

Complexation of Poly(vinylpyrrolidone) and Gelatin with Some Transition Metal Chlorides in Aqueous Solution

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ABSTRACT: Complexation of poly(vinylpyrrolidone) and gelatin with certain metal chlorides (HgCl_2 , CdCl_2 , CoCl_2 , and ZnCl_2) have been investigated by viscosimetric and spectrophotometric techniques in aqueous solutions. While the change in intrinsic viscosity, $[\eta]$, of poly(vinylpyrrolidone) has shown a discontinuity with a concentration of metal chlorides, gelatin showed a steady decrease with increasing metal chloride concentration. The decreasing order of effectiveness of cations in complex formation is $\text{Hg}^{2+} > \text{Cd}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+}$ for poly(vinylpyrrolidone) and $\text{Zn}^{2+} > \text{Co}^{2+} > \text{Cd}^{2+} > \text{Hg}^{2+}$ for gelatin solutions. It has been suggested that the poly(vinylpyrrolidone)/metal cation interaction is a charge-controlled reaction, and gelatin/metal cation is a covalent coordination in character. A similar metal cation effect has been observed for poly(vinylpyrrolidone) by UV-VIS spectrophotometry. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 891–895, 1998

Key words: poly(vinylpyrrolidone); gelatin; transition metal chlorides; aqueous solutions

INTRODUCTION

Water-soluble polymers are often used in various applications, as coating agent, tablet binder, and suspending and/or viscosity modifying agents.¹ The interaction between polymer additives and organic/inorganic substances are of importance from physicochemical and biopharmaceutical aspects.

Polymer–metal complexes are used as a basis for the construction of a vast variety of biomedical preparations and drugs. Transition metal ions as well as other biphilic low molecular weight compounds (e.g., 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. Polyanions form ion-coordinate complexes with proteins by crosslinks via metal ions. Recent studies demonstrate the important role of some metals (Cu, Zn, Fe) in the functional activity of immunocomponent cell.^{2–5}

Poly(vinylpyrrolidone) (PVP), sometimes considered as a model compound for proteins,^{6,7} has increasing pharmaceutical importance. Chemically, PVP is inert, nontoxic, and has a strong tendency for complex formation with small molecules.^{8–11}

Gelatin is an albumin obtained by boiling animal tissue (collagen) under pressure with water. It is composed entirely of amino acid units joined together by peptide linkages to form a linear polymer.

PVP is readily soluble in water, whereas the characteristic property of gelatin is its ability to form a gel or become jelly in aqueous solutions at

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temperatures below 35°C. Gelatin is an amphoteric compound that combines with cations to form "gelatinates" and with anions to form "gelatin salts."

The intrinsic viscosity, $[\eta]$, is a measure of the effective hydrodynamic volume of the polymer chain in solution. It is known that variation in $[\eta]$ of polymers in different solutions results from the interaction among components of the mixtures. The influence additives on the viscosity of PVP has been studied extensively. It has been shown that the addition of denaturing agents,¹² glycine and alanine,¹³ decreases the intrinsic viscosity of PVP in water, whereas inorganic salts exhibit different influences on the viscosity.¹⁴

Rashidova et al.¹⁵ have investigated the hydrodynamic properties of dilute solutions of PVP and Co(II) complexes by viscosimetry and high-speed sedimentation methods. It has been shown that the addition of Co(II) decreases the intrinsic viscosity of PVP in water and ethanol.

The addition of salt to the aqueous solution of polymer changes the hydration and could cause a disruption of oriented water molecules that surround the polymer. According to Frank and Wen,¹⁶ addition of salts to the solution affects the hydrogen-bonded structure of water, depending on the nature of the salt. The effects of the anions on the hydrogen-bonded structure of water^{17,18} and the phase separation temperature of aqueous PVP solutions^{19,20} were studied. These studies revealed that the salts of trivalent anion have the greatest, but the salt of univalent anion (in that particular study, chloride) have the smallest effect on the hydrogen bond disruption of water and the phase separation of PVP/aqueous solutions.

In neutral and in weak basic solutions the decreasing order of effectiveness, for a series of anions, in salting out of water-soluble polymers in aqueous salt solutions was found to follow the given sequence: trivalent anions > divalent anions > univalent anions (in this group, $F^- > HCOO^- > CH_3COO^- > Cl^-$).

The aim of this study is to investigate the complexation of PVP and gelatin with transition metal (Hg, Cd, Co, Zn) chlorides at different salt concentrations by using viscosimetry and UV-VIS spectrophotometry.

EXPERIMENTAL

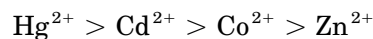
The PVP sample used in this study was commercial product of BDH, and gelatin used was Bacto

Gelatin from Difco Laboratories, USA. Weight-average molecular weight of PVP sample was determined by using a "Brice-Phoenix Light Scattering Photometer, 2000 Series." It has a weight-average molecular weight, $M_w = 548,000 \text{ g mol}^{-1}$ as determined in chloroform at 30°C. Viscosity measurements were made by using an Ubbelohde capillary viscosimeter at 25°C for PVP, and 37.5°C for gelatin solutions. Temperatures were controlled within $\pm 0.02^\circ\text{C}$, and flow times were measured with an accuracy of $\pm 0.1 \text{ s}$. Deionized and bidistilled water was used for the preparation of solutions. The UV-VIS spectra were recorded by using a Hitachi 100-60 model UV-VIS double-beam spectrophotometer at room temperature. All the transition metal chlorides were of reagent grade.

RESULTS AND DISCUSSION

PVP is capable of forming a high degree of hydrogen bonding in aqueous and nonaqueous solvent systems.^{12,21} The possibility of forming hydrogen bonding and some other types of associations with various solvents (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 is observed that the $n \rightarrow \pi^*$ excitations were shifted to the longer wavelengths in aqueous and nonaqueous PVP solutions.²¹ Similar wavelength shifts were also observed in the present study in PVP/metal chloride aqueous systems. It is possible to explain the observed shifting phenomena in aqueous metal chloride solutions of PVP as a result of several combined effects, i.e., change in the water structure, and in the polymer hydration sheath due to the added metal chloride and the interaction of the polymer with metal cations. It is mentioned above that the addition of chloride anion has a small effect on the hydrogen-bonded structure of water and the phase separation temperature of PVP. A small shifting effect of the anion is clearly shown in Figure 1 (Cl^- , NaCl). On the other hand, the cations are more effective on the wavelength shifting.

The effects of transition metal cations on the longest wavelength excitation of PVP are seen in Figure 1. On the basis of molar concentration the following order of bathochromic shifts are obtained:



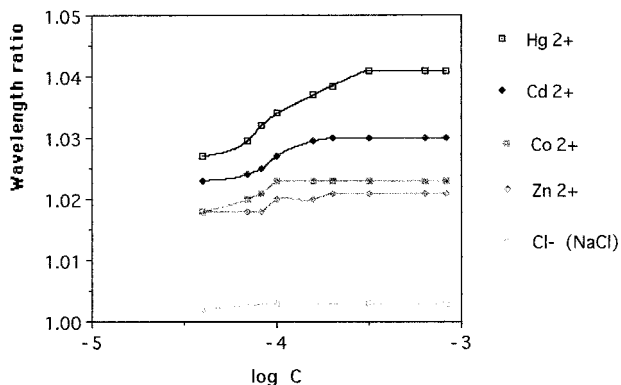


Figure 1 Change of wavelength ratio ($\lambda_{\text{MCl}_2}/\lambda_{\text{H}_2\text{O}}$) of PVP in metal chloride aqueous solutions.

The viscosimetric behaviors of PVP in Hg(II), Cd(II), Co(II), and Zn(II) chloride solutions were followed according to the well-known Huggins equation;

$$\eta_{\text{sp}/c} = [\eta] + k_{\text{H}}[\eta]2C$$

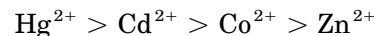
where $\eta_{\text{sp}/c}$ is the reduced specific viscosity, $[\eta]$ intrinsic viscosity, and k_{H} is the Huggins constant. In Figure 2, the intrinsic viscosity ratios, $[\eta]_{\text{MCl}_2}/[\eta]_{\text{H}_2\text{O}}$, of PVP against metal chloride (MCl_2) concentrations (as $\log C$), are shown. As can be seen from this figure, the change in the intrinsic viscosities depends on the molar concentrations of MCl_2 . The discontinuity in the curves is apparent. The intrinsic viscosities decrease until $\log C = -1.88$ ($1.32 \times 10^{-2} \text{M}$) of MCl_2 , then increase around $\log C = -1.55$ ($2.84 \times 10^{-2} \text{M}$), and then decrease again. Although ZnCl_2 brings about small changes, HgCl_2 has the strongest effect on the change of the intrinsic viscosity of polymer solution.

This type of discontinuities in the plots of intrinsic viscosity vs. cosolute concentrations have been previously observed in the system of PVP/propanol-aromatic isomeric components binary solvents²² and PVP/water-hydroquinone, PVP/propan-2-ol-hydroquinone, and PVP/water-urea mixtures.²³ 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 the effect of metal ions on conformational changes in PVP.

The results presented in Figure 2 can be divided into three regions, and a possible explanation for each region in the curve described below.

Region I

The intrinsic viscosity of PVP/ MCl_2 aqueous solutions decreased due to the intramolecular complex formation with the cations. For a series of cations the decreasing order of effectiveness in complexation of PVP in aqueous solutions, on the basis of molar concentrations, was found to be:



Intrinsic viscosity decrement shows the contraction of the polymer coil in solution, most probably due to a complexation between one cation and two or more carbonyl groups of the lactam rings.

Region II

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

Region III

The ions may change the charge distribution of the ring, and strong dipole-dipole interactions may exist or hydrophobic interactions may occur in the solution. The decrease in the viscosity may also be due to some coagulation that has occurred as the cation concentration of the solution is increased.

Investigation of the intrinsic viscosity of gela-

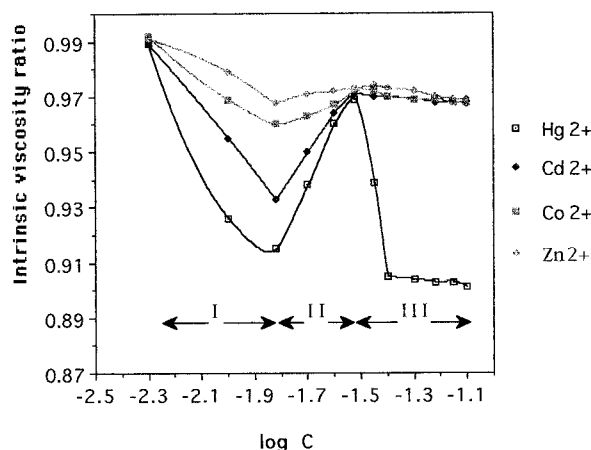


Figure 2 Change of intrinsic viscosity ratio ($[\eta]_{\text{MCl}_2}/[\eta]_{\text{H}_2\text{O}}$) of PVP in metal chloride aqueous solutions.

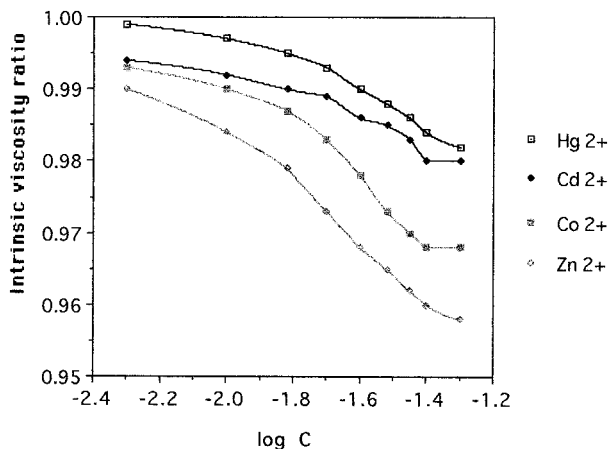
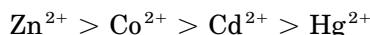


Figure 3 Chance of intrinsic viscosity ratio ($[\eta]_{MCl_2}/[\eta]_{H_2O}$) of gelatin in metal chloride aqueous solutions.

tin/cation complexes showed that the intrinsic viscosity values regularly decrease with increasing cation content (Fig. 3). This phenomenon in gelatin complexes is apparently caused by decreasing hydrodynamic dimensions of the gelatin coil due to metal-ion coordination by several donor groups of the polymer.

In contrast to the series of cations in decreasing order of effectiveness in the complexation of PVP, the series of gelatin was found to be:



The above results of complexation behavior show a similarity to those derived from Pearson's treatment of hard and soft acids and bases.²⁴ In Pearson's empirical classification hard acids (acids, mostly the cations) are mentioned as strong acceptors, soft acids are weak, hard bases (bases, organic functional groups, their anions, and anions) are strong donors, and soft bases are weak. A general principle has been proposed, according to which hard acids coordinate best with hard bases, and soft acids with soft bases.

The hard base-hard acid interaction is a charge-controlled reaction. It results mostly from a favorable electrostatic interaction between a donor of high orbital electronegativity and an acceptor of low orbital electronegativity, but the interaction between a soft acid and a soft base results the covalent coordination of a donor of low orbital electronegativity and an acceptor of high orbital electronegativity.²⁵

In a PVP/MCl₂ aqueous system, the polymer has a carbonyl group (soft base) in the ring, and the cations Hg²⁺ and Cd²⁺ are soft acids, but the

other two cations Co²⁺ and Zn²⁺ are in borderline (ref. 25, pp. 68–69). PVP/Hg²⁺ and Cd²⁺ complexation is a typical soft base-soft acid interaction and seems more predominant than PVP/Co²⁺ and Zn²⁺ complexation.

In the case of gelatin/MCl₂ aqueous solutions, gelatin has amine and carboxylate groups (hard bases), and gelatin/Co²⁺ and Zn²⁺ coordination is more probable than hard base-soft acid complexation.

Finally, the behavior of water (hard base) can be considered. While water/Hg²⁺ and Cd²⁺ interaction is improbable (hard base-soft acid), water/Co²⁺ and Zn²⁺ complexation is always probable, and the complexation between water and Co²⁺ and Zn²⁺ cations may screen the main gelatin/Co²⁺ and Zn²⁺ interactions.

CONCLUSION

Investigation studies for the complexation of PVP and gelatin with certain metal chlorides (HgCl₂, CdCl₂, CoCl₂, and ZnCl₂) were achieved in aqueous solvent systems. $n \rightarrow \pi^*$ 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 change in intrinsic viscosity for PVP showed a discontinuity with concentration of metal chlorides, whereas a steady decrease was observed for gelatin with increasing metal chloride concentration. The effectiveness of cations in complexation with PVP and gelatin solutions decreased in the order of Hg²⁺ > Cd²⁺ > Co²⁺ > Zn²⁺, and Zn²⁺ > Co²⁺ > Cd²⁺ > Hg²⁺, respectively, due to Pearson classification. Although PVP-metal cation interaction proceeded via a charge-controlled reaction, covalent coordination was obtained for gelatin-metal cation interaction.

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