

Full Paper

Impedance Characteristics and Electrical Double Layer Capacitance of Polystyrene Based Nickel Arsenate Membrane

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Abstract- Polystyrene-based nickel arsenate membranes were prepared by sol-gel method for various electrolytes (KCl and NaCl) at different concentrations and found to be quite stable. The membrane capacitance and resistance obtained values were found to dependent on the concentration of the electrolyte and to depend on the applied oscillator frequency at isothermal temperature ($25 \pm 0.1^\circ\text{C}$). 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 to be pushed inside the membrane. Thus, the membrane becomes more conductive to the incoming ions, which in turn, supports the trend in the behaviour of the membrane resistance under discussion. Deviations from the ideal behaviour in the lower frequency range were attributed to the non-homogeneous nature of the membrane used in the investigation.

Keywords- Capacitive Reactance, Capacitance, Frequency, Impedance, Interfacial Double Layer Capacitance

1. INTRODUCTION

Organic–inorganic composite materials have attained a great deal of attention because of their useful integration of properties encompassing both organic and inorganic characteristics within a single molecular-scale. A composite material is consist of two or more physically distinct components and exhibits properties that are entirely different from their original components. These materials with controlled functionality and hydrophobicity have opened new avenues for organo-metallic chemistry [1,2].

A flat electrical double layer is created by a charged plane in contact with an electrolyte solution composed of solvent molecules, counter-ions (ions with the charge of the opposite sign than the plane) and co-ions (ions with the charge of the same sign as the plane). Phenomena involving the electrical double layer are common in systems in contact with the electrolyte solution, such as biological and artificial membranes [3], in liquid crystals [4], in clays [5], and solid electrolytes [6].

The electrical double layer is the most important part of an electrochemical cell, where all reactions and processes take place. But in spite of decades of research, our knowledge of its structure and composition, of the distribution of the various particles, is limited; in particular, there is a lack of reliable models. The universal starting point for double-layer theory is the venerable Gouy–Chapman theory [7,8], which is based on continuum theory. An important step towards a molecular description was made in the 1980, when the statistical mechanics of an ensemble of hard spheres was solved in the mean-spherical approximation and combined with the jellium model [9,10]. This model explained the large effect that the electrode has on the interfacial capacity, and, despite its simplicity, gave the correct trend and order of magnitude for sp metals at the potential of zero charge (pzc). An extension to higher charge densities proved difficult, and not much progress has been made in this line of research since.

This paper describes the analysis of membrane impedance under various conditions of electrolyte concentration and applied oscillator frequency in order to understand the mechanism of ionic transport through the membrane surface. In addition, the values of electrical double layer capacitance were computed as a function of concentration in order to ascertain the influence of further investigations.

2. EXPERIMENTAL

2.1. Preparation of membrane

Nickel arsenate precipitates were prepared by mixing a 0.2 M nickel chloride (99.98%, Merck Chemicals) solution and a 0.2 M sodium arsenate (99.98%, Merck Chemicals) solution. The solution pH was adjusted to 1.0 by adding dilute hydrochloric acid (32%, Merck Chemicals) solution in the precipitate. The precipitates formed were allowed to stand

for 24 h in the mother liquor. The supernatant liquid was later removed and the precipitates were washed several times with demineralized water to remove excess of acid and finally filtered using suction pump. The products were dried at 80 ± 2 °C in a vacuum oven (Binder VD25) and later ground to a free flowing powder using a pestle and mortar. Membranes were prepared employing suitable ratios of polystyrene (99.98%, Otto Kemi) as the binder [11]. The nickel arsenate and polystyrene powders were mixed thoroughly using a pestle and mortar. The resultant mixture was placed in an oven maintained at 200 °C for about an hour to equilibrate the reaction mixture [12]. Composite membranes prepared by embedding 25% polystyrene with nickel arsenate had the highest mechanical stability and gave reproducible results. Those containing greater amounts ($> 25\%$) of polystyrene did not give reproducible result while those with lesser amounts of polystyrene ($< 25\%$) were found to be unstable. All membranes were prepared by pressing the powder of the composite into pellets employing a hydraulic press (Carver Hydraulic Unit Model 3912, Wabash, USA).

2.2. Measurement of membrane resistance and capacitance

The freshly prepared membrane was installed at the centre of the measuring cell, which had two glass tube cells as shown in Fig. 1, with one on either side of the membrane. The half-cell contained 20 mL of the electrolyte solution while the capacity of each of the half cells holding the membrane was about 30 mL. Platinum electrodes connected to the digital multimeter meter (T48 Electronic DMM, Digital Multimeter, HellermannTyton) were used to measure membrane resistance and capacitance. Aqueous solutions of potassium and sodium chloride were used as electrolytes. All the solutions were stored in special airtight bottles to avoid exposure of solutions to air and evaporation. All solutions were prepared by using analytically reagent (AR grade) chemicals and ultra-pure distilled water. The pH of the prepared solutions was found to be between 5.5 and 6. A magnetic stirrer was placed at the bottom of each half-cell to minimize the concentration-polarization at the membrane surfaces and its speed rate was externally controlled. The measurements were carried out at a stirring rate of 500 rpm [13]. All the measurements were carried out under isothermal condition at (25 ± 0.1 °C).

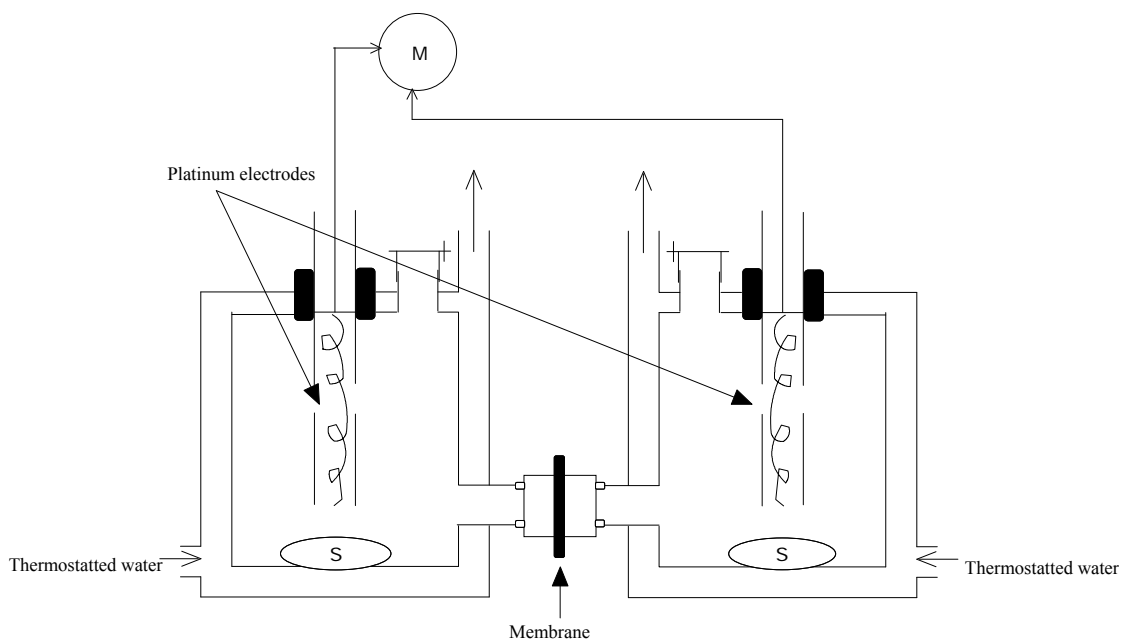


Fig. 1. Apparatus for membrane resistance and capacitance measurements: multimeter (M), magnetic stirring bar (S)

3. RESULTS AND DISCUSSION

A system composed of two identical electrolyte solutions separated by the membrane will be considered as one dimensional [14,15]. The assumptions made are, (a) Two electro-neutral solutions perfectly stirred, (b) two electro-neutral diffusion layers on each side of the membrane, (c) a membrane bulk also electroneutral, and (d) two interfacial Donnan layers.

These last two regions, the interfacial electrical double layers (EDL), generally are very thin, in equilibrium; their thickness is the order of the Debye length [16]. Within these layers there is space electric charge, while beyond these interfacial layers, the solution can be considered as locally electro-neutral. The theory of ion transfer in electrochemical systems where the deviation from the local electro-neutrality is taken into account by using the Poisson equation [17,18] allows the evaluation of the thickness of these charged regions.

The small additional charge was developed on the membrane matrix due to the π electrons of the organic binder (polystyrene). This was verified by prepared membranes which is containing various amounts of the binder. Scanning Electron Microscopy (SEM) was done in the previous work [19].

The variation of electrical resistance with different electrolytes concentration is shown in Fig. 2. The decrease in the values of electric resistance when the electrolyte concentration increase is attributed to the concentration dependence of the eventual electrolyte solution embedded in the membrane network [20]. On the other hand, an increase in applied frequency results in a fast exchange of polarity between the ions and the membrane material.

This, in turn causes leakage of the membrane surface and thus, decreases the resistance, hence, at low electrolyte concentrations, membrane resistance was found to be high [21].

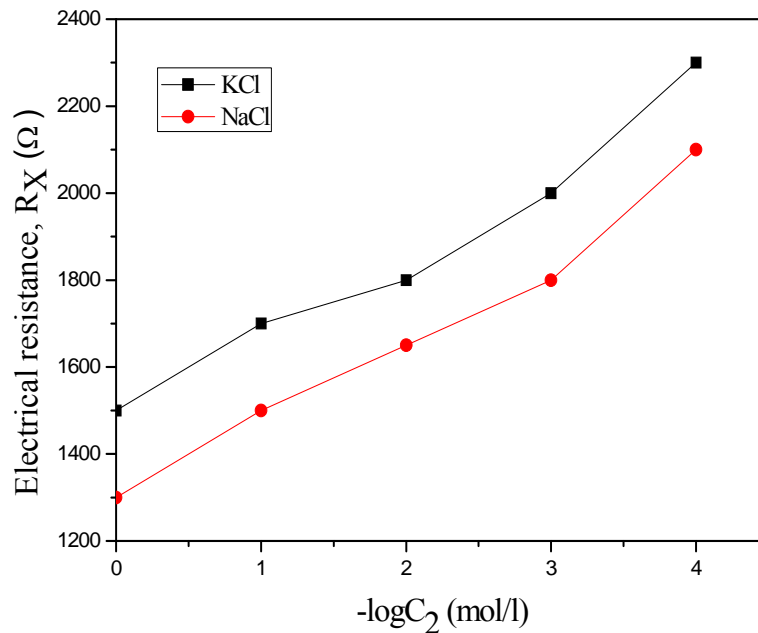


Fig. 2. Plots of electrical membrane resistances vs. $-\log C_2$ for the polystyrene based nickel arsenate membrane using 1:1 electrolytes

The increase of capacitance values with electrolyte concentration (Fig. 3) indicates the rise of an adsorbed charge associated to the double layer developed on the membrane surfaces [22]. On the other hand, the increase of capacitance with the increase of electrolyte concentration is attributable to the changes produced in the dielectric properties and effective thickness of the membrane due to accumulation of ions within the membrane in accordance with the equation for parallel plate capacitor.

$$C_x = \varepsilon/36 \times 10^4 d \quad (1)$$

Thus, the capacitance increases with increase in the dielectric constant as well as with decrease in the effective thickness (d) of the membrane. An increase in the electrolyte concentration results in an accumulation of ions within the membrane. This causes decrease in the effective thickness of the membrane due to squeezing of water molecules from the membrane framework by the incoming ions.

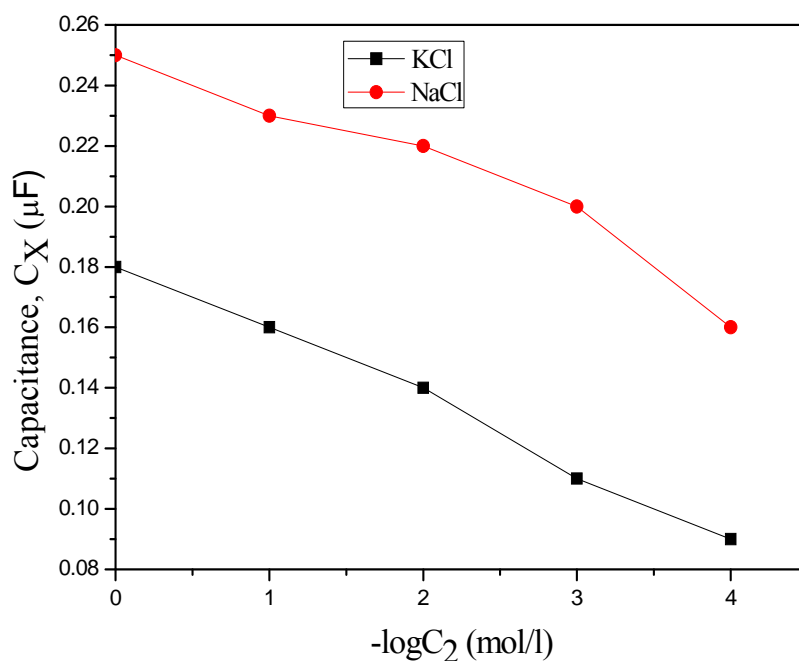


Fig. 3. Plots of capacitances vs. $-\log C_2$ for the polystyrene based nickel arsenate membrane using 1:1 electrolytes

The double layer theory [23] may also be used to interpret the changes produced in the magnitude of capacitance with the change in electrolyte concentration. The variations of electric resistance and capacitance of the electrolytes by raising oscillator frequencies were also investigated as shown in Fig. 4 and 5. It was observed that the electric resistance and capacitance of the electrolyte decreases with the increase in oscillator frequency, hence these values were found to be oscillator frequency dependent. At low frequency, the resistance and capacitance were found to be high, whilst up on increasing frequency of electrolytes the resistance and capacitance decreased.

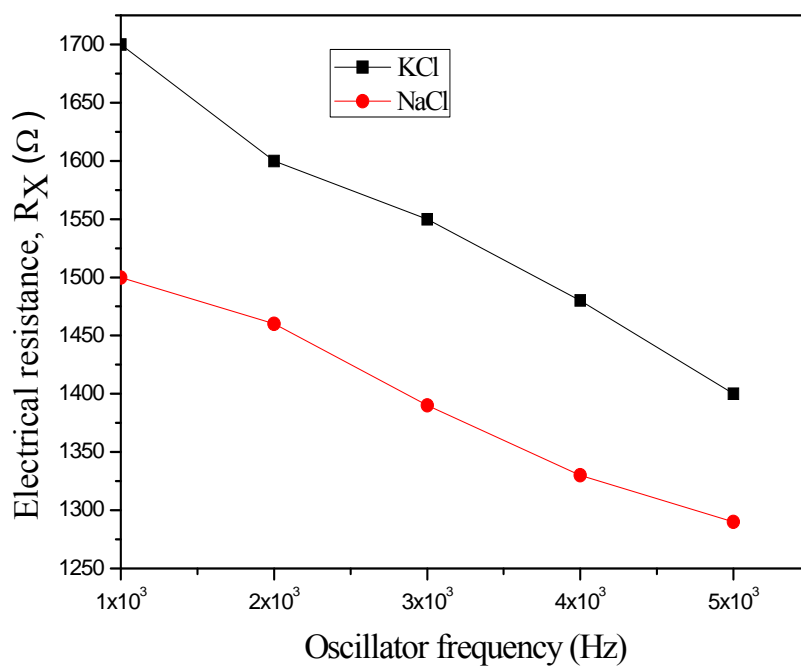


Fig. 4. Plots of electrical resistances vs. oscillator frequency for the polystyrene based nickel arsenate membrane using 1:1 electrolytes

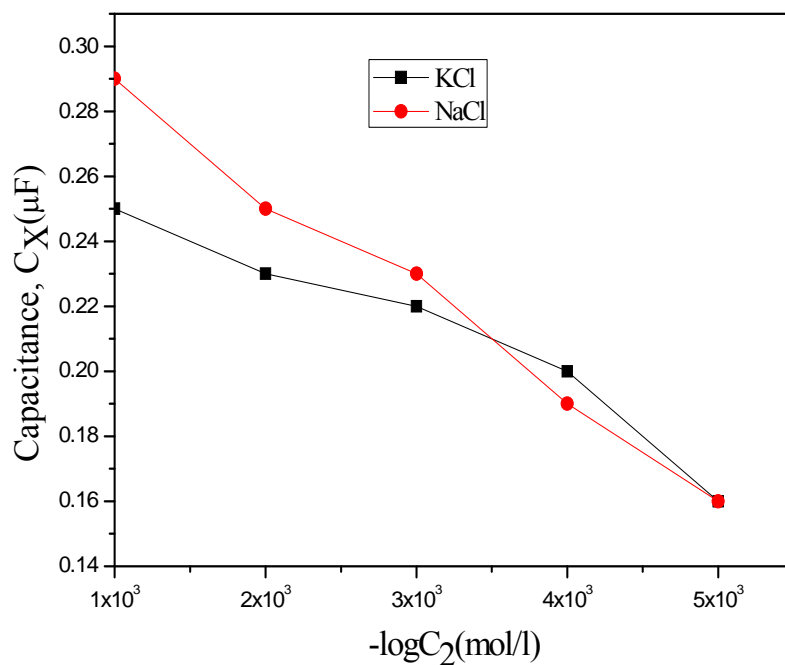


Fig. 5. Plots of capacitances vs. oscillator frequency for the polystyrene based nickel arsenate membrane using 1:1 electrolytes

In order to study the mechanism of flow of ions through the membrane, the impedance, Z along with the membrane resistance, and membrane capacitance, have been evaluated employing the equation proposed by Lakshminarayanaiah and Shanes [24] for an equivalent circuit as shown in Fig. 6 using the following equations:

$$R_M = R_x \left[1 + \left(\frac{X_x}{R_x} \right)^2 \right] \quad (2)$$

$$X_x = \frac{1}{\omega C_x} \quad (3)$$

$$C_M = \left(\frac{X_x}{R_x} \right) \left(\frac{1}{\omega R_M} \right) \quad (4)$$

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

$$\theta = \arctan \left(\frac{X_x}{R_x} \right) \quad (6)$$

In the above equation, R_x is the electrical resistance, X_x is the capacitive reactance, C_x is the capacitance, θ is the phase angle, Z is the impedance of membrane, $\omega = 2\pi f$ and f is the frequency used to measure R_x and C_x . The values of R_M , C_M and Z were calculated as a function of electrolyte concentration and the applied oscillator frequency for membrane, as shown in Fig. 6, 7 and 8. Fig. 6A and B shows that membrane resistance values of the electrolytes were found to be higher at lower concentration and frequency respectively. Thus, membrane resistance values were found to increase with decrease in concentrations and frequency.

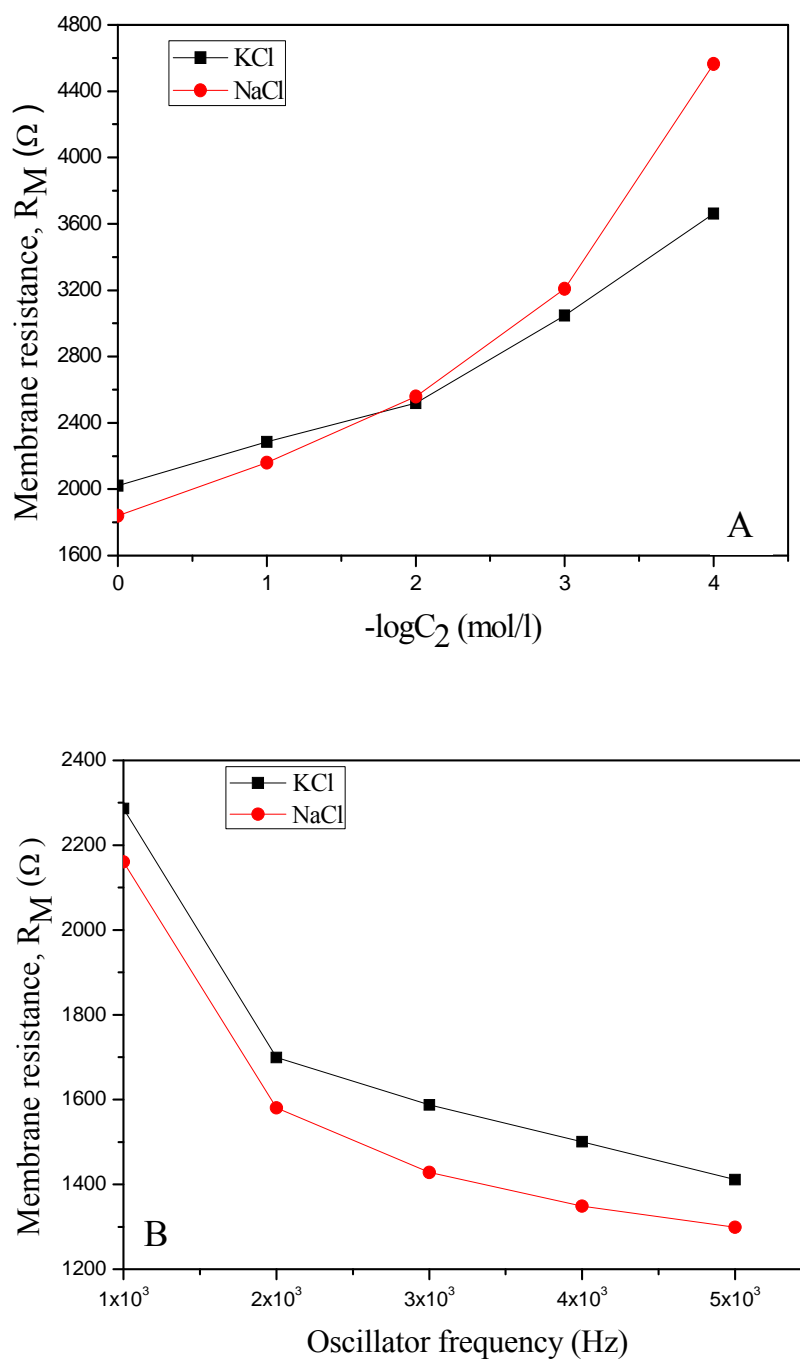


Fig. 6. A) Plots of membrane resistances vs. $-\log C_2$ for the polystyrene based nickel arsenate membrane using 1:1 electrolytes, B) Plots of membrane resistances vs. oscillator frequency for the polystyrene based nickel arsenate membrane using 1:1 electrolytes

The variation of the membrane capacitance with electrolyte concentration is shown in Fig.7A. The increase of the membrane capacitance values is due to the concentration dependence. The values hardly differ even though different electrolytes were employed.

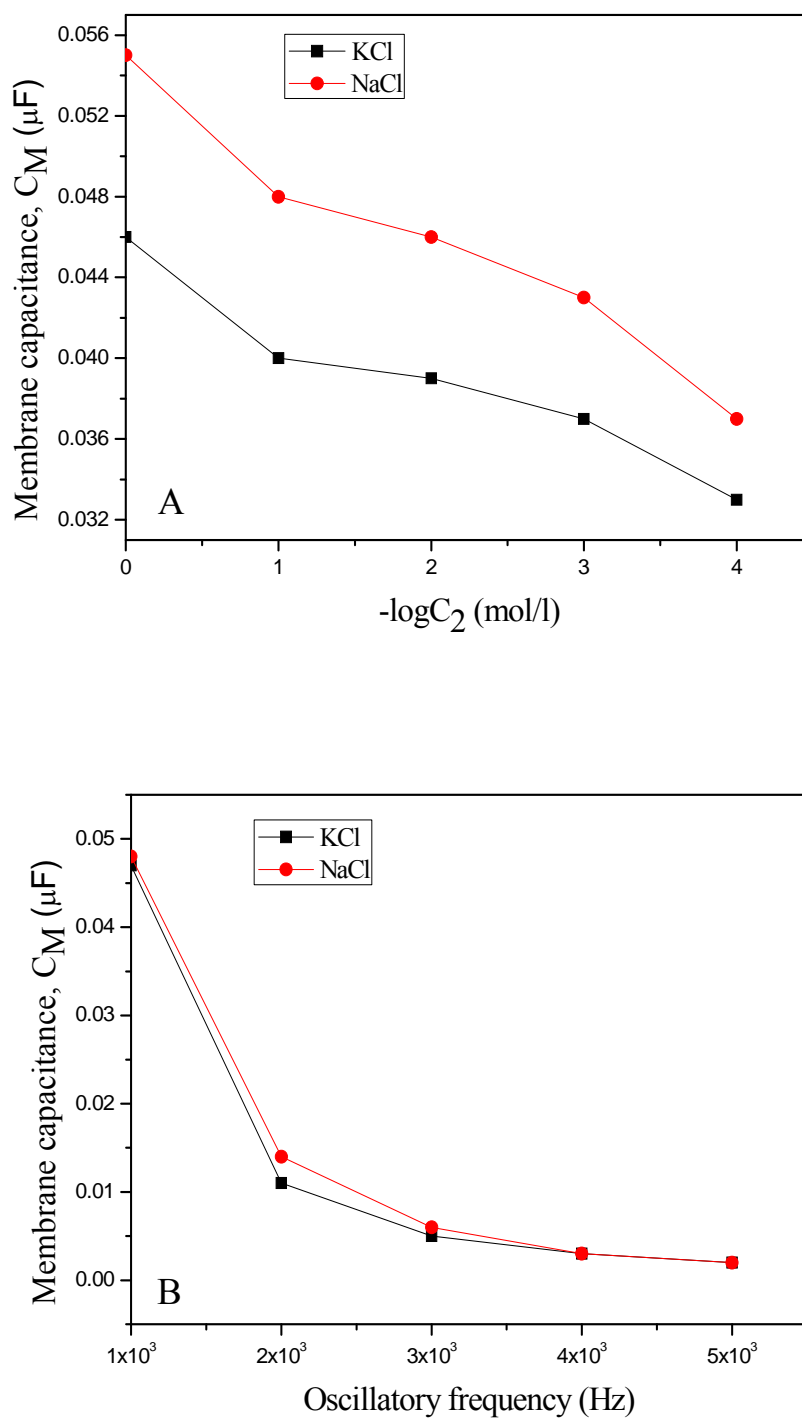


Fig. 7. A) Plots of membrane capacitances vs. $-\log C_2$ for the polystyrene based nickel arsenate membrane using 1:1 electrolytes, B) Plots of membrane capacitances vs. oscillator frequency for the polystyrene based nickel arsenate membrane using 1:1 electrolytes

As shown in Fig. 7B, the value of membrane capacitance decreases significantly with the increase of frequency.

Close look in Fig. 8A and B indicates that, impedance values decrease with increase in electrolyte concentration and applied frequency respectively and this suggests ease in the flow of ions across the membrane.

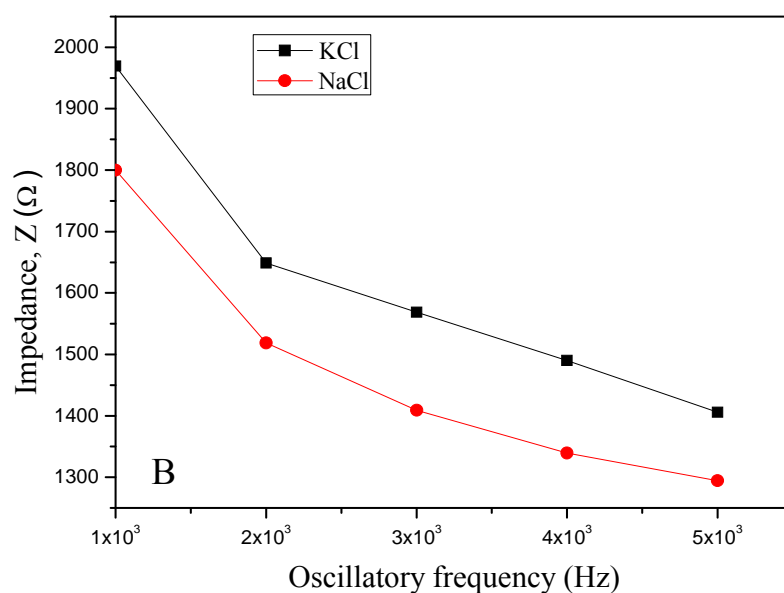
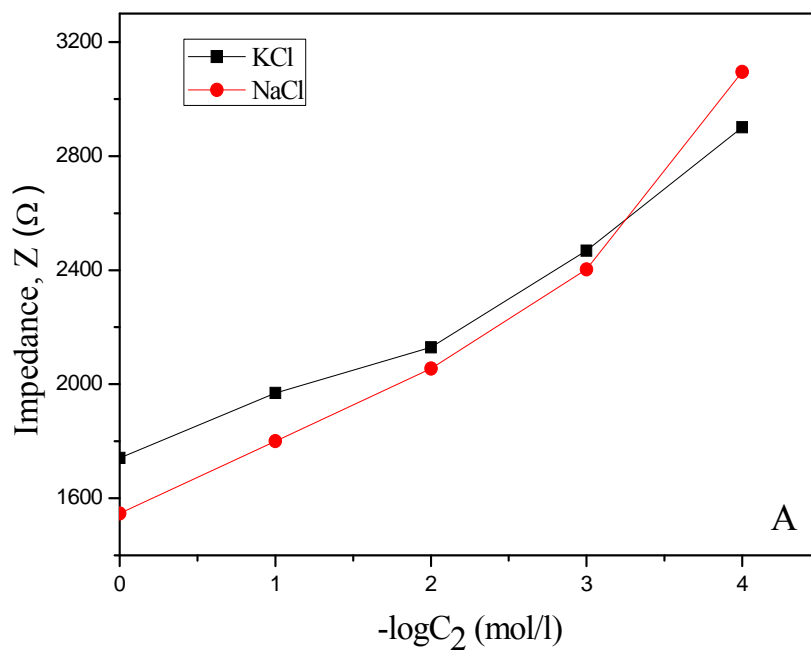


Fig. 8. A) Plots of impedances vs. $-\log C_2$ for the polystyrene based nickel arsenate membrane using 1:1 electrolytes, B) Plots of impedances vs. oscillator frequency for the polystyrene based nickel arsenate membrane using 1:1 electrolytes

In general, the equivalent circuit for a system consists of two parts associated with: (a) the membrane; (b) the electrolyte solution placed between the electrodes and the membrane surfaces; however, in the case of porous membrane that separation is not always possible and a unique electric contribution and, consequently, an equivalent electric circuit for the whole membrane system might be obtained [25]. Impedance is also complex number but it can be separated into real and imaginary parts by algebraic rules where j is the imaginary unit and is used instead of i and in this context to avoid confusion with the symbol for electric current. Electrical resistance is the real part of the impedance and the capacitive reactance is the imaginary part of the impedance.

The obtained results demonstrate that the shape of the capacitance reactance and electrical resistance plot depends entirely on the membrane materials as shown in Fig. 9. The capacitance reactance values increase with an increase of electrical resistance in all the cases.

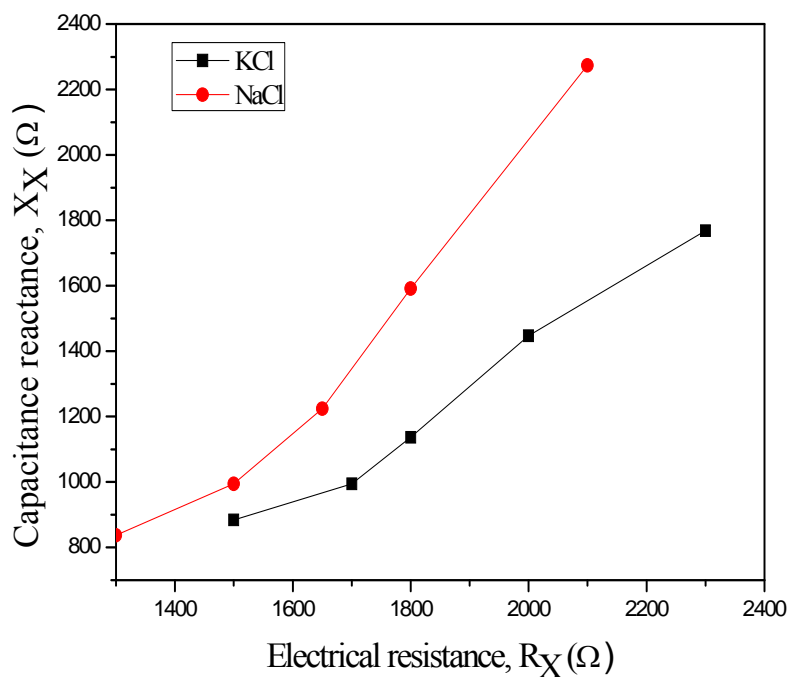


Fig. 9. Plots of capacitance reactances vs. electrical resistance for the polystyrene based nickel arsenate membrane using 1:1 electrolytes

Fig. 10 shows that the capacitance reactance as a function of the oscillatory frequency for membrane with the two electrolytes. The value of capacitance reactance decreases significantly with the increase of oscillator frequency.

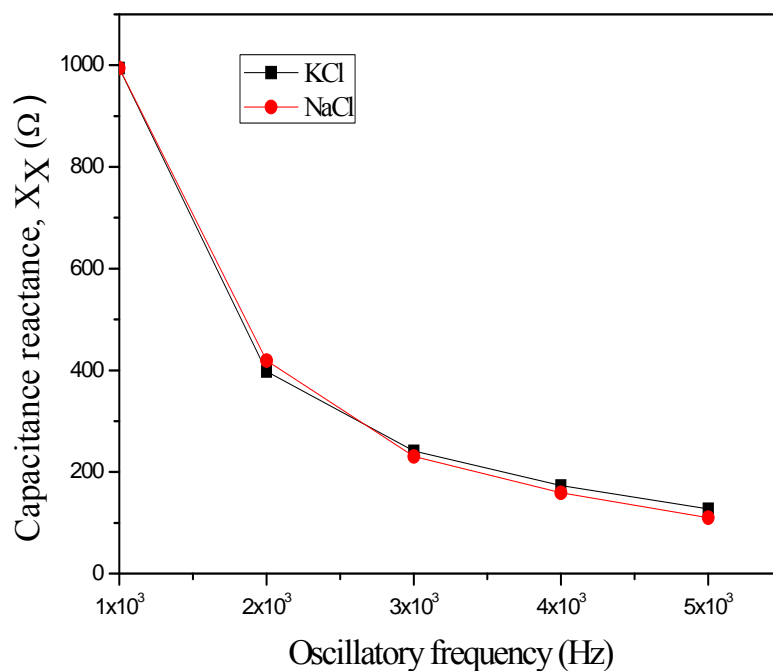


Fig. 10. Plots of capacitance reactances vs. oscillator frequency for the polystyrene based nickel arsenate membrane using 1:1 electrolytes

Fig. 11 shows that, in this specific region of the capacitance reactance and resistance plot (called the planar section [26]), the phase angle approaches asymptotically from 30° to 5° for KCl and from 33° to 4° for NaCl. A unique relaxation process was obtained for the all electrolyte-membrane-electrolyte systems, as was also reported in the literature for highly porous membranes [27,28].

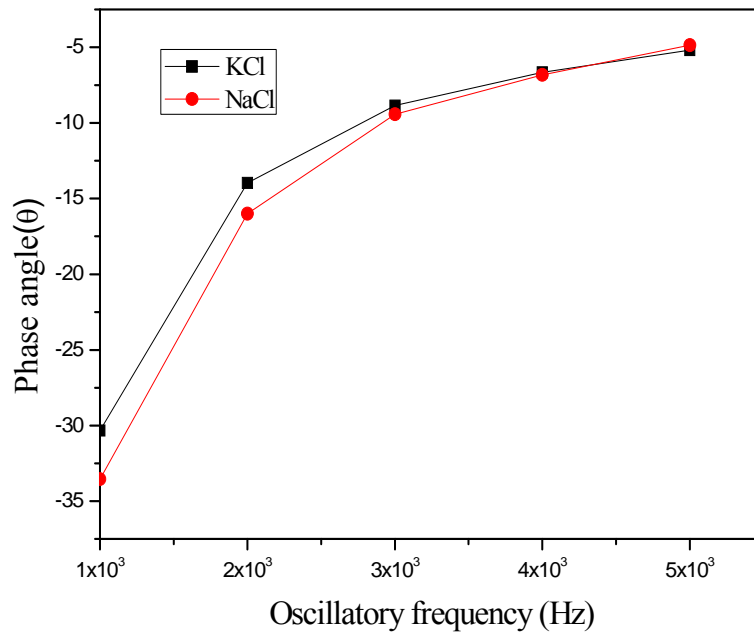


Fig. 11. Plots of phase angles vs. oscillator frequency for the polystyrene based nickel arsenate membrane using 1:1 electrolytes

The electrical double layer at the membrane-solution interface was utilized in several studies for membrane behaviour [29,30]. The polarization charge on the geometric capacitor in the form of diffused doubled layer plays an important role and affects the overall membrane capacitance [31]. The electrical double layer capacitance can be evaluated [32] by employing the expression of the proposed equivalent circuit for the membrane-electrolyte interface is given by

$$\frac{R_M}{1 + j\omega C_M R_M} = \frac{R_T}{1 + j\omega C_D R_T} + \frac{R_B}{1 + j\omega C_G R_B} \tag{7}$$

Where C_G is the specific geometric capacitances, C_D is the interfacial double layer capacitance, R_B is the bulk resistance of the membrane, and R_T is the charge transfer resistance between the membrane-electrolyte interface assuming the transfer to be a single step process. The real and imaginary parts of eq.(1) are given by

$$\frac{R_M}{1 + \omega^2 C_M^2 R_M^2} = \frac{R_T}{1 + \omega^2 C_D^2 R_T^2} + \frac{R_B}{1 + \omega^2 C_G^2 R_B^2} \tag{8}$$

$$\frac{C_M R_M^2}{1 + \omega^2 C_M^2 R_M^2} = \frac{C_D R_T^2}{1 + \omega^2 C_D^2 R_T^2} + \frac{C_G R_B^2}{1 + \omega^2 C_G^2 R_B^2} \tag{9}$$

At higher frequency, Eq. (9) becomes

$$\frac{1}{C_M} = \frac{1}{C_G} + \frac{1}{C_D} \quad (10)$$

This equation indicates that the membrane-electrolyte system may be considered to be composed of two capacitors arranged in series. The geometric capacitor is placed between the two interfacial double layers [32]. For dilute solutions [33], the capacity of the diffuse layer C_G is small compared with the more or less C_D contribution, so that $C_M \approx C_G$. When the diffuse layer becomes more compact and its capacity becomes large compared with that of the C_D , then the latter contribution should dominate. We have to clarify the notion of the potential of zero charge. There are really two such concepts: (1) the potential at which there is no excess electronic charge on the metal; this is called the potential of zero total charge [34], and this we have taken as zero; (2) the potential at which there is no charge in the diffuse double layer; this corresponds to a minimum in the Gouy–Chapman capacity, and is sometimes called the potential of zero free charge.

However, the exact form of the double layer capacitance depends upon the fixed charge (σ_s) and the membrane potential (V_M). If $\sigma_s = 0$, then [35]

$$C_D = \frac{\varepsilon_0 \varepsilon_w \sinh \alpha}{(1/\kappa)\alpha} \quad (11)$$

Where $\varepsilon_0 = 8.85 \times 10^{-14} \text{ F/m}$, ε_w is the dielectric coefficient of water, α is a constant which takes into account the structure details of membrane polymer, F is the Faraday constant and $(1/\kappa)$ is the Debye-Huckle length given by

$$\frac{1}{\kappa} = \left(\frac{4.31 \times 10^{-8}}{\sqrt{2\mu}} \right) \quad (12)$$

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

$$\left[\frac{\varepsilon_0 \varepsilon_w}{(1/\kappa)C_G} \cdot \sinh \alpha + 2 \right] = \frac{V_M}{2(RT/F)} \quad (13)$$

Or alternatively from

$$C_M V_M = \sigma \rho = 4FC(1/\kappa)\sinh \alpha \quad (14)$$

Where $\sigma \rho$ is the polarization charge on the capacitor. Equation (10) can be reduced to

$$C_D = \frac{\varepsilon_o \varepsilon_w}{(1/\kappa)} \quad (15)$$

If $V_M \ll RT/F$ so that $\sinh \alpha = \alpha$. The values of C_D calculated from eq. (15) for the aqueous solutions of all electrolyte, are given in Table I. The data shows that the value of C_D increases with the increase of electrolyte concentration. The difference in the values of C_D calculated from equation (10) and (15) is attributed to the presence of polarizing charge and other structural details of membrane matrix [36].

Table 1. Calculated vales of interfacial double layer Capacitance for polystyrene based nickel arsenate membranes equilibrated with different concentration of KCl and NaCl at 1 kHz (temp=25 ± 0.1 °C)

Electrolyte Conc (M/L)	C_D from eq. (10)		C_D from eq. (15)	
	(μF)		(μF)	
	KCl	NaCl	KCl	NaCl
0.0001	0.063	0.007	1.954	0.779
0.001	0.019	0.011	7.939	1.333
0.01	0.059	0.029	20.492	20.060
0.1	0.152	0.082	50.835	49.325
1.0	0.452	0.203	96.140	82.593

4. CONCLUSIONS

The effects of electrolyte concentration and frequency on the membrane capacitance seemed to be due to some structural changes in the membrane. Increase in electrolyte concentration led to continuous progressive accumulation of ionic species within the membrane surface. Similarly, increase in applied frequency led to a fast exchange of polarity between the ions and the membrane material. The impedance spectra were found to deviate from the theoretical predictions at low frequencies due to non-homogenous and rough surface of the membrane. The electrical double layer at the membrane–electrolyte interface was influenced and controlled by the transport of ions.

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