Effect of Some Selective Aromatic Cosolutes on the Main Thermodynamic Parameters of Aqueous Poly(*N*-vinyl-2-pyrrolidone) Solutions

SERAP KAVLAK, ALI GÜNER

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

ABSTRACT: Cloud-point curves and theta temperatures have been determined for aqueous solutions of poly(*N*-vinyl-2-pyrrolidone) at several concentrations for a variety of aromatic additives (benzoic acid, *o*- and *p*-hydroxy benzoic acid, aniline, *o*- and *p*-hydroxy aniline). The theta temperature of polymer is suppressed at lower temperatures depending on the chemical structure and the concentration of additives. The effectiveness, in decreasing order, of the cosolutes in reducing the temperature is: *p*-hydroxy benzoic acid > *o*-hydroxy benzoic acid > *p*-hydroxy aniline > *o*-hydroxy aniline ≈ benzoic acid > aniline. It is understood that changes in theta temperatures caused by the cosolute result from the changes taking place in the hydrophilic and hydrophobic interactions among polymer, solvent and polymer–solvent interactions from the added cosolute. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 507–510, 2000

Key words: poly(*N*-vinyl-2-pyrrolidone); aromatic cosolutes; cloud points; theta temperatures

INTRODUCTION

Theta temperature (θ), the ideal temperature, is one of the main physicochemical parameters for chosen polymer–solvent system and can be determined by second virial coefficient (at theta temperature, $A_2 = 0$). Extrapolation method was first presented by Stockmayer et al. in the early 1960s, and subsequently many related equations were developed by other research groups.[1] These methods, permit, in addition to short-range interactions, the determination of long-range interactions by viscometric measurement. According to Flory,[2] the theta temperature of a polymer solution can be determined by the long-range interaction parameter–temperature relationship. Theta temperatures of dextran–water[3] and dextran–

DMSO[4] systems have been determined by using various equations and B–T behavior in recent studies.

More rapid methods use turbidity and cloud-point temperature measurements. The turbidimetric technique of Cornet and Ballegooijen,[5] later developed by Talamani and Vidotto[6] and Napper,[7] is not dependent on the molecular weight of the polymer and was subsequently applied to a variety of systems, mostly polymer–solvent systems that exhibit upper critical solution temperature (UCST). This method, also employed for the determination of the theta temperature, assumes that the interaction parameter, χ_1, and the logarithm of the polymer volume fraction, $\log \phi_2$, have a linear dependence. This behavior is verified by the straight line graph of T_{cp}^{-1} against $\log \phi_2$, with $1/\theta$ at $\log \phi_2 = 0$ the intercept of this line.

Poly(*N*-vinyl-2-pyrrolidone), hereafter denoted as PVP, is one of the most important synthetic

water-soluble polymers employed in biological systems and in medicine. The existing similarities between the chemical structure of PVP and proteins have led to the proposal of PVP as a synthetic polymeric model for proteins. PVP exhibits a series of interactions toward small dissolved molecules, which have been studied by many researchers using different cosolute systems.[8–15]

EXPERIMENTAL

The polymer sample used in this study was commercial PVP with a nominal molecular weight of 44,000 g mol^{-1} obtained from BDH. Weight-average and number-average molecular weights of polymers were determined using the Brice-Phoenix Light Scattering Photometer (2000 Series) and the Knauer Membrane Osmometer and were found to be M_w= 78,000 g mol^{-1} and M_n = 46,000 g mol^{-1},respectively. Specifications of these instruments, calculated characteristics,[16] and density measurements[17] were reported previously.

The additives, aniline, o-hydroxy and p-hydroxy aniline, benzoic acid, and o-hydroxy and p-hydroxy benzoic acid were obtained from BDH and Merck. They were of reagent grade and were purified by recrystallization if necessary. Polymer–cosolute aqueous solutions did not show any cloudiness and/or phase separations over the studied temperature range (25–90°C) and atmospheric pressure (670.0 ± 0.5 mmHg). As mentioned previously,[17,18] in order to ascertain the effects of organic additives at lower concentrations below their solubilities, $(NH_4)_2SO_4$ was added to polymer–organic additive aqueous solutions to lower the cloud point to a temperature range in which measurements could be made easily. All chemicals were dried in a vacuum at 40°C and stored in a desiccator over P_2O_5. Deionized and double-distilled water was used for the preparation of each solutions.

Cloud-point temperature measurements of the polymer–organic additive aqueous solutions were carried out in Pyrex tubes containing ammonium sulfate under atmospheric pressure. The solutions were immersed in a well-controlled, stirred, and heated bath (±0.2°C min^{-1}), and they were also stirred by a Teflon magnetic stirring bar while being heated. The first appearance of cloudiness for each PVP–additive aqueous solution system was determined twice, and the average temperature of each system was taken as the cloud-point temperature. Reproducibility of the cloud-point temperature measurements for all polymer–additive aqueous solutions was excellent, within 0.1°C.

RESULTS AND DISCUSSION

PVP aqueous solutions exhibit a lower critical solution temperature (LCST) because they cloud on heating.[19] The effects of various additives (denaturing agents, certain organic compounds, and inorganic salts) on the cloud-point temperature of aqueous solutions of PVP were studied by several research groups.[17,18,20–22] The ability of an aromatic cosolute to lower the cloud-point temperature of a PVP aqueous solution differs depending on its functional groups and the types and/or numbers and positions of its substituents.

The cloud-point temperature of PVP in aniline, o- and p-hydroxy aniline, benzoic acid, and o- and p-hydroxy benzoic acid depended on the concentration of the additive. The presence of organic additives (5.0×10^{-4}–3.0×10^{-3} mol^{-1}) led to a decrease in the cloud-point temperatures of aqueous PVP solutions. This observation is typical of water-soluble polymer–polar solvent systems. The hydrogen bond formation and/or molecular association between polymer and polar solvent molecules is disturbed in the presence of additives or with increments of temperature for LCST systems. The effect of benzoic acid concentration and polymer concentration (as log ϕ_2) on the cloud-point temperatures for PVP in aqueous solutions can be seen in Figure 1. Cloud-point data of PVP–additive aqueous solutions, shown in Figure 2 for the same example, have been used to determine theta temperatures, which also exhibit the effect of a particular concentration of cosolute. The procedure depends on the reciprocal of cloud-point temperature being linearly related to the logarithm of PVP volume fraction. Calculated theta temperatures of PVP are given in Table I as determined by linear regression analysis (correlation coefficients are 0.996 ± 0.003).

The observed effects of aromatic cosolutes on the change of theta temperatures of PVP aqueous solutions were that (1) the theta temperature decreases with increasing additive concentration, (2) aniline has the smallest effect on the decrease of the theta temperature of a polymer, while p-hydroxy benzoic acid has the greatest effect on the decrease of the theta temperature of PVP in aqueous solutions, and (3) the effectiveness of the studied aromatic cosolutes on cloud-point decre-
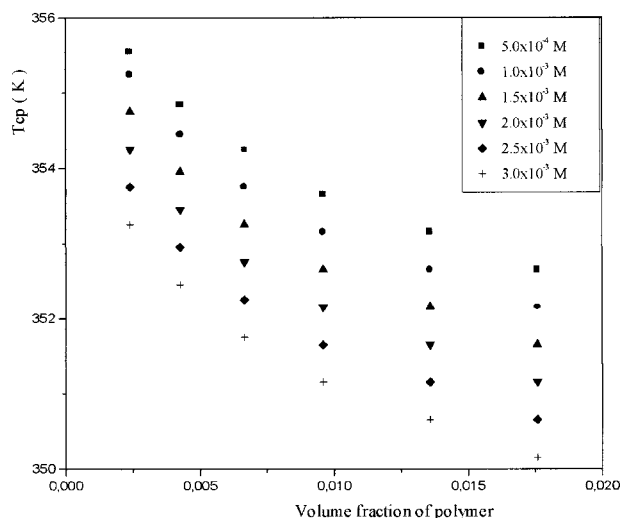
Figure 1 Dependence of cloud-point temperature, T_{cp}, on polymer volume fraction, ϕ_2, for the molar concentration of benzoic acid containing $0.5M$ of ammonium sulfate.

Table I Theta Temperatures (K) at Various Aromatic Additive Concentrations (C) for Poly(N-vinyl-2-pyrrolidone) Aqueous Solutions

$C(M) \times 10^3$	Benzoic Acid	o-Hydroxy Benzoic Acid	p-Hydroxy Benzoic Acid
3.0	343.9	339.7	338.3
2.5	344.4	340.7	340.3
2.0	344.9	342.7	342.4
1.5	345.3	344.5	343.1
1.0	345.8	344.3	344.1
0.5	346.8	345.5	345.0

$C(M) \times 10^3$	Aniline	o-Hydroxy Aniline	p-Hydroxy Aniline
3.0	347.2	343.1	341.6
2.5	348.4	344.5	343.4
2.0	349.2	345.5	344.6
1.5	349.8	346.0	345.6
1.0	350.3	346.7	346.0
0.5	350.8	346.4	346.2

ment and theta temperature is in the order of: p-hydroxy benzoic acid $>$ o-hydroxy benzoic acid $>$ p-hydroxy aniline $>$ o-hydroxy aniline $\approx$ benzoic acid $>$ aniline.

PVP is capable of forming hydrogen bonds with aqueous and nonaqueous solvents,[23] and additives may affect the already-existing hydrogen bonds between polymer and solvent molecules.[9,24] It is well known that the clouding phenomenon mainly depends on the nature of the additive. Cloud-point curves and the evaluation of theta
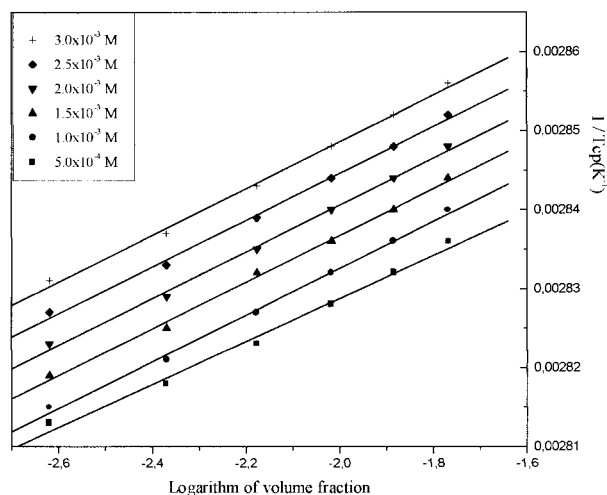
temperatures previously were studied for aqueous solutions of PVP for a variety of inorganic salts[21] and denaturing agents.[17] These studies revealed that the addition of inorganic salts affects the suppression of cloud-point and theta temperatures, while in the case of denaturing agents, the increasing effect of denaturants resulted in salting out the polymer. This observation was explained by the formation of strong hydrogen bonding between polymer and denaturing agents and the prevention of hydrophobic interactions between polymer segments.

The additives used in this study contain various hydrogen donor and acceptor groups that interact with adjoining water molecules or with polymer segments (carbonyl group of the ring) through hydrogen bonding. Denaturing agents (urea, thiourea, and guanidinium salts) are potential hydrogen-bonding amino groups. When the chemical structures of denaturing agents and the cosolutes used in this study are compared, it can be clearly noticed that the denaturants include a larger number of active hydrogen donor and acceptor groups that interact with PVP segments.

In a PVP–aromatic cosolute aqueous system, the effects of additive species in the polymer solution and the suppression of the cloud-point and theta temperatures of PVP can be interpreted as

Figure 2 Reciprocal of cloud-point temperature, $1/T_{cp}$, against log ϕ_2 for molar concentration of benzoic acid containing $0.5M$ of ammonium sulfate.

a combination of several effects: (1) the interaction of the polymer with cosolute molecules, which is not very effective for PVP–denaturing agent systems, (2) the change in the structure of water with an additive, and (3) the disruption of the binding of the water molecules to the polymer and/or the change in the hydration sheath of PVP because of the added aromatic cosolute.

It has been reported that both organic acids and phenols appreciably lower the viscosity of PVP.[13] The results show no clear-cut behavior for the acids, while the phenols exhibit a more noticeable effect with an increasing number of hydroxyl groups. The *p*- and *m*-dihydroxy benzenes are much more effective than the *o*-dihydroxy benzene. A similar correlation has been found for the interaction of proteins with phenols, interpreted as hydrogen bonding between one hydroxyl with the oxygen of the adjacent hydroxyl competing effectively with the intermolecular hydrogen bonding between phenol and protein.[25]

Benzoic acid lowers the theta temperature more than phenol (Table I). Suppression of the theta temperature is also related to the number of substituents. Disubstituted additives seem to be more dominant than monosubstituted samples. The theta temperatures of PVP at 3.0×10^{-3} mol L^{-1} of benzoic acid and aniline were found to be 343.9 and 347.2 K, respectively. However, in the system of *ortho*-substituted benzoic acid and aniline, the values were reduced to 339.7 and 343.1 K, respectively. The position of substituents is another important point. Two substituent groups of salicylic acid at ortho position might interact with each other to form intramolecular hydrogen bonding, and this restrains the availability of these groups to interact with the polymer molecules, as well as that in the behavior of *p*- and *o*-hydroxy aniline.

CONCLUSION

In the present study we have attempted to explain the effects of certain aromatic additives on cloud-point and theta temperatures of PVP in aqueous solutions. The addition of certain aromatic cosolutes into aqueous solutions of PVP changes the association and/or hydration behavior and causes a disruption of water molecules that surround the polymer. Consequently, the increasing hydrophobicity of the polymer chain should result in the lowering of the polymer phase separation temperature. The effects of cosolutes on the suppression of the theta temperature of

polymer in aqueous solutions reveal the structural function of the used aromatic cosolutes.

Disubstituted cosolutes in *o* position are not effective in decreasing the theta temperature because of intramolecular hydrogen bonding, while those in *p* position have significant effects in suppressing the theta temperature of PVP in aqueous solutions.

The dynamics of hydrogen bonding is being surveyed by the authors in areas where spectroscopic studies are still going on. In addition, the position and number of hydroxyl groups of several phenol derivatives are being investigated, using techniques such as detailed cloud-point temperature[26] and spectrophotometric measurements.

REFERENCES

1. Rabek, J. F. Experimental Methods in Polymer Chemistry; Wiley: Chichester, UK, 1980; p 50.
2. Flory, P. J. Principles of Polymer Chemistry; Cornell University Press: New York, 1953.
3. Güner, A. J Appl Polym Sci 1999, 72, 871.
4. Çatıker, E.; Güner, A. Polym Bull 1998, 41, 223.
5. Cornet, C. F.; van Ballegooijen, H. Polymer 1966, 7, 293.
6. Talamani, G.; Vidotto, G. Makromol Chem 1967, 110, 111.
7. Napper, D. H. Polymer 1969, 10, 181.
8. Güner, A. J Appl Polym Sci 1996, 62, 785.
9. Güner, A. J Appl Polym Sci 1997, 65, 1307.
10. Güner, A. J Appl Polym Sci 1998, 67, 1615.
11. Gargallo, L.; Radic, D. Polymer 1983, 24, 91.
12. Sheth, N. S. J Appl Polym Sci 1986, 32, 4333.
13. Bandyopadhyay, P.; Rodriguez, F. Polymer 1972, 13, 119.
14. Inoue, M.; Otsu, T. J Polym Sci Polym Chem Ed 1976, 14, 1933.
15. Molyneux, P.; Frank, H. P. J Am Chem Soc 1961, 83, 3169.
16. Güner, A.; Ataman, M. Polym Int 1997, 44, 30.
17. Güner, A.; Kara, M. Polymer 1998, 39, 1569.
18. Sekikawa, H.; Hori, R.; Arita, T.; Ito, K.; Nakano, M. Chem Pharm Bull 1978, 26, 2489.
19. Sakellariou, P. Polymer 1992, 33(6), 1339.
20. Molyneux, P. In Water: A Comprehensive Treatise; Plenum: New York, 1975; Vol. 4, Chapter 7.
21. Güner, A.; Ataman, M. Colloid Polym Sci 1994, 272, 175.
22. Guttman, D.; Higuchi, T. J Am Pharm Assoc Sci Ed 1956, 45, 659.
23. Türker, L.; Güner, A.; Yiğit, F.; Güven, O. Colloid Polym Sci 1990, 268, 337.
24. Güner, A. J Appl Polym Sci 2000, 75, 1434.
25. Endres, H.; Hoermann, H. Angew Chem Int Ed 1963, 2, 254.
26. Kırcı, B.; Güner, A. Eur Polym J, to appear.