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Ultrafiltration of Aqueous Solutions of PVA-Cu(II) Macromolecular Complex

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Abstract: The hydrodynamic behavior of aqueous solutions of poly(vinyl alcohol) and poly(vinyl alcohol)–cupric complex and its effect on the performance in the concentration of the macromolecular cupric complex by ultrafiltration is considered in this study which implements various synthetic membranes in polyethersulfone. The polyelectrolyte–like behavior of poly(vinyl alcohol) is highlighted. This behavior disappears in the case of the macromolecular complex. The disappearance of the polyelectrolyte–like effect is explained by the modification of the macromolecular conformation induced by the formation of the complex which takes up a tightly packed conformation. The study of the effect of the variation of the pH and the ionic strength made it possible to observe that the increase of the pH is accompanied by the reduction of the medium viscosity and the increase of the flux through the ultrafilters and the increase of the ionic strength of the medium is accompanied by the increase of the thickness of the adsorbed solute layer. The study of the effect of the nature of the ionic species in solution on the hydrodynamic behavior of the aqueous solutions of the macrocomplex leads to the conclusion that the use of the cupric chloride salt, instead of the nitrate or the sulphate salts, in the preparation of the macrocomplex improves the hydrodynamic properties of the solution and enhances the performance of its treatment by means of the ultrafiltration process.

Keywords: Ultrafiltration, viscometry, macromolecular complex, poly(vinyl alcohol), polyethersulfone membrane

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INTRODUCTION

The complexation-ultrafiltration hybrid process was suggested at the end of the sixties by A.S. Michaels (1). Since then, many studies have shown its effectiveness in the purification of aqueous solutions of metal ions sequestered by adequate water–soluble macromolecular substrates (2–14). The study presented in this publication is about the effect of the hydrodynamic characteristics of aqueous solutions of the macromolecular complex Poly(vinyl alcohol)-Cu(II) on the performances of the process, in particular its effect on the flux. For this study, several membranes in polyethersulfone of various cut-off are employed. These membranes have been selected for their capacity to completely reject the macrocomplex Poly(vinyl alcohol)-Cu(II) (15).

The characterization of an ultrafiltration membrane requires the study of parameters as the porosity, the asymmetry, the permeability to solvent and the selectivity for the macromolecular reject. The porosity and the asymmetry of the membrane are given or checked by direct methods of characterization such as adsorption-desorption of nitrogen (for porosity) and scanning electronic microscopy (for asymmetry). The permeability and the selectivity of the membrane are, on the other hand, given by indirect methods of characterization implementing the process of ultrafiltration to measure fluxes and to determine rejection rates.

The mass transfer through a membrane is modelled to allow a simplified approach of the complex phenomena of transfer and selectivity. For ultrafiltration, the model of the molecular sieve, based on a capillary type mechanism, is in a good correlation with the experimental results. This model assimilates the pores of the membrane with cylindrical capillaries of heterogeneous sizes in which the solvent runs out freely, the macromolecular solute being partially rejected by the sieve and the rejection rate R, which measures the separating capabilities of the membrane is given by:

$$R(\%) = (1 - c_P/c_0) \times 100$$

Where: c_0: the concentration of the solute upstream of the membrane; c_p: the concentration of the solute downstream from the membrane; Besides, the solvent flux J is given by Darcy's law (16) that describes the flux of a fluid through a porous medium and which is very largely employed in the ultrafiltration process:

$$J = (B_P/\eta e)\Delta P$$

Where: η: the dynamic viscosity of the fluid; e: the thickness of the active layer; ΔP: the trans-membrane pressure gradient; Bp is the permeability, which is an intrinsic characteristic of the membrane that depends of the average radius of the pores and the number of pores per unit of membrane area.

The Darcy law is verified, in practice, when the solvent flux through the membrane is simultaneously proportional to the applied pressure and inversely proportional to the medium viscosity.

The pressure flux behavior observed during typical ultrafiltration operations of macromolecular solutions, i.e., pressure-controlled at low pressures, pressure-independent at high pressures, can be described using the resistance-in-series approach, employed for determining the fouling mechanism of membranes (17). Indeed, if membrane fouling occurs due to specific membrane-solute interactions, either by surface deposition or by pore blocking, the intrinsic membrane resistance will change, and there may be a series of additional membrane resistances due to membrane fouling. This explains the discrepancy from the linearity of the flux with pressure in the ultrafiltration of aqueous macromolecular solutions. The flux varies with the pressure applied to the solution, on the one hand, and with the inverse of viscosity, on the other hand. When the conditions of temperature and pressure are selected and fixed, the flux becomes affected only by the intensity of the interactions membrane/solution and by the modifications that the nature of the species present in the solution brings to viscosity. Indeed, the viscosity of a solvent is completely modified by the introduction of a macromolecular solute, even in a very small quantity (18). The viscosity of polymer solutions is dependent on the molar mass and also on the polymer concentration, the polymer-solvent interactions, the solvent viscosity, the temperature, and the pressure (18–20). The viscosity of polymer solutions is, in addition, affected by all the parameters which influence the macromolecular conformation. Thus, it is the effect of these parameters, on the viscosity of the medium and the flux through the ultrafilters, which is examined in this study. The parameters considered are, primarily those which intervene in the formation and the stability of the macrocomplex, in particular the pH and the relative concentration of the reagents, than those which intervene in the macromolecular conformation of the complex, in particular the ionic strength of the medium and the nature of the ionic species in the solution.

EXPERIMENTAL

Poly(vinyl alcohol) (PVA) (MW: 15,000, 49,000, and 1,00,000) and cupric chloride, sulfate, and nitrate are used to prepare the macromolecular metal complex solutions. The pH of the solutions are adjusted using the required amount of 0.1 M potassium, sodium, or lithium hydroxide and the ionic strength of the solutions is maintained at the desired value using potassium, sodium, or lithium chloride, or potassium sulfate or nitrate. The simultaneous choice of the base and the added salt is made according to the nature of the counterion in the cupric salt. All chemicals are from Fluka AG and are used without further purification.

The ultrafilters used are PBQK, PBTK, and PBGC polyethersulfone membranes supplied by Millipore. They are asymmetric membranes of hydrophobic nature and their molecular weight cut-off are respectively 50,000, 30, 000, and 10,000. They are employed in a Millipore magnetic stirred cell and the device is operated in a batch mode. The effective membrane area is 45.3 cm^2, the feed volume is 300 mL and the rotational speed is set to be 500 rpm during all the trial runs. The ultrafiltration cell is pressurized with nitrogen and the pressure is controlled by a manometer placed at the top of the cell (Fig. 1).

Viscometric measurements are carried out at 30°C in a Schott-Geräte AVS 360 automated system with Ubbelohde-type capillary viscometer. The temperature is controlled to within ±0.01°C.

RESULTS AND DISCUSSION

Effect of the Formation of the PVA-Cu(II) Complex on the Viscometric Behavior and Flux

In Fig. 2, it is illustrated the variation of the reduced viscosity as a function of concentration for aqueous solutions of poly(vinyl alcohol) 15,000, 49,000, and 1,00,000 is illustrated. Although the poly(vinyl alcohol) is a water-soluble non-ionic polymer (21), the increasing of the reduced viscosity at low concentrations reveals a behavior which seems to correspond to a polyelectrolyte behavior (18, 20).

So as to verify that this behavior is not due to charges which are carried by the PVA macrochains, but to the important elongation of the macromolecular coils, particularly in dilute aqueous solutions, because of the great hydrophily of PVA, the addition of KCl in relatively high concentration is achieved and it is observed that no change occurs after the addition of KCl. In fact, the same

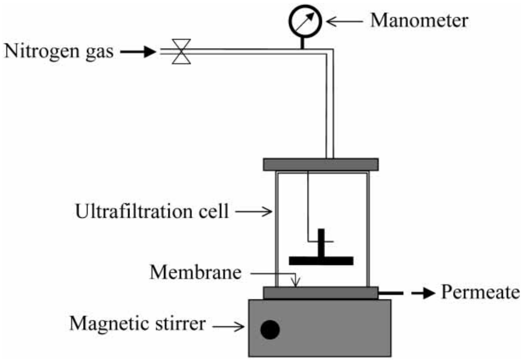

Figure 1. Schematic of the stirred cell used in the experiments.

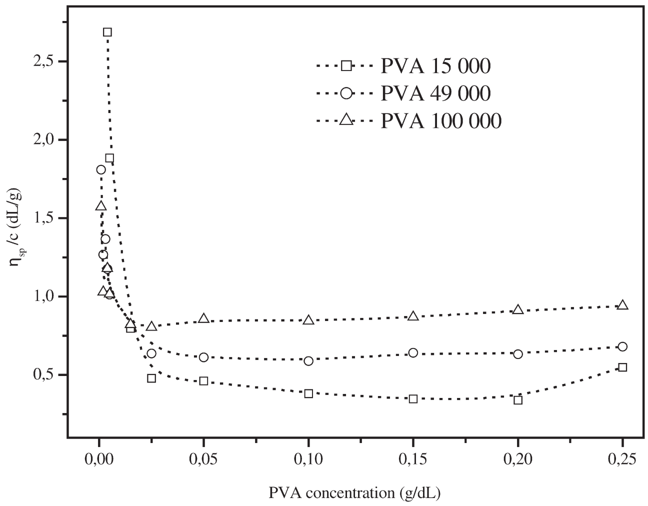

Figure 2. Viscometric behavior of PVA at different molecular weights.

behavior persists in KCl 10^{-1} M medium (Fig. 3). The increase of viscosity at low concentrations must then be attributed to a polyelectrolyte-like effect which disappears when the PVA-Cu(II) macrocomplex is formed (Fig. 4).

Indeed, the extended configuration assumed by the macromolecular chains of PVA, observed in particular at low concentrations is attenuated by the formation of the macrocomplex which takes up a tightly packed

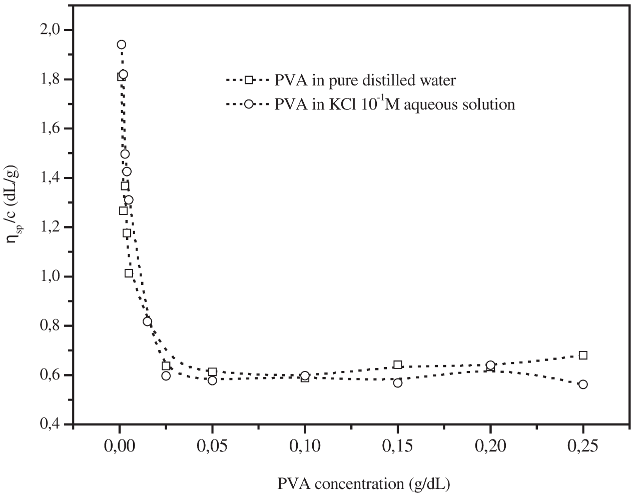

Figure 3. Viscometric behavior of PVA 49,000 in presence and absence of additional electrolyte.

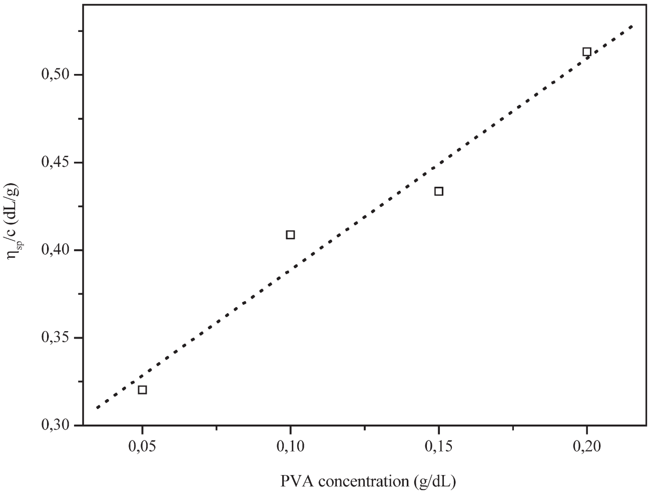

Figure 4. Viscometric behavior of Cu(II)-PVA 49,000 macromolecular complex.

conformation (22). Thus, the macrocomplex formation acts on the hydrodynamic behavior of the solution whose properties become similar to those of solutions of classical non-ionic polymers.

It is worthy to note that the knowledge of the viscometric behavior of PVA and PVA-Cu(II) aqueous solutions is useful because of the evident relationship between the feed solution viscosity and the flux through the ultrafiltration membrane. The correlation between the decrease of flux and the increase of viscosity can be illustrated clearly by Figs. 5 and 6 for each solution of PVA and PVA-Cu(II) respectively.

The effect of the occurrence of modification in the macromolecular conformation, induced by the formation of the complex, on the flow rate is revealed by following the evolution of the flux versus the pressure for aqueous solutions PVA 49,000 and PVA 49,000 Cu(II) macrocomplexes ultrafiltrated through the 50,000 cut-off membrane. Thus, flux is better for the solutions of the macrocomplex than for the corresponding poly(vinyl alcohol) solutions (Fig. 7). Moreover, the discrepancy from straight linear proportionality of flux to applied pressure, which reveals the establishment of the polarization layer near the membrane, is more marked for the macromolecular complex than for the corresponding poly(vinyl alcohol) solutions (Figs. 8, 9). These observations can be explained when one passes from the macromolecular solutions of poly(vinyl alcohol) to its corresponding cupric macrocomplex, by the reduction of the viscosity of the medium (increase of the flux) and by the increase of the interactions polymer/membrane (increase of the phenomenon of polarization concentration). Indeed, when the cupric ions form the complex bonds with PVA, the polymer takes up a tightly packed conformation, thus, the viscosity decreases and the flux increases. In addition, the

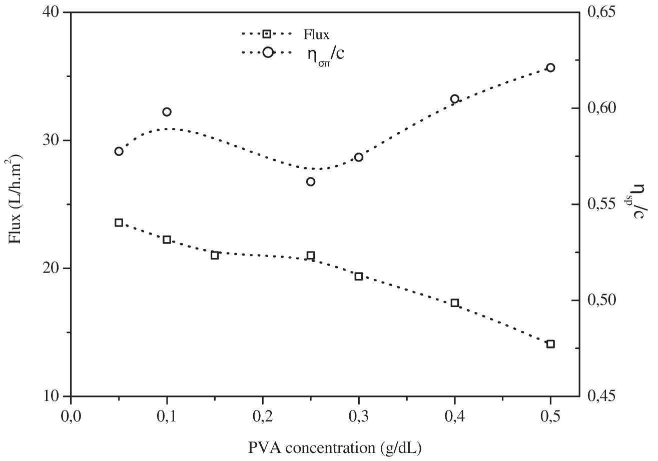

Figure 5. Relationship between viscometric behavior of PVA 49,000 and flux. (KCl: 10^{-1} M).

other cations present in solution (K^+) are moved away from the macromolecular chains by electrostatic repulsion and act as enrichment in free salts in solution, i.e. increase in the ionic strength of the medium, which contribute to the accentuation of the phenomena of adsorption (23).

After the observation of the hydrodynamic properties of the macrocomplex during the process of ultrafiltration, it was useful to study its behavior when various ultrafilters of different porosities and comparable nature are

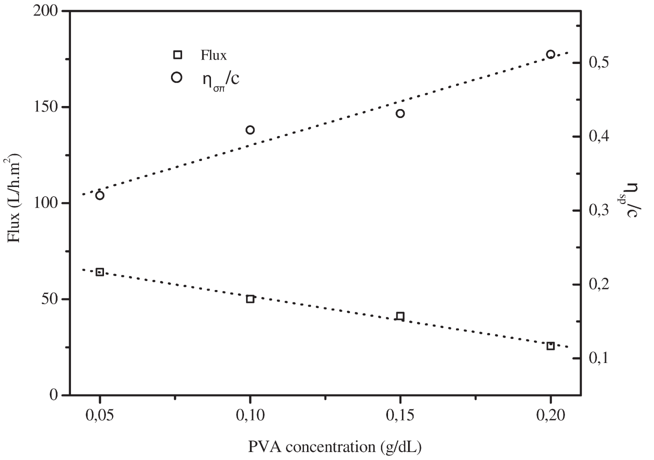

Figure 6. Relationship between viscometric behavior of Cu(II)-PVA 49,000 macromolecular complex. (Cu(II): 5.10^{-4} M; KCl: 10^{-1} M; pH: 7.1).

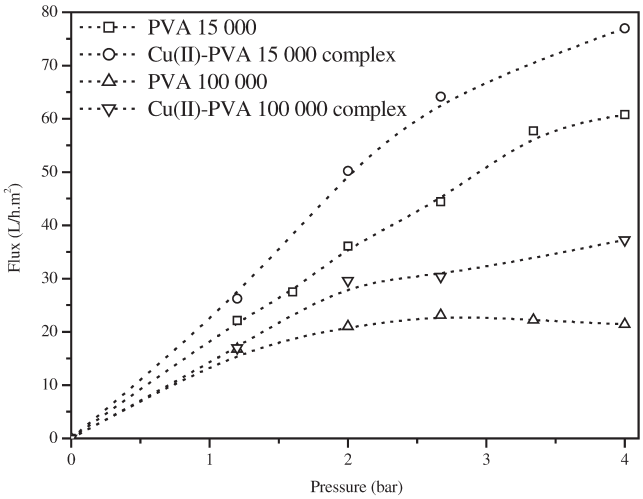

Figure 7. Ultrafiltration of aqueous solutions of PVA and PVA-Cu(II). Effect of the macrocomplex formation on flux (PVA: 1.5 g/L; Cu(II): 5.10^{-4} M; KCl: 10^{-1} M; pH: 7.1).

used. It is worthy to note that these membranes reject completely the PVA 49,000 Cu(II) macrocomplex (24). The results of the comparative study gathered in Fig. 10 make it possible to ensure that the flux evolves in the way of the increase of the cut-off of the membrane and always takes on the same profile.

The intensification of the phenomenon of polarization concentration for the 50,000 cut-off membrane can be explained by the fact that a relatively high-molecular-weight cut-off membrane, even though it may have a higher flux, is more susceptible to internal fouling than a membrane with a lower molecular weight cut-off which have lower pure water flux, but often provides a more sustained flux because less internal fouling occurs (25). Thus, to gather the best operating conditions, the microstructure of the ultrafiltration membrane must be taken into account as well as the hydrodynamic behavior of the treated solutions insofar as the interactions membrane/solution have a dominating effect in the effectiveness of separation by ultrafiltration.

Effect of pH on Viscometric Behavior and Flux

Figure 11 gives the evolution of reduced viscosity and solvent flux versus the pH. This study is done at various gradients of pressure to make it possible to check that the conditions of pressure implemented in the treatment of the solutions do not affect the profile of the flux.

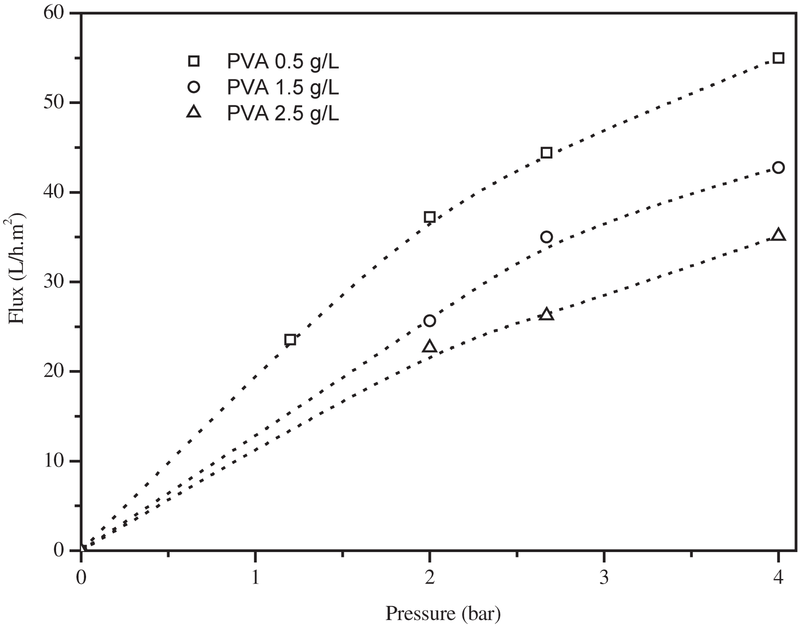

Figure 8. Ultrafiltration of aqueous solutions of PVA 49,000 (KCl: 10^{-1} M).

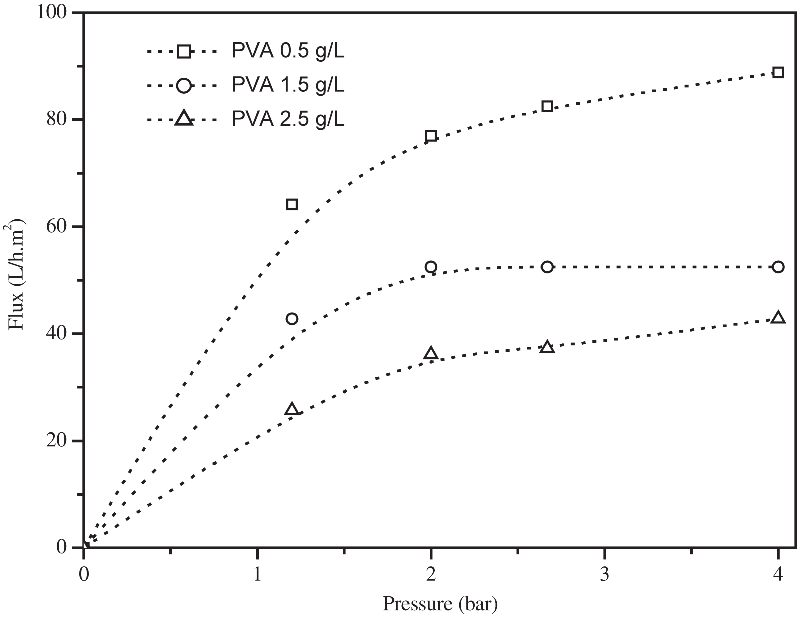

Figure 9. Ultrafiltration of aqueous solutions of Cu(II)-PVA 49,000 (Cu(II): 5.10^{-4} M; KCl: 10^{-1} M; pH: 7.1).

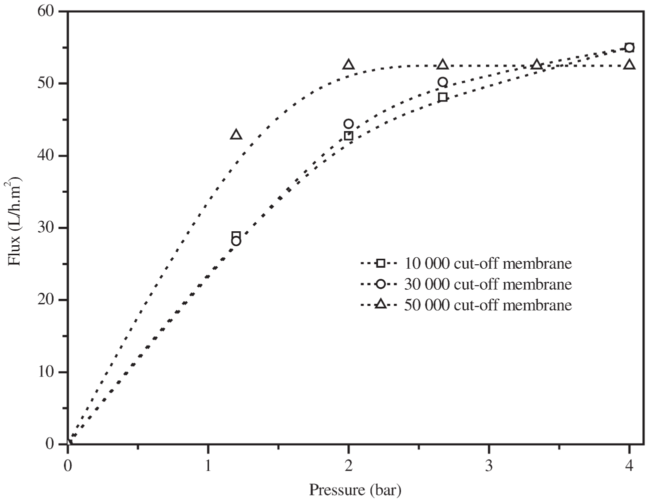

Figure 10. Ultrafiltration of aqueous solutions of Cu(II)-PVA 49,000 macromolecular complex through several cut-off membranes (PVA: 1.5 g/L; Cu(II): 5.10^{-4} M; KCl: 10^{-1} M; pH: 7.1).

The graphs gathered in this figure allow us to note that when the pH increases, the conditions of the complex formation are not being reached, i.e. the cupric ions are free in solution, and one observes a reduction of the medium viscosity. This behavior can be allotted to the reduction of the expansion of the polymer coils when the pH of the formation of the complex is achieved. However, the reduction of the viscosity is accompanied, contrary to what was awaited, with a reduction of the flux, which suggests a rising of the phenomenon of polarization concentration induced by the relatively high concentration of free cupric ions in solution. Indeed, the increase of ionic strength causes an increase of the thickness of adsorbed solute layer (23).

Besides, when the pH of complex formation is reached, the polymer takes up a tightly packed conformation (22) which is accompanied by the reduction of the viscosity of the medium and the increase of the flux.

Effect of Ionic Strength on Flux

At equal concentration in PVA, we observe, for the low KCl concentrations, that the flux of the permeate, during the ultrafiltration of the complex increases in the way of the increase of the concentration of KCl. On the other hand, for the high concentrations of KCl, the increase of the ionic strength of the medium, which is accompanied by a reduction of the viscosity of the macromolecular complex solution, is accompanied, however, by a reduction of the

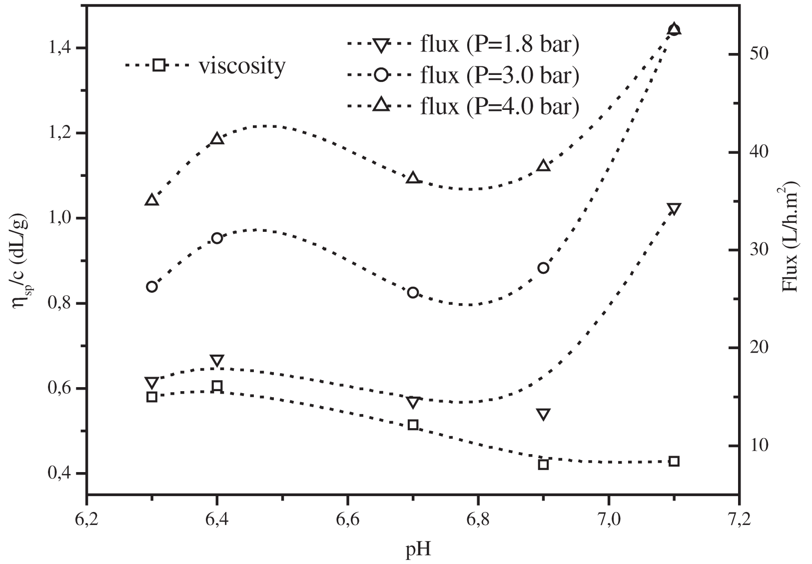

Figure 11. Evolution of reduced viscosity and flux with pH (PVA 49,000: 1.5 g/L; Cu(II): 5.10^{-4} M; KCl: 10^{-1} M).

flux of the permeate. These results are illustrated in Fig. 12 and confirm those of the study of the evolution of the flux with the pH which showed that an increase of the ionic strength of the medium, induced by a high concentration of the free ions in solution, was accompanied by a reduction of the flux

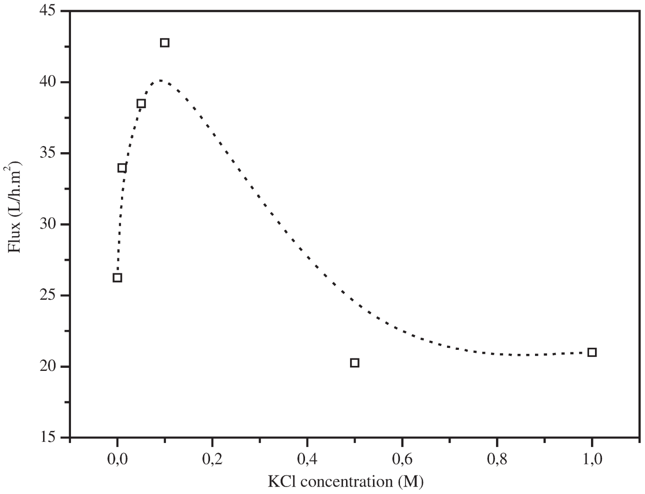

Figure 12. Effect of ionic strength on flux (PVA 49,000: 1.5 g/L; Cu(II): 5.10^{-4} M; pH: 7.1).

because of the increase of the thickness of the adsorbed solute layer. Homberg et al. (21) interpret the emphasis of the adsorption phenomenon of polymers at high salt concentrations by the fact that the added salt causes a shielding of the repulsive forces between the polymer and the surface and also between different polymers as the interchain repulsion becomes more screened at high salt concentrations.

Effect of the Ionic Species in Solution on Flux

Figures 13, 14, and 15 illustrate the effect of the nature of the salt added to the macromolecular solutions and the effect of the nature of the anion in Cu(II) salts, on the evolution of the flux of permeate with the applied pressure. The results gathered in these figures show the importance of the nature of the added ionic species on the hydrodynamic behavior of the aqueous solutions of PVA-Cu(II) macrocomplex during the process of ultrafiltration.

In Fig. 13, we note that even if the profiles of the flux of the permeate are similar, the fluxes relating to the ultrafiltration of PVA-Cu(II) macrocomplex in the presence of KCl are, however, better than those relating to its ultrafiltration in the presence of NaCl or LiCl. Indeed, the small ions, carrying a high charge density tend to be more strongly solvated, attracting and ordering a greater number of solvent molecules around them. This behavior induces a reduction in the interactions of the small ions with the macromolecular chains. The tightly packed conformation, adopted when the conditions of the pH

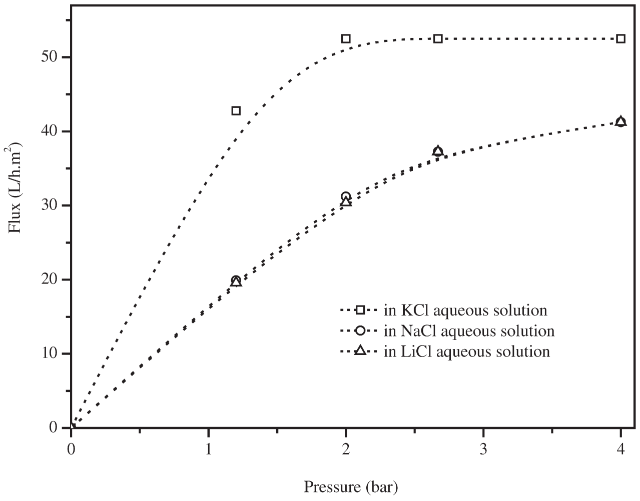

Figure 13. Effect of the nature of the added salt on flux (PVA 49,000: 1.5 g/L; Cu(II): 5.10^{-4} M; XCl: 10^{-1} M; pH: 7.1).

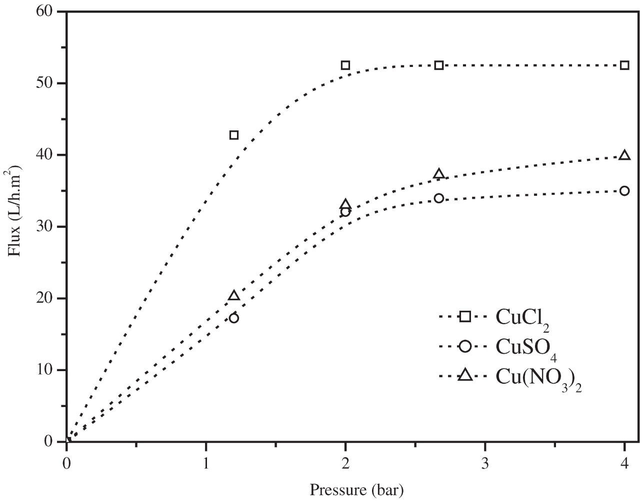

Figure 14. Effect of the nature of the anion in the cupric salt on flux (PVA 49,000: 1.5 g/L; Cu(II): 5.10^{-4} M; KCl, K_2SO_4 or KNO_3: 10^{-1} M; pH: 7.1).

formation of the complex are met, is thus in fact, more marked in the presence of K^+ than Na^+ or Li^+, what explains the differences observed in fluxes.

Figure 14 gathers the results obtained in the study of the evolution of the flux with the pressure during the ultrafiltration of aqueous solutions of PVA-Cu(II) macrocomplex formed from cupric salts are different by the nature of

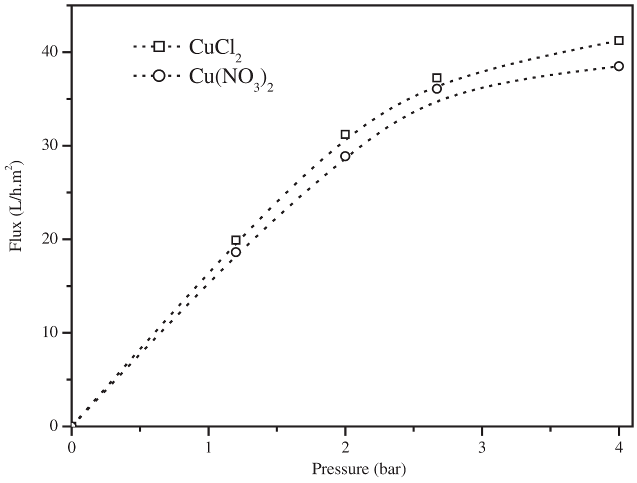

Figure 15. Effect of the nature of the anion in the cupric salt on flux (PVA 49,000: 1.5 g/L; Cu(II): 5.10^{-4} M; NaCl or $NaNO_3$: 10^{-1} M; pH: 7.1).

their anions. Thus, the PVA-Cu(II) macrocomplex formed using cupric sulfate gives a flux lower than that formed using cupric nitrate which is itself weaker than that formed using cupric chloride. The enhancement of the flux in the case of the complex formed from cupric chloride is confirmed by the results gathered in Fig. 15 where added salt is NaCl or $NaNO_3$, instead of KCl, KNO_3, or K_2SO_4.

The enhancement of the flux in the case of the complex formed from cupric chloride can be explained by an increase in the stability of the conformation of the complex when the cupric chloride is used in the presence of KCl. Thus, the presence of KCl seems to act positively with the formation and the stability of the PVA-Cu(II) macrocomplex, and consequently with the improvement of the flux of permeate through the ultrafilter.

CONCLUSION

This experimental study is about the effect of hydrodynamic behavior of aqueous solutions of poly(vinyl alcohol) and poly(vinyl alcohol)–cupric complex on the performance in the concentration of the macromolecular cupric complex by ultrafiltration. The profound discrepancy of the hydrodynamic behavior between the poly(vinyl alcohol) and the poly(vinyl alcohol)–cupric complex in aqueous solution has been highlighted. Indeed, poly(vinyl alcohol) has a polyelectrolyte–like behavior whereas poly(vinyl alcohol)–cupric complex has properties which are similar to those of non–ionic polymers. The modification of the macromolecular conformation is induced by the formation of the complex. It acts on the hydrodynamic properties of the macrocomplex and on the flow rate through the employed membranes. Thus, the flux is better and the phenomenon of polarization concentration is more intense for the solutions of macrocomplex than for the corresponding poly(vinyl alcohol) solutions. These results can be explained by the decrease of the medium viscosity and the increase of the phenomena of adsorption accentuated because of the increase of the ionic strength of the medium. The effect of pH on the viscometric behavior and flux has been evaluated and the results obtained permit to conclude that the medium viscosity decreases and the flux of permeate increases when, in fact, the pH of complex formation is reached. The study of the effect of ionic strength on flux allowed observing that for the low KCl concentrations flow rate increases with the increasing of KCl concentration; and it decreases with the increasing of KCl concentration for the high KCl concentrations. The effect of the nature of the ionic species in solution on flux has been investigated and the obtained results lead to the conclusion that the use of the cupric chloride salt in the preparation of the macromolecular complex improves the hydrodynamic properties of the solution and enhances the performance of its treatment by means of the ultrafiltration process.

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