Polysulfone-Bonded Polyvinylpyridinium Membranes

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Synopsis

Polydivinylbenzene-4-vinyl-*N*-methylpyridinium iodide (MeVP$^+$-DVBI$^-$) membranes are obtained by solvent evaporation from dispersions of copolymer powder in polysulfone dichloroethane solutions. The membranes' macroporosity increases from 2.5 to 46.4% and the pore size distribution concentrates in the 10^3–10^5 Å range upon varying the concentration of polypyridinium polymer from 0 to 67% w/w. Similarly, the specific conductivity increases from 10^{-11} to 10^{-4} ohm^{-1} cm^{-1} and the mechanical strength decreases from 500 to 8.8 kg/cm^2. The ion selectivity is maximum at 40–50% MeVP$^+$-DVBI$^-$ and lower above or below this concentration range. The properties are discussed in relation to the membrane chemical and physical parameters.

INTRODUCTION

Vinylpyridine polymers are mostly known as polyelectrolytes.[1] Crosslinked vinylpyridine(VP)-divinylbenzene(DVB) copolymers (VP-DVB) are insoluble, nonmelting, chemically and thermally stable.[2] Quaternization of the pyridine nucleus yields a copolymer with fixed positive charges (RVP$^+$-DVB), anion-exchanging capacity, and higher wettability than the parent material.[3]

A major disadvantage of crosslinked polymers is mechanical rigidity. Thus, exploitation of the stability and anion-exchanging potential of VP-DVB for industrial applications (i.e., advanced water electrolysis,[4] air purification, and high temperature flue gas desulfurization processes[5]) requires the manufacture of composites (i.e., with asbestos or polyvinylidene fluorides) to yield mechanically flexible electrolytic separators or membrane sheets.

Polysulfone (PS)[6] is a chemically and thermally stable aromatic polymer, which has great mechanical flexibility. It acquires cation-exchanging properties and/or wettability upon sulfonation[7] or incorporation of hydrophilous oxides,[8] while still retaining its desirable mechanical feature. As a support matrix to make composites, this polymer is a valid alternative to toxic asbestos or expensive fluoride materials.

The analysis of the properties of RVP$^+$-DVB and PS has convinced us to undertake the design of the MeVP$^+$-DVB-PS composite where the desirable features of each component might be exploited to tailor the material properties according to industrial demands (i.e., production of ion-selective mem-

branes or electrodialysis membranes suited for use in treatment of metal-polluted waste-waters). This preliminary work was initiated with the intent to find out how the electrical transport and mechanical properties of the new composite were affected by changing the composition over the widest possible range of $MeVP^+$–DVB concentrations and to suggest further development steps.

EXPERIMENTAL

All reagents were C. Erba RPE products, unless otherwise indicated. The VP-DVB copolymer containing 2% mol/mol DVB was of the macroporous type which is synthesized in decaline.[3] Thus, 22.5 mL (~ 0.21 mol) of freshly distilled 4-vinylpyridine (Fluka reagent, 96% purity), 1.2 mL (~ 0.0042 mol) of divinylbenzene (Fluka reagent, 50% in ethylvinylbenzene) and 0.6 g of benzoylperoxide (Merck reagent, containing 25% water) are reacted in 22 mL decaline at 80°C under N_2 blanketing and stirring. A pink solid starts to form after 15 minutes. After 3 h the product is filtered, washed in a soxlet extractor with acetone, toluene, and acetone again, and finally dried at 50°C under vacuum to yield 17.63 g.

The copolymer was converted into its N-methylpyridinium ion form ($MeVP^+$–DVB) by N-methylation with methyl iodide,[5] using 50% mole excess of MeI over the stoichiometric requirement. Thus, 10 g of the VP–DVB copolymer are reacted with 8.77 mL (~ 20 g) of MeI in 70 mL of dimethylformamide under N_2 and stirring for 24 h. The yellow-green product is filtered, washed with Et_2O, and dried at 30°C under vacuum to yield 25.4 g.

The N-methylated copolymer was ground to a fine powder. The fraction passing through a 325 mesh size sieve was used for the preparation of the membranes. Udel polysulfone (Union Carbide), 1 g, was dissolved in the minimum amount (< 10 mL) of syn-dichloroethane. The desired amount of methylated copolymer powder was added under stirring. The membrane was obtained by room temperature evaporation of the solvent in a petri dish overnight. Last traces of solvent were removed by air drying at 30°C to constant weight. By this procedure rust-colored and visually homogeneous membranes were obtained with composition ranging from 0 to 75% w/w of $MeVP^+$-$DVBI^-$.

The potentiometric transport number was measured as previously reported[9] in a concentration cell having a fixed molar ratio of 2 between the membrane external aqueous KCl bounding solutions and by using Ag/AgCl(s)-KCl(s) electrodes.

The membrane 1 KHz a.c. electrical resistance in water was measured by pressing the membrane (5.5 cm diameter) between C-felt discs (4.5 cm diameter) in a sealed stainless steel case.[10] The case flanges were insulated from each other by silicon rubber gasket rings enclosing the C-felt discs and resting on the free edge of the membrane disc. After assembling the cell, CO_2-free deionized water was admitted to fill each half cell chamber space. The cell entrance and exit ports were then closed and the cell was placed in a thermostatted oven. The cell resistance was measured with a Philips PM6303 RCL meter after equilibrating the membrane in water for 24 h at each temperature.

The membrane-specific conductivity (χ, $ohm^{-1} cm^{-1}$) was calculated from the equation $\chi = L/RS$, where R = cell resistance, S = area of the membrane surface in contact with the C-felt disc, L = membrane thickness as in Table II.

Porosity and surface area measurements on the membranes and the copolymer powder were obtained by C. Erba mercury intrusion[11] Model 2000 porosimeter and Model 120 macropore unit.

All other experimental details are known.[3]

RESULTS AND DISCUSSION

Cross-Linked Polyvinylmethylpyridinium Iodide

The elemental analyses of VP-DVB copolymer (found: C 79.98, H 6.73, N 12.64% w/w; theor.: C 80.30, H 6.73, N 13.00% w/w) and of its methylated derivative (found: C 38.39, H 4.38, N 5.29, I 50.9% w/w; theor.: C 39.44, H 4.14, N 5.61, I 50.8% w/w) were close to the theoretical calculations for 2 mol% content of DVB and 100% degree of N methylation.

The methylated copolymer was identified from its infrared (IR) spectrum. The pyridinium methyl C-H stretching band was observed at 3030 cm^{-1}. Methyl stretching vibration bands usually fall below 3000 cm^{-1}. Absorption frequencies above 3000 cm^{-1} are typical for ionized methyl ammonium salts.[12] The 3030 cm^{-1} band was of medium intensity and overwhelmed the weak bands due to the vibrations of the ring (at 3020 and 3070 cm^{-1}) and methylene (at 2850 and 2930 cm^{-1}) C-H bonds. By comparison the parent copolymer spectrum contained only the above weak bands and no band at 3030 cm^{-1}. The C = C and C = N ring-stretching bands of the methylated copolymer fell at higher frequencies (ν = 1520 m, 1575 m, and 1645 s)* than those of the parent copolymer (ν = 1495 w, 1552 w, 1599 s). Similar positive frequency shifts, although not as large, have previously been reported for metal halides (X) complexation of the ring nitrogen of pyridine and formation of polarized $\overset{\delta+}{>} N \rightarrow X$ functions.[13] The magnitude of the frequency shift observed with the N-methylated copolymer is due to the stronger electron-withdrawing effect exercised on the ring by the ionized $\overset{+}{>} N$ —Me function. In agreement with the above results of elemental analysis, the absence of the parent copolymer ring bands in the IR spectrum confirms that nearly all pyridine rings in the methylated copolymer product are present in ionized salt form.†

The salt structure of polyvinylpyridinium iodide was found to be associated with a decrease of thermal stability relative to the parent copolymer. Thermal gravimetric analyses (TGA) scans performed in nitrogen or air (100 mL/min) at 10°C/min showed that the methylated copolymer undergoes thermal

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*s = strong, m = medium, w = weak intensity band.

†By comparison, the reaction of the VP-DVB copolymer with stoichiometric amounts of MeI yields a partially methylated product as confirmed from the presence of both main ring-stretching bands at 1600 and 1645 cm^{-1} in the IR spectrum.
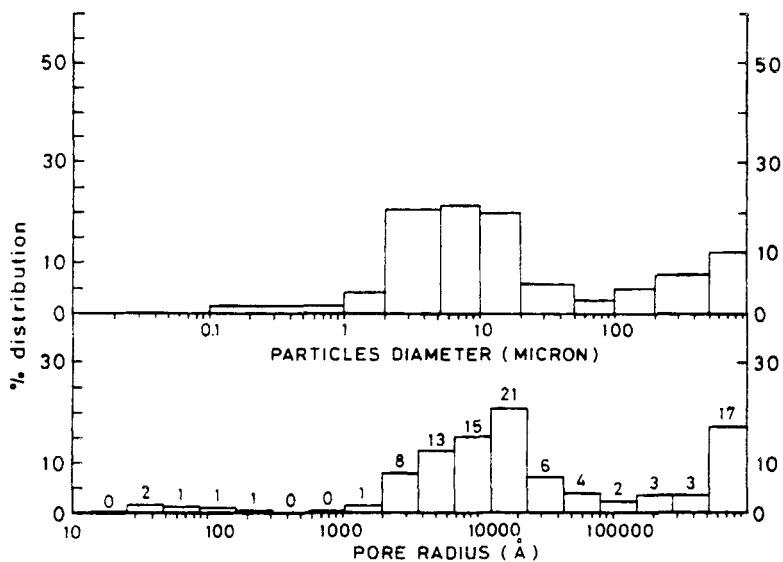
Fig. 1.   Pore size and particle size distribution in polyvinylmethylpyridinium iodide powder.

decomposition with weight loss starting from 200°C. The parent copolymer
was stable up to 320°C in nitrogen and up to 250°C in air.

The physical microstructure characterization of the polyvinylpyridinium
powder which was used to manufacture the composite membranes revealed
that the powder was made of particle aggregates with diameter ranging from
0.1 to 1000 μm, 60% having 2–20 μm diameter (Fig. 1). The powder total
porosity was 41%, nearly all of which concentrated in the range above 10^3 Å
pore radius and associated with aggregates interparticle void fraction.

Polysulfone-Polyvinylmethylpyridinium Membranes
Membrane Preparation

Due to the insolubility and nonmelting properties of VP-DVB, for the
manufacture of polyvinylpyridinium membranes in the form of flexible me-
chanical sheets, two procedures were evaluated: (a) "in situ" polymerization
of the VP and DVB monomers sorbed in a porous mechanically flexible
support in membrane form and methylation of the "in situ" grown polymer,
and (b) dispersion of previously synthesized polyvinylpyridinium iodide powder
in the solution of a film-forming polymer and solvent evaporation to cast the
composite membrane.

The in situ polymerization of VP-DVB has already been reported to be
successful for the manufacture of asbestos-VP-DVB electrolytic separators.[3]
This procedure, however, has been found very sensitive to the nature of the
host phase when other support articles are tried out. A separate investigation
seems necessary to look into the synthesis aspects. The second procedure
yielded almost immediate results which have allowed preliminary structure-
properties investigation to be conducted.

(A)

(B)

Fig. 2.   SEM micrographs at 1000 X magnification (— = 10 μm) of 25 (A), 50 (B), and 67 (C) %
MeVP$^+$-DVBI$^-$ membranes.

Chemical and Morphological Structure

Membranes behavior is a function of chemical and physical factors. In the polysulfone-polyvinylpyridinium composite membrane, polyvinylpyridinium is understood to represent the chemically active component. The ionized salt structure of the pyridine ring is expected to contribute water wettability, low electrical resistance (due to the mobility of the skeleton negative counter-ion), and anion selectivity in aqueous electrolytes (due to the ability of the positive fixed charge to reject migration of the electrolyte-positive co-ions through the membrane). Polysulfone is intended to be a bonding material to incorporate polyvinylpyridinium particles in a mechanically flexible membrane structure.

The presence of ionized polyvinylpyridinium functions in the membrane was confirmed by the 1645 cm^{-1} band in the IR spectra of the membranes. The relative intensity of this band correlated with the expected $MeVP^+$-$DVBI^-$ concentration in the membrane.

The membrane morphology and physical microstructure revealed important features for the explanation of the membrane properties. The scanning electron micrographs (Figs. 2 and 3) clearly show that the membrane morphology is strongly dependent on the relative concentrations of the two components. Polyvinylpyridinium particles are incorporated in the polysulfone matrix layer and become more and more distinct as their concentration increases. At 67% $MeVP^+$-$DVBI^-$ concentration, the particles are distinctly visible; most of them are ~ 1-2 μm in diameter. It appears, therefore, that during the membrane manufacture, the large polyvinylpyridinium aggregates constituting the powder (Fig. 1) break down into smaller particles upon dispersion in
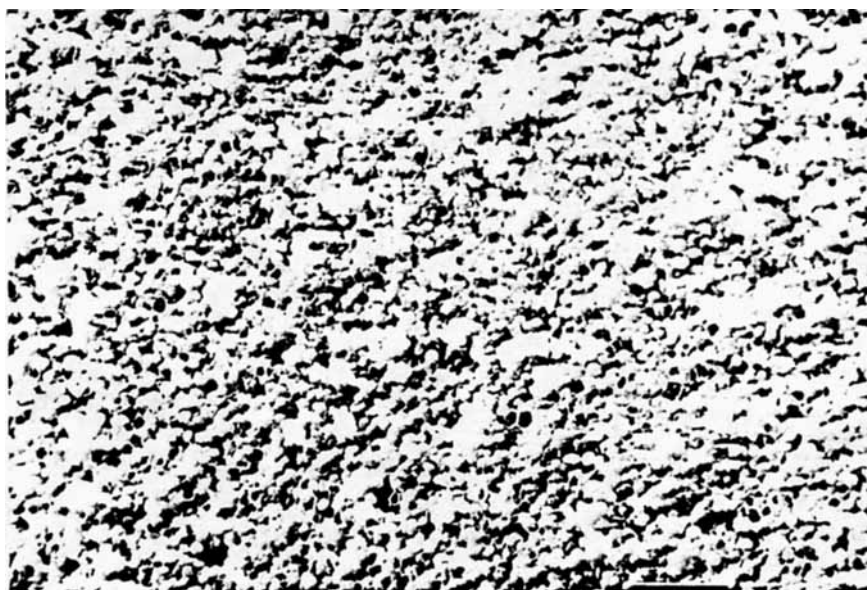
(C)

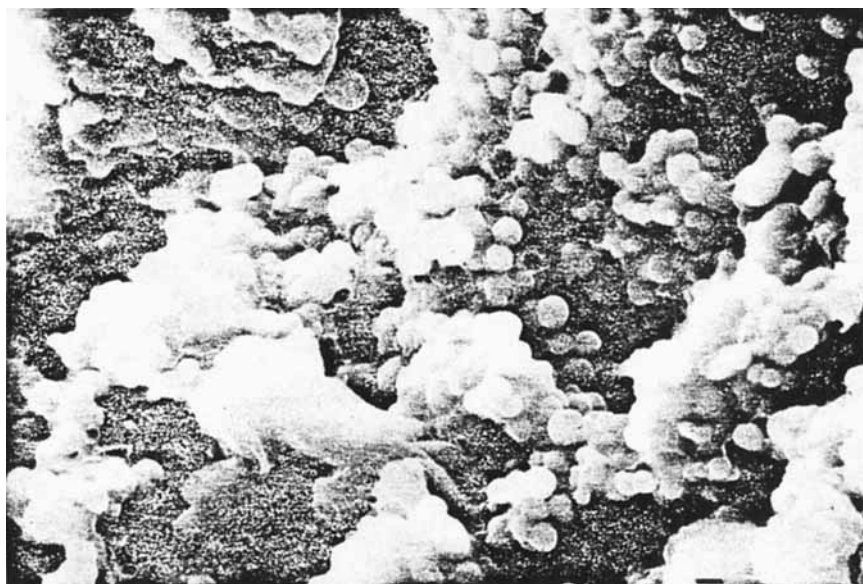Fig. 2. (*Continued from the previous page.*)
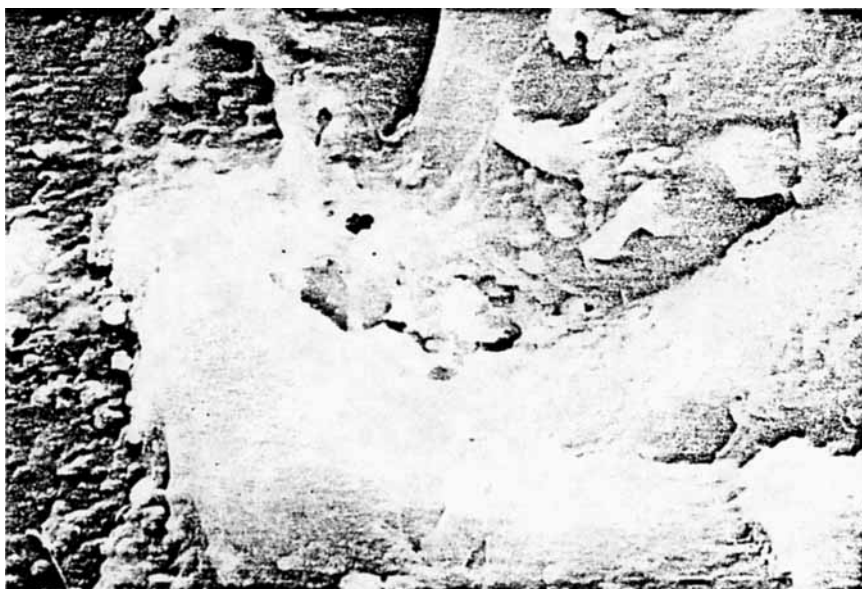
(A)

(B)

Fig. 3.   SEM micrographs at 2500 X magnification (— $\approx$ 1 μm) of 25 (A), 50 (B), and 67 (C) % MeVP$^+$–DVBI$^-$ membranes.

(C)

Fig. 3. *(Continued from the previous page.)*

the membrane-casting solvent and are subsequently bonded to each other by polysulfone when the solvent is evaporated.

The micrographs also show the presence of pores of variable diameter (10^3–10^5 Å) at each MeVP$^+$-DVBI$^-$ level. Significant is the fact that the total porosity and the relative concentration of the larger macropores ($> 10^4$ Å diameter) increase as the concentration of bonding material decreases.

Table I reports the quantitative pore distribution in the 37–2.10^6 Å range and the total specific surface area obtained by mercury intrusion for the composite membranes containing up to 67% MeVP$^+$-DVBI$^-$ copolymer. The

TABLE I
Physical Microstructure of MeVP$^+$–DVBI$^-$ Membranes by Mercury Intrusion Technique

VP[a] %w/w	Pore radius Å	% Porosity distribution				%TP[b]	%MP[c]	SA[d] m²/g
		≥ 37–10^3	$> 10^3$–10^4	$> 10^4$–10^5	$> 10^5$			
00		5.4	1.8	0.0	0.7	7.9	2.5	9.9
25		9.4	2.2	1.5	3.0	17.1	6.7	13.0
40		5.7	4.9	0.0	0.0	10.6	4.9	10.9
50		31.8	17.0	3.3	3.3	55.1	23.6	22.8
67		4.6	9.3	36.6	0.5	51.0	46.4	9.6

[a] MeVP$^+$–DVBI$^-$ % in the membrane.
[b] total porosity in the 37–$2 \cdot 10^6$ Å range.
[c] total macroporosity in the $> 10^3$–$2 \cdot 10^6$ Å range.
[d] specific surface area.

data confirm that the total porosity increases with the polyvinylpyridinium concentration in the membrane and that the pore distribution shifts toward the region of macroporosity ($> 10^3$ Å). Very significant for the membrane properties discussed below is the macro- rather than the total porosity % and the comparison between the 50 and 67% $MeVP^+$-$DVBI^-$ membranes. In the 50% membrane the high concentration of micropores ($\sim$ 32%) results in the highest value for the cumulative pore-specific surface area ($\sim$ 23 m^2/g). In the latter membrane, the high level of macroporosity ($\sim$ 46%), most of which (37%) is concentrated in the 10^4–10^5 Å range, yields the lowest pore-specific surface area.

Properties

All membranes up to 67 $MeVP^+$-$DVBI^-$% exhibited excellent mechanical flexibility and could be bent at almost 180 degrees angle without breaking or cracking. Membranes with higher concentration of $MeVP^+$-$DVBI^-$ were not considered further because they are very fragile and cannot be handled. Table II shows a strong decrease of tensile strength (Ts) with the increase of $MeVP^+$-$DVBI^-$% in the membrane. The decreasing tensile strength is not necessarily to be ascribed to poor mechanical properties inherent with the nature of the pyridine copolymer. For a large part the phenomenon is likely to be due to the increase of void fraction in the membrane structure (Table I). In a different VP-DVB composite made of porous asbestos cardboard and in situ synthesized VP-DVB, Ts was found to increase with the VP-DVB content of the membrane. In this case the copolymer grows over the support matrix fibers and into the structural pores, thus behaving as a pore-filling and bonding agent. It is therefore likely that $MeVP^+$-$DVBI^-$-PS composites obtained by a similar in situ polymerization technique will exhibit very different mechanical properties from the herewith described polysulfone-bonded material.

Figure 4 reports the wettability of the membranes as measured by the weight regain of the dry membrane after 24 h equilibration in water. The neat PS membrane is absolutely nonwettable, but the composite membranes absorb significant amounts of water. Water may be chemisorbed by chemical interaction with the composite materials (in this case with polyvinylmethyl-

TABLE II
Tensile Strength (Ts, kg/cm^2) and Elongation to Break (Eb, %) for
$MeVP^+$–$DVBI^-$–PS Membranes

VP[a] %w/w	W[b] cm	Th[c] cm	Eb %	Ts kg/cm^2
00	1.00	0.009	8.9	502
25	0.99	0.015	6.7	401
40	0.94	0.010	5.0	236
50	1.00	0.015	11.1	177
67	0.97	0.024	3.3	8.8

[a] $MeVP^+$–$DVBI^-$% in the membrane.
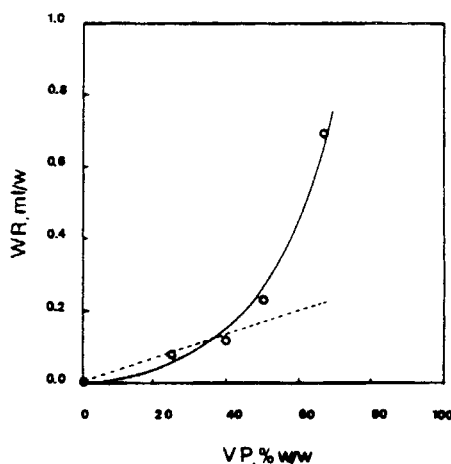[b] sample width.
[c] sample thickness.

Fig. 4. Water regain (WR, mL of sorbed water per gram of dry membrane) vs. polypyridinium iodide concentration (VP %w/w) in dry membrane.

pyridinium iodide) or may simply occupy the membrane void volume. Polysulfone is chemically lipophilic, nor does the physical microstructure of the neat PS membrane contribute any significant water entrapment in the structure. The 25 and 40% MeVP⁺-DVBI⁻ membranes resemble each other from the microstructure point of view and are not greatly different from the neat PS membrane (Table I). However, the water absorption increases significantly and appears to vary linearly with the concentration of polyvinylpyridinium iodide. The slope of the water regain versus polyvinylpyridinium concentration up to 40% MeVP⁺-DVBI⁻ appears constant and equal to ~ 4.1 moles of sorbed water per salt function equivalent. In these membranes, therefore, chemisorption seems to be the main water sorption mechanism. Physisorption is likely to contribute negligibly to the water wettability in the 0–40% MeVP⁺-DVBI⁻ range. At higher polyvinylpyridinium concentration, the water regain increases exponentially and the calculated moles of sorbed water per membrane salt equivalent are 6.5 and 14.0 at 50 and 67% MeVP⁺-DVBI⁻, respectively. The excess water sorption over the amount predicted by the linear portion of the plot is likely to represent all physisorbed water. Furthermore, this excess appears to be related to the level of macroporosity (i.e., the total porosity fraction due to pores with $> 10^3$ Å radius) rather than to that of total porosity. It seems therefore that the main parameters governing the water wettability of the MeVP⁺-DVBI⁻-PS membranes are the polyvinylpyridinium ion concentration and the membrane macroporosity above 10^3 Å.

   The membrane water content is very important in connection with the electrical properties. Table III reports the specific conductivity of the membranes in the ambient 60°C temperature range. The apparent activation energies compare with the values reported for other anion-exchange membranes[5] (i.e., 19.6 Kj mol⁻¹ for 75% polyvinylpyridinium carbonate in polyvinylidene fluoride matrix and 24.5 Kj mol⁻¹ for commercial divinylbenzene-crosslinked polystyrene with quaternary ammonium exchange groups). For the MeVP⁺-DVBI⁻-PS membranes, ionic conduction is also inferred from

TABLE III

Specific Conductivity (χ, ohm^{-1}, cm^{-1}) of MeVP$^+$–DVBI$^-$–PS Membranes in Water at Variable Temperature

VP [a]	I [b]		χ, ohm^{-1}, cm^{-1}			$-E$ [c]
%w/w	mEq/g	T, °C	22	40	60	Kj/mole
00	0.00		$9.9 \cdot 10^{-11}$	$10.5 \cdot 10^{-11}$	$11.5 \cdot 10^{-11}$	3.2
25	0.95		$1.1 \cdot 10^{-9}$	$1.4 \cdot 10^{-9}$	$1.6 \cdot 10^{-9}$	8.9
40	1.45		$1.4 \cdot 10^{-7}$	$2.2 \cdot 10^{-7}$	$3.0 \cdot 10^{-7}$	16.5
50	1.64		$1.1 \cdot 10^{-4}$	$1.6 \cdot 10^{-4}$	$2.6 \cdot 10^{-4}$	19.0
67	1.61		$2.0 \cdot 10^{-4}$	$2.7 \cdot 10^{-4}$	$3.8 \cdot 10^{-4}$	13.9

[a] MeVP$^+$–DVBI$^-$% in the dry membrane.

[b] Iodide ion mEq/g of wet membrane.

[c] Apparent activation energy from log χ vs. $1/T$ (°K^{-1}) linear regressions (correlation coefficients $\geq$ 0.99).

the strong dependence of the specific conductivity on the concentration of polyvinylpyridinium functions in the wet membrane phase. In reality the membrane ionic conductivity is expected to depend on the concentration and mobilities of the dissociated ions in the membrane phase. Ions coming from the dissociation of the sorbed water are estimated in very low concentration (10^{-11}–10^{-12} eq/g) in the wet membrane phase. It is more likely that the main contributors to the increase of conductivity are the membrane skeleton counterions. The water function in the membrane phase is mainly that of changing the medium viscosity and the electrostatic interaction between the skeleton fixed charge and its counterion, thus influencing the mobility and concentration of the latter.

All polypyridinium membranes of this work appear to have anion selectivity. The potentiometric transport number in $2.3 \cdot 10^{-5}$–1.5 M aqueous KCl is shown to be from 0.74 to 1.0 (Fig. 5), depending on the MeVP$^+$–DVBI$^-$ concentration in the membrane and on the external electrolyte concentration. For all membranes, the selectivity decreases on increasing the electrolyte concentration. This phenomenon, which is common to all ion-selective membranes, is known to be associated to the presence of external electrolyte co-ions (with the same sign of the skeleton-fixed charge) in the membrane phase due to salt invasion.[9] The effects of the membranes structural diversities on the ionic transport number are more evident in the low electrolyte concentration range. At $2.3 \cdot 10^{-2}$ M, the transport number reaches a maximum value of ~ 1 for the 40–50% MeVP$^+$–DVBI$^-$ membranes. The 25 and 40% MeVP$^+$–DVBI$^-$ membranes have similar physical microstructure (Table I). Therefore, the increase of the transport number in this case is well explained based on the increase of the fixed positive charge concentration in the membrane and on the expectation of increasing electrical repulsion for the electrolyte co-ion. The highest ion selectivity is still maintained for the 50% MeVP$^+$–DVBI$^-$ membrane. Here the development of the high level of membrane macroporosity (Table I) should lower the ion selectivity, but it is probably still compensated by the fixed charge concentration effect. In the 67% MeVP$^+$–DVBI$^-$ membrane, the macroporosity effect evidently overwhelms by far that of the fixed charge concentration and the selectivity
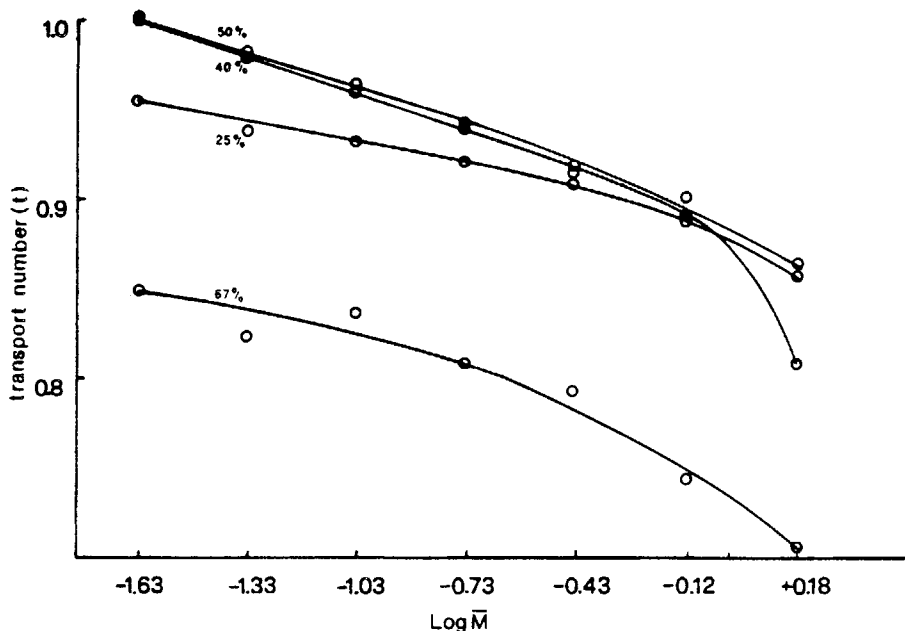
Fig. 5. Potentiometric transport number (t) of 25, 40, 50, and 67% MeVP$^+$–DVBI$^-$ membranes in aqueous KCl at room temperature; $\overline{M}$ = mean molar concentration of the membrane-bounding solutions.

reaches the lowest value. Here a large concentration of macropores ($> 10^4$ Å) is present and the available concentration of skeleton-positive charge on the pores' surface is probably insufficient to inhibit the migration of K$^+$ ions through the membranes phase.

CONCLUSIONS

Polyvinylmethylpyridinium membranes, crosslinked with divinylbenzene, have been manufactured in the form of mechanically flexible sheets by bonding the polymer powder with polysulfone. This procedure yields membranes with variable porosity (7–55%) and pore size (37–2 · 10^6 Å) depending on the concentration of polyvinylpyridinium in the composite membrane (0–67%). Particularly the pore size distribution has been found to shift to and concentrate in the 10^3–10^5 Å range for MeVP$^+$–DVBI$^-$ concentrations $\geq 50\%$ in the membrane. This change of physical microstructure with polyvinylpyridinium concentration in the polysulfone-bonded membranes appears to be specifically connected with the membrane preparation procedure. In another case, where the VP-DVB copolymer was synthesized in a porous asbestos host phase, porosity was found to decrease on increasing the concentration of the guest polymer.

The MeVP$^+$–DVBI$^-$–PS membrane properties have been found to depend both on its chemical and physical nature. The membrane-fixed charge concentration is directly related to the specific conductivity and the anion selectivity by supplying conducting counterions in the membrane phase and

repelling external co-ions. Macroporosity, vice versa, is beneficial only to the specific conductivity by enhancing the membrane water uptake. Large macropores, however, enhance also the uptake of electrolyte salts and decrease the membrane anion selectivity. Finally, the increase of the membrane-void fraction has been shown to lower dramatically mechanical strength.

Possible structural changes, achieved by coating mechanically flexible porous support with polyvinylpyridinium, should allow to combine further the chemical and physical parameters in the membrane and tailor the properties according to specific applications.

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