Ion Exchange Membrane for Acid Recovery by Diffusion Dialysis

Toshio ARITOMI, Takenori ISOMURA, Kenji FUKUTA and Kanji SAKATA
Tokuyama Corporation, Tsukuba Research Laboratory, 40 Wadai, Tsukuba, Ibaraki 300-4247, Japan

(Manuscript submitted February 15, 2003; accepted April 10, 2003)

Abstract
An ion exchange membrane with a high cross-linking structure close to the membrane surface was prepared and evaluated for its diffusion dialysis performance. Cross-linking at the membrane surface was carried out by soaking the base membrane (4-Vinylpyridine and Divinylbenzene copolymer) in n-Hexane containing Dibromoalkane. Then the cross-linking structure was formed next to the surface by pyridine and Dibromoalkane interaction. After that, the inside of the membrane was quaternized by CH₃I. The ion exchange membrane obtained shows a greatly improved metal rejection for diffusion dialysis compared with the membrane having no surface modification.

1 Introduction
Diffusion dialysis is a method for the recovery of free acid using as its driving force a concentration difference between the solutions on both sides of an ion exchange membrane. An anion exchange membrane is generally used because it shows a great difference in diffusivity between acids and salts, such as metals. This allows the separation of an acid from a salt solution.[1] Diffusion dialysis is mainly used for the recovery of acids from spent pickling solutions in the steel, metal refining, and electroplating industry to minimize the waste solutions that cause environmental problems. Since a concentration difference is the driving force for mass transfer, Diffusion dialysis gives low operating costs because of minimizing an energy consumption.

Tokuyama Corp. has been working for many years on ion exchange membranes and the diffusion dialysis technology, and has developed a technology for the economical recovery of acids by using a commercialized membrane: the Neosepta® AFN, based on a 4-Vinylpyridine and Divinylbenzene copolymer.[2] The objective of this study is to develop a membrane that would perform more efficiently for acid recovery, specifically with high acid selectivity and high metal rejection. A high selectivity between acids and metals through the membrane is achieved by increasing the cross-linking of the membrane structure. However, this usually reduces the diffusivity of acid. Our idea is to only introduce the high cross-linking structure around the membrane surface. It is expected that minimizing the thickness of the high cross-linking zone, not all-the-way inside of the membrane but only at the membrane surface, gives an increase of the membrane selectivity without decreasing the acid diffusivity.

The cross-linking at the membrane surface can be introduced by reacting the base membrane (4-Vinylpyridine and Divinylbenzene copolymer) with Dibromoalkane dissolved in an organic solvent. It is important to select a Paraffin hydrocarbon, such as Hexane, for the organic solvent. Hexane suppresses swelling of the base membrane so that the Dibromoalkane is not allowed to easily penetrate inside the membrane. This
results in forming the cross-linked polymer network around the membrane surface.

In the present work, the effect of the membrane surface modification by Dibromoalkane on the diffusion dialysis property is investigated. The influence of an alkyl chain of the Dibromoalkane is also discussed.

2 Experimental

2.1 Preparation of the membranes

The base membrane was prepared by the “Paste method”[3,4]: the paste, consisting mainly of 4-Vinylpyridine, divinylbenzene, styrene, nitrile-butadiene-rubber (NBR), and benzoylperoxide as a polymerization initiator, was coated onto the polyvinylchloride cloth made by Teijin Ltd., and the monomers were polymerized. Then the base membrane was soaked in dibromalkane dissolved in n-Hexane; Br(CH₂)nBr, alkyl chain n = 3 ~ 10, at 25 degC for 3 days, and successively soaked in n-Hexane and Methanol, washed with methanol and dried in vacuum drier. The resultant membrane was quaternized with Methyl iodide (CH₃I). The obtained membrane was washed with methanol and deionized water.

2.2 Cross-linking degree of Dibromoalkane

The amount of reacted dibromalkane was determined by measuring the weight increase of the membrane after soaking in n-Hexane containing the dibromalkane. The weight was measured after completely drying the membrane with a vacuum oven. The amount of reacted dibromalkane in mols per g-dry membrane was calculated from the weight increase per g-dry membrane divided by the molecular weight.

Two types of formation for the reacted Dibromoalkane are considered as shown in Fig. 1. The degree of cross-linking represented by type A was determined from the amount of reacted dibromalkane and the amount of quaternary salt of type A. The amount of quaternizing groups was determined to measure the associated ions following the general way for an ion exchanger[5].

2.3 Diffusion dialysis testing

The characterization of the Diffusion dialysis properties was carried out using two-compartment cells separated by the membrane with an active membrane area of 10 cm². Initially, one compartment was filled with 200 cm³ solution of 1 M-H₂SO₄ and 0.5 M MgSO₄ (M = mol dm⁻³) and another compartment was filled with 100 cm³ of deionized water. The temperature was maintained at 25 degC. After one hour of dialysis with stirring at identical rates of 1500 ~ 1800 rpm for both compartments, the solution on the deionized water side was sampled and analyzed for acid and Mg ion concentrations. The acid concentration was determined by titration with NaOH. The Mg ion concentration was determined by inductively coupled plasma spectrometry (ICP). The permeation properties of acid (Uₜ) and Mg ions (Uₐₘ₃) are given by

\[ Uₜ \text{ or } Uₐₘ₃ = \frac{w}{A \times t \times M} \]

Where \( w \) is the amount of transported component in moles, \( A \) the active membrane area in square meters, \( t \) the time in hours, and \( M \) the log mean of the difference of concentration for the component across the membrane (mol/dm³)

\[ M = \frac{\left(C_{f₀} - C_f + C_{pₜ}\right)}{\ln\left[C_{f₀}/(C_f - C_{pₜ})\right]} \]
Where \( C_{FB} \) is the concentration of the component in the feed solution at time 0, \( C_{Ft} \) the concentration of the component in the feed solution at time \( t \) and \( C_{Rt} \) is the concentration of the component in the permeate solution at time \( t \). The selectivity of acid against Mg ion was calculated by \( U_R / U_{Mr} \). [6]

3 Results and Discussion

3.1 Effect of a solvent on the reaction of 1,4-Dibromobutane

Figure 2 shows that the effect of a solvent on the reaction of 1,4-Dibromobutane with the base membrane. N-Hexane and methyl ethyl ketone (MEK) were studied and compared for their solvent effect. If methyl ethyl ketone is used as a solvent, the amount of reacted 1,4-Dibromobutane increases with higher concentrations of 1,4-Dibromobutane, saturated at around 1.4 mmol/g-dry membrane. However in the case of n-Hexane, 1,4-Dibromobutane reacts with the base membrane much less than with the use of methyl ethyl ketone, even if in the high concentration of 1,4-Dibromobutane. This result indicates that methyl ethyl ketone has an impact on the cross-linking not only at the membrane surface, but also inside the membrane. It is supposed that the 1,4-Dibromobutane easily penetrates inside the membrane due to membrane swelling. A small amount of the reacted 1,4-Dibromobutane using n-Hexane implies that the cross-linking reaction occurred around the membrane surface caused by the suppressed membrane swelling.

The distribution of the reacted 1,4-Dibromobutane across the membrane was analyzed by electron probe micro analysis (EPMA). The membrane reacted with 1,4-Dibromobutane (before quaternization with CH₃I) was soaked in 5wt% KMnO₄ aqua in order to exchange the counter ions MnO₄⁻ with the Br⁻. Then Mn across the membrane was detected by EPMA. As shown in Fig. 3, it is clear that, in the case of n-Hexane, the reacted 1,4-Dibromobutane does not exist in the middle of the membrane but, in the case of methyl ethyl ketone, 1,4-Dibromobutane exists in the middle of the membrane as well as around the membrane surface. A solvent of ketone such as MEK has a good chemical affinity with polyvinyl chloride and polystyrene that are some of the components of the membrane, so that membrane swelling could be accelerated by ketone. Therefore, in order to make a cross-linking reaction around the membrane surface, paraffin hydrocarbon such as n-Hexane is suitable solvents to use. They have the effect of reducing the membrane swelling.
3.2 Effect of an alkyl chain of Dibromoalkane on the cross-linking rate

The amount of reacted Dibromoalkane decreases with a higher number of alkyl chain, as shown in Fig. 4. It is due to the effect of the variation in molecular size. A big-sized molecule is interrupted at the surface. Dibromoalkane with alkyl chain numbers of 4 or 5 is the best to give a high cross-linking rate. However, the big Dibromoalkane reduces the cross-linking rate and the small one \(n=3\) also tends to reduce the cross-linking rate. The possible explanation for this observation is not clear at this point. It is assumed that the most suitable extent of cross-linking exists in the reaction between Dibromoalkane and the 4-Vinylpyridine-Divinylbenzene copolymer.

3.3 The performance of surface modified membrane

Table 1 shows the permeation property of the acid \(U_H\) and the metal rejection \(U_{H/Mg}\) for the surface-modification membranes and for commercialized membranes Neosepta AFN. The listed membranes with the various cross-linking degree were prepared using 1,4-Dibromobutane dissolved in the different concentrations of \(n\)-Hexane. The metal rejection \(U_{H/Mg}\) increases remarkably with slightly higher cross-linking at the membrane surface. But a dramatic decrease in the \(U_H\) is not observed. Comparing to Neosepta AFN, the surface modification membranes shows a much higher metal rejection, even if the \(U_H\) is similar. This high metal rejection can contribute to the development of a highly efficient system for acid recovery.

It is concluded that the surface cross-linking modification approach to ion exchange membranes can lead to an excellent metal rejection without a decrease in acid diffusivity.

Table 1 Diffusion dialysis performance of the surface modified membrane

<table>
<thead>
<tr>
<th>Membrane type</th>
<th>Cross-linking degree (%)</th>
<th>(U_H)</th>
<th>(U_{Mg} \times 10^3)</th>
<th>(U_{H/Mg})</th>
</tr>
</thead>
<tbody>
<tr>
<td>modified membrane No.1</td>
<td>12</td>
<td>10</td>
<td>28</td>
<td>360</td>
</tr>
<tr>
<td>modified membrane No.2</td>
<td>13</td>
<td>10</td>
<td>10</td>
<td>990</td>
</tr>
<tr>
<td>modified membrane No.3</td>
<td>15</td>
<td>9</td>
<td>4</td>
<td>2030</td>
</tr>
<tr>
<td>Neosepta AFN</td>
<td>-</td>
<td>10</td>
<td>53</td>
<td>190</td>
</tr>
</tbody>
</table>

Acknowledgement

The authors thank Ms. Y. Kobayashi and Mr. R. Ishimoto, at the RC center of Tokuyama Corp., for measurements by EPMA.

References