Nickel Transfer and Selective Transport Through Weak Acid Ion-Exchange Membrane Based on Poly(vinyl chloride)/Poly(methylmethacrylate-co-divinylbenzene) System

I. ALEXANDROVA* and G. IORDANOV

Higher Institute of Chemical Technology, 8010 Bourgas, Bulgaria

SYNOPSIS

The transport of nickel and copper through a carboxylic ion-exchange membrane was investigated by using a system containing HCl as a receiver solution and nickel chloride or copper chloride as a feed solution. The transfer rate was found to be greatly affected by the H^+ concentration in the receiver solution and metals concentration in the feed solution. The rate of transfer for nickel was about 60% higher than that of copper under the same experimental conditions ($0.5M$ HCl as a receiver solution, $0.1M$ feed solution, and 5 h dialysis time). © 1996 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.[1-8]

Wen and Hamil[1] reported that transport of Ni^{2+}, Cu^{2+}, Mg^{2+}, and Fe^{3+} ions through sulphonated styrene-grafted or acrylic acid-grafted membranes increases with the increase of membrane ion-exchange capacity. The rate of metal transport through a membrane of low ion-exchange capacity and gel water content decreases with increasing size and valence of the metal cation.

Sudoh and colleagues[2,3] studied the transfer of copper through sulphonated ion-exchange membranes. The membranes with a lower degree of crosslinking showed higher ionic flux and gave a higher enrichment factor. 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 authors[9-11] studied the effect of the nature and ionic strength of the receiver solution on Donnan dialysis enrichment of Cu, Zn, and Fe using poly(styrene sulphonate)/polyethylene and sulphonate/Teflon-based membranes.

The aim of the present paper is to study nickel transport and nickel/copper transport through a carboxylic ion-exchange membrane.

EXPERIMENTAL

Materials

Poly(vinyl chloride) (PVC) used was Devilit E-70, a product of Polychim, Devnia, Bulgaria, with $M_n = 9 \times 10^4$ g/mol. Divinylbenzene (DVB) was supplied by Koch-Light Laboratories, Ltd., and contained 54% of DVB isomers. It was used as a crosslinking agent. Methylmethacrylate (MMA) was a commercial product supplied by Reachim Russia. Benzoyl peroxide (BPO), reagent grade, was recrystallized from absolute methanol and dried at room temperature. It was used as initiator for radical polymerization.

All other chemicals used ($NiCl_2$, $CuCl_2$HCl, EDTA, CH_3OH, and CH_3COOH) were of analytical reagent grade.

---

* To whom correspondence should be addressed.
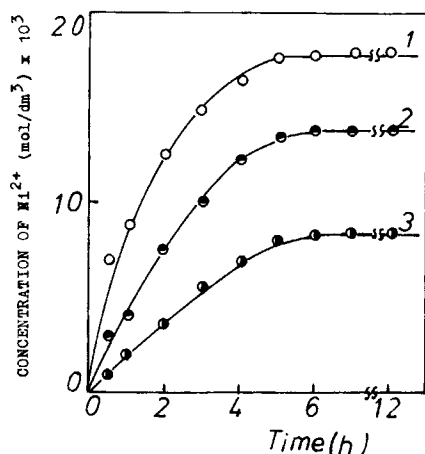
Figure 1 Dependence of nickel concentration in receiver solution on time and HCl concentration: (1) 0.5*M;* (2) 0.3*M;* (3) 0.1*M* HCl.

Membrane Preparation

Fine PVC powder was mixed with a monomer mixture containing MMA, 5 wt % DVB, and 2 wt % BPO to prepare a paste. The composite obtained was cast between two cellophane films and heated at 373 K for 10 h. The PVC/poly(MMA-*co*-DVB) polymer film synthesized (150–200 μm thick) was treated with glacial acetic acid at 353 K for 3 h to convert the ester groups in the MMA units into carboxylic groups. The carboxylic membrane obtained was washed consecutively with acetone, methanol, and water.

Methods

The ion-exchange capacity, water content and electrical resistance of the membrane were measured by ordinary procedures.[12]

Transport experiments were carried out at 298 K using a dialysis cell with two compartments (47 cm³

**Table I Transfer Rate and Transfer Fraction of Nickel and Copper Through the Membrane***

Receiver Solution	Transfer Rate [$10^5 \times J$, mol/ (cm² h)]		Transfer Fraction (%)	
	Nickel	Copper	Nickel	Copper
0.1*M* HCl	1.67	0.71	8.0	3.4
0.3*M* HCl	2.88	1.77	13.8	6.6
0.5*M* HCl	3.69	2.08	18.5	10.5

* Feed solution: 0.1*M* NiCL₂ (or CuCl₂).
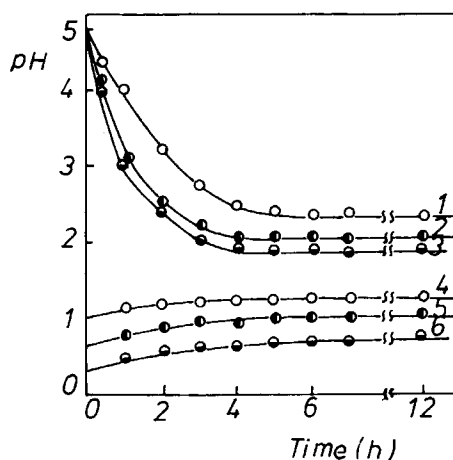
Figure 2 Change in pH of feed and receiver solution with the time and HCl concentration: (1) and (4), 0.1*M;* (2) and (5), 0.3*M;* (3) and (6), 0.5*M.* HCl.

each), equipped with a glass stirrer. The effective membrane area was 4.5 cm². The compartments were filled with NiCl₂ (feed solution) and HCl (receiver solution), respectively. Both solutions were sampled periodically and the metal concentration was determined by titration with EDTA solution. The HCl concentration was determined by titration with NaOH solution. The pH of solutions were monitored by pH-meter model OP 205 (Radelkis, Hungary). The experiments were carried out at a stirring speed of 700–800 rpm.
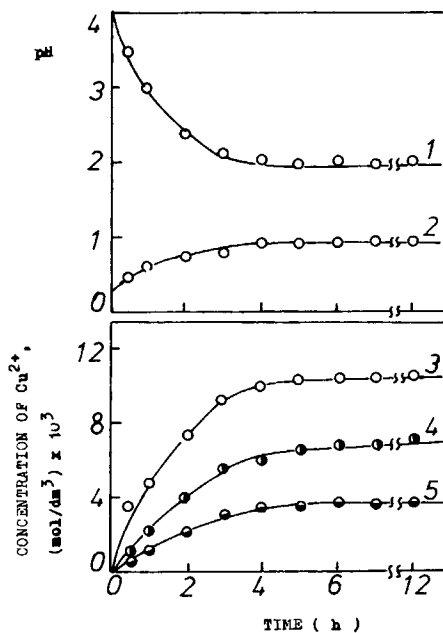
Figure 3 Dependence of copper concentration in receiver solution and change in pH on time and HCl concentration: (1), (2), and (3), 0.5*M;* (4) 0.3*M;* (5) 0.1*M* HCl.

Table II   Effect of the Initial Concentration of Nickel and Copper on the Rate of Transfer

Feed Solution	Transfer Rate $[10^5 \times J, \text{mol}/(\text{cm}^2 \text{ h})]$	
	Nickel	Copper
$0.01M$ NiCl$_2$ (or CuCl$_2$)	0.35	0.30
$0.05M$ NiCl$_2$ (or CuCl$_2$)	1.56	0.94
$0.10M$ NiCl$_2$ (or CuCl$_2$)	3.65	2.08
$0.50M$ NiCl$_2$ (or CuCl$_2$)	19.15	10.02

Membrane transfer rate J [mol/(cm^2 h)] was calculated by linear regression technique from the change of concentration by the formula

$$J = -V/S(dc/dt)$$

where c is the nickel concentration in the solution analyzed, mol/dm^3; V is the volume of solution, cm^3; S is the effective membrane area, cm^2; and t is the time.

The transfer fraction of nickel from the feed to the receiver solution was calculated by the ratio:

$$\alpha = (C_t/C_o) \times 100$$

where C_t is the concentration of nickel in the receiver solution after time t, mol/dm^3 and C_o is the initial concentration of nickel in the feed solution, mol/dm^3.

The selectivity of the membrane was determined in the same dialysis cell but a mixed solution of nickel chloride and copper chloride at 1 : 1 molar ratio was used as feed solution. The concentration of mixed salt solution was 0.1 mol/dm^3.

The selectivity coefficient was calculated from the equation[13]:

$$T = \{(C_{Ni})r/(C_{Ni})f\}/\{(C_{Cu})r/(C_{Cu})f\}$$

where f and r denote the concentration of each ion in the feed and receiver solution after 5 h dialysis time, respectively.

RESULTS AND DISCUSSION

In our previous paper,[14] weak acid ion-exchange membranes were synthesized by the paste method and the effect of membrane composition on copper transfer was studied. The membrane based on PVC/poly(MMA-co-DVB) with 5 wt % DVB was found to be effective for Donnan dialysis. The transport of nickel through this synthesised carboxylic ion-exchange membrane was investigated to determine the metal/proton exchange through the membrane.

Figure 1 represents the dependence of nickel transport through the studied membrane on time and concentration of HCl in the receiver solution. The acid concentration was varied from 0.1 to 0.5 mol/dm^3 and the feed solution was 0.1 mol/dm^3 NiCl$_2$. It can be seen that the amount of nickel removed from the feed solution and appearing in the receiver solution significantly increases with the increase of HCl concentration in the receiver solution during the first 4–5 h of the experiments. The nickel concentration in the receiver solution reached constant values after more than 5 h dialysis time, which indicates that the transfer of nickel through the membrane was affected by H$^+$ concentration in the receiver solution. The transfer rate increased twice when 0.5M HCl was used as receiver solution, compared to that of 0.1M HCl solution (Table I). The transfer fraction of nickel was about 18.5%.

Figure 2 shows the change of pH in both solutions during the nickel transport. In all cases the pH of the feed solution decreased consistently during the first 4–5 h and then remained almost constant up to 12 h (Fig. 1, curves 1–3). The transfer of nickel through the membrane stopped shortly after the pH in the feed solution decreased to 1.9 (Fig. 2, curve 3). The pH difference between feed and receiver solution was about 1.15–1.25. It can be supposed that nickel was transported from feed to the receiver solution by diffusive flow based on the concentration gradient and active transport driven by H$^+$ flux through the membrane.

The same results were obtained for copper transport through the membrane. Figure 3 shows that the amount of copper transported from the feed to the receiver solution increased when higher HCl concentration in the receiver solution was used. The copper transport stopped shortly
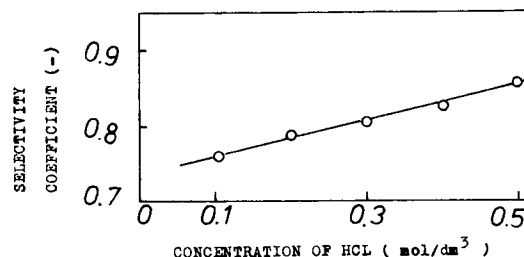
Figure 4 Selectivity coefficient versus HCl concentration.

after the pH of the feed solution decreased to 2.0. The pH difference between the two solutions was 1.05 (Fig. 3, curves 1 and 2). It was found that the copper transfer rate was about 60% lower than that of nickel under the same conditions ($0.5 M$ HCl as a receiver solution, $0.1 M$ $CuCl_2$ as a feed solution, and 5 h dialysis time). The transfer fraction observed for copper was found to be about 10.5%, perhaps due to the fact that the hydrated ionic size of the cupric ion (4.19 Å) is larger than that of the nickel ion (4.04 Å) and to the stronger interaction between carboxylic groups and Cu^{2+} ions. The stability constants observed for metal carboxylic ion complexes (log β) were[15]: 1.7 for Cu^{2+} and 0.72 for Ni^{2+}. These values are related to the isobutanoic acid, which resembles the repeating units of polymethacrylic acid.

The investigations carried out and the results obtained regarding the effect of the initial metal concentration in the fed solution are listed in Table II. The receiver solution was $0.5 M$ HCl. Obviously, the transfer rate of nickel or copper increases with the nickel or copper concentration up to 0.5 mol/dm^3. The dependence of membrane selectivity (Ni^{2+}/Cu^{2+}) on the HCl concentration in the receiver solution is shown in Figure 4. The selectivity coefficient (T) increases with the HCl concentration in the receiver solution. In all cases it was close under unity. It indicates that the copper was permeated more preferentially than nickel into the membrane when the Ni-Cu binary system was used.

REFERENCES

1. C. P. Wen and H. F. Hamil, *J. Membr. Sci.*, **8**, 51 (1981).
2. M. Sudoh, H. Kamei, and S. Nakamura, *J. Chem. Eng. Japan*, **20**, 34 (1987).
3. M. Sudoh, S. Nakamura, and M. Kawamori, *J. Chem. Eng. Japan*, **23**, 680 (1990).
4. T. Shimidzu and H. Okushita, *J. Membr. Sci.*, **27**, 349 (1989).
5. K. Takahashi, K. Tsuboi, and H. Takeuchi, *J. Chem. Eng. Japan*, **22**, 351 (1987).
6. M. Igawa, K. Echizenya, T. Hayashita, and M. Seno, *Bull. Chem. Soc. Japan*, **60**, 383 (1987).
7. O. Kedem and L. Bromberg, *J. Membr. Sci.*, **78**, 255 (1993).
8. T. Tomida, T. Inoue, T. Tsuchiya, and S. Masuda, *Ind. Eng. Chem. Res.*, **33**, 903 (1994).
9. J. A. Cox, T. Gray, K. S. Joon, Y. T. Kim, and Z. Twardowski, *Analyst*, **109**, 1603 (1984).
10. J. Cox and A. Bhatnagar, *Talanta*, **37**(11), 1037 (1990).
11. J. Cox, R. Gajek, G. Litwinski, and J. Carnahan, *Anal. Chem.*, **54**, 1153 (1982).
12. T. Nonaka and H. Egawa, *J. Appl. Polym. Sci.*, **40**, 769 (1990).
13. T. Nonaka, H. Maeda, M. Nakayama, and H. Egawa, *J. Appl. Polym. Sci.*, **37**, 242 (1989).
14. I. Alexandrova and G. Iordanov, *J. Appl. Polym. Sci.*, **57**, 1315 (1995).
15. A. E. Martell and R. M. Smith, *Critical Stability Constants*, Vol. 3, Plenum Press, New York, 1979.