

Effect of Phenol Derivatives on Molecular Dimensions of Poly(*N*-vinyl-2-pyrrolidone) in Aqueous Solution

BETÜL KIRCI, ALI GÜNER

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

Received 24 October 2000; accepted 5 April 2001

ABSTRACT: The unperturbed dimensions and thermodynamic parameters of poly(*N*-vinyl-2-pyrrolidone) (PVP) were studied in aqueous solutions in the presence of certain phenolic cosolutes (phenol, catechol, hydroquinone, resorcinol, and phloroglucinol). The intrinsic viscosities at 25°C and the θ temperature, linear and thermodynamic expansions, and root mean square end to end distances were evaluated for the system that was employed. The sequence was obtained due to the effectiveness of the cosolutes in the order of phloroglucinol > resorcinol > hydroquinone > catechol > phenol. The effects of these cosolutes on the main thermodynamic parameters were reported to be due to the number and position of hydroxyl groups present. The thermodynamic interaction parameter was also evaluated and the enthalpic and entropic contributions were verified. The condition required for the θ temperature to correspond to a Flory interaction parameter of 0.5 was well provided, yielding a θ temperature of almost 0.5 for the system under study. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 473–477, 2002; DOI 10.1002/app.10047

Key words: poly(*N*-vinyl-2-pyrrolidone); aqueous solutions; phenolic cosolutes; thermodynamic study

INTRODUCTION

Poly(*N*-vinyl-2-pyrrolidone) (PVP), a water-soluble synthetic polymer, has a number of interesting properties and applications. It has frequently been the object of different studies to understand the interactions (hydrogen bonding, dipole–dipole, ion–dipole, etc.) among organic small molecules, ionic species, and a polymer.

Because the polymer is soluble in a variety of polar solvents, interaction of PVP with small solvent molecules of different solvating power is possible. The change in the water–hydrogen bonded structure around the polymer caused by the added cosolute plays an important role in its behavior in solution.

Our previous and ongoing studies are mainly focused on the dynamic,^{1,2} thermodynamic,^{3–8} and spectrophotometric^{9–11} aspects of PVP in the presence of certain organic and inorganic additives.

The unperturbed molecular dimension parameter is one of the most important physicochemical parameters as a measure for short-range interactions, and it can be determined by viscosity measurements.^{4,6,12–15}

The long-range interactions for polymer–solvent and polymer–solvent–additive systems can be followed by the interaction parameter (B),^{12–15} hydrodynamic and thermodynamic expansion factors,^{4,6,12–15} and determination of the cloud point and phase separation temperature studies.^{3,5,7,8}

The aim of the present work is to investigate the effect of certain phenolic cosolutes, depending on their nature, on viscometric behavior and to determine the related unperturbed dimensions

Correspondence to: A. Güner (agun@hacettepe.edu.tr).

Journal of Applied Polymer Science, Vol. 84, 473–477 (2002)
© 2002 John Wiley & Sons, Inc.

and thermodynamic magnitudes of PVP and water combined with certain phenolic ternary systems.

EXPERIMENTAL

The polymer sample used in this study was commercial BDH PVP with a nominal molecular weight of 44,000 g/mol. The weight-average molecular weight ($M_w = 78,000$ g/mol) and the number-average molecular weight ($M_n = 46,000$ g/mol) of the polymer sample were previously determined by light scattering and membrane osmometer measurements. The specifications of both instruments and the determined characteristics (second virial coefficient, root mean square radius of gyration) were reported in previous studies.^{1,3,5}

The phenolic cosolutes used in this study were phenol, catechol (*o*-hydroxyphenol), resorcinol (*m*-hydroxyphenol), hydroquinone (*p*-hydroxyphenol), and phloroglucinol (1,3,5-trihydroxybenzene). Phenol was obtained from Hopkin-Williams. Catechol and resorcinol were obtained from Fisher, hydroquinone was obtained from BDH, and phloroglucinol was obtained from Merck. They were reagent grade and were purified by recrystallization if necessary.

The viscosity measurements were carried out by using an Ubbelohde capillary viscometer at 25°C and previously determined θ temperatures.⁷ The temperatures were controlled within $\pm 0.02^\circ\text{C}$, and the flow times were measured with an accuracy of ± 0.01 s. Deionized and double distilled water was used for the preparation of solutions.

The densities of all solutions were determined by using a picnometer at room temperature. The reproducibility of the density measurements for all phenolic cosolutes was excellent.

RESULTS AND DISCUSSION

In the first part of this study we presented the phase separation behavior (lower critical solution temperature or LCST), determination of the cloud point temperatures, and θ temperatures for a PVP-water-phenolic cosolute ternary system. It was revealed that the cloud point, phase separation behavior of aqueous PVP solutions changed systematically with increasing concentrations of additive.⁷ The relationship between the polymer and the nature of the cosolute was also pointed

out for the system under study. The effectiveness of phenolic cosolutes in the decrease of the θ temperature was in the order of phloroglucinol > resorcinol > hydroquinone > catechol > phenol.

Subsequently, hydrogen bond dynamism among the components of the PVP-water-phenolic cosolute system was interpreted thermodynamically:

$$[\eta]_\theta = K_\theta M^{1/2} \quad (1)$$

where K_θ is the unperturbed dimension parameter, a form of the Kuhn-Mark-Houwink-Sakurada (KMHS) equation,

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

for the ideal state, where K and a are KMHS constants; $[\eta]$ and $[\eta]_\theta$ are the intrinsic viscosities determined at 25°C and the θ temperatures,⁷ respectively, which were evaluated as average values of the intercepts of the plots of specific viscosity (η_{sp})/ c versus the polymer concentrations. Straight lines were obtained where the results of the specific viscosity on the polymer concentration were plotted according to the Huggins equation.

The intrinsic viscosity is a characteristic function for the polymer coil in solution. It depends on the molar mass, structure, and conformation of the polymer molecules and on the power of the solvent and temperature. The dimensions of $[\eta]$ are a measure of the effective hydrodynamic volume of the polymer in solution and also represent the interactions between the polymer and cosolute systems.

The association of polymer-solvent molecules by hydrogen bonding is possibly disrupted by using certain organic substances, which are called denaturing agents.¹⁶⁻¹⁸ The requirement of high concentrations of these substances is generally interpreted to be due to either weak binding of the denaturant molecule to the polymer or changes in the local water structure surrounding the polymer.

The phenolic cosolutes used in this work contain hydrogen acceptor and donor hydroxyl substituents that may interact with adjoining water molecules and the carbonyl group of the polymer through hydrogen bonding. The effect of phenolic structures on the hydrodynamic volume of the polymer coil can easily be followed by intrinsic viscosity results. Addition of these phenolic substances led to a decrease in the viscosities of aque-

Table I Intrinsic Viscosity Values

Phenolic Cosolutes	$[\eta]_{25^\circ\text{C}}$ (dL/g)	$[\eta]_\theta$ (dL/g)
0.0030M Phloroglucinol	0.122	0.108
0.0025M Phloroglucinol	0.129	0.110
0.009M Resorcinol	0.145	0.123
0.007M Resorcinol	0.155	0.126
0.010M Hydroquinone	0.166	0.138
0.008M Hydroquinone	0.175	0.142
0.02M Catechol	0.192	0.153
0.01M Catechol	0.201	0.156
0.02M Phenol	0.209	0.159
0.01M Phenol	0.228	0.166

See text for variables.

ous PVP solutions at 25°C. The three most important effects of these additives on the decrease of the intrinsic viscosity of PVP solutions are the following:

1. Phenol has the smallest effect on the decrease of the intrinsic viscosity of PVP solutions. This value drops to 0.228 dL/g in 0.01M phenol and 0.209 dL/g in 0.02M phenol solutions (Table I) while for the aqueous PVP solution the value is 0.231 dL/g.
2. Phloroglucinol has the greatest effect on the decrease of the intrinsic viscosity of polymer solutions (Table I). The original intrinsic viscosity value drops to 0.129 and 0.122 dL/g in more dilute cosolute concentrations of 0.0025 and 0.0030M, respectively.
3. The decreasing order of effectiveness of the phenolic cosolutes in reducing the intrinsic viscosity is phloroglucinol > resorcinol > hydroquinone > catechol > phenol.

The observed decrease in the intrinsic viscosities, as well as the decrease in the intrinsic viscosities measured at the θ temperatures (Table I), can be considered as the disruption of the hydrogen bonding of PVP in aqueous solution, association among polymer segments, and the interactions formed between polymer segments and the phenolic cosolute molecules.

In the theory of Flory and Fox¹⁹ and Kurata et al.^{20,21} the intrinsic viscosity is related to the unperturbed dimension parameter and the molecular weight of the polymer (M) by

$$[\eta]_\theta = K_\theta M^{1/2} \quad (3)$$

and

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

where Φ is the Flory constant (2.5×10^{21}) and $\langle r^2 \rangle_0^{1/2}$ represents the unperturbed root mean square end to end distance of the coil.

According to the concept of the θ state, the unperturbed dimensions should be independent of the temperature, solvent, and molecular weight of the polymer. However, as seen from Table II, the K_θ values vary over a small range and are not constant for all θ conditions. The values for the phenolic cosolutes vary from $(5.04 \text{ to } 7.74) \times 10^{-4}$ dL/g and certain irregularities were observed for different PVP–water–additive systems. It is obvious that the different dimensions of the polymer molecules in different θ solvents may be largely due to the interactions of the solvents, particularly the ionic and functionally substituted organic substances, with the polymer molecules.

Van Krevelen and Hoftyzer calculated the theoretical value of K_θ as 7.5×10^{-4} dL/g.²² Meza and Garallo determined $K_\theta = 5.8 \times 10^{-4}$ dL/g for PVP in 0.55M Na₂SO₄ ($\theta = 303$ K) and in a H₂O/acetone mixture (33.2:66.8, v/v, θ) the $K_\theta = 7.4 \times 10^{-4}$ dL/g, the same as that found in 2-propanol²³ and $(5.25\text{--}5.43) \times 10^{-4}$ for PVP–water–inorganic salt systems.⁴ The ionic species (mostly the anions) may interact with the lactam ring of the polymer or may induce the charge distribution of the ring (mostly expected for polymer–water–inorganic salt systems), depending on the nature of the salt. Similarly, the functional substances may also interact with the carbonyl group of the ring, depending on the number of

Table II Values for PVP/Water/Phenolic Cosolute Systems

Phenolic Cosolutes	$K_\theta \times 10^4$	α	α_η
0.0030M Phloroglucinol	5.04	1.05	1.04
0.0025M Phloroglucinol	5.13	1.07	1.05
0.009M Resorcinol	5.75	1.07	1.06
0.007M Resorcinol	5.87	1.09	1.07
0.010M Hydroquinone	6.43	1.08	1.06
0.008M Hydroquinone	6.62	1.09	1.07
0.02M Catechol	7.13	1.10	1.08
0.01M Catechol	7.27	1.11	1.09
0.02M Phenol	7.41	1.12	1.10
0.01M Phenol	7.74	1.14	1.11

See text for variables.

Table III Values for System Under Study

Phenolic Cosolutes	C_M	$\langle r^2 \rangle_0^{1/2} \times 10^6$ (cm)	χ_H	χ_S	χ
0.0030M Phloroglucinol	0.396	1.256	-0.002	0.501	0.499
0.0025M Phloroglucinol	0.389	1.265	-0.002	0.501	0.499
0.009M Resorcinol	0.348	1.311	-0.002	0.501	0.499
0.007M Resorcinol	0.340	1.323	-0.003	0.501	0.498
0.010M Hydroquinone	0.310	1.363	-0.003	0.501	0.498
0.008M Hydroquinone	0.301	1.378	-0.003	0.501	0.498
0.02M Catechol	0.279	1.411	-0.004	0.502	0.498
0.01M Catechol	0.274	1.421	-0.004	0.501	0.497
0.02M Phenol	0.269	1.428	-0.005	0.502	0.497
0.01M Phenol	0.255	1.449	-0.006	0.502	0.496

See text for variables.

substituents and the nature of phenolic cosolutes (*o*-, *m*-, and *p*- positions), and hence affect the experimental value of K_θ .

The hydrodynamic expansion factor may be expressed in the following form:

$$\alpha_\eta^3 = [\eta]/[\eta]_\theta \quad (5)$$

and the relation between the thermodynamic expansion factor (α) and α_η is given by Kurata and Yamakawa²⁴:

$$\alpha_\eta^3 = \alpha^{2.43} \quad (6)$$

Both expansion factors are also given in Table II.

As is known, α_η depends on the factor $(1/2 - \chi_S)(1 - \theta/T)$, which also measures the intensity of the thermodynamic interaction for the polymer-solvent pairs under study. Depending on the nature of the cosolute and its concentration, there is a slight variation in the α_η and α values in the PVP-water-phenolic cosolute system. According to eq. (5), $\alpha_\eta = 1$ only when $[\eta]_\theta = [\eta]$, and the calculated expansion factors are in a decreasing trend from phenol to phloroglucinol for the employed system (Table II).

Similarly, the effectiveness sequence of phenolic cosolutes on the decrease in $\langle r^2 \rangle_0^{1/2}$ is almost the same as found above (phloroglucinol > resorcinol > hydroquinone > catechol > phenol). Because the addition of phenolic cosolute influences the hydrogen bonded structure of water and the hydration sheath of PVP in aqueous solutions, the interaction of cosolutes with the different conformers of the polymer chain is expected to be

altered; consequently, internal rotations around the main chain change.

The thermodynamic linear expansion factor is related to the Flory interaction parameter (χ) and the excess entropy of the dilution parameter (χ_S) through the Flory-Fox¹⁹ equations

$$\alpha^5 - \alpha^3 = 2C_M(1/2 - \chi)M^{1/2} \quad (7)$$

and

$$\alpha^5 - \alpha^3 = 2C_M(1/2 - \chi_S)(1 - \Theta/T)M^{1/2} \quad (8)$$

The coefficient C_M is given by

$$C_M = \frac{27v_2^2 M_n^{3/2}}{2NV_1(2\pi\langle r^2 \rangle_0)^{3/2}} \quad (9)$$

where v_2 is the partial specific volume of the polymer, N is Avogadro's number, and V_1 is the molar volume of the solvent (water-cosolute) and can be calculated easily by using the densities of water-cosolute solutions.⁴

The interaction parameter is the sum of χ_H and χ_S ; excess entropy of dilution and calculated values for aqueous phenolic cosolute solutions of PVP are shown in Table III. The negative χ_H values are indicative of the negative excess enthalpies of dilution, and positive χ_S values are indicative of the negative excess entropies of dilution for PVP in aqueous phenolic cosolute solutions. Association and hydration of the polymer with water molecules is not preferred entropically; however, the enthalpic factors mainly indicate the solubility of the polymer in polar sol-

vents. The molecular association and hydration between polymer segments and polar solvent molecules (in this study, water) is disrupted in the presence of cosolute or with an increment of temperature for LCST systems. It is shown that PVP exhibits a LCST^{3,25} and there are strong interactions between polymer segments and polar solvent molecules through hydrogen bonding; therefore, χ_H must be negative. In order to reveal the relative contributions of the enthalpy and the entropy to the change of the thermodynamic interaction parameter, certain studies were reported in the literature^{4,26} for PVP–water–inorganic salt systems. Garvey and Robb²⁷ reported the value of χ_H as -0.036 . In the current study the χ_H values are smaller than this value in the presence of phenolic cosolutes (i.e., the original structure of water is most probably destroyed in the aqueous phenolic solution system). However, according to calculated χ_S values, the excess entropy term seems to be the indicative force of χ in the system under study (Table III).

The relation between χ_H , χ_S and the interaction parameter χ is defined by

$$\chi - 1/2 = \chi_H - (1/2 - \chi_S) \quad (10)$$

It is well known that the interaction parameter must be equal to 0.5 at the θ temperatures. This stipulation is found to hold with values of χ_H and χ_S that are equal to $\chi - 0.5 < 0.001$ for the PVP–water–phenolic cosolute system.

CONCLUSION

In the PVP–water system various thermodynamic magnitudes are determined in the presence of phenolic cosolutes. The number and position of hydroxyl groups (the interaction mechanisms are discussed in detail⁷) present in the related cosolutes strongly affects these magnitudes. The effects of phenolic cosolutes on the phase separation and θ temperature of polymer solutions are investigated previously,⁷ and one may recall that a sequence is obtained that is due to the number and position of hydroxyl groups present. Surely, one of the most important methods to verify the hydrogen bond dynamism in the PVP–water–cosolute triple system is to follow the changes occurring in the thermodynamic magnitudes.

The same order is observed for the sequence obtained regarding the θ temperature,⁷ the intrinsic viscosity values obtained at both 25°C and the θ temperature, the unperturbed dimension parameter, the hydro- and thermodynamic expansion factors, and the end to end distance in the unperturbed state (phloroglucinol > resorcinol > hydroquinone > catechol > phenol).

In view of all these aspects, the formation and competition of hydrogen bonding among the components exhibit thermodynamically important proofs of hydrogen bond formation for the polymer–water–phenolic cosolute system under study.

REFERENCES

- Güner, A. *J Appl Polym Sci* 1996, 62, 785.
- Güner, A.; Sevil, A. U.; Güven, O. *J Appl Polym Sci* 1998, 68, 891.
- Güner, A.; Ataman, M. *Colloid Polym Sci* 1994, 272, 175.
- Güner, A.; Ataman, M. *Polym Int* 1997, 44, 30.
- Güner, A.; Kara, M. *Polymer* 1998, 39, 1569.
- Güner, A. *J Appl Polym Sci* 1998, 67, 1615.
- Kırcı, B.; Güner, A. *Eur Polym J* 2001, 37, 361.
- Kavlak, S.; Güner, A. *J Appl Polym Sci* 2000, 78, 507.
- Türker, L.; Güner, A.; Yiğit, F.; Güven, O. *Colloid Polym Sci* 1990, 268, 337.
- Güner, A. *J Appl Polym Sci* 1997, 65, 1307.
- Güner, A. *J Appl Polym Sci* 2000, 75, 1434.
- Çatıker, E.; Güner, A. *Polym Bull* 1998, 41, 223.
- Güner, A. *J Appl Polym Sci* 1999, 72, 871.
- Çatıker, E.; Güner, A. *Eur Polym J* 2000, 36, 2143.
- Güner, A.; Çatıker, E. *J Appl Polym Sci* 2001, 82, 948.
- Güner, A.; Güven, O. *Makromol Chem* 1978, 179, 2789.
- Sabatie, I.; Choplin, L.; Paul, F.; Monsan P. *Rheol Acta* 1986, 25, 287.
- Okubo, T.; Ise N. *J Phys Chem* 1969, 73, 1488.
- Flory, P. J.; Fox, T. G. *J Am Chem Soc* 1951, 73, 1904.
- Kurata, M.; Stockmayer, W. H. *Fortschr Hochpolym Forsch* 1963, 3, 196.
- Kurata, M.; Stockmayer, W. H.; Roig, A. *J Chem Phys* 1960, 33, 151.
- Van Krevelen, D. W.; Hoftyzer, P. J. *J Appl Polym Sci* 1967, 11, 1409.
- Meza, R.; Gargallo, L. *Eur Polym J* 1977, 13, 235.
- Kurata, M.; Yamakawa, H. *J Chem Phys* 1950, 29, 311.
- Sakellariou, P. *Polymer* 1992, 33, 1339.
- Garvey, M. J.; Robb, I. D. In *International Symposium of Water-Soluble Polymers*, Cranfield, U.K., 1976.
- Garvey, M. J.; Robb, I. D. *J Chem Soc Faraday Trans* 1979, 75, 999.