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Cloud points and Θ temperatures of aqueous poly(*N*-vinyl-2-pyrrolidone) solutions in the presence of denaturing agents

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Cloud point curves have been determined for various concentrations of aqueous solutions of poly(*N*-vinyl-2-pyrrolidone) in the presence of a variety of denaturing agents (e.g. thiourea, guanidinium chloride and guanidinium carbonate). From these, θ temperatures have been found. The resulting dependences of the critical temperature theta (between 320 and 350 K) on the molar concentration can be expressed as a sequence showing the increasing effect of denaturants in salting out the polymer. The increasing order of effectiveness of denaturing agents increasing the θ temperature is guanidinium carbonate > guanidinium chloride > thiourea. The change of θ temperature by denaturing agents was found to be the result of the changes taking place in the hydrophobic/hydrophilic interactions among the polymer, solvent and additive denaturing agents, and of the influence of denaturing agent–polymer interactions. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Theta temperature (Flory temperature, ideal temperature) is the temperature at which, for a given polymer–solvent pair, the polymer exists in its unperturbed dimensions. The theta temperature, θ, can be determined by colligative property measurements, by determining the second virial coefficient. At theta temperature the second virial coefficient becomes zero. More rapid methods use turbidity and cloud point temperature measurements[1–3]. In this method, the linearity of the reciprocal cloud point temperature ($1/T_{cp}$) against the logarithm of the polymer volume fraction (ϕ_2) is observed. Extrapolation to $\log \phi_2 = 0$ gives the reciprocal theta temperature.

Poly(*N*-vinyl-2-pyrrolidone) (PVP) is a water-soluble polymer, and is capable of forming a high degree of hydrogen bonding with aqueous and nonaqueous solvent systems[4]. The presence of association among PVP molecules by hydrogen bonding was investigated by the addition of denaturing agents to the solutions[5]. The effects of denaturing agents on the molecular association of certain water-soluble polymers were also studied previously[6,7]. These studies revealed that guanidinium salts are more effective in disrupting hydrogen bonds or molecular association of water-soluble polymers in aqueous media.

It has been reported that the cloud point of aqueous PVP[8] and poly(ethylene oxide)[9] aqueous solutions is depressed by the addition of electrolytes. The addition of an electrolyte to water changes the hydrogen-bonded structure of water, association and/or hydration, and can cause a disruption of water molecules which surround the polymer. Consequently, the increasing hydrophobic behavior of the polymer chain should result in the lowering of the polymer precipitation temperature.

In the present study, the effect of thiourea and of the two guanidinium salts guanidinium chloride and guanidinium carbonate, over a range of concentrations, on the cloud point curves, and the theta temperatures derived therefrom for PVP have been investigated.

EXPERIMENTAL

The polymer sample used in this study was commercial BDH poly(*N*-vinyl-2-pyrrolidone) with a nominal molecular weight of 700 000. The weight-average molecular weight of the polymer sample was determined by light scattering photometer in chloroform at 30°C. In this study, Brice-Phoenix Light Scattering, Photometer, 2000 Series was used for measuring the Rayleigh ratios of the polymer solutions where a high-pressure mercury lamp of type (AH-3), 85 W, was present as a light source vertically unpolarized light of 436 nm wavelength. The interpretation of light scattering data was based on the Zimm method, expressed in the general form

$$K_C/R_\theta = 1/M_W[1 + (16\pi^2/3\lambda^2)\langle s^2\rangle Z \sin^2\theta/2] + 2A_2C + \ldots$$

and the dn/dc value of the polymer in chloroform solution is taken as 0.108 mL g^{-1} [10]. It has a weight-average molecular weight of $M_W = 548\,000$ g mol^{-1}.

Thiourea and guanidinium carbonate were obtained from BDH and guanidinium chloride was obtained from Riedel-de Haen AG. PVP/denaturing agent aqueous solutions did not show any cloudiness over the experimental temperature range (20–94°C). In order to ascertain the effect of denaturing agents at the lower concentration below their solubilities, ammonium sulfate (0.5 M in the mixture) was added to PVP/denaturing agent aqueous solution beforehand to lower the cloud point to a temperature range in which measurements could be made easily.

The determination of cloud point temperatures was carried out in pyrex tubes containing aqueous ammonium

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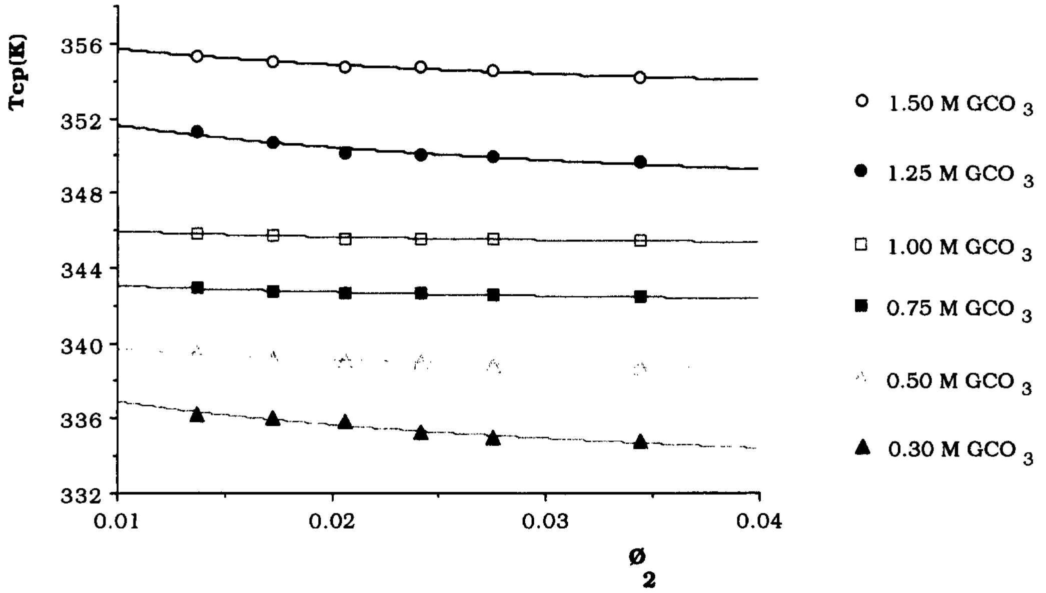

Figure 1 Dependence of cloud point temperature T_{cp}, on polymer volume fraction ϕ_2, for the molar concentration of guanidinium carbonate containing 0.5 M of ammonium sulfate

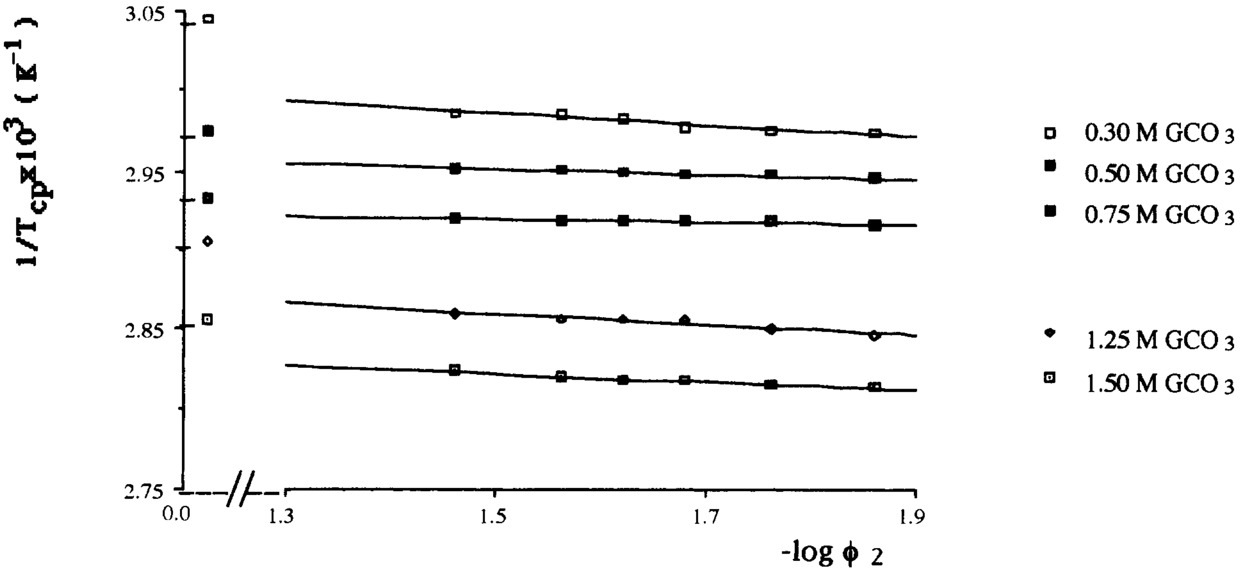

Figure 2 Reciprocal of cloud point temperature $1/T_{cp}$, against log ϕ_2 for molar concentration of guanidinium carbonate containing 0.5 M of $(NH_4)_2SO_4$ (correlation coefficients are 0.98 ± 0.001)

sulfate and denaturing agent solutions of PVP. They were immersed in a well-controlled, stirred and heated bath (0.5°C min^{-1}). The solutions were also stirred by a Teflon magnetic stirring bar while being heated. The first appearance of cloudy aqueous denaturing agent solutions of PVP was taken as the cloud point temperature. Reproducibility of the cloud point measurements was excellent, within the range 0.1°C. Density of PVP sample was determined as 1.16 g cm^{-3} in *n*-hexane and *n*-heptane at 20°C using a pycnometer.

RESULTS AND DISCUSSION

The molecular association between polymer and solvent molecules by hydrogen bonding is destroyed in the presence of additives or with the increment of temperature for lower critical solution temperature (LCST) systems. PVP aqueous solutions exhibit LCST, since they cloud on heating[11].

The effects of some aromatic compounds on the cloud point of PVP aqueous solutions were investigated by Sekikawa and co-workers[12]. It is reported that the abilities of the aromatic compounds to lower the cloud point of PVP solution differed depending upon their functional groups, types and positions of their substituents. Contrary to the effect of aromatic compounds on the cloud point temperatures, urea derivatives increased the cloud point temperature of PVP solution. Guttman and Higuchi[13] reported on a similar clouding phenomenon in the interaction of some phenolic compound with some water-soluble polymers and PVP by titration method. Bandyopadhyay and Rodriquez[14] reported that PVP aqueous solution exhibited the cloud point by addition of hydroquinone, and it is pointed out that hydroquinone played a role of theta solvent.

Cloud point temperatures of PVP in denaturing agents depended on the concentration of the salt. The presence of thiourea (2.0–4.0 M), guanidinium chloride (0.3–1.5 M),

Table 1 Theta temperatures at various denaturing agent concentrations (*C*) for poly(*N*-vinyl-2-pyrrolidone) aqueous solutions

Thiourea		Guanidinium chloride		Guanidinium carbonate	
C (M)	*θ* (K)	*C* (M)	*θ* (K)	*C* (M)	*θ* (K)
4.00	333.43	1.50	336.45	1.50	349.77
3.50	330.24	1.25	333.88	1.25	344.03
3.00	328.22	1.00	330.98	1.00	343.03
2.50	325.10	0.75	329.60	0.75	340.91
2.00	320.10	0.50	327.92	0.50	336.28
-	-	0.30	327.94	0.30	328.77

and guanidinium carbonate (0.3–1.5 M), led to an increase in the cloud point temperatures of aqueous PVP solutions. The effect of denaturing agent concentration and polymer concentration on the cloud point temperatures for PVP in aqueous guanidinium carbonate solutions can be seen in *Figure 1*.

Cloud point data of polymer solutions, shown in *Figure 2*, for guanidinium carbonate as an example, have been used to obtain theta temperatures, which also show the effect of a particular concentration of denaturing agents. The procedure we use depends on $1/T_{cp}$ being linearly related to the logarithm of PVP volume fraction. The theta temperatures given in *Table 1*, for thiourea, guanidinium chloride, and guanidinium carbonate are determined by linear regression analysis.

The most important effects of denaturants on the increase of theta temperatures of PVP solution are as follows.

(1) The increase in theta temperatures of polymer solutions depends on the molar concentrations of denaturing agents. The theta temperature values increase with increasing denaturant concentrations.

(2) Thiourea has the smallest effect on the increase of theta temperatures of polymer solutions, but guanidinium carbonate has the greatest effect on the increase of theta temperatures of PVP solutions.

(3) The effectiveness of denaturing agents on the increase in cloud point temperature is in the order: guanidinium carbonate > guanidinium chloride > thiourea. The theta temperatures for 3.50 M of thiourea, 1.00 M of guanidinium chloride and 0.5 M of guanidinium carbonate are calculated as 330.24 K, 330.98 K and 336.28 K, respectively. Similarly, the theta temperature values for 4.0 M of thiourea and 1.25 M of guanidinium chloride are almost the same (333 K), but is higher for 0.50 M of guanidinium carbonate than for the other two denaturing agents.

Previously, cloud point curves and θ temperatures were studied for aqueous solutions of PVP at several concentrations for a variety of inorganic salts (phosphates, mono- and dihydrogen phosphates, carbonates, sulfates and fluorides of sodium and potassium)[8]. It was observed that the addition of these inorganic salts affects the suppression of T_{cp} and θ temperatures; it seems the anions play an important role[15]. The denaturing agent thiourea has a hydrogen-acceptor thiocarbonyl group and two hydrogen donor and acceptor amino groups. These amino groups interact with adjoining water molecules[16–18] or with polymer molecules[5] through hydrogen bonding. The denaturing effect of guanidinium compounds is greater than that of thiourea. This is due to the hydrogen-bond destroying effect of these salts; guanidinium chloride and sulfate have three and six amino groups per mole of compound, respectively. These two salts provide chloride, carbonate and bicarbonate anions for the aqueous media. The last anion, i.e. bicarbonate, is hydrogen bond acceptor and donor in character, but, when the first two anions (chloride and carbonate) are compared, carbonate is doubly charged and it interacts strongly with the hydrogen bond donors.

It is well known that ions change the hydrogen-bonded structure of water, and the extent to which this occurs depends mainly on the charge and size of the ion. Divalent anions (in this study, the carbonate ion) can destroy the hydrogen-bonded structure of water more effectively than the univalent anion (in this study, the chloride ion)[19,20]. Of course, the ions destroying the hydrogen-bonded structure of water may also affect the PVP–water interaction. The denaturant guanidinium carbonate provides two guanidinium cations per mole of compound compared with guanidinium chloride which provides one guanidinium cation per mole. A kind of interaction may arise between hydrogen bond acceptors and the cations[21–23] and this increases the cloud point temperature of PVP in aqueous solutions. One should keep in mind that the addition of anions affects the suppression of T_{cp} of PVP in aqueous solutions.

Additives interact with PVP chains more strongly than water by forcing the hydrating water molecules to be removed from the polymer. This results in an enhancement of the hydrophobic character of the polymer and its precipitation. The clouding phenomenon depends on the nature of the additive.

The effect of guanidinium salts on the change of T_{cp} of PVP in aqueous solutions appears to be due to the amino group–PVP interactions through hydrogen bonding.

Denaturing agents are potential hydrogen bonding amino groups. These amino groups are acceptor and donor in character, and subsequent interactions of the polymer occur with the acceptor group of PVP–lactam ring. PVP-denaturing agent interactions change hydrophobic/hydrophilic interactions among polymer and solvent molecules, decrease the hydrophobic interactions between polymer segments, and increase its precipitation temperature.

CONCLUSION

Phase separation is a result of the hydrophobic interactions of the polymer, depending on the nature of the additive, solvent and temperature. At the theta point segmental interactions become attractive. In the present study we have attempted to explain the effects of certain denaturing agents on cloud point temperatures and theta temperatures of PVP aqueous solutions, mainly on the basis of polymer–denaturant interactions. These interactions prevent the hydrophobic interactions or segmental attractions between polymer segments, thus causing the T_{cp} and θ temperature increment as a function of the type and number of hydrogen bond donor and acceptor groups in denaturing agents.

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REFERENCES

1. Cornet, C. F. and van Ballegooijen, H., *Polymer*, 1966, **7**, 293.
2. Talamani, G. and Vidoto, G., *Makromol. Chem.*, 1967, **110**, 111.
3. Napper, D. H., *Polymer*, 1969, **10**, 181.
4. Türker, L., Güner, A., Yiğit, F. and Güven, O., *Colloid Polym. Sci.*, 1990, **268**, 337.
5. Guven, O. and Eltan, E., *Makromol. Chem.*, 1981, **182**, 3129.
6. Güner, A. and Güven, O., *Makromol. Chem.*, 1978, **179**, 2789.
7. Güner, A., *J. Appl. Polym. Sci.*, 1995, **56**, 1561.
8. Güner, A. and Ataman, M., *Colloid and Polym. Sci.*, 1994, **272**, 175.
9. Ataman, M., *Colloid and Polym. Sci.*, 1987, **265**, 19.
10. Huglin, M. B., *Light Scattering from Polymer Solutions*. Academic Press, London, 1972, p. 282.
11. Sakellariou, P., *Polymer*, 1992, **33**(6), 1339.
12. Sekikawa, H., Hori, R., Arita, T., Ito, K. and Nakano, M., *Chem. Pharm. Bull.*, 1978, **26**(8), 2489.
13. Guttman, D. and Higuchi, T., *J. Am. Pharm. Assoc. Sci. Ed.*, 1956, **45**, 659.
14. Bandyopadhyay, P. and Rodriguez, F., *Polymer*, 1972, **13**, 119.
15. Güner, A., *J. Appl. Polym. Sci.*, 1996, **62**, 785.
16. Wen, W. Y. and Saito, S., *J. Phys. Chem.*, 1965, **69**, 3569.
17. Wolrafen, G. E., *J. Chem. Phys.*, 1966, **44**, 3726.
18. Molyneux, P., in *Water: A Comprehensive Treatise*, Vol. 3, Ch. 5, ed. F. Franks. Plenum, New York, 1975.
19. James, D. W. and Frost, R. J., *Chem. Soc. Faraday Trans.*, 1978, **1**(74), 583.
20. Hindman, J. C., *J. Chem. Phys.*, 1962, **36**, 1000.
21. Witzchonke, C. R. and Kraus, C. A., *J. Am. Chem. Soc.*, 1947, **69**, 2472.
22. Ralph, E. K. and Gilkerson, W. R., *J. Am. Chem. Soc.*, 1964, **86**, 4783.
23. Coetzee, J. F. and Podmanabhan, G. R., *J. Am. Chem. Soc.*, 1965, **87**, 5005.