JOURNAL OF APPLIED POLYMER SCIENCE VOL. 8, PP. 1491–1496 (1964)

Studies on Cation Exchange Membranes. I. Effect of Porosity on the Rate of Exchange in Rubber-Based Cation Exchange Membranes from CNSL Resin

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

Synopsis

Experimental studies on the exchange capacity of rubber based CNSL resin membranes have been carried out. The rate of exchange was found to decrease with increase in rubber content of the membrane. Determination of the exchange capacity in presence of dioxane showed definite interaction between the resin and the binder. This was confirmed by extracting out the binder with a solvent and subsequent determination of the capacity of the residue.

INTRODUCTION

Ion exchange membranes are finding increasing applications in desalting of seawater,[1] separation of certain organic chemicals and also in the determination of activity of different ions in solution. Recently, newer uses of ion exchange membranes, such as electrolyte in fuel cells (for the conversion of chemical energy directly into electrical energy),[2] have also been reported.

Exhaustive studies on various types of collodion membranes[3] have been able to provide a basis for the electrochemistry of ion exchange membranes. Because of the low mechanical strength of such homogeneous membranes, it is rather difficult to utilize these studies for the development of newer applications.

Heterogeneous membranes, on the other hand, although complicated for the purpose of study, have come into practical applications in varied forms which warrant their detailed study for the understanding of basic phenomena associated with them. The fundamental electrochemistry of any ion exchange resin can be studied in the form of plugs, rods, or membranes rather than in granular state.[4] Most of the theoretical aspects of the mechanism of ion exchange are explained often by reference to their electrochemical behavior in the form of membranes.

More recently[4–6] the properties are being studied with reference to the structure of the membrane. In the case of heterogeneous membrane, the porosity seems to be of great importance in determining the electrochemical characteristics of the membrane.

Sulfonated polystyrene and phenol–sulfonic acid formaldehyde condensates have been extensively studied in the form of membranes by combining them with polystyrene[7] and polyethylene[6] and also by casting on a screen of Saron.[8,9] Rubber[10] has also been found as a suitable binder in making ion exchange membranes.

A modified phenol-sulfonic acid type cation exchanger from cashew nut shell liquid[11] has been used in conjunction with natural rubber and the possibilities of being utilized in electrodialysis[12] have been examined.

An attempt to study this resin in the form of membranes was undertaken in this laboratory. Preliminary investigations showed considerable variation in the property of the resin in the form of membranes. The study of the rate of exchange, the influence of a solvent along with the equilibriating electrolyte, and the study of the interaction of binder and resin (if any) as revealed by the extraction of the binder by solvent under varying conditions are reported and discussed in this paper.

EXPERIMENTAL

Preparation of Membranes

Membranes were prepared by mixing powered resin, (Wasoresin-14) of about 100 mesh size with pale crepe rubber on a 12-in. rubber mill. Rolls were kept cold while milling by the circulation of cold water. Uniform sheets (30–35 mils) were obtained. The membranes were swollen for 24 hr. in cold water before taking them for further experiments.

Determination of Capacity and Moisture Content of Membranes

Samples prepared as above were cut into small pieces and thoroughly regenerated with 5% hydrochloric acid, then washed free of acid, and air-dried.

A 1-g. portion of the sample was equilibriated with 50 cc. of 1*N* barium chloride solution for various time intervals. At the end of a known interval of time, the solutions were titrated against standard alkali. A sample weighing 1 g. was separately kept in a weighing tube in an oven at 100°C. for 20 hr. and the dry weight of the sample was used to evaluate the capacity of the membrane. Samples used for equilibriation with 1*N*-$BaCl_2$ were regenerated and reused. No variation in capacity was noted after successive regeneration and exhaustion.

Determination of Capacity in Presence of a Solvent

Samples weighing 1 g. were placed in 100 cc. conical flasks. A solvent, 5–25 cc. purified dioxane (for the convenience of miscibility with water phase, this solvent was used), was added along with 50 cc. of 1*N* barium chloride solution. After 24 hr. equilibriation, the solutions were titrated against alkali as in the previous case. The dry weights of the samples were determined separately. Samples containing a higher percentage of binder were used in these experiments.

Extraction of Binder

A small portion of the membrane was treated with petroleum ether which is a good solvent for the binder. After few hours, the solution was carefully decanted and the residue kept in contact with fresh quantities of petroleum ether; in this manner, a considerable amount of rubber was removed, and the capacity of the residue was evaluated after regeneration as described above.

Alternatively, membranes were cut into small pieces and were Soxhlet-extracted for 16 hr. with petroleum ether and the residue was used for capacity determination.

RESULTS

The characteristics of the membranes are summarized in Table I. Results of the experiments of extraction of the membrane with solvent are given in Table II. Figure 1 shows the variation in capacity with increasing

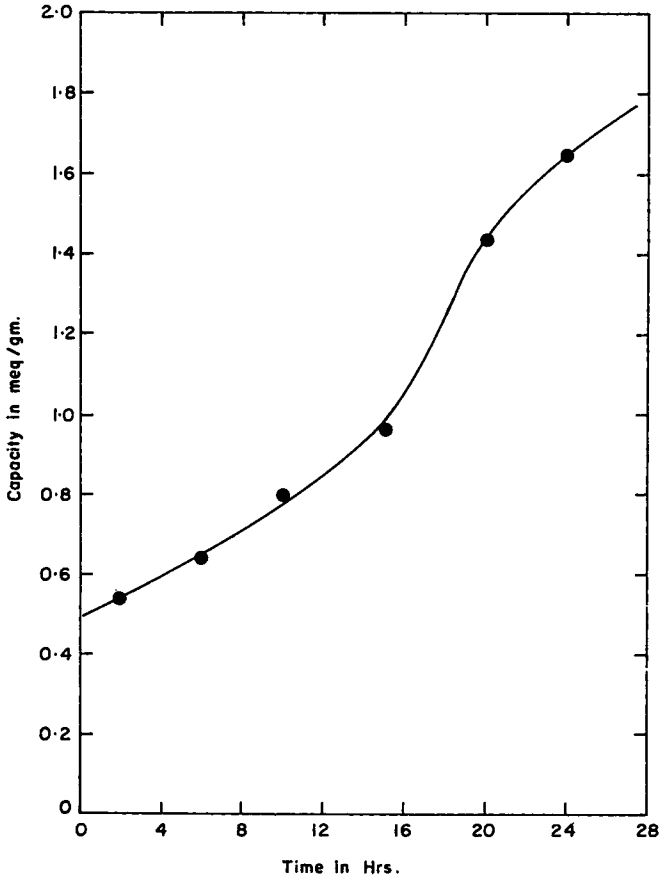

Fig. 1. Rate of exchange in a high capacity membrane.

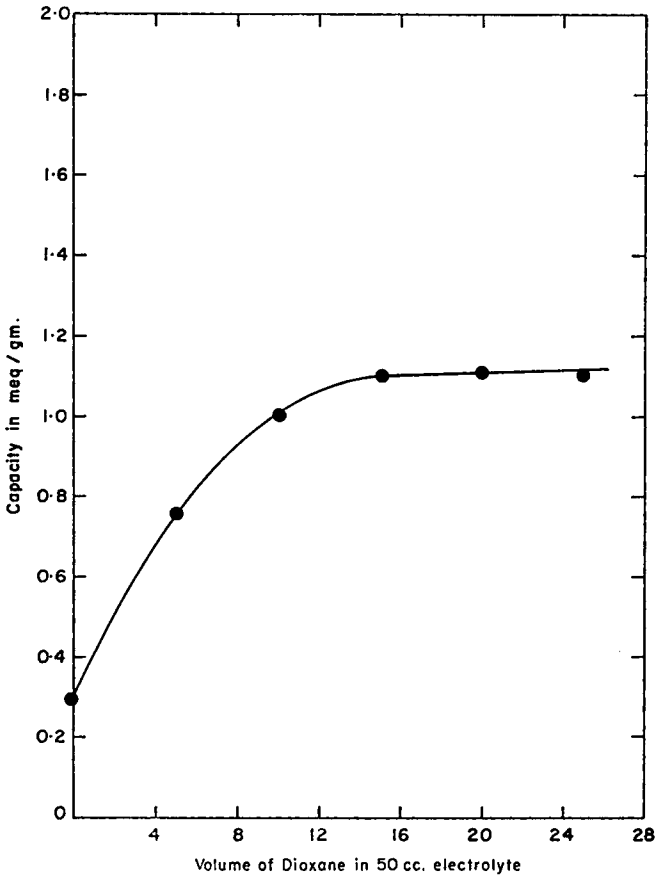

Fig. 2. Variation of capacity with increasing dioxane content of a low capacity membrane

TABLE I
Characteristics of Wet Membranes

Sample no.	Binder, %	Moisture content %	Exchange capacity, meq./g.
1	16	50	1.65
2	20	44	0.25

TABLE II
Extraction Experiments

Method of extraction	Capacity, meq./g.	Moisture content, %
Nil	0.25	35.06
Cold	0.78	32.00
Hot	0.87	32.00

dioxane content of a low capacity membrane. Figure 2 shows the rate of exchange in a high capacity membrane.

DISCUSSION

As observed by many workers,[13] we also find that the ratio of rubber to resin is rather critical and if the ratio increases beyond a critical value, there is a sudden change of electrochemical properties with a relatively small change in the concentration of the binder.

The residual resin obtained on extracting the binder from the membrane shows very much less capacity than the pure resin. This confirms that there is a strong interaction of binder and resin resulting in the covering of the active surface of ion exchanger particle.

The rate of exchange is comparatively very much slower than that of conventional commercial membranes (for example, Permaplex C-10). It can be seen from Figure 1 that there is very slow rise in capacity (about 0.2 meq./g. in 5 hr.).

After 24 hr. exchange, there is about 90% capacity corresponding to the resin content in the membrane. The probable reason for this slow rate of exchange is that rubber, unlike other binders, yields to a considerable extent and stretches itself over the resin particle and thus offers greater resistance for the contact of electrolyte with the resin. As a consequence of this, a small increase in rubber content (from 16 to 20%) will increase the resistance to the imbibition of electrolyte and results in almost negligible capacity.

In order to get a better picture of this slow imbibition, experiments were performed with mixture of an organic solvent with equilibriating electrolyte. It can be seen from Figure 2 that increasing quantities of organic solvent results in improved capacity. With about 15 cc. of dioxane/50 cc. of electrolyte, the capacity increases to 1.12 meq./g. from 0.25 meq./g. Solvent seems to swell the binder resulting in increased porosity and thus higher capacity is observed in presence of solvent.

Comparing the properties of membranes containing polystyrene and poly(methyl methacrylate), Wylie[7] has inferred that the more flexible nature of poly(methyl methacrylate) results in poorer electrochemical characteristics. Our results with natural rubber which is more flexible in comparison with poly(methyl methacrylate) seem to confirm the findings of Wylie.[7]

Hale[6] has recently reported that the increase or decrease in interstitial volumes (i.e., porosity) will greatly influence the properties. Since the rate of exchange in these membranes has revealed certain anamolous results, it is intended to extend our studies to Donnan diffusion electrical conductivity and membrane potentials.

References

1. Wilson, J. R., *Demineralisation by Electrodialysis*, Butterworths, London, 1960.
2. Grubb, W. T., *J. Electrochem. Soc.*, **107**, 131 (1960).
3. Solner, K., *Ann. N. Y. Acad. Sci.*, **37**, 177 (1955).
4. Spiegler, K. S., *J. Electrochem. Soc.*, **100**, 303C (1953).
5. Barrer, R. M., and S. D. James, *J. Phys. Chem.*, **54**, 417 (1960).
6. Hale, D. K., and McCauley, *Trans. Faraday Soc.*, **57**, 132 (1961).
7. Wylie, M. R. J., and H. W. Patnode, *J. Phys. Chem.*, **54**, 204 (1960).
8. Juda, et al., *J. Am. Chem. Soc.*, **74**, 3736 (1952).
9. Krishnaswamy, N., *J. Sci. Ind. Res.*, **13B**, 772 (1954).
10. Ramakrishnan, C. S., and N. Krishnaswamy, (to Council of Scientific and Industrial Research), Ind. Pat. 55546 (1955).
11. Krishnaswamy, N., K. P. Govindan, and R. N. Pandya, *Chem. Ind. (London)*, **1957**, 1456.
12. Krishnaswamy, N., and N. P. Suryanarayana, *J. Polymer Sci.*, **B1**, 491 (1963).
13. Kunin, R., *Ion Exchange Resins*, Reinhold, New York, 1958.

Résumé

On étudié expérimentalement la capacité d'échange de membranes de résine CNSL supportée par du caoutchouc. La vitesse d'échange diminue avec l'augmentation de la teneur en caoutchouc de la membrane. La détermination de la capacité d'échange en présence de dioxane montre une interaction bien définie entrella résime et le liant. Ceci a été confirmé en extrayant le liant avec un solvent et ensuite en déterminant la capacité du résidu.

Zusammenfassung

Die Austauschkapazität von CNSL-Harz-Membranen auf Kautschukbasis wurde experimentell untersucht. Die Austauschgeschwindigkeit nimmt mit steigendem Kautschukgehalt der Membran zu. Auf Grund der Bestimmung der Austauschkapazität wurde eine deutliche Wechselwirkung zwischen Harz und Bindemittel festgestellt. Dieser Befund wurde durch Extraction des Bindemittels mit einem Lösungsmittel und darauffolgende Bestimmung der Kapazität des Rückstandes bestätigt.

Received August 29, 1963