

Impedance Characteristics of Parchment Supported Inorganic Precipitate Membranes

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Synopsis

The impedance characteristics of parchment-supported inorganic precipitate model membranes have been analyzed in order to understand the mechanism of ionic diffusion through biomembranes. The observed values of membrane capacitance and resistance were found to be dependent on the concentration of bathing electrolyte and applied oscillator frequency. The change in membrane capacitance and resistance values with the change in electrolyte concentration and oscillator frequency has been interpreted in terms of changes produced in the electrical double layer at the membrane-solution interface. The values of interfacial double layer capacitance derived by the equations of Armstrong and Longer were found to be different due to the presence of polarising charge and other structural details of membrane matrix. Different model-equivalent electrical circuits have been analyzed using the experimental data. The complex impedance spectra have been found to deviate from the theoretical predictions at low frequencies due to nonhomogenous and rough surface of the membrane.

INTRODUCTION

Impedance measurements provide a powerful diagnostic tool for the analysis of many electro-chemical systems.¹⁻⁴ In order to understand the behavior of complex living membranes, simple polymeric for some time,⁵ liquid bilayer membranes^{6,7} parchment and millipore filter paper supported membranes⁸⁻¹⁰ in recent years have been used as models by a number of investigators. Warburg¹¹ developed the theory of diffusional impedances and derived the expression for it. The work of MacDonald¹² provides a systematic treatment of small signal ac response of conducting cell and membranes. Armstrong and Archur¹³ interpreted the complex impedance spectra for solid/electrolyte interfaces.

This paper describes the analysis of membrane impedance of parchment-supported nickel phosphate, cobalt phosphate, and complex nickel-cobalt phosphate model membranes under various conditions of bathing electrolyte concentration and applied oscillator frequency in order to understand the mechanism of ionic transport through these membranes. The results are interpreted in terms of changes produced in the electrical double layer at the membrane/electrolyte interfaces. The values of membrane resistance, capacitance, and impedance have been computed by considering different equivalent electrical circuit models.

EXPERIMENTAL

Parchment supported nickel phosphate, cobalt phosphate, and a complex nickel-cobalt phosphate membranes have been prepared by the method of

interaction as suggested by Beg and co-workers.⁸⁻¹⁰ The chemicals, nickel chloride, cobalt chloride, and trisodium orthophosphate, are of AR grade. The complex nickel-cobalt phosphate membrane has been prepared by taking a mixture of 0.2M nickel chloride and 0.2M cobalt chloride solutions on one side of parchment paper and on the other side 0.2M trisodium orthophosphate solution. The two solutions were interchanged after 72 h and kept for another 72 h. The resulting membranes were washed with deionized water to remove free electrolyte. The membranes thus obtained were cut into a circular disc form of unit cross-sectional area and sealed between the two half cells of an electrochemical cell. The two half cells were filled with electrolyte solutions to equilibrate the membrane. The solutions were then replaced by purified mercury without removing the adhering surface liquids. Air bubbles, if any, on the membrane surface were removed by tilting the cell assembly. Mercury is likely to be oxidized to form mercuric oxide which would form films on membrane faces and cause irreversibility. Use of purified mercury has eliminated this problem and has given reproducible results.

A Universal LCR bridge 921 has been used to measure the electrical resistance and capacitance of the membranes. The membranes were equilibrated with a lower concentration of potassium chloride initially than the higher concentration while measuring the resistance and capacitance of the membranes. The effect of oscillator frequency on the resistance and capacitance values have been observed for all the membranes. A platinum wire coated with platinum black dipped in Hg was used as the electrode. The use of long electrode was preferred in order to avoid tip impedance.¹⁴ A thermostat was used to maintain the temperature at $25 \pm 0.1^\circ\text{C}$.

RESULTS AND DISCUSSION

The electrical resistance (R_x) and capacitance (C_x) across parchment-supported nickel phosphate, cobalt phosphate, and complex nickel-cobalt phosphate membranes equilibrated with different concentrations of potassium chloride solution at 1 kHz frequency have been measured. The R_x and C_x were also determined for all the three membranes equilibrated with 0.1M KCl solution by applying different ac frequencies. These values are given in Tables I and II. The data refer to the fact that R_x decreases while C_x increases with the increase in bathing electrolyte concentration. The decrease in R_x with the increase in electrolyte concentration may be ascribed due to progressive accumulation of ionic species within the membrane, thus making the membrane more and more conducting. The increase in C_x may be attributed to the changes produced in the dielectric properties (ϵ) and the effective thickness (d) of the membrane/electrolyte system in accordance with the equation for parallel plate capacitor.

$$C_x = \epsilon/36\pi 10^{11}d \quad (1)$$

Thus the increase in C_x may be referred to the increase in ϵ due to accumulation of ions with the increase in electrolyte concentration and decrease in the value of d probably due to the deswelling of membrane because of squeezing of water molecules from the membrane framework by the incoming ions. This behavior of membrane is not unusual to these systems.^{15,16} Among the three membranes, the capacitance values across the complex nickel-cobalt phos-

TABLE I
Electrical Resistance (R_x) and Capacitance (C_x) Observed across Parchment-Supported Nickel Phosphate, Cobalt Phosphate, and a Complex Nickel-Cobalt Phosphate Membranes Equilibrated with Different Concentrations of Potassium Chloride at 1 kHz (Temp = $25 \pm 0.1^\circ\text{C}$)

Electrolyte concn (M/L)	Nickel phosphate membrane		Cobalt phosphate membrane		Complex nickel-cobalt phosphate membrane	
	R_x (Ω)	C_x (μF)	R_x (Ω)	C_x (μF)	R_x (Ω)	C_x (μf)
1×10^{-4}	20×10^2	0.04	34×10^2	0.02	30×10^2	0.03
1×10^{-3}	14×10^2	0.06	30×10^2	0.03	23×10^2	0.04
1×10^{-2}	9×10^2	0.11	22×10^2	0.05	14.5×10^2	0.07
1×10^{-1}	3.2×10^2	0.70	5.1×10^2	0.40	8×10^2	0.30
1×10^0	0.47×10^2	1.20	0.80×10^2	1.25	1.3×10^2	0.65
2×10^0	0.35×10^2	2.40	0.60×10^2	2.00	1×10^2	1.10

phate membrane was found to be lowest. This may be attributed to the relatively compact structure of the membrane and carries lesser charge carrier than the other two membranes. The values of electrical resistance across the three membranes confirm this viewpoint.

Structural simulation is a newer approach to modeling for more complex electrochemical systems.¹⁷ Armstrong has attempted to adopt some of the theoretical models for aqueous electrolyte system in order to obtain simple model for metal/superion conductor.¹³ By the usual analysis, Lakshminarayanaiah and Shane¹⁸ evaluated membrane resistance (R_m), capacitance (C_m), and impedance (Z) of a membrane/electrolyte system from the model equivalent electrical circuit (Fig. 1) using the equations

$$R_m = R_x \left[1 + (X_x/R_x)^2 \right] \quad (2)$$

$$X_x = 1/\omega C_x \quad (3)$$

$$C_m = (X_x/R_x)(1/\omega R_m) \quad (4)$$

TABLE II
Electrical Resistance (R_x) and Capacitance (C_x) Observed across Parchment-Supported Nickel Phosphate, Cobalt Phosphate, and a Complex Nickel-Cobalt Phosphate Membrane Equilibrated with 0.1M Potassium Chloride Solution at Different Oscillator Frequencies (Temp = $25 \pm 0.1^\circ\text{C}$)

Oscillator frequency (Hz)	Nickel phosphate membrane		Cobalt phosphate membrane		Complex nickel-cobalt phosphate membrane	
	R_x (Ω)	C_x (μF)	R_x (Ω)	C_x (μF)	R_x (Ω)	C_x (μF)
1×10^3	3.2×10^2	0.70	5.10×10^2	0.40	8.00×10^2	0.30
2×10^3	2.5×10^2	0.61	4.20×10^2	0.30	7.60×10^2	0.25
3×10^3	2.0×10^2	0.50	3.50×10^2	0.24	7.10×10^2	0.21
4×10^3	1.65×10^2	0.47	3.10×10^2	0.20	6.70×10^2	0.17
5×10^3	1.40×10^2	0.43	2.90×10^2	0.15	5.50×10^2	0.13
6×10^3	1.35×10^2	0.39	2.85×10^2	0.14	6.35×10^2	0.12

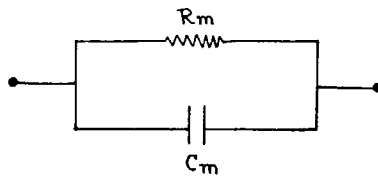


Fig. 1. The equivalent electrical circuit for a simple membrane. R_m and C_m are membrane resistance and capacitance respectively.

and

$$Z = \sqrt{R_x^2 + X_x^2} \quad (5)$$

where $\omega = 2\pi f$ and f is the frequency used to measure R_x and C_x . The values of R_m , C_m , and Z , thus calculated as a function of both bathing electrolyte concentration and the applied oscillator frequency for nickel phosphate and cobalt phosphate membranes, are given in Tables III and IV.

Although the values of R_m and C_m can be easily computed for simple membranes from bridge readings of R_x and C_x , such calculations cannot be done for complex membrane, because it cannot be described by a definite equivalent electrical circuit. However, in an ideal case, if simple nickel phosphate and cobalt phosphate membranes are assumed to form complex nickel-cobalt phosphate membrane by retaining their identity, it may conform to the circuit shown in Figure 2 and the impedance of the circuit for the two units is given by

$$\frac{R_A}{1 + j\omega C_A \cdot R_A} + \frac{R_B}{1 + j\omega C_B \cdot R_B} \quad (6)$$

where $j = \sqrt{-1}$, R_A , R_B and C_A , C_B are the membrane resistances and capacitances of the two units (nickel phosphate and cobalt phosphate membranes). Separating the real and imaginary parts of eq. (6) yields

$$R_e = \left[\frac{R_A}{(1 + \omega^2 \cdot C_A^2 \cdot R_A^2)} \right] + \left[\frac{R_B}{(1 + \omega^2 \cdot C_B^2 \cdot R_B^2)} \right] \quad (7)$$

$$X_e = \left[\frac{\omega C_A \cdot R_A^2}{(1 + \omega^2 \cdot C_A^2 \cdot R_A^2)} \right] + \left[\frac{\omega C_B \cdot R_B^2}{(1 + \omega^2 \cdot C_B^2 \cdot R_B^2)} \right] \quad (8)$$

However, another equivalent electrical circuit has been used to represent the complex membrane in view of uncontrolled simultaneous deposition of nickel phosphate and cobalt phosphate in the interstices of parchment paper.¹⁹ In this case the identity of simple nickel phosphate and cobalt phosphate membranes are lost as shown in Figure 3 and the impedance of the circuit is given by

$$(R_A + R_B) \left/ \left[1 + j\omega \left(\frac{C_A \cdot C_B}{C_A + C_B} \right) (R_A + R_B) \right] \right. \quad (9)$$

TABLE III
 Calculated Values of Membrane Resistance (R_m), Capacitance (C_m), and Impedance (Z) from Eqs. (2), (4), and (5) for Parchment-Supported Nickel Phosphate, Cobalt Phosphate, and a Complex Nickel-Cobalt Phosphate Membrane Equilibrated with Different Concentrations of Potassium Chloride at 1 kHz (Temp = $25 \pm 0.1^\circ\text{C}$)

Electrolyte concn (M/L)	Nickel phosphate membrane			Cobalt phosphate membrane			Complex nickel-cobalt phosphate membrane		
	R_m (Ω)	C_m (μF)	Z (Ω)	R_m (Ω)	C_m (μF)	Z (Ω)	R_m (Ω)	C_m (μF)	Z (Ω)
1×10^{-4}	99.24×10^2	0.032	44.55×10^2	220.44×10^2	0.017	86.57×10^2	123.91×10^2	0.023	60.97×10^2
1×10^{-3}	64.30×10^2	0.047	30.00×10^2	123.90×10^2	0.023	60.97×10^2	91.90×10^2	0.030	45.98×10^2
1×10^{-2}	32.28×10^2	0.080	17.04×10^2	68.10×10^2	0.034	38.71×10^2	50.19×10^2	0.050	26.98×10^2
1×10^{-1}	4.82×10^2	0.235	3.93×10^2	8.21×10^2	0.150	6.47×10^2	11.51×10^2	0.092	3.37×10^2
1×10^0	4.22×10^2	1.060	1.41×10^2	2.83×10^2	0.896	1.50×10^2	5.92×10^2	0.507	2.77×10^2
2×10^0	1.61×10^2	1.877	0.75×10^2	1.66×10^2	1.276	1.0×10^2	3.10×10^2	0.744	1.76×10^2

TABLE IV
 Calculated Values of Membrane Resistance (R_m), Capacitance (C_m), and Impedance (Z) from eqs. (2), (4), and (5) for
 Parchment-Supported Nickel Phosphate, Cobalt Phosphate, and Complex Nickel-Cobalt Phosphate Membranes
 Equilibrated with 0.1M Potassium Chloride Solution at Different Oscillator Frequencies (Temp = $25 \pm 0.1^\circ\text{C}$)

Oscillator frequency (Hz)	Nickel phosphate membrane			Cobalt phosphate membrane			Complex nickel-cobalt phosphate membrane		
	R_m (Ω)	C_m (μF)	Z (Ω)	R_m (Ω)	C_m (μF)	Z (Ω)	R_m (Ω)	C_m (μF)	Z (Ω)
1×10^3	4.82×10^2	0.235	3.93×10^2	8.20×10^2	0.150	6.47×10^2	11.51×10^2	0.092	9.60×10^2
2×10^3	3.18×10^2	0.131	2.82×10^2	5.88×10^2	0.085	4.97×10^2	8.94×10^2	0.037	8.24×10^2
3×10^3	2.56×10^2	0.110	2.26×10^2	4.90×10^2	0.068	4.14×10^2	8.00×10^2	0.024	7.54×10^2
4×10^3	2.10×10^2	0.099	1.86×10^2	4.38×10^2	0.058	3.68×10^2	7.52×10^2	0.018	7.10×10^2
5×10^3	1.80×10^2	0.094	1.59×10^2	4.45×10^2	—	3.59×10^2	—	—	6.95×10^2
6×10^3	1.69×10^2	0.079	1.51×10^2	4.11×10^2	0.043	3.42×10^2	7.12×10^2	0.013	6.72×10^2

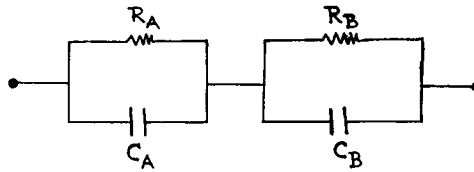


Fig. 2. The equivalent electrical circuit for an ideal complex membrane built from simple membranes. R_A , R_B and C_A , C_B are simple membrane resistances and capacitances, respectively.

Separating the real and imaginary parts of eq. (9), we have

$$R_e = (R_A + R_B) / \left[1 + \omega^2 \left(\frac{C_A \cdot C_B}{C_A + C_B} \right)^2 (R_A + R_B)^2 \right] \quad (10)$$

and

$$X_e = \omega \left(\frac{C_A \cdot C_B}{C_A + C_B} \right) (R_A + R_B)^2 / \left[1 + \omega^2 \left(\frac{C_A \cdot C_B}{C_A + C_B} \right)^2 (R_A + R_B)^2 \right] \quad (11)$$

The values of R_e and X_e determined from eqs. (7) and (8) or eqs. (10) and (11) are comparable to the observed values of R_x and X_x of the complex membrane particularly at higher concentrations of bathing electrolyte as given in Table V.

It may be concluded that the two equivalent circuits may be utilized to represent the behavior of complex membrane at least in higher concentration ranges. The deviation in dilute concentrations may be assigned to the interfacial polarization and structural changes in the interfacial double layers.

The electrical double layer at the membrane/solution interface has been utilized in several studies to account for various membrane behavior.^{4,20} The polarization charge on the geometric capacitor in the form of diffused double layer plays an important role and affects the overall membrane capacitance.^{21,22} The applied frequency across the membrane has been found to affect the double layer capacitance by the movement of ions across it. In order to investigate the impedance characteristics of the membrane/electrolyte system and the double layer effect, the equivalent electrical circuit has been analyzed further and may be represented as in Figure 4. This circuit, according to Armstrong,²³ represents a solid smooth surface in contact with the penetrating electrolyte and refers to ideal impedance spectra on complex plane as shown by the dotted lines in Figure 5, where C_g is the specific geometric

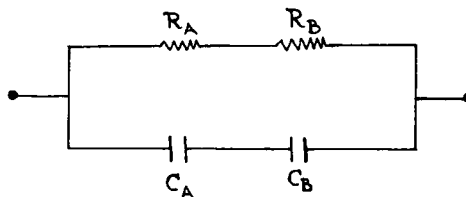


Fig. 3. The equivalent electrical circuit for the complex nickel cobalt phosphate membrane.

TABLE V
 Theoretical and Observed Values of Resistive and Reactive Components of Impedance of Complex Nickel-Cobalt Phosphate Membrane
 Equilibrated with Different Concentrations of Potassium Chloride at 1 kHz (Temp = $25 \pm 0.1^\circ\text{C}$)

Electrolyte concn (M/L)	Theoretical values for Fig. 2		Theoretical values for Fig. 3		Experimental values	
	R_c (Ω)	X_c (Ω)	R_c (Ω)	X_c (Ω)	R_x (Ω)	X_x (Ω)
1×10^{-4}	58.59×10^2	119.41×10^2	53.65×10^2	119.10×10^2	30.0×10^2	53.08×10^2
1×10^{-3}	44.02×10^2	79.69×10^2	42.77×10^2	78.06×10^2	23.0×10^2	39.81×10^2
1×10^{-2}	30.79×10^2	46.32×10^2	30.75×10^2	46.21×10^2	14.5×10^2	22.75×10^2
1×10^{-1}	8.35×10^2	6.62×10^2	8.34×10^2	62.46×10^2	8.0×10^2	5.31×10^2
1×10^0	1.31×10^2	2.74×10^2	1.32×10^2	2.66×10^2	1.3×10^2	2.45×10^2
2×10^0	0.96×10^2	1.52×10^2	0.95×10^2	1.46×10^2	1.0×10^2	1.45×10^2

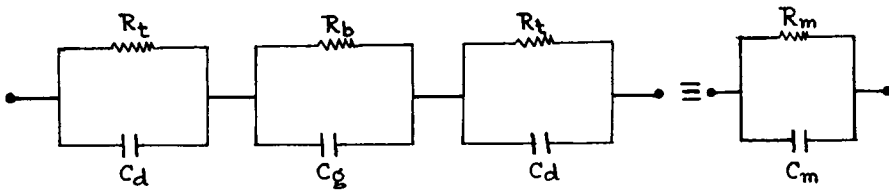


Fig. 4. Equivalent electrical circuit for a membrane-electrolyte system.

capacitance which is assumed to depend upon the structural details of the polymer network of which the membranes are composed, C_d is the interfacial electrical double layer capacitance, R_b is the bulk resistance of the membrane, and R_t is the charge transfer resistance between membrane/electrolyte interface assuming the ion transfer process to be single step.

The impedance of the proposed equivalent electrical circuit (Fig. 4) for the membrane/electrolyte system is given by

$$\frac{2R_t}{1 + j\omega C_d R_t} + \frac{R_b}{1 + j\omega C_g R_b} = \frac{R_m}{1 + j\omega C_m R_m} \tag{12}$$

The real and imaginary parts of eq. (12) are given by

$$\frac{R_m}{1 + \omega^2 C_m^2 R_m^2} = \frac{2R_t}{1 + \omega^2 C_d^2 R_t^2} + \frac{R_b}{1 + \omega^2 C_g^2 R_b^2} \tag{13}$$

$$\frac{C_m R_m^2}{1 + \omega^2 C_m^2 R_m^2} = \frac{2C_d R_t^2}{1 + \omega^2 C_d^2 R_t^2} + \frac{C_g R_b^2}{1 + \omega^2 C_g^2 R_b^2} \tag{14}$$

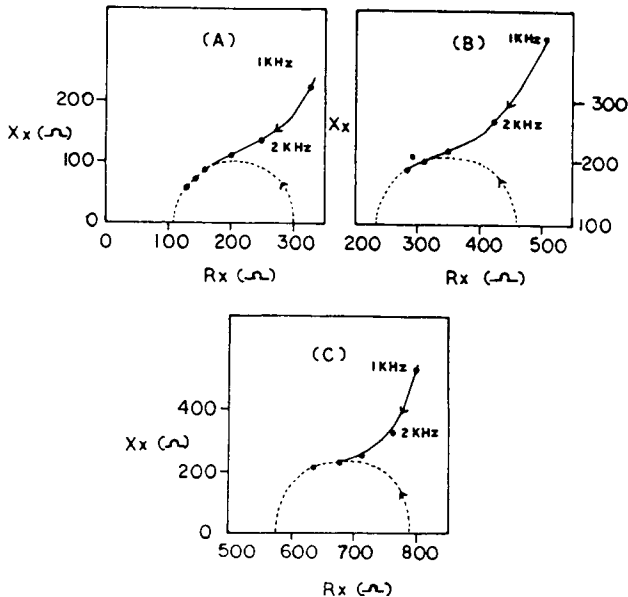


Fig. 5. Theoretical (···) and experimental (—) complex impedance spectra for (A) nickel phosphate, (B) cobalt phosphate, and (C) complex nickel-cobalt phosphate membrane equilibrated with 0.1M solution of KCl.

Equation (14) can be approximated at higher oscillator frequencies as

$$\frac{1}{C_m} = \frac{1}{C_g} + \frac{2}{C_d} \quad (15)$$

which indicates that the membrane/electrolyte system may be considered to be composed of three capacitors arranged in series. The geometric capacitor is placed between the two interfacial double layer capacitors as suggested by Armstrong.¹³ For high electrolyte concentrations and/or significant surface charge,^{4,24} $1/C_g \gg 2/C_d$ so that $C_m \approx C_g$.

Now, taking this value of C_m as C_g (at 2M KCl solution), the different values of C_d at other electrolyte concentrations are calculated using eq. (15). It is found that the value of C_d increases with increase in electrolyte concentration. C_m should differ considerably from C_g when $1/C_g \approx 2/C_d$. This situation prevails in the absence of surface charge at low electrolyte concentrations.

The exact form of the double layer capacitance depends upon the fixed surface charge (σ_s) and the membrane potential (V_m). If $\sigma_s = 0$, then²⁴

$$C_d = \frac{\epsilon_0 \epsilon_w \sinh \alpha}{(1/\kappa)\alpha} \quad (16)$$

where $\epsilon_0 = 8.85 \times 10^{-14} F/C_m$, ϵ_w is the dielectric coefficient of water, α is a constant which takes into account the structural details of membrane polymer, and $(1/\kappa)$ is the Debye-Huckle length given by

$$\frac{1}{\kappa} = \left(\frac{4.31 \times 10^{-8}}{(2/\mu)^{1/2}} \right) \quad (17)$$

where μ is the ionic strength of bathing electrolyte solution. α is determined from the transcendental equation

$$\left[\frac{\epsilon_0 \epsilon_w}{(1/\kappa)C_g} \cdot \sinh \alpha + 2 \right] = \frac{V_m}{2(RT/F)} \quad (18)$$

or alternatively from

$$C_m V_m = \sigma p = 4FC(1/\kappa) \sinh \alpha \quad (19)$$

where σp is the polarization charge on the capacitor. Equation (16) can be reduced to

$$C_d = \frac{\epsilon_0 \cdot \epsilon_w}{(1/\kappa)} \quad (20)$$

if $V_m \ll RT/F$ so that $\sinh \alpha = \alpha$. The values of C_d calculated from eq. (20) at different electrolyte concentrations are given in Table VI. The difference in

TABLE VI
 Calculated Values of Interfacial Double Layer Capacitance (C_d) for Parchment-Supported Nickel Phosphate, Cobalt Phosphate, and the Complex Nickel-Cobalt Membranes Equilibrated with Different Concentrations of Potassium Chloride at 1 kHz (Temp = $25 \pm 0.1^\circ\text{C}$)

Electrolyte concn (M/L)	C_d from eq. (20) (μF)	C_d from eq. (15) nickel phos. memb. (μF)	C_d from eq. (15) cobalt phos. memb. (μF)	C_d from eq. (15) complex nickel-cobalt phos. memb. (μF)
1×10^{-4}	2.28	0.07	0.03	0.05
1×10^{-3}	7.22	0.10	0.05	0.06
1×10^{-2}	22.82	0.17	0.07	0.11
1×10^{-1}	72.18	0.54	0.34	0.21
1×10^0	228.25	4.80	5.91	3.15
2×10^0	322.78	—	—	—

the values of C_d calculated from eqs. (15) and (20) is attributed to the presence of polarizing charge and other structural details of membrane matrix.

The frequency dependence of the electrical impedance of membranes is conveniently represented by the complex impedance spectra.¹³ The impedance spectra of complex plane for all the membranes are represented in Figure 5. The dotted semicircle according to Armstrong represents a solid smooth surface in contact with the penetrating electrolyte and refers to the ideal impedance spectra. The experimental data follow the theoretical predictions at higher frequencies whereas, at a lower frequency region, there is a marked deviation from ideal behavior may be due to nonhomogeneity and rough membrane surface.

It may, therefore, be concluded that the membrane/electrolyte system can be represented by a model equivalent electrical circuit as shown in Figure 4 and the values of membrane capacitance (C_m) as a function of electrolyte concentration is accurately predicted by double layer theory. This type of behavior is in agreement with our earlier findings of membrane potential measurements with nickel phosphate and cobalt phosphate membranes⁹ as well as in agreement with Tien and Ting for bilayer membranes that the electrical double layer at the interfaces control the diffusion process, at least in dilute concentration ranges.^{25,26}

References

1. S. Stephen, *Biochim. Biophys. Acta*, **323**, 343-350 (1973).
2. Y. Kobatake, *Biochim. Biophys. Acta*, **323**, 367-377 (1973).
3. H. P. Schwan, *Phys. Technique in Biol. Res.*, Academic, New York, 1963, Vol. 6.
4. C. T. Everitt and D. A. Haydon, *J. Theor. Biol.*, **18**, 371-379 (1968).
5. N. Lakshminarayanaiah, *Chem. Rev.*, **65**, 491 (1965).
6. G. Claud and S. Roger, *Biochim. Biophys. Acta*, **21**, 33 (1975).
7. R. Beuz and K. Janko, *Biochim. Biophys. Acta*, **14**, 721 (1976).
8. M. N. Beg, F. A. Siddiqui, and R. Shyam, *Can. J. Chem.*, **56**, 1680 (1977).
9. M. N. Beg, F. A. Siddiqui, R. Shyam, and I. Altaf, *J. Electroanal. Chem.*, **89**, 141 (1978).
10. M. N. Beg, K. Ahmad, I. Altaf, and M. Arshad, *J. Memb. Sci.*, **9**, 303 (1981).
11. E. Warburg, *Ann. Phys.*, **67**, 493 (1899); **6**, 125 (1901).
12. J. R. MacDonald and D. R. Fanceschetti, *J. Electroanal. Chem.*, **101**, 307 (1979).
13. R. D. Armstrong and W. I. Archur, *J. Electroanal. Chem.*, **87**, 221 (1978).

14. S. Takashina, R. Yantorno, and R. Hovack, *Biochim. Biophys. Acta*, **469**, 74–88 (1977).
15. T. Hanai, D. A. Haydon, and J. Taylor, *Proc. Royal Soc. London*, **281A**, 377–391 (1964).
16. T. Hanai, D. A. Haydon, and J. Taylor, *J. Theor. Biol.*, **9**, 278–296 (1965).
17. Z. B. Stoyner and B. S. Stoyner, *J. Electroanal. Chem.*, **209**, 11–18 (1986).
18. N. Lakshminarayanaiah and Shane, *J. Appl. Polym. Sci.*, **9**, 689 (1965).
19. N. Lakshminarayanaiah and F. A. Siddiqui, *Biophys. J.*, **11** (1971).
20. A. W. Clower, R. J. Charry, and D. Chapman, *Biochim. Biophys. Acta*, **249**, 301–317 (1971).
21. S. H. White and T. E. Thomson, *Biochim. Biophys. Acta*, **323**, 7 (1973).
22. C. P. Freeman and D. West, *J. Lipid. Res.*, **324**, 7 (1966).
23. R. D. Armstrong and A. A. Matcalfe, *J. Electroanal. Chem.*, **84**, 209 (1977).
24. P. Longer, W. Lesslaner, E. Marti, and J. Richter, *Biochim. Biophys. Acta*, **135**, 20–32 (1967).
25. H. T. Tien and H. P. Ting, *J. Coll. Interface Sci.*, **27**, 702 (1968).
26. F. A. Siddiqui, N. Lakshminarayanaiah, and M. N. Beg, *J. Polym. Sci.*, **9**, 2853–2867 (1971).

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