Conformational and Morphological Changes in Poly(N-vinyl-2-pyrrolidone) Induced by MoCl₅

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ABSTRACT: The influence of MoCl₅ on the conformation and morphology of poly(N-vinyl-2-pyrrolidone) (PVP) was examined in this study. Viscometric, densimetric, solubility, and scanning electron microscopy techniques were carried out. A conformational transition at 75 mM of MoCl₅ and so a more compact conformation of PVP was observed. A preferential exclusion of salt from the inside the polymer structure and a preferential adsorption of water was produced. A salting-in behavior was exhibited at all concentrations studied, the binary mixture being thermodynamically unfavourable. Scanning electron microscopy shows changes on polymer structure due to its interaction with the salt, MoCl₅ being a nucleating agent for PVP.

KEY WORDS Poly(N-vinyl-2-pyrrolidone) / Molybdenum Pentachloride / Preferential Interactions / Unperturbed Dimensions / Viscometry / Densimetry / Scanning Electron Microscopy /

Studies on physiological importance of certain salts, which interact to macromolecules such as polymers, have increased. The interactions cause conformational[1-3] and morphological[4,5] changes in the structures of macromolecules as well as variation in solubility.[6-8]

The pattern of interaction phenomena is determined by a ternary system, formed by a solvent, a macromolecule and a salt. The variation of the system thermodynamic properties, caused by a change of system composition, defines the interaction nature.

Structural alterations can be studied by different techniques, as much in solid state as in dissolution.

Several molybdenum compounds are added to plastics materials to act as a nucleating agents and improve crystallinity and hence mechanical properties. Molybdenum salts increases tensile strength and durability of polymeric materials.[9] The homogeneous particle size of molybdenum is an important parameter to prevent breakdown or centres of weakness in plastics.[10]

In the present work, we used molybdenum pentachloride (MoCl₅). This halide is the most commonly encountered binary halide of the metal and finds extensive use as starting material for the preparation of inorganic an organometallic compounds.[11,12]

We used poly(N-vinyl-2-pyrrolidone) (PVP) with a large number of biological and pharmaceuticals applications[13,14]; it is a water-soluble polymer that forms complexes with other polar or ionic groups.[15-17] Complexing ability is utilized in the textile industry for improving dyeability and dye stripping, in the pharmaceutical industry and agriculture for drug dissolution and sustained release of drugs and chemicals.[18]

Viscometric, densimetric, and solubility techniques were used to study different conformational parameters such as intrinsic viscosity, unperturbed dimensions of marcromolecules and interactions such as preferential hydration, preferential interaction, transfer free energy, or polymer solubility. This way, thermodynamic and hydrodynamic properties of the system are charaterized.

In solid state, scanning electron microscopy has been used to investigate possible nucleating effects and structural modifications induced in PVP due to interaction with MoCl₅.

EXPERIMENTAL PROCEDURES

Materials

Poly(N-vinyl-2-pyrrolidones) (PVP) were purchased from Fluka Chemika (samples I, III, IV) and Merck (sample II).

Molybdenum pentachloride (MoCl₅) (Merck p.a.) was used as received.

Distilled and deionized water was employed.

Solvent and Solutions

The solvent was a binary mixture of water/metal. Molybdenum pentachloride between 5 mM and 100 mM was used. Polymer solutions were made gravimetrically; specific volumes of the binary mixtures (water/metal) at 298 K were added to accurate weights of polymer. The experiments were carried out in triplicate.

Instrumentation and Techniques

Gel Permeation Chromatography (GPC). The molecular weights of the samples were determined by this technique. A standard chromatographic experimental system was used, consisting of a Knauer pump, a Rheodyne inyector, two columns of Ultrahydrogels 250 and 1000 (Waters; molecular range 10³—10⁶), a refractive index detector and UV-V detector. GPC measurements were made in water at 298 K; the columns were calibrated with standard ethylenglycol samples and samples were eluted

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at a flow rate of $1 \, mL \, min^{-1}$. The data obtained were: I = 9765 g mol^{-1}, II = 27300 g mol^{-1}, III = 36630 g mol^{-1}, and IV = 630960 g mol^{-1}.

Viscometry. Viscosity measurements were made in a modified Ubbelohde suspended level viscometer, immersed in a thermostatically controlled bath at 298 K. The temperature control was ±0.01 K. Flow times were reproducible within ±0.03 s.

Densimetry. The densities of the solvents and solutions were measured using pycnometers with a volume between 4 and 5 mL. These were calibrated with distilled water. They were syringe-filled and put in a thermostatically controlled bath at 298 K until temperature equilibrium was reached (10 min). The filled pycnometers were weighed in a Sartorius balance, with 0.1 mg precision. Six concentrations of PVP (sample III) were used, from 0.2% wt/vol to 1% wt/vol.

Equilibrium Dialysis. Dialysis was carried out using dialysis tubing (Spectra/Por Membranes MWCO: 6—8000) to obtain density values of the solution at constant chemical potential of metals (μ_3), and PVP (sample III) was used.

Solubility Measurements. Polymer solubility (sample III) was determined by dissolving the polymer in the desired solvent until the solution turned turbid or viscous. It was then dialysed against several changes of the same solvent for *ca.* 24 h at 298 K. The solution containing the precipitate was removed from the dialysis bags and centrifuged for 10 min at 13000 rpm in a Biofuge B (Heraeus) centrifuge. The polymer concentration of the supernatant was measured spectrophotometrically using a Unicam spectrophotometer at 201 nm and 298 K by diluting it with the dialyzing solvent. This was defined as the solubility.[19]

Scanning Electron Microscopy (SEM). To observe the effects of the interaction of MoCl$_5$ on polymer structure, solutions of PVP (sample III) in 75 mM MoCl$_5$ were dialyzed using dialysis tubing (Spectra/Por Membranes MWCO: 6—8000) against several changes of water for 15 days at 298 K. PVP solution was removed from the dialysis bag and concentrated in a Savant SVC-200H SpeedVac concentrator. PVP, MoCl$_5$, and PVP/MoCl$_5$ mixture obtained before and after dialysis and concentration were shadowed with gold. All samples were rinsed in an ultrasonic bath.

Photographs were taken by of a JEOL JSM-6400 scanning electron microscope and a dispersion energy spectrophotometer RX Pentafet to carry out a semi-quantitative analysis samples.

Theorical Equations

The intrinsic viscosity for a minimum of six concentrations for each fraction and composition was determined by double extrapolation to zero concentration using Huggins[20] and Kraemer[21] equations.

The unperturbed dimensions of the macromolecule (K_θ) and long-range polymer–solvent interactions (B) as a function of MoCl$_5$ concentration were calculated by the Burchard–Stockmayer–Fixman equation[22]:

$$[\eta]/M^{1/2} = K_\theta + \phi 0.51 B M^{1/2} \qquad (1)$$

where $[\eta]$ is the intrinsic viscosity of the polymer, M the molecular weight of the polymer and ϕ the Flory con-

stant ($\phi = 2.5 \, 10^{21} \, mol^{-1}$ if $[\eta]$ is expressed in dL g^{-1}).

The parameter a for every solvent composition was obtained using the Mark–Houwink–Sakurada equation[23]:

$$[\eta] = KM^a \qquad (2)$$

The partial specific volume of the PVP (sample III) in the saline medium was determined as,[24]

$$\bar{v}_2 = [1 - (\partial \rho / \partial C_2)_{T,P,m_3}]/\rho_0 \qquad (3)$$

where ρ_0 and ρ are the densities of solvent and solutions, respectively, and $(\partial \rho / \partial C_2)_{T,P,m_3}$ is the change in the density of the solution with polymer concentration (C_2) at constant temperature (T), pressure (P) and molal metal concentration (m_3). Scatchard[25] and stockmayer[26] notations were followed: 1, water; 2, macromolecule; 3, salt.

The preferential adsorption coefficient λ_3 was determined using the Kratochvil *et al.*'s equation[27]:

$$\lambda_3 = [(\partial \rho / \partial C_2)_{T,P,\mu_3} - (\partial \rho / \partial C_2)_{T,P,m_3}]/$$
$$(\partial \rho / \partial C_3)_{T,P,m_2} \qquad (4)$$

where $(\partial \rho / \partial C_2)_{T,P,\mu_3}$ is the change in density with polymer concentration at constant chemical potential (μ_i) and $(\partial \rho / \partial C_3)_{T,P,m_2}$ is the change in the density of the solution with respect to the metal concentration at constant temperature (T), pressure (P), and mass of polymer (m_2).

λ_3 can also be given by:

$$\lambda_3 = (\partial g_3 / \partial g_2)_{T,\mu_1,\mu_3}$$

where g_i is the weight of component i in grams; for diluted solution, the error is not significant.[28] Thus, the preferential hydration, $(\partial g_1 / \partial g_2)_{T,\mu_1,\mu_3}$, can be obtained from the equation[29,30]:

$$(\partial g_1 / \partial g_2)_{T,\mu_1,\mu_3} = -(1/g_3)(\partial g_3 / \partial g_2)_{T,\mu_1,\mu_3} \qquad (5)$$

The preferential interaction parameter, $(\partial \mu_2 / \partial m_3)_{T,P,m_2}$, shows the relationship between mutual perturbation of the chemical potential of components 2 and 3[31,32]:

$$(\partial \mu_2 / \partial m_3)_{T,P,m_2} = -(\partial m_3 / \partial m_2)_{T,\mu_1,\mu_3}$$
$$\times (\partial \mu_3 / \partial m_3)_{T,P,m_2} \qquad (6)$$

The term $(\partial m_3 / \partial m_2)_{T,\mu_1,\mu_3}$ can be determined as follows[33]:

$$(\partial m_3 / \partial m_2)_{T,\mu_1,\mu_3} = (M_2/M_3)(\partial g_3 / \partial g_2)_{T,\mu_1,\mu_3} \qquad (7)$$

where M_i and m_i are the molecular weight and molality of component i, respectively.

The self-interaction term $(\partial \mu_3 / \partial m_3)_{T,P,m_2}$ can be calculated from:

$$(\partial \mu_3 / \partial m_3)_{T,P,m_2} = nRT/m_3 + nRT(\partial \ln \gamma \pm / \partial m_3)_{T,P,m_2} \qquad (8)$$

where n is number of ions ($n = 6$ for MoCl$_5$), R is the gas constant and $\gamma \pm$ is the ionic activity coefficient of the salt.

Starting from the preferential interaction parameter, it is possible to determine the transfer free energy, $\Delta \mu_2$, of the polymer from water to the salt medium according to the equation[34,35]:

$$\Delta \mu_2 = \mu_{2,m_3} - \mu_{2,w} = \int_0^{m_3} (\partial \mu_2 / \partial m_3)_{T,P,m_2} dm_3 \qquad (9)$$

where μ reflects the relative affinity of salt and water for

the polymer at a given solvent composition, and the subscript w refers to water.

RESULTS AND DISCUSSION

One way to analyze the variation of hydrodynamic properties of macromolecules in solution is by the intrinsic viscosity parameter [η] related to macromolecular size and shape in dissolution. This parameter can be modified due to macromolecule-salt interactions.

Figure 1 plots the variation of [η] with binary mixture composition. As can be seen there is no linear variation, and this could indicate changes on the structure of the macromolecule, all polymeric fractions behavior being the same, independently of molecular weight. This parameter can be related to the partial specific volume $\bar{v}_2$ determined from densimetric measurements.[36] Variation of this parameter values would reflect conformational changes in macromolecules.[37,38] The salt concentration from which the partial specific volume parameter begins to decrease (50 mM) is the same at which a drastic decrease of intrinsic viscosity is produced (Figure 2), and a minimum is obtained in [η] at 75 mM MoCl$_5$ for all samples studied.

The unperturbed dimensions, K_θ, and long-range polymer–solvent interactions, B, were determined by the Stockmayer–Fixman equation.[22] The unperturbed dimensions of the macromolecule (Figure 3A) increase with salt concentration up to 50 mM MoCl$_5$ and sig-
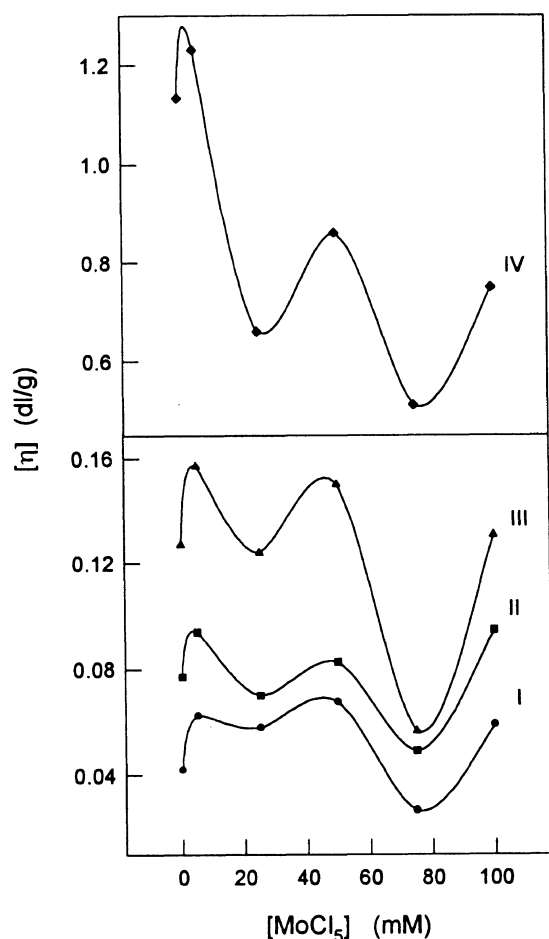
nificant decrease of K_θ is exhibited at 75 mM of salt indicating a more compact shape of the macromolecular coil, which is in accordance with the minimum observed for intrinsic viscosity at this salt concentration. This more compact shape of the macromolecule structure can be due to the PVP–salt interaction and conformational change may occur.

The long-range polymer–solvent interaction B (Figure 3B) decreases starting from the first salt concentration, and an enhancement is observed at 50 mM of salt; this indicates a higher macromolecule-binary mixture interaction.

The Mark–Houwink–Sakurada[23] a parameter (Figure 4), that measures the permeability of macromolecular coil for solvent molecules presents a maximum at 75 mM of salt. At first, this parameter decreases, so the thermodynamic quality of the binary mixture makes worse, which is in accordance to the B parameter (Figure 3B). Starting from 25 mM of MoCl$_5$, the thermodynamic
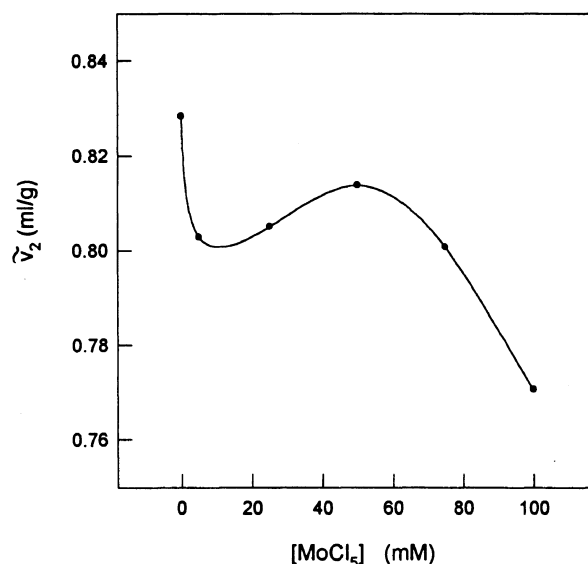

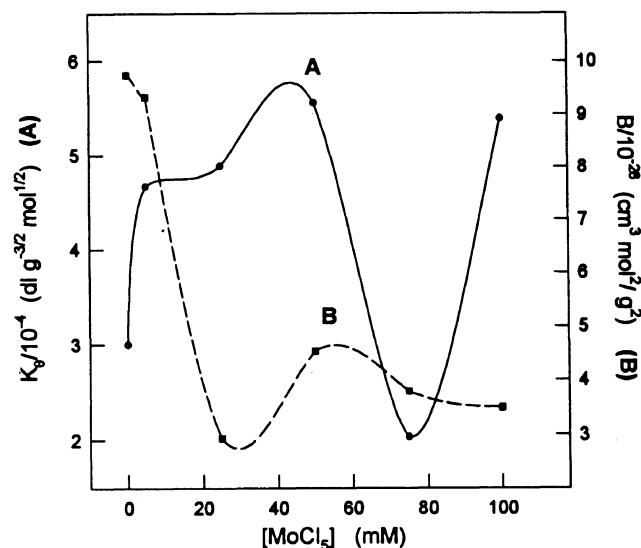**Figure 2.** Plots of partial specific volume of PVP in different water [1]/MoCl$_5$ [3] solvent mixtures at 298 K.

Figure 1. Intrinsic viscosity of PVP samples (I, II, III, and IV) in a binary water [1]/MoCl$_5$ [3] mixture at 298 K.

Figure 3. Variation of K_θ (A) and polymer–binary mixture interaction B (B) as a function of MoCl$_5$ concentration of the binary mixture at 298 K.
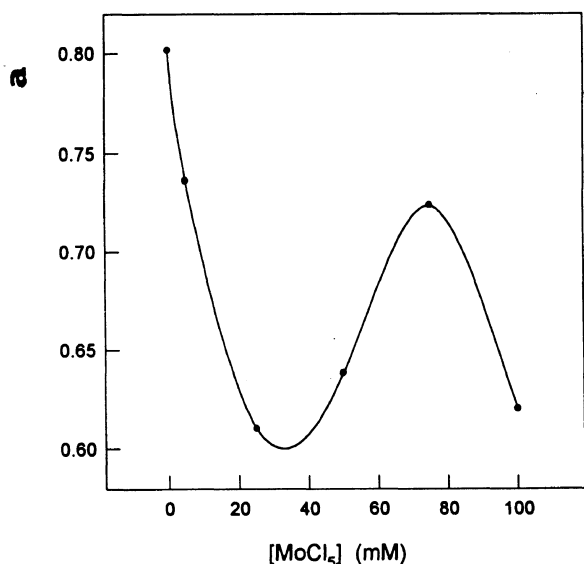
Figure 4. Dependence of Mark Houwink exponent a on the MoCl$_5$ for the PVP [2]/water [1]/MoCl$_5$ [3] system at 298 K.
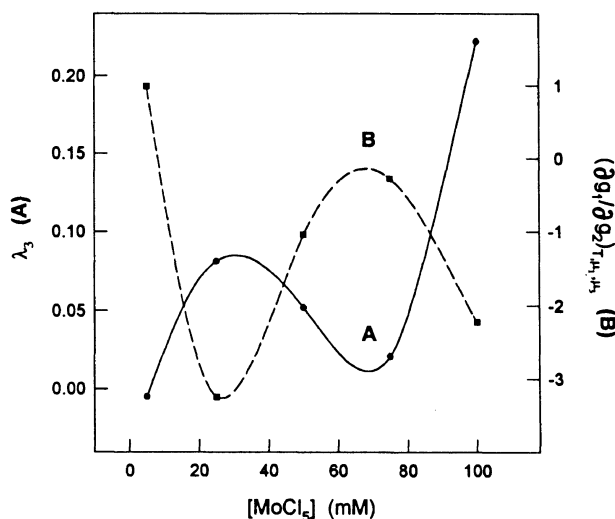

Figure 5. Preferential adsorption coefficient (A) and preferential hydration (B) of PVP in the water [1]/MoCl$_5$ [3] mixtures as a function of MoCl$_5$ concentration.

quality of solvent improves up to 75 mM of MoCl$_5$.

Preferential adsorption or solvation parameter (λ_3) indicates which component of the binary mixture (water [1] or metal [3]) interacts preferentially inside the macromolecular structure.[27] Negative values of this parameter reveal preferential salt adsorption, whereas positive values indicate preferential exclusion of salt from the macromolecule.

Figure 5A shows light preferential adsorption of salt at 5 mM and from this salt concentration preferential absorption of water is observed, so this parameter increases showing positive values, meaning preferential exclusion of the salt from the inside the macromolecular coil.

The correlation of these results with preferential hydration, $(\partial g_1/\partial g_2)_{T,\mu_1,\mu_3}$, is clear. This parameter exhibits negative values from 25 mM of salt, indicating the salt is preferentially placed in the macromolecular external domain (Figure 5B). This behavior has been observed for PVP with other salts.[5]
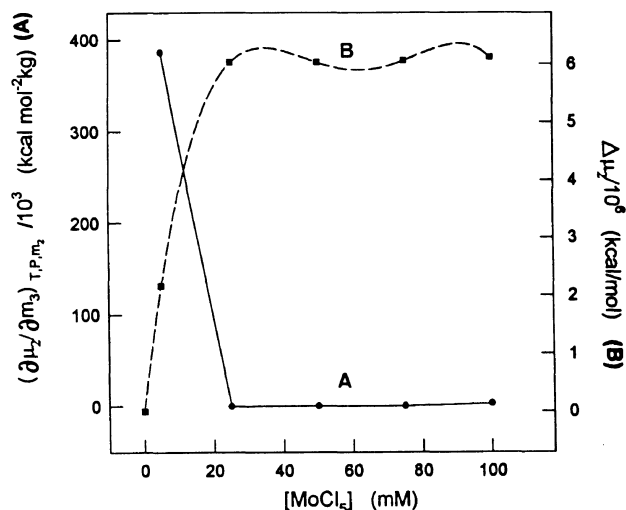
Figure 6. Variation of preferential interaction $(\partial\mu_2/\partial m_3)_{T,P,m_2}$, (A) and transfer free energy from water to salt solution, $\Delta\mu_2$ (B) for PVP as a function of MoCl$_5$ concentration.

Preferential adsorption (λ_3) exhibits a minimum at 75 mM MoCl$_5$, showing the least preferential water adsorption. At this salt concentration intrinsic viscosity is minimum (Figure 1), partial specific volume begins to decrease (Figure 2) and a more compact macromolecular coil is observed (Figure 3A). Correlation between the decrease of preferential adsorption of water and the minimum value of the unperturbed dimensions of the macromolecule is observed. A similar behavior has been described in the system PVP/water/VOSO$_4$, too.[39]

Starting from preferential adsorption, preferential interaction, $(\partial\mu_2/\partial m_3)_{T,P,m_2}$, can be obtained,[31,32] representing a change in the system thermodynamic stability due to a variation of solvent composition. As can be seen in Figure 6A, this parameter becomes quite high at the lowest salt concentration. The interaction is thus thermodynamically unfavorable, althougt at MoCl$_5$ concentrations higher than 25 mM the interaction of the polymer with solvent components is thermodynamically more favorable. Thus the preferential interaction parameter is close to zero. These results are in accordance with the enhancement of the polymer–solvent mixture interaction (Figure 3B) and increase of the thermodynamic quality solvent (Figure 4) from 25 mM of salt.

The transfer free energy, $\Delta\mu_2$, expresses the difference between the affinity of a macromolecule for the specific solvent system and for pure water. This parameter was calculated by eq 9. The integration was carried out by treating the data as two straight lines intersecting at 25 mM of salt. The values of $\Delta\mu_2$ calculated in this manner are presented in Figure 6B and indicate that the transfer of energy from water to salt solution is thermodynamically unfavorable, although starting from 25 mM MoCl$_5$, stability in the system was observed.

Information given by the transfer free energy of the macromolecule in solution was complemented by the results of polymer solubility studies.[19] Densimetric and solubility studies show that MoCl$_5$ is a salting-in agent for PVP at all salt concentrations because in all cases no precipitate is obtained after dialysis.

The MoCl$_5$ structure has been extensively studied in the solid state[9]: it is a dimer in which two distorted

octahedra share an edge to form two chloride bridges. This salt, by scanning electron microscopy, certainly presents small and homogeneous clustering crystallines (Figure 7A).

PVP is an amorphous polymer with a non-crystalline structure as is observed in Figure 7B.

The variation in the polymer structure in the presence of molybdenum pentachloride is observed in Figures 7C and 7D. In PVP/MoCl$_5$ samples, regular formation with different sizes and morphologies are presented. When dialysis is carried out, large and homogeneous structures are obtained (Figure 7C), while if this process is not realized, small particles appear, which are eliminated after dialysis due to pore size of the dialysis tubing allows this small particles leak out of dialysis bag (figure 7D).

This change in the polymer structure from an amorphous to regular appearance can be produced by polymer–salt interaction. The semiquantitative analysis of the samples shows the existence of C, N, O, Mo, and Cl, which indicates that PVP and MoCl$_5$ are present. These elements are detected in samples obtained with or without dialysis. There is decrease of Cl in the dialyzed samples and thus the regular structure obtained is constituted by polymer and salt.

Molybdenum ions in low charged states such as Mo^{3+} are able to bind to soft donors such as RS$^-$ and neutral nitrogen bases as well as to RO$^-$ donors. Higher oxidation states the reaction of the cation is in competition with hydrolysis. This competition is so strong in fact that the ions are usually treated as oxo-cations MoO^{2+} and MoO^{3+}. These oxo-cations have effective charges of aproximately $n+1$ where n is the formal charge on the cation Mo^{n+} and they are bound to anions much more strongly than Mo^{n+} cations of approximately the same size.[9] In an early study Mitchell and Williams[40] were able to show that the higher oxidation state of molybdenum favors its binding to S and O-donors.

PVP complexes with lithium salts have been examined[17] where the cation is coordinated through the carbonyl group of the polymer due to the resonance structure [$-$N$-$C$=$O$> \cdots <-$N$^+=$C$-$O$^-$]. The amide group of PVP may interact to MoO^{3+} cation to form a polymer–metal complex.

We conclude that the addition of MoCl$_5$ to the polymer influences the structure by modifying the overall properties in solution and solid state. Sudden changes in the slope of intrinsic viscosity and partial specific volume of the polymer are produced and related with a conformational transition at 75 mM of salt. The PVP–MoCl$_5$ interaction induces decrease of the macromolecule unperturbed dimensions with a more compact macromolecular coil, the binary mixture being thermodynamically unfavorable and a salting-in behavior is exhibited at all salt concentrations.
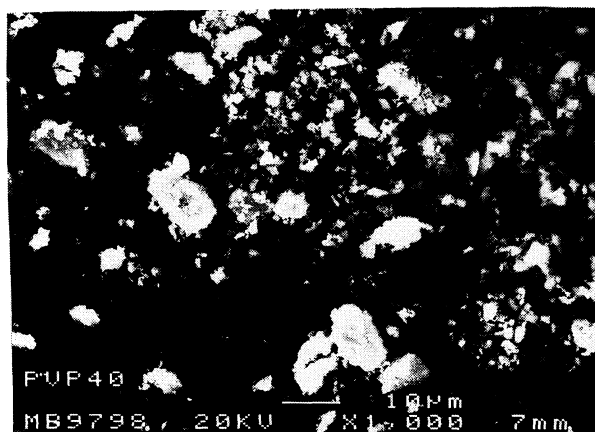
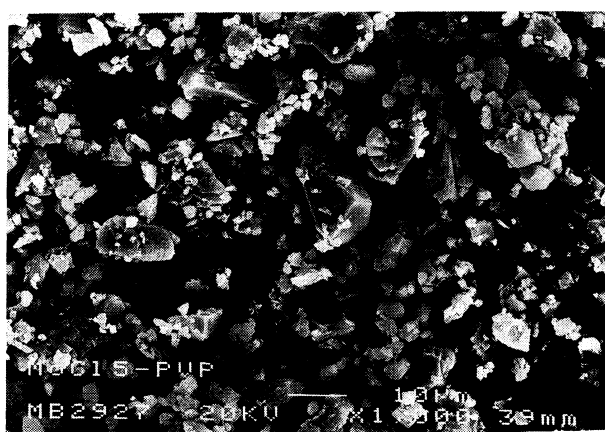The present results agree with those obtained by scanning electron microscopy. In the presence of MoCl$_5$,

(A)

(B)

(C)
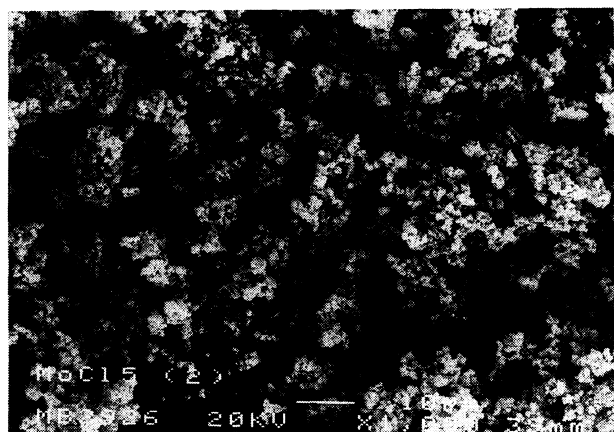
(D)

Figure 7. Scanning electron micrographs of MoCl$_5$ (A), PVP (B), dialyzed PVP/MoCl$_5$ (C), and undialyzed PVP/MoCl$_5$ (D) samples.

the polymer structure changes and PVP presents a regular structure as a consequence of its interaction with the salt. $MoCl_5$ is thus a nucleating agent of PVP.

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616