

Studies on the Radiation Stability of Ion Exchange Membranes

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Synopsis

This article deals with some aspects of γ -radiation stability of (phenolsulfonic acid, PSA) cation exchange membranes synthesized in the laboratory. The changes in cation exchange capacity, moisture content, coion sorption, concentration potential, area resistance, counterion transference number, and solute flux of the membranes were evaluated before and after irradiation. The membrane samples were irradiated under wet conditions using a ^{60}Co source up to a total dose of 18.65 Mrads. The experimental data point out the possibility of degradation of PSA membranes beyond a dose of 9.78 Mrads, resulting in the loss of functional groups from membrane matrix.

INTRODUCTION

Synthetic semipermeable membranes are used in a variety of industrial applications on commercial scale. A large number of neutral and charged membranes have been developed recently for use in desalination as well as in waste water treatment. The possibility of radioactive separations using membranes has been well recognized.¹ Development of suitable membranes for radioactive separations require adequate knowledge about the stability of various membrane systems in radiation as well as in adverse chemical environments. Though extensive research work has been reported on radiation stability aspects of polymers in general,² information with respect to membrane systems is scarce. We have earlier reported some studies on the radiation stability of cellulosic and noncellulosic neutral polymeric membranes useful in reverse osmosis process.^{3,4}

Recently we have initiated studies on the application of charged membranes useful in electrodialysis process for radioactive separations.⁵ Though ionic membranes are generally described as ion exchange resins in sheet forms, they differ considerably from the latter in certain specific electrochemical properties which are vital for electrochemical applications. The chemical and radiation stability of synthetic organic ion exchange resins are widely reported.^{6,7} These are known to be damaged due to higher radiation doses resulting in loss of exchange capacity, release of water-soluble products, and volume changes.⁸ However, data on the changes in the other physicochemical and electrochemical properties of ion exchange membrane are not widely reported. In this paper, we report some aspects of the γ -radiation stability of cation exchange membranes of phenolsulfonic acid (PSA) synthesized in the laboratory.

EXPERIMENTAL

Cation exchange membranes were synthesized by *in situ* polymerization⁹ of freshly synthesized phenolsulfonic acid and GR grade 39% formaldehyde solution using the procedure described elsewhere.¹⁰ The membrane samples were irradiated in wet conditions using a ⁶⁰Co source having a dose rate of 0.28 Mrad/h. The γ -source was calibrated using a Fricke's dosimeter. The membrane samples were irradiated for various doses up to a total dose of 18.65 Mrad.

The radiation stability of membranes was studied by evaluating changes in cation exchange capacity, moisture content, coion sorption, concentration potential, area resistance, counterion transference number, and solute flux. The cation exchange capacity and coion sorption data were evaluated with respect to hydrogen-sodium exchange and chloride ion sorption using standard methods.¹¹

The moisture content was determined using loss in weight at 105°C. The concentration potential, area resistance, and counterion solute flux were measured using a suitably designed two compartment cell.¹¹ The counterion transference number was computed from the measured concentration potential values using the Nernst equation.

RESULTS AND DISCUSSION

Moisture Content

The % moisture content and counterion solute flux measured for PSA membranes irradiated to different doses are shown in Figure 1. It can be seen from the figure that the % moisture content increases with increase in dose of irradiation beyond 9.78 Mrad dose. The increase in moisture content were found to be around 4%. The variation of moisture content could be apparently

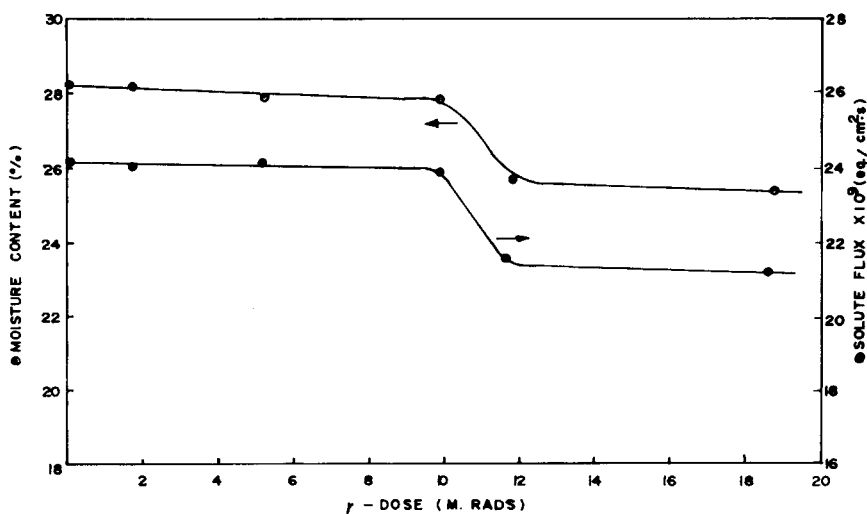


Fig. 1. Effect of γ -radiation on the moisture content and counterion solute flux of PSA membranes.

due to degradation (increase in swelling) or due to crosslinking (decrease in swelling) of the membrane matrix. In the case of PSA membranes the effect noticeable in the dose range studied are mainly degradative, and the increase in swelling of the membrane samples after irradiation is an outcome of the loss of functional groups. In the case of anion exchange resins, it was observed that the water content decreased with radiation dose,¹² which was ascribed to crosslinking. Since ion exchange groups are responsible for water absorption properties of the resins, the effect of radiations to produce swelling or shrinkage seems to be influenced by the nature of the ionic sites present in the polymer. Also it is possible that cleavage of a heavy functional group from the membrane matrix would cause a significant reduction in dry weight of the polymer which also could effect a net increase in swelling.

Solute Flux

The solute flux for PSA membranes measured in terms of equivalents of sodium for various doses of irradiation under identical conditions using 0.025*N* sodium chloride as feed are also shown in Figure 1. It can be seen from the figure that the measured solute flux remain more or less steady up to a dose level of 9.78 Mrad, beyond which the solute flux values tend to decline. The decline in solute flux indicates the possibility of loss in selectivity of the membrane samples due to degradation. It appears that these membranes are more radiation resistant compared to uncharged cellulose acetate (CA) membranes used in reverse osmosis. CA membranes are reported³ to undergo radiolytic degradation, resulting in loss in solute separation and enhanced water transport beyond 500 Krad dose. The observed decline in solute flux data beyond the dose level of 9.78 Mrad is explainable due to the degradation of the membrane polymer, resulting in the loss of exchange capacity. It is to be pointed out that the transport of solute ions through ion exchange membranes under electrical gradient is successive migration through ionogenic groups. Loss of exchangeable groups restrict the transport of solute ions, when all other parameters are kept constant.

The changes in area resistance, counterion exchange capacity and transference number due to irradiation are presented in Table I.

TABLE I
Physicochemical Data of Irradiated PSA Membranes

Sample no.	Dose (Mrad)	Area ^a resistance (Ω cm ²)	Exchange capacity [meq/g (wet)]	Transference number	Acid generation (m)
1	0	41.5	0.48	0.87	6.17×10^{-7}
2	1.69	41.7	0.48	0.87	5.34×10^{-7}
3	5.09	41.4	0.47	0.87	5.95×10^{-7}
4	9.78	41.8	0.47	0.86	5.95×10^{-7}
5	11.76	37.7	0.45	0.81	2.34×10^{-4}
6	18.65	36.4	0.44	0.72	2.95×10^{-4}

^a Measured in 0.1*N* KCl.

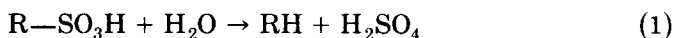
Area Resistance

The area resistance of ion exchange membranes primarily depends on its porosity and charge density as well as on the concentration of the electrolyte solution in which it is in contact. When the resistance is measured under identical conditions, changes in the resistance values before and after irradiation could indicate the possible changes in porosity and charge density of membranes.

It can be seen from Table I that the area resistance decreases at higher doses. The decrease in the area resistance at larger doses supports the degradation of the membrane matrix. The loss in exchange capacity of the membranes resulting from the loss of functional groups cause more open channels for the electrolyte solution to freely pass through.

Counterion Exchange Capacity

The exchange capacity decreases with the dose rate. The decrease in exchange capacity is around 9%. The chemical changes brought out by radiation typical of most synthetic organic ion exchange resins, namely, crosslinking, degradation, gas evolution, changes in degree of unsaturation, and changes in physical and physicochemical parameters, are expected to take place in the case of ion exchange membranes also. When ion exchange membranes are irradiated in wet conditions, the reactions involving the macroradicals of the membrane matrix increases the possibility of degradation. The chances of recombination and crosslinking within the membrane matrix are greatly reduced when irradiation is carried out in presence of water and other degradable support materials. It is reported⁷ that the exchange capacity values of ion exchange resins, derived from the condensation polymerization of phenolsulfonic acid and formaldehyde, decrease to about 3–9% when irradiated to 50–100 Mrad dose. The radiation-induced decomposition of PSA membranes may be occurring mainly due to the following reactions:



This is confirmed by the presence of acid (Table I) in the aqueous medium contacting the membrane during irradiation. This indicates that the major part of the sulfonic acid groups do not undergo the type of simple reaction as indicated in eq. (1) but become inactive through the formation of sulfinic acid groups or sulfone bridges:⁶



Counterion Transference Number

When a concentration gradient is applied across an ideally selective ion exchange membrane, the diffusion of free electrolyte is restricted due to Donnan exclusion of coions and electrical neutrality criteria. If a concentration cell is formed with such a membrane using a set of electrodes which are reversible to the coions, then the measured concentration potential indicates the selectivity of the membrane. The concentration potential and counterion transference number are interrelated by the Nernst equation. The concentration potential and transference number measured before and after irradiation indicate changes in the selectivity properties of the membranes.

It can be seen from Table I that the counterion transference number decrease beyond a dose level of 9.78 Mrad. These indicate the loss of selectivity of the membrane samples brought out as a result of membrane degradation.

CONCLUSIONS

The effect of γ -radiation on the PSA membranes synthesized in the laboratory on the various physicochemical and electrochemical properties was studied up to a total dose of 18.65 Mrad. It was observed that the counterion solute flux, counterion transference number, area resistance, concentration potential, and exchange capacity decrease beyond a dose of 9.78 Mrad. The decrease in the exchange capacity data may be attributed to the decomposition of sulfonic acid functional groups of the membrane samples, which is confirmed by the presence of acid in the contacting aqueous medium. The amount of acid generated is not quantitatively accountable to the loss in functional groups, indicating its subsequent chemical changes, leading to more inactive products.

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References

1. V. Ramachandhran and B. M. Misra, *J. Appl. Polym. Sci.*, **28**, 1641 (1983).
2. A. Chapiro, *Radiation Chemistry of Polymeric Systems*, Wiley (International Edition), New York, 1962.
3. V. Ramachandhran and B. M. Misra, *J. Appl. Polym. Sci.*, **27**, 3427 (1982).
4. V. Ramachandhran and B. M. Misra, *J. Appl. Polym. Sci.*, **30**, 35 (1985).
5. V. Ramachandhran and B. M. Misra, *Sep. Sci. Tech.*, **34**, 35 (1985).
6. E. V. Egorov and P. D. Novikov, *Action of Ionising Radiation on Ion-Exchange Materials*, Israel Program for Scientific Transactions, Jerusalem, 1967.
7. V. A. Nikashina et al., *Int. J. Appl. Radiation Isotopes*, **4**, 201 (1958).
8. L. L. S. Smith and H. J. Groh, USAEC, D.P. 549 (1961).
9. W. R. Sorenson and T. W. Campbell, *Preparative Methods of Polymer Chemistry*, Wiley-Interscience, New York, 1961.
10. N. Lakshminarayaniah, *Transport Phenomena in Membranes*, Academic, New York, 1972.
11. J. N. Weinstein, B. M. Misra, Dorit Kabif, and S. Roy Caplan, *Desalination*, **12**, 1 (1973).
12. R. S. Shetiya, V. K. P. Unny, and D. G. Vartak, *Indian J. Chem.*, **16A**, 24 (1978).

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