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VISCOSIMETRIC STUDIES OF WATER AND WATER-SALT SOLUTION OF POLYETHYLENE GLYCOL

The complex analysis of a state of PEG macromolecules of various molecular weights in water and water-salt solutions is carried out. Temperature factors, the constants characterizing intermolecular interaction in these systems are defined. The intrinsic viscosity is defined with the use of the various linear extrapolation equations. Influence of temperature and electrolytes on thermodynamic properties in PEG – water and PEG – water-salt solution systems is shown.

Introduction. Properties of polymer solutions are due to the configuration and conformational characteristics of macromolecules in a solvent. Currently two methods of determining the dimensions of macromolecules are mainly used – light scattering and viscosimetry [1–3]. The errors inherent to the method of light scattering, are unacceptably high in determining such parameters as temperature coefficient. The basis of viscosimetric method is the Flory equation, according to which to determine mean square distance between the ends of the chain it is necessary to determine the intrinsic viscosity $[\eta]$. In determining $[\eta]$ Huggins equation are often use [4–8]. However, we know a large number of other extrapolation dependencies, allowing to determine the intrinsic viscosity [1, 10–14].

The aim of this work was to determine how are comparable values $[\eta]$, defined using a series of linear extrapolation dependencies.

Main part. According to [1], the relationship between the solution viscosity and polymer concentration determined by the following equation:

$$\frac{\eta_2 - \eta_1}{\eta_1 \cdot c} = [\eta] + K_1 [\eta]^2 c + K_2 [\eta]^3 c^2 + \dots, \quad (1)$$

where η_2 и η_1 – is the polymer solution viscosity and solvent viscosity; c – concentration of the solution; K_1 and K_2 – constants.

To estimate the concentration dependence of the viscosity of dilute solutions of the polymers many linear equations are proposed, but most often the following equation are used.

– Huggin's equation [10]

$$\frac{\eta_{SP}}{c} = [\eta] + K_h [\eta]^2 c; \quad (2)$$

– Schulz-Blasschke equation [11]:

$$\frac{\eta_{SP}}{c} = [\eta] + K_{SB} [\eta] \eta_{SP}; \quad (3)$$

– Martin equation [12]:

$$\ln\left(\frac{\eta_{SP}}{c}\right) = \ln[\eta] + K_M [\eta] c; \quad (4)$$

– Kremer equation [13]:

$$\frac{\ln \eta_{RL}}{c} = [\eta] - K_K [\eta]^2 c; \quad (5)$$

– Arrhenius-Roher equation [12]:

$$\frac{\ln \eta_{RL}}{c} = [\eta] + K_{AR} [\eta] \ln(\eta_{RL}); \quad (6)$$

– Kreiss equation [1]:

$$\frac{\eta_{SP}}{c} = [\eta] + K_{KR} \frac{\eta_{SP}^2}{c}; \quad (7)$$

– Heller equation [14]:

$$\frac{c}{\eta_{SP}} = \frac{1}{[\eta]} - K_{He} c; \quad (8)$$

– Find-Shramek equation [1]:

$$\frac{\eta_{SP}}{c} = [\eta] + K_1 [\eta]^2 c + \left[\frac{m-1}{2m} \right] K_1^2 [\eta]^3 c^2 + \dots, \quad (9)$$

where K_h , K_{SB} , K_M , K_K , K_{AR} , K_{KR} , K_{He} – constants of Huggin, Schulz-Blasschke, Martin, Kremer, Arrhenius-Roher, Kreiss, Heller, Find-Shramek; η_{RL} – relative viscosity; η_{SP} – specific viscosity.

On the basis of experimental data on the densities of water and aqueous salt solutions of PEG, given in [7, 8] were determined values $[\eta]$ and constants for equations 2-9 for PEG-20 000 (Table 1).

In [6], the authors note that different extrapolation relations may give different values $[\eta]$ due to measurement error, the availability of data in a limited range of concentrations, as well as possible changes in chain conformation and structure formation with increasing concentration of the solution.

Analysis of the data in table 1 shows that the values $[\eta]$, defined by equations 2-8 differ by 1,3-4,0 %. For all other samples PEG deviation values $[\eta]$ did not go beyond the specified interval. This indicates that for determining $[\eta]$ may be used any extrapolation from these equations.

Table 2 shows the average value $[\eta]$ for the studied of systems PEG – water and PEG – wa-

ter-salt solution. It is seen that aqueous solutions of low molecular weight PEG intrinsic viscosity with increasing temperature is slightly increased, while for PEG with molecular masses of 2000 and above is reduced. In the case of aqueous salt solutions for all investigated samples with increasing temperature there is a decrease of intrinsic viscosity.

Studying the influence of temperature on the intrinsic viscosity is the subject of many experimental and theoretical studies, in which the complex nature of these relationships is pointed [1-3]. It is believed that the causes of the change in viscosity with increasing temperature can be very different: an increase in the degree of order in the ar-

rangement of the segments and the solvent macromolecules, desolvation of macromolecules, changes in the content of trans, gauche and cis conformations, the helix – ball transformation and etc .

According to [3], valuable information on the circuit configuration and energy conformations of bond can give the temperature coefficient, which is defined by the formula [6]:

$$\frac{d \ln[\eta]}{dT} = \frac{3}{2} \frac{d \ln \overline{h_0^2}}{dT} + \frac{d \ln \alpha^3}{dT},$$

where $\overline{h_0^2}$ – the mean square distance between the ends of the chain; α^3 – the swelling coefficient of the macromolecule.

Table 1

**Intrinsic viscosity and constant equations
of systems PEG-20000 – Water and Peg-20000 – water-salt solution***

T, °C	Water solution of PEG-20 000													
	[η], dl/g							K						
	(2)	(4)	(5)	(6)	(7)	(8)	среднее	K_h	K_M	K_K	K_{AR}	K_{KR}	K_{He}	
20	0.373	0.378	0.378	0.378	0.388	0.381	0.379	0.590	0.491	-0.026	-0.027	0.313	0.419	
25	0.389	0.392	0.391	0.391	0.399	0.394	0.393	0.420	0.365	-0.115	-0.125	0.256	0.322	
30	0.380	0.382	0.381	0.382	0.389	0.385	0.383	0.417	0.364	-0.116	-0.125	0.258	0.323	
40	0.351	0.354	0.353	0.354	0.360	0.356	0.354	0.459	0.399	-0.093	-0.099	0.282	0.353	
45	0.334	0.337	0.338	0.338	0.344	0.340	0.339	0.538	0.461	-0.048	-0.049	0.315	0.403	
50	0.346	0.347	0.345	0.346	0.349	0.348	0.347	0.269	0.248	-0.199	-0.226	0.200	0.230	
Water-salt solution of PEG-20 000														
20	0.190	0.191	0.191	0.192	0.194	0.192	0.192	0.746	0.657	0.121	0.117	0.474	0.586	
25	0.168	0.170	0.171	0.171	0.174	0.172	0.171	1.165	0.977	0.418	0.371	0.637	0.840	
30	0.162	0.164	0.164	0.165	0.168	0.165	0.165	1.148	0.969	0.412	0.368	0.644	0.837	
35	0.154	0.156	0.156	0.157	0.160	0.157	0.157	1.357	1.128	0.570	0.491	0.718	0.963	
40	0.136	0.139	0.139	0.141	0.146	0.142	0.140	2.155	1.670	1.149	0.890	0.928	1.357	
45	0.137	0.139	0.140	0.141	0.144	0.141	0.141	1.788	1.445	0.903	0.735	0.865	1.209	

* Similar results were obtained for PEG – 400, 1000, 1500, 2000, 4000, 9000.

Table 2

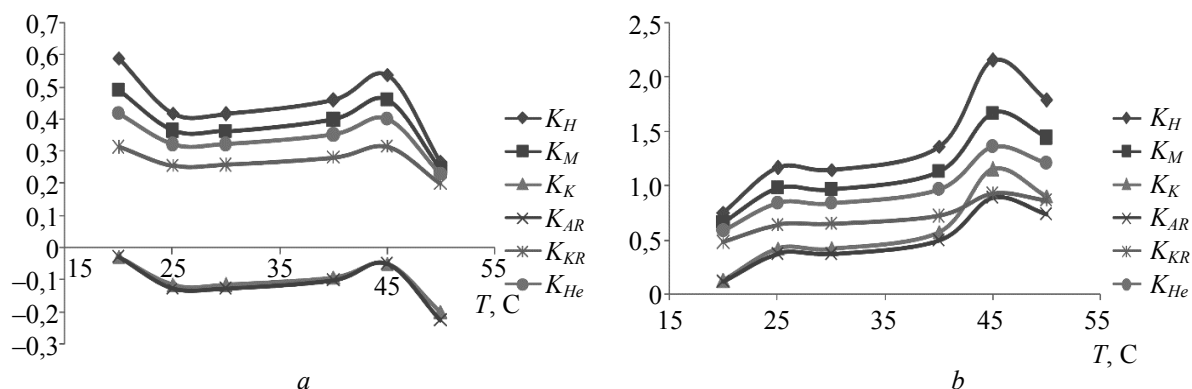
Intrinsic viscosities of the PEG solutions depending on the temperature

T, °C	Intrinsic viscosity [η], dl/g						
	PEG-400	PEG-1000	PEG-1500	PEG-2000	PEG-4000	PEG-9000	PEG-20 000
Water solution							
20	0.0231	0.0440	0.0572	0.0898	0.136	0.220	0.379
25	0.0265	0.0528	0.0668	0.0962	0.143	0.260	0.393
30	0.0257	0.0432	0.0666	0.0950	0.141	0.249	0.383
40	0.0234	0.0485	0.0622	0.0911	0.136	0.227	0.354
45	0.0280	0.0554	0.0667	0.0932	0.139	0.210	0.339
50	0.0295	0.0468	0.0693	0.0923	0.133	0.214	0.347
Water-salt solution							
20	0.0447	–	0.0544	0.0637	0.0970	–	0.192
25	0.0405	–	0.0505	0.0603	0.0913	–	0.171
30	0.0409	–	0.0479	0.0584	0.0905	–	0.165
35	0.0377	–	0.0468	0.0543	0.0867	–	0.157
40	0.0346	–	0.0433	0.0532	0.0791	–	0.140
45	0.0346	–	0.0419	0.0520	0.0790	–	0.141

Table 3

Temperature coefficient of water and aqueous salt solutions of PEG $\frac{d \ln[\eta]}{dT} \times 10^3, K^{-1}$

PEG-400	PEG-1000	PEG-1500	PEG-2000	PEG-4000	PEG-9000	PEG-20 000
Water solution						
5.363	2.858	3.603	-0.166	-1.241	-4.296	-4.593
Water-salt solution						
-10.47	-	-10.24	-8.310	-8.545	-	-13.00



Dependence of the constants of PEG-20000 on temperature:

a – Water solution; *b* – Water-salt solution

Table 3 shows the values of the temperature coefficients for the investigated water and aqueous salt solutions of PEG. As can be seen, with increasing molecular weight of PEG in aqueous solution a reduction of the temperature coefficient occurs, while for PEG with molecular masses above 2000 a temperature coefficient has a negative value. For aqueous salt solutions all temperature coefficients are negative and have smaller values than for water. This indicates that, in aqueous salt solutions PEG macromolecule have higher rigidity, and equilibrium flowability of molecules (i.e., between the circuit elements there is no hydrodynamic interaction transmitted through the solvent).

Constants are presented in Table 1, represent the interaction between segments of the macromolecule with the solvent molecules [1, 2]. The figure shows that the behavior of the constants with increasing temperature is the same.

The most widely for the analysis of the thermodynamic properties of the solutions Huggins constant (K_h) is used [4–8]. In the literature [1–3] for comparison among the polymer homologues we use not only the Huggins constant, but other constants obtained in the construction of experimental dependences $\eta = f(c)$. However, in this case, it should be noted that the accuracy of finding of all the above constants are not always high enough to do so only on the basis of the numerical values of these constants definite conclusion about the conformational and structural features of mac-

romolecules is not always correct. Based on these dependencies (figure) it may be concluded that the qualitative evaluation of the thermodynamic affinity for the solvent any of the presented equations can be used.

Thus, apparently, for determining the intrinsic viscosity, constants equation of Mark – Kuhn – Houwink when analyzing thermodynamic affinity of the polymer and the solvent, etc., it is advisable to use one of the above extrapolation equations. This will eliminate errors arising from the assumptions that have been adopted in the derivation of data of the linear extrapolation dependencies.

Conclusion. Based on the above it can be argued that an increase in temperature, and the introduction of electrolyte aggravates thermodynamic quality of solvent respectively to PEG. In determining the affinity between the polymer and the solvent as a criterion, you can use either of the constants of known linear extrapolation equations, since the variation of these constants with increasing temperature for all versions of the calculation is the same.

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Received 27.02.2013