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Viscometric Determination of the Conformations and Sizes of Polyethylene Glycol Macromolecules in Aqueous Solutions

E. A. Masimov[a], **B. G. Pashayev**[a,*], **G. Sh. Gasanov**[a†], **and Sh. N. Gadzhieva**[a]

[a] *Baku State University, Baku, 1148 Azerbaijan*

**e-mail: p.g.bakhtiyar@gmail.com*

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Abstract—The kinematic viscosities of solutions of polyethylene glycol (PEG) of different molecular weights (1000, 1500, 3000, 4000, and 6000) are studied at 293.15–323.15 K in the 0–5 g/dL range of concentrations. Parameters are calculated according to the obtained data: characteristic viscosity, the Huggins constant, parameter α in the Kuhn–Mark–Houwink equation, characteristic viscosity in a θ solvent, the coefficient of swelling of the macromolecular coil in solution, root-mean-square distance of PEG macromolecular chain, and the length of Kuhn segments. It is found that the macromolecular coil is partially permeable for the surrounding liquid (water) and opens slightly. It was shown that the PEG molecules shrink as the temperature is raised, as is typical of flexible chain polymers.

Keywords: aqueous solution, polyethylene glycol, characteristic viscosity, root-mean-square distance, swelling coefficient, Kuhn segment

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INTRODUCTION

The structure of water and the conformation and size of macromolecules change during the dissolution of polymers containing polar groups (e.g., polyethylene glycol ($HO–(–CH_2–CH_2–O–)_n–H$)), due to interaction between the components of the system. The structural characteristics of a solution depend largely on temperature and are characterized by the conformation and size of macromolecules, hydration, and other parameters [1–10]. It is known that both the upper and lower critical solution temperatures (UCSTs and LCSTs) are observed upon the dissolution of polyethylene glycol (PEG) in water, depending on the temperature [1, 2].

The aim of this work was to determine the effect temperature has on the structural parameters (e.g., the conformation and size of macromolecules) of aqueous solutions of PEG.

THEORETICAL

According to current concepts, the macromolecules of flexible chain polymers exist in coil conformation in diluted solutions. Friction forces that raise the viscosity of solutions arise in the flow of a solution, due to interaction between molecules of the solvent and the dissolved substance. The rotational motion of individual macromolecules results in the characteristic viscosity of a solution, which in turn determines the loss of energy during a flow. Determining the value of characteristic viscosity allows us to estimate certain parameters of a solution (e.g., the conformation and size of macromolecules). Reduced viscosity (η_{red}) is first found to determine the characteristic viscosity [1, 2]:

$$\eta_{red} = \frac{\nu_{sol} - \nu_{solv}}{c\nu_{solv}}, \qquad (1)$$

where ν_{sol} and ν_{solv} are the kinematic viscosities of solutions and solvents, respectively; c is the concentration of the solution.

The reduced viscosity is described by the Huggins equation:

$$\eta_{red} = [\eta] + K_H[\eta]^2 c, \qquad (2)$$

where $[\eta] = \lim\limits_{c\to 0}(\eta_{red})$ is the characteristic viscosity; K_H is the Huggins constant, which characterizes the intensity of interaction between particles in system [6]. The characteristic viscosity and the Huggins constant are determined from dependence $\eta_{red} \sim c$ using Eq. (2). It is known that the characteristic viscosity of polymer solutions correlates with the molecular weight of the polymer and is described by the Kuhn–Mark–Houwink equation [1, 2]:

$$[\eta] = KM^{\alpha}, \qquad (3)$$

where K is a constant that depends on the properties of the dissolved substance and the solvent; α is a param-

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[†] Deceased.

eter that characterizes the conformation of macromolecules in the solution and is determined by the slope of direct dependence $\ln[\eta] \sim \ln M$:

$$\ln[\eta] = \ln K + \alpha \ln M. \quad (4)$$

The value of the characteristic viscosity in a θ solvent is normally (and logically) used to determine the undisturbed size of a macromolecule. It should be noted that different interactions between particles are compensated for in a θ solvent. Thermodynamic equilibrium is established in a θ solvent, while molecules of the polymer remain undisturbed. However, it is difficult to select a θ solvent for a given polymer, even though the theory of polymer solutions was created for θ solvents [8]. In the Flory theory [8], the characteristic viscosity of a polymer solution in a θ solvent ($[\eta]_\theta$) is determined by the equation

$$[\eta]_\theta = \Phi_\theta \frac{(\bar{h}_\theta^2)^{3/2}}{M} = K_\theta M^{1/2}, \quad (5)$$

where Φ_θ is the Flory coefficient. If the characteristic viscosity is expressed in dL/g, $\Phi_\theta = 2.1 \times 10^{23}$; $(\bar{h}_\theta^2)^{1/2}$ is the root-mean-square distance between the ends of macromolecules. In the same θ solvent, K_θ is the θ constant, and M is the molecular weight of the polymer.

Equation (5) shows the values of K_θ or $[\eta]_\theta$ are needed to determine $(\bar{h}_\theta^2)^{1/2}$. It should be noted that the value of $[\eta]_\theta$ cannot be determined when there is no θ solvent. However, there are many empirical ratios between the characteristic viscosity of solutions measured in "good" (as opposed to θ) solvents and constant K_θ. One such ratio is the Stockmayer–Fixman equation [9]:

$$\frac{[\eta]}{\sqrt{M}} = K_\theta + 0.51 B \Phi_\theta \sqrt{M}, \quad (6)$$

where B is a long-range interaction parameter expressed in liters. Characteristic viscosity $[\eta]$ of polymers with different molecular weights must be determined in order to use Eq. (2) at certain temperatures. Equation (6) is thus used after measuring $[\eta]$ in "good" (as opposed to θ) solvents, and dependence $\frac{[\eta]}{\sqrt{M}} = f(\sqrt{M})$ is extrapolated. Parameter K_θ can be determined when $\sqrt{M} \to 0$, and the values of $[\eta]_\theta$ and $(\bar{h}_\theta^2)^{1/2}$ can then be found using Eq. (5). On the other hand, the conformation of a macromolecule in a solution is characterized by such parameters as coefficient β of swelling and length A of Kuhn segments. Polymer macromolecules swell in "good" solvents. Coil volume β grows and characteristic viscosity can be determined as [8]

$$[\eta] = \beta^3 \Phi_\theta \frac{(\bar{h}_\theta^2)^{3/2}}{M}. \quad (7)$$

Equations (5) and (7) allow us to obtain

$$\beta^3 = [\eta]/[\eta]_\theta. \quad (8)$$

The Kuhn length is then determined using the following formula to estimate the flexibility of macromolecules:

$$A = \frac{(\bar{h}_\theta^2)}{L} = \frac{(\bar{h}_\theta^2)}{n l_0}, \quad (9)$$

where L is the length of a completely unfolded macromolecule; n is the degree of macromolecule polymerization of; and l_0 is the contour length of the monomer, expressed in angstroms. In [10], the value of this parameter for the monomer of polyethylene glycol ($-CH_2-CH_2-O-$) was $l_0 = 2.36$ Å.

EXPERIMENTAL

In this work, we studied the density and kinematic viscosity of aqueous solutions of polyethylene glycol fractions characterized by molecular weights of 1000, 1500, 3000, 4000, and 6000 at 293.15–323.15 K in the 0–5 g/dL range of concentrations. The PEGs were of chemically pure grade, and the solutions were prepared using bidistilled water. Viscosity was measured with a VPZh-2 viscometer. The accuracy of determining the duration of a liquid flow was ±0.01 s.

RESULTS AND DISCUSSION

The values of the reduced viscosity in the investigated ranges of concentration and temperature were obtained using Eq. (1), according to the experimentally measured density and kinematic viscosity. The characteristic viscosity was determined by extrapolating dependence $\eta_{red} \sim c$ to zero concentration. The value of the Huggins constant was calculated using the slope of dependence (2). Our results are given in Tables 1 and 2.

Table 1 shows the values of characteristic viscosity of solutions grow along with the molecular weight of the polymer at a constant temperature. At the given molecular weight, these values fall slightly when the temperature is raised. The rise in the characteristic viscosity as molecular weight of polymer grew was clearly due to an increase in the sizes of the macromolecules and stronger interaction between the macromolecules and the solvent (water). This magnified the friction force between the macromolecules and the solvent as the former rotated in solution. The drop in the characteristic viscosity of the solution with the given molecular weight upon a rise in temperature shows there was a reduction in the solvent's affinity toward the polymer, resulting in less swelling of the macromolecular coils. This behavior of the system is typical of flexible

Table 1. Temperature dependences of the characteristic viscosities of aqueous PEG solutions ([η], dL/g)

T, K	PEG-1000	PEG-1500	PEG-3000	PEG-4000	PEG-6000
293.15	0.0341	0.0471	0.0675	0.0837	0.1343
298.15	0.0331	0.0467	0.0674	0.0824	0.1325
303.15	0.0310	0.0466	0.0672	0.0817	0.1299
308.15	0.0301	0.0465	0.0670	0.0803	0.1277
313.15	0.0273	0.0463	0.0666	0.0794	0.1257
318.15	0.0266	0.0463	0.0665	0.0780	0.1240
323.15	0.0255	0.0460	0.0663	0.0774	0.1216

Table 2. Temperature dependences of Huggins constant K_H of aqueous PEG solutions

T, K	PEG-1000	PEG-1500	PEG-3000	PEG-4000	PEG-6000
293.15	5.269	3.627	1.998	1.431	1.117
298.15	5.284	3.546	1.983	1.407	1.111
303.15	5.001	3.534	1.926	1.391	1.114
308.15	4.832	3.523	1.831	1.382	1.112
313.15	4.699	3.485	1.786	1.349	1.083
318.15	4.471	3.411	1.740	1.332	1.079
323.15	4.274	3.395	1.717	1.322	1.053

Table 3. Temperature dependence of parameter α in the Kuhn–Mark–Houwink equation for an aqueous PEG system

T, K	293.15	298.15	303.15	308.15	313.15	318.15	323.15
α	0.715	0.722	0.741	0.744	0.779	0.781	0.791

Table 4. Temperature dependence of θ constants (K_θ) in aqueous PEG solutions

T, K	293.15	298.15	303.15	308.15	313.15	318.15	323.15
$K_\theta \times 10^4$, dL/g	6.69	6.48	6.04	5.98	5.24	5.21	5.03

chain polymers characterized by lower critical solution temperatures (LCSTs).

Table 2 shows that the Huggins constant, which (like the characteristic viscosity) characterizes the rheological properties of polymer solutions, is reduced when T = const as the molecular weight of the polymer is raised. In a solution of a polymer with the given molecular weight, it falls slightly as the temperature rises. If we consider the physical sense of the Huggins constant, which characterizes the deformability of macromolecules and the permeability of a macromolecular coil for a solvent, our results can be interpreted as the macromolecular coil being deformed by the solvent as the molecular weight of polymer grows. The coil then deviates from spherical form due to resistance against the solvent's penetration, and the Huggins constant is reduced.

Parameter α in the Kuhn–Mark–Houwink equation (Table 3) is a quantitative parameter that determines the shape of a polymer molecule; its value varies from 0 to 2 ($0 \leq \alpha \leq 2$). When a macromolecule is spherical, the surrounding medium cannot penetrate into it, and parameter $\alpha = 0$. With a rod-like conformation of a rigid macromolecule, $\alpha = 2$. With a completely permeable coil, $\alpha = 1$ [1]. The obtained values of parameter α in PEG aqueous solutions are 0.7–0.8 (Table 3), showing that PEG molecules exist in permeable coil conformation in aqueous solutions. Table 3 shows a partial increase of parameter α due to a rise in temperature. This shows the coil of a PEG macromolecule opens slightly as the temperature rises.

The values of θ constants K_θ at different temperatures (Table 4) were then calculated, using the obtained values of characteristic viscosity and allowing for Eqs. (6).

The characteristic viscosities of solutions of PEG in θ solvents (Table 5) were calculated using the obtained values of constant K_θ (Table 4). The data presented in Table 5 show that the characteristic viscosities of solutions of PEG in θ solvents grow along with the molecular weight of PEG, and $[\eta]_\theta$ falls slightly as the temperature rises. The temperature dependence of the characteristic viscosity of PEG in a θ solvent and its dependence on the molecular weight of polymer exhibit similar behavior.

Table 5. Characteristic viscosities of PEG solutions in a θ solvent ($[\eta]_\theta$, dL/g)

T, K	PEG-1000	PEG-1500	PEG-3000	PEG-4000	PEG-6000
293.15	0.0212	0.0259	0.0366	0.0423	0.0518
298.15	0.0205	0.0251	0.0355	0.0410	0.0502
303.15	0.0191	0.0234	0.0331	0.0382	0.0468
308.15	0.0189	0.0232	0.0328	0.0378	0.0464
313.15	0.0166	0.0203	0.0287	0.0331	0.0406
318.15	0.0165	0.0202	0.0285	0.0329	0.0404
323.15	0.0159	0.0195	0.0276	0.0318	0.0390

Table 6. Swelling coefficients (β) of PEG macromolecules in solution

T, K	PEG-1000	PEG-1500	PEG-3000	PEG-4000	PEG-6000
293.15	1.173	1.220	1.226	1.255	1.373
298.15	1.173	1.230	1.238	1.262	1.382
303.15	1.175	1.258	1.266	1.288	1.405
308.15	1.167	1.261	1.269	1.285	1.402
313.15	1.181	1.317	1.325	1.338	1.458
318.15	1.173	1.319	1.326	1.333	1.454
323.15	1.170	1.331	1.340	1.345	1.461

Table 7. Root-mean-square distance between the ends of chains of PEG molecules in solution ($(\bar{h}_\theta^2)^{1/2}$, Å)

T, K	PEG-1000	PEG-1500	PEG-3000	PEG-4000	PEG-6000
293.15	21.6	26.5	37.4	43.2	52.9
298.15	21.4	26.2	37.0	42.7	52.3
303.15	20.9	25.6	36.2	41.8	51.1
308.15	20.8	25.5	36.0	41.6	51.0
313.15	19.9	24.4	34.5	39.8	48.8
318.15	19.9	24.3	34.4	39.7	48.7
323.15	19.6	24.1	34.0	39.3	48.1

The swelling of a macromolecular coil in a nonideal solvent is β times higher than in a θ solvent. Coefficients β of the swelling of PEG macromolecules were determined according to Eq. (8), using the obtained values of $[\eta]$ and $[\eta]_\theta$. Our values of β depending on *M* and *T* are given in Table 6. Table 6 shows that parameter β grows along with the molecular weight of the polymer, but it is virtually independent of temperature.

The root-mean-square distances between the ends of macromolecules, calculated using the θ value of constant K_θ, are given in Table 7. Table 7 shows that the value of $(\bar{h}_\theta^2)^{1/2}$ grows along with the molecular weight of the polymer. It falls slightly as the temperature rises. This effect is explained by an increase in the mobility of a molecule's segments, which allows its ends to approach each other in space.

The rigidity and mobility of a macromolecular chain play an important role in shaping the conformation of a polymer macromolecule. It is known that Kuhn segment length (*A*, Å) is a characteristic of the rigidity and flexibility of a macromolecule. With a very flexible molecule, the Kuhn length is almost the length of a monomer unit; with a very rigid macromolecule, it is the length of completely branched chain. The values of the Kuhn segment length for aqueous solutions of PEG, calculated according to formula (7), are given in Table 8.

Table 8. Lengths *A* of Kuhn segments in an aqueous PEG solution at different temperatures

T, K	293.15	298.15	303.15	308.15	313.15	318.15	323.15
A, Å	8.70	8.51	8.13	8.07	7.39	7.36	7.19

Table 8 shows that the Kuhn length falls from 8.70 to 7.19 Å as the temperature rises. It should be noted that the Kuhn length does not depend on the molecular weight of the polymer. PEG can be considered a flexible polymer, since the Kuhn length in an aqueous PEG solution is less than 100 Å. The temperature-dependent reduction in the Kuhn length can be explained by parameter $(\bar{h}_\theta^2)^{1/2}$ changing along with temperature.

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