

Transport of Nickel and Copper Against a Concentration Gradient Through a Carboxylic Membrane, Based on Poly(vinyl chloride)/Poly(methyl methacrylate-co-divinylbenzene)

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SYNOPSIS

Carboxylic exchange membranes were prepared from poly(vinyl chloride)/poly(methyl methacrylate-co-divinylbenzene) (PVC) [poly(MMA-co-DVB)]. Transport of nickel and copper against a concentration gradient through the membrane was investigated by using a system containing NiCl_2 or CuCl_2 aqueous solution on the left side (L) and mixed solution of NiCl_2 (or CuCl_2) and HCl on the right side (R) of the membrane. It was found that nickel and copper were actively transported through the membrane from the L to the R side during the first 5 h of the experiments. The rate of transport of the ions increased with increasing H^+ ion concentration on the R side and the initial concentration of the metals ions on both sides. The highest rate of transport was observed when 0.1 mol/L MeCl_2 on the L side and 0.1 mol/L MeCl_2 -0.5 mol/L HCl on the R side were used. The nickel and copper transport fractions were 34 and 24%, respectively. © 1997 John Wiley & Sons, Inc.

INTRODUCTION

In recent years, synthetic-charged polymeric membranes were used in studies of active ion transport. Uragami et al.¹⁻⁵ studied the transport of alkali metal ions and alkali earth metal ions against their concentration gradient through poly(styrene-sulfonic acid)/poly(vinyl alcohol) and poly(isobutylene-alternating-maleic anhydride) membranes, respectively. Alkali metal ions such as Li^+ , K^+ , and Na^+ were also transported against their concentration gradient through 2,3-epithiopropyl methacrylate-methacrylic acid copolymer membranes.⁶⁻⁸

Schwahn and Woermann⁹ reported that K^+ , Na^+ , Ca^{2+} , and Mg^{2+} ions were transported against their concentration gradient through sulfonated ion-exchange membranes. The active transport of ions through polymeric membranes was found to depend on the membrane composition and pH difference

between the bulk phases. The efficiency of transport may be improved by the formation of a dense membrane.

From a practical point of view, the polymeric membranes are rather stable membranes and have advantages in energy compared with the liquid membrane for this transport. In this respect, poly(vinyl chloride)/poly(methacrylate-co-divinylbenzene) [PVC/poly(MMA-co-DVB)] carboxylic exchange membranes were synthesized. The purpose of this article was to study the transport of nickel and copper against a concentration gradient through a carboxylic membrane.

EXPERIMENTAL

Materials

The poly(vinyl chloride) (PVC) used was Devilit E-70, a product of Polychim, Devnia, Bulgaria, with a number-average molecular weight of $9 \cdot 10^4$ g/mol. The methyl methacrylate (MMA) was a commercial product supplied by Reachim, Russia. Divinylben-

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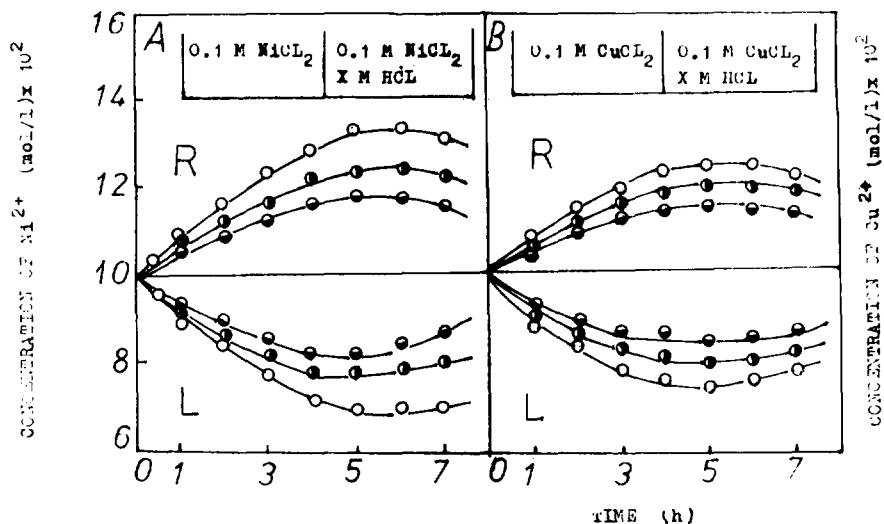


Figure 1 Changes in nickel and copper concentrations on both sides of the membrane with time at different H^+ ion concentrations on the R side: (○) 0.5 mol/L, (●) 0.3 mol/L, and (◐) 0.1 mol/L, and 0.1 mol/L $NiCl_2$ (or $CuCl_2$).

zene (DVB), supplied by Koch-Light Laboratories Ltd., was used as a crosslinking agent. Benzoyl peroxide (BPO), reagent grade, was used as an initiator for the polymerization. All other reagents used were of pure grade from commercial sources.

Preparation of the Membrane

Fine PVC powder was mixed with a monomer mixture containing MMA, DVB (5 wt %), and BPO (2 wt %) to prepare a paste. The composite was placed between two cellophane films and heated at 373 K for 10 h. The PVC/poly(MMA-co-DVB) polymer film synthesized was treated with acetic acid for 3 h at 353 K. The membrane obtained was washed consecutively with acetone, methanol, and water. The carboxylic exchange membrane used in this study has an ion-exchange capacity of 3.41 meq/g (dry membrane in the H form), a water content of 0.320 g/g, an electrical resistance of 40 cm^2 , and a thickness of 0.180 mm.

Apparatus and Measurements

Transport experiments were carried out at 298 K using a dialysis cell with two compartments (24 cm^3 each) equipped with a stirrer. The compartments were designated as L (left compartment) and R (right compartment), respectively. The effective membrane area was 12.56 cm^2 . The L compartment was filled with a $NiCl_2$ or $CuCl_2$ aqueous solution. The R compartment was filled with a mixed solution of $NiCl_2$ (or $CuCl_2$) and HCl. The concentration of

metal ions on the R side was equal to that on the L side at the beginning of the experiments. Both solutions on the L side and on the R side of the membrane were periodically sampled and the concentration of nickel or copper was determined by chelatometry with EDTA. The experiments were carried at a stirring speed of 500–600 rpm.

RESULTS AND DISCUSSION

The transport of nickel and copper against a concentration gradient through a carboxylic exchange membrane was investigated under various conditions. The membrane was obtained from a PVC/poly(MMA-co-DVB) interpolymer system crosslinked with 5 wt % DVB.

Figures 1(A), 2(A), and 3(A) show the changes in Ni^{2+} ion concentration on the L side and the R side of the membrane with the time, the H^+ ion concentration on the R side, and the initial concentration of the nickel on both sides. As can be seen from the figures, in all cases, the amount of nickel increased on the R side consistently during the first 5 h of the experiments. Since the initial concentration of the Ni^{2+} ion was the same on both the L and R sides, the increase of the Ni^{2+} concentration on the R side suggests active transport of ions from the L side to the R side through the membrane, against the concentration gradient between both sides. It may be due to the fact that the dissociation of the carboxylic groups in the membrane on the R side is depressed compared with

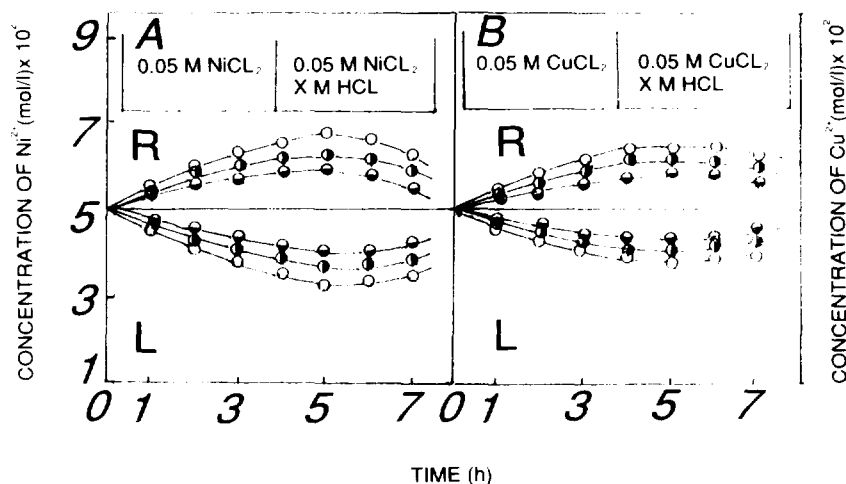


Figure 2 Changes in nickel and copper concentrations on both sides of the membrane with time at different H^+ ion concentrations on the R side: (○) 0.5 mol/L, (●) 0.3 mol/L, and (◐) 0.1 mol/L and 0.05 mol/L NiCl_2 (or CuCl_2).

that on the L side. The second electrolyte was HCl on the R side of the membrane and the pH of solution was lower than unity. At the same time, the initial pH of the solution on the L side was higher than 5. Therefore, the membrane surface is denser on the R side than on the L side. The concentration of Ni^{2+} ions was higher at the left phase boundary of the membrane and the nickel ion transport from the L side to the R side was observed.

On the other hand, the hydrogen ions were transported through the membrane from the R side to the L side, according to the concentration gradient of their ions. It can be supposed that the H^+ ions drive the transport of nickel through the membrane.

The same results were obtained for copper transport through the membrane.

Figures 1(B), 2(B), and 3(B) show the dependence of copper transport on the time, H^+ ion concentration, and initial concentration of copper. The Cu^{2+} ions were also transported through the membrane from the L side to the R side against the concentration gradient.

The results obtained for the transfer rate and transport fraction of nickel and copper are listed in Table I. The H^+ ion concentration was varied from 0.1 to 0.5 mol/L on the R side. The initial concentration of ions was varied from 0.01 to 0.1 mol/L on both sides of the membrane.

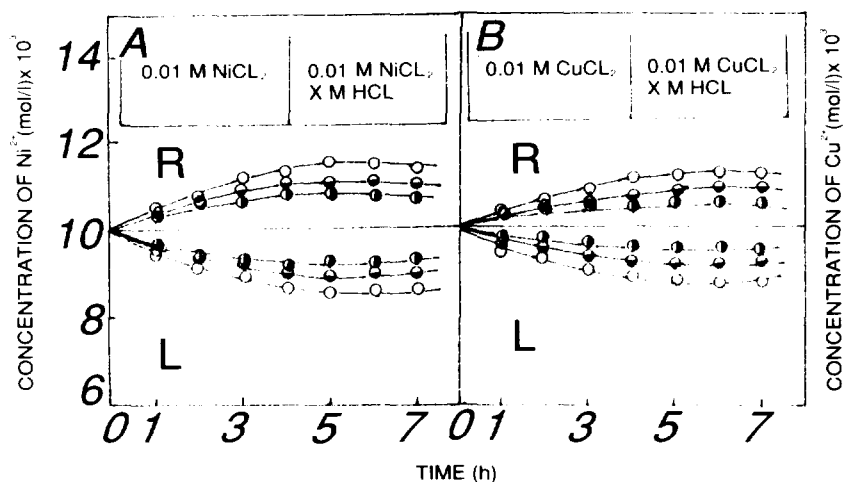


Figure 3 Changes in nickel and copper concentrations on both sides of the membrane with time at different H^+ ion concentrations on the R side: (○) 0.5 mol/L, (●) 0.3 mol/L, and (◐) 0.1 mol/L and 0.01 mol/L NiCl_2 (or CuCl_2).

Table I Results of Transport Experiments

Solutions		Transfer Rate $J \times 10^6$ (mol/cm ² h)	Transport Fraction (%)
L Side	R Side		
0.1M NiCl ₂	0.1M NiCl ₂ 0.1M HCl	6.88	18.5
0.1M NiCl ₂	0.1M NiCl ₂ 0.5M HCl	12.61	34.1
0.05M NiCl ₂	0.05M NiCl ₂ 0.5M HCl	6.51	17.0
0.1M CuCl ₂	0.1M CuCl ₂ 0.1M HCl	5.35	14.1
0.1M CuCl ₂	0.1M CuCl ₂ 0.5M HCl	9.17	24.0
0.05M CuCl ₂	0.05M CuCl ₂ 0.5M HCl	4.85	12.4

The transfer rate was calculated from the amount of transported nickel (or copper) through the membrane from the L side to the R side after 5 h (in mol) and with respect to the effective membrane area. The transport fraction was calculated from the relationship $(C_t - C_0/C_0) \times 100$, where C_t is the concentration of nickel or copper on the R side after 5 h (mol/L) and C_0 is the initial concentration of nickel or copper (mol/L). It was found that the ion transport increased when a higher HCl concentration on the R side was used. The highest rate of the

transfer of ions through the membrane was observed when a 0.1 mol/L initial concentration of nickel or copper on both sides was used and a 0.5 mol/L H⁺ ion concentration on the R side. The ionic strength of the solution was 0.8 on the R side, while on the L side, it was 0.3. The transport fractions of nickel and copper were 34 and 24%, respectively, at the above conditions.

REFERENCES

1. T. Uragami, in *Membrane Science and Technology*, Y. Osada and T. Nakagawa, Eds., Marcel Decker, New York, 1991, p. 377.
2. T. Uragami, S. Watanabe, R. Nakamura, and M. Sugihara, *Polym. Bull.*, **7**, 71 (1982).
3. T. Wada, T. Uragami, and M. Sugihara, *Polym. Bull.*, **14**, 219 (1985).
4. T. Uragami, K. Moriyama, M. Yamamoto, and M. Sugihara, *Makromol. Chem.*, **187**, 583 (1986).
5. T. Uragami, M. Yamamoto, and K. Moriyama, *J. Membr. Sci.*, **61**, 227 (1991).
6. T. Nonaka, H. Maeda, M. Nakayama, and H. Egawa, *J. Appl. Polym. Sci.*, **34**, 1025 (1987).
7. T. Nonaka, H. Maeda, M. Nakayama, and H. Egawa, *J. Appl. Polym. Sci.*, **37**, 241 (1989).
8. T. Nonaka and H. Egawa, *J. Appl. Polym. Sci.*, **40**, 769 (1990).
9. P. Schwahn and D. Woerman, *Ber. Bunsenges Phys. Chem.*, **90**, 773 (1986).

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