

## Electrochemistry of Poly(Methyl Vinyl Ether-Maleic Anhydride)-Polyvinyl Alcohol Membranes

H. G. SPENCER and O. L. HUNT\*

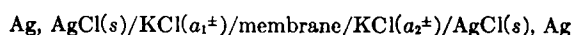
*Department of Chemistry, Clemson College, Clemson, South Carolina*

The ultrafiltration properties of baked poly-(methyl vinyl ether-maleic anhydride)-polyvinyl alcohol membranes have been presented.<sup>1</sup> This account presents their electrochemical properties.

### Experimental Procedures

The membranes were cast from aqueous solutions and rendered insoluble by baking in a drying oven at  $110 \pm 5^\circ\text{C}$ . as described previously.<sup>1</sup> The poly(methyl vinyl ether-maleic anhydride) (PVM/MA) was a high viscosity polymer obtained from General Aniline and Film Corp. The polyvinyl alcohol (PVA) was Du Pont, Grade 72-60, a high viscosity, greater than 99% alkaline-hydrolyzed polymer. The compositions are designated by the carboxyl group fraction  $X_f$ , i.e., the fraction of the hydrophilic groups, carboxyl plus hydroxyl, which are carboxyl.

Concentration potentials were determined over the range of 0.00196*m* to 0.721*m* using cells of the type:



where  $a_1^\pm$  and  $a_2^\pm$  are the mean ionic activities. The mean ionic activity ratio,  $a_1^\pm/a_2^\pm$ , was  $3 \pm 0.01$  for all measurements. The solutions were passed through the cell at a rate of 160 ml./min. while measurements were being made. This rate was such that a large additional increase in flow rate was required to increase the potential significantly. The temperature was controlled at  $30 \pm 0.1^\circ\text{C}$ . The measuring circuit employed a Gray Instrument Co., model E-3040, three-range potentiometer with a Rubicon galvanometer which had a sensitivity of  $1.39 \times 10^{-6}$  amp./mm. Readings were made at one hour intervals following a conditioning period of several hours. The potential values of subsequent measurements were reproducible within  $\pm 0.02$  mv., except for the pure PVA membranes,

\* Based on the M.S. thesis of O. L. Hunt, February 1961.

for which the reproducibility was only  $\pm 0.3$  mv. Measurements were made over the concentration range and then repeated for the initial pair of solutions. This final measurement duplicated the initial reading within the limits specified above.

The bi-ionic potentials were evaluated using the same cells and conditions. The mean ionic activities of the solutions were the same, with the concentrations approximately 0.02*m*. All potentials were repeated using new membranes and electrodes within an accuracy of  $\pm 0.2$  mv.

The membrane resistance was measured in a similar cell with a film area of 3.8 cm.<sup>2</sup>, but with platinized platinum electrodes. The measurements were made at  $30 \pm 0.1^\circ\text{C}$ . using a 0.1*M* KCl solution with a 1000-cycle/sec. Wheatstone bridge. Several days of conditioning between KCl solutions of different concentrations were required before consistent readings were obtained. The specific resistance was determined by taking the difference between the reciprocal of the specific conductances of the cell obtained with and without a membrane.

The osmotic flow rates were determined using a simple osmometer described by Gregor et al.<sup>2</sup> The osmometer, which contained a small volume of water, was placed in contact with a much larger volume of a 1*M* sucrose solution, which was stirred vigorously. The rate of loss of water from the osmometer was observed. Extrapolated values are reported for the PVA since the sucrose leaked through these membranes and the flow rate decreased with time. The flow rates are reported as microliters per hour per square centimeter of membrane area ( $\lambda/\text{hr.}/\text{cm.}^2$ ).

The thickness of the membranes was measured with a micrometer caliper to an accuracy within  $\pm 0.4 \mu$ . The thickness at room conditions and per cent swelling in a 0.1*M* KCl solution are reported.

## Results

The characterization data for the PVM/MA-PVA membranes are summarized in Table I. The concentration potentials for the series of solutions are listed in Table II. The maximum concentration potential was calculated to be 57.4 mv. using the modified Nernst equation with  $T^+ = 1$ , and  $(a_1^{\pm}/a_2^{\pm}) = 3$ ,

TABLE I

Characterization Data for the PVM/MA-PVA Membranes

Membrane	Baking time, hr.	Specific resistance, ohm-cm.	Osmotic flow rate, $\lambda$ /hr./cm. <sup>2</sup>	Thickness, $\mu$	Swelling, %
0.00	2	0.9	290	25.0	52
0.05	2	2.4	85.4	20.0	34
0.10	2	2.0	55.0	23.5	8
0.15	2	2.4	14.8	25.0	2
0.00	36	1.1	298	24.1	41
0.05	36	3.7	43.0	24.0	6
0.10	36	3.3	23.6	25.4	2
0.15	36	3.7	4.6	24.0	1
0.00	84	0.7	295	23.6	41
0.05	84	3.5	32.0	24.0	10
0.10	84	3.9	11.6	23.0	2
0.15	84	4.3	4.1	25.0	0

$$e = \frac{2T^+RT}{F} 10^3 \ln (a_1^{\pm}/a_2^{\pm}) \quad (1)$$

where  $e$  is the e.m.f. of the cell in mv.;  $T^+$  is the transport number of the cation in the membrane;

and  $R$ ,  $T$ , and  $F$  have their usual significance. Equation (1) assumes the transference number of water in the membrane to be zero.<sup>3</sup> The value of  $T^+$  for any membrane is given by  $T^+ = e/57.4$ . Table III contains the bi-ionic potentials for four membranes which exhibited near-maximum concentration potentials. The transport number ratios are also included in this table. They were calculated using the equation introduced by Sollner,<sup>4</sup>

$$e = \frac{RT}{F} 10^3 \ln (T_1^+/T_2^+) \quad (2)$$

TABLE III  
Bi-ionic Potentials and Transport Number Ratios for Univalent Ions in Selected Membranes

Membranes	Baking time, hr.	Solution pairs			
		KCl NaCl	KCl LiCl	KCl (CH <sub>3</sub> ) <sub>4</sub> NCl	HCl KCl
Bi-ionic Potentials, mv.					
0.10	36	7.71	14.81	56.86	103.46
0.10	84	7.02	12.77	63.12	112.21
0.15	2	8.37	17.97	25.10	73.46
0.15	84	8.01	15.55	67.86	116.34
Transport Number Ratios					
		$T^+_{K}/T^+_{Na}$	$T^+_{K}/T^+_{Li}$	$T^+_{K}/T^+_{(CH_3)_4N}$	$T^+_{H}/T^+_{K}$
0.10	36	1.34	1.76	8.75	52.5
0.10	84	1.31	1.63	11.2	74.3
0.15	2	1.37	1.99	2.62	16.6
0.15	84	1.36	1.81	13.35	87.5

TABLE II  
Concentration Potentials of the Membranes for the Series of Solution Pairs

Membranes	Baking time, hr.	$e^a$ in mv. for solution pairs, $m$				
		0.721	0.2104	0.0627	0.0192	0.00604
$\lambda_f$		0.2104	0.0627	0.0192	0.00604	0.00196
0.00	2	28.04	29.35	30.67	33.12	39.05
0.05	2	42.92	50.22	54.40	55.67	55.27
0.10	2	50.41	53.70	55.76	55.94	55.34
0.15	2	54.24	55.37	56.78	56.93	55.42
0.00	36	28.01	30.85	34.20	39.68	48.08
0.05	36	44.98	52.45	56.00	56.80	56.26
0.10	36	53.64	56.27	56.96	56.90	56.38
0.15	36	55.27	56.52	57.28	56.70	56.15
0.00	84	28.51	31.98	38.09	46.03	50.85
0.05	84	45.12	53.15	56.00	56.55	54.61
0.10	84	54.20	56.17	57.12	56.90	55.29
0.15	84	55.79	56.81	57.19	57.04	55.48

<sup>a</sup> Here,  $e_{max}$  is 57.4 mv.

where  $e$  is the bi-ionic potential in mv., and  $T_1^+$  and  $T_2^+$  are the transport numbers of the two univalent critical ions in the membrane.

### Discussion

Increased baking time and PVM/MA content reduced swelling, osmotic flow rates, and anion transport numbers, and increased the concentration potentials or cation transport numbers. Anion transport limits the rate of salt flow in the ultrafiltration process. Thus this result is parallel to the ultrafiltration result that salt flow decreased with increased baking time and PVM/MA content.<sup>1</sup>

Near maximum values of the concentration potential were obtained in the intermediate concentration range for the PVM/MA-PVA membranes. However, maximum values were obtained at the lowest concentrations for the PVA membranes, which have a much reduced fixed charge concentration. Deviation from the maximum potential in the concentrated solutions is usually attributed to anion penetration into the membrane and increased water transport. This result was also evident in the ultrafiltration measurements, where salt and water flow increased with concentration in the range of 0.11 to 0.54M NaCl, for a membrane with  $X_f = 0.09$ .<sup>1</sup> Deviation from the maximum potential at low concentrations has been attributed to water transport and hydrolysis.<sup>3,5</sup> It is likely that both phenomena contribute in these membranes because the water content is high and the extent of dissociation of PVM/MA in solution was shown to decrease sharply as the ionic strength was reduced.<sup>6</sup>

The results of the bi-ionic potential measurements illustrate the effect of pore size on the transport number ratios of the univalent cations. Membranes with the same  $X_f$ , but baked for different lengths of time, exhibited similar transport number ratios for ions of comparable size,

but also exhibited much different ratios when the sizes of the ions differed appreciably.

### References

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### Synopsis

The electrochemical properties of a series of baked poly(methyl vinyl ether-maleic anhydride)-polyvinyl alcohol membranes were investigated. Increased baking time and carboxylic acid content reduced swelling and osmotic flow, and increased the concentration potentials. Near-maximum concentration potentials were obtained for some membranes in a limited concentration range.

### Résumé

Les propriétés électrochimiques d'une série de membranes recuites à base de poly(méthyl-vinyléther-anhydride maléique) et d'alcool polyvinylique ont été étudiées. L'augmentation du temps de cuisson et de la quantité d'acide carboxylique diminue le gonflement et l'écoulement osmotique et augmente les potentiels de concentration. Des potentiels de concentration quasi maxima ont été obtenus pour certaines membranes dans une gamme limitée de concentration.

### Zusammenfassung

Die elektrochemischen Eigenschaften einer Reihe wärmebehandelter Poly(methylvinyläthermaleinsäureanhydrid)-Polyvinylalkoholmembrane wurden untersucht. Zunehmende Dauer der Wärmebehandlung und höherer Carbon säuregehalt verminderten die Quellung und den osmotischen Fluss und erhöhten die Konzentrationspotentiale. Für einige Membranen wurden in einem begrenzten Konzentrationsbereich nahezu maximale Konzentrationspotentiale erhalten.

Received October 16, 1961