

Transport of Cadmium and Iron Through a Carboxylic Membrane Based on a Poly(vinyl chloride)/Poly(methyl methacrylate-*co*-divinyl benzene) System

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ABSTRACT: The transport of cadmium and iron through a poly(vinyl chloride)/poly(methyl methacrylate-*co*-divinyl benzene) carboxylic ion-exchange membrane was investigated with a system containing HCl as the receiver solution and CdCl₂ or FeCl₃ as the feed solution. Transport of the ions through the membrane depended on the H⁺ concentration in the receiver solution and the metal concentration

in the feed solution. The rate of transfer for cadmium was about 35% higher than that for iron under the same conditions (0.5 mol/dm³ of HCl, 0.1 mol/dm³ of CdCl₂ or FeCl₃, and 5 h of dialysis). © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 705–707, 2005

Key words: membranes; diffusion; selectivity

INTRODUCTION

The current and rapid development of membrane technology involves Donnan dialysis as one method for the separation of metal ions. The transport of metal ions was investigated with solutions containing monovalent and divalent cations on several types cation exchange membranes.

Wen and Hamil¹ studied the transport of Cu²⁺, Ni²⁺, Co²⁺, Mg²⁺, and Fe³⁺ through sulfonated styrene-grafted or acrylic acid grafted membranes.

Other authors^{2–6} have described the effect of the nature and ionic strength of the receiver solution on the Donnan dialysis enrichment of copper, zinc, and iron with poly(styrene sulfonate)/polyethylene and sulfonated Teflon-based membranes.

Mecenauer et al.⁷ described the transport of divalent cations, such as Cu²⁺, Ni²⁺, Co²⁺, Zn²⁺, and Fe²⁺, through a perfluorsulfonate ion-exchange membrane (Nafion 427) with metal sulfate–sulfuric acid dialysis systems.

In previous studies,^{8,9} we examined the transport of Cu²⁺, Ni²⁺, Co²⁺, and Zn²⁺ ions through a carboxylic ion-exchange membrane. The membrane was based on a poly(vinyl chloride) (PVC)/poly(methyl methacrylate-*co*-divinyl benzene) [poly(MMA-*co*-DVB)] polymer system.

The purpose of this study was to examine cadmium and iron transport through the obtained carboxylic membrane.

EXPERIMENTAL

Materials

The carboxylic membrane was prepared by the paste method. PVC powder was mixed with a monomer mixture containing methyl methacrylate (MMA), 5 wt % divinyl benzene (DVB), and 2 wt % benzoyl peroxide to prepare a paste. The obtained composite was cast between two cellophane films and heated at 373 K for 10 h. The synthesized PVC/poly(MMA-*co*-DVB) polymer film (170–180 μm thick) was treated with glacial acetic acid at 353 K for 3 h. The obtained carboxylic membrane was washed consecutively with acetone, methanol, and water.

All of the other chemicals (MMA, DVB, benzoyl peroxide, CH₃COOH, CdCl₂, FeCl₃, HCl, and ethylenediaminetetraacetic acid) were analytical reagent grade.

Methods

Transport experiments were carried out at 298 K with a dialysis cell with two compartments (47 cm³) equipped with a glass stirrer. The effective membrane area was 4.5 cm². The compartments were fitted with CdCl₂ or FeCl₃ as the feed solution and HCl as the receiver solution. Both solutions were sampled periodically, and the metal concentration was determined by titration with ethylenediaminetetraacetic acid solu-

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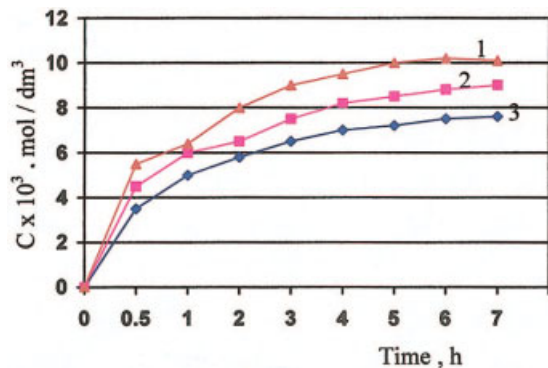


Figure 1 Dependence of the cadmium concentration in the receiver solution on the time and HCl concentration: (1) 0.5, (2) 0.3, and (3) 0.1M HCl. Feed solution: 0.1 mol/dm³ of CdCl₂.

tion. The HCl concentration was determined by titration with NaOH solution. The pH of the solutions was monitored by a pH meter (model OP 205, Radelkis, Budapest, Hungary). The experiments were carried out at a stirring speed of 700–800 rpm.

The membrane transfer rate (J ; mol cm⁻² h⁻¹) was calculated by a linear regression technique from the change of the concentration by the following equation:

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

where C is the cadmium or iron concentration in the solution (mol/dm³), V is the volume of the solution (cm³), S is the effective membrane area (cm²), and t is the time(h).

The transfer fraction of metal ions (α ; %) was calculated from the following relationship:

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

where C_t is the concentration of cadmium or iron in the receiver solution after time t (mol/dm³) and C_0 is

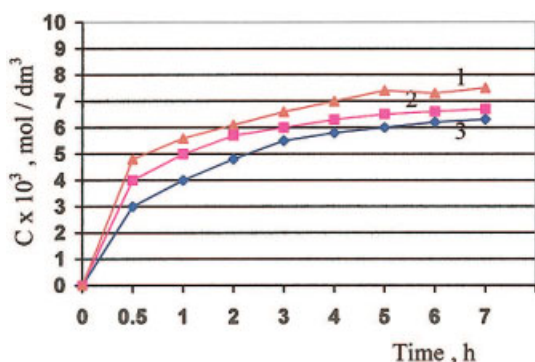


Figure 2 Dependence of the iron concentration in the receiver solution on the time and HCl concentration: (1) 0.5, (2) 0.3, and (3) 0.1M HCl. Feed solution: 0.1 mol/dm³ of FeCl₃.

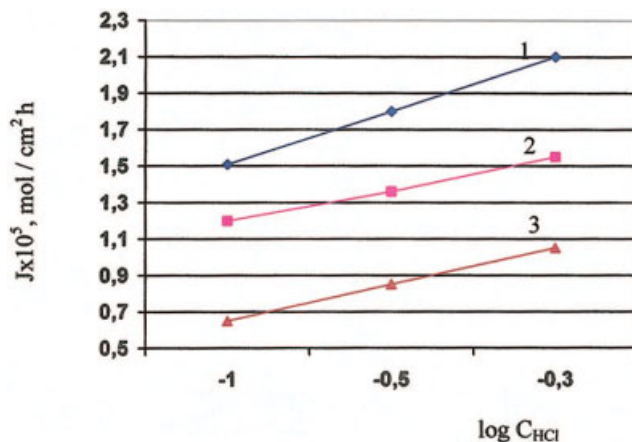


Figure 3 Dependence of the transport rate on the H⁺ concentration in the receiver solution: (1) 0.1M CdCl₂, (2) 0.1M FeCl₃, and (3) 0.01M CdCl₂. C_{HCl} is the concentration of the hydrochloric acid as receiver solution.

the initial concentration of cadmium or iron in the feed solution (mol/dm³).

RESULTS AND DISCUSSION

The transport of cadmium and iron through a carboxylic membrane based on a PVC/poly(MMA-co-DVB) polymer system was investigated under various conditions. Figure 1 represents the dependence of cadmium transfer through the membrane on the time and concentration of HCl in the receiver solution. The acid concentration was varied from 0.1 to 0.5 mol/dm³, and the concentration of CdCl₂ in the feed solution was 0.1 mol/dm³.

The amount of cadmium removed from the feed solution and appearing in the receiver solution was affected by the H⁺ concentration in the receiver solu-

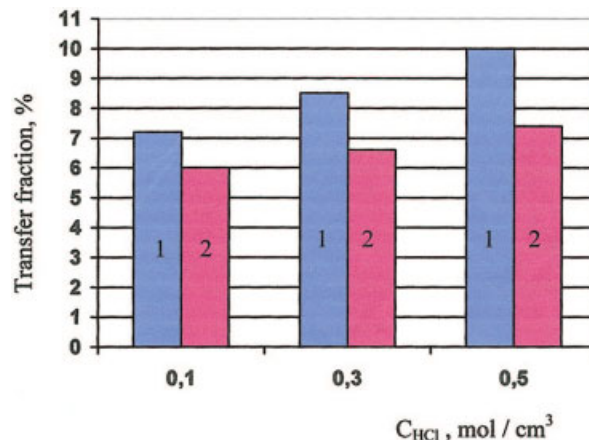


Figure 4 Effect of the H⁺ concentration in the receiver solution on the transfer fraction of (1) cadmium and (2) iron. Feed solution: 0.1 mol/dm³ of CdCl₂ or FeCl₃ and 5 h of dialysis.

tion. The transfer rate of cadmium increased by 40% when 0.5M HCl was used as the receiver solution compared to that when 0.1M HCl was used. The transfer fraction of cadmium was 10% after 5 h of dialysis.

This indicates that the transfer of cadmium from the feed to the receiver solution through the membrane was based on the concentration gradient and active transport driven by H^+ flux in the opposite direction. The pH of the feed solution decreased from 5.4 to 4.5 for 0.5M HCl after 5 h of dialysis.

The same results were obtained for iron transport through the membrane. Figure 2 shows the dependence of iron transport on the time and acid concentration in the receiver solution. The number of Fe^{3+} ions transported from the feed solution to the receiver solution through the membrane increased when a higher HCl concentration in the receiver solution was used. The transfer rate of iron was about 35% lower than that of cadmium under the same conditions [Fig. 3(2)]. This may have been due to the fact that the valence and the hydrated ionic size of the Fe^{3+} ion (4.59 Å) were higher than that of the Cd^{2+} ion. Also, the carboxylic groups on the membrane were weakly dissociated. The pH of the feed solution was 2.4 (0.1M $FeCl_3$), and it changed negligibly during the iron transport. We suggest that the transport of iron through the membrane was controlled by the boundary layer diffusion on the feed side of the membrane. The transfer fraction observed for iron was about 7.5% (Fig. 4, column 2).

The investigation carried out and the results obtained for the effect of the initial metal concentration in the feed solution are shown in Figure 5. The receiver solution was 0.5M HCl. The rate of transfer of ions through the membrane decreased with decreasing initial metal concentration of $CdCl_2$ or $FeCl_3$ in the

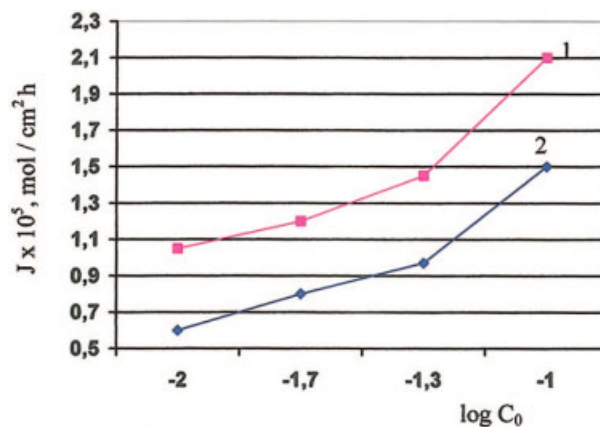


Figure 5 Effect of the initial metal concentration on the transfer rate of (1) cadmium and (2) iron. Receiver solution: 0.5M HCl.

feed solution. The transfer rate of ions observed for 0.01M $CdCl_2$ (or 0.01M $FeCl_3$) was about 2–2.5 times lower than that of 0.1M $CdCl_2$ (or 0.1M $FeCl_3$) as a feed solution.

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