

Rheological Properties of Aqueous Solutions Based on Polyvinylpyrrolidone

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Abstract

The study describes the dependences of the density and viscosity of aqueous solutions of polyvinylpyrrolidone (1 -5%) on temperature (15-50°C) were investigated and the intrinsic viscosity $[\eta]$ and the Huggins constant (k) were determined. It was obtained that the viscosity decreases monotonically and Huggins constant increases with increasing temperature.

Keywords: Polyvinylpyrrolidone (PVP), Polymer, Aqueous Solution, Huggins constant, Intrinsic Viscosity

Introduction

Polyvinylpyrrolidone (PVP) is an extensively used polymer due to its low toxicity to humans and the environment as well as high water solubility. The aqueous solutions of PVP are used in cosmetics (toothpastes, shampoos), pharmacy (tablets), medicine (blood plasma substitute, biomaterials) [1-10].

It is known that high molecular weight (HMW) compounds solutions, in contrast to low molecular weight compounds, have an abnormally high viscosity, which is highly dependent on temperature and concentration [11]. According to modern concepts, long mobile molecules of HMW solid solutions receive different conformations [11, 12]. As a result of temperature and external influences, the conformation of the coil is changed, and these changes determine the structure and properties of the solution. This conformation can vary from a rigid spherical shape (in poor solvents) to a rigid rod [11, 13].

At a certain velocity gradient during laminar flow, different parts of the macromolecule move with different speeds. As a result, macromolecules are under the influence of double forces that cause it to collapse during flow. During rotation of the macromolecule, a friction force arises between its segments and the solvent molecule, which also increases the viscosity of the solution relative to the solvent.

In this paper, we present the results of the investigations of the dependences of the density and viscosity of aqueous solutions of polyvinylpyrrolidone (1 -5%) on temperature (15-50°C).

Experimental Part

Materials

Polyvinylpyrrolidone with molecular weight 10 000, 12 000, 25 000 and 44 000, and 45 000 g/mol were purchased from Alfa Aesar. The provenance and purity of the polyvinylpyrrolidone are listed in Table 1.

Table 1: The provenance and purity of the polyvinylpyrrolidone

Chemical	CAS number	Source	Formula	Form	Purification
polyvinylpyrrolidone	9003-39-8	Alfa Aesar	$(C_6H_9NO)_n$	powder	as stated by supplier

Sample preparation

Stoichiometric amounts of the Polyvinylpyrrolidone were weighed with accuracy ± 0.00001 g. Then they were dissolved in bidistilled water to obtain a solution of a certain concentration and left 1 day for polymer swelling. Then the solution was heated in a water bath without boiling ($\sim 80-90^\circ\text{C}$) to completely polymer dissolve. For experiments, the optimal solution volume was 60 ml.

Methods

The rheological properties were measured using Ostwald viscometer. The measurements uncertainty was 3%. The rheological properties were measured within temperature interval 15-50°C.

The increase in solubility due to the rotation of individual macromolecules is determined by intrinsic viscosity $[\eta]$. The density value varies depending on the intensity of the interaction of the macromolecule with the solvent and is described by Mark-Kuhn-Houwink equation [14, 15]:

$$[\eta] = KM^\alpha \quad (1)$$

Here K and α are constants for given polymer-solvent system and temperature. M- The weight of macromolecule. The α constant varies between 0÷2 depending on the shape of the polymer molecule. Taking into account that the solvent cannot penetrate into the spherical shape of the molecule, then $\alpha=0$ while for rigid molecules $\alpha=2$. If the solvent penetrates into the spherical molecules, then $\alpha=2$. Intrinsic viscosity η_{int} is determined by extrapolation of the viscosity to zero concentration. This dependence is illustrated by the empirical Huggins equation:

$$\frac{\eta_{int}}{\tilde{n}} = [\eta] + k'[\eta]^2 \tilde{n} \quad (2)$$

Here c is solution concentration, k' - Huggins constant [16, 17], which characterizes the rheological properties of the solution. From here

$$[\eta] = \lim_{\tilde{n} \rightarrow 0} \frac{\eta_{int}}{\tilde{n}} \quad (3)$$

For each polymer, 5-6 concentrations were measured and then found the average data.

Based on the obtained experimental results, the intrinsic viscosity and Huggins constant were calculated. The results для one sample (5% polymer solution with a molecular weight 25 000) are listed in Table 2 and Figures 1, 2.

Table 2

$t^{\circ}\text{C}$	$\rho_{\text{water}}, \text{q/m}^3$	$\eta_{\text{water}}, \text{mPa}\cdot\text{s}$	$\tau_{\text{water}}, \text{s}$	$\rho_{\text{sol}}, \text{q/m}^3$	$\tau_{\text{sol}}, \text{s}$	$\eta_{\text{sol}}, \text{mPa}\cdot\text{s}$
15	0.99862	1.1383	13.36	0.996226	29.1	2.473067
20	0.99823	1.0020	12.36	0.995988	27.2	2.200968
25	0.99681	0.8902	11.34	0.995962	23.5	1.842876
30	0.99568	0.7973	10.51	0.995742	20.8	1.577108
35	0.99372	0.7191	9.6	0.995478	18.8	1.409554
40	0.99225	0.6527	9.15	0.995214	17	1.215227
45	0.98898	0.5961	8.7	0.994906	15.7	1.082167
50	0.9881	0.5471	8.39	0.994599	14.4	0.944504

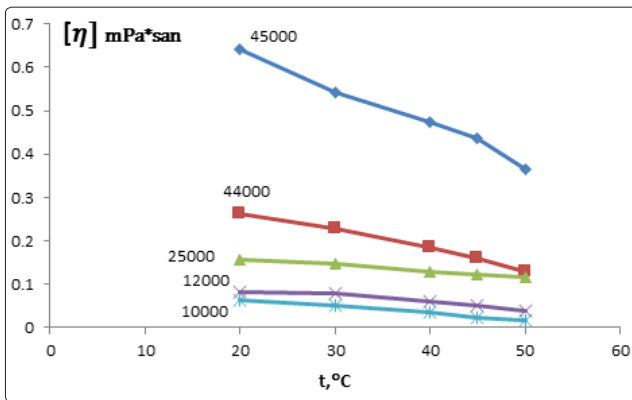


Figure 1: The density as a function of temperature for several polymers

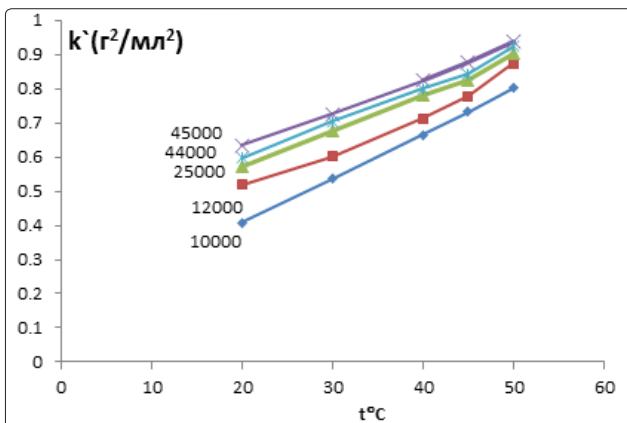


Figure 2: Huggins constant dependences from temperature for several polymers

Results

Apparently, with increasing temperature, the intrinsic viscosity monotonically decreases with monotonicity, but the parameter

k' increases. The nature of this relationship indicates that the polyvinylpyrrolidone (PVP) water system has a low critical solubility temperature. Thus, with increasing temperature, the viscosity of the PVP decreases, which means that the thermodynamic quality of the water is deteriorating. At this time, the coils are compressed, their size decreases, and the viscosity, which characterizes the hydrodynamic resistance during flow, decreases.

The Huggins constant, which characterizes the resistance of solvent permeability to macromolecules in polymer solutions, increases with temperature. It is well known that the Huggins constant characterizes the degree of deformation of a stable molecular particle. For elastic molecules, the value of k' is greater, and its shape differs from sphericity.

It should be noted that at low molecular weights, the dependence on concentration $\frac{\eta_{max} - \tilde{\eta}}{\tilde{n}}$ is parallel to the c axis, i.e.

$k' = 0$. The permeability of the solvent is high.

Conclusion

Thus, the work presents the results of a study of the dependence of the rheological properties of polyvinylpyrrolidone (1-5%) on temperature (15-50 °C) and the characteristic viscosity $[\eta]$ and the Huggins constant (k) are determined. The obtained data could be used in different applications.

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