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ACIDITY IN NAFION*

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ABSTRACT

Hammett acidity functions have been measured for Nafion films equilibrated with a series of nitroaniline dyes in hydrochloric acid solutions. The effect of ionic strength of alkali metal and tetraalkylammonium bromides on the ability of the Nafion film to donate a proton to Bronsted bases is the reverse of that expected for acid in solution. Absorption of neutral and charged dye is also influenced by the concentration and hydrophobicity of the salt in solution. An interpretation based upon structural spectroscopic studies is discussed.

INTRODUCTION

Although there have been many studies of the effect of solution pH and ionic strength on the characteristics of ion-exchange polymer-coated electrodes [1–4], it has been noted that polymer electrostatic sites have not been studied as acids [5]. The ability of the solvent or acidic group within a polymer to donate protons to a base is crucial to the consideration of acidity and acid catalysis in polymers at electrode surfaces. Also, the Bronsted acidity of the electrostatic binding sites affects the ability of ion-exchange polymers to preferentially incorporate electroactive or cata-

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lytic molecules into their matrix. The focus of this work is the definition of acidity in Nafion as a function of equilibrating solution acidity and ionic strength [6–8].

The Hammett acidity function, H_0 , has been used to define the ability of Nafion polyelectrolyte membranes to donate a proton to an acceptor [9–11]:

$$H_0 = pK_a - \ln [BH + /B]$$

The equilibrium constant and concentration of a series of protonated and unprotonated organic indicator dyes has been measured spectrophotometrically in Nafion membranes. Then, using the Hammett acidity function, the effect of varying equilibrating solution acid, alkali metal ion, and tetraalkylammonium ions on Nafion acidity and dye absorption has been investigated.

EXPERIMENTAL

Materials and Solutions

Organic dyes *p*-nitroaniline (I), *o*-nitroaniline (II), and 4-chloro-2-nitro-*N*-methylaniline (IV) were purified by recrystallization from ethanol (Aldrich). The 4-chloro-2-nitro-aniline (III) was synthesized by the method of Krishnamurthy [12], purified by sublimation, and subsequently characterized by NMR and melting point (106°C). Inorganic salts were used without further purification (Baker). The organic salts tetramethyl and tetraethylammonium bromide (Aldrich) were recrystallized from methanol. HCl (Baker, reagent grade) was titrated with 5 M NaOH standard solution (VWR) by using a phenolphthalein indicator to determine the acid concentration.

Nafion films (Aldrich, 0.018 cm thick) were cut into pieces measuring 1 × 2 cm, were boiled for 30 min in 0.1 M NaOH, and were boiled in two changes of deionized water for an additional 30 min. This procedure hydrated the films and replaced all protons in the commercially prepared film with sodium ions. The treated films were then stored in distilled water until used. The films were handled with plastic tweezers when contacting acid solutions.

Solutions of HCl were prepared with dye at 110% of the final concentration, and salts were added to desired concentrations after dilution. Dye

solutions were heated to dissolve 0.4 mM dye, and acid and dye solutions were then mixed in a ratio of 9 : 1 to 40 μ M dye concentration. A piece of prepared Nafion film was placed in each bottle with 20 mL acid/dye mixture, and it was equilibrated for approximately 12 h with constant stirring.

Instrumentation and Measurements

Spectrophotometric measurements were made by using an HP8452 spectrophotometer with an HPIB interface to an IBM-PC. Successive measurements from 200–600 nm were made at 25°C to ± 0.0016 absorbance units. Spectra were taken in a cell consisting of two matched quartz spectrophotometric cells that were connected by a bridge to allow for equilibration of solutions from either side. The cells measured $1 \times 1 \times 4$ cm, so that the cut pieces of Nafion fit into the bottom of the cells in such a way that the path of the light passed through them. Spectra were taken of each side of the cells, one with solution only and one with solution plus the film contained in the cell. Cell measurements containing Nafion film were accurate to approximately 0.006 absorbance units. Nafion films were not necessarily identical, and light scattering effects differ from film to film. However, these differences in baseline due to scattering were small compared to the absorbance of the dye.

Absorption coefficients for the protonated and unprotonated species were determined by measuring a known concentration of dye in neutral water and in 6.0 M acid solution. Shifts in absorption maxima due to changes in medium were small (= 5 nm). Data analysis was performed by subtracting the absorption of each side of the cell at the wavelength of interest, so that the absorption due to the film could be determined. This treatment assumes that the path length of the film is negligible as compared to the path length of the cell. It was also assumed that changes in the film path length due to swelling changes in the film with ionic strength or acidity are small.

Concentrations were determined by solving a system of simultaneous equations with two unknowns. The path length was 1 cm for the solution side of the cell and was measured at 0.018 cm for Nafion. (The thickness of Nafion film is determined by Du Pont Corporation.) The temperature dependence of the ratio of protonated to unprotonated dye in solution was negligible. Changes in concentration of the dye due to addition of salt were less than 5% for alkali metal halides and less than 10% for tetraalkylammonium ions [13].

RESULTS

Choice of Indicators

The accuracy of the Hammett acidity function depends upon the choice of a series of indicator dyes that will result in a well-behaved function over the acid concentration range of interest [14]. The suitability of a series of nitroaniline dyes for determination of an acidity function in Nafion has two criteria: the sigmoid test and the determination of successive pK_a 's.

The ratio of protonated to unprotonated dye in solution was a sigmoid function of acid concentration around the pK_a of the indicator. Nafion films that have been equilibrated in solution show the same sigmoid relation of the ionization ratio, where ionization occurs over less than 2.5 pH units. The response of the indicator dye to changes in hydrogen ion concentration within the film was found to be comparable to that in solution and was consistent for the chosen dyes. H_0 as a function of the absorbance coefficient has shown the same sigmoid relationship, and changes in absorbance were proportional to changes in film acid concentration.

The dyes chosen for the Hammett indicator series must all respond to film acidity in the same way, and this parallel response has been found to be necessary for determination of the pK_a of indicator dyes in concentrated acid solutions. Successive determinations of an effective pK_a in the film demonstrated parallel behavior in the overlapping ranges of acid concentration. The first pK_a of the series, the strong base *p*-nitroaniline, was graphically extrapolated to its value at zero acid concentration in Nafion. The linear extrapolation of *p*-nitroaniline to zero acid concentration assumes the minimization of interactions between dye molecules and that activity coefficients of the dye in the film are close to 1. Semilog plots of the ionization ratio versus the acid concentration in solution showed parallel behavior for dye in both the solution and film, and the difference between the successive lines on the plot allowed for the determination of the value for each successive pK_a . Because of the choice of neutral aniline bases, the H_0 scale of acidity is the proper one for experimental purposes.

Acidity in Nafion

The extent of ionization of an indicator dye in Nafion can be represented by the Hammett acidity function. The Hammett acidity function

for the solution versus the film at 50 mM NaCl and zero to 5.0 M HCl allowed the determination of the partitioning of protons between the solution and the film (Fig. 1). In the film, acidity at 50 mM NaCl is high at low acid concentration, and it increased slowly with solution acid concentration. As the acid concentration continued to increase, the film acidity leveled off to a relatively constant value. In contrast, solution values of H_0 increased slowly as acid concentration was increased. At dilute acid and salt concentrations (0.1 M), the difference between the solution and film acidity functions was approximately 2.5 H_0 units. The values of H_0 for the solution and the film converge at about 4.5 M HCl. The solution acidity function then increased more rapidly than Nafion at concentrations of solution acid greater than 4.5 M.

Effect of Salt

To examine the effect of salt on Nafion acidity, the change of the ratio of protonated to unprotonated dye as a function of salt concentration in equilibrating solution was examined. The change in ratio reflects the

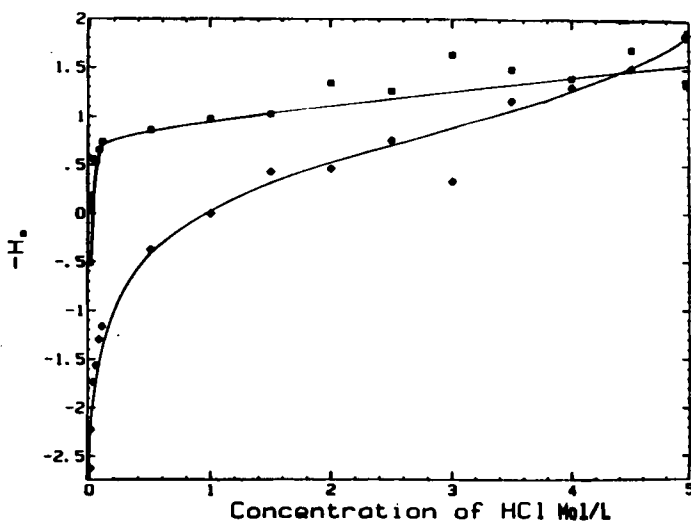


FIG. 1. The Hammett acidity function H_0 has been determined from zero to 5 M HCl for both solution (◆) and Nafion (■) in the presence of 50 mM NaCl.

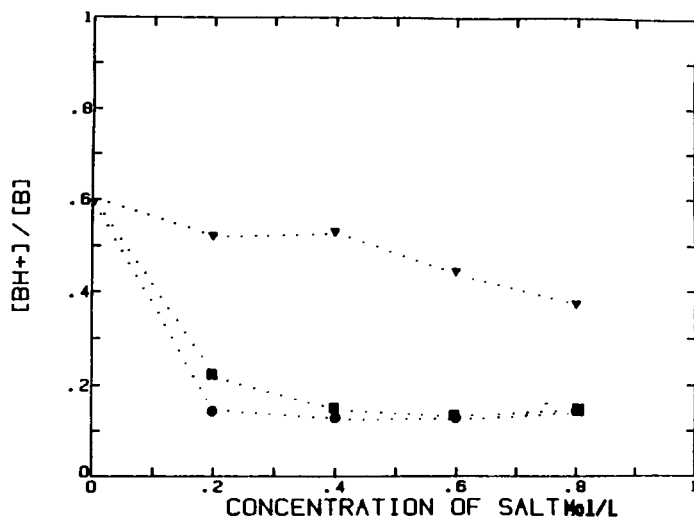


FIG. 2. The ionization ratio of 4-chloro-2-nitro-*N*-methyl aniline is plotted as a function of alkali metal bromide. Sodium (▼), potassium (■), and cesium (●) ion concentration ranges from 0 to 1.0 *M* in the presence of 0.5 *M* HCl.

effect of salt on the Hammett acidity function in Nafion. Alkali metal bromides (Fig. 2) caused an effective decrease in acidity in Nafion. Tetraalkylammonium ions produced the same decrease in acidity initially, but further addition of cations increased acidity again. This increase is observed as the tetraalkylammonium salt concentration was increased above 0.2 *M* (Fig. 3). The effect of salt in Nafion established a clear order in its influence on the ionization ratio. Alkali metal ions were generally found to decrease the ionization ratio in Nafion in the order $\text{Na} < \text{K} < \text{Cs}$. For hydrophobic cations, tetraethylammonium cation had a greater effect on the film ionization ratio than tetramethylammonium cation.

An effect of salt on the ionization ratio is to change the concentration of protonated and unprotonated dye species in the film and to change the total absorbed dye. 4-Chloro-2-nitro-aniline has been used to illustrate the effects of Nafion acidity and ionic strength on the ionization ratio and dye absorption. The protonated dye was displaced by both alkali metal and tetraalkylammonium ions for all dyes (Fig. 4). The unprotonated base was reduced by tetraalkylammonium ions (Fig. 5), while alkali metal ions increased the concentration of unprotonated dye in the film.

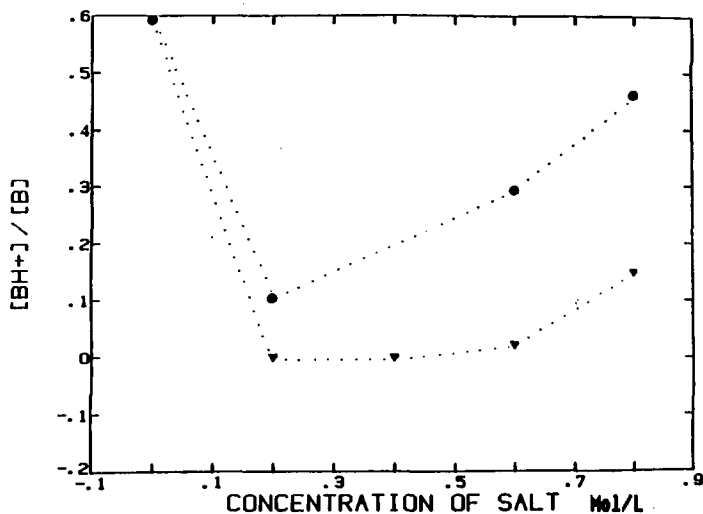


FIG. 3. The ionization ratio of 4-chloro-2-nitro-*N*-methyl aniline is plotted versus the concentration of alkylammonium bromide. Tetramethylammonium (●) and tetraethylammonium (▼) bromide concentrations vary from 0 to 0.8 *M* salt with a constant concentration of 0.5 *M* HCl.

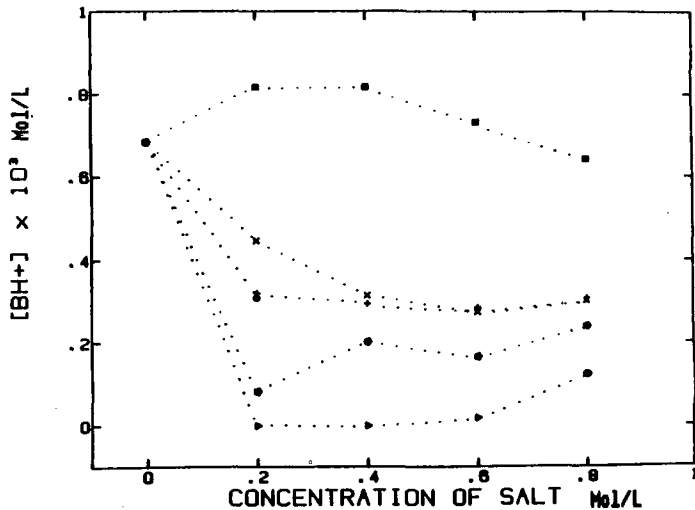


FIG. 4. The ionization ratio of a Hammett dye was plotted as a function of increasing concentration of bromide salts. Sodium (■), potassium (×), cesium (+), tetramethylammonium (●), and tetraethylammonium (▼) bromide concentrations range from 0 to 0.8 *M* with a constant concentration of 0.5 *M* HCl.

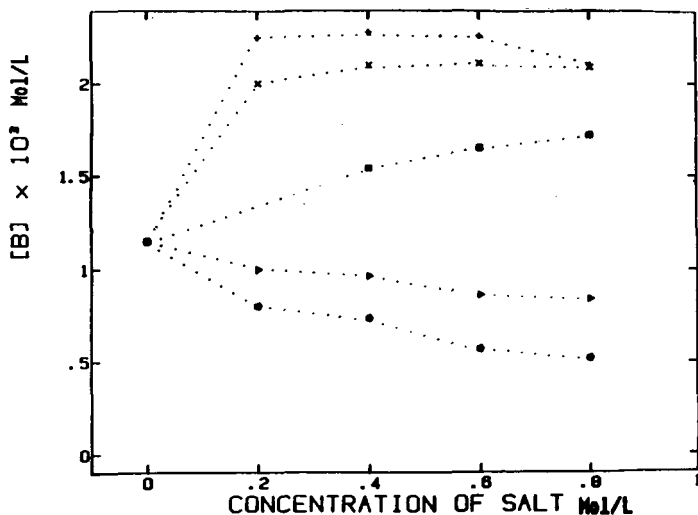


FIG. 5. The concentration of unprotonated 4-chloro-2-nitro-*N*-methylaniline is plotted as a function of bromide salt concentration (0–0.8 *M* salt in 0.5 *M* HCl). The alkali metal bromides sodium (+), potassium (×), and cesium (■); and tetraalkylammonium bromides tetramethylammonium (▼) and tetraethylammonium (○) bromide were utilized.

Total dye concentration in the film was decreased for all cations as salt concentration in solution increased (Fig. 6). Alkali metal ions displaced protonated dye to a greater extent than neutral dye. Tetraalkylammonium ions displaced both protonated and unprotonated dye, and a larger fraction of total dye was displaced from the film (Fig. 7).

The majority of the effects of salt on acidity and concentration of dye in the film occurred over a concentration ranging from zero to 0.2 *M* for alkali metal ions. Increases in alkali metal salt concentration greater than 0.2 *M* did not lead to a continuation in the trend established in more dilute solution. Instead, the dye ionization ratios tended to remain at a constant value. Tetraalkylammonium ions behave in the same way up to 0.2 *M* as alkali metal ions by displacing dye from the film, but the acidity did not show signs of leveling off as the concentration of salt increased.

Large variations or irreproducibility in acidity occurred when examining the effect of salt using chloride ions, and for this reason bromide salts were chosen. Similar effects also occurred at 0.5 to 1.0 *M* chloride ion in 0.5 *M* HCl and at higher concentrations of bromide ion (>1.5 *M*).

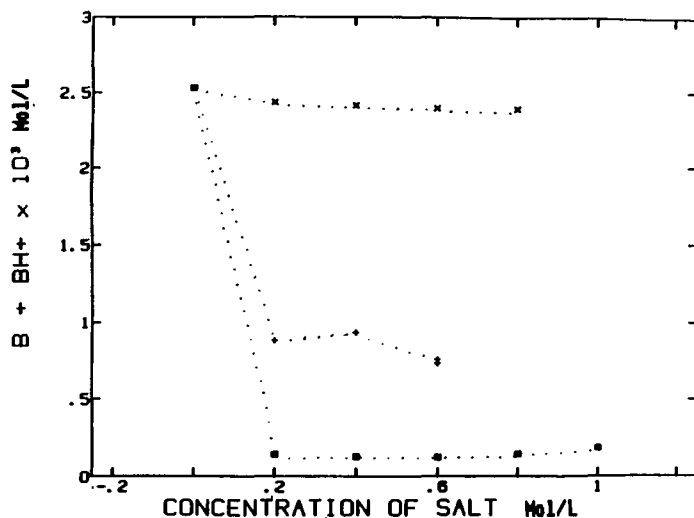


FIG. 6. Total dye absorbed into the Nafion film is represented as a function of salt concentration. Sodium (\times), potassium ($+$), and cesium (\blacksquare) alkali metal bromide concentrations vary between 0 and 0.8 M , while acid concentration is held constant at 0.5 M HCl.

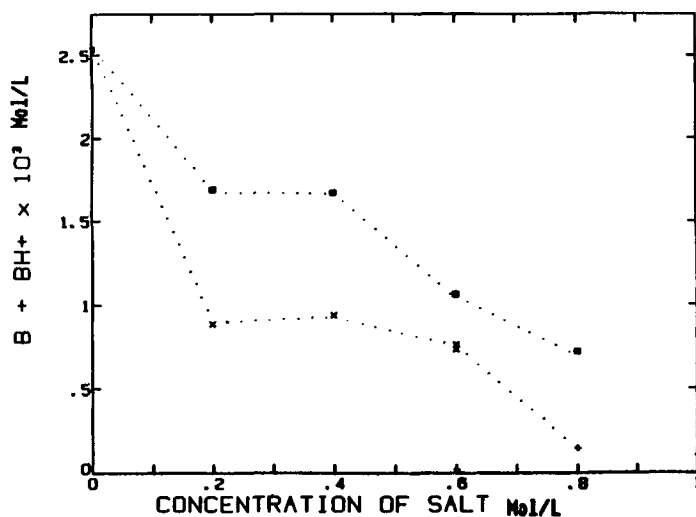


FIG. 7. Total dye absorbed into the Nafion film is plotted as a function of salt concentration. Tetramethylammonium (\blacksquare) and tetraethylammonium (\times) bromide is varied between 0 and 0.8 M , while acid is held constant at 0.5 M HCl.

Ammonium ion also showed large variations and irreproducibility from sample to sample, but did behave similarly to alkali metal ions. These variations are attributed to a loss of permselectivity in Nafion.

DISCUSSION

A proposed structure of Nafion membranes has emerged based upon spectroscopic studies of varying acid and salt forms of the membrane which can be used as a basis for interpretation of data [15, 16]. The membrane separates into both crystalline polymer regions and aqueous clusters, i.e., water-swollen domains, which contain the sulfonate side chains and counterions. The size of the clusters is dependent upon the extent of hydration of the membrane which is related to the counterion incorporated into the film. The concentration and type of salt in the outside solution also affects hydration of the film, as water molecules will be taken up from solution to solvate ions. Although cluster size is in the 2–4 nm range, hydrogen bonding of water is disordered as compared to bulk solution. In addition, absorption of organic compounds and ions to the fluorocarbon backbone is strong [17, 18]. The membrane structure of Nafion allows for the exclusion of approximately 15 *M* or greater sodium hydroxide in industrial chloralkali applications.

The comparison of the value of H_0 in solution with that of Nafion at 10 mM NaCl and increasing HCl concentration begins to illustrate some of the characteristics of the membrane suggested by spectroscopic studies. The concentration of sulfonates in the bulk film has been estimated at approximately 1.4 *M* (calculated from the equivalent weight and void volume), and the sulfonates must have a much higher local concentration due to clustering. Nafion is consistently more acidic than acid solution up to 4.5 *M* solution HCl, and the acidity does not vary greatly between 0.2 and 4.5 *M*. As solution HCl concentration is increased to 0.2 *M*, protons displace all other cations in the Nafion membrane, and a further increase in proton concentration does not change the value of H_0 greatly. Beyond a concentration of 4.5 *M* HCl, however, the solution becomes more acidic than that of the film. This suggests that the concentration of coions in the film (additional negative charges) is still low at 5–6 *M* solution HCl, and no additional protons can enter the membrane since charge neutrality is preserved. Dehydration effects due to the high ionic strength of the equilibrating solution may account for any small increases in film acidity between 0.2 and 4.5 *M* HCl. An additional contribution to the high

acidity in the film clusters is due to alteration of solvent structure from water-fluorocarbon interactions.

The effects of salt on acidity in Nafion can be accounted for in several ways. First, protons are displaced by the increasing concentration of alkali metal ions in solution that equilibrate with the film in order to preserve charge neutrality. Although decreased hydration of the film and altered cluster size are a result of the hydration of each ion, the effects of differing hydration are not as strong as the maintenance of charge neutrality and the partition coefficient. The effect of addition of tetraalkylammonium ions on Nafion acidity, however, is not the same as that of the alkali metal ions. Protons are displaced from the film sulfonate sites by cations at low concentration (0.2 *M*), and there are fewer protons in the film to donate to the indicator dye. As the concentration of the tetraalkylammonium salt is increased above 0.2 *M*, the ionization ratio of the film begins to increase again toward the initial high ionization ratio value at zero salt concentration. In this case the alteration of the clusters due to the effect of absorption of the hydrophobic ammonium cation may alter the structure of water inside the cluster, allowing the solution to more easily donate a proton to the dye. Cluster size may also be affected, altering the effective concentration of sulfonates within the cluster. Interestingly enough, both of these salt effects are macroscopically the opposite of a solution salt effect. In the latter, water molecules participate in solvation of ions which allows protons to be more easily donated to an indicator dye molecule.

Dye concentration in Nafion also changes as solution salt concentration is varied. Positively charged dye is expelled in preference to cation incorporation into the film for both the alkali metal and tetraalkylammonium cations, and uncharged dye increases due to expulsion of protons and the resulting shift in pH. Continued addition of tetraalkylammonium ions also expels uncharged dye, in contrast to the increase in uncharged dye in the presence of alkali halide ions. Interaction of the organic ligands of the salt may alter hydration, cluster size, and water structure such that the number of sites for absorption are altered or decreased for neutral dye sorption.

Nafion-H, the protonated form of the polymer, has been utilized as a solid substrate in organic synthesis as a superacid catalyst [19, 20]. Additional research [21] examined the effect of nonaqueous solvents upon the acidity of Nafion beads by using Hammett dyes. These results clarify the effect of experimental conditions upon the ability of the polymer to act as an acid catalyst.

SUMMARY

The experimental results give a glimpse of the complexity of the effects of various equilibria on the acidity of Nafion films equilibrated in acidic solutions. Acidity in Nafion at low salt concentration is much greater than that of its equilibrating solution due to the unique properties of Nafion's cluster morphology. The addition of alkali metal cations to solution decreases Nafion acidity through displacement, and tetraalkylammonium cations exhibit a more complex alteration of acidity as their concentration increases. Finally, the sorption sites of neutral dye are affected by changes in ionic species and strength of the equilibrating solution.

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REFERENCES

- [1] N. Oyama, T. Shimomura, K. Shigehara, and F. C. Anson, *J. Electroanal. Chem.*, **112**, 271 (1980).
- [2] Y. Tsou and F. C. Anson, *J. Electroanal. Chem.*, **131**, 595 (1984).
- [3] Z. Twardowski, H. L. Yeager, and B. O'Dell, *J. Electrochem. Soc.*, **129**(2), 328 (1982).
- [4] D. J. Harrison, K. A. Daube, and M. S. Wrighton, *Ibid.*, **163**, 93 (1984).
- [5] R. W. Murray, A. G. Ewing, and R. A. Durst, *Anal. Chem.*, **59**(5), 379A (1987).
- [6] S. J. Sondheimer, N. J. Bunce, and C. A. Fyfe, *Rev. Macromol. Chem. Phys.*, **C26**(3), 353 (1986).
- [7] W. T. Ford (Ed.), *Polymers, Reagents, and Catalysis*, (ACS Symp. Ser. 308), American Chemical Society, Washington, D.C., 1986.
- [8] F. J. Waller, *Catal. Rev. - Sci. Eng.*, **28**, 1 (1986).
- [9] L. P. Hammett, *Physical Organic Chemistry; Reaction Rates, Equilibria, and Mechanisms*, 2nd ed., McGraw-Hill, New York, 1970, Chap. 9.
- [10] M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957).

- [11] F. A. Long and W. F. McDevitt, *Ibid.*, 57, 119 (1957).
- [12] S. Krishnamurthy, *Tetrahedron Lett.*, 23, 3315 (1982).
- [13] B. E. Conway, *Ionic Hydration in Biochemistry and Biophysics*, Elsevier, New York, 1981, Chaps. 16, 17, 29, 31.
- [14] C. H. Rochester, *Acidity Functions*, Academic, London, Chaps. 1, 2.
- [15] A. Eisenberg and H. S. Yeager (eds.), *Perfluorinated Ionomer Membranes* (ACS Symp. Ser. 180), American Chemical Society, Washington, D.C., 1982. These spectroscopic methods include low and wide angle scattering, infrared spectroscopy, NMR, etc. to characterize the physical structure of the polymer, and the chemical environment of the polymer backbone, charged sulfonates, sorbed water, and cations.
- [16] S. P. Rowland (ed.), *Water in Polymers* (ACS Symp. Ser. 127), American Chemical Society, Washington, D.C., 1980.
- [17] C. R. Martin and K. A. Dollard, *J. Electroanal. Chem. Interfacial Electrochem.*, 159(1), 127-135 (1983).
- [18] P. C. Lee and D. Meisel, *J. Am. Chem. Soc.*, 102, 5477 (1980).
- [19] G. A. Olah, P. S. Dyer, and G. K. S. Prakash, *Synthesis*, 7, 513-531 (1980).
- [20] S. J. Sondheimer, N. J. Bunce, and C. A. Fyfe, *J. Macromol. Sci—Rev. Macromol. Chem. Phys.*, C26(3), 353-413 (1986).
- [21] S. J. Sondheimer, N. J. Bunce, M. E. Lambe, and C. A. Fyfe, *Macromolecules*, 19(2), 339-343 (1986).

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