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Use of Partial Molar Volume for Determining Conformations of Macromolecules in a Solution

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Abstract—A formula was derived for determining the partial molar volume (PMO) of solute at various concentrations and on this basis a method was developed for determining the PMO at infinite dilution. The partial molar volumes of the homologous series of poly(ethylene glycol) with molecular masses 400, 1000, 1500, 2000, 4000, 20000 in aqueous solutions at infinite dilution were determined. Analysis of the calculated and experimental PMO showed that poly(ethylene glycol) molecules exist in dilute solutions in the conformations of elongated helices. In addition, the high-molecular polyethylene glycol molecules include the areas of statistical chaos, which leads to sites unavailable for the solvent molecules. Based on literature data were revealed the values of PMO for highly concentrated solutions of poly(ethylene glycol) PEG 400, PEG 4000, and PEG 6000. Effect of concentration on the structure of PEG solutions was demonstrated. We found that in the temperature range 25–40°C the conformational transitions were not observed.

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An important task of the physical chemistry is the study of the structure and properties of molecules. Of paramount importance is the relation between the properties of compounds and structure of the molecules in a solution. One approach to solving this problem is the study of the partial molar properties of components and, in particular, the partial molar volume [1]. According to the literature [1–10], the analysis of the values of partial molar volumes allows revealing the features of behavior of compounds in solution: the structure of solvation shells, effect of the background salt on the solvation, conformation of macromolecules, and more. Bulk thermodynamic properties of liquids are most directly related to the packing of the molecules and changes in this packing with changing parameters of the state. Therefore any changes of the solvent structure should be reflected in the partial molar properties of the dissolved substance in a dilute solution. In this regard, the study of the volume characteristics of dilute aqueous solutions of substances is an important way to study structure of the latter [2]. However, the theoretical interpretation of the partial molar volumes is a challenge.

Mixing or dissolving substances usually results in a change in the volume of the solution [2, 3], that is, the free volume is changed (the volume not occupied by the proper volume of the molecules of the substance). Therewith, the proper volume of molecules remains practically unchanged. Therefore, the change of volume on mixing of materials corresponds to the difference between the volume of one mole of a substance, measured at a given temperature, and the proper volume of the molecules contained in one mole of substance. The change in free volume on mixing liquids or dissolving solids may be due to differences in cohesive energy between the molecules of the components, in the molecular size, and in the shape of the molecules [3]. The investigation of these causes is important when studying the structure of macromolecules in solution.

Many works are known, which show the properties of solutions of poly(ethylene glycol) of different molecular weight [4–10]. However, they concern the bulk properties of concentrated aqueous solutions of poly(ethylene glycol) containing more than 5 wt % of the solute, or the solutions in hydrocarbons or salt-containing solvents. But we could not find any information on the properties of dilute solutions of poly(ethylene glycol) with the concentration less than 5 wt %.

The aim of this work was to study the bulk properties of solutions of poly(ethylene glycol) in a wide range of concentrations and spatial structures of aqueous solutions of poly(ethylene glycol) on the basis of molar volumes. For this purpose it was necessary to achieve the following objectives: (1) to derive a formula for determining the partial molar volume of substances that can be applied in a wide range of concentrations, (2) to calculate the partial molar volumes of poly(ethylene glycol) in aqueous solution on the basis of the experimental density values for different concentrations, and (3) to calculate the partial molar volume of poly(ethylene glycol) from the theoretical values of partial molar volumes of individual groups of atoms, and to compare these results with those obtained from experimental data.

To derive the formula for determining partial molar volumes in the whole concentration range we used the following concepts.

The partial molar quantity $\bar{Q}_i$ is equal to [11]:

$$\bar{Q}_i = (\partial Q/\partial n_i)_{T,P,nj}. \tag{1}$$

The $\bar{Q}_i$ value is a change of extensive property of a solution at adding to 1 mol of it an infinitesimal amount of the *i*th component at the constant temperature, pressure, and unchanged number of moles of the other components. In the general case the $\bar{Q}_i$ is not a thermodynamic function and it can be both positive and negative. For a pure component the partial molar quantity is equal to its molar quantity [11].

If the extensive quantity is the volume, the equation becomes:

$$\bar{V}_i = (\partial V_\text{p}/\partial n_i)_{T,P,nj}, \tag{2}$$

where V_solution is the volume of the solution, ml mol^{-1}, $\bar{V}_i$ is the partial molar volume of *i*th substance, ml mol^{-1}.

To derive the formula relating the mass fraction and the solution density to the partial molar volume, we used the following magnitudes: the solution density (ρ, g cm^{-3}), which is equal to the ratio of the solution weight (m_solution, g) to the volume of solution (V_solution, cm^3); the solution weight, which is equal to the sum of products of a component amount (n_i, mol) on its molecular weight (M_i, g mol^{-1}); specific volume (V_spec, cm^3 g^{-1}), which is the value of the inverse solution density; the weight fraction of substance (w, %), calculated as a ratio of the weight of a substance (m_subst, g) to the weight of solution (m_solution, g), expressed as a percentage.

The derivative of the specific volume of solution on the weight fraction of solute equals to the ratio of the derivatives of the specific volume and weight fraction on the amount of the solute:

$$(\partial V_\text{spec}/\partial\omega_1)_{P,T,n2} = (\partial V_\text{spec}/\partial n_1)_{P,T,n2}/(\partial\omega_1/\partial n_1)_{P,T,n2}. \tag{3}$$

The partial derivatives of the specific volume and mass fraction on the number of substances are:

$$\begin{aligned}\partial V_\text{spec}/\partial n_1)_{P,T,n2} &= [\partial(1/\rho_\text{solution})/\partial n_1]_{P,T,n2}\\ &= \{\partial[V_\text{solution}/(n_1M_1 + n_2M_2)]/\partial n_1\}_{P,T,n2},\end{aligned} \tag{4}$$

$$(\partial\omega_1/\partial n_1)_{P,T,n2} = \{\partial[n_1M_1/(n_1M_1 + n_2M_2)]/\partial n_1\}_{P,T,n2}. \tag{5}$$

Differentiating the Eqs. (4) and (5) gives:

$$\begin{aligned}(\partial V_\text{spec}/\partial n_1)_{P,T,n2} &= -[V_\text{spec}M_1/(n_1M_1 + n_2M_2)^2]\\ &+ (\partial V_\text{solution}/\partial n_1)_{P,T,n2}/(n_1M_1 + n_2M_2),\end{aligned} \tag{6}$$

$$\begin{aligned}(\partial\omega_1/\partial n_1)_{P,T,n2} &= M_1/(n_1M_1 + n_2M_2)\\ &- M_1^2n_1/(n_1M_1 + n_2M_2)^2.\end{aligned} \tag{7}$$

The transformation of Eqs. (6), (7), taking into account the fact that $(\partial V_\text{p}/\partial n_1)_{P,T,ni} = \bar{V}_1$ gave the following general expression:

$$(\partial V_\text{spec}/\partial\omega_1)_{P,T,n2} = [1/(n_1M_1 + n_2M_2)]\cdot(\bar{V}_1 - V_\text{spec}M_1), \tag{8}$$

$$(\partial\omega_1/\partial n_1)_{P,T,n2} = [1/(n_1M_1 + n_2M_2)]\cdot(M_1\omega_2). \tag{9}$$

Substituting expression (8) and (9) into Eq. (3) and performing the appropriate mathematical transformations, we obtain an equation which relates the partial molar volume of the substance with its weight fraction in the solution:

$$(\partial V_\text{spec}/\partial\omega_1)_{P,T,n2} = [V_\text{уд} - (\bar{V}_1/M_1)]/\omega_2. \tag{10}$$

This expression allows the calculation of partial molar volumes of substances in the concentration range from 0 to 100%. At the calculation of partial molar volumes of substances it is necessary to know the equation describing the dependence of the density of the solution (ρ_solution) or the specific volume of solution (V_spec) on the weight fraction of solute (ω): $V_\text{spec} = f(\omega)$.

Now we consider the obtained results in the framework of above theoretical analysis of the problem.

Poly(ethylene glycol) dilute aqueous solutions. According to [2, 4, 5], in dilute solutions the dependence $V_\text{spec} = f(\omega)$ is described by a polynomial of the first order. Then equation 10 for the dilute solutions takes the following form:

$$\bar{V}_1 = (V_\text{spec} - \tan\alpha\cdot\omega_2)M_1, \tag{11}$$

where tan α is the slope of the function $V_\text{spec} = f(\omega_2)$.

Densities of the dilute poly(ethylene glycol) solutions under study are listed in Table 1. From the data on the density of the solutions (Table 1) using Eq. (11) the missing in the literature partial molar volumes of poly(ethylene glycol) at infinite dilution were calculated (Table 2). Additive partial molar volumes V_{add} of the poly(ethylene glycol)s were calculated according to [1, 2] as follows:

$$\bar{V}_{\mathrm{add}} = nV(\mathrm{CH_2{-}CH_2{-}O}) + (n-1)V(\mathrm{CO}), \qquad (12)$$

where n is the polymerization degree, $V(\mathrm{CH_2CH_2O})$ is the additive molar volume of the elementary unit, $\mathrm{cm^3\ mol^{-1}}$, $V(\mathrm{CO})$ is the increment of the molar volume of the C–O bond , $\mathrm{cm^3\ mol^{-1}}$.

Since the polymerization degree of poly(ethylene glycol) is high, in the calculation of the partial molar volume the contribution of the terminal hydroxy groups was not considered.

To calculate the increments of the partial molar volumes of $\mathrm{CH_2CH_2O}$ and CO groups, we suggest the following formulas in the framework of the known procedure of calculation of the molar volume increments [2]:

$$V(\mathrm{CH_2{-}CH_2{-}O}) = V[\mathrm{HO(CH_2)_2O(CH_2)_2OH}] - V(\mathrm{HOCH_2CH_2OH}),$$

$$V[\mathrm{CH_2{-}CH_2{-}O}) = V[\mathrm{HO(CH_2)_2O(CH_2)_2O(CH_2)_2OH}] - V[\mathrm{HO(CH_2)_2O(CH_2)_2OH}],$$

$$V(\mathrm{CO}) = 4V(\overline{\mathrm{CH_2{-}CH_2{-}CH_2{-}O}}) - 3V(\overline{\mathrm{CH_2{-}CH_2{-}CH_2{-}CH_2{-}O}}),$$

$$V(\mathrm{CO}) = [5V(\overline{\mathrm{CH_2{-}CH_2{-}CH_2{-}O}}) - 3V(\overline{\mathrm{CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}O}})]\cdot 1/2.$$

Table 3 includes the data on the partial molar volume of substances in aqueous solutions necessary for the calculation of the partial molar volume of a group [2].

Table 2 shows that for the studied systems the ε_v value characterizing the deviation of the experimental V_{part} values from the additively calculated amounts is 28.1–42.9%. Apparently, this is due to the difference in the solvation of the low-molecular and high-molecular compounds, containing hydroxyethyl group. The spatial structure of molecules of ethylene glycol, diethylene glycol and triethylene glycol does not allows the water molecules to surround the hydroxyethyl groups on all sides. As a consequence, in these cases there are voids increasing the partial molar volume. On the contrary, the molecules of poly(ethylene glycol) acquire in solution *spiral* conformation with the spatial step that ensures the availability of hydroxyethyl groups to water molecules.

In [12] the effect has been studied of the number of hydroxyethyl groups in the glycol molecules on the structural organization and intermolecular association in the water–glycol systems. It was found that the strength of intermolecular hydrogen bonds decreases significantly with increasing number of the hydroxyethyl groups per molecule of glycol. This is due to the replacement of the strong hydrogen bonds between the hydroxy groups by the bonds between the OH and aromatic C–O–C groups. The process of association, which is very sensitive to steric effects, is also hampered by a lengthening of the molecular chain of glycol.

According to computer simulations [13], ethylene glycol does not significantly affect the network of hydrogen bonds of water in the concentration range $0 < x < 0.1$. However, according to [12], the concentration range when the additives influence the network of hydrogen bonds in water is markedly lower for ethoxylated glycols than for aqueous solutions of ethylene glycol. Moreover, at the introduction in the water of the molecules of nonelectrolytes the framework of hydrogen bonds remains unchanged at 298.15 K, and further increase in temperature affects the network of hydrogen bonds insignificantly [12, 13].

As Table 2 shows, the values of the relative deviation (ε_v) increase with the increase of the molecular weight of poly(ethylene glycol) to PEG-4000. However, the ε_v value of PEG-20000 is less than for PEG-4000. Apparently, upon increasing the polymer molecular weight and hence its chain length, it undergoes twisting, therefore, begin to form the areas of statistical chaos in the mutual arrangement of chains, which leads to the appearance of the sites inaccessible for the solvent molecules.

The change in the partial molar volumes of poly (ethylene glycol) with increasing temperature is insignificant, in agreement with published data [1, 6]. Therefore, in a given temperature range the conformational transitions do not occur.

It was found earlier [14, 15] that with increasing temperature in aqueous solutions of PEG 400, PEG 1000, and PEG 1500 the thermodynamic parameters of

Table 1. Temperature and concentration dependences of the density of dilute aqueous solutions of poly(ethylene glycol)

Weight fraction of poly(ethylene glycol), wt %	Density of solution, g cm^{-3}			Weight fraction of poly(ethylene glycol), wt %	Density of solution, g cm^{-3}		
	25°C	30°C	40°C		25°C	30°C	40°C
PEG-400				PEG-1000			
0.468	0.9965	0.9957	0.9934	0.536	0.9980	0.9968	0.9933
0.927	0.9970	0.9962	0.9939	0.832	0.9985	0.9975	0.9938
1.510	0.9976	0.9969	0.9948	1.493	0.9995	0.9984	0.9949
2.090	0.9982	0.9975	0.9953	1.862	0.9999	0.9990	0.9958
2.588	0.9988	0.9981	0.9962	2.503	1.0013	1.0003	0.9968
2.863	0.9992	0.9985	0.9964	2.994	1.0022	1.0011	0.9980
3.634	1.0000	0.9994	0.9976	4.191	1.0038	1.0030	0.9998
PEG-1500				PEG-2000			
0.463	0.9977	0.9962	0.9935	0.527	0.9979	0.9959	0.9930
0.838	0.9982	0.9968	0.9941	0.815	0.9984	0.9965	0.9936
1.469	0.9991	0.9978	0.9950	1.496	0.9994	0.9974	0.9948
1.910	0.9998	0.9986	0.9957	1.865	0.9999	0.9982	0.9952
2.635	1.0011	0.9996	0.9972	2.500	1.0010	0.9990	0.9963
3.078	1.0019	1.0005	0.9982	3.151	1.0020	1.0001	0.9972
4.288	1.0034	1.0022	1.0002	4.249	1.0036	1.0018	0.9991
PEG-4000				PEG-20000			
0.437	0.9979	0.9963	0.9932	0.193	0.9972	0.9960	0.9926
0.725	0.9984	0.9968	0.9938	0.411	0.9976	0.9964	0.9929
1.282	0.9992	0.9976	0.9948	0.807	0.9983	0.9970	0.9937
1.747	0.9999	0.9986	0.9956	1.152	0.9990	0.9977	0.9942
2.367	1.0012	0.9997	0.9966	1.520	0.9995	0.9982	0.9949
2.932	1.0022	1.0005	0.9980	1.882	1.0001	0.9989	0.9955
3.730	1.0034	1.0020	0.9991	2.641	1.0012	1.0001	0.9968

the interaction of poly(ethylene glycol) with water significantly deteriorate (the Huggins constant increases). However, for poly(ethylene glycol) with a molecular weight more than 2000 the thermodynamic quality of solvent does not vary significantly with increasing temperature (the Huggins constant change is insignificant). Since at the increase in temperature the partial molar volume of poly(ethylene glycol) does not change, the deterioration of the poly(ethylene glycol)–water thermodynamic interaction is apparently due to an increase in the kinetic energy of a low molecular weight poly(ethylene glycol) and to the rupture of hydrogen bonds. The interaction energy in the macromolecular poly(ethylene glycol)–water system is rather high, therefore the mobility of macromolecules does not increase significantly and as a consequence the solvent quality does not fall.

Thus, the study of temperature and concentration dependences of the density of dilute aqueous solutions of poly(ethylene glycol) of various molecular weights allowed us to propose a methodology of estimation of the conformations of macromolecules in aqueous solutions. Therewith, the comparison of rheological and volumetric properties revealed more completely the behavior of macromolecules of poly(ethylene glycol) in water.

Poly(ethylene glycol) concentrated aqueous solutions. On the basis of density of aqueous solutions of PEG 400, 4000, 6000 [6] specific volumes of solutions were calculated. According to the data of [6, 7], the density dependence on the solution concentration is described by a third degree polynomial:

$$\rho(\omega) = a + b\omega + c\omega^2 + d\omega^3, \tag{13}$$

where $\rho(w)$ is the solution density, g cm^{-3}; *a, b, c, d* are the depending on the temperature coefficients of polynomial equations; *w* is the mass fraction of a component.

Therefore, Eq. (10) for the region of high concentration of the polymer becomes:

$$\bar{V}_1 = [V_{\text{spec}} - (b + c\omega_2 + d\omega_2^{\,2})\cdot\omega_2]\cdot M_1 \tag{14}$$

The figure shows the plots of partial molar volumes of PEG 400, PEG 4000, and PEG 6000 vs. the concentration. With increasing content of poly(ethylene glycol) in water up to 20–25 wt % the value of partial molar volume decreases. Further increase in the poly(ethylene glycol) concentration in the solution increases the value of partial molar volume.

It was found in [12] that at mixing di- and triethylene glycols with water at concentrations above 30–40 wt % the network structures break both in water and in the glycol. But the network of hydrogen bonds between water and the poly(ethylene glycol) molecules on the whole is retained. Due to their strong electron-donating properties ethylene glycols form associates with water.

According to [16], in the water–glycol system there are three concentration areas. The first area corresponds to the dilute solutions, where the glycol does not appreciably affect the network of hydrogen bonds of water molecules. Calculations indicate that in the second area of concentration of the mixtures of water with glycols the temperature factor most strongly influences the specific interactions which become noticeably weaker when temperature increases. In solutions of glycols with higher concentrations of the non-aqueous component with a large number of hydroxyethyl groups more effective destruction of the structure of water occurs not only at 298.15 K but also at other temperatures. The network of hydrogen bonds of water molecules now includes the molecules of glycols, which leads to its gradual change and the formation of a common network of hydrogen bonds.

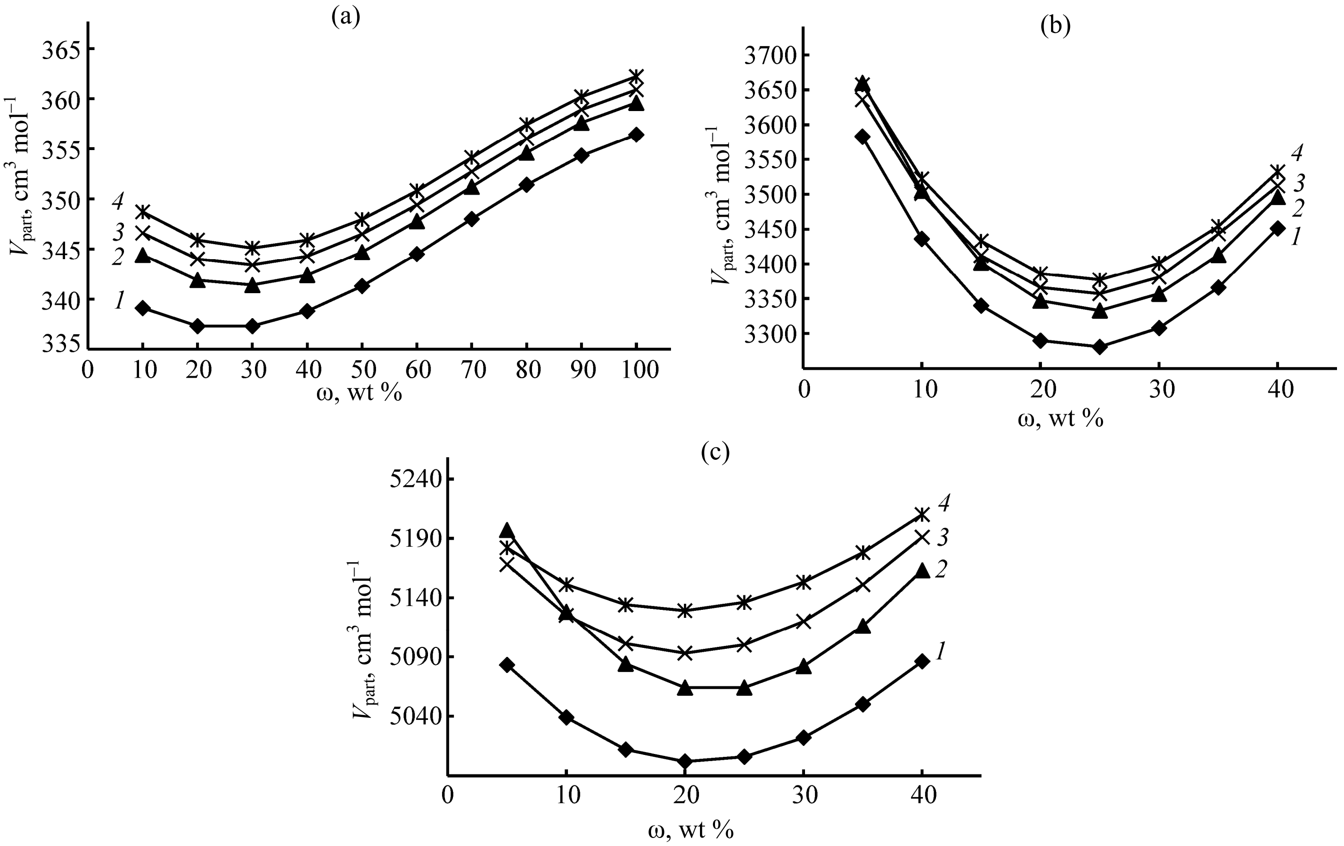
Table 2. Partial molar volumes

T, °C	$\bar{V}_{\text{part}}$, cm^3 mol^{-1}	$\bar{V}_{\text{ad}}$, cm^3 mol^{-1}	ε_v,%
Aqueous solution PEG-400, *n* = 9			
25	357±13	457	28.1
30	355±13	–	–
40	350±13	–	–
Aqueous solution PEG-1000, *n* = 22			
25	840±50	1140	35.6
30	835±50	–	–
40	825±50	–	–
Aqueous solution PEG-1500, *n* = 34			
25	1275±85	1770	38.9
30	1270±85	–	–
40	1240±85	–	–
Aqueous solution PEG-2000, *n* = 45			
25	1700±130	2347	38.2
30	1695±130	–	–
40	1690±130	–	–
Aqueous solution PEG-4000, *n* = 91			
25	3330±400	4762	42.9
30	3325±400	–	–
40	3300±400	–	–
Aqueous solution PEG-20000, *n* = 454			
25	18150±900	23820	31.1
30	18100±900	–	–
40	18050±900	–	–

The third area, with a high content of organic component, is of greatest length. It is characterized by a high concentration of free OH groups of water. Computer simulations [13] showed that under these conditions a small number of water molecules is self-associated to form dimers and clusters. This indicates

Table 3. Partial molar volumes of substances in aqueous solutions at 298 K

Compound	*V*, cm^3 mol^{-1}	Compound	*V*, cm^3 mol^{-1}
Ethylene glycol	54.65	Triethylene glycol	129.28
Dithylene glycol	92.25	Oxetan	61.35
Oxolane (tetrahydrofuran)	76.90	Oxane (tetrahydropyrane)	91.80



Isotherms of partial molar volumes of (a) PEG 400, (b) PEG 4000, and (c) PEG 20000.

that in the region of high concentration of the organic component water is dispersed, existing mainly as individual molecules included in the heteroassociates with glycols.

The figure shows that the partial molar volume of poly(ethylene glycol) decreases with its increasing concentration. Apparently, there is the introduction of poly(ethylene glycol) macromolecules in a tetrahedral cage of water molecules and the network of hydrogen bonds of water molecules breaks. When the concentration of poly(ethylene glycol) is more than 25%, a cage is formed of the poly(ethylene glycol) molecules with water molecules in the cavity. These data support the statements on the influence of the concentration of substances on the structure of water presented in [12, 13, 16].

According to [17] an increase in temperature causes the rupture of hydrogen bonds between water molecules, which leads to changes in both direction and topology of the network of hydrogen bonds. With increasing temperature the contribution increases of the weak specific and possibly van der Waals interactions, which along with strong hydrogen bonds plays an important role in the structural organization of liquid water.

The graphic data in the figure show that with increasing temperature an increase occurs in the partial molar volume of PEG-400. Apparently, there is a destruction of tetrahedral structure of water and strengthening of the interactions in the system of poly(ethylene glycol)–water due to the rupture of hydrogen bonds and increase the contribution of van der Waals forces in the intermolecular interactions. The obtained data on the effect of temperature on the partial molar volume of poly(ethylene glycol), as well as on the structure of water, are consistent with the experimental data obtained for the different carbohydrates in aqueous solutions [18].

EXPERIMENTAL

We investigated the concentration dependences of the density of dilute aqueous solutions of poly(ethylene glycol) at 25, 30, and 40°C. The investigated polymers were commercial samples having an average molecular weight of 400 (385–415), 1000 (940–1060), 1500 (1400–1600), 2000 (1900–2200), 4000 (3900–

4800), and 20000 (17000–20000). Solutions were prepared by gravimetric method. As the solvent twice distilled water was used. Densities of solutions were measured by pycnometric method [19]. Temperature was controlled with an accuracy of ±0.1 K.

Data on the values of the concentration dependences of the densities of poly(ethylene glycol) solutions with average molecular weights of 400 (385–415), 4000 (3500–4500), 6000 (5000–7000) and the poly(ethylene glycol) content exceeding 5 wt % are taken from [6].

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