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Electrical Double Layer Capacitance And Impedance Characteristics of Inorganic Precipitate Membranes

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Abstract

To understand the mechanism of ionic diffusion through membranes the membrane resistance, capacitance and impedance of parchment supported Iron phosphate, cupric phosphate and complex iron-cupric phosphate membranes have been analyzed. The electrical resistance (R_x), and capacitance(C_x) developed across these membranes have been measured at different electrolyte concentrations and oscillator frequencies.

The obtained the values of membrane resistance(R_m), membrane capacitance(C_m), impedance(Z) were found to dependent on the concentration of the electrolyte and on the applied oscillator frequency at isothermal temperature (25±0.1°C). The electrical double-layer at the membrane-electrolyte interface was influenced and controlled by the transport of ions. An increase in concentration of electrolyte solution causes the counter ions in the form of double-layer inside the membranes makes membrane more conductive. Different model-equivalent electrical circuits against to membranes have been analyzed using the experimental data. There is a deviation from theoretical predictions in Membrane resistance, capacitance and impedance due to roughness and non homogeneity of the membranes used in present investigation.

Key words : Resistance, Capacitance, Impedance, Frequency, Double layer capacitance

Introduction

There are several areas of membrane research which have potentially far reaching consequences to medicine and chemical industry. Ion exchange membranes are one of the most advanced separation membranes, which have been widely used in various industries. The natural membranes are complex and always easily reproducible. Inorganic membranes show a number of advantageous properties, which make them attractive to filtration tasks.[1-4].

A flat electrical double layer is created by a charged plane in contact with an electrolyte solution composed of solvent molecules, counter-ions and co-ions. It is also the most important part of electrochemical cell, where all reactions and process takes place. Impedance measurement provide a powerful diagnostic tool for the analysis of many electro-chemical system[5-7]. It has been resolved into a "resistance" term (of the ohmic type) and a "reactance" term the latter being usually regarded as due to a "capacity" residing in the membrane structure. Many speculations have been devoted to the significance of these impedance terms. Although it is true that the impedance method have offered excellent service in permeability research as sensitive indicators. A common interpretation has been that the resistance term is connected with the ion permeable structures and the capacitance term with the ion impermeable parts of the membranes. This paper describes the analysis of impedance of parchment supported inorganic precipitate Iron phosphate, cupric phosphate and complex iron-cupric phosphate model membranes under various conditions of bathing electrolyte concentrations and applied oscillator frequency in order to understand the mechanism of ionic transport through these membranes.

Experimental

Parchment supported iron phosphate, cupric phosphate and complex iron-cupric phosphate membranes have been prepared by the method of interaction as used in our previous study[8].

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 as shown in fig-1

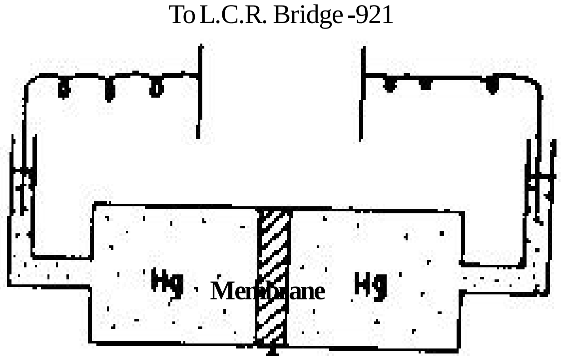

Fig. 1 : Cell for measuring the electrical resistance and capacitance of the membrane

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 causes 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, Then 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[9]. A thermostat was used to maintain the temperature at 25 ± 0.1°C.

Results and Discussion

The electrical resistance (R_x) and capacitance (C_x) across parchment-supported iron phosphate, cupric phosphate and complex iron-cupric phosphate membranes equilibrated with different concentrations of potassium chloride electrolyte solution at 1 KHz frequency have been measured. The R_x and C_x were also determined for all three membranes equilibrated with 0.1 M solution of same electrolyte by applying different ac frequencies. These values are given in Tables-1 and 2.

Structural simulation is a newer approach to modeling for more complex electrochemical systems[10]. Armstrong[11,12] has attempted to adopt some of the theoretical models for aqueous electrolyte system in order to obtain simple model for metal/super-ion conductor. By using equivalent electrical circuits for the membrane electrolyte system[13], the values of membrane resistance (R_m), capacitance (C_m), and impedance (Z) are calculated with the help of the following equation and given in Tables-3and4.

Table - 1. Electrical Resistance (R_x) and Capacitance (C_x) Observed Across Parchment Supported Iron Phosphate, Cupric Phosphate and Complex Iron-Cupric Phosphate Equilibrated with Different Concentrations of Potassium Chloride At 1 Khz (Temp 25 ± 0.1°C)

Electrolyte Concen. (M/L)	Iron phosphate Membrane		Cupric phosphate Membrane		Complex Iron-Cupric phosphate Membrane	
	R_X (Ω)	C_X (μF)	R_X (Ω)	C_X (μF)	R_X (Ω)	C_X (μF)
1 x 10^{-4}	47.30 x 10^{2}	1.60 x 10^{-2}	33.00 x 10^{2}	1.80 x 10^{-2}	43.90 x 10^{2}	2.20 x 10^{-2}
1 x 10^{-3}	31.50 x 10^{2}	3.20 x 10^{-2}	22.00 x 10^{2}	5.50 x 10^{-2}	26.90 x 10^{2}	4.30 x 10^{-2}
1 x 10^{-2}	18.90 x 10^{2}	5.30 x 10^{-2}	12.10 x 10^{2}	7.70 x 10^{-2}	16.10 x 10^{2}	6.50 x 10^{-2}
1 x 10^{-1}	8.40 x 10^{2}	10.50 x 10^{-2}	5.60 x 10^{2}	13.20 x 10^{-2}	7.50 x 10^{2}	11.80 x 10^{-2}
1 x 10^{0}	3.20 x 10^{2}	16.80 x 10^{-2}	2.60 x 10^{2}	18.70 x 10^{-2}	3.20 x 10^{2}	17.20 x 10^{-2}
2 x 10^{0}	1.40 x 10^{2}	18.90 x 10^{-2}	1.10 x 10^{2}	20.90 x 10^{-2}	1.20 x 10^{2}	18.80 x 10^{-2}

Table - 2. Electrical Resistance (R_x) and Capacitance (C_x) Observed Across Parchment Supported Iron Phosphate, Cupric Phosphate and Complex Iron-Cupric Phosphate Membrane Equilibrated with 0.1 M Pottassium Chloride at Different Oscillator Frequencies (Temp 25 ± 0.1°C)

Oscillator Frequency (Hz)	Iron phosphate Membrane		Cupric phosphate Membrane		Complex Iron-Cupric phosphate Membrane	
	R_X (Ω)	C_X (μF)	R_X (Ω)	C_X (μF)	R_X (Ω)	C_X (μF)
1 x 10^{3}	7.00 x 10^{2}	29.00 x 10^{-2}	4.60 x 10^{2}	51.00 x 10^{-2}	8.50 x 10^{-2}	24.30 x 10^{-2}
2 x 10^{3}	4.50 x 10^{2}	21.50 x 10^{-2}	3.10 x 10^{2}	43.70 x 10^{-2}	6.60 x 10^{2}	19.50 x 10^{-2}
3 x 10^{3}	3.50 x 10^{2}	17.40 x 10^{-2}	2.40 x 10^{2}	35.70 x 10^{-2}	5.70 x 10^{2}	16.30 x 10^{-2}
4 x 10^{3}	3.20 x 10^{2}	14.50 x 10^{-2}	1.90 x 10^{2}	33.30 x 10^{-2}	5.30 x 10^{2}	13.40 x 10^{-2}
5 x 10^{3}	2.80 x 10^{2}	11.90 x 10^{-2}	1.80 x 10^{2}	30.50 x 10^{-2}	4.50 x 10^{2}	11.70 x 10^{-2}
6 x 10^{3}	2.40 x 10^{2}	10.40 x 10^{-2}	1.50 x 10^{2}	27.90 x 10^{-2}	4.30 x 10^{2}	10.50 x 10^{-2}

Table - 3. Calculated Values of Membrane Resistance (R_m), Capacitance (C_m), and Impedance (Z) for Parchment Supported Iron Phosphate, Cupric Phosphate and Complex Iron-Cupric Phosphate Membrane Equilibrated With Different Concentrations of Potassium Chloride at 1 KHz (Temp 25 ± 0.1°C)

Electr-olyte Conc. (M/L)	Iron phosphate Membrane			Cupric phosphate Membrane			Complex Iron-cupric Carbonate 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 X 10^{-4}	256.69X10^{2}	1.30X10^{-2}	110.19X10^{2}	270.12X10^{2}	1.50X10^{-2}	94.45X10^{2}	164.47X10^{2}	1.60X10^{-2}	58.95X10^{2}
1 X 10^{-3}	110.00X10^{2}	2.20X10^{-2}	58.89X10^{2}	60.10X10^{2}	3.40X10^{-2}	36.36X10^{2}	77.87X10^{2}	2.80X10^{-2}	39.00X10^{2}
1 X 10^{-2}	66.65X10^{2}	3.70X10^{-2}	35.52X10^{2}	47.40X10^{2}	5.70X10^{-2}	23.95X10^{2}	53.35X10^{2}	4.50X10^{-2}	25.66X10^{2}
1 X 10^{-1}	35.76X10^{2}	8.00X10^{-2}	17.33X10^{2}	31.57X10^{2}	10.80X10^{-2}	13.30X10^{2}	31.76X10^{2}	9.00X10^{-2}	10.96X10^{2}
1 X 10^{0}	31.23X10^{2}	15.00X10^{-2}	9.99X10^{2}	28.96X10^{2}	17.00X10^{-2}	9.01X10^{2}	29.93X10^{2}	15.30X10^{-2}	2.55X10^{2}
2 X 10^{0}	1.90X10^{2}	1.26X10^{-2}	1.67X10^{2}	1.62X10^{2}	68.00X10^{-2}	1.33X10^{2}	1.81X10^{2}	59.10X10^{-2}	1.54X10^{2}

Table - 4. Calculated Values of Membrane Resistance (R_m), Capacitance (C_m), and Impedance (Z) for Parchment Supported Iron Phosphate, Cupric Phosphate and a Complex Iron-Cupric Phosphate Membrane Equilibrated with 0.1 M Potassium Chloride Solution at Different Oscillator Frequencies (Temp 25 ± 0.1ºC)

Oscillator Frequency	Iron phosphate Membrane			Cupric phosphate Membrane			Complex Iron-cupric Carbonate Membrane		
Conc. (Hz)	R_m (Ω)	C_m (μF)	Z(Ω)	R_m (Ω)	C_m (μF)	Z(Ω)	R_m (Ω)	C_m (μF)	Z(Ω)
$1X10^3$	$11.31X10^2$	$11.00X10^{-2}$	$8.90X10^2$	$6.67X10^2$	$16.00X10^{-2}$	$5.54X10^2$	$13.58X10^2$	$9.00X10^{-2}$	$10.74X10^2$
$2X10^3$	$7.54X10^2$	$8.60X10^{-2}$	$5.83X10^2$	$4.17X10^2$	$11.00X10^{-2}$	$3.60X10^2$	$9.12X10^2$	$5.30X10^{-2}$	$7.75X10^2$
$3X10^3$	$6.14X10^2$	$7.60X10^{-2}$	$4.60X10^2$	$3.31X10^2$	$9.80X10^{-2}$	$2.81X10^2$	$7.56X10^2$	$4.00X10^{-2}$	$6.57X10^2$
$4X10^3$	$5.54X10^2$	$6.70X10^{-2}$	$4.21X10^2$	$2.66X10^2$	$9.20X10^{-2}$	$2.25X10^2$	$6.93X10^2$	$3.20X10^{-2}$	$6.03X10^2$
$5X10^3$	$5.32X10^2$	$5.60X10^{-2}$	$3.86X10^2$	$2.36X10^2$	$8.00X10^{-2}$	$2.04X10^2$	$6.11X10^2$	$3.10X10^{-2}$	$5.22X10^2$
$6X10^3$	$5.10X10^2$	$5.50X10^{-2}$	$3.50X10^2$	$1.97X10^2$	$8.00X10^{-2}$	$1.69X10^2$	$5.74X10^2$	$2.70X10^{-2}$	$4.94X10^2$

$$R_m = R_x\,[(1 + X_x/R_x)^2] \tag{1}$$

$$X_x = \frac{1}{\omega C_x} \tag{2}$$

$$C_m = \left(\frac{X_X}{R_X}\right)\left(\frac{1}{\omega R_m}\right) \tag{3}$$

and

$$Z = \sqrt{R^2_x + X^2_x} \tag{4}$$

where ω=2π f and f is the frequency used to measure R_x and C_x.

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 membranes because it cannot be described by a definite equivalent electrical circuit. However, in an ideal case, if simple iron phosphate and cupric phosphate membranes are assumed to form complex iron-cupric phosphate membrane by retaining their identity, it may conform to the circuit shown below-

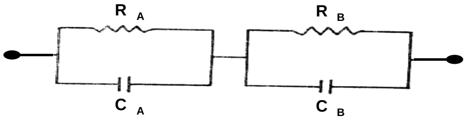

Fig. 2 The equivalent electrical circuit for an ideal complex membrane built from simple membranes R_A, R_B and C_A, C_B are simple membrane resistances and capacitances, respectively.

The impedance of the circuit given in Fig-2 for two units is given by equation

$$\left(\frac{R_A}{1 + J\omega\, C_A.R_A}\right) + \left(\frac{R_B}{1+J\omega\, C_B.R_B}\right) \tag{5}$$

where J= $\sqrt{-1}$, R_A, R_B and C_A, C_B are the membrane resistances and capacitances of the two units (Iron phosphate and cupric phosphate). Separating the real and imaginary parts of Eq. (5) yields.

$$Re = \left(\frac{R_A}{1 + \omega^2.C^2_A.R^2_A}\right) + \left(\frac{R_B}{1 + \omega^2.C^2_B.R^2_B}\right) \tag{6}$$

$$Xe = \left(\frac{\omega C_A.R^2_A}{1 + \omega^2.C^2_A.R^2_A}\right) + \left(\frac{\omega C_B.R^2_B}{1 + \omega^2.C^2_B.R^2_B}\right) \tag{7}$$

However, another equivalent electrical circuit has been used to represent the complex membranes in view of uncontrolled simultaneous deposition of Iron phosphate and cupric phosphate in the interstices of parchment paper[14] as shown in Fig. 3

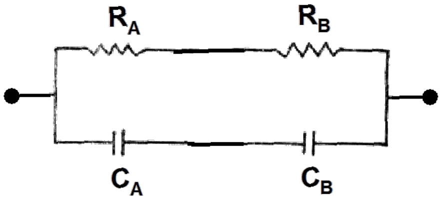

Fig. 3 : The equivalent electrical circuit for the complex

Table - 5. Theoretical and Observed Values of Resistive and Reactive Components of Impedance of Complex Iron-Cupric Phosphate Membrane Equilibrated with Different Concentration of Potassium Chloride at 1 KHz (Temp 25 ± 0.1°C)

Electrolyte Concen. (M/L)	Theoretical Values for Fig. 2		Theoretical Values for Fig. 3		Experimental Values	
	R_e (Ω)	X_e (Ω)	R_e (Ω)	X_e (Ω)	R_e (Ω)	X_e (Ω)
1×10^{-4}	83.78×10^2	192.58×10^2	83.57×10^2	192.42×10^2	43.20×10^2	72.38×10^2
1×10^{-3}	55.95×10^2	79.71×10^2	55.99×10^2	79.94×10^2	26.90×10^2	37.03×10^2
1×10^{-2}	31.82×10^2	51.09×10^2	18.21×10^2	51.16×10^2	16.10×10^2	24.49×10^2
1×10^{-1}	13.93×10^2	27.14×10^2	13.93×10^2	27.30×10^2	7.50×10^2	13.49×10^2
1×10^{0}	5.98×10^2	17.99×10^2	5.98×10^2	17.99×10^2	3.20×10^2	9.25×10^2
2×10^{0}	2.50×10^2	1.59×10^2	2.51×10^2	1.60×10^2	1.25×10^2	0.84×10^2

Table - 6. Theoretical and Observed Values of Resistive and Reactive Components of Impedance of Complex Iron-Cupric Phosphate Membrane Equilibrated with 0.1 M Potassium Chloride at Different Oscillator Frequencies (Temp 25±0.1°C)

Osciallator Frequency (Hz)	Theoretical Values for Fig. 2		Theoretical Values for Fig. 3		Experimental Values	
	R_e (Ω)	X_e (Ω)	R_e (Ω)	X_e (Ω)	R_e (Ω)	X_e (Ω)
1×10^3	13.77×10^2	7.57×10^2	13.83×10^2	7.53×10^2	8.50×10^2	6.57×10^2
2×10^3	8.08×10^2	6.54×10^2	8.05×10^2	6.53×10^2	6.60×10^2	4.08×10^2
3×10^3	5.88×10^2	4.52×10^2	5.98×10^2	4.55×10^2	5.70×10^2	3.26×10^2
4×10^3	4.89×10^2	3.94×10^2	5.00×10^2	3.99×10^2	5.30×10^2	2.97×10^2
5×10^3	4.59×10^2	3.69×10^2	4.68×10^2	3.74×10^2	4.50×10^2	2.72×10^2
6×10^3	3.88×10^2	3.42×10^2	4.07×10^2	3.52×10^2	4.30×10^2	2.50×10^2

In this case the identity of simple iron phosphate and cupric phosphate are lost and the impedance of the circuit is given by

$$\left[\frac{R_A + R_B}{+ J\omega \left(\dfrac{C_A.C_B}{C_A + C_B} \right) (R_A + R_B)} \right] \qquad (8)$$

Now separating the real and imaginary parts of Eq. (8), we have

$$R_e = \frac{(R_A + R_B)}{\left[1 + \omega^2 \left(\dfrac{C_A\, C_B}{C_A + C_B} \right)^2 (R_A + R_B)^2 \right]} \qquad (9)$$

and

$$X_e = \frac{\omega \left(\dfrac{C_A.C_B}{C_A + C_B} \right) (R_A + R_B)^2}{1 + \omega^2 \left(\dfrac{C_A.C_B}{C_A + C_B} \right)^2 (R_A + R_B)^2} \qquad (10)$$

The values of R_e and X_e determined from Eq-6 and7 or Eq-9 and 10 equilibrating the membranes with different concentrations of various electrolytes at 1KHz oscillator frequency are given in Table-5. These values are comparable to the observed values of R_X and X_X of the both complex membrane particularly at higher concentrations of bathing electrolyte as given in Table-6. The calculated values of R_e and X_e determined from eqs-6 and 7 or Eqs-9 and 10 at different frequencies equilibrated with 0.1 M solutions of various electrolytes are given in Table-6. These values are also comparable to the observed values of R_X and X_X of the complex membrane particularly at higher oscillator frequencies.

It may be concluded that the two equivalent circuits may be utilized or 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[15,16]. The polarization charge on the geometric capacitor in the form of diffused double layer plays an important role and affects the over-all membrane capacitance[17,18]. 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 membrane/electrolyte system and the double layer effect, the equivalent electrical circuit has been analyzed further and may be represented as in Fig.-4. This circuit according to Armstrong[19], 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 the Figs 5and6 where C_g is the specific geometric 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.

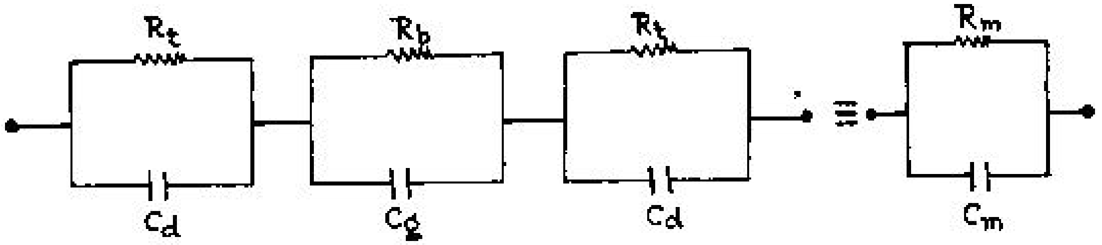

Fig. 4 : Equivalent electrical circuit for a membrane electrolyte system

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

$$\frac{2R_t}{1 + J\omega C_d R_t} + \frac{R_b}{1 + J\omega C_g R_b} = \frac{R_m}{1 + J\omega C_m R_m} \qquad (11)$$

The real and imaginary parts of Eq. 11 are given by

$$\frac{R_m}{1 + \omega^2 C^2_m R^2_m} = \frac{2R_t}{1 + \omega^2 C^2_d R^2_t} + \frac{R_b}{1 + \omega^2 C^2_g R^2_b} \qquad (12)$$

$$\frac{C_m R^2_m}{1 + \omega^2 C^2_m R^2_m} = \frac{2C_d R^2_t}{1 + \omega^2 C^2_d R^2_t} + \frac{C_g R^2_b}{1 + \omega^2 C^2_g R^2_b} \qquad (13)$$

Eq. 13 can be approximated at higher oscillator frequencies as

$$\frac{1}{C_m} = \frac{1}{C_g} + \frac{2}{C_d} \qquad (14)$$

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[19]. For higher electrolyte concentrations and/or significant surface charge[20,21].

$$1/C_g >> 2/C_d \text{ so that } C_m \approx C_g$$

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. 14. 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 (E_m). If $\sigma_s = 0$, then according to Longer *et al.*[21].

$$C_d = \frac{\in_0 \in_\omega \operatorname{Sin} h\alpha}{(1/K)\,\alpha} \qquad (15)$$

where $\in_0 = 8.85 \times 10^{-14}$ F/C_m, $\in_\omega$ is the dielectric coefficient of water, $\propto$ is a constant which takes into account the structural details of membrane polymer, and (1/K) is the Debye-Huckel length given by

$$\frac{1}{K} = \frac{4.31 \times 10^{-8}}{(2/\mu)^{1/2}} \qquad (16)$$

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

$$\left[\frac{\in_0 \in_\omega}{(1/K)\, C_g} \operatorname{Sin} h\alpha + 2 \right] = \frac{E_m}{2\,(RT/F)} \qquad (17)$$

Or alternatively from

$$C_m E_m = \sigma_p = 4FC\,(1/K) \operatorname{Sin} h\alpha \qquad (18)$$

where σ_p is the polarization charge on the capacitor. Eq.15 can be reduced to

$$C_d = \left[\frac{\in_0 \in_\omega}{(1/K)} \right] \qquad (19)$$

If $E_m << RT/F$ so that $\sin h\alpha = \alpha$. The values of C_d calculated from Eq. 17 at different electrolyte concentrations are given in Table-7. The different values of C_d calculated from Eq. 12 for parchment supported Iron phosphate, Cupric phosphate and complex Iron-Cupric Phosphate membranes for potassium chloride electrolyte solution are also given in Table-7. The difference in the values of C_d calculated from Eqs. 15 and 19 is attribute to the presence of polarizing charge and other structural details of membrane matrix.

Table - 7. Calculated Values of Interfacial Double Layer Capacitance (Cd) for Parchment Supported Iron Phosphate,Cupric Phosphate and the Comlex Iron-Cupric Phosphate Membranes Equilibrated with Different Concentrations of Potassium Chloride at 1 KHz (Temp 25 ± 0.1°C)

Electrolyte Concentrations (M/L)	Cd from eq. 19 (μF)	Cd from eq. 15 Iron phosphate Membrane (μF)	Cd from eq. 15 Cupric phosphate Membrane(μF)	Cd from eq. 15 Complex Iron-Cupric phosphate Membrane(μF)
1×10^{-4}	2.28	0.035	0.030	0.033
1×10^{-3}	7.22	0.078	0.072	0.058
1×10^{-2}	22.82	0.285	0.125	0.097
1×10^{-1}	72.18	-0.267	0.257	0.212
1×10^{0}	228.25	-0.150	0.454	0.413
2×10^{0}	322.78	–	–	–

The frequency dependence of the electrical impedance of membranes is conveniently represented by the complex impedance spectra[22]. The impedance spectra of complex plane for all the membranes are represent in Figs. 5 and 6. 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 non-homogeneity and rough membrane surface as examined by previous workers[21-23]. It may, therefore, be concluded that the membrane/electrolyte system can be represented by a model equivalent electrical circuit as shown in Fig. 4 and the values of membrane

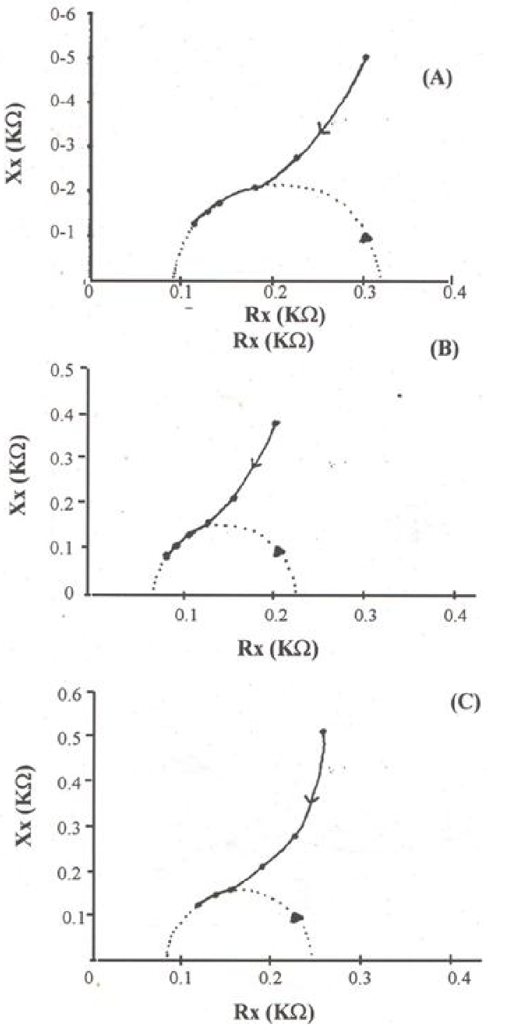

Fig. 5. Theoretical (----) and experimental (——) complex inpedance spectra for (A) Iron phosphte (B) Cupric phosphate (C) complex Iron-Cupric phosphate membrane equilibrated with

capacitance (C_m) as a function of electrolyte concentration is accurately predicted by double layer theory.

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