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Viscosity properties of aqueous solution of poly(allylamine)-metal complexes

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SUMMARY

Poly(allylamine)-metal complexes with Co(II), Cu(II), and Ni(II) in conjunction with an ultrafiltration membrane were prepared. They were obtained varying the polymer/metal ion ratio and the pH (1, 3, 5, 7).

The viscosimetric behavior of these poly(allylamine)-metal complexes as well as the poly(allylamine) and mixture of poly(allylamine) with each metal ion was also studied. All the aqueous solutions showed a pseudoplastic behavior. However, it is not far away from that of Newtonian behavior. The viscosity depends strongly on the pH and on the metal salt concentration.

INTRODUCTION

The water-soluble polymers are of increasing interest in different fields for enchanced oil recovery drilling operations oil well production (1-6). In medicine and biology they are widely used applied as plasma substitutes, and for the controlled release of drugs.

The physicochemical properties of solutions of synthetic water-soluble polymers have gained attention mainly to their hydrodynamic properties, among which the intrinsic viscosity is determined in great detail. They have been also studied as chelating agents to metal ions in combination with an ultrafiltration membrane (7-12). These properties give the water-soluble polymers interesting applications to fields such as hydrometallurgy, environmental, *etc*.

An interesting polymer with ability to form complexes with metal ions is the poly(allylamine), (PALA). It has a side amino group as ligand group. The chelation properties for heavy metal ions as Ni(II), Cu(II), Cd(II), Zn(II), and their properties have been previously reported (13). For a better understanding the phenomena present in the polymer-metal ion interaction in aqueous solution it is necessary to study the aqueous solution behavior of the polymers, as well as mixtures of polymers and metal salt, and polymer-metal ion.

The aim of this paper is prepare poly(allylamine)-metal complexes with different metal ions in conjunction with an ultrafiltration membrane, and to carry out a viscosity study of poly(allylamine), mixtures of poly(allylamine) with metal salts, and poly(allylamine)-metal ion in aqueous solution.

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EXPERIMENTAL PART

Materials: All reagents used were analytical grade. Poly(allylamine) Mw=60.000, from Polysciences was used as the chlorhydrate. The metal salts (Merck) of Cu(II), Co(II), and Ni(II) were prepared from nitrate and chloride salts. The pH was adjusted by HNO_3, HCl, and NaOH.

Preparation of poly(allylamine)-metal complexes. These complexes were prepared by mixing of an aqueous solution of poly(allylamine) (4.0 g/dL) with an aqueous solution of Cu(II), Co(II), and Ni(II). The polymer/metal ratios (in mol) employed were: 4:1, 3:1, 2:1, 1:1 and at pH 1, 3, 5, and 7. The final concentration of poly(allylamine) was always 2.0 g/dL. Subsequently, the sample was placed in the filtration cell. The non-complexed metal ion passed through the ultrafiltration membrane. Either the volume and pH in the cell are kept constant. It corresponds to using the Liquid-Phase Polymer Based-Retention (LPR) method.

Measurements: The viscosity was measured by a Haake VT 500 rotation viscosimeter. The variables studied were: shear rate, concentration, and pH.

RESULTS AND DISCUSSION

The poly(allylamine)-metal complexes were synthesized in conjunction with the liquid phase polymer based retention technique (LPR) (14).

The membrane used has an exclusion limit of molecular mass of 3.000 g mol^{-1}. It allows the separation of the polymer-metal complexes which stay in the cell solution from the non-complexed metal ion which passes through the membrane to the filtrate. The initial volume of the reaction mixture is kept constant, 20 mL.

Viscosimetric Measurements

Flow curves.The relationship between the shear stress and the shear rate are represented by the Figures 1, 2, and 3, which describes the flow behavior of aqueous solutions of poly(allylamine), mixtures of poly(allylamine) with metal salts, and poly(allylamine)-metal complexes. All the solutions present a behavior which can be approximated to the Ostwald model, $t=AD^B$. It allows the description of the Newtonian flow behavior, pseudoplastic, and dilatant behavior. A is related with the amount of the resistance to the flow and for Newtonian fluids corresponds to the viscosity (Pa·s). B is called index of flow and measures the degree of non Newtonian flow behavior. For B=1,the solution is a Newtonian fluid, B > 1, a dilatant fluid, and B < 1 a pseudoplastic fluid.

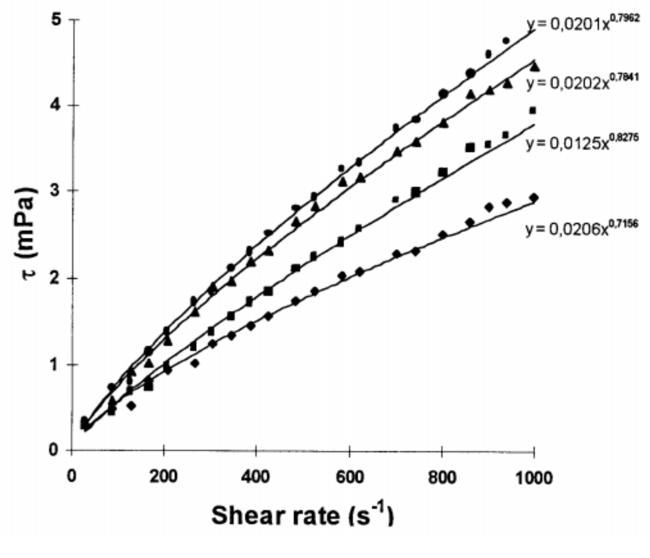

Figure 1. Flow curves of mixtures of poly(allylamine) with $CoCl_2$ in different ratios (-◆-) 1:1; (-■-) 2:1; (-▲-) 3:1; (-●-) 4:1; at pH 3.0. 20ºC and 2.0 g/dL of poly(allylamine).

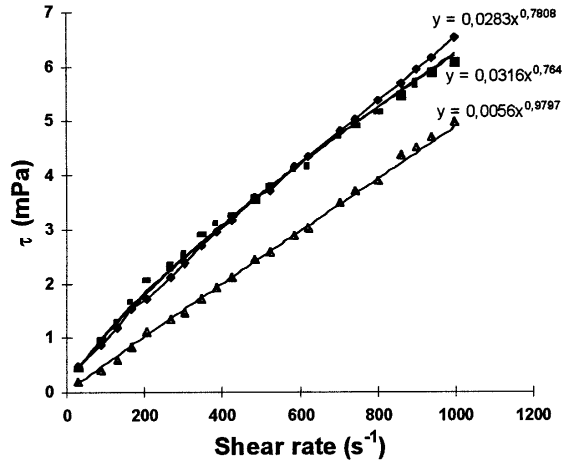

Figure 2. Flow curves of mixtures of poly(allylamine) with (-◆-) $CuNO_3$; (-■-) $Co(NO_3)_2$ and (-▲-) $Ni(NO_3)_2$ in a polymer: metal ratio 1:1 pH 3.0, 20°C and 2.0 g/dL of poly(allylamine).

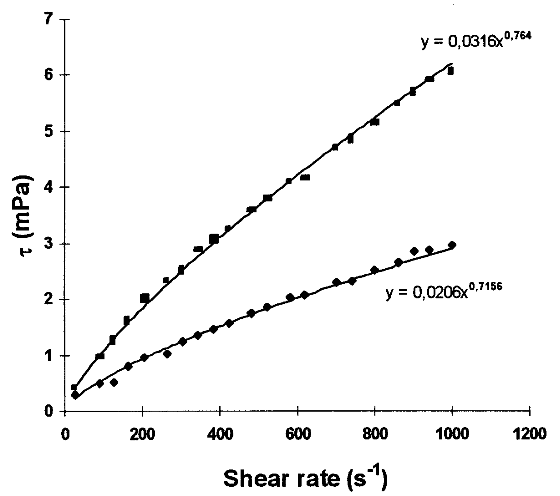

Figure 3. Flow curves of mixture of poly(allylamine) with to $CoCl_2$ (-◆-) and poly(allylamine)-Co(II) (-■-) at pH 3.0; 20°C, and 2.0 g/dL of poly(allylamine).

In this case, all the solutions have a pseudoplastic fluid behavior with values of B varying between 0.72 and 0.98. It may be corroborated by Figure 4 which represents the apparent viscosity as a function of the shear rate and the shape of the curves is characteristic of pseudoplastic fluids. Thus, a high apparent viscosity at low shear rate and a decrease of these values as the shear rate is increased. It can be attributed to the fact that, the particles or polymeric chains keep a disordered state, raising a high internal resistance to a forced flow, and therefore high viscosity.

By increasing of the shear rate the particles are oriented in direction of the flow. In polymer solutions, the chains are oriented parallel to the flow direction. Some particles are be better shaped yielding a low viscosity. This behavior is expected for polymers with a rigid rod conformation.

The metal salt shows no an effect on the shape of the flow curves. For a poly(allylamine): $CoCl_2$ 2:1 ratio a B= 0.83 was obtained, implying a behavior more close to Newtonian whereas for a 1:1 ratio is obtained a B= 0.72 was obtained.

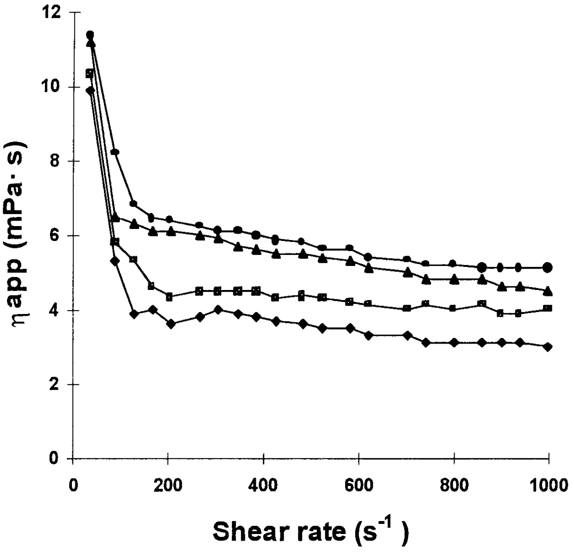

Figure 4. Effect of the shear on the apparent viscosity for mixtures of poly(allylamine): $CoCl_2$ (-◆-) 1:1; (-■-) 2:1; (-▲-) 3:1, and (-●-); 4:1 at pH 3.0, 20ºC and 2.0 g/dL of poly(allylamine).

Figure 4 shows also that with a higher $CoCl_2$ ratio, the apparent viscosity decreases in all range of shear rate studies. This is characteristic of polyelectrolytes. The poly(allylamine)-metal solutions with Cu(II), and Co(II) show similar viscosity values whereas with Ni(II) lower values (see Figure 5) are obtained. This can be attributed to a higher intrachain interaction of the poly(allylamine) with Ni(II), coiling and decreasing the viscosity.

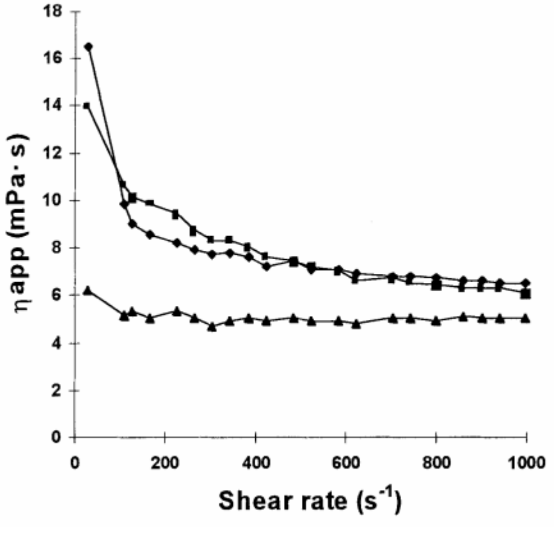

Figure 5. Effect of the shear rate on the apparent viscosity for poly(allylamine)-metal complexes. (-◆-) Cu; (-■-) Co, and (-▲-) Ni at pH 3.0 and 20ºC. 2.0 g/dL of poly(allylamine).

Effect of the pH and metal salts on the viscosity of poly(allylamine) solutions.

There is a significant dependence of the pH on the viscosity (see Figure 6). It increases as the pH increases, achieving the highest value at pH 3.0, then it remaining constant up to pH 5.0, and thereafter a decrease was observed. It corresponds basically to the polyelectrolyte behavior at lower pH than 5.0. As the polymer chain is charged, there is repulsion between the segments, yielding an extension, increasing the hydrodynamic volume and the viscosity. In order to decrease the pH (<3) HNO_3 was added, increasing the ionic strength, the polymeric coil was contracted and the viscosity decreased. This effect disappears by increasing the metal ion concentration.

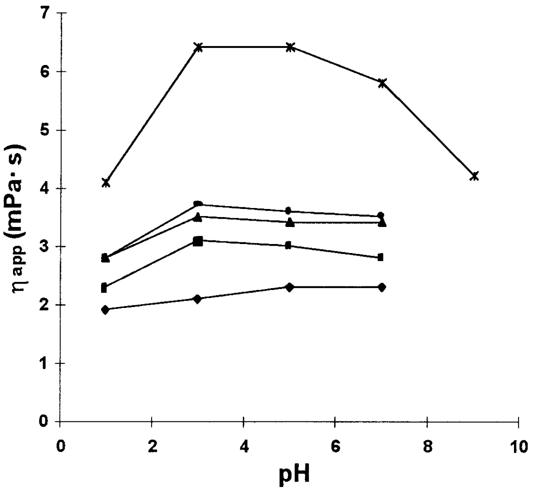

Figure 6. Apparent viscosity in function of pH for poly(allylamine) (-✳-) and mixtures of poly(allylamine)/$Co(NO_3)_2$, (-◆-) 1:1; (-■-) 2:1; (-▲-) 3:1; and (-●-) 4:1 at 20°C and shear rate: $200s^{-1}$.

At pH >5.0 amino groups remain to an important degree as the free base. The equilibrium state of the protonated and free amino group is strongly dependent on the pH and is shifted to the free amino group as it increases. Thus, poly(allylamine) without charge is obtained, which allows a higher interaction among the backbone segments adopting preferentially a coiled macroconformation, therefore a smaller viscosity. Moreover, it was observed that an important decrease of the viscosity of an aqueous solution of poly(allylamine) respect to a solution that contains poly(allylamine) and metal salt occured. It is higher as the metal salt concentration increases (see Figure 7). For chloride metal, the effect on the viscosity was Ni(II)>Co(II)>Cu(II), but for nitrate salts the order was Co(II)>Cu(II)>Ni(II). It may be attributed to the larger size of the nitrate ions.

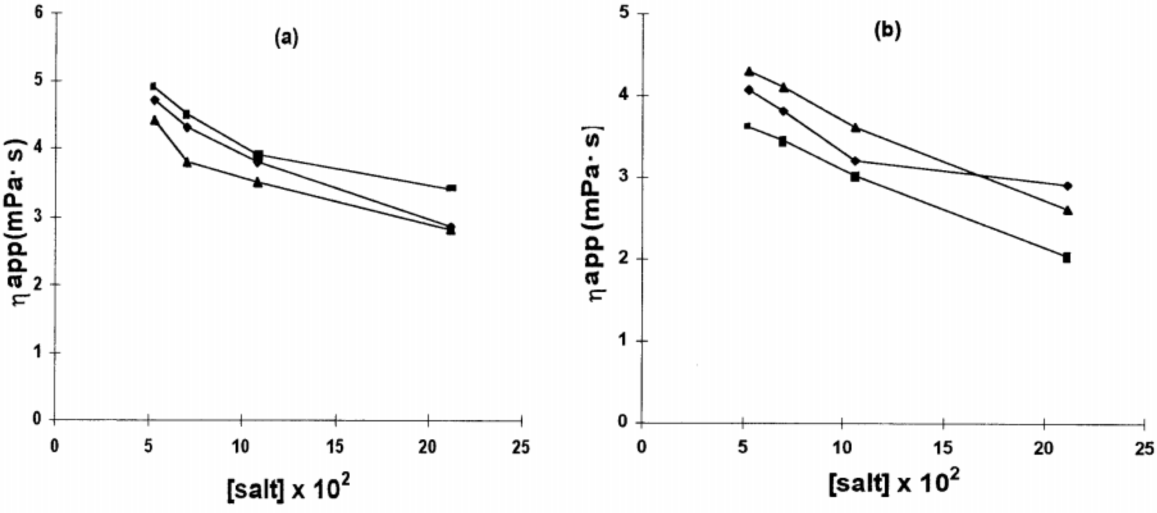

Figure 7. Effect of the salts (a) chloride, (b) nitrate on the viscosity of poly(allylamine).

Dependence of the viscosity with the concentration of poly(allylamine) and poly(allylamine)-metal complex.

The diagrams of apparent and reduced viscosity as function of the polymer-metal concentration show a typical polyelectrolyte behavior (see Figures 8 and 9). This behavior is due to the fact that, as polyelectrolyte concentration decreases, the ionization degree increases and the produced ions form an ionic atmosphere greater than the diameter of polymeric coil. The repulsion among the ions increases the rigidity of the chain, expanding the polymeric coil with a consequent increase of the viscosity.

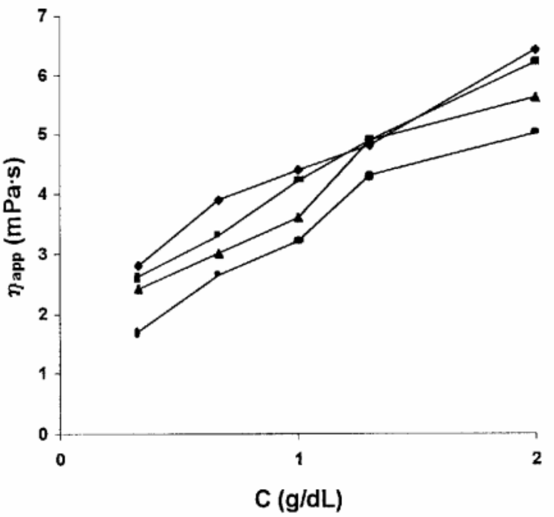

Figure 8. Effect of the concentration on the viscosity (-◆-) poly(allylamine);(-■-) poly(allylamine)-Cu;(-▲-) poly(allylamine)-Co;(-●-) poly(allylamine)-Ni at 20°C. Shear rate: 200s^{-1}, pH 3

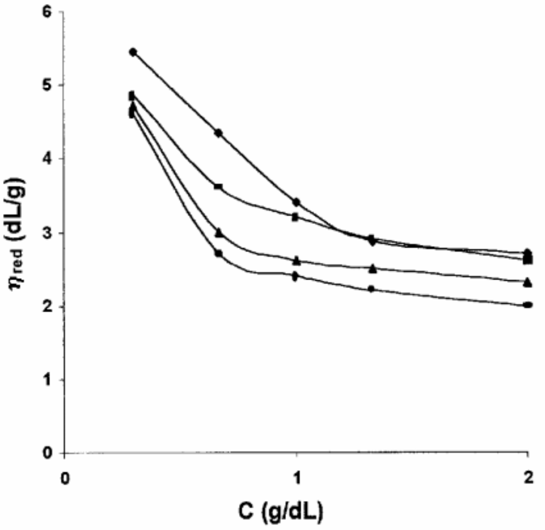

Figure 9. Reduced viscosity in function of the concentration for (-◆-) poly(allylamine), (-■-) poly(allylamine)-Cu;(-▲-), poly(allylamine)-Co and (-●-) poly(allylamine)-Ni at 25ºC. Shear rate: 200s^{-1}, pH 3.

At middle polyelectrolyte concentrations, the ions are placed either inside and outside of the polymeric coil, but at higher concentration, they are preferably outside yielding an osmotic effect, increasing the expansion of the coil. Therefore, at low concentration the electrostatic effect predominates, whereas at higher concentration it is the osmotic effect.

The high apparent viscosity values are due to the large hydrodynamic volume of the polyelectrolytes. The calculations of the intrinsic viscosity were carried out by the Fuoss equation (15). The results are shown in Figure 10.

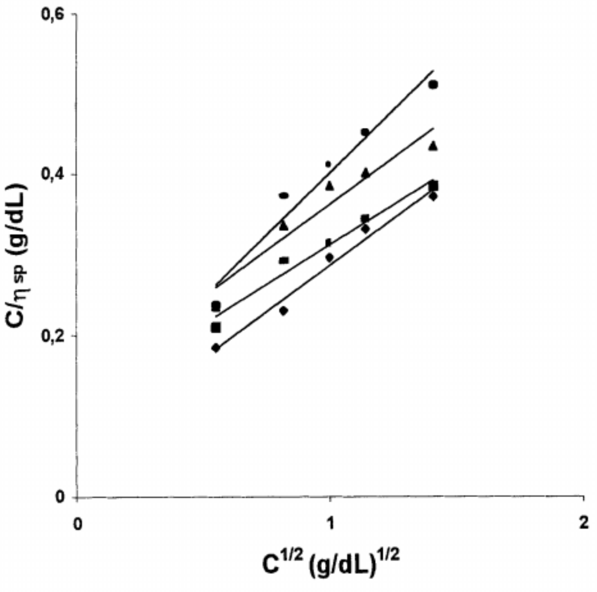

Figure 10. Plots of Fuoss for (-◆-) poly(allylamine), (-■-) poly(allylamine)-Cu; (-▲-) poly(allylamine)-Co, and (-●-) poly(allylamine)-Ni at 20ºC. Shear rate: 200s^{-1}, pH 3.

CONCLUSIONS

The viscosity measurements of poly(allylamine), poly(allylamine)-metal complexes, and poly(allylamine)/metal ion mixtures showed a high dependence of the shear rate. All the aqueous solutions showed a pseudoplastic behavior. However, this behavior is not far away from a Newtonian. The viscosity of poly(allylamine) and its metal complexes is strongly dependent on the metal salt concentration. It is due to basically to the change in the ionic strength which induces the polymer coil to take a more compact or extended conformation. There is always a high dependence on the pH. It is explained by the protonation and deprotonation equilibrium of the amino groups as well as by the ionic strength. The preferred macroconformation is the rigid rod forming compact coils. The excluded volume of the poly(allylamine)-metal complexes is lower than that poly(allylamine) indicating the intrachain polymer-metal ion interaction is the preferred.

ACKNOWLEDGEMENTS

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