

Hydrodynamic Characteristics of Aqueous Poly(*N*-vinyl-2-pyrrolidone) Solutions in the Presence of Denaturing Agents

ALİ GÜNER

Hacettepe University, Faculty of Science, Chemistry Department, Beytepe, 06532, Ankara, Turkey

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ABSTRACT: The aqueous solution properties of poly(*N*-vinyl-2-pyrrolidone) (PVP)-denaturing agents (i.e., thiourea, guanidinium chloride, and carbonate) were studied by viscosity measurements. The polymer dimensions were calculated at 25°C and at previously determined theta temperatures. The unperturbed dimension parameter, K_0 , hydrodynamic expansion factor, α_η , and unperturbed root-mean-square end-to-end distance, $\langle r^2 \rangle_0^{1/2}$, have been evaluated. Viscosimetrically determined characteristics (e.g., intrinsic viscosity, Huggins constants) and the high values of α_η and $\langle r^2 \rangle_0^{1/2}$ can be explained by the interaction between the polymer and denaturing agents. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 1615–1618, 1998

Key words: poly(*N*-vinyl-2-pyrrolidone), aqueous solutions, denaturing agents, hydrodynamic characteristics

INTRODUCTION

Denaturing agents are the source of potential hydrogen-bonding substances. The effects of denaturing agents on the molecular association of poly(ethylene oxide),¹ dextran,² periodate-oxidized dextran,³ PVP,⁴ and cloud point and theta temperatures of PVP⁵ in aqueous solutions were studied previously. Poly(*N*-vinyl-2-pyrrolidone) has polar lactam groups, capable of forming hydrogen-bond^{6,7} and hydrophobic methylene groups; hence, it should exhibit different unperturbed states if the solution media are changed suitably.⁸

In previous studies, the effect of inorganic salts on the cloud points and theta temperatures,⁹ polymer dimensions and thermodynamic quantities,¹⁰ and viscosity characteristics¹¹ of aqueous PVP solutions were reported. The aim of the present work was to study the denaturing agent effects on

the hydrodynamic characteristics (e.g., intrinsic viscosity, unperturbed dimensions, hydrodynamic expansion, and root-mean-square end-to-end distance) of PVP in a dilute solution at 25°C and at theta temperatures.

EXPERIMENTAL

The polymer sample used in this study was commercial BDH PVP and has a nominal molecular weight of 700,000. The weight-average molecular weight of the PVP sample was determined by a light-scattering photometer in chloroform at 30°C. In this study, the Brice-Phoenix light scattering photometer, 2000 Series, was used for measuring the Rayleigh ratios of the polymer solutions. The interpretation of the light-scattering data was based on the Zimm method. It has a weight-average molecular weight of $M_w = 548,000 \text{ g mol}^{-1}$.

The denaturing agents used, thiourea (TU) and guanidinium carbonate (GCO_3), were ob-

Table I Viscosity Characteristics of Poly(*N*-vinyl-2-pyrrolidone) Aqueous Solutions in the Presence of Denaturing Agents

Solutions	<i>T</i> (K)	$[\eta]H$	$[\eta]K$	k_H	k_K	$k_H - k_K$
2.00 <i>M</i> TÛ	298	0.53	0.52	1.27	0.39	0.88
	320 ^a	0.32	0.33	3.05	1.79	1.26
0.50 <i>M</i> GCl	298	0.71	0.73	1.26	0.34	0.92
	328 ^a	0.45	0.46	1.69	0.74	0.95
0.75 <i>M</i> GCl	298	0.69	0.70	1.47	0.47	1.00
	330 ^a	0.41	0.42	2.33	1.18	1.15
0.50 <i>M</i> GCO ₃	298	0.68	0.69	1.12	0.28	0.84
	336 ^a	0.48	0.50	1.16	0.46	0.70
0.75 <i>M</i> GCO ₃	298	0.65	0.67	1.27	0.39	0.88
	341 ^a	0.44	0.45	1.69	0.73	0.96

Correlation coefficients are 0.997 ± 0.002 , except in 0.75*M* GCO₃, Θ .

^aTheta temperatures, from ref. 5.

tained from BDH, and guanidinium chloride (GCl) was obtained from Riedel-de Haen AG. All the chemicals and the polymer sample were used without further purification.

Viscosity measurements were made by using an Ubbelohde capillary viscosimeter at 298 K and at the theta temperatures.⁵ Temperatures were controlled within a range of $\pm 0.02^\circ\text{C}$ and flow times were measured with an accuracy of ± 0.1 s. Deionized and twice-distilled water was used for the preparation of PVP-denaturing agent solutions. The concentration dependence of the viscosity of dilute polymer solutions ($0.40\text{--}0.25$ g dL⁻¹) is described by the well-known Huggins equation:

$$\eta_{sp}/c = [\eta] + k_H[\eta]^2c$$

and the Kraemer equation:

$$\ln \eta_r/c = [\eta] - k_K[\eta]^2c$$

RESULTS AND DISCUSSION

Viscosity Characteristics

$$[\eta]\Theta = K_0M^{1/2} \quad (1)$$

is the form of the Kuhn–Mark–Houwink–Sakurada equation

$$[\eta] = KM^a \quad (2)$$

where $[\eta]$ and $[\eta]\Theta$ are the intrinsic viscosities determined at 25°C and at the theta tempera-

tures⁵ which were evaluated as average values of the intercepts of the plots of η_{sp}/c versus c and $\ln \eta_r/c$ versus c . Straight lines were obtained when the results of the specific viscosity and logarithmic viscosity on polymer concentration (c) at a particular denaturing agent concentration were plotted according to the Huggins and Kraemer equations. The dimension of $[\eta]$ is a measure of the effective hydrodynamic volume of the polymer in solution. The constants k_H and k_K are the Huggins and Kraemer slope coefficients. Table I gives the k_H and k_K obtained from slopes and intrinsic viscosities $[\eta]$ from intercepts where $c = 0$. As can be seen from Table I, an agreement is observed between the $[\eta]$ values calculated from the Huggins and Kraemer equations.

The Huggins constant is a measure of the polymer–solvent interaction and it is about 0.35 in good solvents. However, in some polymer–solvent systems, higher values have been observed and this was interpreted to be due to molecular association.^{2,12,13} The molecular association of PVP in aqueous solutions and the effects of some denaturing agents were discussed previously.⁴ The high k_H values found for aqueous solutions of PVP may be a result of the interactions of lactam groups of the polymer with water molecules/ionic species¹¹ or hydrogen-bond acceptor–donor denaturing agents in solution by hydrogen bonding.

The value of $k_H - k_K = 0.94 \pm 0.6$ is higher than the expected value of 0.5. Sakai¹⁴ reported that since nonpolar polymer–solvent combinations should lie between 0.5–0.7 under theta conditions k_H may also be influenced by the aggrega-

tion of the polymer segments in a solution. Most of the k_H values found in this study were higher than the predicted range of 0.5–0.7, and $k_H - k_K$ values were found to be 1.00 ± 0.3 (Table I). The high values of k_H for some polymer–solvent systems (under theta conditions) were discussed in a previous study.¹¹ If the $[\eta]$ and k_H values are reconsidered, in contrast to this increase of $k_H - k_K$ in the presence of denaturing agents in aqueous solutions, the value of $[\eta]$ is decreased. This point shows mainly that, with an increasing degree of hydrophobic interactions of polymer segments, the contraction of the polymer coil occurs in solution.

Polymer Dimensions

In eq. (1), K_0 is the unperturbed dimension parameter, independent of solvent, temperature, and molecular weight and can be calculated by extrapolation methods.¹⁵ In the theory of Flory and Fox¹⁶ and Kurata et al.,^{17,18} the intrinsic viscosity $[\eta]$ is related to K_0 , the molecular weight M , and the hydrodynamic expansion factor α_η by

$$[\eta] = K_0 M^{1/2} \alpha_\eta \quad (3)$$

and

$$[\eta] = \Phi \langle r^2 \rangle_0 / M)^{3/2} M^{1/2} \alpha_\eta^3 \quad (4)$$

where Φ is a universal constant, which was taken as 2.5×10^{21} , and $\langle r^2 \rangle_0^{1/2}$ denotes the unperturbed root-mean-square end-to-end distance.

The information on unperturbed dimensions, starting from the viscosity results, was also given by the Stockmayer–Fixman equation¹⁹

$$[\eta] M^{-1/2} = K_0 + 0.51 B \Phi M^{1/2} \quad (5)$$

where

$$K_0 = [\eta] \Theta M^{1/2} \quad (6)$$

The unperturbed dimension parameter values for PVP in a water/denaturing agent system (at theta temperature) are given in Table II. The determined values, $K_0 = 5.31 \times 10^{-4}$ dL g⁻¹ ($\pm 1.031 \times 10^{-4}$), are in agreement with the values of PVP

Table II Hydrodynamic Characteristics of Poly(*N*-vinyl-2-pyrrolidone) Aqueous Solutions in the Presence of Denaturing Agents

Solution	$K_0 \times 10^4$ (dL g mol g)	α_η	$\langle r^2 \rangle_0^{1/2} \times 10^6$ (cm)
2.00M TU	4.30	1.19	4.12
0.50M GCl	6.07	1.16	4.62
0.75M GCl	5.50	1.20	4.47
0.50M GCO ₃	6.32	1.13	4.68
0.75M GCO ₃	5.93	1.15	4.58

in 0.55M Na₂SO₄ ($\Theta = 303$ K), $K_0 = 5.8 \times 10^{-4}$ dL g⁻¹ PVP/aqueous salt solutions (at theta temperatures), $K_0 = 5.1 \times 10^{-4}$ dL g⁻¹ ($\pm 0.5 \times 10^{-4}$),¹⁰ and PVP in a urea–hydroquinone system, $K_0 = 5.2 \times 10^{-4}$ dL g⁻¹.²⁰

The hydrodynamic expansion factor, α_η , measures the intensity of the thermodynamic interaction and it has been calculated by using the definition

$$\alpha_\eta^3 = [\eta]/[\eta]\Theta \quad (7)$$

There is a slight variation in the α_η values (1.17 ± 0.3) in PVP aqueous denaturing agent solutions. However, the α_η values for the system of PVP–denaturing agent aqueous solutions are rather high compared to those in a PVP–aqueous salt solution system (1.03 ± 0.03).¹⁰ Similarly, the calculated values of the root-mean-square end-to-end distances (Table II) of the PVP–denaturing agent system, $\langle r^2 \rangle_0^{1/2} = 4.4 \times 10^{-6}$ cm ($\pm 0.3 \times 10^{-6}$), are higher than those of the PVP–salt solution system, $\langle r^2 \rangle_0^{1/2} = 1.65 \times 10^{-6}$ cm ($\pm 0.4 \times 10^{-6}$).¹⁰

As mentioned previously, denaturing agents are the source of potential hydrogen bonding where amino groups interact with the lactam group of the polymer for hydrogen bonding. On the other hand, at the theta point or unperturbed state, segmental interactions become attractive, leading to the contraction of the polymer coil. If these two types of interactions are compared, the long-range interactions prohibit the predominance of the short-range interactions, thus causing the α_η and $\langle r^2 \rangle_0^{1/2}$ increment for the system of aqueous PVP solutions in the presence of denaturing agents.

Actually, this result is expected, especially when an PVP–inorganic salt solution and a PVP–

denaturing agent system are considered, since, in the prior solution, the anionic charge of the salt destructs the hydrogen-bonded structure of water, consequently leading to a decrease in α_η and $\langle r^2 \rangle_0^{1/2}$ values, whereas in the latter, the amino group of the denaturing agent is capable of hydrogen bonding with the lactam group of the polymer, yielding significantly higher values of α_η and $\langle r^2 \rangle_0^{1/2}$ due to the slightly more expanded conformation of the polymer coil. As a result, the solubility of the denaturing agent in solution anions may as well exist in the latter system; however, it has been determined spectrophotometrically⁴ that the effect of the ions are less predominant than that of the amino group of the denaturing agent. This argument is quite in agreement with the viscosimetric results where an increment was observed in the k_H value followed by a decrease in $[\eta]$, as well as with the previously determined cloud point temperature and theta temperature increments.⁵

REFERENCES

1. A. Güner and O. Güven, *Makromol. Chem.*, **179**, 2786 (1978).
2. A. Güner, *J. Appl. Polym. Sci.*, **56**, 1561 (1995).
3. I. Uraz and A. Güner, *Carbohydr. Polym.*, **65**, 1307 (1997).
4. A. Güner, *J. Appl. Polym. Sci.*, to appear.
5. A. Güner and M. Kara, *Polymer*, to appear.
6. L. Türker, A. Güner, F. Yiğit, and O. Güven, *Colloid Polym. Sci.*, **268**, 337 (1990).
7. O. Güven and E. Eltan, *Makromol. Chem.*, **182**, 3129 (1981).
8. R. Meza and L. Gargallo, *Eur. Polym. J.*, **13**, 235 (1977).
9. A. Güner and M. Ataman, *Colloid Polym. Sci.*, **272**, 175 (1994).
10. A. Güner and M. Ataman, *Polym. Int.*, **44**, 30 (1997).
11. A. Güner, *J. Appl. Polym. Sci.*, **62**, 785 (1996).
12. N. Sütterlin, in *Polymer Handbook*, 2nd ed., J. Brandrup and E. H. Immergut, Eds., Wiley, New York, 1975, p. IV-135.
13. M. Bohdanecky, *Coll. Czech. Chem. Commun.*, **35**, 1972 (1970).
14. T. Sakai, *J. Polym. Sci. Part A-2*, **6**, 1535 (1968).
15. J. F. Rabek, in *Experimental Methods in Polymer Chemistry*, 1st ed., Wiley, New York, 1980, p. 50.
16. P. S. Flory and T. G. Fox, *J. Am. Chem. Soc.*, **73**, 1904 (1951).
17. M. Kurata and W. H. Stockmayer, *Fortschr. Hochpolym.-Forsch.*, **3**, 196 (1963).
18. M. Kurata, W. H. Stockmayer, and A. Roig, *J. Chem. Phys.*, **33**, 151 (1960).
19. W. H. Stockmayer and M. Fixman, *J. Polym. Sci. C1*, 137 (1963).
20. L. Gargallo and D. Radic, *Polymer*, **24**, 91 (1983).