

Electrical resistance of polybenzimidazole membranes

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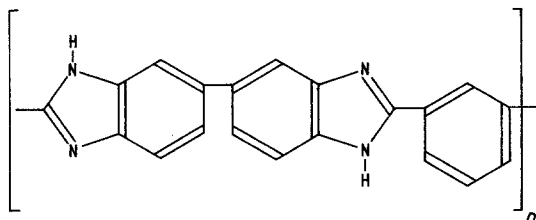
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Measurements of electrical resistance were made on several polybenzimidazole membranes prepared for use in reverse osmosis. In contact with 1 M KCl, different samples had resistances which ranged from 0.087 to 22 $\Omega \text{ cm}^2$. Smaller ranges of resistance were seen with membranes in contact with 36% H_2SO_4 (0.022 to 0.030 $\Omega \text{ cm}^2$) and 40% KOH (0.0063 to 0.096 $\Omega \text{ cm}^2$). With all three electrolytes, however, increasing resistance followed increasing salt rejection measured under reverse osmosis conditions. This offers a rapid and convenient diagnostic test for reverse osmosis performance of the membranes.

1. Introduction

Synthetic membranes are finding increasing application in the separation and purification of components in liquid and gaseous mixtures, as well as for separators in electrochemical cells [1, 2]. In this paper we examine one such synthetic membrane, polybenzimidazole (PBI), more correctly known as poly(2,2'-(*m*-phenylene)-5,5'-bibenzimidazole). The PBI membranes studied



were prepared for reverse osmosis (RO) so as to have a thin, continuous skin on one side (the 'active side'), supported by a thick, porous layer of the same chemical composition. This structure is shown in Fig. 1. Since the membrane functions in RO by rejecting the passage of dissolved electrolytes while permitting the passage of water, it was of interest to examine how the electrical resistance of the membranes in contact with electrolyte related to the RO behaviour and to determine, if possible, what structural features of the membrane control both of these.

2. Experimental

PBI membranes, prepared and characterized for reverse osmosis [3], were obtained from M. Tan and H. J. Davis of these laboratories. Typically, the membranes were prepared by casting *N,N*-dimethylacetamide solution on to glass plates, followed by heating to cause partial evaporation of solvent from the surface of the cast film. The temperature and duration of this heating controls the thickness of the dense top skin of the membrane. This step is followed by immersion of the film in water, causing coagulation and establishing the porous structure of the thick support layer on the bottom of the membrane. The final step consists of annealing the membrane in ethylene glycol at 180°C, which causes a reduction in molecular void volume and enhances the RO properties of the membrane.

RO characterization was carried out at a

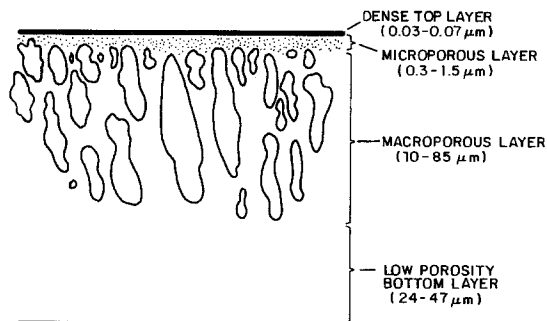


Fig. 1. Cross-section based on TEM photomicrograph of representative membrane.

pressure of 4.14×10^6 Pa using 0.5% NaCl solution over a period of 24 hours. Salt rejection (%) is given by $100(1 - C_p/C_f)$, where C_p is the product salt concentration and C_f is the feed salt concentration, these being measured by conductivity and titration methods.

Membrane resistance was measured using the procedure described by Lander and Weaver [4]. In this measurement the membrane is clamped between two halves of a Lucite cell in contact with electrolyte on either side. A d.c. current is applied between two platinum-wire electrodes across the electrolyte/membrane/electrolyte. The voltage drop across the membrane is measured using electrodes adjacent to either side of the membrane. The voltage-measuring electrodes were as follows: (a) Hg/Hg₂SO₄/H₂SO₄ with 36% H₂SO₄ electrolyte; (b) Hg/Hg₂Cl₂/KCl with 1 M KCl electrolyte; (c) Hg/HgO/KOH with 40% KOH electrolyte. For each sample, the current direction was reversed and the voltage drop (without regard to sign) averaged. The area resistance was then obtained by application of the formula

$$R_{\text{area}} = (E - E_0)A/I$$

where E is the voltage drop with the membrane in place, E_0 the voltage drop due to the electrolyte measured in the absence of the membrane, A is the working area of the membrane (1.27 cm^2 in our cell) and I is the applied current. The membranes were stored under water and then conditioned by several hours soaking in the appropriate electrolyte prior to measurement.

3. Results and discussion

3.1. KCl as electrolyte

Although resistance measurements were usually made at a single setting of applied current (typically 40 mA), measurements on one sample in contact with 1 M KCl showed the membrane resistance to be constant over an applied current range of 3 to 75 mA. The membrane in contact with electrolyte thus exhibits the same ohmic behaviour as do simple solutions of electrolytes [5].

When three different samples of PBI membrane were evaluated by this technique after two hours conditioning in 1 M KCl, the area resistance was found to vary by two orders of magnitude.

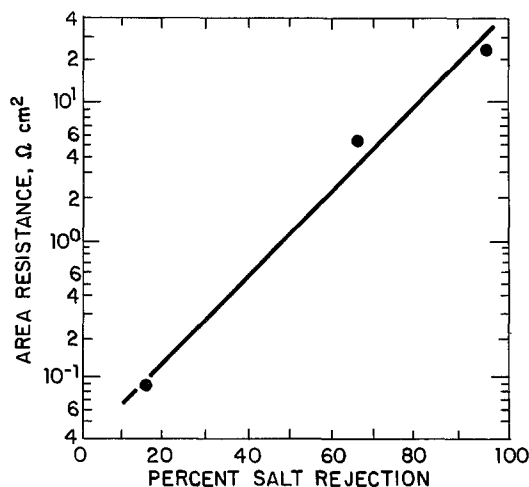


Fig. 2. Area resistance versus salt rejection (%) for three PBI membranes in 1 M KCl after 2 hours conditioning.

(Longer conditioning times resulted in somewhat lower area resistance.) As shown in Fig. 2, the resistance follows the salt rejection as measured in the RO characterization and may be represented by the following empirical correlation

$$\log R_{\text{area}} = 0.0311 (\% \text{ salt rejection}) - 1.527.$$

Although the relationship is not rigorously derived, the fact that it exists is, in retrospect, not surprising, since both resistance and salt rejection depend on the ease of movement of ionic species through the membrane.

3.2. H₂SO₄ as electrolyte

In contrast to the above, the electrical resistances of PBI membranes in contact with 36% H₂SO₄ are uniformly low and differ only slightly from one another. Their relation to the RO salt rejection data are shown in Fig. 3 and may be described by the empirical correlation

$$\log R_{\text{area}} = 0.00160 (\% \text{ salt rejection}) - 1.702.$$

The behaviour of the PBI membranes in contact with strong acid may be understood in terms of the basic nature of the benzimidazole units of the polymer[†]. Under these conditions both nitrogen atoms are protonated and will readily conduct

[†] We have determined by potentiometric titration the pK_a of a small molecule analogue, 2-phenylbenzimidazole. This value, 3.75, is presumably not greatly different in PBI.

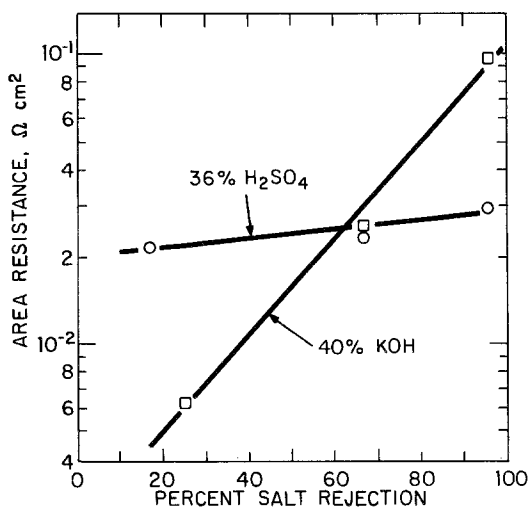


Fig. 3. Area resistance versus salt rejection (%) for PBI membranes in 36% H₂SO₄ (24 hours conditioning) and in 40% KOH (1.5 hours conditioning).

SO₄²⁻ and HSO₄⁻ counterions and possibly H₃O⁺ co-ions as well. In addition, the positively charged units of the polymer chain will result in a higher degree of solvation and greater swelling than occurs with neutral electrolyte. If this swelling occurs to an appreciable amount, then differences among the individual membranes (clearly seen with 1 M KCl) will be largely masked when the membranes are in contact with strong acid. It follows that the more open, swollen films should offer less resistance to the passage of other electrolytes present in solution. This agrees with the observation [3] that when used as an RO membrane, PBI shows a marked drop in salt rejection in the presence of acid.

A second possibility is that the lower electrical resistance of PBI in contact with acid is due to a proton-hopping mechanism, as suggested by Hoel and Grunwald [6] based on somewhat different experimental conditions. In the present work, however, protonation and swelling of the membranes as discussed above seem adequate to explain the results without invoking specific proton conductivity.

3.3. KOH as electrolyte

The electrical resistance of PBI in contact with 40% KOH electrolyte clearly reflects the relative ease of migration of ions measured in RO charac-

terization. This is shown in Fig. 3 and is described by the empirical equation

$$\log R_{\text{area}} = 0.0165 (\% \text{ salt rejection}) - 2.637.$$

The low values of area resistance may be understood if concentrated KOH, like H₂SO₄, is able to invade the membrane and effect its swelling so as to facilitate the passage of ions. That this does occur is supported by the observation that dry films of PBI undergo 10–20% increase in linear dimensions when immersed in strong caustic solutions.

3.4. Relation to membrane morphology

Since the membrane samples examined have identical chemical structure, it was of interest to determine what morphological features might be responsible for the ease of migration of ionic species, as evidenced in the RO and electrical measurements. Examination of three PBI membranes characterized by salt rejection of 91.8%, 37.3% and 18.3% by transmission electron microscopy showed that each had the structure shown in Fig. 1. Within these three samples there was an apparent trend toward increasing salt rejection with increasing thickness of the microporous layer. This trend is certainly fortuitous, since transport properties will be dominated by the dense top layer of the membrane, rather than the porous support structure. Further, while both salt and solvent flux are inversely proportional to membrane thickness, salt rejection should, according to Lonsdale's solution-diffusion model [7], be independent of membrane thickness.

A second possibility is that salt rejection is controlled by the degree of crystallinity in the membrane [8]. However, when the three samples were examined by wide-angle X-ray diffraction, crystalline reflections were not observed. It may be suggested, then, that the differences in behaviour are due to differences in annealing which occurred in the samples. Although not imparting any observable crystallinity to the membranes, annealing can result in shrinkage and tightening of the polymeric structure which impedes the passage of diffusing ions across the membrane. In any case, electrical resistance clearly reflects the salt rejection ability of the membranes studied and

offers a rapid and convenient diagnostic test for their RO performance.

Acknowledgements

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