

Transport of Cobalt and Zinc Through a Carboxylic Membrane Based on Poly(vinyl chloride)/Poly(methyl metacrylate-co-divinylbenzene) System

I. ALEXANDROVA, G. IORDANOV

Higher Institute of Chemical Technology, 8010, Bourgas, Bulgaria

Received 4 October 1999; accepted 16 June 2000

ABSTRACT: The transport of cobalt and zinc through a carboxylic ion-exchange membrane was investigated by using a system containing HCl as a receiver solution and cobalt chloride or zinc chloride as a feed solution. The transfer rate was found to be greatly affected by the H^+ concentration in the receiver solution and metal concentration in the feed solution. The rate of transfer for zinc was about 25% higher than that of cobalt under the same experimental conditions (0.5M HCl as a receiver solution, 0.1M feed solution, and 5 h dialysis time). © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 47–50, 2001

Key words: PVC; poly(MMA-co-DVB)system; membrane; transport; ions; dialysis

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 the membrane's physical and chemical structure and properties.^{1–8}

Wen and Hamil¹ reported that the transport of Cu^{2+} , Ni^{2+} , Co^{2+} , Mg^{2+} , and Fe^{3+} ions through sulfonated styrene-grafted or acrylic acid-grafted membranes increases with increase of the membrane ion-exchange capacity. Macenauer et al.² studied the transport of divalent cations, such as Ni^{2+} , Cu^{2+} , Co^{2+} , Zn^{2+} , and Fe^{2+} , through a perfluorosulfonate ion-exchange membrane (Nafion 427) with metal sulfate–sulfuric acid systems. The efficiency of the dialysis was found to depend on the initial concentration ratio of the metal sulfate and sulfuric acid solutions.

Cox et al.^{9,10} described the effect of the nature and ionic strength of a receiver solution on Donnan dialysis enrichment of Cu, Zn, and Fe using poly(styrene sulfonate)/polyethylene and sulfonate/Teflon-based membranes. Other authors^{11–15} studied the transport of Ag^+ , Co^{2+} , Cu^{2+} , Zn^{2+} , Ni^{2+} , and Fe^{3+} through microporous membranes containing an organic complexing agent in the pores as a carrier.

In our previous articles,^{16,17} carboxylic ion-exchange membranes were synthesized and the transport of copper and nickel through the membranes was studied. The purpose of this article was to investigate cobalt and zinc transport through the carboxylic membrane based on the poly(vinyl chloride)/poly(methyl methacrylate-co-divinylbenzene) [PVC/poly(MMA-co-DVB)] system.

EXPERIMENTAL

Materials

The PVC used was Devilit E-70, a product of Polychim (Devnia, Bulgaria) with $M_n = 9 \times 10^4$

Correspondence to: I. Alexandrova.

Journal of Applied Polymer Science, Vol. 80, 47–50 (2001)
© 2001 John Wiley & Sons, Inc.

g/mol. DVB was supplied by the Koch–Light Laboratories, Ltd. (England), and contained 54% of DVB isomers. It was used as a crosslinking agent. MMA was a commercial product supplied by Reachim (Russia). Benzoyl peroxide (BPO), reagent grade, was used as an initiator for the polymerization. All other chemicals used (CoCl_2 , ZnCl_2 , HCl, EDTA, CH_3OH , and CH_3COOH) were of analytical reagent grade.

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 was treated with glacial acetic acid at 353 K for 3 h. The carboxylic membrane obtained was washed consecutively with acetone, methanol, and water. The membrane used in this study had 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 $40 \Omega \text{ cm}^2$, and a thickness of 0.180 mm.

Methods

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

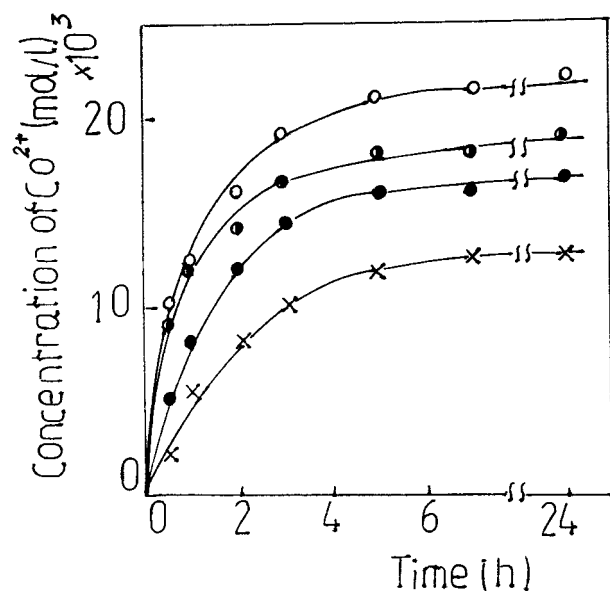


Figure 1 Dependence of cobalt concentration in receiver solution on time and HCl concentration: (○) 0.5M, (●) 0.3M, (●) 0.1M, and (X) 1.0M HCl.

Table I Results of Transport Experiments

Feed Solution	Receiver Solution	Transfer Rate ($J \times 10^5 \text{ mol cm}^{-2} \text{ h}^{-1}$)	
		Cobalt	Zinc
0.01M CoCl_2 (or ZnCl_2)	0.1M HCl	0.65	1.15
	0.3M HCl	0.85	1.25
	0.5M HCl	1.25	1.32
0.1M CoCl_2 (or ZnCl_2)	0.1M HCl	3.35	4.40
	0.3M HCl	3.74	5.01
	0.5M HCl	4.37	5.43

cm^3 each), equipped with a glass stirrer. The effective membrane area was 4.5 cm^2 . The compartments were filled with CoCl_2 or ZnCl_2 (as a feed solution) and HCl (as a receiver solution). Both solutions were sampled periodically and the metal concentration was determined by titration with an EDTA solution. The HCl concentration was determined by titration with a NaOH solution. The pH of solutions were monitored by a pH-meter, Model OP 205 (Radelkis, Hungary). The experiments were carried out at a stirring speed of 700–800 rpm.

The membrane transfer rate J ($\text{mol cm}^{-2} \text{ h}^{-1}$) was calculated by a linear regression technique from the change of the concentration by the formula

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

where C is the cobalt or zinc concentration in the solution analyzed (mol/dm^3), V , the volume of the solution (cm^3); S , the effective membrane area (cm^2), and t , the time (h).

The transfer fraction (α , %) was calculated from the relationship

$$\alpha = (C_t/C_0) \times 100$$

where C_t is the concentration of cobalt or zinc in the receiver solution after 5 h dialysis time (mol/dm^3) and C_0 is the initial concentration of cobalt or zinc in the feed solution (mol/dm^3).

RESULTS AND DISCUSSION

The transport of cobalt and zinc through a carboxylic membrane, based on the PVC/poly(MMA-

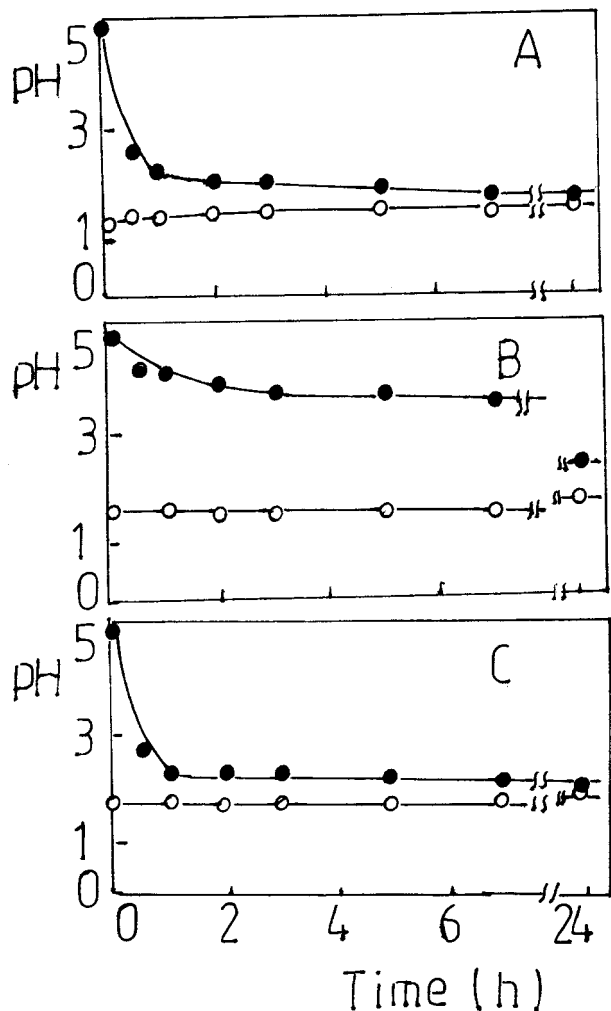


Figure 2 Changes in pH of (●) feed and (○) receiver solutions with the time and HCl concentration: (A) 0.5M; (B) 0.3M, and (C) 0.1M HCl. Feed solution: 0.1M CoCl₂.

co-DVB) system, was investigated under various conditions. Figure 1 represents the dependence of cobalt transport through the membrane on the time and concentration of HCl in the receiver solution. The acid concentration was varied from 0.1 to 1.0 mol/dm³ and the feed solution was 0.1 mol/dm³ CoCl₂. It can be seen that the amount of cobalt removed from the feed solution and appearing in the receiver solution significantly increases with increase of the H⁺ ion concentration in the receiver solution up to 0.5 mol/dm³ and during the first 5 h of the experiments. The transfer rate increased 1.3 times when 0.5 mol/dm³ HCl was used as the receiver solution, compared to that of a 0.1 mol/dm³ HCl solution (Table I). The transfer fraction of cobalt was about 21.4% after 5 h dialysis time.

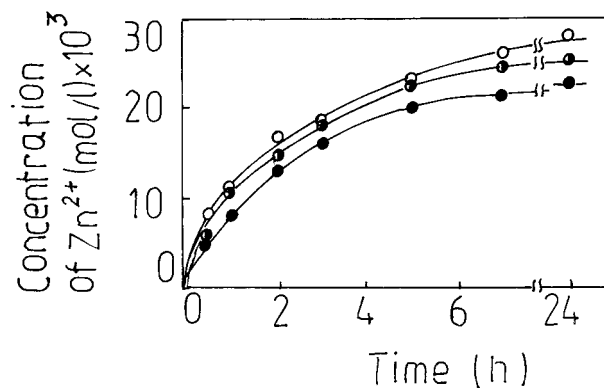


Figure 3 Dependence of zinc concentration in receiver solution on time and HCl concentration: (○) 0.5M, (◐) 0.3M, and (●) 0.1M HCl.

Figure 2 shows the changes in pH of the feed and receiver solutions, respectively, with the time at different H⁺ ion concentrations. It was found that the pH value in the feed solution decreases up to 1.8 during the first 5 h in the case of 0.5M HCl as the receiver solution [Fig. 2(A)]. For the

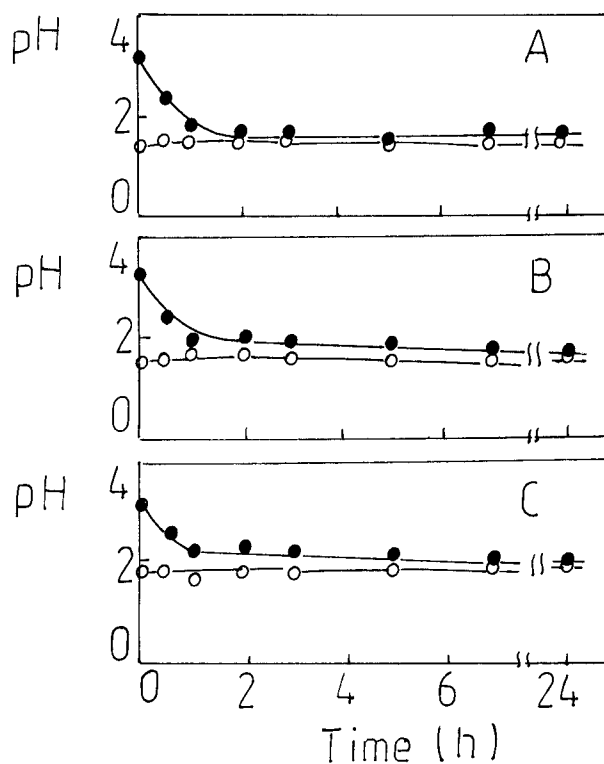


Figure 4 Changes in pH of (●) feed and (○) receiver solutions with the time and HCl concentration: (A) 0.5M, (B) 0.3M, and (C) 0.1M HCl. Feed solution: 0.1M ZnCl₂.

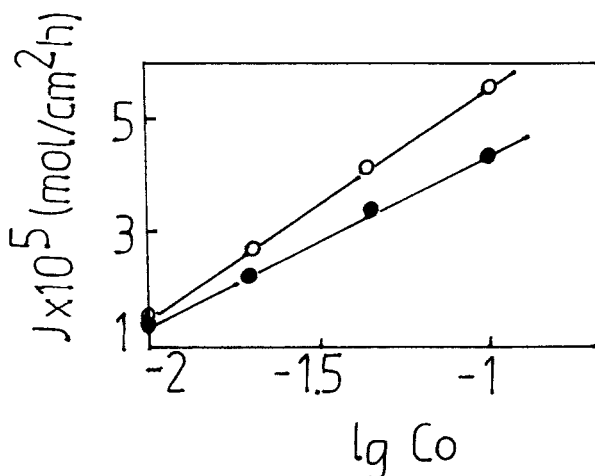


Figure 5 Effect of the initial metal concentration on the transfer rate: (○) zinc, (●) cobalt. Receiver solution: 0.5M HCl.

receiver solution, the pH changed slightly up to 24 h. It can be supposed that the cobalt is transported from the feed to the receiver solution by the diffusion flux based on the concentration gradient and active transport driven by the H^+ flux through the membrane. The mobility of H^+ ions in the membrane phase is higher than that of the Co^{2+} ions.

The results obtained for zinc transport through the membrane are shown in Figures 3 and 4. Figure 3 shows the dependence of the zinc transport on the time and acid concentration in the receiver solution. The amount of zinc transported through the membrane increased when a higher concentration of HCl in the receiver solution was used. It was found that the transfer rate of zinc was about 25% higher than that of the cobalt under the same conditions (0.5 mol/dm³ HCl as the receiver solution, 0.1 mol/dm³ ZnCl₂ as the feed solution, and 5 h dialysis time). The transfer fraction observed for zinc was found to be about 23.9%. Figure 4 shows the change of pH in the feed and receiver solutions during the zinc transport.

The investigation carried out and the results obtained regarding the effect of the initial metal concentration in the feed solution are shown in Figure 5 and Table I. The receiver solution was

0.5M HCl. As can be seen from the figure, the transfer rate of cobalt and zinc decreased with decrease of the initial metal concentration in the feed solution. The rate of transfer of ions observed for 0.01M CoCl₂ (or 0.01M ZnCl₂) was 3.5–4.0 times lower than that of 0.1M MeCl₂ as a feed solution.

On the basis of these results and the results obtained for copper and nickel,¹⁷ it could be suggested that the mobility of the corresponding ions in the membrane phase decreases in the order $Zn^{2+} > Co^{2+} > Ni^{2+} > Cu^{2+}$. The transfer rate of the ions was greatly affected by the H^+ concentration in the receiver solution and the metal concentration in the feed solution.

REFERENCES

1. Wen, C. P.; Hamil, H. F. *J Membr Sci* 1981, 8, 51.
2. Macenauer, J.; Handlirova, M.; Machac, I. *J Membr Sci* 1991, 60, 157.
3. Sudoh, M.; Nakamura, S.; Kawamori, M. *J Chem Eng Jpn* 1990, 23, 680.
4. Shimidzi, T.; Okushita, H. *J Membr Sci* 1989, 27, 349.
5. Osseo-Asare, K.; Xue, T. *J Membr Sci* 1989, 43, 5.
6. Takahashi, K.; Tsuboi, K.; Takeuchi, H. *J Chem Eng Jpn* 1987, 22, 353.
7. Kedem, O.; Bromberg, L. *J Membr Sci* 1993, 78, 255.
8. Tomida, T.; Inoue, T.; Tsuchiya, T.; Masuda, S. *Ind Eng Chem Res* 1994, 33, 903.
9. Cox, J.; Gray, T.; Joon, K.; Kim, Y.; Twardowski, Z. *Analyst* 1984, 109, 1603.
10. Cox, J.; Bhatnagar, A. *Talanta* 1990, 37, 1037.
11. Kataoka, T.; Nishiki, T.; Kimura, S.; Tomioka, Y. *J Membr Sci* 1989, 46, 67.
12. Chandry, M.; Malik, M.; Ali, A. *Sep Sci Technol* 1990, 25, 263.
13. Goto, M.; Yamamoto, H.; Kondo, K.; Fumiyuki, T. *J Membr Sci* 1991, 57, 161.
14. Bromberg, L.; Levin, G.; Kedem, O. *J Membr Sci* 1992, 71, 41.
15. Kalachev, A.; Kardivarenko, L.; Plate, N.; Bagreev, V. *J Membr Sci* 1992, 75, 1.
16. Alexandrova, I.; Iordanov, G. *J Appl Polym Sci* 1995, 57, 1315.
17. Alexandrova, I.; Iordanov, G. *J Appl Polym Sci* 1996, 60, 721.