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DEVELOPMENT OF ANION-SELECTIVE MEMBRANES

by

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Southern Research Institute
2000 Ninth Avenue, South
Birmingham, Alabama 35205

Prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

NASA Lewis Research Center
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16. Abstract

Studies were made of methods of preparing anion-exchange membranes that would have low resistance, high selectivity, and physical and chemical stability when used in acidic media in a redox energy-storage system being developed by NASA. Of the twelve systems selected for study, only the system that was based on crosslinked poly-4-vinylpyridinium chloride produced physically strong membranes when equilibrated in 1 M HCl. The resistivity of the best membrane was 12 ohm-cm, and the transference number for chloride ions was 0.81.

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FOREWORD

This document constitutes the final report for the work accomplished between 19 June 1974 and 18 June 1975 by Southern Research Institute for the National Aeronautics and Space Aministration, Lewis Research Center, under Contract NAS3-18898, on Development of Anion-Selective Membranes. Dr. Richard W. Lauver of NASA Materials and Structures Division served as Project Manager.

The work at Southern Research Institute was performed under the technical direction of Mr. Robert E. Lacey, Senior Chemical Engineer, and Dr. Donald R. Cowsar, Head, Biomaterials Section.

Dr. Thomas St. Pierre, Adjunct Research Advisor; Dr. O. Reed Tarwater, Senior Chemist; Mr. Hollis Hill, Assistant Chemist; and Mrs. Rita D. Wingo, Assistant Chemist, aided in planning and performing the research. Mr. W. E. Richardson, Assistant Biologist; Mr. R. Eugene Godwin, Engineering Technician; and Mr. Ray Thornton, Chemical Technician, assisted in some of the experiments.

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DEVELOPMENT OF ANION-SELECTIVE MEMBRANES

I. SUMMARY

The objective of this study was to develop anion-exchange membranes with low values of resistivity, high values of selectivity, and acceptable physical strength and chemical stability when exposed for long periods to acidic media in which oxidation and reduction reactions occur alternately. Such membranes are needed for use in a redox energy-storage system being developed by NASA.

Twelve membrane systems were selected for study on the basis of theory. Seven of the systems were based on polyamines (e.g., polyethyleneimine and poly-4-vinylpyridine) crosslinked by alkylation with dihaloalkanes. The crosslinking reaction also formed charged moieties to impart ion-exchange characteristics. Four of the systems were based on copolymerization of amine-containing and divinyl-type monomers with free-radical catalysts followed by alkylation of the amine groups by monohaloalkanes. The twelfth system was based on polymers that contained alkyl halogen atoms which were crosslinked by reaction with diamines.

Experimental membranes were prepared from three of the polyamine systems by a method that involved mixing the dihaloalkane crosslinking agent into a solution containing 50% by weight of the polyamine, pouring the reaction mixture into a membrane mold, and heating the mold to crosslink the polymer. The type of dihaloalkane, the molar ratio of dihaloalkane to polymer repeating unit, and the curing conditions were all varied in a systematic manner in unsuccessful attempts to prepare membranes with acceptable physical properties. Similar extensive studies were also performed with two of the four copolymer systems, but membranes with acceptable mechanical properties were not produced.

During the latter part of the program our studies were directed entirely toward the development of methods for preparation of membranes with improved physical strength. These studies resulted in a method for preparing membranes in which polyamines were first partially alkylated by reaction with only one of the two halogen atoms on dihaloalkane molecules. The modified polyamines from this reaction were separated from the solvent used in the first reaction, and were then dissolved in water to form the most concentrated solution possible without gelation occurring in the reaction flask. The resulting viscous syrup was poured into membrane molds, and the molds were heated to crosslink the polymer and form a solid membrane. Only one set of experimental membranes with acceptable physical strength could be prepared before the time and funds in the contract were exhausted. This membrane was based on poly-4-vinylpyridine. The resistivity was 12 ohm-cm and the transference number for chloride ions

was 0.81 for membranes equilibrated in 1 M HCl. With further development this membrane could be of great utility for many purposes, but with a transport number of only 0.81 in acidic media, the membrane cannot be recommended for use in the energy-storage cells being developed by NASA.

II. INTRODUCTION

Southern Research Institute has carried out a 12-month research program to develop anion-exchange membranes suitable for use in a new redox energy-storage system being developed by the National Aeronautics and Space Administration (NASA). The main objective of the research program was the preparation and evaluation of membranes having low values of resistivity, high values of selectivity, and good physical and chemical stability during service for 10,000 hours at temperatures to 80°C.

Economic factors in the electric utility industry have led to a search for means of storing energy for use in meeting peak loads. Methods of storage that involve the storage of water, which is pumped during off-peak periods, have been in use for some time. Since limited plant sites are suitable for pumped-water storage systems because of topographical or other reasons, a number of other energy-storage systems are being considered or studied. The redox battery system being developed by NASA is one such system.

Prior reports (ref. 1, 2) have discussed the concept of the NASA redox system, its economic potential, and some of the problems that require research. One of the major problems is the development of improved membranes. The concept of the redox flow cell, and the necessary features of membranes for use in the flow cell are discussed below.

The simplest form of the flow cell and auxiliary equipment is illustrated schematically in Figure 1. In addition to the flow cells, two storage tanks and two pumps are needed. (Only one flow cell is shown, but many would be used). Each flow cell consists of two solution compartments. Each compartment is provided with solution inlets and outlets, and contains an inert electrode. The two solution compartments are separated by a membrane that prevents ions from the redox couple that flows through the cathode compartment from mixing with the redox couple that flows through the anode compartment.

A redox couple that is primarily in its reduced state is circulated through the anode compartment; a different redox couple that is primarily in its oxidized state is circulated through the cathode compartment. If an electrical load is connected to the electrodes, electrochemical reactions take place in which the couple flowing through the anode compartment changes from its reduced state to its oxidized state by loss of electrons from cationic species to the electrode. A similar, but opposite, electrochemical reaction occurs in the cathode compartment in which the cationic species gains electrons and the cationic redox couple goes from its oxidized to its reduced state.

The entire system can be recharged by removing the electrical load and connecting a voltage source to the electrodes. The solution flowing through the cathode compartment is reoxidized; the one

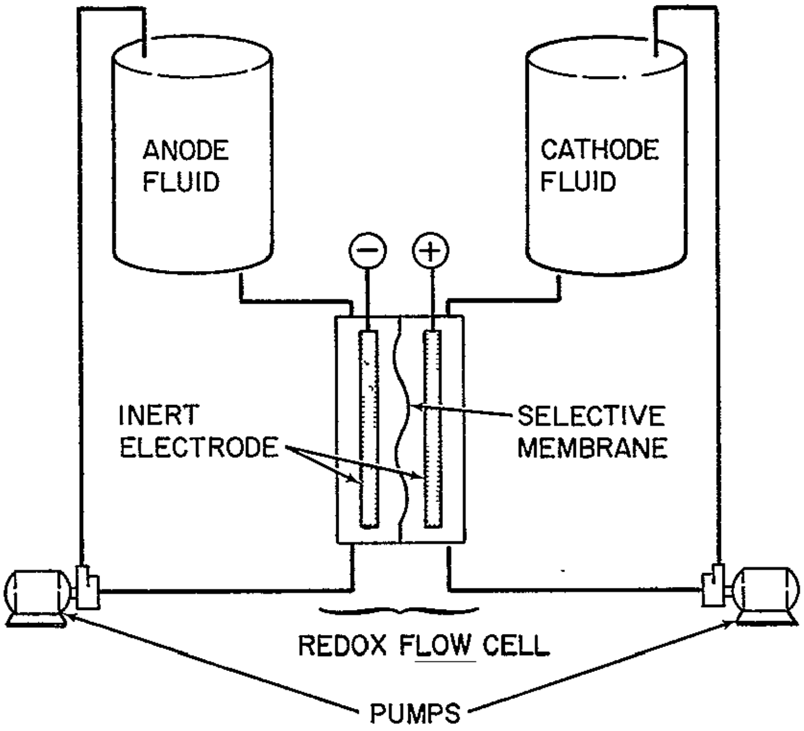

Figure 1. Representation of a System for Energy Storage with Rechargeable Redox Flow Cells

flowing through the anode compartment is reduced.

Membranes for use in the flow cells must provide an impermeable barrier to solution flow from one compartment to the other and provide a barrier to the electrolytic transfer of both cationic redox species in both states of charge. The membranes must also provide a means of transferring anions so that electrical neutrality can be provided for both solutions as the cell is charged and discharged. The above requirements indicate anion-exchange membranes should be used.

It is desirable that the anion-exchange membranes have as high a selectivity and as low a resistivity as possible. With ideally high selectivity, the anodic redox couple cannot transfer to the cathode compartment and *vice versa*, and the energy capacity of the cell remains constant. With low membrane resistivity the internal resistance of the cell is low. The membranes must also have adequate physical strength and acceptable durability when exposed to the alternate cycles of oxidative and reductive reactions that occur and to the acidic solutions that are used to ensure solubility of the redox couples.

III. EXPERIMENTAL

Twelve membrane systems were selected for study on the basis of theoretical considerations of the relationships among polymer structure and membrane resistivity, selectivity, physical strength, and chemical stability. The more important aspects of the theoretical analysis are given in the Appendix.

A. Materials

Materials used to prepare membranes from polyamines include polymers and dihaloalkanes obtained from the sources given below:

- Polymers:
  - polyethyleneimine(grades PEI-6, PEI-18, and PEI-100) were obtained from the Dow Chemical Company*
  - poly-2-vinylpyridine and poly-4-vinylpyridine (no designated grade or molecular weight) were obtained from Polysciences, Inc.*
  - poly-p-aminostyrene (no designated grade) was obtained from Polysciences, Inc.*

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* See page 7

Dihaloalkanes:

- 1,2-dibromoethane, 1,3-dibromopropane; 1,4-dibromobutane, and 1,10-dibromodecane were obtained from Eastman Organic Chemicals*

Materials used to prepare membranes by copolymerization include monomers and catalysts obtained from the sources listed below:

Monomers:

- 2-vinylpyridine and 4-vinylpyridine were obtained from Polysciences, Inc.*

- divinylbenzene (50% active) was obtained from Polysciences, Inc.*

Catalysts:

- azobisisobutyronitrile (AIBN) was obtained from Eastman Organic Chemicals*

- benzoyl peroxide was obtained from the Fisher Scientific Company*

The prepolymers used in Membrane Systems VII, VIII, IX, and X were synthesized from the materials listed below.

- acrylyl chloride (used to prepare polyvinylamine for System VII and the vinylamine for System VIII) was obtained from Polysciences, Inc.*

- sodium azide (used for Systems VII, VIII) was obtained from Research Organic Chemicals Corporation*

- diallylamine (97%), 1,6-dibromohexane, and iodomethane (99%) (used in the synthesis of the dimethyldiallylammonium iodide and the N,N,N',N'-tetraallyl-N,N'-dimethyl-1,6-hexanediammonium chloride used in System IX) were obtained from the Aldrich Chemical Company*

- polystyrene (125,000 to 250,000 molecular weight) (used to prepare the chloromethylated polystyrene for System X) was obtained from Polysciences, Inc.* The methylal used in this synthesis was obtained from the Aldrich Chemical Company.*

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* See page 7

- aluminum chloride and ethylene chloride were obtained from the Sargent-Welch Scientific Company.*

B. Membrane Preparative Procedures

Initially, one of two general methods (Methods A and B) of preparing membranes was used. Later Method C, which resulted in membranes with improved physical strength, was developed.

1. Method A - crosslinking polyamines

Polyamines (e.g., polyethyleneimine, polyvinylamine, and polyvinylpyridine) were dissolved in a suitable solvent, mixed with an appropriate amount of a dihaloalkane (e.g., 1,3-dibromopropane and 1,4-dibromobutane), and cast into membrane-forming molds made from plate glass and Teflon gaskets. The membrane-forming molds were sealed, and the molds and mixtures were either allowed to stand at room temperature or warmed to an appropriate temperature to effect N-alkylation. Crosslinking was effected by the reaction of both of the halogen atoms of the dihaloalkane. Simultaneously, charged moieties were formed by the N-alkylation. If additional charge density was desired, the crosslinked membrane was exhaustively alkylated with a monofunctional alkylating agent (e.g., dimethylsulfate or methyl bromide). After removing the membranes from the molds (and after further alkylation, if used), the solvent used in the preparative procedure was exchanged for water by one of the solvent-exchange techniques described later. The membranes were then stored in 1 M KCl for subsequent evaluation.

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* Dow Chemical Company, South 2005, 20 Perimeter Center East, Atlanta, Georgia 30346.

Polysciences, Inc., Paul Valley Industrial Park, Warrington, Pennsylvania 18976.

Eastman Organic Chemicals, 343 State Street, Rochester, New York 14650.

Fisher Scientific Company, 2775 Pacific Drive, P. O. Box 829, Norcross, Georgia 30071.

Research Organic Chemicals Corporation, 11686 Sheldon Street, Sun Valley, California 91352.

Aldrich Chemical Company, 940 W. St. Paul Avenue, Milwaukee, Wisconsin 53233.

Sargent-Welch Scientific Company, 7300 North Linder Avenue, Skokie, Illinois 60076.

2. Method B - polymerization of amine-containing monomers

Ethylenically unsaturated amine-containing monomers (e.g., 4- or 2-vinylpyridine) were dissolved in a suitable solvent, mixed with a divinyl type of crosslinking agent (e.g., divinylbenzene) and a free-radical catalyst (e.g., benzoylperoxide or azobisisobutyronitrile), and the mixture was poured into membrane molds. The molds were sealed and then heated to effect polymerization. After cooling, the membranes were removed from the molds and alkylated with a monofunctional alkylating agent, if desired. The solvent used in the preparative procedure was then exchanged for water, and the membranes were stored in either 1 M HCl or 1 M KCl to await evaluation.

After many unsuccessful attempts to prepare membranes with acceptable physical strengths by Methods A and B a third method, Method C, was developed and tried for membrane Systems I and II. In Method C the amine prepolymer was modified to give a water-soluble prepolymer, and membranes were cast from water solutions.

3. Method C - crosslinking of modified amine-containing polymers

A dilute solution (5% to 15% by weight) of the prepolymer in a solvent comprising 4 parts of ethanol and 1 part of water was treated with an appropriate amount of dihaloalkane at 45 to 65°C for 16 to 18 hours. The dilute solutions were used in an attempt to obtain alkylation of the nitrogen atoms on the prepolymer with only one of the two halogen atoms of the dihaloalkanes. The concentration of modified polymer in the reaction mixture was then increased by evaporating the solvent under vacuum at 25° to 35°C. At the first sign of precipitate formation, which was taken to indicate crosslinking, the reaction mixture was cooled quickly and centrifuged. The pH was then adjusted to a high value (11 to 12) with 5 M KOH so that the alkylation reaction with the second of the two halogen atoms originally on the dihaloalkane could proceed readily. Water was added to the viscous syrup to adjust the concentration of the modified polymer to 50% by weight, and the reaction mixture was poured in membrane molds.

The molds were then heated at 65° to 85°C to effect crosslinking by complete alkylation of unreacted nitrogen atoms. After cooling the molds, the membranes were removed and equilibrated in a 1 M KCl solution to prepare them for evaluation.

C. Solvent-Exchange Procedure

The solvent-exchange procedure described below as Procedure 1 was used initially. After studies of solvent exchange, described later, Procedure 2 was used for a few membranes prepared toward the end of the program.

Procedure 1

This solvent-exchange procedure was used by Hills, Kitchener, and Ovendon (ref. 3), and we used the procedure in some of our prior work with graft-polymerized ion-exchange membranes. The procedure consists of immersing membrane samples in a concentrated solution of the desired electrolyte (12 M HCl, or 4 M KCl for the present work). After equilibration for two hours, deionized water is added slowly while the solution is vigorously stirred until the desired final concentration is reached (1 M HCl or KCl). The concentrated solution is used to minimize the swelling stresses on the membrane that might be imposed by osmotic pressure. With slow dilution, the environment surrounding a membrane is changed very slowly to minimize sudden changes in osmotic pressure that could impose swelling stresses.

Procedure 2

Procedure 2, which involves an extremely slow exchange of solvents, was developed during studies to improve the physical strength of the membranes. In Procedure 2 the membrane samples are suspended in the vapor space above a pool of 1 M HCl in a closed container. Over a period of three days at room temperature, the vapors from the pool of HCl exchange with vapors of ethanol from the membrane samples. After three days, the membrane samples are equilibrated and can be immersed in 1 M HCl or 1 M KCl and stored until evaluations are performed.

D. Membrane Evaluation Procedures

The procedures used in evaluating the experimental membranes are based on standard methods given in the Office of Saline Water Tests Manual for Permselective Membranes (ref. 4 (hereafter called the OSW Test Manual)). Prior to a measurement, the membrane samples are equilibrated with the solution to be used in the measurement by method 202.1 in the OSW Test Manual. This procedure involves immersion of the membrane samples in the desired solution for 48 hours at room temperature in a closed container placed in a shaker, followed by rinsing with deionized water for 4 hours. In evaluating membranes, determinations of resistivities, selectivities, water contents, and ion-exchange capacities were made.

1. Resistivity

The determination of resistivity is based on methods 401.1 and 601.1 in the OSW Test Manual. First, the thickness of the equilibrated membrane is measured by method 401.1. This procedure as adapted by Southern Research Institute involves measuring the thickness of the specimen at multiple locations with a Randall-Stickney thickness gage provided with a one-square-centimeter foot. We found that thicknesses of soft membranes are almost always in error when they were measured with the machinists micrometer specified in method 401.1 because the small area of the measuring foot on micrometers results in indentations in the membrane.

The areal resistance of the membrane is then measured by a procedure based on method 601.1. In this determination two identical Micarta* half-cells are used and the membrane is clamped between them. With the membrane in place, each half-cell has a solution compartment bounded on one side and the edges by the Micarta plastic and on the other side by the membrane. In each half-cell a platinized-platinum electrode is mounted on the face of the solution compartment opposite to the membrane. Lead wires extend through the Micarta so that the electrodes can be connected to an ac resistance bridge. The resistance bridge used has a variable capacitor for balancing reactive capacitance, a null current indicator, and a 1000-cps, 1-volt voltage source. Each of the two solution compartments is provided with solution inlet and outlet tubes which are connected to an external hydraulic circuit that includes a solution reservoir, a heater, a flow meter, a thermometer, and a circulation pump.

To make a measurement of areal resistance, the pump is started, the heater is adjusted to give the desired temperature to the circulating solution and cell (e.g., 25°C)**, and the resistance of the cell plus the membrane is measured with the resistance bridge. The membrane is then removed, and the resistance of the cell without the membrane is measured.

The resistivity, ρ, of the membrane material is calculated by:

$$\rho = \frac{A}{h} R$$

where: ρ = resistivity, ohm-cm
A = area of membrane exposed to solution, cm^2
h = thickness of membrane, cm
R = difference between the resistance measurements made with and without the membrane, ohm

The estimated accuracy of the determination of resistivities is ±0.8 ohm-cm.

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* Micarta is a glass-fabric-filled phenolic polymer made by the Micarta Division of Westinghouse, Inc.

** The measurements of resistivities and selectivities were made in a room held at 23 ±0.2°C.

2. Selectivity by the concentration-potential method

This procedure is based on method 602.1 in the OSW Test Manual. The flow apparatus and temperature-control features are improvements developed at Southern Research Institute. The cell used to measure concentration potentials consists of two half-cells made of Micarta that can be clamped together with a membrane between them to form two solution compartments. Each solution compartment is provided with inlet and outlet tubes that are attached to separate external hydraulic circuits. Each of the two closed-loop hydraulic circuits is provided with a heater and temperature controller, a flow meter, a thermometer, a solution reservoir, and a peristaltic circulation pump. Each half-cell is provided with a silver-silver chloride electrode probe that extends into the solution compartment.

To measure the concentration potential across a membrane, a solution of known concentration (e.g., 1 M NaCl or 1 M HCl) is introduced into one solution reservoir and closed-loop hydraulic circuit. A solution of the same electrolyte but of lower concentration (e.g., 0.5 M NaCl or 0.5 M HCl) is introduced into the other solution reservoir and hydraulic circuit. The solutions are circulated, and the heaters and temperature controller are adjusted to bring the entire system to a desired temperature (e.g., 25°C). The potential between the silver-silver chloride electrodes is measured with a potentiometer. (The asymmetry potential of the pair of electrodes is measured before and after the measurement of cell potential and the value is corrected for the asymmetry potential.)

The potential across a membrane may be expressed as:

$$E_m = E_{Ag} + \frac{RT}{F}(t^- - t^+) \ln \frac{\gamma_1 C_1}{\gamma_2 C_2}$$

Where: E_m = the potential measured across the membrane corrected for asymmetry of the electrodes
E_{Ag} = concentration potential due to the Ag:AgCl electrodes = $\frac{RT}{F} \ln \frac{\gamma_1 C_1}{\gamma_2 C_2}$
R = gas constant
T = temperature
F = Faraday's constant
t^- = transference number of the anion in the membrane
t^+ = transference number of the cation in the membrane = $1-t^-$
γ_1 = activity coefficient of the more concentrated solution
γ_2 = activity coefficient of the less concentrated solution
C_1 = solute concentration in the more concentrated solution
C_2 = solute concentration in the less concentrated solution

For an anion-selective membrane, the potential due to the membrane opposes the potential due to the Ag:AgCl electrodes. Therefore, it has a negative sign.

The transference number of the anion in the membrane is a measure of membrane selectivity. It is calculated from measured values of E_m, C_1, and C_2, and known values of γ_1 and γ_2. The estimated accuracy of determining transference numbers by this method is ± 0.003.

3. Water content

This procedure is based on method 412.1 in the OSW Test Manual. For anion-exchange membranes the samples are equilibrated to the chloride form in the desired solution (1 M HCl or 1 M KCl). Each equilibrated sample is removed from the equilibrating solution, blotted dry, folded into a tared piece of aluminum foil (to avoid evaporation), and weighed. The sample is then removed from the foil, and dried to constant weight in a vacuum oven at 90°C. The difference between the initial and final weights is taken to be the amount of water originally in the wet membrane. The water contents are expressed as percentages of the weight of the wet membranes. The estimated accuracy is ± 0.1%.

4. Ion-exchange capacity

This procedure is based on method 502.1 in the OSW Test Manual. Each dried sample from the determinations of water contents is immersed in 50 ml of 4% $NaNO_3$ solution in a container that can be closed. The containers are shaken at room temperature on a mechanical shaker for 24 hours. During this equilibration the chloride ions within the membrane are exchanged for nitrate ions. The equilibrating solutions are then titrated with standardized 0.1 M $AgNO_3$ solution, and the milliequivalents of chloride in the solution (originally in the membrane) are calculated from the milliliters of $AgNO_3$. The ion-exchange capacity is expressed as milliequivalents per dry gram of membrane. The estimated accuracy of the determination is ± 0.05 meq/dry gram.

E. Membrane Preparation and Evaluation

Twelve membrane systems were selected for study on the basis of theoretical considerations. (The theoretical considerations used in selection are discussed in the Appendix.) The studies made and the results obtained for membranes in each selected system are discussed below.

1. Membrane System I

a. Preparation of membranes

These membranes were based on polyethyleneimine and were prepared by Method A with ethanol as a solvent. Samples of commercially available polyethyleneimine (PEI) with three different nominal molecular weights (MW=600, 1800, and 10,000) were tried in the preparative procedures.

Four dihaloalkanes were tried: 1,2-dibromoethane, 1,3-dibromopropane, 1,4-dibromobutane, and 1,10-dibromodecane. With dibromopropane (DBP) as the dihaloalkane and the PEI with a molecular weight of 1800, which was found to be the best, the effects of changes in several of the variables on the characteristics of the membranes were studied. The variables explored were:

- the concentration of PEI in the ethanol solvent (concentrations of 20 through 70% by weight were studied and the range of 45 to 55% appeared to be best)

- the temperatures and times to be used for the crosslinking reaction (a temperature of 65°C for 16-18 hours was found to be satisfactory)

- the ratio of DBP to the formula weight of a repeating unit in PEI (ratios of 0.1, 0.2, 0.33, 0.5, and 1.0 equivalent weights of DBP* to the formula weight of PEI repeating units were tried)

- partial alkylation of PEI with monofunctional alkylating agents having 2 and 3 carbon atoms prior to neutralization and treatment with the difunctional alkylating agent.

Membranes based on polyethyleneimine (System I) were also prepared by Procedure C with the polyethyleneimine of 1800 molecular weight and with a 4:1 mixture of ethanol and water as solvent. In two of the preparations 1,3-dibromopropane (DBP) was used as the dihaloalkane; in the other two preparations 1,4-dibromobutane (DBB) was used. In the first preparation with both DBP and DBB, the molds were sealed (as had been done with Methods A and B). No solid membranes were obtained even after heating at 80°C for 85 hours.

In the second preparation with both DBP and DBB, the membrane molds were left unsealed so solvent could evaporate. Solid membranes were obtained with the reaction mixture containing DBP but not with the one containing DBB. The reason for the lack of cure with DBB was not pursued because we considered that membranes based on poly-4-vinylpyridine (P4VP) would have lower charge density than those those based on polyethyleneimine, and the probability of producing physically strong membranes from P4VP was higher.

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* One equivalent weight of DBP is the weight that contains one atomic weight of bromine (i.e., 1 equivalent weight = 0.5 formula weight).

b. Results of studies on System I

Selected data are presented in Table I to show the effects of variables, such as the molecular weight of the prepolymer or the ratio of dihaloalkane crosslinking agent to prepolymer, on the characteristics of the experimental membranes based on System I.

c. Discussion of System-I membranes

System I was used to explore the effects of changes in starting materials and processing conditions on the characteristics of the membranes. With the entirely new methods of preparing membranes used in this study, such exploratory studies were necessary to determine a fairly narrow range of variables that held the most promise for use with all systems involving prepolymers and dihaloalkanes.

Runs 1 through 7 in Table I show the effects on the membranes of changes in the molecular weight of PEI and of changes in the dihaloalkane. When dibromoethane was used (Runs 1 and 4), the alkylation reaction was so rapid at room temperature that the reaction mixture gelled in the flask before membrane molds could be filled. When dibromobutane was used (Runs 3 and 6) no solid membranes were obtained with the normal heating schedule of 18 hours at 65°C. In Run 6, Table I, PEI-100 and DBB in a 5:1 ratio were heated at 65°C for a total of 65 hours and a solid membrane did result. Thus, we concluded the rate of the alkylation reactions decreased as the number of carbon atoms in the dihaloalkane increased.

The membranes from Runs 2 and 7 were both made with DBP but PEI-6 was used in Run 2 and PEI-18 was used in Run 7. The ion-exchange capacity of the two membranes did not differ greatly, but the water contents did. This difference suggests a difference in the degree of crosslinking.

Runs 7, 8, and 9 show the effects of increasing the degree of crosslinking. All of the membranes in this series were prepared with PEI-18 and DBP, but the amount of crosslinking agent used was increased. If the alkylation reaction was complete, every fifth nitrogen on the PEI-18 in Run 7, and every fourth and third nitrogen on the PEI-18 in Runs 8 and 9, respectively, would be alkylated. Thus, both the crosslinking density and the charge density (ion-exchange capacity) should be higher for Run 9 than for Runs 8 or 7. There was only a slight increase in ion-exchange capacity (from 4.5 to 4.7 mg/dry gram) but a decided decrease in water content, which indicates an increase in crosslinking density. The inconsistency in water contents of membranes obtained in Runs 8 and 9 suggests (along with other factors found later) that control of the alkylation reaction is difficult.

Table I

Characteristics of Membranes in System I

Run No.	Sample Number	Description							Characteristics			
		Preparative Method	Amino-containing Reactant		Crosslinking Agent		Ratio[a] of Crosslinking Agent to Nitrogen atoms	Pre-alkylating Agent and Equivalent % Added	Water Content %	Ion-exchange capacity meq/dry g	Resistivity ohm-cm At 25°C	Transport Number of Cl⁻
			Prepolymer	Monomer	Dihaloalkine	Monomer						
	Samples Equilibrated in 1 M KCl											
1	7616-123-1	A	PEI-6[b]	-	DBE[c]	-	1:5	none	Gelled in reaction flask			
2	-123-2		PEI-6	-	DBP[c]	-	1:5		58.6	4.4	e	e
3	-123-3		PEI-6	-	DBB[c]	-	1:5		Did not cure to solid			
4	-73-1		PEI-100[d]	-	DBE	-	1:5		Gelled in reaction flask			
5	-73-2		PEI-100	-	DBP	-	1:5		h	h	h	h
6	-73-3[d]		PEI-18[d]	-	DBB	-	1:5		h	h	h	h
7	119		PEI-18	-	DBP	-	1:5		67.7	4.5	e	e
8	113-11		PEI-18	-		-	1:4		60.4	4.6	e	e
9	113-2		PEI-18	-		-	1:3		61.9	4.7	e	e
10	127-35[f]		PEI-18	-	DBP	-	1:5		86.4	7.3		
11	127-40[f]		PEI-18	-		-	1:5		82.1	6.1		
12	127-45[f]		PEI-18	-		-	1:5		76.5	5.5	e	e
13	127-50[f]		PEI-18	-		-	1:5		69.1	4.8	e	e
14	127-55[f]		PEI-18	-		-	1:5	none	67.0	4.8	e	e
15	110-7		PEI-18	-		-	1:5	EtBr[g]-100%[i]	64.5	-	h	h
16	110-8		PEI-18	-		-	1:5	EtBr -200%[i]	61.5	6.3	h	h
17	110-6		PEI-18	-		-	1:5	i-PrBr[g]- 50%[i]	60.1	6.9	h	h
18	110-9		PEI-18	-		-	1:5	i-PrBr -100%[i]	48.6	-	h	h
19	110-10		PEI-18	-		-	1:5	i-PrBr -200%[i]	47.6	-	h	h
	Samples Equilibrated in 1 M HCl											
1a	123-1	A	PEI-6	-	DBE	-	1:5	none	Gelled in reaction flask			
2a	123-2		PEI-6	-	DBP	-			65.7	6.0		e
3a	123-3		PEI-6	-	DBB	-			Did not cure to solid			
4a	73-1		PEI-100	-	DBE	-			Gelled in reaction flask			
5a	73-2		PEI-100	-	DBP	-			h	h	h	h
6a	73-3		PEI-100	-	DBB	-			h	h	h	h
7a	119		PEI-18	-	DBP	-		none	69.7	8.1	e	e
8a	113-11			-		-	1:4		65.6	6.2	e	e
9a	113-2			-		-	1:3		61.9	7.6	e	e
10a	127-35		PEI-18	-	DBP	-	1:5		89.7	9.0		
11a	127-40			-		-			83.5			
12a	127-45			-		-			80.4	4.8	e	e
13a	127-50			-		-			78.6	8.7	e	e
14a	127-55			-		-			75.4		e	e
15a	110-7		PEI-18	-		-	1:5	EtBr -100%[i]	63.1		f	f
16a	110-8			-		-		EtBr -200%[i]	61.9	6.3	f	f
17a	110-6			-		-		i-PrBr - 50%[i]	59.6	7.0	f	f
18a	110-9			-		-		i-PrBr -100%[i]	55.0		f	f
19a	110-10			-		-		i-PrBr -200%[i]	51.9		f	f
	Samples Equilibrated in 1 M KCl											
20	7956-9	C	PEI-18	-	DBP	-	1:1				<2[f]	e
	Samples Equilibrated in 1 M HCl											
20a	7956-9	C	PEI-18	-	DBP	-	1:1		72.0	7.7	<2[f]	e

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a. Total atomic weights of halogen atoms in relation to the total atomic weights of nitrogen atoms in the reaction mixture

b. PEI-6, PEI-18, and PEI-100 refer to commercial grades of polyethyleneimine with nominal molecular weights of 600, 1800, and 10,000 respectively

c. DBE, DBP, DBB, and DBD refer to 1,2-dibromoethane; 1,3-dibromopropane and 1,4-dibromobutane and 1,10-dibromodecane respectively

d. In run 6 the reactant mixture was heated in the membrane molds for 65 hours

e. These samples either crumbled, or fractured under the clamping pressure needed to mount them in the cells to measure resistance or transport numbers

f. The last two numbers in the sample number indicate the percentage of reactants in the solvent

g. EtBr and i-PrBr represent ethylbromide and iso-propyliodide, respectively

h. Shattered during solvent exchange by Procedure I

i. Enough monohaloalkane added to react with 50%, 100% or 200% (i.e. 100% excess) of the nitrogen atoms

j. Two ohm-cm was the minimum resistivity that could be determined with the method used

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Runs 10 through 14 illustrate the effect of changes in reactant concentration on characteristics of the membranes. Concentrations of 25 to 75% by weight were studied, but data are presented only for samples prepared from reaction mixtures with reactant concentrations of 35 to 55%. With concentrations of 25 and 30% no solid membranes were obtained. With concentrations of 60 to 75% the membranes were cracked, brittle, and too fragile to remove from the membrane molds.

The more dilute solutions shown in Table I (35 and 40% in Runs 10 and 11) were so water swollen after solvent exchange they could not be handled without damage. The membranes prepared with reactant concentrations of 45, 50, and 55% (Runs 12, 13, and 14) had the best physical properties of the membranes prepared in this series of experiments, and even they were not strong enough to be clamped in the cells used to measure resistivities and transference numbers.

Based on this series of experiments, a solute concentration of 50% was used in most of the remaining experiments (other Systems as well as System I). (The membranes prepared before Runs 10 through 14 had also been made with solutions containing 50% by weight of reactants.)

Runs 15 through 19 show the effects of partially alkylating the prepolymers with monofunctional alkylating agents before the treatments with difunctional alkylating agents. The monofunctional agents used were ethyl bromide, EtBr, and 2-propyl bromide, i-PrBr. Enough of the monofunctional agents were added to react with 50 to 200% (i.e. 100% excess) of the total nitrogen atoms in the PEI-18. An increase in the amount of monofunctional agents attached to the polymer chain prior to crosslinking resulted in a decrease in the water contents (from 64.5 to 61.5% for Runs 15 and 16 with EtBr, and from 60.1 to 47.6% for Runs 17, 18, and 19 with i-PrBr). This decrease in water content was expected because of the increase in formula weight per unit of charge on the membranes. Comparison of the water contents of membranes from Runs 16 and 19 shows that the membranes made with 200% of the i-PrBr (Run 19) had a lower water content (47.6%) than the membranes made with 200% of the EtBr (61.5% for Run 16), which was also expected.

Meaningful comparisons of the effects of EtBr and i-PrBr on ion-exchange capacities cannot be made because data are only available for membranes made from the two monohaloalkanes under different conditions (200% of EtBr and 50% of i-PrBr). Meaningful comparisons can be made, however, to show the effects of equilibration in 1 M KCl versus 1 M HCl. For example, with the membranes made in Run 7, equilibration in acid resulted in much higher ion-exchange capacity (8.1 meq/g for 7a) than equilibration in KCl (4.5 meq/g for 7). The water contents were also slightly higher when membranes were equilibrated in acid (69.7% for 7a compared with 67.7% for 7). As the crosslinking density increased, these differences decreased (compare the water contents and ion-exchange capacities for 9 and 9a with those of 7 and 7a). Higher ion-exchange capacities are encountered with acid equilibration because many of the nitrogenous moieties that are not ionized in KCl solution become ionized in acid solution. However, with increasing crosslinking density the proportion of alkylated moieties to the total nitrogenous moieties increases. Therefore, the difference in ion-exchange capacity (i.e., charge density) decreases because the proportion of non-alkylated nitrogenous moieties that are not ionized in KCl but ionized in acid is lower.

Finally, the most notable feature of the data in Table I is that none of the membranes based on polyethyleneimine made by Method A were strong enough to be mounted in the cells used to measure resistivities or transference numbers. However, when Method C was used (Runs 20 and 20a) the membranes were strong enough to withstand being clamped in the cell used to measure resistivity, but crumbled when mounted in the cell for transference number.

2. Membrane Systems II and III

a. Preparation of System-II membranes by Method A

Membranes in System II are based on poly-4-vinylpyridine (P4VP); those in System III are based on poly-2-vinylpyridine (P2VP). Only one set of experimental membranes was made by Method A based on System II because there were fibrous impurities in the P4VP, (as received) that were time-consuming to remove. Moreover, information pertinent to System II could be obtained by the studies made on System III since the two prepolymers differ only in steric features. For this one set of System II membranes, enough 1,3-dibromopropane was used to react with all nitrogenous moieties in the P4VP.

b. Preparation of System-II membranes by Method C

After preparative Method C was developed late in the program, membranes based on poly-4-vinylpyridine (P4VP) were prepared. A 4:1 weight ratio of ethanol and water was used as solvent for all of the preparations. In the first attempt to prepare these membranes, the molar ratio of P4VP to 1,4-dibromobutane (DBB) was 1:1. The concentration of reactants in the ethanol-water solvent was 7.4% by weight. The reaction mixture was heated at 40°C for 5 hours. The pH of the reaction mixture changed from 7.6 to 5.4 during the first two hours but did not change further during the last three hours. The reaction appeared to have stopped. Accordingly, the temperature was increased. When the temperature reached about 55°C an exothermic reaction began, and the temperature increased spontaneously to 73°C, and the reaction mixture gelled in the flask.

In the second attempt to prepare membranes in System II by Method C a 2:1 ratio of P4VP to DBB was used and the concentration of reactants in the solvent was decreased to 4.7% by weight. The stirred reaction mixture was heated to 60°C. The pH decreased slowly over 8 hours from 7.6 to 6.3. During the next 24 hours at 60°C, the pH decreased to 4.9, and during the next 12 hours it became constant at 4.7. The total time of heating was 44 hours. No precipitate or gel was visible during or after heating.

The solvent was vacuum evaporated at 35 ±2°C from an aliquot of the solution. During the evaporation the solution was carefully observed to detect the first signs of precipitate formation as an indication of crosslinking. No precipitation was seen. Instead, the entire reaction mixture gelled quickly when the concentration of modified prepolymer in the solution was about 39-40% by weight.

We then repeated the experiment, but stopped the evaporation when the concentration was 28% to be sure gelation would not occur. This viscous solution was poured into membrane molds. Two of the molds contained a nylon scrim for reinforcement, and one contained no scrim. The molds were sealed and heated at 65°C for 22 hours. The molds were cooled, opened, and inspected. Crosslinking had occurred (at least partially), but there was so much solvent present that only soft gels were formed. We then attempted to cure these gels further to obtain additional crosslinking and simultaneously allow the membranes to reach a lower equilibrium water content.

The soft-gel membranes were immersed in saturated NaCl solution. (The use of a saturated salt solution minimized the stresses imposed on the soft gels by osmotic pressure.) The solution was heated at 65°C for 24 hours. The membranes that resulted were much tougher and stronger than any made previously. However, both the membranes with scrim reinforcement and those without reinforcement had shrunk appreciably from the dimensions of the soft gels, and the resulting membranes were curled and wrinkled. Nevertheless, the membranes were stored in 1 M KCl for evaluation.

It was desirable to find some method of preparing solutions for casting that would have higher concentrations of modified prepolymer than the 28% used in this preparation. After several attempts to obtain higher concentrations of modified prepolymer by vacuum evaporation at low temperatures, we tried acidifying the dilute solution of modified prepolymer with HBr before evaporation. The rationale for acidification was that if the unreacted nitrogen atoms on the modified prepolymer were converted to the HBr salt prior to removal of solvent, the undesired crosslinking reaction to cause premature gelling that had been occurring during evaporation would be inhibited.

When HBr was added to the ethanol-water solution of modified prepolymer, a precipitate formed. The HBr salt of the modified prepolymer was only sparingly soluble in the 4:1 mixture of ethanol and water. Acidification appeared to be a good way of recovering the HBr salt of the modified prepolymer so the slurry of precipitate was centrifuged and the centrifugate was decanted. The wet cake remaining contained 65% solvent and 35% solids. The solids content of the wet cake from the acidification and centrifuging was not much higher than that obtained by evaporation. There were several ways in which the solids content of the wet cake could have been increased (*e.g.*, washing with acetone or freeze drying), but the time and funds provided by the contract were exhausted.

The results of the studies made of System II along with those of the studies of System III are given in Table II.

3. Membrane System III

a. Preparation of membranes

Membrane System III is based on poly-2-vinylpyridine (P2VP). All of the experimental membranes were made by Method A. The concentration of reactants in ethanol and the method and temperature of curing (65°C) were identical to the conditions used for the membranes made by Method A in System II. Three dihaloalkanes were used: 1,2-dibromoethane, 1,3-dibromopropane, and 1,10-dibromodecane. The ratios of equivalent weights of dihaloalkane to the formula weight of a repeating unit in P2VP were varied from 0.1 to 1.0.

b. Results

The effects on membrane characteristics of changes in the number of carbon atoms in the alkylating agent, of the crosslinking density, and of equilibration in near-neutral (KCl) or acidic (HCl) solutions are shown in Table II.

c. Discussion of membranes in Systems II and III

System II

Membranes in System II were prepared by Methods A and C. Enough dibromopropane was used to react with all nitrogen atoms, if the alkylation reaction was complete. In KCl solution all of the nitrogenous moieties that reacted would be ionized, but virtually none of the unreacted nitrogen moieties would be. In HCl solution essentially all nitrogenous moieties would be ionized, either as quaternary species or as HCl salts. Since the ion-exchange capacity of the membranes made by Method A is only slightly lower in KCl (5.4 meq/g) than in HCl (5.8 meq/g), a high proportion of the total nitrogenous moieties (>90%) must have been quaternized. Also, since quaternization results from the crosslinking reaction, the crosslinking density must have approached the maximum possible. Thus, the membranes produced by Method A had both high charge density and high crosslinking density, and a combination of high charge density and high crosslinking density is desirable to meet the goals of low resistivity and high selectivity. However, the membranes crumbled when attempts were made to mount them in the cells used to measure resistivities and transference numbers.

The membranes in System II that were prepared by Method C were much stronger physically than any membranes prepared in this program. With the exception of being badly wrinkled, the physical characteristics of these membranes appeared good enough to be used. The resistivities were also low enough to be promising. The transference number

Table II

Characteristics of Experimental Membranes Based on Systems II and III

Run No.	Sample Number	Preparative Method	Amine-containing Prepolymer	Dihaloalkane Used	Ratio of Crosslinking Agent to Nitrogen Atoms[a]	Water Content %	Ion-exchange Ion-exchange capacity, meq/dry g	Resistivity ohm-cm at 25°C	Transference Number of Cl
System II									
Samples Equilibrated in 1 M KCl									
21	7616-117	A	P4VP	DBP[b]	1:1	63.6	5.4	c	c
22	7687-131	C	P4VP	DBP	1:1	-	-	26	0.95
Samples Equilibrated in 1 M HCl									
21a	7616-117	A	P4VP	DBP	1:1	65.2	5.8	c	c
22a	7687-131	C	P4VP	DBP	1:1	-	-	12	0.81[d]
System III									
Samples Equilibrated in 1 M KCl									
23	7616-92-5	A	P2VP	DBE[b]	1:10	26.5	<0.1	c	c
24	-92-6			DBE	1:5	27.0	<0.1	c	c
25	-92-11			DBP[b]	1:10	34.5	1.2	c	c
26	-92-33			DBP	1:2	41.0	1.8	390	c
27	-108-2			DBD[b]	1:5	27.5	1.3	1920	c
28	-108-3			DBD	1:2	29.6	1.7	2030	c
Samples Equilibrated in 1 M HCl									
25a	-92-11	A	P2VP	DBP	1:10	95.0	6.5	4	c
26a	-92-33			DBP	1:2	88.3	6.1	8	-
27a	-108-2			DBP	1:5	75.3	7.3	-	-
28a	-108-3			DBP	1:2	73.9	6.9	-	-

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[a] Total atomic weights of halogen atoms in relation to the total atomic weights of nitrogen atoms in the reaction mixture

[b] DBE, DBP, and DBD refer to 1,2-dibromoethane, 1,3-dibromopropane, and 1,10-dibromodecane respectively

[c] These samples either crumbled or fractured when clamped in test cells

[d] Transference numbers measured between 1.0 and 0.5 molar solutions of KCl or HCl

for Cl^- of 0.81 measured between 1.0 and 0.5 M HCl compared favorably with values of 0.66 to 0.78 measured for commercially available membranes.* However, a value of 0.81 in 1 M HCl is not acceptable for use in the proposed redox cells.

System III

Several variations were tried in the preparation of membranes based on System III. Membranes prepared from dibromopropane had higher water contents than those prepared from either dibromoethane or dibromodecane. The values of resistivity for the three samples (Runs 26, 27, and 28) that did not crumble in the resistivity cell were higher than expected on the basis of their ion-exchange capacities. However, the samples crumbled when attempts were made to clamp them in the cell for transference numbers even though the water contents and ion-exchange capacities were low.

The poor physical properties of these membranes despite low water contents and ion-exchange capacities (combined with similar observations about System V membranes, described later) was sufficient evidence to conclude that strong membranes could not be prepared by Method A.

4. Membrane System IV

Attempts were made to prepare membranes in System IV by the copolymerization of N-methyl-4-vinylpyridinium sulfate and divinylbenzene. In this membrane preparation, which was based on a method described for 2-vinylpyridine in U. S. Patent 2,732,350, 4-vinylpyridine (4VP) was dissolved in an equal weight of 2-propanol. The solution of 4VP was first treated with the amount of dimethylsulfate required for complete quaternization of the tertiary nitrogen atoms in the 4VP, and then treated with a weight of divinylbenzene (50% DVB and 50% ethylstyrene) equal to the weight of the 4VP.

During the treatment of 4VP with dimethylsulfate, the 4VP polymerized into a viscous syrup. Since the polymerized 4VP would have no unsaturated bonds left, treatment with divinylbenzene was not attempted.

5. Membrane System V

These membranes were prepared by copolymerization of N-methyl-2-vinylpyridinium sulfate and divinylbenzene (DVB). This membrane preparative technique was based on U. S. Patent 2,732,350. 2-Vinylpyridine (2VP) was dissolved in an equal weight of 2-propanol and then treated at room temperature with the amount of dimethyl sulfate

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* MA3148 and MA3475 anion-exchange membranes from Ionac Chemical Company (t^- = 0.66 and 0.78 respectively)

required to effect quaternization of all of the nitrogen atoms. A weight of DVB equal to the weight of 2VP was added to the solution of quaternized 2VP. The solution was poured into membrane molds, sealed, and then heated to 60°C for 5 hours to effect polymerization and crosslinking. After cooling, the membranes were removed from the molds, and the 2-propanol was exchanged for water. The membranes were then stored in either 1 M HCl or 1 M KCl.

Two other sets of experimental membranes were prepared by procedures that were identical to the above except that the amount of DVB added to the solution of quaternized 2VP was 1/2 of the weight of the 2VP for one set, and 1/4 of the weight of 2VP for the other set. Both of these less-crosslinked membranes were so water swollen after solvent exchange they could be handled only with extreme care, whereas the first set of membranes could be handled.

The water contents of the membranes prepared from equal weights of 2VP and DVB was 58.1% when equilibrated in 1 M KCl and 61.4% when equilibrated in 1 M HCl. The ion-exchange capacity of the membranes was the same in both KCl and HCl (1.6 meq/dry g). However, the samples crumbled when attempts were made to clamp them in the test cells used for resistivity and transference number.

This extreme fragility of experimental membranes with relatively high crosslinking densities and relatively low charge densities indicated Method B held little promise for preparing satisfactory membranes

6. Membrane System VI

Membranes in System VI were to be made from poly(p-aminostyrene) (PAS) crosslinked with a dihaloalkane. The PAS supplied to us would not dissolve in methanol, ethanol, tetrahydrofuran, dimethylformamide, pyridine, or dimethyl sulfoxide. We concluded that the PAS, which is known to be susceptible to crosslinking by air oxidation, was crosslinked. Further work on System VI was delayed until some of the urgent problems pertaining to the poor physical strength of the experimental membranes could be resolved.

7. Membrane System VII

Membranes in System VII are based on polyvinylamine (PVAm) crosslinked with a dihaloalkane. Polyvinylamine hydrochloride was prepared from acrylyl chloride by the method of St. Pierre and Hughes, which is described in Appendix B, and neutralized with NaOH in methyl alcohol. After evaporation of the methyl alcohol, the PVAm was dissolved in a 9:1 mixture of ethanol and water. The most concentrated solution that could be used for preparation of membranes contained 30% of PVAm by weight. (More concentrated solutions were too viscous for use.) Enough 1,3-dibromopropane was added to react with 20% of the available nitrogen atoms. The reaction mixture was cast in membrane molds and cured at 60°C for 24 hours. After cooling, the membranes were removed from the molds and saved for the solvent-exchange procedure. The solvent-exchange procedure used (Procedure I) involved immersing the samples in concentrated solutions of electrolytes (4 M KCl or 12 M HCl) and then slowly diluting the electrolyte solutions until 1 M concentrations were reached. The samples of membranes shattered before the concentration of 1 M was reached. At this time in the course of the project, a decision was made to delay further work on new membrane systems until problems relating to the physical strength of the membranes could be resolved. Therefore, the membranes based on System VII were not evaluated.

8. Membrane Systems VIII through XII

Membranes in System VIII were based on copolymers of vinylamine and divinylbenzene (DVB). The membrane preparation involved the copolymerization of DVB and N-vinyl-t-butylcarbamate prepared by the method of St. Pierre and Hughes, followed by stepwise treatment of the crosslinked copolymer with alcoholic HCl and methyl iodide. However, because of the emphasis on studies to improve the physical strength of the membranes, System VIII was not studied.

Membranes in System IX were based on polydiallylamine. The preparation of membranes involved the copolymerization of N,N'-diallyldimethylammonium iodide (DDAI) and N,N,N',N',-tetraallyl-N,N'-dimethyl-1,6-hexanediammonium chloride (TADMH) with ammonium persulfate as a catalyst by the method of Booth, Flock and Hoover (ref. 5).

DDAI was prepared by the reaction of diallylamine and methyl iodide followed by neutralization and further alkylation with methyl iodide. TADMH was prepared by the reaction of 1,6-dibromohexane and diallylamine followed by neutralization and alkylation with methyl iodide. Both DDAI and TADMH were identified by nuclear magnetic resonance (NMR) spectroscopy. However, when attempts were made to dissolve TADMH after storage for about 10 days, no adequate solvent was found. It was suspected that the TADMH had crosslinked during storage, but no further work was done with System IX due to emphasis on studies to improve mechanical properties of earlier more promising membranes.

Membranes in System X were based on crosslinking of polyvinylbenzylchloride (PVBC) with a diamine. Three attempts were made to prepare PVBC by chloromethylation of polystyrene by treatment with formaldehyde and $AlCl_3$ under anhydrous conditions (ref. 6). The product from the first attempt was insoluble. Almost certainly crosslinking had occurred as a result of an alkylation reaction that competes with the chloromethylation reaction. In the subsequent attempts to chloromethylate polystyrene, precautions were taken as advocated by Jones (ref. 7) for preventing crosslinking (i.e., dilute solutions were used and the reaction was stopped with water before complete chloromethylation occurred.) However, the products from these two attempts were also insoluble. No further work was done on System X when the intensive studies to improve physical strength of more promising membranes were started.

Membranes in System XI were based on the crosslinking of polyallylamine with a dihaloalkane, and membranes in System XII were based on the copolymerization of 2-methyl-5-vinyl-pyridine and divinylbenzene.

After discussions of the poor physical properties of all experimental membranes with the Project Officer and other personnel at NASA, it was decided to concentrate our efforts on methods of improving the physical strength of the experimental membranes. Therefore, work on membrane Systems VIII through XII was held in abeyance until methods of producing membranes with acceptable physical strengths were developed.

F. Studies to Improve the Physical Strength of the Membranes

Many of the experimental membranes had acceptable physical strength when removed from the membrane molds, but during the solvent-exchange procedure (Procedure I), the membrane samples either shattered or became so water swollen they were too weak for use. There was a possibility that the solvent-exchange procedure itself placed so much stress on the polymeric structure that either microscopic shattering or crazing occurred which was responsible for the weakness of the membranes. On the other hand, there was a possibility that some step in the preparative procedures was critical to the development of adequate strength, or that the desired high charge densities were too high to obtain acceptable physical strengths. Therefore, the solvent-exchange procedures and the procedures for preparing membranes were both investigated.

1. Solvent-exchange procedures

Solvent-exchange Procedure I, which had been used for all of the experimental membranes prepared by Methods A and B, had been used successfully by Hills, Kitchener and Ovendon (ref. 3) to exchange water for solvent in the preparation of cation-exchange membranes of high charge density. Procedure I consisted of first equilibrating membrane samples in a concentrated solution of electrolyte (e.g., 12 M HCl or 4 M KCl) and then slowly diluting the solution with water until a desired concentration was reached. The concentrated solutions were used to minimize the osmotic pressure difference between the external solution and the interstitial solution within the membranes, and thus minimize the stresses imposed by swelling pressures.

Two other solvent-exchange procedures were studied. In one procedure, samples of membranes based on System I (polyethyleneimine crosslinked with enough dibromopropane (DBP) to react with 20% of the nitrogen atoms) and System III (poly-2-vinylpyridine crosslinked with enough DBP to react with 20% of the nitrogen atoms) were placed in a 1:9 mixture of water and ethanol. (Ethanol was the solvent used in the membrane preparations.) The intent of the experiment was to follow the initial equilibration in the 1:9 mixture by successive equilibrations in water-ethanol mixtures that contained more and more water (e.g., 2:8; 3:7; 4:6 mixtures). However, the surfaces of the samples crazed even when they were immersed in the 1:9 mixture. A second attempt was made in which the initial mixture was 98% ethanol. The membranes survived this equilibration, but crazed at the surfaces when the next mixture (96% ethanol and 4% water) was used.

In the second modification of the solvent-exchange procedure, samples of the membranes based on Systems I and III were placed in a closed vessel above the surface of a pool of 1 M HCl so that the membranes were exposed only to the vapors from the 1 M HCl. After 3 days, the samples based on System I were cracked, but the samples based on System III were still intact. These latter samples were placed directly in a 1 M HCl solution. After 24 hours, they were swollen to about three times their former dimensions but remained intact. Although intact, these samples were so swollen and weak they could not be mounted in the cell used to measure resistivity. This procedure, described previously as Procedure II, was used for some of the experimental membranes.

These studies suggested that a solvent-exchange procedure in which the environment of the membrane samples is changed very gradually might have advantages over Procedure I. However, the fact that membranes based on System I cracked even with the extremely gradual change of solvent obtained with the vapor-phase method suggested that if the charge density is too high, difficulties with physical strength would be encountered even with extremely gradual solvent-exchange. The extremely swollen and weak membranes resulting from immersion of System III in 1 M HCl after the vapor-phase exchange of solvent also suggested the charge density was too high or the degree of crosslinking was too low to achieve good physical strength.

2. Studies of procedures for strengthening membranes

In addition to the studies of solvent-exchange, methods were explored for strengthening membranes by the formation of interpolymers. We hypothesized that the formation *in situ* of a non-charged polymer matrix, such as styrene polymerized by a free-radical catalyst, in ion-exchange membranes could improve the strength of the charged membranes. These interpolymers would consist of uncharged polymer chains intertwined with the chains of a charged polymer. The network of non-charged chains could provide physical support to aid the charged polymer in resisting the stresses imposed by swelling pressure when the membrane is immersed in an aqueous solution.

To test this hypothesis we used samples of previously prepared membranes based on Systems I and III. Membranes based on System I (polyethyleneimine treated with enough DBP to react with 20% of the nitrogen moieties) and on System III (poly-2-vinylpyridine plus 20% of DBP) were soaked in one of three baths containing styrene. The compositions of the three baths were: (a) 100% styrene, (b) 50% styrene and 50% tetrahydrofuran (THF), and (c) 25% styrene and 75% THF. The three concentrations of styrene were used to determine whether the amount of styrene absorbed by the membranes would alter the strength, ion-exchange capacity, and equilibrium water contents of the membranes. The membrane samples were allowed to imbibe styrene at room temperature for 18 hours and were then removed from the baths and stored in a 50:50 mixture of THF and toluene that contained 1% of benzoyl peroxide. After two weeks, the samples were removed and equilibrated in 1 M KCl or 1 M HCl by solvent-exchange Procedure II. The membranes based on System I shattered but those based on System III remained intact. The ion-exchange capacities and water contents of the styrene-treated samples based on System III are shown in Table III.

Table III

Effect of Treatment with Styrene on the Properties

of Poly-2-vinylpyridine/20%-DBP Membranes

Treatment	Equilibrating Solution	Ion-exchange capacity, meq/g	Water content %
None	1 M KCl	-	54.6
	1 M HCl	6.3	88.0
100% styrene	1 M KCl	2.1	42.2
	1 M HCl	6.1	88.5
50% styrene-50% THF	1 M KCl	-	51.5
	1 M HCl	6.0	88.0
25% styrene-75% THF	1 M KCl	-	53.5
	1 M HCl	6.1	88.2

The styrene-treated samples were stronger than untreated membranes based on System III and were strong enough for use after equilibration in KCl. However, when they were equilibrated in HCl, the membranes were too water swollen for use.

If a larger proportion of non-charged polystyrene could be incorporated into the membranes, the strength might be improved further. Moreover, if divinylbenzene could be incorporated, the non-charged polymer, which would be crosslinked within the charged membrane, might enhance the physical strength still further. Accordingly, styrene and divinylbenzene were mixed together in a 9:1 ratio and added to a solution of P2VP in ethanol. The mole ratio of styrene to the repeating unit of P2VP was 1:1. The solution was divided into two equal portions, and enough DBP was added to each portion to react with 20% of the amine moieties. Benzoyl peroxide was added to one portion and both were heated for 65 hours at 65°C. At the end of 65 hours both portions were still fluid. Apparently, adding styrene and divinylbenzene to the reaction mixture of System III inhibits crosslinking by the dihaloalkane. There was also no evidence of polymerization of the styrene or DVB.

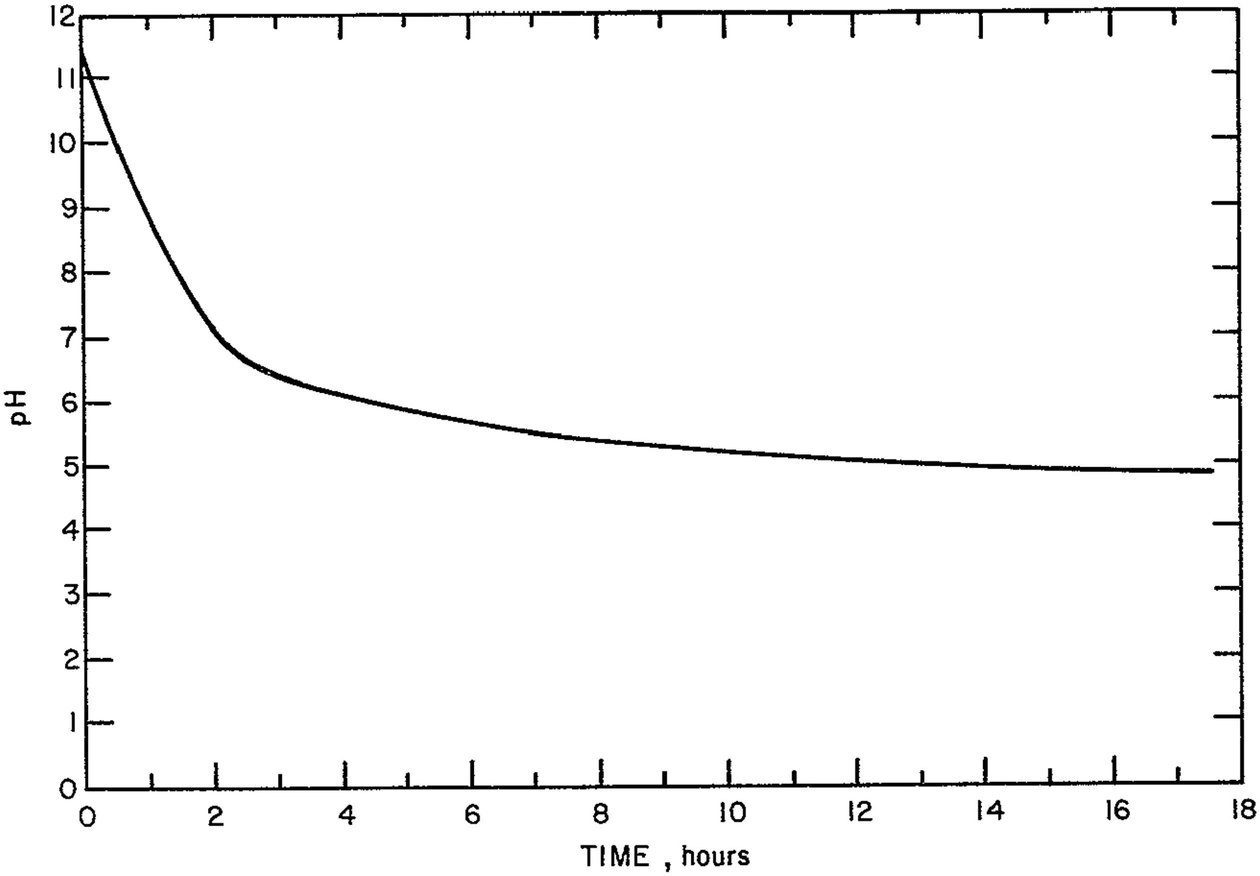
The experiments in which non-charged polymers were incorporated into ion-exchange membranes showed promise of increasing the physical strength of the membranes, but some method for incorporating more non-charged polymer into the ion-exchange resin is needed if the membranes are to be used in acidic media.

A second study to improve the strength of membranes led to Method C for preparing membranes. We hypothesized that if only one of the two halogen atoms on the dihaloalkanes could be made to react with the amine prepolymers, the modified prepolymers might be soluble in water and membranes could be prepared in an aqueous media so there would be no need for solvent exchange.

After exploration of a number of different reaction conditions, it was found that the reaction of only one of the two halogen atoms on dihaloalkanes was favored by the use of a dilute solution (5% to 15% by weight) of an amine prepolymer, and of relatively low reaction temperatures (45 to 65°C). With a secondary-amine prepolymer (e.g., polyethyleneimine) the course of reaction could be monitored by following the pH of the reaction mixture. As the alkylation proceeded, HBr was formed and the pH of the reaction mixture decreased.

The following experiment with polyethyleneimine of 1800 nominal molecular weight and 1,3-dibromopropane is used to illustrate several features of the reaction.

When a 1:1 mole ratio of the two reactants was dissolved in a solvent comprising 80% of ethanol and 20% of water to give a solution containing 11.5% by weight of the reactants, the pH was 11.1. The stirred reaction mixture was held at 60°C. The pH decreased rapidly at first and more slowly as time went on. The change in pH with time is shown in Figure 2. When the pH reached a value of 4.9, precipitate began forming. The rapid change at first followed by slower changes indicates that with an increasing number of protons in the reaction mixture, the rate of the alkylation reaction decreases. Thus, the reaction tends to be self limiting.



Fiure 2. Change in pH During the Reaction of Polyethyleneimine with Dibromopropane

The reaction mixture was cooled to minimize further reaction, and the solution was filtered to remove the precipitate. An aliquot of the filtrate was adjusted with 5 M KOH to a pH of 12.2 so that the reaction of the second halogen of the dibromopropane molecules with unreacted nitrogen atoms to crosslink the polymer could occur readily. The reaction mixture was poured into a tared Petri dish, which was placed in a vacuum desiccator. Solvent was evaporated at room temperature under vacuum until a thick syrup remained. Deionized water was added until the weight of the Petri dish and contents indicated the solution contained 50% by weight of the modified prepolymer. The Petri dish and its contents were heated at 80°C for two hours. A crosslinked, clear membrane resulted that was tougher and stronger than any membrane based on polyethyleneimine that had been made previously. A portion of this membrane was placed directly into 1 M KCl; the second portion was immersed directly in 1 M HCl. The membrane samples withstood both of these extreme treatments and remained intact. The small membrane samples were highly swollen and probably too weak for use, but they were much stronger than any membranes made previously.

In summary, the following things were learned from the reaction of polyethyleneimine with dibromopropane in a dilute ethanolic solution, followed by the crosslinking reaction.

> It is possible to cause an amine-containing prepolymer to react with essentially only one of the two halogen atoms on a dihaloalkane.
>
> The modified prepolymer is water soluble.
>
> The progress of the reaction can be monitored by measuring the pH of the reaction mixture.
>
> When the "single-ended" reaction has reached a characteristic degree of completion, a precipitate begins to form. This precipitate could be a result of the second of the two halogen atoms reacting with unreacted nitrogen moieties on the prepolymer, which would result in crosslinking and insolubility.
>
> By filtering the reaction mixture to separate any insoluble matter, adjusting the pH to a high value, and increasing the solids content of the reaction mixture to about 50% solids, the second halogen atoms on the dihaloalkane reactant can be made to react to give a crosslinked ion-exchange membrane that is stronger than the membranes produced by all previous attempts.

Method C for preparing membranes was based on the above observations.

Work was begun immediately to repeat the preparation of membranes based on polyethyleneimine (System I) so that membranes large enough for evaluation of their properties could be made. Work was also started to prepare membranes based on poly-4-vinylpyridine (System II) by Procedure C. However, only one set of membranes that could be evaluated resulted from these efforts. The one good set of membranes was based on System II and was discussed previously.

3. Studies of membrane systems in addition to the selected systems

Toward the end of the contract a few experiments were performed to explore other membrane systems that seemed to have promise for producing membranes with good physical strength.

One experiment was performed to prepare membranes from chloroethylvinyl ether (CEVE) and 4-vinylpyridine (4VP) monomer. A dilute solution (9.2% solids) of CEVE and 4VP in a one-to-one mole ratio was prepared. The solvent used was a mixture of 4 parts of ethanol and 1 part of water. The solution was heated with stirring for 24 hours at 60°C. The solution was then cooled and the solvent removed by vacuum evaporation. The resulting powder, which was almost solvent free (94% solids), was dissolved in an equal weight of water. Ammonium persulfate (1% of the weight of the solid) was added as a catalyst. A membrane was cast in a Petri dish. The Petri dish was sealed and heated at 65°C for 4 days. After 4 days the membrane was still highly tacky, so it was placed in a saturated NaCl solution and cured overnight at 85°C.

The membrane was rubbery and relatively strong after the cure in NaCl solution. The resistivity at 25°C was 98 ohm-cm when the membrane was equilibrated in 1 M HCl. The transference number for chloride ions was 0.73 (measured between 1.0 and 0.5 M HCl).

Unsuccessful attempts were made to prepare crosslinked membranes by the copolymerization of 2-vinylpyridinium sulfate and diallydimethylammonium iodide in 2-propanol with benzoyl peroxide as a catalyst. Attempts to prepare solid membranes from mixtures of diallyldimethylammonium iodide and 2-vinylpyridine with 2-propanol as solvent were also unsuccessful with benzoyl peroxide, methylethylketone peroxide, and azobisisobutyronitrile (AIBN) as catalysts.

The results of the experiments with the CEVE membranes showed promise for obtaining physically strong membranes, but unfortunately time and funds in the contract were exhausted.

IV. CONCLUSIONS

In this research program to develop anion-exchange membranes of low resistivity and high selectivity for use in acidic media in a redox energy-storage system being developed by NASA, the main conclusion is that none of the membranes had acceptable physical characteristics for use in the proposed energy-storage system. Only one of the experimental membranes (a membrane based on poly-4-vinylpyridine prepared by Method C) was strong enough for use, and this membrane had such a wrinkled surface and was so distorted in the planar dimensions that its utility in clamped cells is doubtful. With further effort it appears possible that an undistorted, wrinkle-free membrane with low resistivity might be developed from the poly-4-vinylpyridine system, and that the membrane might have great utility for uses other than the proposed redox energy-storage system. However, unless the transference number (i.e., selectivity) in 1 M HCl could be greatly improved, the usefulness of the membrane for the redox energy-storage cells is highly unlikely.

APPENDIX A

Relationship of Polymer Structure to Membrane Properties

Rigorous thermodynamic treatments of the equilibrium between ion-exchange membranes and solutions, such as those developed by Kieland (ref. 8), and by Gaines and Thomas (ref. 9), are quite general and correct, but they reveal little about the physical causes of equilibrium phenomena. Therefore, models with particular properties resembling those of an ion exchanger have been introduced for deriving equations that reflect the action of various physical forces. As the sophistication and complexity of the models increased, the amount of information that could be obtained about the relationship between structure and properties also increased. But the difficulty of using the mathematical expressions also increased, since their use required the measurement of more and more physical features of the polymers, and the features become more and more difficult to measure. The models that are based on molecular considerations are more revealing than the models based on more macroscopic considerations (ref. 10, 11, 12, 13).

Models based on considerations on a molecular scale were first developed by Katchalsky and his students (ref. 14, 15, 16). These models for weakly crosslinked and weakly ionized polyelectrolytes, are not directly applicable to modern ion-exchange membranes. The later developments of Rice and Nagasawa (ref. 17), more nearly explain the behavior of the strongly crosslinked and strongly ionized resins that would be applicable for the proposed redox cell.

The theoretical developments of Rice and Nagasawa are based on a model for ion-exchange resins in which the resins are considered as polyelectrolyte gels with the following five properties. First, the gel contains fixed-charge moieties that either bind exchangeable ions or remain unfilled; and at the unfilled sites, electroneutrality is maintained by counterions in the interstitial solution near the sites but not bound to them. Second, neighboring fixed charges interact electrostatically with allowance for shielding by mobile counterions; each exchange site (fixed charge group) is treated as a point charge. Third, the gel assumes an equilibrium volume that depends on the electrostatic repulsions of the fixed-charge sites, and on the forces characteristic of an uncharged three-dimensional network of polymer chains. Fourth, the total amount of ion binding is such as to minimize the free energy, including contributions of binding, charge interaction, distribution of bound ions among the sites, and configurational free energy. And fifth, no differentiation exists with the resin as to unbound ions; that is, the ratio of different kinds of unbound counterions of the same valence, (*i.e.* Cl^-, Br^-) within the interstitial volumes of the resin is the same as their ratio in the external solution, while the ratio of the bound ions within the resin may or may not be the same as in the external solution.

The mathematical developments of these authors were based in part on ideas developed previously by Katchalsky and his co-workers (ref. 14, 15, 16) for weakly crosslinked (highly swollen) gels of weak polyelectrolytes, such as poly(methacrylic acid). The Rice and Nagasawa theory is lengthy, and only the important features of the theory and the conclusions drawn from it will be discussed here (see ref. 17 for a complete discussion of the theory and validation of the model).

As shown by mathematical expressions based on the above model, binding of counterions to fixed charges, and the interactions between neighboring fixed charges, are dominant factors in determining the behavior of ion-exchange resins. Moreover the interactions between fixed charges are affected by shielding provided by bound and unbound counterions, and the shielding by bound ions is stronger than that by unbound ions.

Some of the conclusions that follow from the Rice-Nagasawa model are:

- With a given degree of crosslinking, increasing the ion-exchange capacity increases the number of bound ions. An increase in ion-exchange capacity above a given value increases the fraction of bound ions and therefore decreases the fraction of unbound ions. Since the specificity of a resin (i.e. the preference for one kind of ion over another of the same valence) is related to the ratio of bound to unbound ions (Item 5 in the model), the specificity of a resin increases with increasing capacity.

- With a given number of fixed charges per repeating polymer unit, increasing the crosslinking density increases the number of fixed charge sites per unit of resin volume because crosslinking decreases the ability of the resin to swell. Therefore, an increase in the number of exchange sites per unit volume results from increased crosslinking. This causes the number of bound counterions, and thus the specificity to increase.

- The resistance to ion transport through an ion-exchange resin depends in part on the average number of charged groups per repeating polymer unit and in part on the crosslinking density. With a fixed number of charged groups per repeating polymer unit, increasing the crosslinking density increases the total number of counterions per unit of swollen volume (i.e. the molality of the interstitial solution) because the crosslinking decreases the swelling of the resin. However, increasing crosslinking density also increases the ratio of bound ions to unbound ions, and the number of polymer chains per unit of swollen volume. Increases in interstitial molality would tend to decrease resistance, but the increases in the ratio of bound to unbound ions would increase the relative number of ions that are retarded by electrostatic interactions with fixed charges. Ions that are so retarded require more energy to transport them. An increase in the number of polymer chains per unit of swollen volume by an increase in crosslinking density results in an increase in the amount of energy dissipated by collisions between moving ions and polymer chains, hence an increase in resistance. Thus, an increase in crosslinking density results in one factor that tends to decrease resistance, and two factors that tend to increase resistance. The result of the interaction of these factors on total resistance is not predictable by the theory developed to date.

The data developed by Hills, Kitchener, and Ovendon (ref. 3), for a series of resins with increasing crosslinking density illustrate the changes that occur with increasing crosslinking density of a resin with a given number of fixed charges per polymer repeating unit. The data are given in Table I.

Table I. Effects of Crosslinking on Membrane Properties

Percent Crosslinking	Interstitial Molality of Counterions	Volume resistivity, ohm-cm	Transference number for counterions[a]
5	2.84	9.3	-
10	4.03	11.6	0.92
15	4.41	10.9	0.95
20	4.71	10.3	0.98

(a) in 0.1 N KCl

As the crosslinking was increased from 5% to 10%, the resistivity increased, even though the interstitial molality also increased, but

> with further increases of crosslinking density, the resistivity decreased slightly. The data indicate that the goals of a highly selective resin ($t^-=0.98$) with resistivity of 20 ohm-cm or less appear to be attainable. Although the data are for cation-exchange resin, similar anion-exchange resins should be possible.
>
> Usually, with a fixed degree of crosslinking, swelling of an ion-exchange resin increases with an increase in the number of fixed charges. However, with a high number of fixed charges and high degrees of crosslinking, the probability of two or more fixed charges being on the same polymer segment (*i.e.* polymer chain between points of crosslinking) is high. The combined effects of fixed valence angles between atoms on the chain and of hindered rotation about bonds between atoms are to make fixed charges on the same polymer segment largely ineffective in expanding the polymer molecule. Therefore, with resins that have a large number of fixed charges, *at some high degree of crosslinking some of the fixed charges are not effective in swelling the resin and the amount of swelling is small*. (In addition, of course, the short polymer segments that occur with high degrees of crosslinking tend to limit swelling even if there are not multiple fixed charges on the same polymer segment.)

Three different theoretical approaches have been used to characterize ion transport: (1) the Nernst-Planck flux equations; (ref. 18, 19, 20) (2) the phenomenological equations of irreversible thermodynamics (ref. 21, 22, 23, 24) and (3) the theory based on the transport of ions from site to site (ref. 25, 26). Each of these theoretical approaches has limitations. The theory based on the Nernst-Planck equations requires detailed knowledge about the structure and thermodynamic properties of the ion exchanger, some of which are virtually impossible to measure. The theory based on irreversible thermodynamics makes use of membrane properties that can be measured, and reveals much about the macroscopic phenomena of ion transport, but it cannot be used to distinguish among the various types of ion transport or the effects on ion transport of structural features on a molecular level. The theory based on the statistical-mechanical aspects of site-to-site transport of ions requires even more detailed knowledge of membrane structure than the Nernst-Planck theory. Nevertheless, by the judicious use of assumptions, all three theoretical approaches have led to qualitative ideas about the effects of membrane structure on ion transport. These have been summarized by Eisenman, Sandblom and Walker (ref. 27).

Eisenman and his co-workers have discussed in depth the relationships between membrane structure and ion transport. Since their discussion supplements the theory of Rice and Nagasawa, some of the points brought out by Eisenman will be discussed.

There are four mechanisms of ion transport in homogenous membranes. They are: ion migration involving (1) a collision mechanism, (2) a site-to-site jump mechanism, (3) a carrier mechanism, and (4) a solvent drag mechanism.

Solid polymeric ion exchangers consist of interpenetrating three-dimensional networks of polymer chains and aqueous channels. The polymer chains have charged groups affixed to them. All solid polymeric ion exchangers can be considered to have only two variables: (1) the number of fixed charges on the polymer chains, and (2) the distances between the polymer chains (the interstitial distances). When the interstitial distances are sufficiently large, the effects of interactions between fixed charges and counterions on the transport processes are negligibly small. For exchangers with large interstitial distances the mobile ions move as though in an aqueous solution with a concentration of counterions at least equal to the concentration of fixed charge groups. With large interstitial distances coions may be expected to intrude into the aqueous channels. Therefore, coions and the counterions that accompany them contribute to the electrolytic conduction process. In this type of membrane the resistance to ion transport primarily involves dissipation of energy as a result of (1) collisions between moving ions and polymer chains, (2) collisions between moving ions and water (solvent drag), and (3) collisions between counterions and coions moving in opposite directions. Of these energy dissipative processes collisions between moving ions and polymer chains dissipate the most energy. Since there are relatively few polymer chains per unit of swollen volume the resistances of membranes with large interstitial spaces are low. The absolute magnitude of electrical resistance of a membrane depends on the fixed-charge density (i.e. the number of fixed charges per unit volume of membrane) since the fixed-charge density determines the concentration of counterions in the interstitial solution.

In exchangers with small interstitial distances (e.g. less than about 10Å), different factors are of importance to the ion-transport process. In such "tight" membranes much of the water in the interstitial volumes is associated with either the mobile ions or the fixed charges on the polymer chains by an ion-dipole type of association. Transport of ions through this "bound" water dissipates more energy than the transport of ions through "unbound" water (e.g. water in an aqueous solution). Moreover, most of the ions transported in the interstitial solution of a tight membrane pass so close to the fixed charges that the electrostatic interactions between moving counterions and fixed charges contribute strongly to energy dissipation. For this reason the mechanism of ion transport in tight membranes approaches a site-to-site jump mechanism. As might be expected, ion mobilities are greater if the fixed-charge sites have greater freedom of movement (sites in the middle of polymer segments that are in thermal motion or sites that are pendant to polymer chains) than if the fixed-charge sites are less free to move (sites on a polymer chain at or near a point of crosslinking). Also, ion mobilities are higher if the fixed-charge sites are close to each other than with greater distances between sites.

In tight membranes there are more polymer chains per unit of swollen volume than there are in "loose" membranes. Therefore, the energy dissipative effects of collisions between moving ions and polymer chains are greater for tight membranes than for loose ones.

All of the relationships between membrane structure, selectivity, and conductivity described in the preceding paragraphs were based on the assumption that the membrane structure was uniform. However, many of the commercially available membranes have been shown to be molecularly heterogenous (ref. 28, 29), and these heterogeneities affect the performance of the membranes. Figure 2 shows a representation of the type of heterogeneities thought to occur in membranes made by addition polymerization of styrene and divinylbenzene with subsequent chloromethylation and amination. Figure 2 was developed on the basis of inferences made from measurements performed for a typical commercial membrane containing 5% to 8% of divinylbenzene. In Figure 2 an attempt has been made to show areas in which the polymer chains are closely packed in a somewhat linear fashion. The close packing is thought to be due to interchain attractions of the van der Waals type. These areas are separated by areas in which crosslinking maintains a more open spacing of the polymer segments. These crosslinked areas are less ordered than the areas of close-packed polymer chains, and chloromethylation and amination will occur primarily in these regions. Also, the swelling of the membrane by water will occur primarily in the less-ordered regions. Thus, only a fraction of the total volume of this type of membrane is available for conduction. Moreover, the highly-ordered regions will cause greater tortuosity of the path the ions must travel. The conductivity of membranes could be increased if ways were found to eliminate these more ordered regions.

Block (ref. 29) made electronmicrographs of commercial membranes based on the chloromethylated-aminated styrene-divinylbenzene system (Asahi Chemical Industry's anion-selective membranes). His electronmicrographs showed inhomogeneities that could well have been of the nature shown in Figure 2. The electronmicrographs

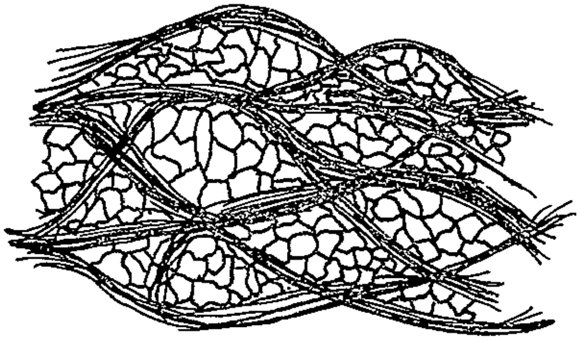


Figure 2. Representation of the Heterogenous Structure of Chloromethylated-styrene Based Membranes.

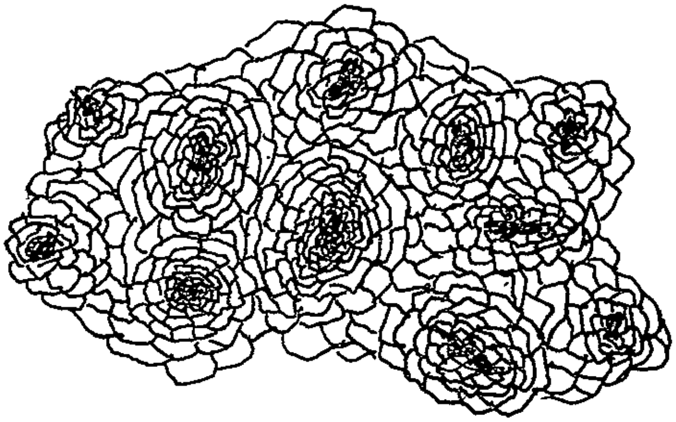


Figure 3. Representation of Sub-micro-heterogenous Nature of Condensation-type Ion-exchange Polymers.

also showed sub-microscopic voids in these membranes. The largest voids were less than 0.5 micron in maximum dimension. Block also made electronmicrographs of membranes made by graft polymerizing imbibed styrene onto polyethylene sheets and then chloromethylating and aminating. These membranes (American Machine and Foundry Company's A-60 membranes) also were heterogeneous on a sub-microscopic scale.

Koschel and Schogl (ref. 30) showed a different type of microheterogeneity for ion-exchange membranes made from condensation-type resins (e.g., guanidinium nitrate, melamine, and formaldehyde, or phenolsulfonic acid, phenol, and formaldehyde). In membranes based on condensation resins there are "micro-grains" surrounded by more amorphous areas. The "micro-grains" found by Koschel and Schogl for a phenolsulfonic acid ion exchanger were about 25 Å in diameter and the thickness of the amorphous regions between grains varied from about 10 to 50 Å, as represented in Figure 3. The micro-grains are thought to occur because the polymerization of condensation resins begins at many nucleation centers and grows outward from each nucleous. The polymer at the nucleation centers is "tighter" than the polymer formed later, which bridges from one nucleous to another. Regardless of the origin of the heterogeneity, the conductivity of the resin would be higher if the "micro-grains" were minimized or eliminated.

Requirements for Stability at High Temperatures in Acid Medium

The proposed anion-selective membranes must be stable to high temperatures (80°C) when bathed in acid solutions (pH=1). Studies of membranes for potential use in high-temperature electrodialysis (ref. 31, 32, 33) reveal the main requirements for stability of membranes at temperatures up to 90°C. Other studies made of electrodialytic processes in acidic media (ref. 34, 35) are informative about the requirements of membranes for use at low values of pH.

On the basis of Forgac's studies (ref. 31, 32) of membranes for high-temperature electrodialysis, a number of polymer systems might be suitable for forming the polymer matrix of membranes for use at high temperatures. Hydrolytic attack at the temperatures and conditions of use appears to be the main consideration in choosing a polymer for the matrix. Polymers with hydrolytically unstable groups, such as ester or ether groups, should be avoided. But polymers with carbon-to-carbon linkages in the backbone (e.g., polyolefins, polystyrene or polymers of halocarbons) should be satisfactory as matrix materials, and the choice of a polymer for the matrix will probably be made on a basis other than that of deterioration at high temperatures.

Initially, it was thought that if quaternary ammonium compounds were used as the positively charged groups, degradation would occur at high temperatures by the well known reaction in which a quaternary ammonium compound is split into a tertiary amine and an alcohol or an alkyl halide (depending on pH). Conversion of quaternary ammonium compounds into tertiary amines during use of an anion-exchange membrane might tend to decrease selectivity and increase resistivity. However, for the intended use at low values of pH tertiary amines should be strongly ionized, and the decrease in selectivity and increase in resistance would be slight.

This anticipated degradation of the transport properties of strong-base anion-exchange membranes did not materialize. Gregor showed that commercially available anion-exchange membranes* based on quaternary ammonium compounds were stable during storage in neutral and acidic solutions at 80°C for 8 months. Work performed later by Forgacs (ref. 32) confirmed Gregor's findings and expanded them to include special membranes** developed in Israel.

Kramer (ref. 33) and Lacey (ref. 34) used strong-base anion-exchange membranes in 1N H_2SO_4 at temperatures to 80°C. Kramer showed that anion-exchange membranes made by the American Machine and Foundry Co., and the Ionac Chemical Co., were slightly more stable at 80°C in acid than the membranes made by the Asahi Glass Co., the Asahi Chemical Industries Co., or Permutit, Ltd., London. Lacey showed that membranes made by the Ionac Chemical Co., and the Tokuyama Soda Co., Ltd., were stable in an acidic solution of $FeSO_4$ and $Fe_2(SO_4)_3$ at 70°C, but that the membranes made by the Asahi Glass Co., suffered mechanical disintegration at 70°C in that solution.

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*Selemion, Am-10(Asahi Glass Co., Yokohama), ACI type A membranes (Asahi Chemical Industries, Tokyo), AMFion 63 membranes (American Machine and Foundry Co., Stamford, Conn). TCX-2 membranes (Tokuyama Soda Co., Tokyo), and MA3148 membranes (Ionac Chemical Co., Birmingham, N.J.).

**Neginst PVC-TEPA and Neginst P.S.M. membranes (Negev Institute of Arid Zone Research, Beersheva, Isreal).

The membranes made by the American Machine and Foundry Co. are polyethylene films to which styrene is graft polymerized to about 30% by weight styrene. The anion-exchange membranes are formed by chloromethylation and amination of the styrene groups. The graft polymerization of the styrene has been done in two ways, one by a method involving chemical initiation (ref. 35) and one by a method involving irradiation (ref. 36).

The MC 3148 anion-exchange membranes of the Ionac Chemical Company are made by calendering a finely ground anion-exchange resin containing quaternary ammonium groups into a vinylidene fluoride polymer and incorporating the mixture into a textile scrim that increases mechanical strength (ref. 29).

The anion-exchange membranes of the Asahi Chemical Industries, Ltd., Co. are made by polymerizing blocks of styrene, divinylbenzene, and ethylvinylbenzene, with dimethyl phthalate plasticizer and benzoylperoxide as catalyst. Thin films are skived from the blocks of polymer in a manner similar to that used for making veneers for plywood. The plasticizer is extracted from the films, and the styrene groups are chloromethylated and aminated to form quaternary compounds (ref. 37).

The anion-exchange membranes of the Asahi Glass Co., are made by doctoring a styrene-butadiene latex onto a polypropylene cloth and drying. The linear styrene-butadiene chains are crosslinked in the presence of a Friedel-Crafts catalyst and the styrene groups are chloromethylated and then aminated to form quaternary ammonium compounds (ref. 34).

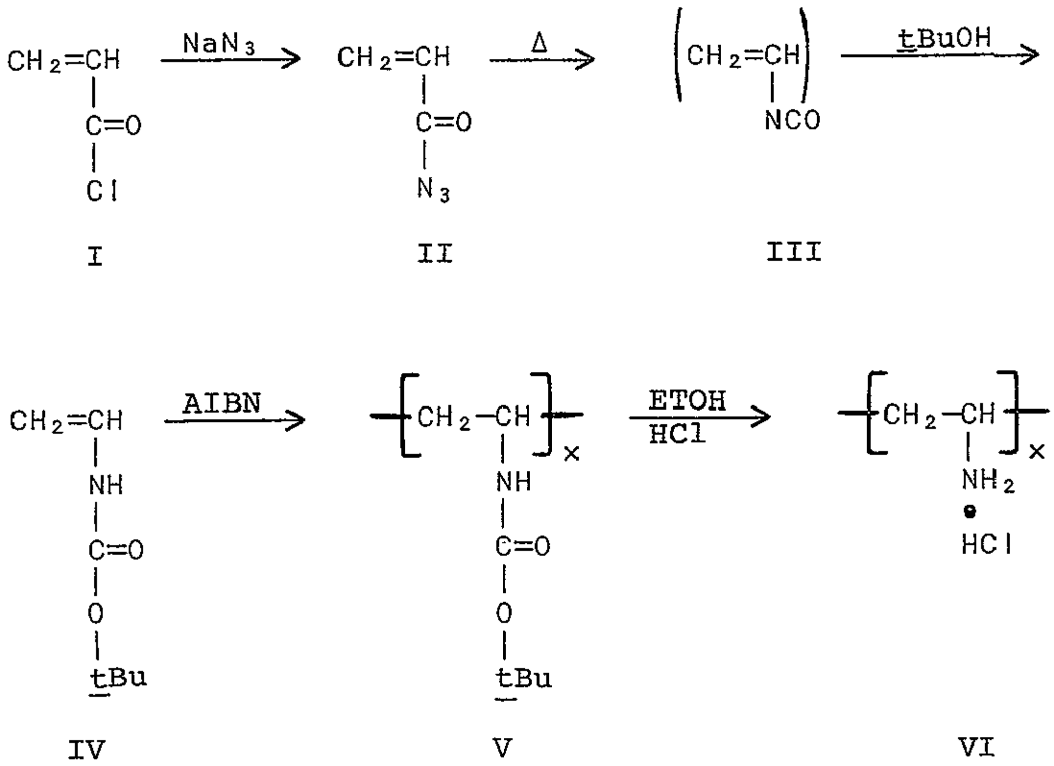
The anion-exchange membranes of the Tokuyama Soda Co., are made by reacting linear polyvinylpyridine with an epoxide oligomer, and then curing for 10 hours at 25°C. Quaternization of the pyridyl-groups and crosslinking occur simultaneously (ref. 29).

Thus, all of the membranes shown to be stable at high temperatures and under acid conditions contained quaternary ammonium groups on a carbon-to-carbon polymeric backbone.

APPENDIX B

Synthesis of Polyvinylamine Hydrochloride

A method for the preparation of polyvinylamine hydrochloride (VI Fig.) has been developed by Hughes and St. Pierre. (Macromolecular Syntheses, in press). Since this article has not appeared, a brief description of the synthesis is given below:



Reaction Series for the Synthesis of Polyvinylamine Hydrochloride

Preparation of Acrylyl Azide: (II)

A solution of 250 g of acrylyl chloride (I) in 700 ml of toluene was added dropwise to a stirred solution of 250 g of sodium azide in 600 ml of water. The reaction temperature was maintained at 0-5°C by the use of an ice bath. After the addition was complete (approximately 3 hr) the reaction mixture was allowed to stand at 0°C for an additional 3 hr. After the toluene layer was separated from the squeous phase, it was washed twice with two 250-ml portions of ice-cold 10°C sodium carbonate solution and then washed with cold water until the washings were neutral. The toluene layer containing acrylyl azide II was dried over $CaCl_2$.

Preparation of N-vinyl-t-butylcarbamate: IV

The solution of acrylyl azide in toluene described above was added dropwise to a solution of 7 g of m-dinitrobenzene in 50 ml of toluene which was heated to reflux. This first flask was connected by glass tubing to a flask containing 500 ml of redistilled t-butanol and 7 ml of pyridine which was in turn connected to a flask containing 250 ml of t-butanol and 5 ml of pyridine. The first flask was held at reflux during the reaction, the two flasks containing t-butanol were kept just above their freezing point. The addition of the acrylyl azide solution required approximately 4 hr. As the isocyanate (III) evolved it distilled into the flasks containing t-butanol and reacted with the t-butanol. The flasks containing t-butanol were allowed to stand overnight at room temperature to ensure complete reaction. The t-butanol solutions of N-vinyl-t-butylcarbamate (IV) were combined and poured over 2 liters of cracked ice. Finally, 5 liters of ice cold water was added and the product was collected by filtration. The product was washed several times with cold water and dried in vacuum. The yield of crude product was 140 g (35% yield). The product was purified by sublimation at 50°C and 1 mm pressure.

Polymerization

N-vinyl-t-butylcarbamate (20 g), 100 mg of azobisisobutyronitrile and 67 ml of redistilled hexane were combined in a round-bottom flask and purged with nitrogen for 30 min. The mixture was frozen with liquid nitrogen, and alternately evacuated and pressurized with nitrogen for 10 times. The flask was then heated at 606-65°C for 30 hr. Precipated polymer appeared after the first 10-12 hr. The polymer was dissolved in acetone, precipitated from hexane, collected by filtration, washed with hexane, and dried in vacuum. The yield of polymer (V) was 16.5 g (82.5% of theory).

Hydrolysis

Poly (N-vinyl-t-butylcarbamate) (V) (16.5 g) was dissolved in 100 ml of 95% ethanol. This solution was added dropwise to 200 ml of 1:1 ethanol/concentrated HCl with vigorous stirring. Hydrochloric acid was also added to the reaction mixture at the same rate as the solution of poly (N-vinyl-t-butylcarbamate) to keep the 1:1 volume ratio of ethanol/acid constant. After the addition was complete, stirring was continued for 6 hr. The product was separated by filtration and washed with acetone to give 9.9 g of poly(vinylamine hydrochloride) (VI), a 97% yield.

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