

# Effects of Inorganic Salts on the Spectral Behavior of Poly(*N*-vinyl-2-pyrrolidone) in Aqueous Solutions

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**ABSTRACT:** Electronic spectral behavior of poly(*N*-vinyl-2-pyrrolidone) (PVP) was determined in aqueous solutions including a variety of inorganic salts (phosphates, mono- and dihydrogen phosphates, sulfates, chlorides, nitrates, bisulfites, and persulfates) for several concentrations. The  $n \rightarrow \pi^*$  excitations are shifted to longer wavelengths depending on the nature and the concentration of salt. The resulting dependence of  $\lambda_{\max}$  on the molar concentration can be expressed to show the increasing effect of anionic and cationic species in bathochromic shift. The increasing order of effectiveness of anions in shifting the  $\lambda_{\max}$  is  $\text{S}_2\text{O}_8^{2-} > \text{S}_2\text{O}_5^{2-} > \text{PO}_4^{3-} > \text{HPO}_4^{2-} > \text{SO}_4^{2-} > \text{H}_2\text{PO}_4^{2-} > \text{Cl}^-$ . The order for the cation is as  $\text{Na}^+ \approx \text{K}^+ \approx \text{NH}_4^+$  in the 0.1–0.6M concentration range and  $\text{Na}^+ \approx \text{K}^+ > \text{NH}_4^+$  in  $> 0.6M$  aqueous solutions. The changes observed in  $\lambda_{\max}$  by the salt were correlated with the changes occurring in the structure of water and the polymer–solvent interactions. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 1434–1439, 2000

**Key words:** poly(*N*-vinyl-2-pyrrolidone); inorganic salts; spectrophotometric behavior

## INTRODUCTION

Organic and inorganic additives affect the different solution properties of water-soluble nonionic polymers.<sup>1–7</sup> Poly(*N*-vinyl-2-pyrrolidone) (PVP) is a nonionogenic synthetic water-soluble polymer. PVP is rather hygroscopic and because of its hydrophilicity and high proclivity to complexation/association, it is widely used in many technologies. Especially, the existing similarities between the structure of PVP and proteins have led to proposing PVP as a synthetic polymeric model for proteins.<sup>8,9</sup> PVP has a polar lactam group and also a hydrophobic structure and it exhibits a series of interactions toward small dissolved molecules.

In previous studies, the phase separation and theta temperature of PVP, in the presence of denaturing agents,<sup>10</sup> inorganic salts,<sup>11</sup> and their

thermodynamic behavior,<sup>12,13</sup> viscosity characteristics,<sup>14</sup> and complexation with certain transition metal chlorides<sup>15</sup> were reported. These studies revealed that the dynamic and thermodynamic behavior of polymer mainly depend on the nature of the additive, their concentrations, and the temperature.

The main purpose of the present study is to investigate the electronic spectral behavior of aqueous PVP solutions in the presence of certain inorganic salts, determine the maximum wavelengths of  $n \rightarrow \pi^*$  electronic excitations, indicate an anionic and a cationic sequence, and compare the ionic sequences found by different methods.

## EXPERIMENTAL

The polymer sample used in this study was commercial BDH (British Drug House, England) poly(*N*-vinyl-2-pyrrolidone) with a nominal molecular weight of 44,000 g mol<sup>-1</sup>. The weight-average molecular weight of the sample was de-

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terminated 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 of vertically unpolarized light of 436-nm wavelength. The interpretation of light scattering data was based on the Zimm method, expressed in the general form:

$$K_c/R_\theta = 1/M_w[1 + (16\pi^2/3\lambda^2)\langle s^2 \rangle_z \sin^2 \theta/2] + 2A_2c + \dots$$

and the  $dn/dc$  value of the polymer in chloroform solution is taken as 0.108 mL g<sup>-1</sup>.<sup>16</sup> The polymer sample had a weight-average molecular weight,  $M_w = 78,000$  g mol<sup>-1</sup>, second virial coefficient  $A_2 = 7.07 \times 10^{-4}$  cm<sup>3</sup> mol g<sup>-1</sup>, and root-mean-square radius of gyration  $\langle s^2 \rangle^{1/2} = 7.2 \times 10^{-9}$  m. The number-average molecular weight of PVP sample was also determined by Knauer membrane osmometer and found to be  $M_n = 4.6 \times 10^4$  g mol<sup>-1</sup> with  $A_2 = 2.20 \times 10^{-3}$  cm<sup>3</sup> mol g<sup>-2</sup> in aqueous solutions.

All the inorganic salts (NaNO<sub>3</sub>, NaCl, KCl, NH<sub>4</sub>Cl, Na<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, Na<sub>3</sub>PO<sub>4</sub>, Na<sub>2</sub>HPO<sub>4</sub>, NaH<sub>2</sub>PO<sub>4</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub>, K<sub>2</sub>S<sub>2</sub>O<sub>5</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) were of reagent grade and obtained from BDH and Fisher Scientific Company. Deionized and twice-distilled water was used for the preparation of PVP/inorganic salt solutions and all the polymer solutions were freshly prepared and used.

The spectrophotometric measurements were carried out by a Hitachi 100–60 model UV-Vis double-beam spectrophotometer at room temperature. Each spectrum was recorded twice and the maximum wavelengths were determined both digitally and on recording paper. The possible impurities were eliminated by dialyzing the aqueous polymer solutions through cellulose nitrate membranes for 3 days. The same spectral behavior was observed for the dialyzed and undialyzed polymer samples. Some selected samples were also checked by using another spectrophotometer, Hitachi 150–20 model double-beam spectrophotometer at room temperature, and no spectral differences were observed for both instruments in the UV region. Electronic spectra of aqueous PVP solutions were followed at constant polymer concentration (0.05 g dL<sup>-1</sup>). The multivalent cations are not used in this study because of the compl-

exation occurring between polymer and multivalent cations in a solution which may in turn screen the effect of anions.

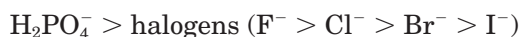
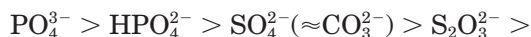
## RESULTS AND DISCUSSION

PVP contains a polar carbonyl group on the lactam ring and the formation of hydrogen bonding, existing between the carbonyl group, and certain polar solvents (water, alcohols, chloroform, etc.) can be followed by a spectrophotometric technique.<sup>17</sup> It is obvious that various additives affect the degree of hydrogen bonding (or molecular association) existing between the polymer and the solvent molecules. Electronic spectral behavior of aqueous PVP solutions was also investigated by UV-Vis spectrophotometry in the presence of certain denaturing agents.<sup>18</sup> The  $n \rightarrow \pi^*$  electronic excitations were observed to shift to longer wavelengths (bathochromic shift) with a variety of denaturing agents (urea, guanidinium sulfate, guanidinium carbonate, guanidinium chloride) depending on their concentrations. In this previous study, the observed shift of  $\lambda_{\max}$  for PVP/aqueous solutions, as well as the decrease in the intrinsic viscosity characteristics, was interpreted by the effectiveness of the denaturing agents in the rupture of hydrogen bonds between the polymer and the solvent molecules. Naturally, the observation of strongly hydrogen-bonded species needs high excitation energy or, vice versa, low excitation at maximum wavelength. Similar  $\lambda_{\max}$  shifts were also observed in PVP/aqueous salt solution system depending on the nature of the salt and their concentrations. Before discussing the spectrophotometric behavior of PVP/aqueous salt solution system, it is better to recognize the structure of water and the influence of electrolytes.

One of the most important questions in applied chemistry is the structure of water in the presence/absence of additives in solution.<sup>19,20</sup> The model of Frank and Wen<sup>21</sup> still provides a basis for discussing water which is supposed to consist of three regions in the presence of ionic species in aqueous solutions. Region A is the innermost region of polarized bound-water molecules around the ion (cation or anion); B, comprising the water molecules partially ordered by region A, the electronic field of the ion; and third, Region C, where the intermolecular hydrogen bonding occurs as in bulk water. Region B can be considered as one where the normal hydrogen-bonded structure was destroyed and the size of this region depends on

the nature of central ion (univalent, divalent, etc.).

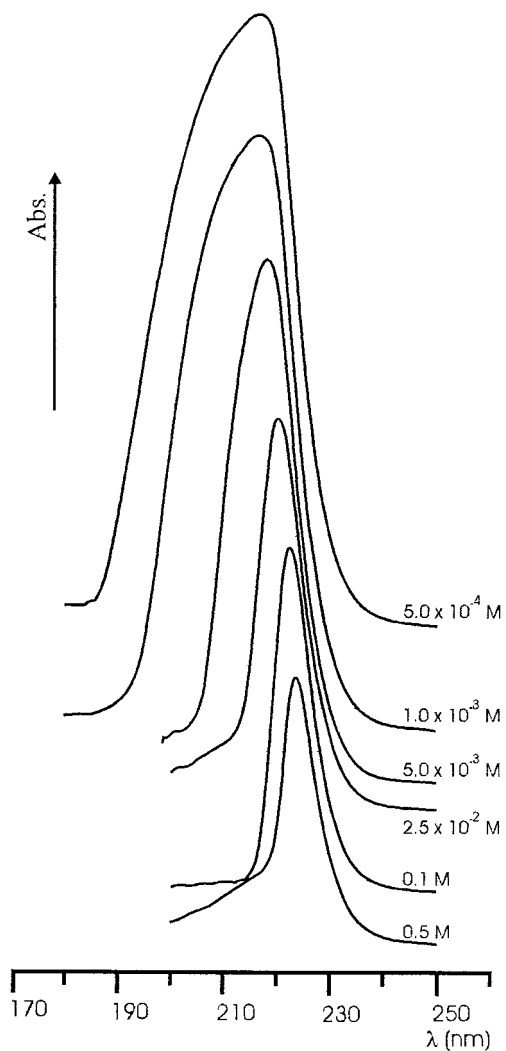
The effects the solution behavior of macromolecules and the orders for anions and cations were obtained for different salts when added to aqueous solutions of amino acids,<sup>22</sup> collagen, and gelatin.<sup>23</sup> Hofmeister has investigated the precipitation of proteins in the presence of salts and the Hofmeister sequence of decreasing effect in reducing the cloud point temperature ( $T_{cp}$ ) for anions incorporating some of the previous results can now be extended on molar concentration basis as follows:



Most applications of absorption spectroscopy to organic compounds are based on transitions of  $n$  or  $\pi$  electrons to the  $\pi^*$  excited state because the energies required for these processes bring the absorption peaks into an experimentally convenient spectral region. The main characteristic difference between the two types of absorption ( $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$ ) may be interpreted by the effect of solvent on the wavelength of the peaks and/or the symmetry of distribution as well as the molar absorptivities. The peak arising from  $n \rightarrow \pi^*$  transitions are generally shifted to shorter wavelengths as the polarity of the solvent is increased. Usually, but not always, a reverse behavior (red shift) is observed for  $\pi \rightarrow \pi^*$  transitions. The competition of these two electronic transitions can easily be followed by peak symmetry. As can be clearly seen from Figure 1, these two effects were also observed in this study, where the peak symmetry was disturbed by increasing polarity of the solvent (water) with shifts toward shorter wavelengths due to the occurrence of  $\pi \rightarrow \pi^*$  transitions besides  $n \rightarrow \pi^*$  transitions.

In spectrophotometric studies of aqueous salt solutions of PVP, it is observed that the  $n \rightarrow \pi^*$  electronic excitations (carbonyl group of the lactam ring) were shifted to longer wavelengths depending on the nature and the concentrations of the salt. The effect of sodium phosphate on the  $n \rightarrow \pi^*$  electronic excitations for PVP in aqueous solutions can be seen in Figure 1. The most important effects of  $\text{PO}_4^{3-}$ ,  $\text{HPO}_4^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{H}_2\text{PO}_4^-$ , and  $\text{Cl}^-$  on the shift of  $\lambda_{\max}$  of PVP/aqueous salt solutions are as follows:

- i. The shift in  $\lambda_{\max}$  of PVP/aqueous salt solutions depends on the molar concentrations

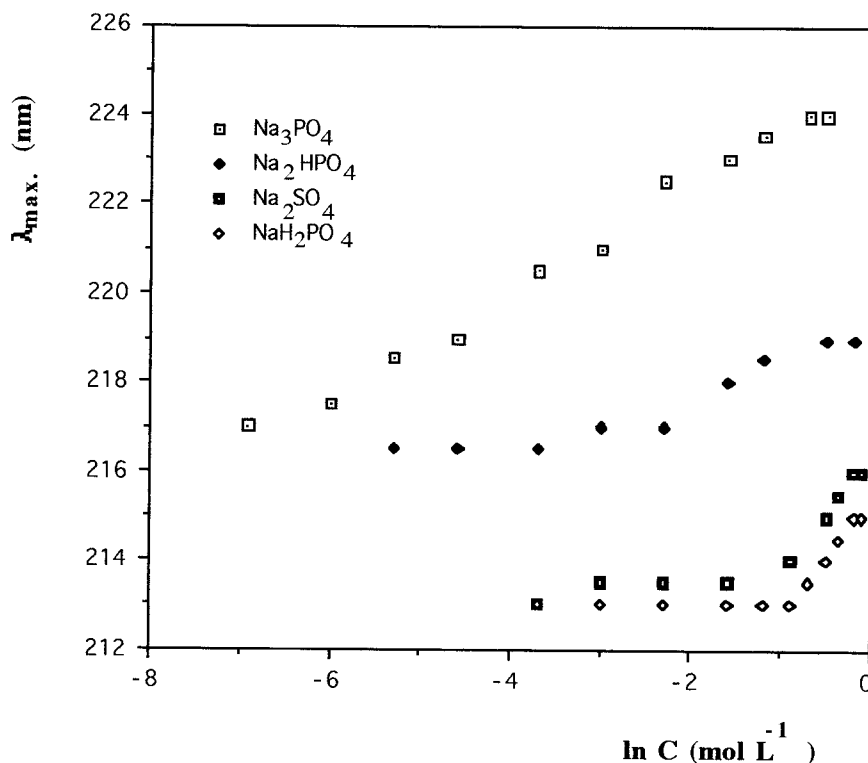


**Figure 1** The UV absorption spectra of PVP in the presence of  $\text{Na}_3\text{PO}_4$  in aqueous solutions.

- of inorganic salt and the  $\lambda_{\max}$  values shift to longer wavelengths by increasing the salt concentrations (Fig. 2),
- ii. The salt  $\text{NaCl}$  has the smallest effect on the shift of  $\lambda_{\max}$  of PVP solutions,
- iii. The salt  $\text{Na}_3\text{PO}_4$  has the greatest effect on the shift of  $\lambda_{\max}$  of polymer in aqueous solutions,
- iv. The shifting order of effectiveness of the salt increasing the  $\lambda_{\max}$  of this series (series A) is

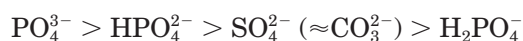


The anionic sequence found in this study is in good agreement with the series found for sodium



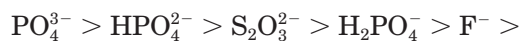
**Figure 2** Changing of the maximum wavelength of PVP in the presence of sodium salts in aqueous solutions.

anions in decreasing order of effectiveness in coacervation of PVP in aqueous salt solutions,<sup>24</sup> tribasic sodium phosphate > dibasic sodium phosphate > monobasic sodium phosphate. The sequence of effectiveness of the anions in reducing the theta temperature and the cloud point temperature of polymer,<sup>11</sup> is



(for sodium and potassium anions)

and the sequence of effectiveness of the anions in reducing the thermodynamic magnitudes for poly(ethylene oxide) (PEO)/aqueous salt solution system, is



as was reported by Ataman,<sup>25</sup> on the basis of molar concentrations.

Verrall's<sup>26</sup> anionic sequence and James and Frost's<sup>27</sup> studies for the decreasing ability to

destroy the hydrogen-bonded structure of water, based on infrared, and Hindman's<sup>28</sup> anionic sequence based on nuclear magnetic resonance studies are in general agreement with the trends found in electronic spectral studies. These spectrophotometric studies revealed that the trivalent anions are the most effective in both destroying the hydrogen-bonded structure of water and the interactions between the polymer segments and the solvent molecules. However, the monovalent anions (in this study  $\text{Cl}^-$  and  $\text{NO}_3^-$ ) follow the structure-making sequence and no significant  $\lambda_{\text{max}}$  shifting is observed in both  $\text{NaCl}$  and  $\text{NaNO}_3$  (almost  $\lambda_{\text{max}} = 213 \pm 0.5$  nm) solutions in the concentration range of 0.1–1.0M. Thus, the observed  $\lambda_{\text{max}}$  values are smaller than the univalent anion  $\text{H}_2\text{PO}_4^-$  and also agree with the sequence mentioned above.

The effects of cations on the shift of  $\lambda_{\text{max}}$  PVP/ aqueous salt solutions were also investigated and no significant spectral behavior was observed. The cationic sequence depends on the anion, especially for the relative position of the sodium and potassium ion. Henceforth, the cation sequence of the shifting in  $\lambda_{\text{max}}$  for PVP in aqueous solutions

**Table I** Maximum Wavelengths of Poly(*N*-vinyl-2-pyrrolidone) in the Presence of Certain Inorganic Salts in Aqueous Solutions

C(M)	$\lambda_{\max}$ (nm)		
	Na <sub>2</sub> SO <sub>4</sub>	K <sub>2</sub> SO <sub>4</sub>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>
0.1	213.5	213.5	213.0
0.2	213.5	213.5	213.5
0.3	213.5	213.5	213.5
0.4	214.0	213.5	213.5
0.5	214.0	214.0	214.0
0.6	215.5	215.5	215.0
0.7	215.5	215.5	215.0
0.8	216.0	216.0	215.0

C(M)	$\lambda_{\max}$ (nm)		
	NaCl	KCl	NH <sub>4</sub> Cl
0.1–1.0	213.0	213.0	213.0
1.2	214.0	214.0	213.0
1.4	215.0	215.0	213.5
1.6	216.5	216.5	214.0

of sulfates are given in Table I and can be formulated as

$$\text{Na}^+ \approx \text{K}^+ \approx \text{NH}_4^+ \text{ (0.1–0.6M concentration range)}$$

$$\text{Na}^+ \approx \text{K}^+ > \text{NH}_4^+ \text{ (>0.6M solutions)}$$

and for PVP in aqueous solutions of chlorides,

$$\text{Na}^+ \approx \text{K}^+ \approx \text{NH}_4^+ \text{ (0.1–1.0M concentration range)}$$

$$\text{Na}^+ \approx \text{K}^+ > \text{NH}_4^+ \text{ (>1.0M solutions)}$$

The cationic sequences found in this work and the sequence reported by Ataman<sup>25</sup> for PEO/aqueous salt solution system ( $\text{Na}^+ \approx \text{K}^+ > \text{NH}_4^+$ , for chloride), and those by Boucher and Hines<sup>2</sup> ( $\text{Na}^+ \approx \text{K}^+ > \text{NH}_4^+$ , for sulfate) are in good agreement. However, the cationic sequences found as a consequence of decreasing salting out power for PVP<sup>11</sup> ( $\text{Na}^+ > \text{K}^+$ ), measurements of shrinkage temperature of gelatin<sup>23</sup> ( $\text{Na}^+ > \text{K}^+$ ), and the salting out of amino acids<sup>22</sup> ( $\text{Na}^+ > \text{K}^+$ ) are different, and certain irregularities were observed for aqueous salt solutions of PVP.<sup>24</sup>

Despite keen interest in the binding properties of persulfate ( $\text{S}_2\text{O}_8^{2-}$ ) containing PVP aqueous solutions, no references were found in literature concerning the effect of bisulfite anion ( $\text{S}_2\text{O}_5^{2-}$ ) on dynamic properties of polymer in aqueous solutions. The effect of persulfate, depending on its concentration, on the properties of aqueous PVP solutions might be different and can be explained by different methods. It is known that the aqueous solutions of PVP are converted to stable gels by the reaction with  $\text{K}_2\text{S}_2\text{O}_8$ .<sup>29,30</sup> However, the mechanism of PVP/ $\text{K}_2\text{S}_2\text{O}_8$  linkage is not known exactly and it is also reported that in addition to intermolecular crosslinking processes, chain scission, and other competing reactions may take place in aqueous solutions. The most interesting feature of gelation of PVP with persulfate is the requirement of an extremely high concentration of persulfate to form the network structure.<sup>31</sup> However, in kinetic investigations<sup>32</sup> and in the radiation studies<sup>33</sup> of the persulfate-containing polymer solutions, it is revealed that the chain-scission process is more dominant than crosslinking for the lower amount of persulfate in aqueous solutions.

In spectrophotometric studies of bisulfite- and persulfate-containing aqueous solutions of PVP, it is indicated that the  $n \rightarrow \pi^*$  electronic excitations were more significantly shifted to longer wavelengths in more dilute solutions of bisulfite and persulfate ions (in the range of  $0.62\text{--}5.00 \times 10^{-2}\text{M}$ ) (Table II). The effectiveness of the bisulfite and persulfate salts in shifting the  $\lambda_{\max}$  is

$$(\text{S}_2\text{O}_5^{2-}) > (\text{S}_2\text{O}_8^{2-}) > \text{series A,}$$

and the cationic behavior is found as

$$\text{Na}^+ \approx \text{K}^+ \text{ (Table 2).}$$

Changes in the PVP and water structure, due to the addition of inorganic salts (depending on the nature and concentration of salt), are responsible for the different properties of dilute polymer solutions. If certain salts are added to aqueous solutions of PVP, the anions and cations introduced disturb the regularity of hydrogen-bonded structure of water and should affect the strength of the hydrogen bonding already existing between the polymer and solvent molecules. The effect of salts on the phase separation, polymer dimensions,



**Table II** Maximum Wavelengths of Poly(*N*-vinyl-2-pyrrolidone) in the Presence of Sodium and Potassium Bisulfite and Persulfate in Aqueous Solutions

C(M) × 10 <sup>-2</sup>	$\lambda_{\max}$ (nm)	
	Na <sub>2</sub> S <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> S <sub>2</sub> O <sub>5</sub>
0.62	220.0	220.0
1.25	221.0	221.0
2.50	221.5	221.5
5.00	222.5	222.5

C(M) × 10 <sup>-2</sup>	$\lambda_{\max}$ (nm)	
	Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>
0.62	221.0	221.5
1.25	223.0	223.0
2.50	225.0	225.0
5.00	227.0	226.5

and thermodynamic parameters of PVP in aqueous solution,<sup>11,13,24</sup> as well as poly(ethylene oxide)/aqueous salt solution system,<sup>2,25</sup> the salt effect to aqueous solutions of amino acids, collagen and gelatin,<sup>22,23</sup> and the precipitation of proteins in the presence of salts appeared to be a combined effect of the anion and cation, with the anion effect being predominant. In the present study, the effect of certain salts on the spectral behavior of PVP solutions was investigated and a parallelism found between the hydrodynamic/thermodynamic and the spectral behavior, indicating exactly the same anionic sequences. The observed facts imply that the changing of the structure of water and the effects to polymer-solvent interactions are the main factors responsible for the spectral behavior of PVP in aqueous solutions.

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