

## Effect of Metal Chlorides on the Spectral Behavior of Poly (vinylpyrrolidone) in Aqueous Solution

M. S. KHAN\* AND K. GUL

*National Center of Excellence in Physical Chemistry,  
University of Peshawar, Peshawar 25120 Pakistan*

(Received 20<sup>th</sup> March, 2004, revised 27<sup>th</sup> February, 2006)

**Summary:** Electronic spectral behavior of poly (vinylpyrrolidone) i.e. PVP, was determined in aqueous solution including a variety of metal chlorides (MgCl<sub>2</sub>, CaCl<sub>2</sub>, KCl and BaCl<sub>2</sub>). The  $n \rightarrow \pi^*$  excitations shifted to longer wavelengths depending on the nature and the salt concentration of different cations. The order of effectiveness of cation is  $K^{1+} > Ca^{2+} > Mg^{2+} > Ba^{2+}$  for poly (vinylpyrrolidone) solution. Changes observed in  $\lambda_{max}$  by the salt were correlated with the polymer solvent interactions. These changes were attributed to interaction of PVP molecules with the co solute molecules. As the concentration of the co solute increased, a red shift in the peaks was observed indicating an increase in interaction between PVP and co solutes.

### Introduction

Organic and inorganic additives affect the different solution properties of water-soluble non-ionic polymers [1-7]. PVP [polyvinyl pyrrolidone] sometimes considered as a model compound for proteins, has increasing pharmaceutical importance. Chemically PVP is inert nontoxic, and has a strong tendency for complex formation with small molecules [8].

Polymer-metal complexes are formed as a result of the reaction between macromolecular functional groups and metals ions [9]. Usually the bond between metal ions and polymers ligands occurs by donor acceptor interactions with the formation of a coordination sphere or as a result of the exchange of the protons in the ligands by metal ions with the formation of ionic bonds. Metal ions are the acceptors, polymer chain atoms like -O-, N-, S-, F-, Cl-, giving a pair of electrons for formation of the bond, are the donors [10]

There has been a growing interest a few years ago, to investigate the interactions between metal ions and neutral macromolecules, which have no electric charges on the molecular chains. Such interactions play a fundamental role not only in the selective transport of metal ions through membranes, and in the solubilisation of inorganic salts in organic solvents or phase transfer catalysis by polymeric additive but also in the biological enzyme systems [8].

The addition of salt to the aqueous solutions of polymer chains produces hydration and could cause a disruption of oriented water molecules that surround the polymer. According to Frank and Wen addition of salts to the solution affects the hydrogen-bonded structure of water, depending on the nature of the salts [11]. The effect of the anions on the hydrogen-bonded structure of water and the phase separation temperature of aqueous PVP solutions, were studied. These studies revealed, that the salt of trivalent anion has the greatest, but the salt of univalent anion [in that particular study, chloride] has the smallest effect on the hydrogen bond disruption of water and the phase separation of PVP /aqueous solution [12].

Since the polymer is soluble in a variety of solvents, interaction of PVP with small solvent molecules of different solvating power is possible, it is observed that change in the water structure around the polymer caused by the added salt could play an important role in its behavior in solution [13].

In the case of PVP structure, polymer cations N-C=O units on the lactam ring, and these polar groups are involved for the association with water molecules by hydrogen bonding [14]. The association of lactam units (especially, with the unshared electron pairs of carbonyl) of PVP with water has been observed both by viscometric and spectrophotometric studies [15].

\*To whom all correspondence should be addressed.

## 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, alcohol, chloroform, etc) can be followed by spectrophotometric technique [16]

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 solution was also investigated by UV-Visible spectrophotometry in the presence of certain denaturing agent [17].

The  $n \rightarrow \pi^*$  electronic excitations were observed to shift longer wavelengths (bathochromic shift) with variety of denaturing agents (urea, guanidinium sulfate, guanidinium carbonate, guanidinium chloride) depending on their concentrations. In this previous study, the observed shift of  $\lambda_{\max}$  of 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 bond between the polymer and the solvent molecules.

The possibility of forming hydrogen bonding and some other types of association with various solvents (or solvent plus co solute or solvent mixtures) should affect the many observable properties of the system containing PVP. In the electronic spectral behavior of PVP it is observed that the  $n \rightarrow \pi^*$  excitation were shifted to the longer wavelengths in aqueous and non-aqueous PVP solution [12]. Similar wavelength shifts were also observed in the present study in PVP/metal chloride aqueous system. It is possible to explain the observed shifting phenomena in aqueous metal chloride solution of PVP as a result of several combine effects, i.e., change in the water structure, and the polymer hydration sheath due to added metal chloride and the interaction of the polymer with metal cations. Naturally, the observation of strongly bonded species needs high excitation energy and vice versa, low excitation at maximum wavelength. Changes in the PVP and water structure, due to the addition of inorganic salts (depending on the nature and concentration of salts), are responsible for their different properties of dilute polymer solutions. If certain salts are added to aqueous solution 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 effects of metal cations on the longest wavelength excitation of PVP are seen in Fig 1. On the basis of molar concentration the following order of bathochromic shifts are obtained:

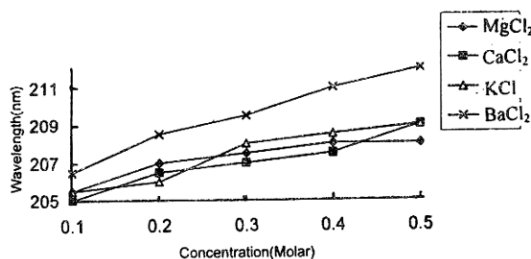
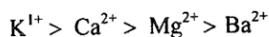


Fig. 1: Plot of wavelength vs concentration.

Table-I: Maximum wavelength (nm) of PVP in the presence of certain metal chloride in aqueous solution

$\lambda_{\max}$ (nm)	KCl	CaCl <sub>2</sub>	MgCl <sub>2</sub>	BaCl <sub>2</sub>
Con. (Molar)				
0.1	204.7	204.2	205.1	205.3
0.2	205.3	205.7	206.3	205.8
0.3	206.7	206.4	206.7	206.5
0.4	207.5	207.0	207.0	207.0
0.5	208.1	207.2	207.2	207.2

## Experimental

The PVP sample used in this study was commercial product of BDH. Weight-average molecular weight of PVP sample was determined by using a "Brice-phenix light scattering photometer, 2000 Series". It has a weight-average molecular weight,  $M_w = 700,000 \text{ g mol}^{-1}$  as determined in chloroform at 30°C. All the inorganic salts (MgCl<sub>2</sub>, CaCl<sub>2</sub>, KCl and BaCl<sub>2</sub>) were of reagent grade and obtained from BDH. Deionized and twice-distilled water was used for the preparation of PVP/metal chlorides solutions and all the polymer solutions were freshly prepared and used. The UV-VIS spectra were recorded by using a SHIMADZU 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 solution mixtures were prepared keeping polymer concentration constant (0.005%) with varying concentrations of metal chlorides in the ranges 0.1-0.5M.

### Conclusions

In presence of PVP peaks appear in the absorption range of the instrument from 200 nm to 210nm. From appearance of these peaks it is inferred that PVP interacts with cosolutes in aqueous medium. The peaks appeared in presence of PVP red shift with increase in concentration of cosolutes.  $n \rightarrow \pi^*$  excitations were shifted to the longer wavelengths, which was explained due to synergistic effects such as the change in water structure, in the polymer hydration sheath with the addition of metal chloride and the interaction of the polymer with metal cations. The shifting effect of the anion was not as significant as the cations. The observed fact 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. The effectiveness of cation interaction with PVP decrease in order of:  $K^{1+} > Ca^{2+} > Mg^{2+} > Ba^{2+}$

### References

1. E. A. Boucher and P. M. Hines, *J. Polym. Sci., Poly. Phys. Ed.*, **16**, 501 (1978).
2. E. A. Boucher and P.M.Hines, *J. Polym. Sci., Poly. Phys.Ed.*, **14**, 2241 (1976).
3. A. Guner and O.Guven, *Makromol. Chem.*, **179**, 2789 (1978).
4. M. A Basedow, K. H. Ebert and W. Feigenbutz, *Makromol. Chem.*, **181**, 1071 (1980).
5. K. H. Ebert, *Montash Chem.*, **98**, 1128 (1967).
6. A. Guner, *J. Appl. Polym.Sci.*, **56**, 1561 (1995).
7. I. Uraz and A. Guner, *Carbohydr. Polym.*, **34**, 127 (1997).
8. I. R. Prohaska and O.A. Zukasewayez *Science*, **213**, 559 (1983).
9. K. Geckeler, *Pure Appl. Chem.*, **52**, 1883 (1980).
10. P. I. Fracex and S. M. Hass, *Nature*, **107**, 1889 (1977).
11. O. Guven and E. Eltan, *Makromol Chem.*, **182**, 3129 (1981).
12. L. Turker, A. Gunner, F. Yigit and O. Guve, *Colloid and Polym. Sci.*, **268**, 337 (1990).
13. A. Guner, *J. Appl. Polym. Sci.*, **62**, 785 (1996).
14. H. S. Frank and W. Y. Wen, *Discuss. Faraday Soc.*, **24**, 133 (1957).
15. A. Guner and M. Ataman, *Colloid and Polym. Sci.*, **272**, 175(1994).
16. R. D. Windberg and E. F. Bally, *J. Polym Sci.*, **A1.4**, 563 (1996).
17. A. Guner, *J. Appl. Poly. Sci.*, **65**, 1307 (1997)