Swelling Studies of Perfluorinated Ionomer Membranes

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Synopsis

The swelling behavior of perfluorinated ionomer membranes in various solvents were studied. It was found that the sample pretreatments and the type of the functional group have a strong effect on the swelling properties of these membranes. The swelling of sulfonate membrane is higher than that of the carboxylate membrane. Also, the membrane swelling can be increased by quenching the sample and increasing solvent temperature. Finally, the dissolution properties of this membrane are discussed.

INTRODUCTION

The structure–property relationship of perfluorinated ionomers has been the subject of many recent investigations.[1-9] The microstructure of these polymers and their effects on properties are currently understood only qualitatively. Although there are diverse opinions on the detailed morphology of these polymers, it is generally agreed that microphase separation and ion clusters do exist.

These perfluorinated ionomer membranes have been used in a wide variety of applications,[10] such as industrial electrolytic processes,[11-15] energy conversion and storage processes,[16-18] waste water treatment and metal recovery,[19,20] electrochromic display,[21] catalyst,[22-24] and ion selective electrode.[25]

The perfluorinated ionomer membranes[26] currently used in chloralkali cells contain carboxylate functional groups to lower the rate of hydroxide ion transport. A satisfactory explanation[11,27-32] on the ability of the carboxylate group to provide better hydroxide ion rejection than the sulfonate group has not yet emerged. But, it is generally observed that the membranes with lower water content yield better permselectivity and higher current efficiency. In a recent study, Chandran et al.[11] have correlated the high current efficiency in concentrated caustic solution to the membrane sorption properties. There is a pronounced change of sorption behavior for perfluoro carboxylate membranes in caustic solution of more than $9.0M$, while the sulfonate membrane does not show any significant variation in sorption properties.

Much effort has been directed in recent years to the preparation and characterization of Nafion-coated modified electrodes.[33-35] The preparation of these "polymer electrodes" involves the dissolution of the polymer in appropriate alcohol solvents and the electrodes are dip-coated with the polymer in the solution. The swelling and dissolution properties of perfluorinated ionomer membranes is very different from that of conventional polymers.

While polymer with equivalent weight (EW) less than 1000 dissolves readily in most solvents, materials with EW more than 1000 undergo dissolution only in certain mixed solvents at elevated temperatures and pressure.[36,37]

Several swelling studies on perfluoro sulfonate membranes[38-40] and radiation grafted membranes[39,41] have been reported. Membranes containing sulfonic acid groups display two swelling envelopes. On the other hand, there is no distinct swelling for membranes with carboxylic acid groups, but increased swelling in water has been observed when the membranes are neutralized. In this study, the difference of the swelling properties between the perfluorinated carboxylate and sulfonate membranes was investigated. Also, the effect of polymer pretreatment on the swelling properties was determined.

EXPERIMENTAL

Membrane Samples

Nafion-110, perfluorosulfonic acid membrane,[1,3] was kindly supplied by DuPont. The membranes are derived from copolymers of tetrafluoroethylene (TFE) and a perfluorovinyl ether terminating in a sulfonic acid group and having the structure

$$-(CF_2CF_2)_n-CF_2CF-$$
$$O-CF_2CFOCF_2CF_2SO_3H$$
$$CF_3$$
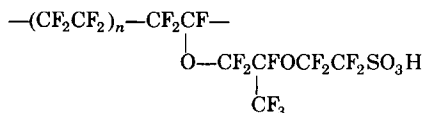
The ion exchange capacity of these membranes is commonly given in terms of the equivalent weight (EW) of the polymer. EW is defined as the weight of polymer which will neutralize one equivalent of base. It is related to the amount of TFE copolymer and is given by: $EW = 100n + 446$. The copolymer of commercial interest fall within the limits of $n = 5-12$.

The perfluorocarboxylic acid membrane[1,8] was prepared from the sulfonic acid membrane ($Nf-SO_3H$) using the method described previously.[8] The membrane was converted into $Nf-SO_2NH_4$ by soaking the sample in 5% NH_4OH. The $Nf-SO_2NH_4$ sample was refluxed with $PCl_5/POCl_3$ for 3 days to obtain sulfonyl chloride form ($NfSO_2Cl$). The membrane was then refluxed with CCl_4 for 19 h and dried under vacuum. The $Nf-SO_2Cl$ membrane was further reacted with HI at 80°C for 5 days to obtain the carboxylic acid form, $Nf-CO_2H$. The sample was then washed with methanol. The sample became translucent after conversion into $Nf-CO_2H$ form.

Nafion-901,[1,11] obtained from DuPont, was also used in this study. It is a composite membrane consisting of both the sulfonic acid and carboxylic acid groups. Nafion-901 was received as K-form.

Degraded Samples

The perfluorosulfonic acid membranes were dried at 170°C,[3] while the other membranes were dried at 120°C, due to the lower thermal stability of the carboxylic acid group. Perfluoro sulfonic acid membranes were darkened when completely dried.[3] Thermal degradation of the membrane begins at ca. 250°C. Significant weight loss was found when the dry samples were further heated

TABLE I
Densities, Molar Volumes, and Solubility Parameters of Solvents

Solvent	Density (g/cm^3)	Molar vol (cm^3/mol)	Solubility parameter $(cal/cm^3)^{1/2}$
Water	1.00	18.	23.4
Formamide	1.134	39.8	19.2
Glycerol	1.2613	73.3	16.5
Ethylene glycol	1.104	55.8	14.6
Methanol	0.7914	40.7	14.5
Ethanol	0.7893	58.5	12.7
1-Propanol	0.8035	75.2	11.9
2-Propanol	0.7855	76.8	11.5
Butanol	0.8098	91.5	11.4
Cyclohexanol	0.9624	106.0	11.4
Amyl alcohol	0.811	109.0	10.9
Decyl alcohol	0.8297	190.8	10.0
2-Ethyl hexanol	0.8328	158.0	9.5
Diethyl amine	0.7056	103.2	8.0
Triethyl amine	0.7275	139.4	7.4

at 260°C for 2 days. The sample became transparent again and the weight loss was found to be 15.5%.

Quenched Samples

The samples were first converted to sodium form. The $Nf-CO_2Na$ and $Nf-SO_3Na$ samples were heated at 315 and 340°C, respectively, for more than 1 h. The lower quenching temperature for the carboxylate sample is due to the lower thermal stability of the material. The sample was then removed from the oven, and cold air was immediately passed over the samples for quenching. The quenched samples were then acidified for uptake measurements. The quenched $Nf-SO_3H$ is tough and soft, while the quenched $Nf-CO_2H$ is brittle.

Uptake Measurements

The method used was similar to those described previously.[38, 39] The samples were immersed in the desired solvent in a plastic container at room temperature for at least 1 day, then removed, blotted dry, and weighed immediately in a closed weighing bottle. The membranes were then replaced in the same solvent and reweighed more than 1 day later to insure that no further solvent uptake had occurred.

The solvents used in this study were high hydrogen bonding solvents and are listed in Table I, along with their solubility parameter values, densities, and molar volumes.

RESULTS

Perfluoro Sulfonate Membranes

The solvent uptake for the perfluoro sulfonate membrane with various types of counterion is plotted against the solubility parameter of solvent in
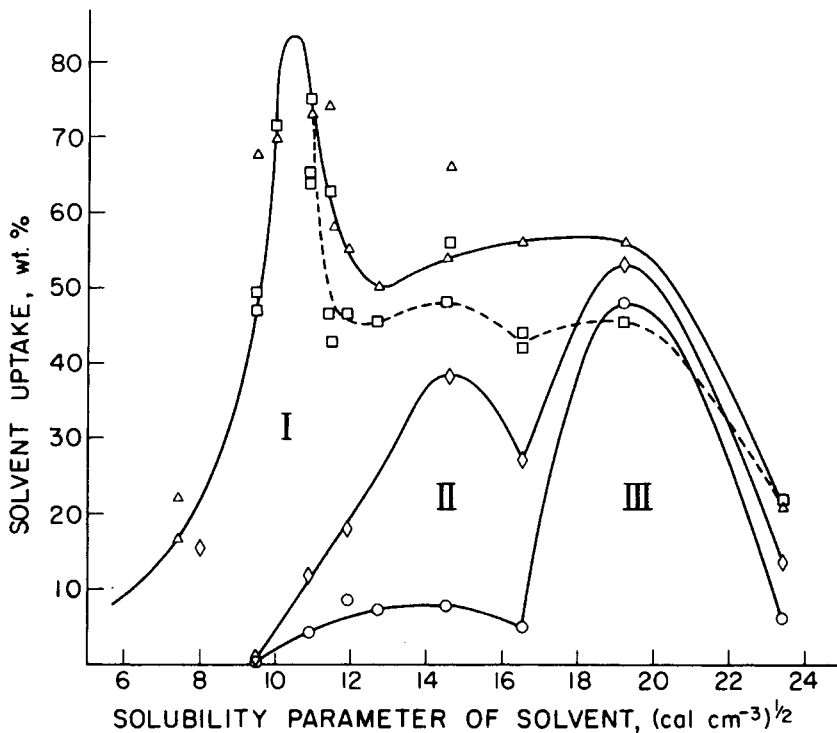
Fig. 1. Solvent uptake of perfluoro sulfonate membrane vs. solubility parameter of solvent: (△) H; (□) Li; (◇) Na; (○) K.

Figure 1. Three swelling envelopes are evident in these plots; they are envelope I, with solvent uptake of ca. 80%, envelope II present as a shoulder or a small peak, and envelope III occurring at ca. 19 Hb. The counterion influences the solvent uptake of the membrane drastically and the amount of solvent uptake decreases in the following sequence $H^+ > Li^+ > Na^+ > K^+$. The counterion effect is more pronounced for envelopes I and II. The swelling envelope I of the Li-form sample resembles that of the H-form material. Envelopes II and III of both the H-form and Li-form samples merges into a broad swelling envelope, as was observed previously.[38,39] It is worth mentioning that the two amine solvents (δ_1 between 7.5 and 8.0 Hb) form salts with the membrane in H-form, as is evident from the color change of the membrane, and would yield a higher uptake value. However, the weight increase due to solvent uptake is higher than that due to neutralization.

Figure 2 shows the solvent uptake of perfluoro sulfonic acid membranes which have been subjected to various thermal pretreatments. The results for the untreated Nafion are also included for comparison.[38] The solvent uptake for most solvents, except the two amine solvents, increases by quenching the sample. On the other hand, the solvent uptake decreases as the sample degraded, especially for solvents within envelopes II and III.

The swelling of the perfluoro sulfonic acid membrane in 40 : 60 water/iso-propanol mixed solvent has been investigated. Figure 3 shows the solvent uptake for quenched and untreated samples as a function of temperature. The
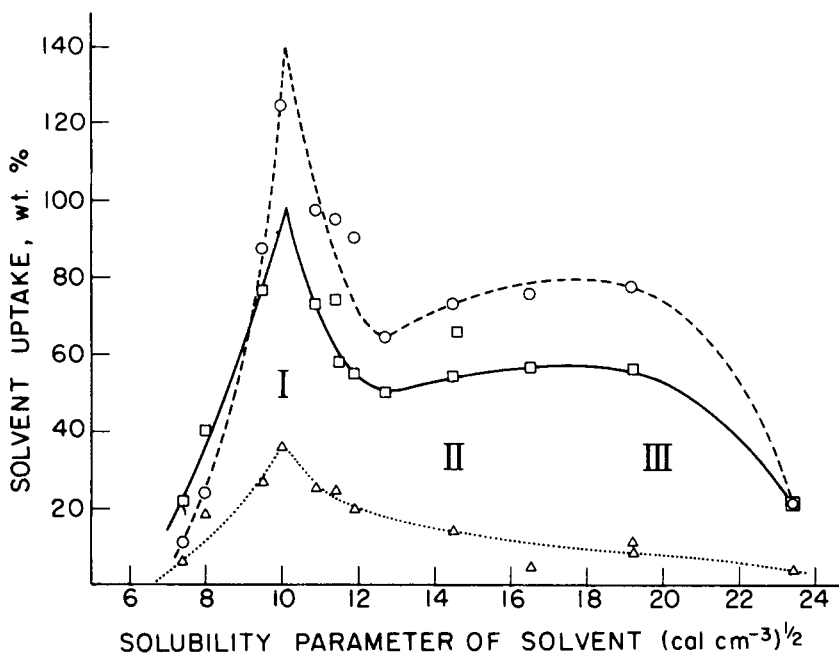
Fig. 2.   Solvent uptake of perfluoro sulfonic acid membrane vs. solubility parameter of solvent: (□) untreated; (○) quenched; (△) degraded.
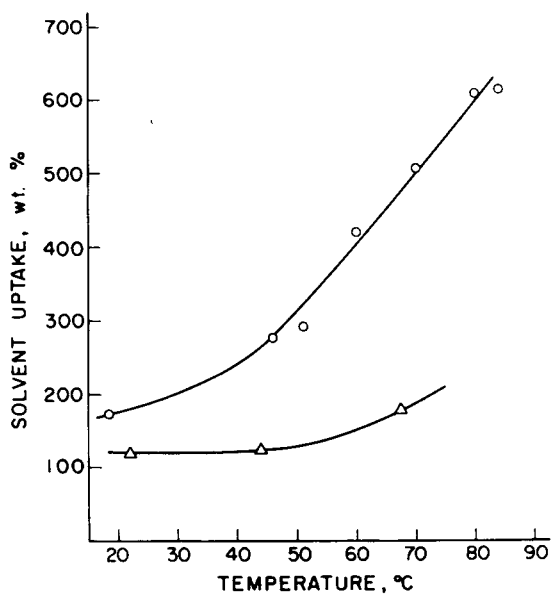
Fig. 3.   Solvent uptake of perfluoro sulfonic acid membrane for isopropanol/water mixed solvent as a function of temperature: (△) untreated; (○) quenched.
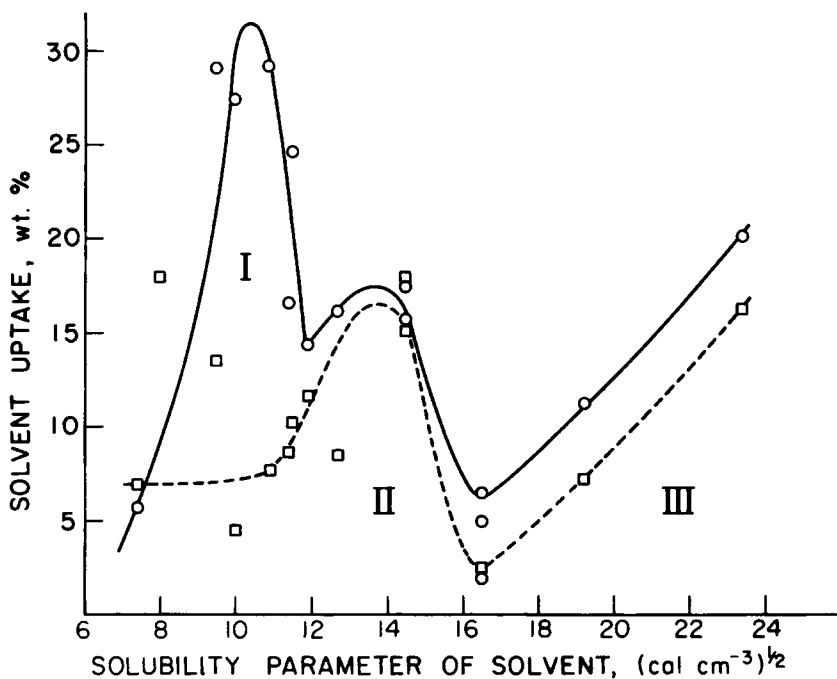
Fig. 4. Solvent uptake of perfluoro carboxylic acid membrane vs. solubility parameter of solvent: (□) untreated; (○) quenched.

solvent uptake of the mixed solvent is also enhanced by quenching the sample. The effect of quenching on membrane swelling becomes stronger at elevated temperatures.

Perfluoro Carboxylate Membranes

Figure 4 represents the sorption behavior of perfluoro carboxylic acid membrane. The solvent uptake for the carboxylic acid membrane is lower than that for the sulfonic acid membrane. The untreated carboxylic acid membrane displays two swelling envelopes, namely, envelopes II and III. In contrast to the sulfonic acid membranes, the water uptake for the carboxylic acid membrane is higher than the formamide uptake. A strong swelling envelope (envelope I) appears by quenching the sample. The quenched sample also shows a higher uptake for solvents with δ_1 higher than 16 Hb.

Figure 5 compares the sorption behavior of perfluoro carboxylate membranes in H-form and K-form. The solvent uptake for most solvents, except formamide, decreases when the membrane is in K-form. The uptake data for solvents with δ_1 less than 10 Hb is rather scattered.

Figure 6 shows the solvent uptake for Nafion-901, which contains both the sulfonate and carboxylate groups. While the swelling envelope III of Nafion-901 resembles that of perfluoro sulfonic acid membrane, the swelling envelope I becomes a broad envelope. Similar to the homogeneous sulfonic acid membrane, the neutralization of Nafion-901 has a strong effect on the swelling envelopes I and II. The solvent uptake of Nafion-901 in K-form is generally higher than that for the homogeneous potassium sulfonate membrane.
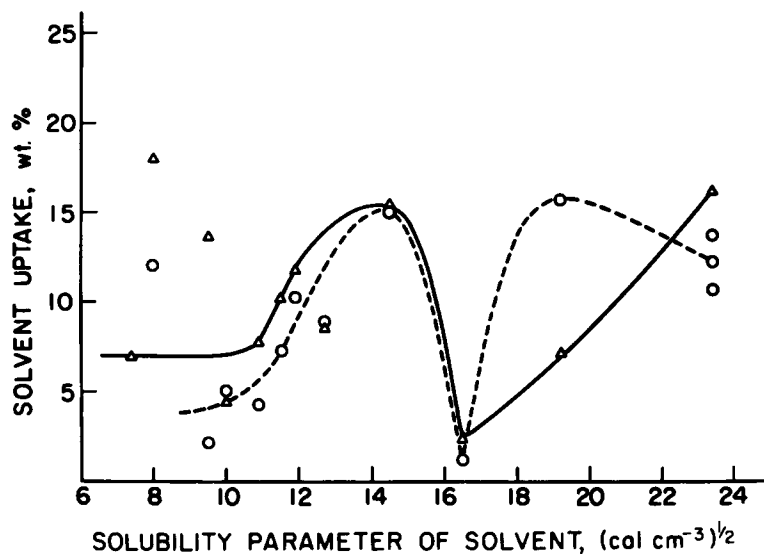
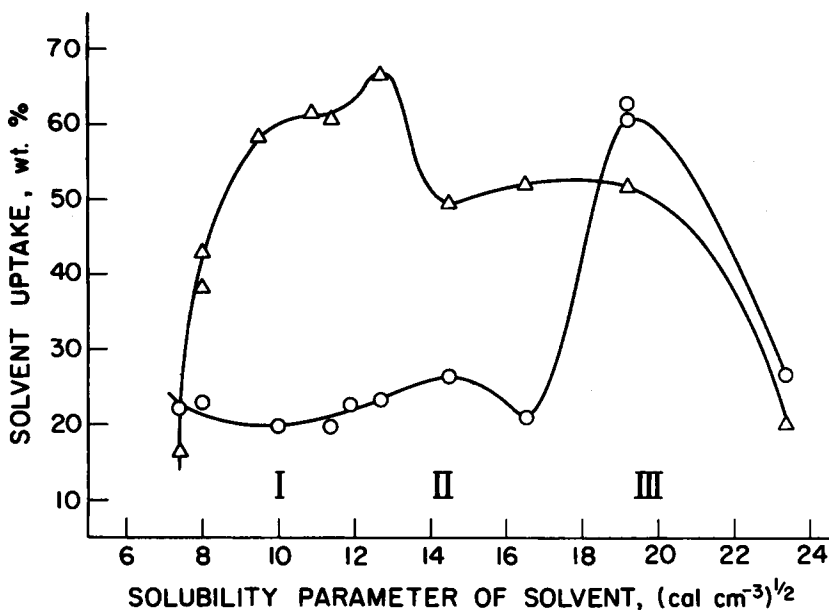Fig. 5. Solvent uptake of perfluoro carboxylate membrane vs. solubility parameter of solvent: (Δ) H; (○) K.

Fig. 6. Solvent uptake of Nafion-901 vs. solubility parameter of solvent: (Δ) H; (○) K.

DISCUSSION

Membrane Swelling and Dissolution

Conventional ion exchange membranes and resins depend on their crosslinkings to prevent swelling and dissolution. These perfluorinated ionomer membranes, with no crosslinking, rely upon their crystalline domains to inhibit the

dissolution.[37,38] The crystalline domains originating from the tetrafluoroethylene material act as crosslinked points. The degree of crystallinity decreases with decreasing EW.[42] Perfluoro sulfonate polymers with EW of less than 1000 are soluble,[37] primarily due to the absence of crystallinity.[42] The degree of crystallinity of a fluorocarbon polymer can generally be reduced by quenching the sample, resulting in enhanced swelling in solvents. The degree of swelling also increases with increasing temperatures. At temperatures higher than 180°C, crystalline domains of these polymers melt down and the polymers are dissolved.[36,37]

The ion exchange groups decompose when the acid samples are heated above 250°C.[3] The loss of the ionic portion leads to the *relatively* increase of the organic material of the polymer, and, in turn, the degree of crystallinity increases accordingly. The decrease of the solvent uptake is likely related to the *relatively* higher crystallinity in the degraded sample. The loss of the ionic groups further decreases the polymer swelling in high δ_1 solvents.

Effect of Ion Exchange Groups

The swelling of the perfluorinated carboxylate membranes is lower than that for the sulfonate membranes. Although the EW for the carboxylic acid membrane is 1200, while that for the sulfonic acid membrane is 1100, the effect of EW on solvent uptake should be small in comparison to that due to the difference in functional groups. The lower acidity of the carboxylic acid group likely accounts for the lower solvent uptake of the carboxylic acid membrane.[32,39]

The swelling envelope I is drastically affected by the quenching of the samples, and the same effect is seen in both the sulfonic acid membrane and carboxylic acid membranes, suggesting envelope I is linked to the crystallinity of the tetrafluoro ethylene material of the membrane. This is consistent with results reported previously.[38,39]

The type of counterion has a pronounced effect on the swelling of the perfluorinated sulfonated membrane. The swelling envelope I gradually disappears as the atomic weight of the counter-ion increased. This result is consistent with the behaviour observed in the radiation grafted membranes containing sulfonate groups.[39] Several explanations for this phenomenon come to mind: The first possibility is that the ionic character of the membranes increases as the atomic weight of the counterion increased. The enhanced ionic character of the materials reduces the uptake of less "ionic" solvents, as dictated by the "like dissolves like" rule. The other possibility is that the degree of crystallinity of the membrane probably increases with increasing atomic weight of the counterion.

The swelling behavior of Nafion-901 resembles that of perfluoro sulfonate material rather than the carboxylate material. It is because the sample contains a thin carboxylate layer, while the bulk of the material is of the sulfonate type.

References

1. R. S. Yeo and H. L. Yeager, in *Modern Aspects of Electrochemistry*, B. E. Conway, J. O'M. Bockris, and R. E. White, Eds., Plenum, New York, 1985, Vol. 16, Chap. 6, 437.

2. A. Eisenberg and E. Besso, in *Membranes and Ionic and Electronic Conducting Polymers*, E. B. Yeager, et al. Eds., Electrochem. Soc., Pennington, NJ, 1983, p. 1.

3. R. S. Yeo and A. Eisenberg, *J. Appl. Polym. Sci.*, **21**, 875 (1977).

4. N. G. Boyle, V. J. McBrierty, and A. Eisenberg, *Macromolecules*, **16**, 80 (1983).

5. W. Y. Hsu, *Macromolecules*, **16**, 745 (1983).

6. H. L. Yeager and A. Steck, *J. Electrochem. Soc.*, **128**, 1880 (1981).

7. E. J. Roche, M. Pineri, and R. Duplessix, *J. Polym. Sci., Polym. Phys. Ed.*, **20**, 107 (1982).

8. M. Fujimura, T. Hashimoto, and H. Kawai, *Macromolecules*, **14**, 1309 (1981).

9. W. Y. Hsu, in *Advances in the Chlor-Alkali and Chlorate Industry*, M. M. Silver and E. M. Spore, Eds., Electrochem. Soc., Pennington, NJ, 1984, p. 35.

10. B. Kipling, in *Perfluorinated Ionomer Membranes*, A. Eisenberg and H. L. Yeager, Eds., Am. Chem. Soc., Washington, DC, 1982, p. 475.

11. R. R. Chandran, R. S. Yeo, and D.-T. Chin, *Electrochim. Acta*, **30**, 1585 (1985).

12. S. Stucki, G. Theis, R. Kotz, H. Davantay, and H. J. Christen, *J. Electrochem. Soc.*, **132**, 367 (1985).

13. R. S. Yeo, J. McBreen, G. Kissel, F. Kulesa, and S. Srinivasan, *J. Appl. Electrochem.*, **10**, 741 (1980).

14. S. C. Stinson, *Chem. Eng. News*, 22 (March 15, 1982).

15. R. S. Yeo, in *Perfluorinated Ionomer Membranes*, A. Eisenberg and H. L. Yeager, Eds., Am. Chem. Soc., Washington, DC, 1982, p. 453.

16. F. G. Will, *J. Electrochem. Soc.*, **126**, 36 (1979).

17. D. G. Oei, *J. Appl. Electrochem.*, **12**, 41 (1982).

18. P. Bratin and M. Tomkiewicz, *J. Electrochem. Soc.*, **129**, 2469 (1982).

19. J. A. Cox and Z. Twardowski, *Anal. Chem.*, **52**, 1503 (1980).

20. P. K. Ng and D. D. Snyder, *J. Membr. Sci.*, **13**, 327 (1983).

21. J. Randin, *J. Electrochem. Soc.*, **129**, 1215 (1982).

22. H. L. Chum, A. K. Hauser, and D. W. Sopher, *J. Electrochem. Soc.*, **130**, 2507 (1983).

23. Z. Ogumi, K. Nishio, and S. Yoshizawa, *Electrochim. Acta*, **26**, 1779 (1981).

24. P. C. Lee, *J. Catalysis*, **70**, 160 (1981).

25. C. R. Martin and H. Freiser, *Anal. Chem.*, **53**, 904 (1981).

26. W. Kramer and D. Bergner, in *Advances in the Chlor-Alkali and Chlorate Industry*, M. M. Silver and E. M. Spore, Eds., Electrochem. Soc., Pennington, NJ, 1984, p. 1.

27. K. A. Mauritz and C. L. Gray, *Macromolecules*, **16**, 1279 (1983).

28. W. Y. Hsu and T. D. Gierke, *J. Membr. Sci.*, **13**, 307 (1983).

29. Z. Twardowski, H. L. Yeager, and B. O'Dell, *J. Electrochem. Soc.*, **129**, 328 (1982).

30. H. Reiss and I. C. Bassignama, *J. Membr. Sci.*, **11**, 219 (1982).

31. M. Suhara and Y. Oda, in *Ion Exchange: Transport and Interfacial Properties*, R. S. Yeo and R. P. Buck, Eds., Electrochem. Soc., Pennington, NJ, 1981, p. 290.

32. K. Kimoto, *J. Electrochem. Soc.*, **130**, 334 (1983).

33. I. Rubinstein and A. J. Bard, *J. Am. Chem. Soc.*, **102**, 6641 (1980).

34. D. A. Buttry and F. C. Anson, *J. Am. Chem. Soc.*, **104**, 4824 (1982).

35. N. E. Prieto and C. R. Martin, *J. Electrochem. Soc.*, **131**, 751 (1984).

36. C. R. Martin, T. A. Rhoades, and J. A. Ferguson, *Anal. Chem.*, **54**, 1641 (1982).

37. W. C. Grot, U.S. Pat. 4,433,082 (1984).

38. R. S. Yeo, *Polymer*, **21**, 432 (1980).

39. R. S. Yeo, S. F. Chan, and J. Lee, *J. Memb. Sci.*, **9**, 273 (1981).

40. G. H. McCain and M. J. Covitch, *J. Electrochem.* **131**, 1350 (1984).

41. M. N. Szentirmay and C. R. Martin, *J. Electrochem. Soc.*, **131**, 1652 (1984).

42. H. W. Starkweather, Jr., *Macromolecules*, **15**, 320 (1982).