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RESEARCH ARTICLE

Complex Impedance Spectra of Charged Membranes A Frequency Dependent Parameter

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ABSTRACT

The electrical double layer is the most important part of an electrochemical cell where all the reactions and process take place. To understand the mechanism of ionic transport through the membrane surface, impedance of parchment supported electrochemically charged complex membranes have been analyzed. The observed values of membrane resistance (R_m), capacitance (C_m) and impedance(Z) were found to be dependent on the concentration of bathing electrolyte and applied oscillator frequencies at isothermal temperature 25 ± 0.1 °C. With the change in electrolytic concentration and oscillator frequencies, the changes in membrane resistance and capacitance have been interpreted in terms of changes produced in the electrical double layer present at the membrane solution surface. The electrical double-layer at the membrane electrolyte interface was influenced and controlled by the transport of ions. The complex impedance spectra have been found to deviate from the theoretical predictions at low frequencies due to non homogenous and rough surface of the charged membrane.

Key words- Electrical Resistance, Electrical Capacitance, Electrical Impedance, Frequency

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INTRODUCTION

Membrane phenomena is widely distributed in chemical science and life science. Membrane technology offers many advantages which correspond to the general tendencies of resources. The performance of a membrane technology process depend essentially on physicochemical properties and hydrodynamic conditions of the membranes. Ion exchange membranes are one of the most advanced separation membranes, which have been widely used in various fields [1-5].

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. Impedance measurement provide a powerful diagnostic tool for the analysis of many electro-chemical system [6-8]. 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 Lead phosphate, Manganese phosphate and complex Lead-Manganese 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.

MATERIAL AND METHODS EXPERIMENTAL

Parchment supported lead phosphate, manganese phosphate and complex lead-manganese phosphate membranes have been prepared by the method of interaction as used in our previous study [9].

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.



Membrane

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 [10]. A thermostat was used to maintain the temperature at $25 \pm 0.1^{\circ}$ C.

RESULTS AND DISCUSSION :

The electrical resistance (R_x) and capacitance (C_x) across parchmentsupported lead phosphate, manganese phosphate and complex lead-manganese 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-1and2.

Table - 1: Electrical Resistance (R_x) And Capacitance (C_x) Observed Across Parchment Supported Lead Phosphate, Manganese Phosphate and Complex Lead-Manganese Phosphate Membranes Equilibrated With Different Concentrations Of Potassium Chloride At 1 KHz (TEMP 25 ± 0.1°C)

Electrolyte Conc.	Lead Phosp Membrane	hate	Manganese p Membrane	hosphate	Complex Lead-Manganese Phosphate Membrane	
(M/L)	R _X (Ω)	C _x (μ F)	R _X (Ω)	C _x (μF)	R _X (Ω)	C _x (μF)
1 x 10-4	49.50x 10 ²	1.60 x 10-2	36.00 x 10 ²	3.50 x 10-2	46.00 x 10 ²	2.30 x 10-2
1 x 10-3	33.00×10^2	3.30 x 10-2	24.00 x 10 ²	6.00 x 10 ⁻²	28.70 x 10 ²	4.60 x 10-2
1 x 10-2	$19.80x \ 10^2$	5.50 x 10 ⁻²	$13.20 \ge 10^2$	8.40 x 10 ⁻²	$17.20 \ge 10^2$	6.90 x 10 ⁻²
$1 \ge 10^{-1}$	$8.80 \ge 10^2$	11.00 x 10 ⁻²	$6.00 \ge 10^2$	14.40 x 10 ⁻²	$8.00 \ge 10^2$	12.60 x 10 ⁻²
$1 \ge 10^{\circ}$	$3.30 \ge 10^2$	17.60 x 10 ⁻²	$3.00 \ge 10^2$	20.40 x 10 ⁻²	$3.10 \ge 10^2$	18.40 x 10 ⁻²
$2 \ge 10^{\circ}$	$1.30 \ge 10^2$	198.0 x 10 ⁻²	$1.20 \ge 10^2$	228.0 x 10 ⁻²	$1.20 \ge 10^2$	205.0 x 10 ⁻²

TABLE - 2: Electrical Resistance (R_x) And Capacitance (C_x) Observed Across Parchment Supported Lead Phosphate, Manganese Phosphate And Complex Lead-Manganese Phosphate Membranes Equilibrated With 0.1 M Potassium Chloride At Different Oscillator Frequencies (TEMP 25 + 0.1°C)

Oscillator	Lead phosphate Membrane		Manganese j Membrane	phosphate	Lead-manganese phosphate Membrane	
(Hz)	R _x (Ω)	C _x (μ F)	$R_{\rm X}(\Omega)$ $C_{\rm X}(\mu F)$		R _x (Ω)	C _x (μF)
1 x 10 ³	8.80 x 10 ²	11.00 x 10 ⁻²	6.00 x 10 ²	14.40 x 10 ⁻²	8.00 x 10 ²	12.60 x 10 ⁻²
$2 \ge 10^3$	$4.40 \ge 10^2$	7.90 x 10 ⁻²	$3.60 \ge 10^2$	9.60 x 10 ⁻²	$4.20 \ge 10^2$	8.90 x 10 ⁻²
3 x 10 ³	$3.00 \ge 10^2$	6.60 x 10 ⁻²	$2.60 \ge 10^2$	7.70 x 10 ⁻²	$2.90 \ge 10^2$	7.20 x 10 ⁻²
4 x 10 ³	$2.50 \ge 10^2$	5.50 x 10 ⁻²	$2.00 \ge 10^2$	7.00 x 10 ⁻²	$2.50 \ge 10^2$	6.40 x 10 ⁻²
5 x 10 ³	$2.20 \ge 10^2$	4.80 x 10 ⁻²	$1.70 \ge 10^2$	6.40 x 10 ⁻²	$2.20 \ge 10^2$	5.90 x 10 ⁻²
6 x 10 ³	$2.00 \ge 10^2$	4.40 x 10 ⁻²	$1.40 \ge 10^2$	6.00 x 10 ⁻²	$2.00 \ge 10^2$	5.70 x 10 ⁻²

Structural simulation is a newer approach to modeling for more complex electrochemical systems [11]. Armstrong [12, 13] 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 [14], 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 - 3:_Calculated Values Of Membrane Resistance (R_m), Capacitance (C_m), And Impedance (Z) For Parchment Supported Lead Phosphate, Manganese _Phosphate And A Complex Lead-Manganese Phosphate Membrane __Equilibrated With Different Concentrations Of _Potassium Chloride At 1 Khz (TEMP 25 ± 0.1°C)

Electrolyte Conc.	Lead Phosphate Membrane		Manganese phosphate Membrane			Complex Lead-Manganese Phosphate Membrane			
(M/L)	R _m (Ω)	C _m (μF)	Ζ(Ω)	R _m (Ω)	C _m (μF)	Ζ(Ω)	R _m (Ω)	C _m (μF)	Ζ(Ω)
1 X 10 ⁻⁴	249.59 X 10 ²	1.20 X 10 ⁻²	111.15 X 10 ²	93.50 X 10 ²	2.10 X 10 ⁻²	73.73 X 10 ²	150.20 X 10 ²	3.40 X 10 ⁻²	108.17 X 10 ²
1 X 10⁻³	103.56 X 10 ²	2.20 X 10 ⁻²	58.46 X 10 ²	53.34 X 10 ²	3.30 X 10 ⁻²	35.78 X 10 ²	70.45 X 10 ²	3.70 X 10 ⁻²	44.97 X 10 ²
1 X 10 ⁻²	62.13 X 10 ²	3.70 X 10 ⁻²	35.07 X 10 ²	40.42 X 10 ²	5.60 X 10 ⁻²	23.10 X 10 ²	48.16 X 10 ²	4.40 X 10 ⁻²	36.89 X 10 ²
1 X 10 ⁻¹	32.61 X 10 ²	8.00 X 10 ⁻²	16.94 X 10 ²	26.38 X 10 ²	11.10 X 10 ⁻²	16.75 X 10 ²	27.96 X 10 ²	8.90 X 10 ⁻²	14.96 X 10 ²
1 X 10º	28.10 X 10 ²	15.50 X 10 ⁻²	9.63 X 10 ²	23.31 X 10 ²	17.70 X 10 ⁻²	8.36 X 10 ²	27.26 X 10 ²	16.30 X 10 ⁻²	12.62 X 10 ²
2 X 10°	1.31 X 10 ²	74.90 X 10 ⁻²	1.52 X 10 ²	1.61 X 10 ²	57.70 X 10 ⁻²	1.39 X 10 ²	1.70 X 10 ²	60.60 X 10 ⁻²	1.63 X 10 ²

Table - 4: Calculated Values Of Membrane Resistance (R_m), Capacitance (C_m), And Impedance (Z) For Parchment Supported Lead Phosphate, Manganese Phosphate And A Complex Lead-Manganese Phosphate Membrane Equilibrated With 0.1 M Potassium Chloride Solution At Different Oscillator Frequencies (Temp $25 \pm 0.1^{\circ}$ c)

Oscillator Frequency	Lead Phosphate Membrane			Manganese phosphate Membrane			Complex lead-Manganese Phosphate Membrane		
(Hz)	R _m (Ω)	C _m (μF)	Ζ(Ω)	R _m (Ω)	C _m (μF)	Ζ(Ω)	R _m (Ω)	C _m (μF)	Ζ(Ω)
1 X 10 ³	32.61 X 10 ²	8.00 X 10 ⁻²	16.94 X 10 ²	26.38 X 10 ²	11.10 X 10 ⁻²	16.75 X 10 ²	27.96 X 10 ²	8.90 X 10 ⁻²	14.96 X 10 ²
2 X 10 ³	27.49 X 10 ²	6.60 X 10 ⁻²	11.00 X 10 ²	22.71 X 10 ²	8.00 X 10 ⁻²	9.04 X 10 ²	23.25 X 10 ²	7.20 X 10 ⁻²	9.88 X 10 ²
3 X 10 ³	24.56 X 10 ²	5.70 X 10 ⁻²	8.58 X 10 ²	20.87 X 10 ²	6.70 X 10 ⁻²	7.36 X 10 ²	21.64 X 10 ²	6.20 X 10 ⁻²	7.92 X 10 ²
4 X 10 ³	23.45 X 10 ²	4.90 X 10 ⁻²	7.66 X 10 ²	18.17 X 10 ²	6.20 X 10 ⁻²	6.02 X 10 ²	17.97 X 10 ²	5.50 X 10 ⁻²	6.70 X 10 ²
5 X 10 ³	22.20 X 10 ²	4.30 X 10 ⁻²	6.99 X 10 ²	16.27 X 10 ²	5.70 X 10 ⁻²	5.26 X 10 ²	15.44 X 10 ²	5.00 X 10 ⁻²	5.83 X 10 ²
6 X 10 ³	20.19 X 10 ²	3.90 X 10 ⁻²	6.35 X 10 ²	15.35 X 10 ²	5.40 X 10 ⁻²	4.64 X 10 ²	12.84 X 10 ²	4.80 X 10 ⁻²	5.07 X 10 ²
		D [/1	· X (D)				(1)		

$$R_{m} = R_{x} \left[(1 + X_{x}/R_{x})^{2} \right]$$
(1)
$$X_{x} = -----$$
(2)

$$\omega C_x$$

$$C_{m} = \begin{pmatrix} X_{X} \\ R_{X} \end{pmatrix} \begin{pmatrix} 1 \\ 0 R_{m} \end{pmatrix}$$

$$Z = \sqrt{R^{2}_{x} + X^{2}_{x}}$$
(3)

and

where $\omega = 2\pi f$ 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 lead-manganese 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

$$\left(\frac{R_{A}}{1 + J\omega C_{A}.R_{A}}\right) + \left(\frac{R_{B}}{1 + J\omega C_{B}.R_{B}}\right)$$
(5)

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

$$Re = \begin{pmatrix} R_{A} \\ 1 + \omega^{2} \cdot C^{2}{}_{A} \cdot R^{2}{}_{A} \\ \hline 1 + \omega^{2} \cdot C^{2}{}_{B} \cdot R^{2}{}_{B} \\ \hline 1 + \omega^{2} \cdot C^{2}{}_{B} \cdot R^{2}{}_{B} \end{pmatrix} + \begin{pmatrix} R_{B} \\ \hline 1 + \omega^{2} \cdot C^{2}{}_{B} \cdot R^{2}{}_{B} \\ \hline 1 + \omega^{2} \cdot C^{2}{}_{B} \cdot R^{2}{}_{B} \end{pmatrix} + (7)$$
(6)
(7)

However, another equivalent electrical circuit has been used to represent the complex membranes in view of uncontrolled simultaneous deposition of lead phosphate and manganese phosphate in the interstices of parchment paper¹⁵ as shown in Fig.3



Fig. 3 : The equivalent electrical circuit for the complex membrane

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

$$\left(\begin{array}{c} R_{A} + R_{B} \\ \hline \\ C_{A} - C_{B} \\ \hline \\ 1 + J \omega \\ \hline \\ \hline \\ C_{A} + C_{B} \\ \hline \\ \hline \\ C_{A} + C_{B} \\ \end{array}\right) (R_{A} + R_{B})$$
(8)

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

$$R_{e} = \frac{(R_{A} + R_{B})}{\left(1 + \omega^{2} \left(\frac{C_{A} C_{B}}{C_{A} + C_{B}}\right)^{2} (R_{A} + R_{B})^{2}\right)}$$
(9)
$$X_{e} = \frac{\omega \left(\frac{C_{A} C_{B}}{C_{A} + C_{B}}\right)^{2} (R_{A} + R_{B})^{2}}{\left(\frac{C_{A} + C_{B}}{C_{A} + C_{B}}\right)^{2} (R_{A} + R_{B})^{2}}$$
(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.

and

Impedance Of Complex Lead-Maganese Phosphate Membrane Equilibrated With Different						
Concentration Of Potassium Chloride AT 1 Khz (TEMP $25 \pm 0.1^{\circ}$ c)						
Electrolyte	ctrolyte Theoretical Values for Theoretical Values for Fig. Experimental					
•				•	-	
Conc.	Fig. 2		3	U	Values	
Conc. (M/L)	Fig. 2 R _e (Ω)	Χ _e (Ω)	3 R _e (Ω)	Χ _e (Ω)	Values Re (Ω)	Χ _e (Ω)

58.29 x10²

32.73 x10²

 $14.87 \ x10^{2}$

 $6.33 \text{ x} 10^2$

 $2.15 \text{ x} 10^2$

75.86 x10²

 $44.45 \text{ x}10^2$

25.65 x10²

16.90 x10²

 $1.29 \text{ x} 10^2$

28.70 x10²

17.20 x10²

 $8.00 \text{ x}10^2$

 $3.10 \text{ x} 10^2$

 $1.20 \text{ x} 10^2$

34.62 x10² 23.08 x10²

12.64 x10²

8.65 x10²

 $0.78 \ x10^{2}$

TABLE - 5: Theoretical And Observed Values Of Resistive And Reactive Components Of

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.

Table - 6: Theoretical And Observed Values Of Resistance And Reactive Components Of Impedance Of Complex Lead-Manganese Phosphate Membrane Equilibrated With 0.1 M Potassium Chloride At Different Oscillator Frequencies (TEMP $25 \pm 0.1^{\circ}$ C)

Oscillator Frequency	Theoretical Fig. 2	l Values for	Theoretical Values for Fig. 3		Experimental Values	
(Hz)	R _e (Ω)	Χ _e (Ω)	R _e (Ω)	Χ _e (Ω)	R _e (Ω)	Χ _e (Ω)
1 x 10 ³	14.87×10^{2}	25.62 x10 ²	14.87 x10 ²	25.65 x10 ²	8.00 x10 ²	12.64 x10 ²
2 x 10 ³	$8.10 \text{ x} 10^2$	17.41 x10 ²	8.09 x10 ²	18.46 x10 ²	4.20 x10 ²	8.94 x10 ²
3 x 10 ³	$5.69 \text{ x} 10^2$	$15.07 \text{ x} 10^2$	$5.69 \text{ x} 10^2$	15.00 x10 ²	2.90 x10 ²	$7.37 \text{ x} 10^2$
4 x 10 ³	$4.53 \text{ x} 10^2$	12.96 x10 ²	$4.53 \text{ x} 10^2$	12.96 x10 ²	$2.50 \text{ x} 10^2$	$6.22 \text{ x} 10^2$
5 x 10 ³	$3.94 \text{ x} 10^2$	11.66 x10 ²	$3.94 \text{ x} 10^2$	$11.84 \text{ x} 10^2$	$2.20 \text{ x} 10^2$	$5.90 \text{ x} 10^2$
6 x 10 ³	$3.49 \text{ x} 10^2$	$10.51 \text{ x} 10^2$	$3.48 \text{ x} 10^2$	$10.57 \text{ x} 10^2$	$2.00 \text{ x} 10^2$	$5.70 \text{ x} 10^2$

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 behavior¹⁶⁻¹⁷. 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 [18, 19]. The applied frequency across the membrane has been found to affect the double layer capacitance by the movement of ions across order to investigate the impedance characteristics it. In 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 [20], 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 Fig.-5 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.

1 x 10-3

1 x 10⁻²

 $1 \ge 10^{-1}$

 $1 \ge 10^{\circ}$

 $2 \ge 10^{\circ}$

57.99 x10²

33.53 x10²

14.87 x10²

6.33 x10²

 $2.15 \text{ x} 10^2$

75.19 x10²

48.10 x10²

25.62 x10²

16.90 x10²

 $1.29 \text{ x} 10^2$





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

$$\frac{2R_{t}}{1 + J\omega C_{d}R_{t}} + \frac{R_{b}}{1 + J\omega C_{g}R_{b}} = \frac{R_{m}}{1 + J\omega C_{m}R_{m}}$$
(11)
eal and imaginary parts of Eq. 11 are given by

The re

$$\frac{R_{m}}{1 + \omega^{2}C_{m}^{2}R_{m}^{2}} = \frac{2R_{t}}{1 + \omega^{2}C_{d}^{2}R_{t}^{2}} + \frac{R_{b}}{1 + \omega^{2}C_{g}^{2}R_{b}^{2}}$$
(12)

$$\frac{C_m R_m^2}{1 + \omega^2 C_s^2 R_s^2} = \frac{2C_d R_t^2}{1 + \omega^2 C_s^2 R_s^2} + \frac{C_g R_b^2}{1 + \omega^2 C_s^2 R_s^2}$$
(13)

 $1 + \omega^2 C_m^2 R_m^2$ $1 + \omega^2 C_d^2 R_t^2$ $1 + \omega^2 C_{g}^2 R_{b}^2$ Eq. 13 can be approximated at higher oscillator frequencies as 1 1 2 (14) C_{g} C_{m} C_{d}

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 Armstrong²⁰. For higher electrolyte concentrations and/or significant surface charge[21, 22].

 $1/C_{g} >> 2/C_{d}$ 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.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. [22].

$$C_{d} = \frac{\epsilon_{0} \epsilon_{\omega} \sin h\alpha}{(1/K) \alpha}$$
(15)

where $\epsilon_0 = 8.85 \times 10^{-14} \text{ F/C}_m$, ϵ_{ω} is the dielectric coefficient of water, ∞ is a constant which takes into account the structural details of membrane polymer, and (1/K) is the Debye-Huckel length given by

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

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

$$\left[\begin{array}{c} \underbrace{\epsilon_{0} \epsilon_{\omega}}{(1/K) C_{g}} & \operatorname{Sin} h\alpha + 2 \end{array}\right] = \frac{E_{m}}{2 (RT/F)}$$
(17)

Or alternatively from

 $C_m \ E_m = \sigma_p = 4FC \ (1/K) \ Sin \ h\alpha \qquad (18)$ where σ_p is the polarization charge on the capacitor. Eq.15 can be reduced to

 $C_{d} = \left(\begin{array}{c} \frac{\epsilon_{0} \epsilon_{\omega}}{(1/K)} \end{array}\right)$ (19)

If $E_m << RT/F$ so that sin $h\alpha = \alpha$. The different values of C_d calculated from Eq.15 and 19 for parchment supported lead phosphate, manganese phosphate and complex lead-manganese Phosphate membranes for potassium chloride electrolyte solution at different electrolyte concentrations 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 Lead Phosphate, Manganese Phosphate And The Comlex Lead-Manganese Phosphate Membranes Equilibrated With Different Concentrations Of Potassium Chloride AT 1 Khz (TEMP $25 \pm 0.1^{\circ}$ c)

Electrolyte Concentrations (M/L)	Cd from eq. 19 (μF)	C₄ from eq. 15 lead phosphate Membrane (μF)	C _d from eq. 15 manganese phosphate Membrane (μF)	C _d from eq. 15 Complex lead- manganese phosphate Membrane (µF)
1 x 10-4	2.28	0.02	0.04	0.07
1 x 10-3	7.22	0.04	0.07	0.08
1 x 10-2	22.82	0.08	0.12	0.09
1 x 10-1	72.18	0.18	0.27	0.21
$1 \ge 10^{\circ}$	228.25	0.39	0.51	0.44
$2 \ge 10^{\circ}$	322.78			

The frequency dependence of the electrical impedance of membranes is conveniently represented by the complex impedance spectra²³. The impedance spectra of complex plane for all the membranes are represent in Fig.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 non-homogeneity and rough membrane surface as examined by previous workers²²⁻²⁴. 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 capacitance (C_m) as a function of electrolyte concentration is accurately predicted by double layer theory.



Fig. 5 : Theoretical (----) and experimental (----) complex impedance spectra for (A)lead phosphate (B) manganese phosphate (C) complex lead-manganese phosphate membrane equilibrated with 0.1M KCl solution.

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