

Studies on Cation-Exchange Membrane.

II. Sorption of Electrolyte by Rubber-Based Cation-Exchange Membrane from CNSL Resin

N. P. SURYANARAYANA and K. M. JOSHI, *Department of Physical Chemistry, Institute of Science, Bombay, India*

Synopsis

Electrolyte sorption of a rubber-based cation-exchange membrane has been studied for two samples of different rubber contents. The sorption behavior is discussed in terms of the capillary volume between rubber and the resin, and an explanation is provided for the difference in the behavior of the two samples.

INTRODUCTION

It is customary to consider ion-exchange materials as strong electrolytes and interpret their behavior in terms of physicochemical concepts of a highly charged solid phase with a pore liquid due to the three-dimensional network. It follows from this that the sorption behavior of such material with strong electrolytic solution would be of considerable interest, and this has indeed been the subject of several investigations.¹⁻³

Generally, the ion-exchange materials are commercially available in a granular form and as such can be used only with difficulty for investigations of sorption behavior, and they are therefore shaped into rods⁴ or membranes which are convenient to handle for sorption experiments. However, this process of making them into the required form introduces swelling effects which in turn affect the sorption behavior. In many investigations, this seems to have received little attention in considering the sorption data.

The porosity of a membrane depends, for several reasons, on the structure of resin, binder, and of the interphase between resin and the binder. In a recent communication,⁵ Hale has studied these effects using resins of varied degrees of cross-linking and taking into account the porosity of the resin. However, the effect of capillary volume between resin and binder has received very little attention.

Recently, membranes using rubber⁶ as a binding material have been prepared. These membranes showed rather low rates of exchange with electrolytic solutions, indicating a change in the behavior of the resin while in the membrane due to presence of rubber.⁷ In this paper, the results of studies of sorption behavior of these rubber based membranes are presented.

EXPERIMENTAL

Membranes

Rubber-based membranes, prepared as described in our earlier work^{6,7} were completely converted to the sodium form and were washed free of chloride. A known weight (about 1.25–1.5 g.) of this sample was used for sorption studies.

Concentration of the Sorbed Electrolyte

A leached sodium form of the membrane was kept in excess of sodium chloride solution of known strength. After 10 hr. equilibration the sample was taken out, and the surface electrolyte was removed by pressing in the folds of a filter paper. The weight of this sample was determined, and the membrane was then transferred to a clean beaker and repeatedly stirred with known volumes of fresh distilled water. All the washings were titrated together (to get the total chloride uptake) against standard 0.01*N* silver nitrate solution.²

Moisture Content

The moisture contents of both resin and membrane were determined separately. The samples used for these experiments were always cut out from the same uniform sheet of membrane for which the moisture content was known with reasonable accuracy, so as to determine the volume of sorbed electrolyte.

RESULTS

The variation of concentration of the imbibed electrolyte with external solution concentration for the two samples of membranes with rubber contents of 16 and 20% are shown in Figure 1.

The variation of the distribution coefficient (ratio of absorbed concentration to the external solution concentration) as a function of concentration is shown in Figure 2.

DISCUSSION

We observe that there is a qualitative agreement between the sorption and permselectivity, in that the membrane containing the larger percentage of resin shows a better permselectivity than the other membrane. This type of behavior observed has been reported by Rosenberg⁸ for glass cloth-reinforced membranes. The straight line plot of the distribution coefficient with concentration points out to the significant role of the capillary volume in the membrane.

Since ion-exchange resins are highly charged bodies, their sorption behavior in general is a function of the fixed charge on them. In the sorption of electrolyte by a membrane, however, the porosity seems to play a very im-

portant role. In our earlier observations,⁷ the exchange capacities of such membranes revealed that the physical structure of the membrane influenced not only the exchange rate but also the total realizable exchange capacity. Because of its elastic nature, the binder tends to stretch itself on to the surface of resin grains on swelling; thus to some extent the binder

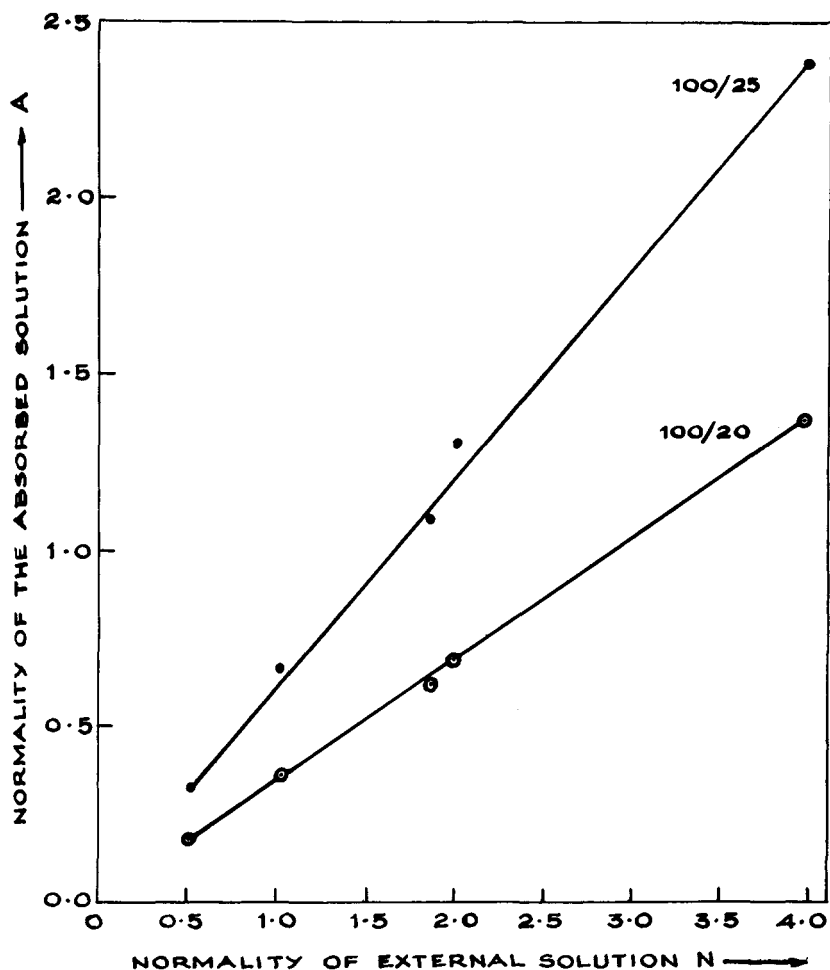


Figure 1.

shields the resin granules. As the permeability of the rubber film is considerably less, this film spread over the resin grain will keep the electrolyte away from contact with the resin. Thus, in spite of the presence of a large amount of resin, only a relatively small portion of the resin will be accessible for the contact with electrolyte.

On analysis of the electrolyte sorption data, it was observed that the sample with higher rubber content and lower moisture content showed

higher electrolyte sorption, indicating a low fixed ion concentration in the sample.

The moisture content of the membrane depends on (1) the resin network, (2) the rubber, and (3) the capillaries between resin and rubber. Since the resin is a highly charged body, the moisture sorption by the resin is small in comparison with holding of electrolytes held in the capillaries. The electrolyte released can therefore be accounted for on the basis of capillary volume. Since the water sorption of resin and the membrane is known, the capillary volume can be calculated from the difference, as rubber is known to have negligible water sorption.

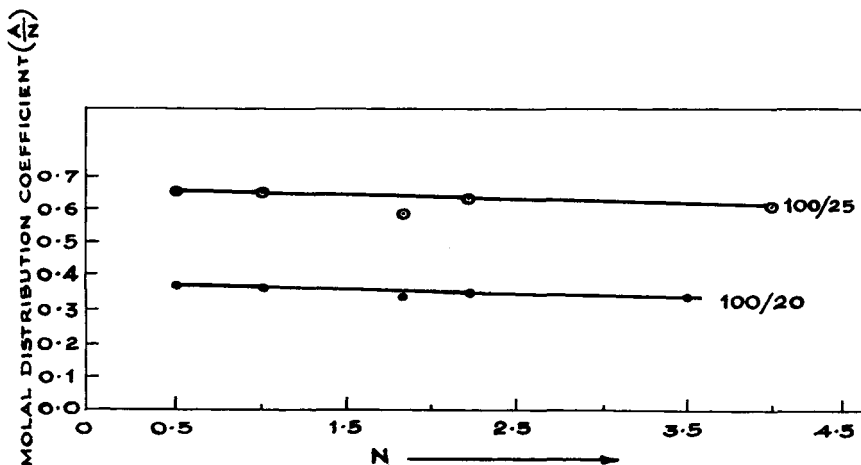


Figure 2.

If the capillaries are not exposed to the resin grain, the concentration of imbibed electrolyte would be the same as that of external solution. However, the capillary walls are charged to varying degrees depending on the binder content, and the membrane with a larger proportion of charged capillary walls would more powerfully exclude the electrolyte than the other.

Table I gives the experimental results obtained with two membranes having different rubber concentrations.

It can be seen from the data of sample containing 20% rubber that the entire sorption of electrolyte is due only to capillary volume, and the resin which is the major constituent of the membrane does not seem to have any effect on the walls of these capillaries. However in sample containing 16% rubber, a considerable number of capillaries seem to be charged, thus effectively excluding the electrolyte. On increasing the binder content beyond 20% we observed that the sorption behavior remained more or less the same as that of sample containing 20% rubber.

Although above explanation seems to be satisfactory on a qualitative basis, conclusions based on such sorption measurements seem to be of less

quantitative importance, since the porosity is controlled to a great extent by the method of processing the resin with rubber to obtain a membrane. Our results show conclusively that sorption of electrolyte is greatly affected by slight variations in rubber content. Hence, conclusions about the behavior of a resin based on electrolyte sorption by a membrane containing the resin will not be very precise. One of the factors that must be carefully

TABLE I
Salt Contents in Capillaries of the Membranes*

Sample no.	Binder content, %	Moisture content, %	Capillary volume, cc./g.	External solution concentration, <i>N</i>	Salt concentration observed, mg. NaCl/g.	Maximum salt content possible, mg. of NaCl/g.
100/20	16	50	0.39	0.5	5.85	11.4
				1.0	10.35	22.8
				2.0	19.86	45.6
				4.0	38.68	91.2
100/25	20	47.5	0.365	0.5	9.10	10.73
				1.0	18.18	21.46
				2.0	35.97	42.92
				4.0	67.20	85.84

* The resin used had a moisture content of 20%.

studied is the compatibility of the rubber with the resin. CNSL resin, unlike harder resins such as polystyrene resins, is very easily mixed with rubber. Though rubber has considerable flexibility⁷ in contrast to other binding materials used for this purpose, it is clear that this binder has a profound influence on the sorption behavior of the resin.

References

1. Helfferich, F., *Ion Exchange*, McGraw-Hill, New York, 1962, p. 82.
2. Juda, W., et al., *J. Am. Chem. Soc.*, **74**, 3736 (1952).
3. Pepper, K. W., D. Reichenberg, and D. K. Hale, *J. Chem. Soc.*, **1952**, 3129.
4. Lakshminarayanaiah, N., *J. Polymer Sci.*, **A1**, 139 (1963).
5. Hale, D. K., and D. J. Mecauley, *Trans. Faraday Soc.*, **57**, 135 (1961).
6. Suryanarayana, N. P., and N. Krishnaswamy, *J. Polymer Sci.*, **B1**, 491 (1963).
7. Suryanarayana, N. P., and K. M. Joshi, *J. Appl. Polymer Sci.*, **8**, 1491 (1964).
8. Rosenberg, et al., *J. Elect. Chem. Soc.*, **104**, 111 (1957).

Résumé

On a étudié la sorption d'électrolyte par membranes échangeuses de cations à base de caoutchouc dans le cas de deux échantillons de teneur différente en caoutchouc. Le comportement à la sorption a été discuté en fonction du volume capillaire compris entre le caoutchouc et la résine et on a fourni une explication de la différence de comportement de deux échantillons.

Zusammenfassung

Die Elektrolytsorption einer Kationenaustauschermembran auf Kautschuk-grundlage wurde an zwei Proben mit verschiedenem Kautschukgehalt untersucht. Das Sorptionsverhalten wurde in bezug auf das Kapillarvolumen zwischen Kautschuk und Harz diskutiert und eine Erklärung für den Unterschied im Verhalten der beiden Proben geliefert.

Received April 17, 1964