can be seen in table 4 and fig. 2, for the studied systems, the parsial molar volume ($\tilde{V}$) of the PEGin the solution decreases with the increase in PEG concentration. We can say that when large-scale associates are divided into a volume fraction and volume fraction of its individual parts smaller than their sum. According to model of the two-structured water [19], 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. This, with the increase in concentration in the

solution causes a decrease in the parsial molar volume of the PEG. This indicates that the solution has become more structured due to increase in PEG concentration.

4. CONCLUSION

Depending on the concentration of both the entropy of the activated flow and the parsial molar volume of PEG in solution, we can say that the PEG has a structural impact on both water and KCl, water-KBR and water-KI systems, but the presence of KC1, KBr, KI weakens the structural impact of the PEG in sequence.

[1] *E.A. Masimov, H.Sh. Hasanov, B.G. Pashayev.* Liquid viscosity. Baku, "Publishing House Laman", p. 285, 2016.

[2] *C. Goncalves, N. Trevisan, A. Meirelles.* Kinematic Viscosity of Systems Containing Polyethylene Glycol+Salt+Water at 298.2 K. J. Chem. Eng.50, p.177-181, 2005.

[3] *I.V. Shulyak, E.I. Grushova, A.M. Semenchenko.* Russian Journal of Phys. Chem., vol. 85, № 3, p. 419-422, 2011.

[4] *F.F.Bailey, J.V.Koleske.* Poly(Ethylene Oxide). Academic press: NY, p.173, 1976.

[5] *K.P. Lange.* Surfactants, synthesis, properties, analysis, application. "Professiya", p.240,2005.

[6] *D.H. Napper.* J.Colloid and Interface Sci., v.58, №2, p. 390-407, 1977.

[7] *Th.F. Tadroq, B. Vincent.* J.Colloid and Interface Sci., v. 66, №1, p. 77-84, 1978.

[8] *I.V. Shulyak, E.I. Grushova.* Russian Journal of Phys. Chem.,vol. 87, № 3, p. 453-456, 2013.

[9] *C. Bhanot, S. Trivedi, A. Gupta, S. Pandey.* Dynamic viscosity versus probe-reported microviscosity of aqueous mixtures of poly(ethylene glycol). J. Chem. Thermodyn., 45, p.137-144, 2012.

[10] *E.A. Masimov, B.G. Pashayev, H.Sh. Hasanov, S.I. Musayeva.* Russian Journal of Physical Chemistry, vol. 87, № 12, p. 2105-2107, 2013.

[11] *E.A. Masimov, B.G. Pashayev, H.Sh. Hasanov, N.H.Hasanov.* Russian Journal of Phys. Chem., vol. 89, №7, p. 1244-1247, 2015.

[12] *E.A. Masimov, B.G. Pashayev, H.Sh. Hasanov.* Russian Journal of Physical Chemistry, vol. 93, № 5, p. 988-990, 2019.

[13] *E.A. Masimov, B.G. Pashayev.* Azerbaijan Journal of Phys., vol. XXIV, №4,p.19-22,2018.

[14] *E.A. Masimov, B.G. Pashayev, H.Sh. Hasanov.* Russian Journal of Physical Chemistry, vol. 93, № 6, p. 1054-1058, 2019.

[15] *Sh.N. Hajiyeva.* Russian Journal of Phys. Chem., vol. 93, № 6, p. 1054-1058, 2019.

[16] *M.A. Sibileva, E.V. Tarasova.* Russian Journal of Phys. Chem.,vol. 78, №7, p.1240-1244, 2004.

[17] *A.A. Tager.* Physico-chemistry of polymers. M.: Scientific world, p. 576, 2007.

[18] *P. Atkins.* De Paula J. Phys. Chem. Oxford University Press., p. 1067, 2006.

[19] *O.Y. Samoylov.* The structure of aqueous solutions of electrolytes and ion hydration. M., AN SSSR, 1957, p.76-182.

[20] *G. Nemethy.* The structure of water and the thermodynamic properties of aqueous solutions. Istituto superiore di sanita-V.le Regina Elena, 299-Roma. vol. VI, fascicolo speciale 1, p. 492-592, 1970.