

Selective Separation of Some Heavy Metals by Poly(vinyl alcohol)-Grafted Membranes

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ABSTRACT: A poly(vinyl alcohol) membrane (PVA) was modified by radiation graft copolymerization of acrylic acid/styrene (AAc/Sty) comonomers. The Cu and Fe ion-transport properties of these membranes were investigated using a diaphragm dialysis cell. In the feed solution containing CuCl₂ or a mixture of CuCl₂ and FeCl₃, the PVA-g-P(AAc/Sty) membranes showed high degrees of permselectivity toward Cu²⁺ rather than toward Fe³⁺. The permeation of Cu²⁺ ions through the membranes was found to increase with decrease in the grafting yield. However, as the content of Cu²⁺ ions in the Cu/Fe binary mixture feed solutions decreased, the rate and the amount of transported Cu²⁺ through the grafted membrane decreased, with no appreciable permselectivity toward Fe³⁺. When Fe²⁺ ions were used instead of Fe³⁺ ions in the feed solution containing Cu²⁺, the transport of both Cu²⁺ and Fe²⁺ through the membrane was observed. The rate of transport of Fe²⁺ was higher than that of Cu²⁺. In addition, it was found that the selective transport of ions was significantly influenced by the pH difference between both sides of the membranes. As the pH of the feed or the received solution decreased, both Cu²⁺ and Fe³⁺ passed through the membrane and were transported to the received solution. The role of carboxylic acid and the hydroxyl groups of the grafted membranes in the transportation process of ions is discussed. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 125–132, 2000

Key words: poly(vinyl alcohol); copolymerization; membrane; separation; dialysis; permselectivity; transport

INTRODUCTION

Recovery of Cu²⁺ from aqueous solutions that contain other metal ions is an important industrial endeavor, which can be accomplished with conventional ion exchange or chelating resins,¹ but such processes are insufficient. Because of inadequate ion selectivity² provided by such resins, liquid extraction with certain organosoluble ligands such as polyether³ affords superior selectivity but lacks the mechanical convenience and operational flexibility inherent in a solid–liquid

system. In view of this, we searched for a new technique which would have the advantage of both solid–liquid and liquid–liquid systems.

The ability to carry out active and selective transport of ion is of great interest in connection with the technological applications of membranes. Much attention has been paid recently to the development of metal transport in Donnan dialysis using ion-exchange membranes.^{4–7}

With time, dialysis has come to be used widely as a simple laboratory method of separating very large molecules from small ones, on the basis of different rates of diffusion. The kinetic movement of the solute molecules will tend to drive them through the membrane in the direction of low concentration. On the other hand, as a result of

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an osmotic-pressure difference, the net movement of the solvent molecules will be in the opposite direction. The rate of diffusion of any single solute through a membrane depends on many factors, among which are the solute, temperature, physical setup, pH of the solutes, and types of membranes.

Synthetic membranes do not show appreciable selective transport properties for metal ions for some polymers such as polyamine sulfone derivatives⁸ and other copolymers containing acrylonitrile groups.⁹ The ability to transport metal ions through the membrane can be improved by modification of the physical properties and the chemical structure properties of the membrane.¹⁰ A number of unique properties associated with water-soluble polymers such as poly(vinyl alcohol) (PVA) allow them to have wide applications in transport processes.¹¹ In previous studies,¹² PVA-g-P(acrylic acid/styrene) (AAc/Sty) membranes were prepared by radiation grafting of the AAc/Sty comonomer onto PVA films which were used as permselective membranes for the separation of Ni ions from the feed solution containing Co ions. In the present work, a trial was made using PVA-g-P(AAc/Sty) as a separating membrane for Cu and Fe ions using a diaphragm dialysis cell. Factors affecting the transport of Cu or Fe through the membrane were also investigated.

EXPERIMENTAL

Materials

PVA powder (Hanawa Chemical Pure, Osaka, Japan), DP = 1700, and degree of saponification, 98 %, was used. Sty GRG (Avondale Laboratories, Banbury, Oxon, England), purity 99%, and AAc (Merck, Darmstadt, Germany), purity 99.9%, were used without further purification. The other chemicals, such as solvents and reagents were reagent grade and used as received.

Methods and Apparatus

Graft Copolymerization

Strips of PVA films of thickness 50–60 mgr:m were weighed and then immersed in a 20% (2:1 mol/mol) AAc/Sty comonomer solution using ethanol/water of 80/20 composition as a diluent. The direct radiation grafting method was used in an air atmosphere. The glass ampules containing all reactants and the polymer substrate were then subjected to ⁶⁰Co gamma rays at dose rate of 1.2

Gy/s at different doses. The grafted films were removed and washed thoroughly with methanol, benzene, and a mixture of benzene/methanol (1:1) and then immersed in a mixture of water/methanol (2:1) to extract the residual monomer or homopolymer which may accumulate in the grafted films. The films were then dried in a vacuum oven at 50°C. The degree of grafting was determined by the percent increase in weight as follows:

$$\text{Degree of grafting(\%)} = [(W_g - w_0/w_0)] \times 100$$

where W_0 and W_g are the weights of the initial and grafted films, respectively. Details of this technique were described in a previous study.¹²

Swelling Measurements

Clean, dried, grafted films of known weights were immersed in distilled water at room temperature until equilibrium had been reached (24 h in almost all cases). The films were removed and the excess water on the surface was removed, blotted by absorbent paper, and quickly weighed. The water uptake (swelling %) was calculated as follows:

$$\text{Water uptake (\%)} = [(w_s - w_g/w_g)] \times 100$$

where w_g and w_s represent the weights of the dry and wet membranes, respectively.

Ultraviolet Spectroscopy

Analysis by a UV spectrophotometer was carried out using a Milton Roy Spectronic 1201 in the range from 190 to 900 nm.

X-ray Fluorescence (XRF)

An HNU TEFA-PC XRF automated nondestructive elemental analyzer was used for the X-ray measurements.

Dialysis Apparatus and Procedure

The dialysis permeability measurements were carried out at 25°C using a dialysis cell consisting of two compartments (18 cm³ each) made of poly(methyl methacrylate) as shown in Figure 1. The prepared membrane, with a 19.5-cm² effective area, was placed in between the two compartments. In the left-hand side of the cell, a metal solution of 1000 ppm concentration was introduced, and in the right-hand side, distilled water

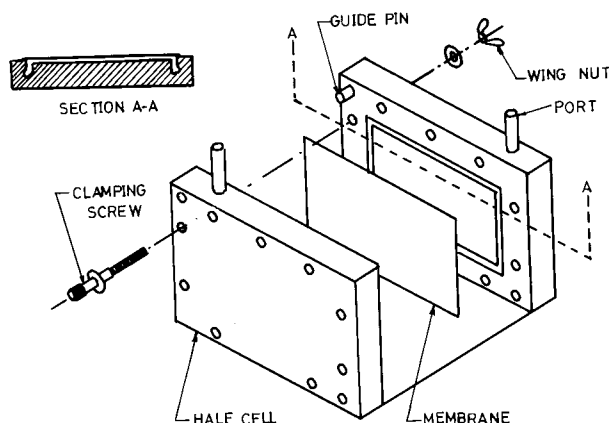


Figure 1 Sketch of dialysis cell.

was introduced. The sample was withdrawn from both sides of the membrane at 5, 10, 30, . . . , and 100 min.

Determination of Copper Ions¹³

1. A volume of the sample containing less than 0.05 mg Cu (25.00 mL max) was put in a 50-mL beaker and the volume was adjusted to 25.0 mL with metal-free water.
2. A blank of 25.0 mL metal-free water and sufficient standards was prepared and the volume adjusted to 25.0 mL with metal-free water.
3. Add 1.0 mL of 5% HNO₃.
4. Add 1.0 mL of 10% sodium citrate.
5. Add 1.0 mL concentrated NH₄OH. Stir the solutions vigorously.
6. Add 1.0 mL dihydroxyethylthiocarbamic acid and mix well.
7. Determine the absorbance of each sample against the blank at 425 nm.

Determination of Iron Ions

This method is based on the reaction between ferrous ion and 2,2'-bipyridine that yields a red complex.¹⁴ Hydroxylamine hydrochloride reduces ferric iron to ferrous ion. The color develops immediately and is stable for hours. The color intensity is independent of pH in the range of 3–10.

1. Use a volume of the sample containing less than 100 μg Fe (25 mL max) in a 50-mL beaker and adjust the volume to 25.0 mL with metal-free water
2. Prepare a blank of 25.0 mL metal-free wa-

- ter and a sufficient standard and adjust the volume to 25.0 mL with metal-free water.
3. Add 1.0 mL bipyridine solution (2.0 g/L demineralized water).
4. Add 2.0 mL NH₂ · OH—HCl reagent (100 g NH₂ · OH—HCl dissolved in 40 mL HCl and adjust the volumes to 1 L).
5. Add 10.0 mL CH₃ · COONa solution (350 g/L demineralized water).
6. Determine the absorbency of each sample against the blank at 520 nm.

RESULTS AND DISCUSSION

Separation of Cu²⁺ from Solution That Contained Fe³⁺

To determine the selective transport of Cu and Fe through the grafted membranes, the transport properties of PVA-*g*-P(AAc/Sty) membranes toward Cu, Fe, and a mixture of Cu and Fe ions were studied. The transport of Cu and Fe from feed solutions containing Cu, Fe, or a mixture of both Cu and Fe ions was investigated and results are shown in Figures 2 and 3. It is obvious that, in the feed solution containing FeCl₃ or a mixture of CuCl₂ and FeCl₃, the PVA-*g*-P(AAc/Sty) membrane does not allow Fe³⁺ to transport through to the received solution. However, Cu²⁺ ions can

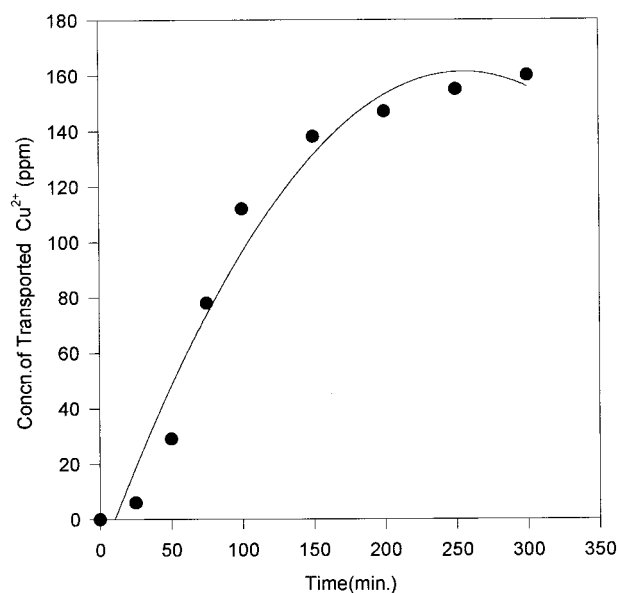


Figure 2 Transport of Cu²⁺ through PVA-*g*-P(AAc/Sty) membrane having degree of grafting of 55%; pH of feed solution/received solution, 4.7/6.7.

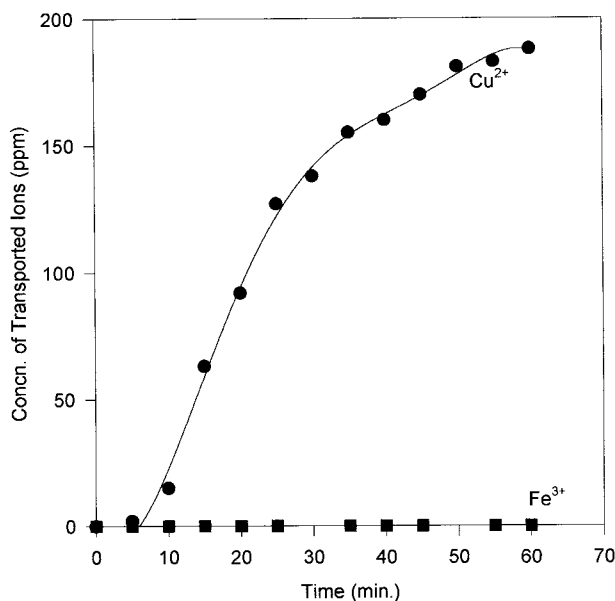


Figure 3 Transport of Cu^{2+} from solution containing Fe^{3+} through PVA-*g*-P(AAc/Sty) membrane having a degree of grafting of 52%; pH of the feed solution/received solution, 4.03/6.7; and Cu/Fe composition, 1/1 (ppm/ppm).

penetrate through the membrane either if the ions exist alone in the feed solution or in presence of Fe^{3+} ions. Also, it was observed that the presence of Fe^{3+} ions in the feed solution enhances the rate and the amount of Cu^{2+} ions transported through the membranes.

This result can be explained by taking into account that Fe^{3+} is chelated with reactive functional groups of the membrane to form a stable complex. This is may be due to the trivalent property of Fe. As a result, the hydrogen bonding of the carboxylic acid and hydroxyl functional groups broke down and the penetration rate of Cu from the feed solution to the receiver solution increased.

XRF study of the PVA-*g*-P(AAc/Sty) membrane, which was used in the separation of Cu^{2+} from Fe^{3+} , shows a clearly distinguishable peak responsible for the Fe^{3+} metal. This indicates that such a membrane formed a stable complex with Fe^{3+} ions and prevents Fe^{3+} to transport through it (Fig. 4). Figures 2 and 3 show also that, for the feed solution containing Cu, the transport of Cu^{2+} takes place slowly and the rate of transport of Cu via the membrane is not as high as that obtained from a feed solution containing a mixture of Cu and Fe under experimental conditions.

These results suggest that in the feed solution containing Cu^{2+} the grafted membrane of

—COOH and —OH functional groups (those responsible for hydrogen bonding) chelated with Cu^{2+} . This process delays the transport of Cu and may regulate the pore size of the membranes to be suitable for transporting of the residual Cu^{2+} ion from the feed solution to the received one. Therefore, transport of Cu^{2+} through a membrane takes a longer time if compared with that found in the presence of Fe^{3+} ions. In addition, the restriction of Cu^{2+} ion transport can be attributed to its lower concentration in the feed solution (because of consuming some of them in the complexation process with the membrane) and result in decrease of its rate of transport. It is known that the concentration of metal ion in the feed solution affects its transport through the membrane. The higher the concentration of the ion in the feed solution, the higher the rate of its transport.

Factors Affecting the Transport of Cu or Fe Through the PVA-*g*-P(AAc/Sty) Membrane

Among the factors affecting the transport of metal ions through the membrane are the porosity and amount of functional groups, that is, the degree of grafting, pH, and concentration of the metal feed solution, the valence of the metal ion, and the type of anion of the metal salt. The influence of such parameters on the transport of Cu^{2+} and Fe^{3+} ions through the prepared grafted membranes is presented in the following.

Effect of Degree of Grafting

Figure 5 shows the effect of grafting yield on the transport process of Cu^{2+} and Fe^{3+} through the

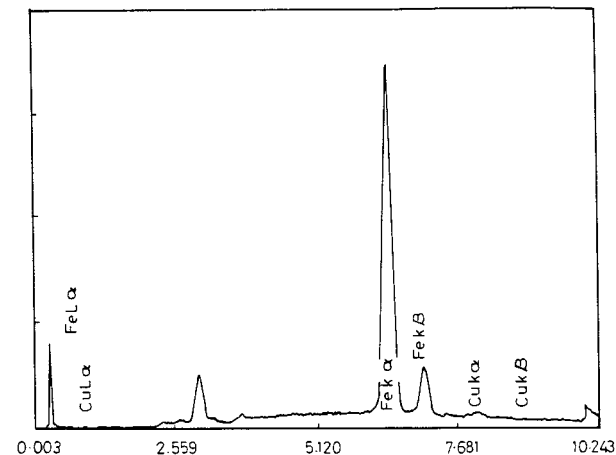


Figure 4 XRF scan for PVA-*g*-P(AAc/Sty) membrane used in separation of Cu^{2+} from its feed solution containing Fe^{3+}

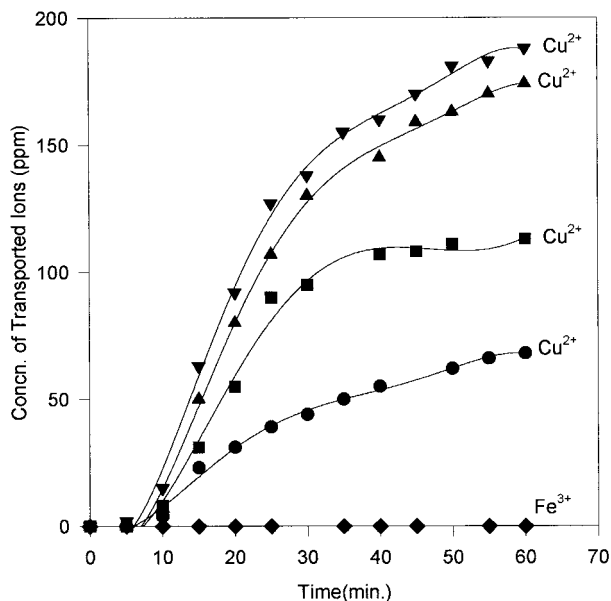


Figure 5 Effect of grafting yield on separation process of Cu^{2+} from Fe^{3+} through PVA-g-P(AAc/Sty) membrane. Degree of grafting (%): (\blacktriangledown) 52; (\blacktriangle) 66; (\blacksquare) 79; (\bullet) 99. Cu/Fe composition, 1/1 (ppm/ppm); pH of the feed solution/received solution, 4.03/6.7.

PVA-g-P(AAc/Sty) membrane. It is obvious that the amount of transported Cu^{2+} ions increases with time and it has a nonlinear relationship. This behavior is observed for all membranes that have different degrees of grafting. However, the rate and amount of transported Cu^{2+} increases as the degree of grafting decreases. Meanwhile, the Fe^{3+} ions do not transport but they are chelated by the membranes.

The results suggested that, at a higher grafting yield, the content of the crosslinked network structure is greater than that at a lower grafting yield. Also, as the degree of grafting increases, the content of polystyrene graft chains increases in the whole graft copolymer. This is based on the fact that polystyrene is hydrophobic in nature. As a consequence, the diffusion of water through the membrane decreased, resulting in retarding the diffusion of Cu^{2+} throughout the membrane. Therefore, at a higher grafting yield, the rate and the amount of transported Cu^{2+} metal decreased and a much longer time was needed for its transportation. To confirm such assumptions, the water content in the grafted films was determined.

Determination of the degree of swelling serves as a method of assessing the degree of crosslinking of polymer chains by grafting AAc and Sty binary monomers onto PVA films. From Figure 6,

which represents the effect of the degree of grafting of AAc/Sty chains on the water content of PVA films, it can be seen that as the degree of grafting increases the water-uptake percent decreases. This indicates that the branches of AAc–Sty-grafted chains affect the hydrophilic properties of PVA: Three-dimensional network structures of the grafted polymer were formed during the grafting process, resulting in reduction of the swelling property of the grafted films that affect its metal-ion transport property.

Effect of pH

As is well known, the transport or chelation of metal ions through membranes is very dependent on the pH of the metal feed and the received solutions.^{15–16} Figure 7 shows the concentration of transported metal ions as a function of time at different pH's of the feed and the received solutions. It can be seen that when a pH ratio of 4.03/6.7 (metal feed solution/received solution) is used no Fe^{3+} ion passed through the membrane (as mentioned previously). However, as the pH of the metal feed solution or the received solution decreases, both Cu^{2+} and Fe^{3+} ions pass through the membrane and are transported to the received solution. The decrease in pH of the received solution (4.03/2.2) results in increasing the concentration of transported Cu^{2+} and Fe^{3+} if compared with that obtained at higher pH (4.03/

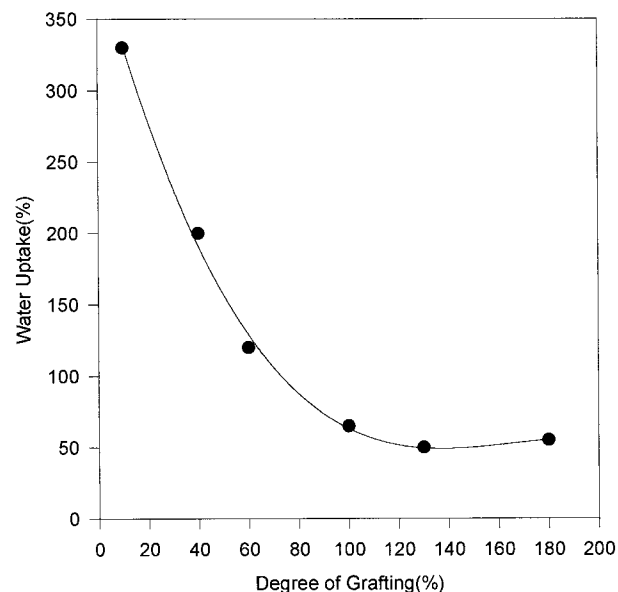


Figure 6 Water uptake (%) versus degree of grafting for PVA-g-P(AAc/Sty) membranes.

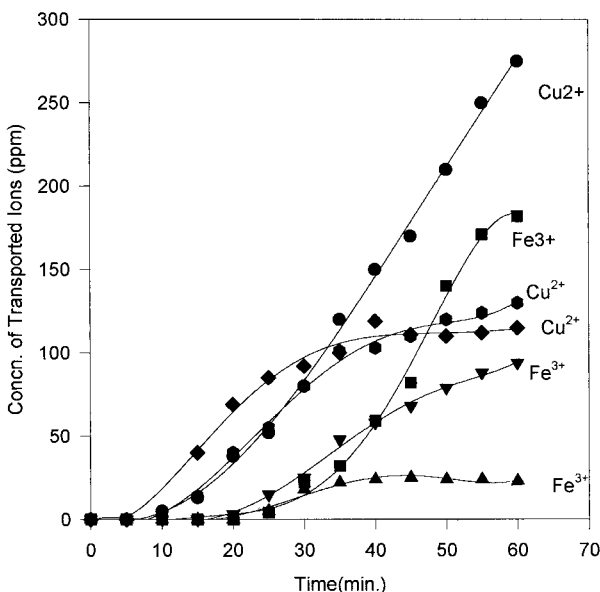


Figure 7 Effect of pH change on transport process of Fe^{3+} or Cu^{2+} through PVA-g-P(AAc/Sty) membrane having degree of grafting of 99%. pH of feed solution/received solution: (\blacktriangle , \blacklozenge) 2.3/6.7; (\blacklozenge , \blacklozenge) 2.3/2.2; (\bullet , \blacksquare) 4.03/2.2. Cu/Fe composition, 1/1 (ppm/ppm).

6.7). It is also observed that, at a given pH, the concentration of transported Cu^{2+} is higher than that of Fe^{3+} .

The transport of Fe^{3+} through the membrane at low pH can be attributed to desorption of the complex formed between Fe^{3+} and its chelated groups. Also, the high amount of Cu^{2+} transported through the membrane, in comparison with that observed at normal pH (4.03/6.7), can be attributed to H^+ flux driving the transport of Cu^{2+} through the membrane.⁷ The transport rate is related to proton activity. It means that a larger pH difference between the feed and the receiver solutions is necessary to obtain high ion transfer.

The results also suggest that the chelating properties of functional group membranes are affected by the pH. When the pH decreases in the feed solution, the transport of Fe^{3+} and Cu^{2+} may take place by a concentration gradient mechanism and the chelating properties of the functional group membrane toward Fe^{3+} is weakened.

Effect of Cu Concentration on Its Transportation Through the Membrane

It is expected that the transport of metal ions through the membrane is affected by the concentration of metal in its feed solution. Figure 8

shows the effect of different $\text{Cu}^{2+}/\text{Fe}^{3+}$ compositions on the transportation process. It can be seen that as the Cu^{2+} concentration increases in the feed solution the amount and rate of transported Cu^{2+} increases in the received compartment. Also, the permselectivity of PVA-g-P(AAc/Sty) toward Cu^{2+} is observed with no appreciable permselectivity toward Fe^{3+} . The results suggest that the reduction of the Cu^{2+} amount in the feed solution does not affect its transport through the membranes. Also, reducing the amount of Cu in the feed solution does not enhance the transport of Fe^{3+} .

Effect of Valence of Fe on Its Transportation in the Presence of Cu

The effect of the valence of Fe metal on the transport process of Cu^{2+} and Fe^{2+} was studied and is shown in Figure 9(A). It can be seen that the transport of Cu^{2+} and Fe^{2+} in the sulfate form occurs through the membrane and the rate of transport of Fe^{2+} is higher than that of Cu^{2+} . However, in the feed solution containing Fe^{3+} and Cu^{2+} , only the permeation of Cu ions takes place [Fig. 9(B)].

These results show that the valence of metal plays an important role in the transport process and the behavior of the membranes toward Fe^{3+}

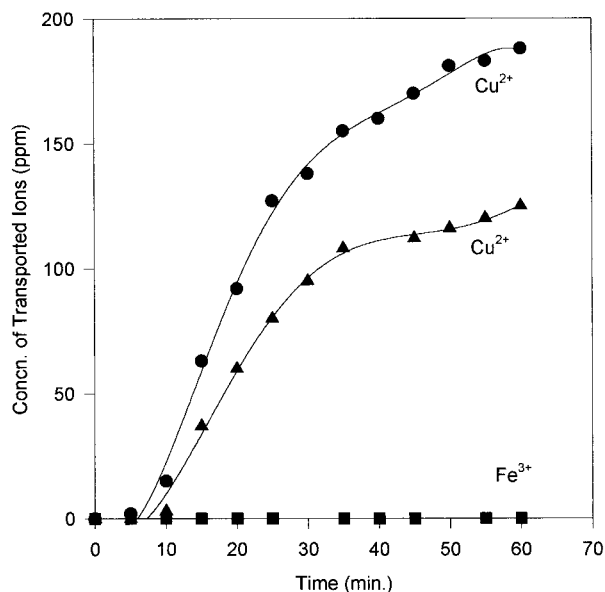


Figure 8 Effect of Cu^{2+} concentration on the transport process of Fe^{3+} through PVA-g-P(AAc/Sty) membrane having degree of grafting of 52% at composition of Cu/Fe of (\bullet) 1/1 (ppm/ppm) and (\blacktriangle) 1/4 (ppm/ppm). pH of feed solution/received solution, 4.0/6.7.

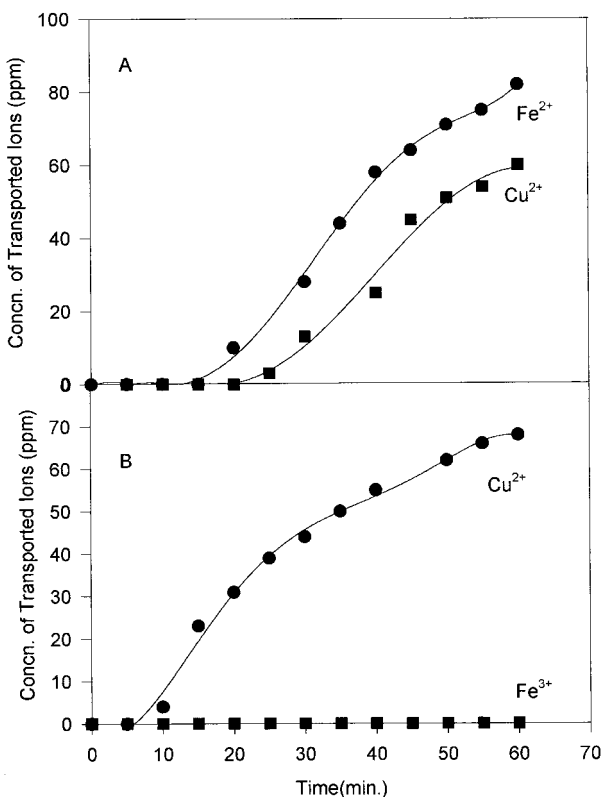


Figure 9 Effect of valence of Fe ion on its transportation in the presence of Cu²⁺ through PVA-g-P(AAc/Sty) membrane having degree of grafting of 99% at composition of Cu/Fe of 1/1 (ppm/ppm) and pH of feed solution/receiver solution of 4/6.7.

is quite different from that toward Fe²⁺. This means that the PVA-g-AAc/Sty membranes prefer Fe³⁺ to chelate with rather than Fe²⁺ ions. It has been reported that the higher the valence and the lower the atomic radii the higher the ability of metal to complex with ligand groups.¹⁷

Effect of Anion Types on the Transport Process

As mentioned before, when Cu²⁺ and Fe³⁺ are used together in the form of chloride salts, the Cu²⁺ ions only are transported but Fe³⁺ is chelated with the membrane and does not transport to the receiver solution. However, when CuSO₄ is used instead of CuCl₂, both Cu²⁺ and Fe³⁺ are transported through the membrane. The transport of Fe³⁺ shows an inductive period within the first 30 min; thereafter, it increases with time (Fig. 10).

The results suggest that the Fe₂ · (SO₄)₃ that may be formed as a result of the replacement reaction between CuSO₄ and FeCl₃ is responsible

for the transport of Fe³⁺. This means that the Cl ion may play a role by participating as a ligand in the stability of the Fe-polymer complex when FeCl₃ is used. Also, the selective transport of anions may be taken into account.

Role of Carboxylic and Hydroxyl Groups of the Grafted Membrane in Transport Process

The selective separation of Cu²⁺ ions from one side of the cell of a high concentrated solution to the other side of the cell of lower concentration is accomplished by selective capture of the Fe ions. The change in pH affects the properties of functional groups that can interact with Fe³⁺. The effect of pH changes on the grafted membranes can be explained by that the —COOH and —OH groups of PVA-g-P(AAc/Sty) may exhibit tautomerism and transform very rapidly in lower pH solutions.⁹ The transform structure prevents the capture of Fe and/or Cu; therefore, they transport through the membrane to the receiver solution. To alter this, the —COOH group of poly(AAc) in the grafted membrane was replaced by the —CONH₂ group by grafting of PVA with acrylamide (AAM) instead of AAc.

Figure 11 shows the transport of Cu²⁺ and Fe³⁺ through the membrane grafted with AAM in

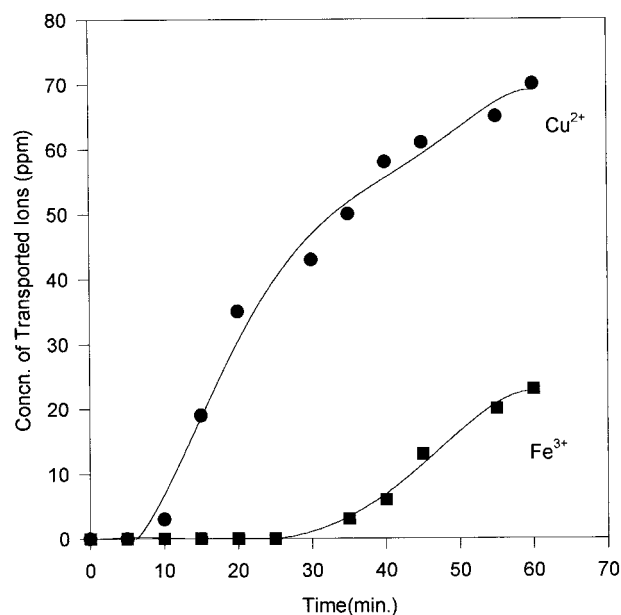


Figure 10 Effect of anion changes on its transportation in the presence of Cu²⁺ and Fe³⁺ through PVA-g-P(AAc/Sty) membrane having degree of grafting of 99% at Cu/Fe composition of 1/1 (ppm/ppm), and pH of feed solution/receiver solution, 4.4/6.7.

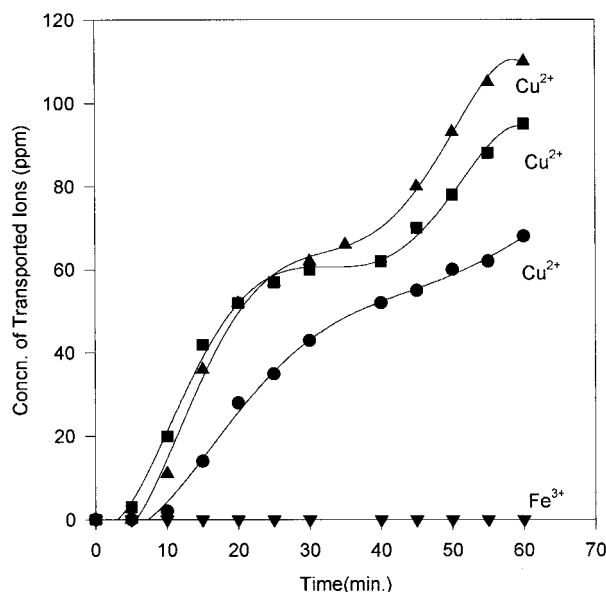


Figure 11 Transport of Cu^{2+} from solution containing Fe^{3+} through PVA-g-P(AAm/Sty) membrane having degree of grafting of 30% at different pH's. pH of feed solution/received solution: (■) (2.3/6.7); (▲) 4.03/2.2; (●) 2.3/ 2.2. Cu/Fe composition, 1/1 (ppm/ppm).

the feed solution containing both Fe^{3+} and Cu^{2+} ions at different pH's. It can be seen that the permselectivity of PVA-g-P(AAm/Sty) toward Cu^{2+} was observed with no appreciable permselectivity toward Fe at all different pH's investigated here. The results indicated that the change in pH in such systems does not affect the permeability of Cu^{2+} or enhance the transport of Fe^{3+} . Such a case is not found when a membrane with $-\text{COOH}$ functional groups is used, for which the Fe^{3+} transport is pH-dependent. This means that the functional groups of membranes play an important role in the separation process, especially at different pH's.

SUMMARY AND CONCLUSIONS

A PVA-g-P(AAc/Sty) comonomer was prepared. These grafted copolymers were investigated as selective transport membranes for Cu^{2+} from a feed solution containing Fe^{3+} . Transport of Cu^{2+} and/or Fe^{3+} through PVA-g-P(AAc/Sty) was determined and it was found that AAc/Sty membranes have a high affinity to chelate with Fe^{3+} and allowed the Cu^{2+} transport to reach the received solution at a pH of 4.03/6.7 (feed/received

solution). When the pH of the metal feed solution or the received solution is decreased, both Cu^{2+} and Fe^{3+} are passed through the membrane and transported to the received solution. In feed solution containing both Fe^{3+} and Cu^{2+} , PVA-g-P(AAc/Sty) has a higher permselectivity property toward Fe^{2+} than for Cu^{2+} . Functional groups of the grafted membranes play a role in the transport process of Fe^{3+} at low pH. As the $-\text{COOH}$ group of poly(AAc) in the grafted membrane is replaced by $-\text{CONH}_2$ groups by grafting PVA with AAm instead of AAc, the transport of Fe^{3+} through the grafted membrane is inhibited at different pH's. It can be concluded that the PVA-g-P(Sty/AAm)-grafted membranes can be used in the separation of CuCl_2 from a solution containing FeCl_3 at different pH's. However, The PVA-g-P(AAm/Sty) grafted membranes are candidates for separating of Cu^{2+} from its feed solution containing Fe^{3+} at pH 4/7 (feed /received solution).

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