

Copper (II) Transfer Through Carboxylic Ion-Exchange Membranes Prepared by Paste Method

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SYNOPSIS

Interpolymer carboxylic membranes were prepared by the paste method. Transport of copper through the membrane was investigated by using a system containing HCl (receiver solution) and CuCl_2 (feed solution). The transfer rate was found to be greatly affected by the membrane composition and HCl concentration in the receiver solution. A membrane based on poly(vinyl chloride)/poly(methyl methacrylate-co-divinylbenzene) with 5 wt % divinylbenzene showed the highest transfer rate. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Much attention has been paid recently to the development of metal transport in Donnan dialysis using ion-exchange membranes. It was considered that the ability to transport metal ions through the membrane can be improved by modification of membrane physical and chemical structure and properties.¹⁻⁷

Wen and Hamil¹ reported that transport of Co^{2+} , Ni^{2+} , Mg^{2+} , and Fe^{3+} ions through sulfonated styrene-grafted or acrylic acid-grafted membrane increases with the increase of membrane ion-exchange capacity and that the styrene-grafted membrane was more effective than the acrylic acid-grafted one.

Sudoh et al.^{2,3} studied the transfer of copper through sulfonated ion-exchange membranes prepared by the paste method. The ratio (ion-exchange capacity) (self-diffusion coefficient of cupric ion) / (membrane thickness) was used as a criterion for the ionic flux through the membrane.

Other authors⁸⁻¹¹ studied active and selective transport of alkali metal ions through copolymer ion-exchange membranes. Metal's transport rate was found to depend considerably on the membrane composition.

The effect of membrane composition on the copper transfer rate through carboxylic ion-exchange

membranes prepared by the paste method was the purpose of this study.

EXPERIMENTAL

Materials

The poly(vinyl chloride) (PVC) used was Devilit E-70, product of Polychim Devnya (Bulgaria) with $M_n = 9 \times 10^4$ g/mol.

Divinylbenzene (DVB, supplied by Koch-Light Laboratories, Ltd.) contained 54 wt % isomers of DVB and 46% isomers of ethylvinylbenzene and diethylbenzene. DVB was used as a crosslinking agent.

Methylmethacrylate (MMA) and glacial acetic acid (AA) (products of E. Mark, Darmstadt, Germany) were used without further purification.

Benzoyl peroxide (BPO), reagent grade, was recrystallized from absolute methanol and dried at room temperature.

All other chemicals used [CuCl_2 , HCl, NaOH, ethylenediamine tetraacetic acid (EDTA), CH_3OH] were of analytical reagent grade.

Membrane preparation and characterization

Fine PVC powder was mixed with monomer mixture containing DVB (2–15 wt %), BPO (2 wt %), and MMA to prepare a paste.¹² The composite was placed between two cellophane films and heated at 373 K

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for 10 h. The PVC/(MMA-co-DVB) copolymer film synthesized (150–200- μm thick) was treated with AA at 353 K for 3 h to convert the ester groups in the MMA units into carboxylic groups. The carboxylic membranes obtained were washed consecutively with acetone, methanol, and water. In the alphanumeric abbreviations of the membranes the letters represent the monomers (V for PVC, M for MMA, and D for DVB) and the numbers represent DVB content in the initial monomer mixture. Thus, VM designates membranes obtained from PVC and MMA and MD₅ from MMA and DVB (5 wt %). All membranes were prepared by the same method and conditions.

Methods

The ion-exchange capacity (Z) and water content (W) were determined by standard procedure.⁸ The swelling ratio (S) of the membranes was calculated from the volumes of dry (V) and swollen (V_1) membrane by the formula $S = V_1/V$.

Transport experiments were carried out at 298 K by using a dialysis cell with two compartments (47 cm³ each) equipped with a glass stirrer. The effective membrane area was 4.5 cm². The compartments were filled with 0.1 M CuCl₂ (feed) and 1.0 M HCl (receiver) solutions in deionized water, respectively. Both solutions were periodically sampled and the metal concentration was measured by chelatometric titration with EDTA. The HCl concentration was determined by neutralization titration with NaOH. The pH of both solutions was monitored by pH meter Model OP 205 (Radelkis, Hungary). Membranes were kept for 48 h in 0.1 M CuCl₂. The experiments were carried out at a stirring speed of 500–600 rpm.

Membrane transfer rate J (mol cm⁻² s⁻¹) was calculated by the linear regression technique from the change of concentration by the formula

$$J = -(V/S) \frac{dC}{dt}$$

where C is the copper concentration in the solution analyzed, mol/dm³; V , solution volume, cm³; and S , the effective membrane area.

Permeability P (cm s⁻¹) was calculated from the values of J and initial copper concentration ($C_0 = 0.1$ M CuCl₂).

Diffusion coefficient D (cm² s⁻¹) was determined from the slope of the linear plot $\log(C_0/C_0 - 2C_t)$ vs. t :

$$D = \frac{V \cdot d \cdot \text{tg} \alpha}{2S}$$

where $\text{tg} \alpha$ is the slope, C_0 is the initial copper concentration in the feed solution (mol/dm³), C_t is the copper concentration in receiver solution at moment t (mol/dm³), V is the volume of the receiver solution (cm³), and d is the membrane thickness (cm).

For the determination of $\bar{D}_{\text{Cu}^{2+}}$, the feed solution used was 1.0 M HCl containing 1×10^{-3} mol/dm³ copper and the receiver solution was 1.0 M HCl.

RESULTS AND DISCUSSION

The transport properties of the carboxylic membranes synthesized were investigated to determine the copper/proton exchange through the membrane.

Figure 1 represents the dependence of copper transport through the membranes studied on time. It can be seen for VMD₂, VMD₅, VMD₁₀, and VMD₁₅ membranes that the amounts of copper removed from the feed solution and appearing in the receiver solution increased during the first 3–9 h of the experiment and then remained almost constant up to 48 h (Fig. 1, curves 1–4, respectively). For VM and MD₅ membranes, copper concentration in the receiver solution reached constant values after more than 12 h (Fig. 1, curves 5 and 6, respectively). It indicates that the transport of Cu²⁺ ions was greatly affected by the composition of the membrane. Copper transfer rates observed for VM and MD₅ membranes were found to be 3 and 6 times lower than

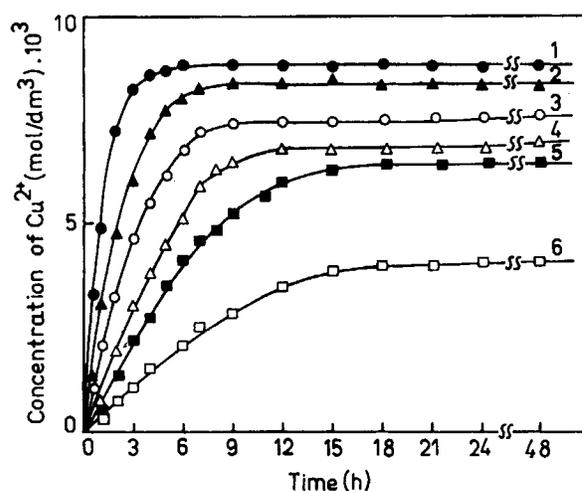


Figure 1 Dependence of copper concentration in receiver solution on time: (1) VMD₅; (2) VMD₁₀; (3) VMD₂; (4) VMD₁₅; (5) VM; (6) MD₅.

Table I Transfer Rate, Permeability, and Diffusion Coefficient of Membranes for Copper at 298 K

Membrane	Transfer Rate, $10^9 \times J$ (mol cm ⁻² s ⁻¹)	Permeability, ^a $10^5 \times P$ (cm s ⁻¹)	Diffusion Coefficient, $10^7 \times D$ (cm ² s ⁻¹)	$ZD/d^b \times 10^{10}$ (meq cm ⁻² s ⁻¹)
VMD ₂	2.51	2.51	5.02	0.73
VMD ₅	5.68	5.68	10.79	1.79
VMD ₁₀	2.71	2.71	5.42	0.64
VMD ₁₅	2.22	2.22	4.50	0.45
VM	1.55	1.55	3.10	0.35
MD ₅	0.85	0.85	1.59	0.28

^a $C_0 = 0.1M$ CuCl₂.^b Z (meq cm⁻³ wet membrane).

that of VMD₅. Copper was transported most rapidly through the VMD₅ membrane. These results showed that membranes prepared from PVC and MMA-co-DVB copolymer yielded higher copper transport rate than those prepared from PVC and PMMA (Table I). In this case, a continuous network of polyelectrolyte was formed in PVC. In addition, the transport rate was affected by the degree of crosslinking (DVB content).

The results obtained for permeability and diffusion coefficients of copper ions are listed in Table I. The diffusion coefficients were calculated from the slopes of the curves in Figure 2.

The results obtained for the influence of DVB content on membrane properties are listed in Tables I and II. The ion-exchange capacity, water content, and swelling ratio show a tendency to decrease with the increase of the DVB content from 2 to 15 wt %

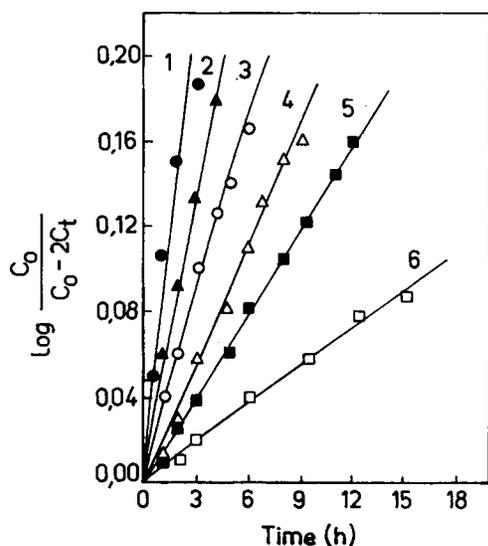


Figure 2 Plot of $\log(c_0/c_0 - 2c_t)$ vs. time for copper transfer across the membranes: (1) VMD₅; (2) VMD₁₀; (3) VMD₂; (4) VMD₁₅; (5) VM; (6) MD₅.

(Table II). The permeability of the membranes decreased also with the increase of DVB content (Table I). The diffusion coefficients show a maximum at 5 wt % DVB. The ratio ZD/d for VMD₁₅ membrane (15 wt % DVB) was 1.5 times lower than that of the VMD₂ membrane (2 wt % DVB). The highest value of the ratio ZD/d was observed for the VMD₅ membrane. This membrane showed the highest copper transport rate among the other membranes and higher ion-exchange capacity. These results indicated that membranes with a higher degree of crosslinking (DVB above 10%) show higher tortuosity and slower diffusion of Cu²⁺ ions. Figure 3 shows the change of pH of the feed solution with time during the copper transport. In the case of VM membranes, pH of the feed solution was found to decrease during the first 3 h of the experiment; for VMD₂, VMD₅, VMD₁₀, and VMD₁₅ membrane pH decreased during the first 6 h. For MD₅ membranes, the pH of the feed solution changed slightly up to 48 h. It indicates that H⁺ did not diffuse across the MD₅ membrane. The copper transfer from feed to receiver solution stopped shortly after the pH in the feed solution decreased to 2.5 (Fig. 3, curve 3). It can be supposed that the H⁺ flux drives the transport of Cu²⁺ through the membrane. The transport rate is related with proton activity. The flux of H⁺ ions

Table II Characteristics of Membranes

Membrane	Ion-Exchange Capacity (meq/g)	Water Content (g/g)	Swelling Ratio
VMD ₂	3.0	0.370	1.20
VMD ₅	3.4	0.320	1.10
VMD ₁₀	2.7	0.260	1.06
VMD ₁₅	2.3	0.200	1.00
VM	2.5	0.420	1.26
MD ₅	3.5	0.312	1.08

from receiver to feed solution through the VMD₅ membrane was $1.32 \times 10^{-10} \text{ mol cm}^{-2} \text{ s}^{-1}$.

The effect of the initial concentration of HCl in the receiver solution on the copper transport was also studied in the range from 0.1 to 1.0 mol/dm³. The concentration of feed CuCl₂ solution was 0.1 mol/dm³.

Figure 4 shows the increase of the copper transfer rate with the increase of the HCl concentration up to 1.0 mol/dm³. It means that a larger pH difference between feed and receiver solutions is necessary to obtain higher copper transfer.

CONCLUSION

PVC-(PMMA-co-DVB) carboxylic membranes were prepared by the paste method. These membranes transported Cu²⁺ ions more rapidly than PVC-PMMA based membranes. Thus, the transport rates were affected mainly by the membrane composition, degree of crosslinking (DVB content), and pH difference between feed and receiver solutions. Cu²⁺ was transported more rapidly across the membrane containing 5% DVB and 1.0M HCl in the receiver solution.

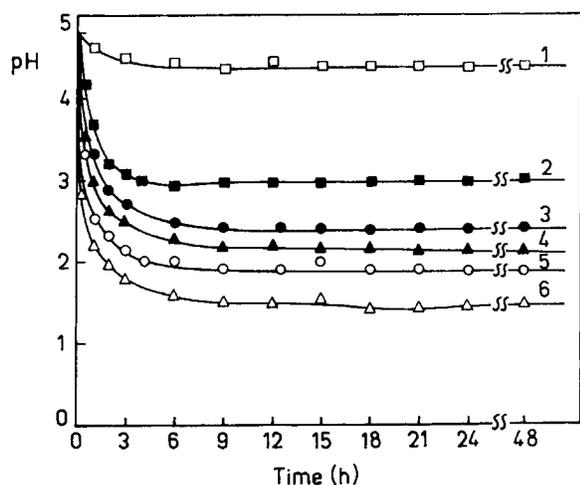


Figure 3 Dependence of pH of feed solution on time: (1) MD₅; (2) VM; (3) VMD₅; (4) VMD₁₀; (5) VMD₂; (6) VMD₁₅.

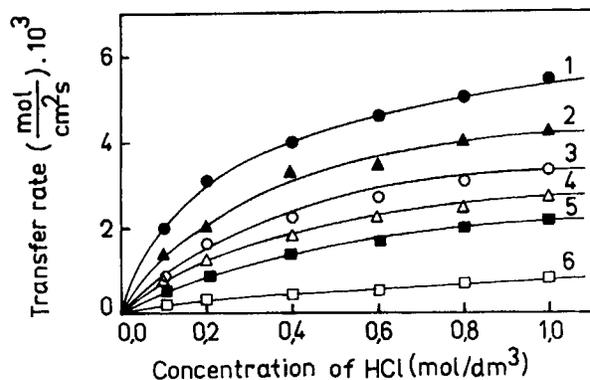


Figure 4 Effect of HCl concentration on copper transfer rate: (1) VMD₅; (2) VMD₁₀; (3) VMD₂; (4) VMD₁₅; (5) VM; (6) MD₅.

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