

STUDIES ON ELECTROCHEMICAL CHARACTERIZATION OF MEMBRANES

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Electrochemical characterization of membranes on the basis of membrane potentials and mixed membrane potentials in terms of permselectivity is described with the object of understanding its variation with nature and composition of the electrolytic environment. The ability of a membrane to discriminate between variously charged ionic species depends in substantial measure on tendency of the membrane matrix to undergo swelling/deswelling upon equilibration with solutions having different electrolytic content. Most often membranes exhibit reduced permselectivity when equilibrated with concentrated electrolyte solutions because of distinct possibility of accompanying lowered coion exclusion. Ion adsorption in some cases, however may modify the permselective behaviour of the membranes.

Studies presented herein deal with electrochemical characterization of cellulose acetate and Dowex-50 (sulphonated styrene divinyl benzene) membranes. Sodium chloride and magnesium chloride solutions of variable composition; and sodium chloride and potassium chloride mixtures have been used for membrane potential and mixed membrane potential studies respectively. Effect of the presence of a representative non electrolyte alongwith an electrolyte on electrochemical behaviour of the Dowex-50 membrane has also been investigated.

Key Words : Electrochemical Characterization; Membrane Potentials; Donnan Potentials; Liquid Junction Potentials; Permselectivity; Transport Number; Ion-Selectivity

Introduction

Membranes allow transmission of charged and uncharged species with varying degrees of restriction. The relative ease with which charged species migrate through a membrane is commonly expressed in terms of permselectivity¹⁻³. A membrane is said to be ideally ion selective if only either positively or negatively charged ions pass through it. On the other hand if migration of ions through a membrane is not affected at all, the membrane is said to be non-selective. Most often the membranes are neither ideally ion selective nor entirely non-selective in nature; they exhibit ion-selectivity in some measure depending on the nature of the membrane forming material, its dimensional and electrochemical characteristics. Membrane potential studies are commonly used for the electrochemical characterization of membranes^{2,3}. In many situations of practical interest mixtures of electrolytes communicate through a membrane. Characterization of membranes in such cases is possible on the basis of mixed membrane potentials^{4,5}. Even characterization of membranes when non-electrolytes are present alongwith electrolytes is also of interest. We present herein some of our recent work carried out with the object of electrochemical characterization of

membranes on the basis of membrane potential and mixed membrane potential studies.

Materials and Methods

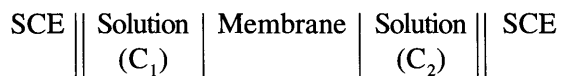
Cellulose acetate and Dowex-50 membranes used in these studies were prepared in the following manner^{2,6}.

For the formation of cellulose acetate membrane a binary casting solution prepared by dissolving 2 g cellulose acetate (BDH Chemicals Ltd., Poole England) in 10 ml of acetone by constant agitation for several hours was spread on a glass plate and allowed to dry at about 30°C. It was then immersed in distilled water to detach the membrane. The membrane thereafter was kept pressed between filter paper sheets to avoid wrinkles.

Similar method was used for the formation of Dowex-50 membrane. A desired quantity of Dowex-50 (J.T. Baker Chemical Co., Philipsburg NJ) was dispersed in 20% solution of kynar (Polyvinylidene fluoride) in N, N-dimethyl acetamide by constant agitation. The slurry thus formed was spread on a clean dried glass plate, dried and immersed in distilled water to detach the membrane.

The thickness and cross-sectional area of the membrane used in these studies are $\sim 2.5 \times 10^{-2}$ cm and 1.56 cm² respectively.

The electrochemical set-up used for the measurement of membrane potential may schematically be represented as



|| denotes KCl salt bridge and SCE, the saturated calomel electrode.

The experimental set-up is shown in Fig. 1. The membrane was equilibrated with 1M sodium or magnesium chloride to convert it to the appropriate ionic form. Solutions of unequal concentrations were then kept on the two sides of the membrane. The solutions were connected to saturated calomel electrodes through salt bridges. Membrane potential was measured by digital voltmeter (HIL2665). To remove asymmetry, the salt bridges were interchanged and membrane potential measured again. The experimental solutions were renewed till a reproducible value of membrane potential could be obtained.

The experimental procedure described above was also used for the mixed membrane potential studies. The membrane under examination was equilibrated with mixtures of sodium chloride and potassium chloride having desired composition. The solutions were renewed and the resulting membrane potential was noted. The measurements were repeated to ensure reproducibility of the results.

Results and Discussion

When a membrane separates solutions of an electrolyte having unequal concentration, a difference of potential across the membrane is developed because of inherent tendency of the ions to move with unequal speeds even if the membrane is non-selective. The observed potential across the membrane corresponds to the so called liquid function potential, $[(\Delta\phi)_{I=0}]_L$, given by⁷.

$$[(\Delta\phi)_{I=0}]_L = \left(\frac{t_+}{Z_+} - \frac{t_-}{Z_-} \right) \frac{RT}{F} \ln \frac{a_1}{a_2} \quad \dots (1)$$

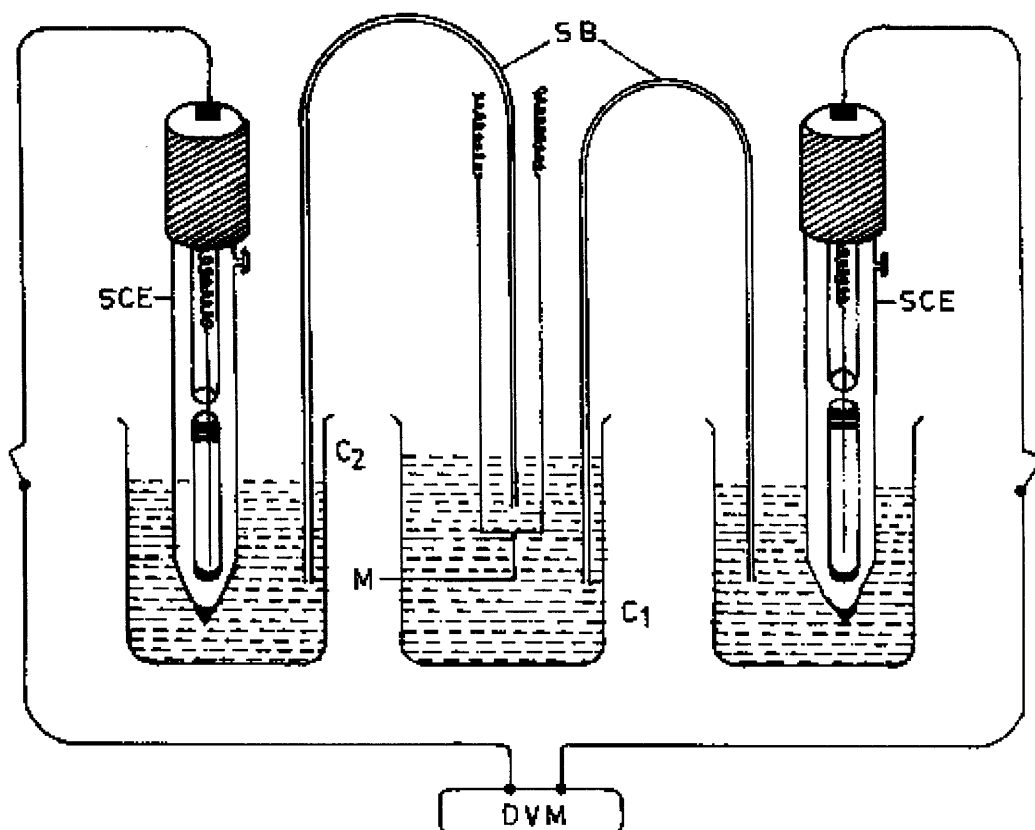


Fig. 1 Experimental setup for measurement of membrane potentials. DVM = Digital Voltmeter; SB = Salt bridges; SCE = Saturated Calomel Electrode; M = Membrane; C₁ and C₂ = Electrolyte Solutions having concentrations C₁ and C₂

t_+ and t_- respectively denote transport numbers of the cation and the anion in solution. Z_+ and Z_- are valences of the respective ions. a_1 and a_2 are activities of the electrolyte solutions used. If the membrane were ideally ion selective, the membrane potential is given by⁷.

$$[(\Delta\phi)_{I=0}]_i = \frac{RT}{F} \ln \frac{a_1}{a_2} \quad \dots (2)$$

Most often the experimentally measured membrane potential, $[(\Delta\phi)_{I=0}]_e$,

$$[(\Delta\phi)_{I=0}]_e \neq [(\Delta\phi)_{I=0}]_L \neq [(\Delta\phi)_{I=0}]_i \quad \dots (3)$$

Some representative values in case of cellulose acetate membrane are included in Table I. In both the cases the membrane is neither non-selective nor ideally selective. The membrane exhibits cation selectivity when sodium chloride solutions are used. On the other hand, it exhibits anion selectivity when magnesium chloride solutions are used. Obviously the extent to which these systems are selective and its variation with the nature and composition of the electrolyte is of interest. Activity coefficients f , needed for the estimation of activities, in all cases, were calculated using the relationship⁸.

$$\log f = -A \cdot Z_+ \cdot Z_- \cdot \sqrt{I} \quad \dots (4)$$

A is constant and I denotes ionic strength.

Ion selectivity of a membrane is quantitatively expressed in terms of permselectivity, P_s , defined as⁹

$$P_s = \frac{\bar{t}_i - t_i}{1 - t_i} \quad \dots (5)$$

\bar{t}_i denotes transport number of the ion in the membrane phase, with respect to which the membrane is selective and t_i , its transport number in the absence of the membrane. For the estimation of permselectivity of the membrane, a knowledge of transport numbers of ions is thus essential. Membrane potential measurements can be used with advantage to accomplish this task.

The electrical potential difference across a membrane when it separates two electrolyte solutions of unequal concentration is made up of a diffusion potential and two Donnan potentials acting in opposition; and may be expressed as¹⁰

$$[(\Delta\phi)_{I=0}]_e = \left(\frac{\bar{t}_+}{Z_+} - \frac{\bar{t}_-}{Z_-} \right) \frac{RT}{F} \ln \frac{a_1}{a_2} \quad \dots (6)$$

For a uni-univalent electrolyte, we may write

$$[(\Delta\phi)_{I=0}]_e = (2\bar{t}_+ - 1) \frac{RT}{F} \ln \frac{a_1}{a_2} \quad \dots (7)$$

This relationship has been used for the estimation of transport numbers of the Na⁺ ions on the basis of membrane potentials given in Table I. For MgCl₂, eq. (6) may be written as

$$[(\Delta\phi)_{I=0}]_e = \left(\frac{3\bar{t}_-}{2} - \frac{1}{2} \right) \frac{RT}{F} \ln \frac{a_1}{a_2} \quad \dots (8)$$

Table I

$[(\Delta\phi)_{I=0}]_L$, $[(\Delta\phi)_{I=0}]_i$ and $[(\Delta\phi)_{I=0}]_e$ Values for Cellulose Acetate / NaCl and Cellulose Acetate / MgCl₂ Systems

Concentration (M)		Sodium Chloride			Magnesium Chloride		
C ₁	C ₂	$[(\Delta\phi)_{I=0}]_L$ (mV)	$[(\Delta\phi)_{I=0}]_i$ (mV)	$[(\Delta\phi)_{I=0}]_e$ (mV)	$[(\Delta\phi)_{I=0}]_L$ (mV)	$[(\Delta\phi)_{I=0}]_i$ (mV)	$[(\Delta\phi)_{I=0}]_e$ (mV)
0.06	0.02	5.8	28.6	13.4	10.7	28.6	19.4
0.08	0.04	3.6	18.1	7.2	6.5	18.1	11.2
0.10	0.06	2.6	13.8	4.8	5.1	13.8	09.1
0.12	0.08	2.0	10.5	3.1	4.1	10.5	06.7
0.14	0.10	1.7	08.8	2.4	3.3	08.8	04.6

Table II

Transport Numbers and Permselectivity Values of Cellulose Acetate / Sodium Chloride and Cellulose Acetate / Magnesium Chloride Systems

Concentration (M)		Sodium Chloride		Magnesium Chloride	
C ₁	C ₂	\bar{t}_+	P_s	\bar{t}_-	P_s
0.06	0.02	0.734	0.568	0.859	0.572
0.08	0.04	0.699	0.514	0.835	0.504
0.10	0.06	0.674	0.475	0.822	0.468
0.12	0.08	0.648	0.435	0.813	0.442
0.14	0.10	0.637	0.420	0.742	0.258

The transport numbers alongwith permselectivity values derived using eq. (5) are included in the Table II. The membrane exhibits cation selectivity when sodium chloride solutions are used. On the other hand it exhibits anion selectivity when magnesium chloride solutions are used. In both the cases membrane permselectivity decreases with increase in concentration of the electrolyte. This could happen as result of the combined effect of alteration in membrane void volume and coion exclusion⁹.

It may be pointed out that cellulose acetate is a weak cation exchanger because of the sparsely distributed carboxylic groups along the cellulose chains¹¹. When sodium chloride is used, cellulose acetate membrane does exhibit mild cation selectivity. However, when magnesium chloride is used the membrane exhibits anion selectivity which decreases with increase in concentration³⁻¹¹. Adsorption of Mg^{2+} ions, has been found to be responsible for observed anion selectivity of the membrane. Alteration in membrane ion selectivity with concentration could arise on account of (i) increased absorbability of Mg^{2+} ion, (ii) reduced swelling of the membrane matrix with increase in concentration and (iii) reduced coion exclusion resulting in increase in membrane conductivity at higher concentrations. Factor (i) is expected to enhance membrane anion selectivity. Factors (ii) and (iii) on the other hand may lead to reduction in membrane selectivity. The results show that factors (ii) and (iii) together predominate because of which

anion selectivity of the membrane decreases with increase in concentration of magnesium chloride solutions used. Similar ion selective behaviour is shown by titanium dioxide membrane-magnesium chloride system¹².

Membrane potential studies were also carried out using Dowex-50 membrane, a typical cation selective membrane using sodium chloride and magnesium chloride solutions. Some representative data are included in Table III alongwith transport number and permselectivity values derived using eqs. (7), (8) and (5). Unlike cellulose acetate membrane, the Dowex-50 membrane exhibits significant cation selectivity in both the cases. Furthermore, relatively mild decline in permselectivity with increase in electrolyte concentration is observed in the case of Dowex-50 membrane.

Till now we were concerned with situations wherein solutions of an electrolyte having unequal concentration communicated through the membrane. Situations wherein mixtures of electrolyte solutions having unequal composition are involved are also of considerable interest. To demonstrate that the electrochemical characterization of membranes can be carried out in such cases, mixed membrane potential studies were carried out.

Mixed membrane potentials obtained using mixtures of sodium chloride and potassium chloride of variable composition; and cellulose acetate and Dowex-50 membranes are summarized in Table IV. Liquid Junction

Table III

Membrane Potential, Transport Number and Permselectivity of Dowex-50/Sodium Chloride and Dowex-50/Magnesium Chloride Systems

Concentration (M)		Sodium Chloride			Magnesium Chloride		
C_1	C_2	$[(\Delta\phi)_{I=0}]_e$ (mV)	\bar{t}_+	P_s	$[(\Delta\phi)_{I=0}]_e$ (mV)	\bar{t}_+	P_s
0.06	0.02	18.4	0.859	0.812	6.4	0.844	0.799
0.08	0.04	11.2	0.842	0.788	3.8	0.840	0.793
0.10	0.06	7.7	0.839	0.786	3.0	0.832	0.785
0.12	0.08	5.8	0.826	0.767	2.1	0.822	0.772
0.14	0.10	4.0	0.786	0.709	1.6	0.815	0.764

Table IV

Mixed Membrane Potential and Liquid Junction Potential for Dowex 50 / KCl + NaCl System

Sl. No.	Concentration (M)		$[(\Delta\phi)_{I=0}]_L$	$[(\Delta\phi)_{I=0}]_e$
	KCl + NaCl	KCl + NaCl	(mV)	(mV)
I	0.00 + 0.09	0.00 + 0.01	11.6	50.0
II	0.01 + 0.09	0.00 + 0.01	6.0	28.0
III	0.02 + 0.09	0.02 + 0.01	4.8	20.6
IV	0.03 + 0.09	0.03 + 0.01	4.0	16.3
V	0.01 + 0.00	0.09 + 0.01	0.0	39.0

potentials obtained using relationship (1) are also included in the Table IV. The t_+ now denotes combined transport number of the cations in solution and t_- , the transport number of the anion in solution.

t_+ values were estimated using the relationship⁸

$$t_+ = \frac{\sum Z_i C_i \lambda_i}{\sum Z_i C_i \lambda_i} \quad \dots (9)$$

are also included in the Table. C_+ and λ_+ denote concentration and equivalent conductance of the cations. C_i and λ_i are values for the i^{th} ion. λ_i values were obtained using the relationship⁸

$$\lambda_i = \lambda_i^0 - A_i \sqrt{C_i} \quad \dots (10)$$

λ_i^0 represents equivalent ionic conductance at infinite dilution. Values of A_i for Na^+ , K^+ and Cl^- are 41.57, 46.93 and 47.58 respectively⁸.

When electrolyte mixtures communicate through a membrane, the membrane potential is given by^{4,6}

$$[(\Delta\phi)_{I=0}]_e = (2\bar{t}_+ - 1) \frac{RT}{F} \ln \frac{a_1}{a_2} \quad \dots (11)$$

\bar{t}_+ denotes transport number of the cations in the membrane phase

$$\bar{t}_+ = \bar{t}_{\text{Na}^+} + \bar{t}_{\text{K}^+} \quad \dots (12)$$

Validity of eq. (11) was established by plotting $[(\Delta\phi)_{I=0}]_e$ against $\log a_1/a_2$. \bar{t}_+ values were then derived from the slopes of these plots. \bar{t}_+ is the combined transport number of the cations. For the description of permselective behaviour of the membrane with respect to the cations separately estimation of \bar{t}_{Na^+} and \bar{t}_{K^+} is needed. Using thermodynamic considerations it is possible to write⁴

$$[(\Delta\phi)_{I=0}]_e = \bar{t}_{\text{Na}^+} \cdot \frac{RT}{F} \ln \frac{(a_{\text{Na}^+})_1}{(a_{\text{Na}^+})_2} + \bar{t}_{\text{K}^+} \cdot \frac{RT}{F} \ln \frac{(a_{\text{K}^+})_1}{(a_{\text{K}^+})_2} + \bar{t}_{\text{Cl}^-} \cdot \frac{RT}{F} \ln \frac{(a_{\text{Cl}^-})_2}{(a_{\text{Cl}^-})_1} \quad \dots (13)$$

Above equation alongwith eq. (12) has been used for the estimation of transport of the cations separately. These values are included in Table V. The membrane permselectivities with respect to the constituent ions separately estimated using the relationships

$$(P_s)_{\text{Na}^+} = \frac{(\bar{t}_{\text{Na}^+} - t_{\text{Na}^+})}{(1 - t_+)} \quad \dots (14)$$

$$\text{and } (P_s)_{\text{K}^+} = \frac{(\bar{t}_{\text{K}^+} - t_{\text{K}^+})}{(1 - t_+)} \quad \dots (15)$$

are summarized in Table V. In spite of mean concentration of sodium chloride having been kept fixed, permselectivity of the membrane changes with respect to both Na^+ and K^+ ions when composition of the mixture is changed, infact both the counter ion permselectivities decline with increase in concentration of potassium chloride in the mixture. Enhancement in membrane void volume and the resulting lowering in coin exclusion with increase in concentration are obviously responsible for the observed alteration in ion-selective character of the membrane¹³.

So far we have dealt with electro-chemical characterization of membranes in a state of equilibrium with electrolyte mixtures having variable composition. Effect of the presence of a non-electrolyte alongwith an electrolyte on the permselective nature of the membrane is also of interest. We carried out electrochemical characterization of the cation selective Dowex-50 membrane using sodium chloride and urea solutions of variable composition. Some representative membrane potential data are given in Table VI. \bar{t}_+ and permselectivity values derived using eqs. (7) and (5) respectively are also included in Table VI. A distinct change in electrochemical character of the membranes occurs when urea is present alongwith sodium chloride in the solution.

An ion exchange membrane undergoes swelling because of the osmotic intake of the solvent by the

Table V

Transport Numbers of Ions in Solution Phase and Dowex 50 Membrane Phase when KCl + NaCl Mixtures are Used; and Permselectivity Values

Sl. No.	Transport numbers in solution			Transport numbers in membrane phase			$(P_s)_{\text{Na}^+}$	$(P_s)_{\text{K}^+}$
	t_{Na^+}	t_{K^+}	t_{Cl^-}	\bar{t}_{Na^+}	\bar{t}_{K^+}	\bar{t}_{Cl^-}		
I	0.383	0.000	0.617	0.974	0.000	0.026	0.958	0.000
II	0.309	0.104	0.587	0.742	0.169	0.089	0.737	0.111
III	0.260	0.171	0.569	0.664	0.219	0.117	0.709	0.085
IV	0.226	0.217	0.557	0.589	0.258	0.152	0.653	0.073
V	0.000	0.490	0.510	0.000	0.841	0.159	0.000	0.688

Table VI
t₊ and P_s Values for Dowex 50 / NaCl + Urea System

Side 1 Urea + NaCl (M)	Side 2 Urea + NaCl (M)	\bar{t}_+	P_s
0.00 + 0.01	0.00 + 0.09	0.968	0.948
0.01 + 0.01	0.01 + 0.09	0.951	0.921
0.02 + 0.01	0.02 + 0.09	0.940	0.903
0.03 + 0.01	0.03 + 0.09	0.930	0.886

membrane network¹⁴. This osmotic action depends on the solute concentration; it decreases with increase in concentration as a result of which solvent uptake by the membrane matrix decreases leading to deswelling of the membrane. Because of this, membrane openness increases accompanied by lowered exclusion of co-ions. Permselectivity of the membrane, therefore decreases. Thus even when electrolyte concentration remains unchanged, a reduction in membrane permselectivity is expected with increase in concentration of the solution with respect to urea. The membrane permselectivity thus decreases with increase in urea concentration although electrolyte concentration is not changed. It may, therefore, be inferred that even the presence of non-electrolytes alters the electrochemical character of the ion exchange

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membrane because of a distinct possibility of reduced coion exclusion as a result of the accompanying deswelling of the membrane. Membrane conductance measurements also lead to similar conclusions⁵.

The results presented herein demonstrate that information in respect of the permselective behaviour of membranes can be had on the basis of membrane potential and mixed membrane potential studies. Alteration in the membrane permselectivity can be understood in terms of change in membrane openness when composition of the electrolyte solutions is varied and the resulting changes in coion exclusion. Furthermore, presence of non-electrolyte in the electrolyte solutions may also alter electrochemical behaviour of the membranes precisely for similar reasons.

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