

INTERACTION OF POLYVINYLPIRROLIDONE WITH METAL CHLORIDE AQUEOUS SOLUTIONS*

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Abstract Interactions of polyvinylpyrrolidone (PVP) with metal chlorides (MgCl_2 , CaCl_2 , KCl and BaCl_2) have been investigated by viscometric and spectrophotometric techniques in aqueous solutions. Intrinsic viscosity $[\eta]$ of (PVP) has shown a discontinuity with varying concentration of metal chlorides. The decreasing order of effectiveness of cation is $\text{K}^{1+} > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{Ba}^{2+}$ for poly(vinylpyrrolidone) solution. Changes in the absorption spectra of the cosolutes were observed in the presence of PVP in the lower limit of the UV-visible region *i.e.* 200–210 nm. These changes were attributed to interaction of PVP molecules with the cosolute molecules. As the concentration of the cosolute increased, a red shift in the peaks was observed, indicating an increase in interaction between PVP and cosolutes.

Keywords Polyvinylpyrrolidone, PVP, Metal chlorides, Interaction, Intrinsic Viscosity

INTRODUCTION

Polymer-metal complexes are formed as a result of the reaction between macromolecular functional groups and metals ions^[1]. Usually the bond between metal ions and polymer 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 with 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^[2].

Polymer-metal complexes are used as a basis for the construction of a vast variety of biomedical preparations and drugs. Metal ions as well as other biphilic low molecular weight compounds (surface active substances) possess the ability to bind to neutral or weakly charged water soluble polymers, and they confer on them adhesive properties and the capacity to form complexes with complementary surfaces^[3].

There was a growing interest a few years ago in investigating 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 dissolution of inorganic salts in organic solvents or phase transfer catalysis by polymeric additive, but also in biological enzyme systems^[4].

Polyvinylpyrrolidone (PVP), 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^[4].

The present study has been undertaken to determine the interaction of PVP with inorganic salts by viscometric and spectrophotometric techniques. This will help in understanding the interaction of an important polymer like PVP with common inorganic salts and will help in application of this polymer in drugs and pharmaceutical industries where interaction between a polymer and salt, *etc.*, are important.

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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-Phoenix Light Scattering Photometer, BP-2000 Series. It has a weight-average molecular weight, $M_w = 700,000 \text{ g mol}^{-1}$ as determined in chloroform at 30°C . Viscosity measurements were made by using an Ubbelohde capillary viscometer at 25°C for PVP solutions. Temperature was controlled within $\pm 0.02^\circ\text{C}$, and flow times were measured with an accuracy of $\pm 0.1 \text{ s}$. Deionised twice-distilled water was used for the preparation of solutions. The UV-Vis spectra were recorded by using a Shimadzu UV-Vis double-beam spectrophotometer at room temperature. All the metal chlorides were of reagent grade. The solution mixtures were prepared keeping polymer concentration constant (0.005%) with varying concentrations of metal chlorides in the ranges 0.1–0.5 mol/L and 0.027–0.06 mol/L for spectroscopic and viscometric studies, respectively.

RESULTS AND DISCUSSION

PVP is capable of a high degree of hydrogen bonding in aqueous and non-aqueous solvent systems^[5, 6]. The possibility of forming hydrogen bonds and some other types of association with various solvent (or solvent plus cosolute or solvent mixtures) should affect the many observable properties of the system containing PVP. In the electronic spectral behavior of PVP it was observed that the $n \rightarrow \pi^*$ excitation was shifted to longer wavelengths in aqueous and nonaqueous PVP solution^[6]. 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 combined 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.

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 is obtained:

$$\text{K}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{Ba}^{2+}$$

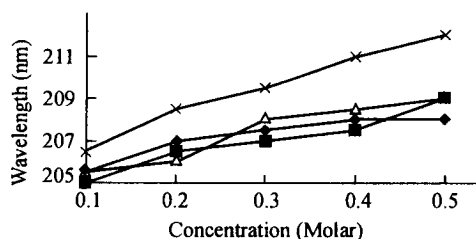


Fig. 1 Effect of metal cations on the wavelength excitation of PVP

◆ MgCl, ■ CaCl₂, △ KCl, × BaCl₂

The viscometric behaviors of PVP in K^+ , Mg^{2+} , Ca^{2+} and Ba^{2+} chloride solutions followed according to the well-known Huggin's equation

$$\eta_{sp}/c = [\eta] + k_H [\eta]^2 c \quad (1)$$

where η_{sp}/c is the reduced specific viscosity, $[\eta]$ the intrinsic viscosity, and k_H is the Huggin's constant. In Fig. 2, the intrinsic viscosity ratio, $[\eta]_{\text{MCl}_x}/[\eta]_{\text{H}_2\text{O}}$, of PVP is plotted against metal chloride (MCl_x) concentration (Molar).

As can be seen from this figure, the change in the intrinsic viscosity depends on the molar concentration of MCl_x . The discontinuity in the curves is apparent. The intrinsic viscosities decrease until 0.045 mol/L and then increase for CaCl_2 , KCl and MgCl_2 . In the case of BaCl_2 , intrinsic viscosities decrease around 0.053 mol/L and then increase. Although BaCl_2 brings about small changes, KCl has the strongest effect on the change of intrinsic viscosity of the polymer solution.

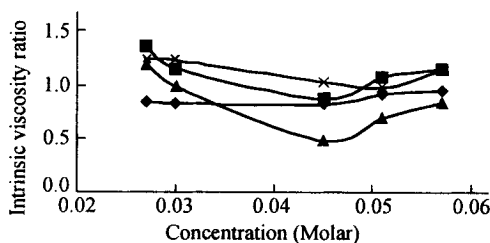


Fig. 2 Change of intrinsic viscosity ratio ($[\eta]_{MCl_x} / [\eta]_{H_2O}$) of PVP in metal chloride aqueous solution
 ◆ Mg^{2+} , ■ Ca^{2+} , ▲ K^{1+} , × Ba^{2+}

This type of discontinuity in the plots of intrinsic viscosity versus cosolute concentration has been previously observed in the system of PVP/propanol-aromatic isomeric components binary solvents^[7] and PVP/water-hydroquinone, PVP/propan-2-ol-hydroquinone, and PVP/water-ureamixtures^[8]. The discontinuity in the curve could be attributed to a probable conformational transition of the polymer chain due to the interaction of PVP with cosolutes, but no references have been found in the literature relating to the effect of metal ions on conformational changes in PVP. The results presented in Fig. 2 can be divided into two regions, and a possible explanation for each region in the curve is described below.

Region 1

The intrinsic viscosity of PVP/ MCl_x aqueous solution decreases due to intermolecular complex formation with cation. For a series of cations the decreasing order of effectiveness in interaction of PVP in aqueous solutions, on the basis of molar concentration, was found to be:

$$K^{1+} > Ca^{2+} > Mg^{2+} > Ba^{2+}$$

The intrinsic viscosity decrement indicates the contraction of the polymer coil in solution, most probably due to interaction between one cation and two or more carbonyl groups of the lactam rings. As discussed before, the lactam carbonyl of the pyrrolidone ring and cosolutes studied have binding sites and have hydrogen bonding capability. Cosolute molecules form hydrogen bonds with PVP pyrrolidone rings. This interaction of cosolute molecules with the PVP chain causes coiling of the molecule. The shrunken compact coil of PVP-cosolutes can easily pass through the capillary of the viscometer compared to the irregular molecules of PVP in absence of cosolutes and thus a decrease in viscosity occurs.

Region 2

The increase in the viscosity in this region indicates the repulsion of polymer segments of the same character, leading to an increase in dimensions. As a results of all these, the interaction between one cation and one carbonyl group of the polymer would be valid.

CONCLUSION

In the presence of PVP, peaks appeared in the absorption range of the instrument from 200 nm to 210 nm. From the appearance of the peaks it is inferred that PVP interacts with cosolutes in aqueous medium. The peaks which appeared in the presence of PVP were red shifted with increasing concentration of cosolutes. $n \rightarrow \pi^*$ excitations were shifted to longer wavelengths, which was explained as being 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 that of the cations. The change in intrinsic viscosity for PVP showed a discontinuity with concentration of metal chlorides. The effectiveness of cation interaction with PVP decreases in the order:

$$K^{1+} > Ca^{2+} > Mg^{2+} > Ba^{2+}$$

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