

Spectrophotometric Behavior of Polyvinylpyrrolidone in Aqueous Solutions. II. The Effects of Denaturing Agents

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ABSTRACT: Electronic spectral behavior of aqueous polyvinylpyrrolidone solutions have been investigated by UV-vis spectrophotometry. $n \rightarrow \pi^*$ electronic excitations of the polymer were observed to shift longer wavelengths with a variety of denaturing agents. The shifting effect of denaturing agents on the λ_{\max} increased in the order guanidinium carbonate \approx guanidinium sulfate > guanidinium chloride > urea. Intrinsic viscosities of different concentrations of aqueous solutions of polyvinylpyrrolidone with the same denaturing agents have also been determined. Intrinsic viscosity number, $[\eta]$, of polymer solutions decreased with the addition of denaturing agents. The slope, $k_H[\eta]^2$, of the polymer was also observed to decrease in the presence of denaturing agents. Shift to the longer wavelengths and decrease in the viscosity characteristics can be explained by the break of the molecular association between the polymer and the water molecules.

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INTRODUCTION

Polyvinylpyrrolidone (PVP) is a well-known water-soluble polymer and it is subject to interaction with aqueous and nonaqueous solvents.^{1–5} Hydrogen bonding is the main type of interaction prevailing in the aqueous solutions of PVP. The investigation of molecular association can be followed by group-specific (spectrophotometry) and molecule-specific (viscosimetry, osmometry, LS, and GPC) methods.⁶ Obviously, various additives affect the degree of hydrogen bonding or molecular association existing between the polymer and the solvent molecules. Denaturing agents have a special importance among the organic additives, and are the source of potential hydrogen bonding amino groups.

Effects of denaturing agents on the molecular association of certain water-soluble polymers were studied previously.^{5,7,8} It is observed that guanidinium salts are more effective in destroying the hydrogen bonds or molecular association of these polymers in aqueous media.

In the present study, the effects of denaturing agents (e.g. urea, guanidinium chloride, guanidinium carbonate, and guanidinium sulfate) on the electronic spectral behavior of PVP aqueous solutions have been investigated. The viscosimetric method has also been studied to follow the hydrodynamic volume changes of the polymer in solution.

EXPERIMENTAL

The PVP sample used in this study was a commercial product obtained from BDH. It has a weight-average molecular weight of 548,000 g mol⁻¹ as determined by light-scattering photometer. "Brice-Phoenix Light Scattering Photometer, 2000 Series" was used for measuring the Rayleigh ratios.

Considering the denaturing agents used, urea was obtained from Fisher Scientific Company, guanidinium salts, guanidinium chloride, guanidinium carbonate, and guanidinium sulfate were obtained from Riedel-De Haen AG, BDH, and Merck, respectively. All the organics were used without further purification and the solutions

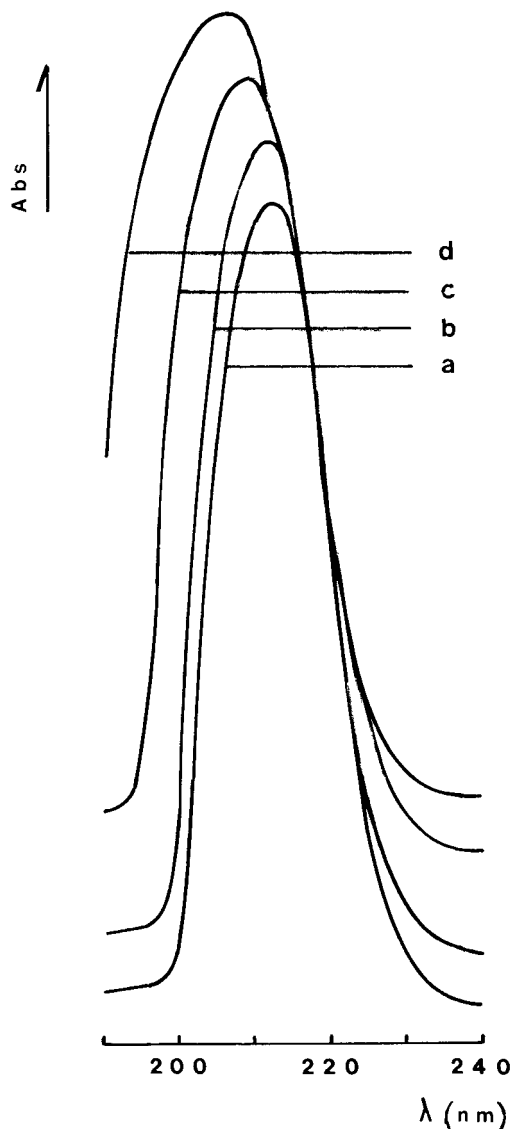


Figure 1 The UV absorption spectra of PVP in urea (a) $3.5 \times 10^{-2}M$, (b) $2.5 \times 10^{-2}M$, (c) $5.0 \times 10^{-3}M$, (d) $5.0 \times 10^{-4}M$ solutions.

were all prepared and used fresh to prevent any degradation.

The spectrophotometric studies were carried out by a Hitachi 100-60 Model UV-vis double-beam spectrophotometer at room temperature. The possible impurities were eliminated by dialyzing the aqueous PVP solutions through cellulose nitrate membranes for 5 days. The same spectral behavior was observed for the dialyzed and undialyzed polymer samples. Some selected samples were also checked by using a Hitachi 150-20 Model double-beam spectrophotometer at room temperature, and no spectral differences

were observed in both of the instruments between the range of 190-340 nm.

Viscosities of the polymer solutions were measured by an Ubbelohde type viscosimeter. The measurements were made in a thermostat bath regulated to $25.0 \pm 0.1^\circ C$.

RESULTS AND DISCUSSION

In the aqueous solution of PVP, the polymer and water molecules are hydrogen bonded, the former

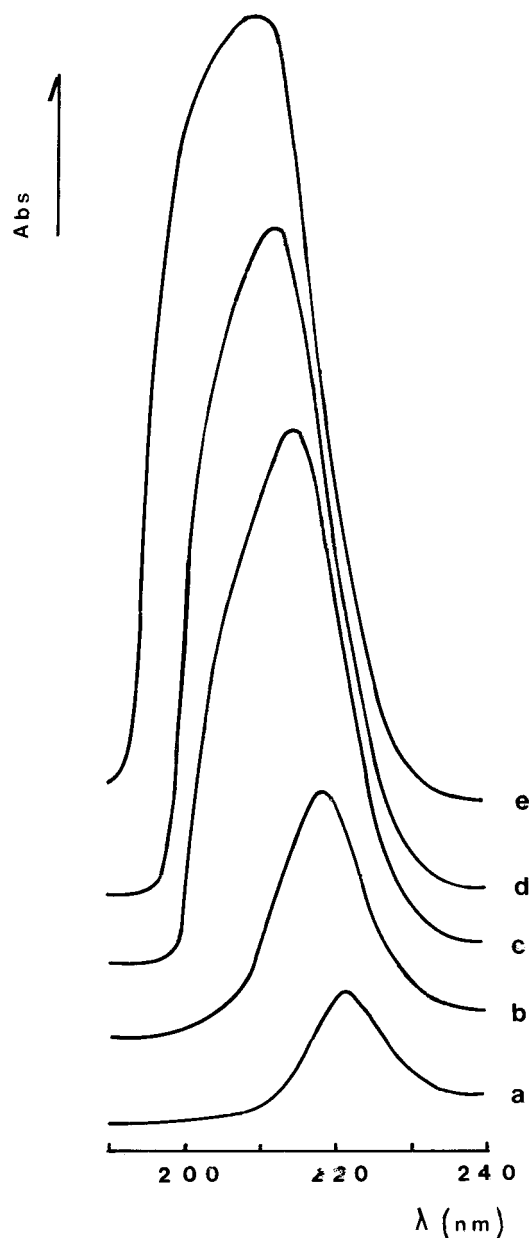


Figure 2 The UV absorption spectra of PVP in guanidinium chloride (a) $3.5 \times 10^{-2}M$, (b) $2.5 \times 10^{-2}M$, (c) $1.0 \times 10^{-2}M$, (d) $5.0 \times 10^{-3}M$, (e) $1.0 \times 10^{-3}M$ solutions.

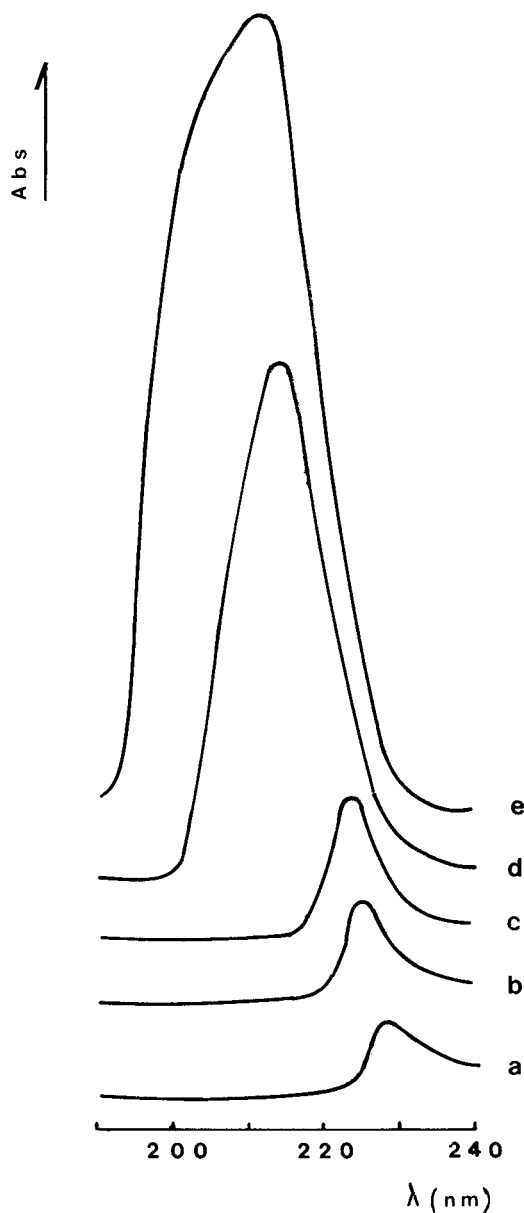


Figure 3 The UV absorption spectra of PVP in guanidinium carbonate (a) $5.0 \times 10^{-2}M$, (b) $3.5 \times 10^{-2}M$, (c) $2.5 \times 10^{-2}M$, (d) $5.0 \times 10^{-3}M$, (e) $5.0 \times 10^{-4}M$ solutions.

being an acceptor of hydrogen bond. As reported previously,⁹ the spectral properties of PVP solutions should be dependent on the extent of hydrogen bond formation between the polymer and the solvent molecules. Certain inorganic and organic additives should affect the many observable properties of PVP in aqueous solutions. In spectrophotometric studies of PVP, it is observed that the $n \rightarrow \pi^*$ electronic excitations (carbonyl group of the lactam ring) were shifted to the longer wave-

lengths (bathochromic shift) in aqueous solutions in the presence of denaturing agents.

PVP is capable of forming a high degree of hydrogen bonding with water molecules, and the ability to bind reversibly to water molecules forming association complexes needs a high excitation energy. If certain additives are added without changing the polymer concentration (in this study 0.05 g dL^{-1}), the additives introduced will disturb the evenness of molecular association and thus affect the strength of the hydrogen bonding already existing between the polymer and water molecules. Disturbing of the association between the polymer and solvent molecules can be followed

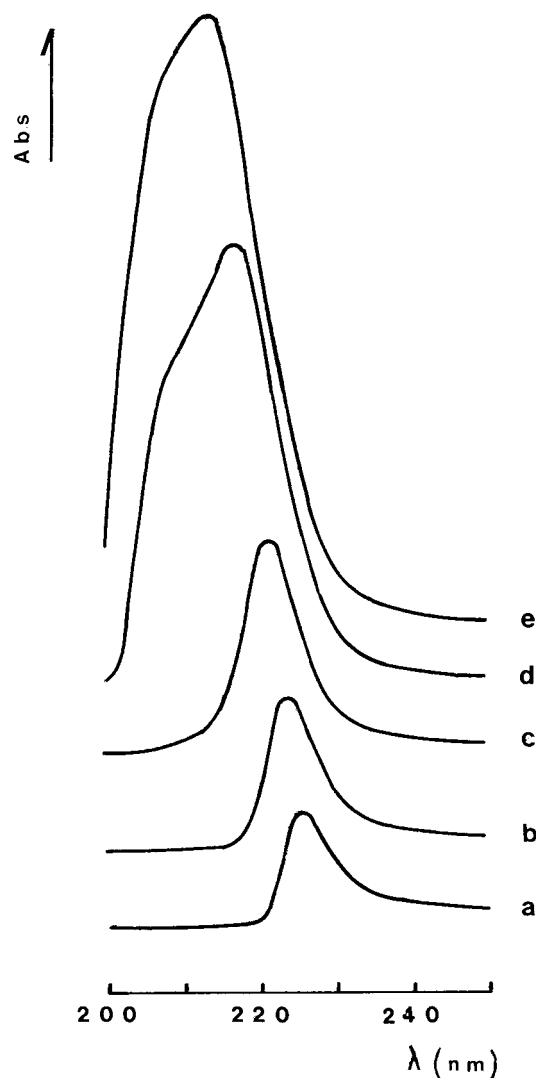


Figure 4 The UV absorption spectra of PVP in guanidinium sulfate (a) $5.0 \times 10^{-2}M$, (b) $3.5 \times 10^{-2}M$, (c) $2.5 \times 10^{-2}M$, (d) $1.0 \times 10^{-2}M$, (e) $5.0 \times 10^{-3}M$ solutions.

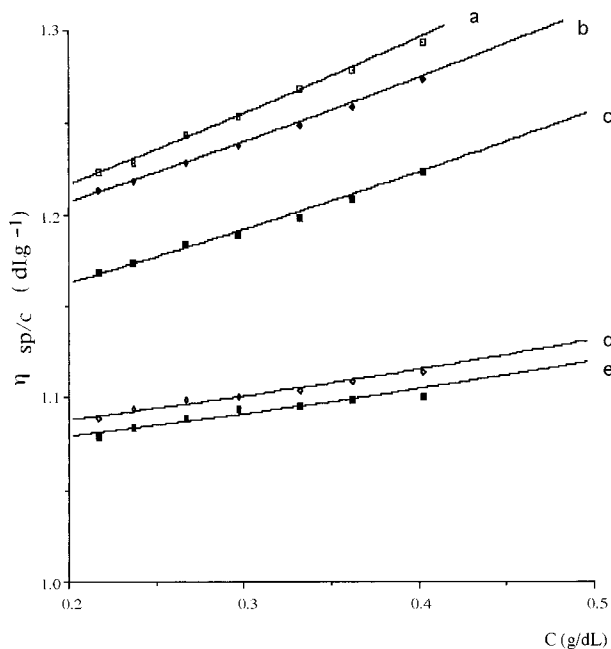


Figure 5 Change of reduced viscosity of PVP in (a) water, (b) 0.1M urea, (c) 0.1M guanidinium chloride, (d) 0.1M guanidinium sulfate, (e) 0.1M guanidinium carbonate solutions (correlation coefficients are 0.998 ± 0.001 , except in guanidinium carbonate solution).

with the excitation energy decrement easily. In addition to that, a kind of interaction that may arise between hydrogen bond acceptor carbonyl and denaturing agents can also be observed.

The most important effects of these denaturing agents on the shift of λ_{\max} of PVP–aqueous solutions are as follows: (1) The shift in λ_{\max} of PVP–aqueous solutions depends on the molar concentrations of denaturing agents, and the λ_{\max} values shift to longer wavelengths by increasing the cosolute concentrations. (2) Denaturing agent urea has the smallest effect on the shift of λ_{\max} of polymer solutions (Fig. 1), whereas guanidinium salts have greater effect on the shift of λ_{\max} of PVP aqueous solutions than that of urea. The spectra of guanidinium chloride, guanidinium carbonate, and guanidinium sulfate are given in Figures 2, 3, and 4, respectively. (3) The shifting order of effectiveness of the cosolutes increasing the λ_{\max} is: guanidinium carbonate \approx guanidinium sulfate $>$ guanidinium chloride $>$ urea. The λ_{\max} for 3.5×10^{-2} mol L $^{-1}$ of denaturing agents are observed as 212.5, 222, 224, and 225 nm, and for 5.0×10^{-3} mol L $^{-1}$, 209, 213, 214, and 214 for urea, guanidinium chloride, guanidinium sulfate, and guanidinium carbonate, respectively.

It is possible to explain the observed shifting

phenomena with the nature of the added cosolute. The denaturing agent urea has two amino groups and a hydrogen-acceptor carbonyl group. The amino groups interact with the carbonyl groups of the polymer molecules through hydrogen bonding⁵ or with the adjoining water molecules.¹⁰ In the case of guanidinium salts, guanidinium chloride has three, guanidinium sulfate and carbonate have six amino groups per molecule of compound, and also provide chloride, sulfate, and carbonate anions for the aqueous media. Of course, the anions change the hydrogen-bonded structure of water, depending on the charge and the size of the anion (trivalent anion $>$ divalent anion $>$ univalent anion) or interact with the lactam ring of the polymer in aqueous solutions.^{11,12} However, only a small shifting (208.0–208.5 nm) effect of the chloride, sulfate, and carbonate is observed in PVP aqueous inorganic salt solutions in the same concentration range (3.5×10^{-2} – 1.0×10^{-3} mol L $^{-1}$) of NaCl, Na₂SO₄, and Na₂CO₃.

The hydrodynamic properties of polymer solutions are very sensitive to molecular association. Thus, information on the presence/the extent of molecular association can be gathered from any experimental method involving aqueous/non-aqueous polymer solutions. Among different experimental techniques, the viscosimetric method has been very frequently used due to its simplicity and high sensitivity to aggregation.^{13,14}

The concentration dependence of the viscosity of dilute polymer solutions (in this study, in the range of 0.215–0.400 g dL $^{-1}$) is described by the well-known Huggins equation:

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

where $\eta_{sp/c}$ and $[\eta]$ are the specific and intrinsic viscosities of the solutions, respectively, and k_H is the Huggins constant. The intrinsic viscosity is a measure of the shape and the size of the polymer in solution, while Huggins constant is a measure of polymer–solvent interaction. The slope, $k_H[\eta]^2$, is generally taken as a measure of interaction between the polymer molecule and the solvent.¹⁵ In Figure 5, the dependence of specific viscosity of PVP in water, urea, guanidinium chloride, guanidinium sulfate and carbonate solutions are shown. In order to make a better comparison of the effect of denaturing agents on the $[\eta]$ values and slopes of the Huggins equation, all these calculated values are also listed in Table I. Addition of denaturing agents has led to a decrease in the

Table I Viscosity Characteristics of PVP in Aqueous Solutions in the Presence of Denaturing Agents

	$[\eta]$ (dL g ⁻¹)	$k_H[\eta]^2$
Water	1.137	0.385
Urea ^a	1.139	0.323
Guanidinium chloride ^a	1.102	0.289
Guanidinium sulfate ^a	1.059	0.125
Guanidinium carbonate ^a	1.053	0.123

^a 0.1M denaturing agent solutions.

viscosities of aqueous PVP solutions at 25°C. The effects of denaturing agents on the decrease of the intrinsic viscosity of PVP solutions are as follows: (1) Urea has no effect on the decrease of the intrinsic viscosity of PVP solution. Intrinsic viscosity of PVP is observed as 1.139 in urea solution, while for the aqueous PVP solution $[\eta] = 1.137$ dL g⁻¹. (2) Guanidinium sulfate and carbonate have the greatest effect on the decrease of the intrinsic viscosity of polymer solution. The value of $[\eta] = 1.137$ dL g⁻¹ in aqueous solution has dropped to 1.059 in guanidinium sulfate and to 1.053 in guanidinium carbonate. (3) The decreasing order of effectiveness of the denaturing agents in reducing the intrinsic viscosity is as follows: guanidinium carbonate \approx guanidinium sulfate > guanidinium chloride > urea \approx water.

A large $k_H [\eta]^2$ value indicates more complete solvation or more association of the polymer with solvent molecules. The slope values take the continuously decreasing values as: 0.385, 0.323, 0.289, 0.125, and 0.123 for water, urea, guanidinium chloride, and sulfate and carbonate, respectively.

The observed decrease in both the intrinsic vis-

cosity and the slope values as well as the shift of λ_{\max} of PVP–aqueous solutions could be taken as an indication of the effectiveness of the denaturing agent in breaking the molecular association in aqueous media.

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