

THE DEFINITION OF POLYETHYLENE GLYCOL MACROMOLECULE CONFORMATION IN WATER SOLUTIONS

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The kinematic viscosity dependences of (PEG) polyethylene glycol water solutions of different molecular masses in temperature interval 293,15 -323,15 K and concentrations 1 – 5% are investigated. The characteristic viscosity, Huggins constants K_H and Mark-Kun-Hauwink constants α are calculated. The temperature dependences of these parameters are defined. The assumptions on polymer macromolecule conformation in solution are made.

Keywords: water solutions, characteristic viscosity, Huggins constants.

PACS: 77.22.Ej, 64.75.Bc, 31.70.Dk, 61.20.Og.

INTRODUCTION

The properties of polymer water solutions are caused by interactions between component molecules and also conformation peculiarities of macromolecules. The viscosimetry is more detail method for definition of macromolecule sizes. The characteristic viscosity $[\eta]$ is defined by this method. The characteristic viscosity is connected with hydrodynamic volume of polymer solutions, i.e. with volume of molecular coil together with trapped solvent. Obviously, the solution structure changes with variation of macromolecule size and conformation in solution. It is necessary to measure the temperature and concentration dependences of solution kinematic viscosity for definition of solution structural change.

The aim of the work is the investigation of rheological properties of heterochain polymer-polyethylene glycol (PEG) water solution which is widely used in different fields of agriculture: medicine, food, pharmaceutical industries and etc [1].

EXPERIMENTAL PART

The water solutions of PEG polymer of molecular masses 1000, 1500, 3000, 4000 and 6000 g/mol are investigated by viscosimetric method. The samples with concentrations from 1% up to 5% are prepared from each polymer of given molecular mass. At sample preparation the polymer joint hinge is weighed with accuracy $\pm 2 \cdot 10^{-3}$ mg and it is solved in bidistilled water in flask of volume 50ml. Each sample is endured in water bath during not less 5-6 hours and they are investigated in temperature interval from 288,15 up to 323,15K. The measurements are carried out in viscosimeter BИДЖ-1 with capillary diameter $d=0,54$ mm put into thermostat. The thermostating time is not less 15 min. The time is measured with accuracy $\pm 0,2$ sec. The obtained values of kinematic viscosity are presented in table.

RESULT DISCUSSION

The table data show that kinematic viscosity of PEG water solutions increases with temperature decreasing and increasing of polymer concentration in solution. Such

change of PEG solution viscosity is character for many liquids.

The values of characteristic viscosity $[\eta]$, Huggins constants K_H of activation energy of viscous flow ΔE_p are used for description of macromolecule state in solution. Firstly the reduced viscosity is calculated for finding of characteristic viscosity of PEG solutions, using the following relation [1,2]:

$$\eta_{red.} = \frac{\eta_{sol} - \eta_0}{\eta_0 c} \quad (1)$$

where c is solution concentration in percents, η_0 is pure solvent viscosity. Later, the dependence on concentration $\eta_{red.} = f(c)$ is constructed which is processed by least square procedure. The characteristic viscosity $[\eta]$ and slope are defined by extrapolation of $\eta_{red.} = f(c)$ dependence to zero concentration. The correlation coefficient is not less 0,99. $\eta_{red.} = f(c)$ dependence for systems PEG-1000-water at 293,15K is presented in fig.1.

The direct line presented in fig.1 is described by formula

$$\eta_{red.} = 0.0341 + 0.0061c \quad (2)$$

In this formula 0,0341= $[\eta_1]$ is characteristic viscosity of system PEG-1000-water at temperature 293,15K; 0,0061 = $K_1 = tg \alpha_1$ is slope of direct line shown in fig.1. The characteristic viscosities of all investigated systems at other temperatures are found by the same way. That's why the formula (2) in general form we can write by the following way:

$$\eta_{red.} = [\eta] + K \cdot c \quad (3)$$

On the other hand, the characteristic viscosity $[\eta]$ is connected with given viscosity by Huggins equation [2-4]:

$$\eta_{red.} = [\eta] + K_H [\eta]^2 c \quad (4)$$

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From formulae (3) and (4) let's obtain formula for calculation of Huggins constant:

$$K_H = \frac{tg\alpha}{[\eta]^2} \quad (5)$$

The temperature dependences of characteristic viscosity and Huggins constants for the investigated systems are given in fig.2 and fig.3.

According to data given in fig.2, the value of characteristic viscosity, which is connected with hydrodynamic flow reaction [4] for PEG with big molecular mass, is bigger than for PEG with less molecular mass.

Table

The values of kinematic viscosity $\left(\nu, \frac{mm^2}{sec} \right)$ of PEG solutions in temperature interval from 293.15 up to 323.15K and concentration 1 up to 5 %.

<i>c, % , T, K</i>	293,15	298,15	303,15	308,15	313,15	318,15	323,15
0	1,0038	0,8928	0,8008	0,7234	0,6578	0,60	0,5537
PEG-1000							
1	1,044	0,927	0,829	0,748	0,678	0,620	0,569
2	1,099	0,974	0,868	0,781	0,703	0,641	0,589
3	1,158	1,027	0,907	0,816	0,732	0,668	0,610
4	1,240	1,095	0,964	0,862	0,768	0,697	0,635
5	1,330	1,168	1,020	0,911	0,804	0,729	0,662
PEG-1500							
1	1,059	0,941	0,844	0,763	0,693	0,634	0,583
2	1,132	1,005	0,901	0,812	0,739	0,676	0,621
3	1,216	1,080	0,967	0,872	0,793	0,726	0,666
4	1,322	1,167	1,048	0,947	0,858	0,782	0,718
5	1,443	1,275	1,141	1,030	0,933	0,852	0,781
PEG-3000							
1	1,070	0,951	0,853	0,770	0,700	0,640	0,589
2	1,153	1,025	0,917	0,828	0,751	0,687	0,631
3	1,253	1,115	0,999	0,895	0,813	0,745	0,683
4	1,371	1,217	1,090	0,982	0,888	0,808	0,740
5	1,508	1,334	1,191	1,065	0,964	0,878	0,809
PEG-4000							
1	1,098	0,975	0,874	0,788	0,716	0,654	0,601
2	1,212	1,074	0,961	0,865	0,784	0,715	0,657
3	1,344	1,190	1,063	0,955	0,864	0,786	0,721
4	1,504	1,326	1,182	1,060	0,956	0,868	0,795
5	1,674	1,473	1,315	1,174	1,060	0,959	0,878
PEG-6000							
1	1,165	1,034	0,924	0,833	0,755	0,690	0,633
2	1,368	1,211	1,080	0,970	0,877	0,798	0,729
3	1,615	1,425	1,267	1,134	1,022	0,929	0,847
4	1,909	1,680	1,484	1,332	1,189	1,084	0,983
5	2,241	1,971	1,739	1,550	1,386	1,253	1,136

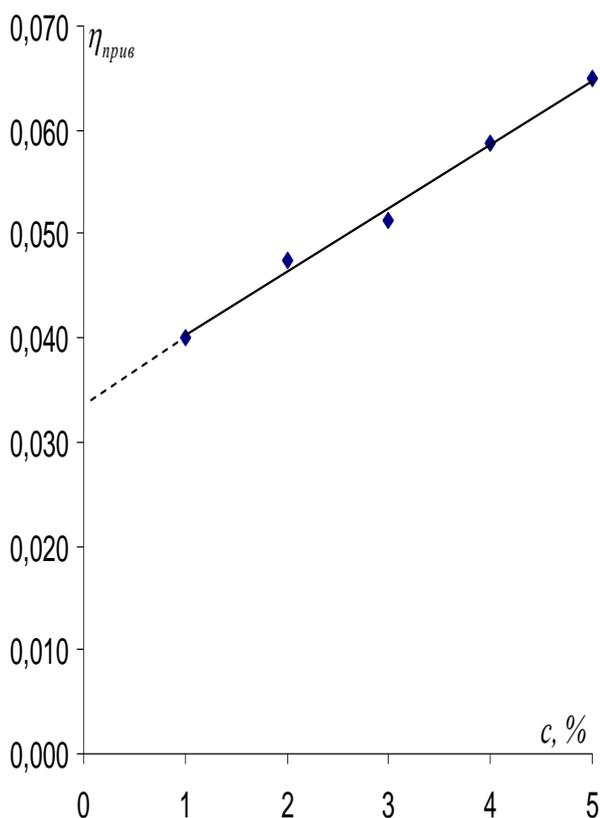


Fig.1. The definition of characteristic viscosity for systems PEG-1000-water at 293,15K.

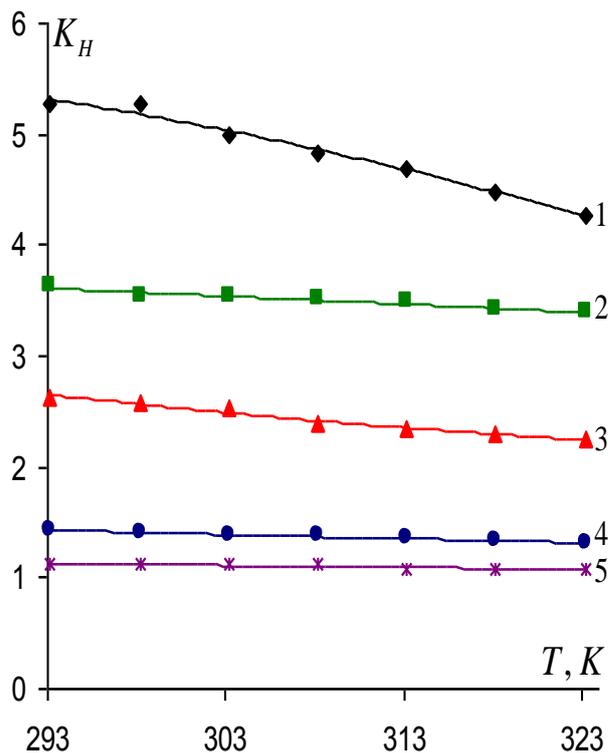


Fig. 3. The dependence of Huggins constant (K_H) on temperature for system PEG-water 1 is PEG (1000), 2 is PEG (1500), 3 is PEG(3000), 4 is PEG (4000), 5 is PEG (6000).

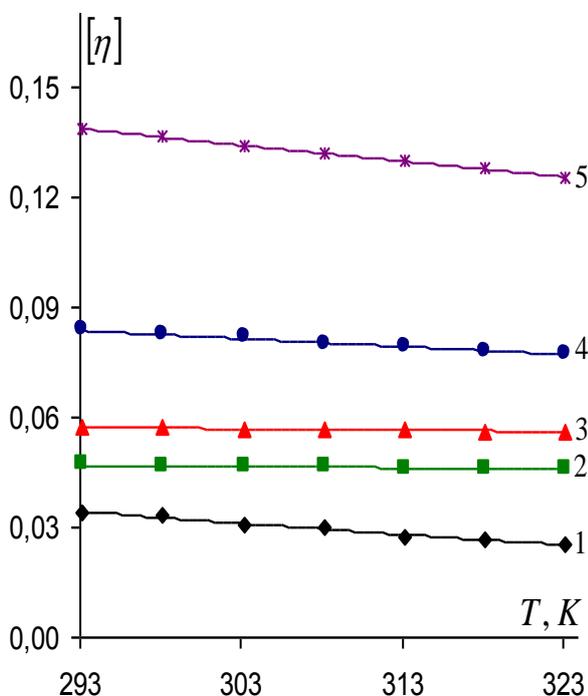


Fig. 2. The dependence of characteristic viscosity ($[\eta]$) on temperature for system PEG-water: 1is PEG(1000), 2 is PEG (1500), 3 is PEG (3000), 4 is PEG (4000), 5 is PEG (6000).

This, probably, is connected with the fact that polymer macromolecule rolls up because of hydrogen bond appeared between water molecules connected with polymer macromolecule with increasing of molecular mass.

As a result the macromolecule transforms into water impermeable coil. At flow of liquid the macromolecule rotating oscillation increases that leads to increase of characteristic viscosity. The characteristic viscosity decreases for all investigated systems with temperature increasing. This means that temperature increase causes the decrease of flow reaction because of hydrogen bond breakage between water molecules.

It is known that Huggins constant [2,3,5] including into equation (4) characterizes the interaction intensity between polymer and solvent molecules. The value is bigger the solvent is worse for the given polymer. According data of fig.3 the interaction between PEG and water molecules decreases with PEG molecular mass increasing. The most interaction is observed in system PEG (1000) – water. Probably, it is connected with the fact that PEG macromolecule with less molecular mass has the more linear conformation. Such PEG macromolecule conformation simplifies the access of water molecules to ethereal oxygen of PEG macromolecules for hydrogen bond formation. Temperature dependence is also observed (fig.3) for system with PEG low molecular mass. The temperature increase weakens the hydrogen bonds between molecules

of polymer and water and that's why increases the probability to roll up PEG macromolecule in loose coil.

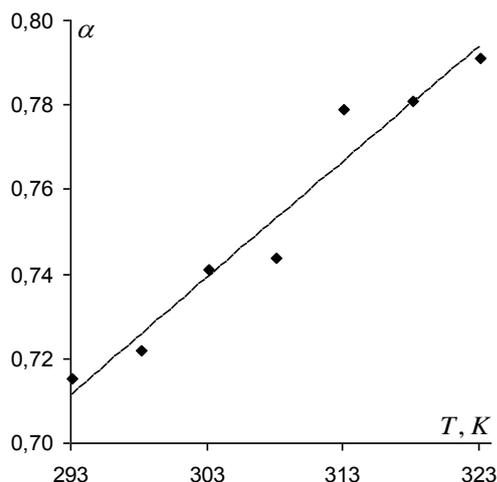


Fig. 4. The dependence of α parameter including into Mark-Kun-Hauwink formula on temperature for system PEG – water.

Temperature dependence of α parameter (fig.4) including into following Mark-Kun-Hauwink formula [2,5]

$$[\eta] = KM^\alpha \quad (6)$$

also shows that PEG macromolecule strive to have the form of loose coil

CONCLUSION

The temperature dependences of characteristic viscosity, Huggins constants K_{H_1} and Mark-Kun-Hauwink constants α , the analysis of which allows us to determine the conformations of PEG molecules, are defined on the base of investigation of kinematic viscosity of PEG water solutions.

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Received:07.04.2017