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Title Synthesis, Influence of Electrolyte Solutions on Impedance Properties and In-vitro Antibacterial Studies of Organic-inorganic Composite Membrane

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Abstract: As stated in the previous work of ours in composite polystyrene-titanium arsenate (PS-Ti-As), both of us studied the impedance behaviour of the PS-Ti-As composite membrane for distinct electrolytic conditions arranged for an experiment. In the present prescribed report, the capacitance and resistance measurements were conducted by enhancing contrary concentrations that is 0.0001 (c (M) (1 of BaCl₂ as well as CaCl₂ of 1:1 electrolyte solutions at isothermal process where temperature remains constant basically at 25 ± 0.1°C. For calculating the membrane resistance (RM), capacitance (CM), reactance (Xx), the measurement of capacitance and resistance were used again and were also formulated to create the impedance (Z) value, as such impedance is an essential characteristic for controlling the membrane phenomena. The dielectric constant also increased with an increase of temperature at 1 kHz oscillatory frequency. According to the simple equivalent electrical circuit model, the data of impedance was evaluated which was found following the theoretical prediction which ranges high frequency. At the membrane-electrolyte interface, the electrical double layer was influenced systematically. The important role played on the geometric capacitor by the charge of polarization forming a diffused double layer which later affected the overall membrane capacitance. The motion of ions through it, which was marked on double-layer capacitance was affected due to the applied frequencies across the membrane. Finally, the composite material was also tested for its antibacterial activity against numerous bacterial cultures that includes *Escherichia coli*, *Bacillus thuringiensis* and *Pseudomonas aeruginosa*. The result of these studies also signifies the activity of the composite as compared with a well-known antibiotic that is tetracycline and therefore, can be specifically used as an antibacterial agent.

Keywords: Polystyrene-titanium-arsenate (PS-Ti-As) composite; capacitive reactance; capacitance; impedance; interfacial double layer capacitance; antibacterial activity

1 INTRODUCTION

In recent years, the hybrid nano-composites which are composed of conducting polymers interacted a great deal of interest for electrochemical-related applications because of their remarkable improvement in the properties of materials, as compared with the virgin polymers. The inorganic and organic entities interact with a kind of hybrid organic and inorganic materials at various molecular level which lies in the nanoscopic domain, and generally represent the best among all properties of each of its components in a very synergic way. It also offers a unique opportunity and characteristic to prepare novel tailor-made materials with its optimal physical, chemical, mechanical as well as electrical properties [1]. It was this multi-functional nature of these materials which made them potentially useful and productful in multiple fields [2,3].

At present, the impedance measurements are used to differentiate a worldwide form of specialized phenomena of electrochemical for the man-made and biological membranes, liquid electrolytes and solid state porous materials. [4]. When compared with different instruments and operation which is devastating and that require special conditions of x-ray, microscopy, vacuum, electromagnetic waves, and so on for those electrical techniques that is earmarked for a reproducible “*in situ*” analysis of the arrangement under a significant operating condition required during the phenomena [5]. In particular, for investigating complex electrochemical system the suitable non-steady skilled method such as AC impedance spectroscopy was used. The electrochemical system pertains to follows a relaxation process, when a minor perturbation is simplified to a regular state. The time response can be analyzed to analyze the overall process as many other basic process changes at various expected rates [6].

A large simplification to the dilemma has come across the leading condition because of the presence of an excess amount of helping electrolyte which pertains to suppress the resettlement of the element of the magnetic fields of electro-active species. It makes their transfer in the bulk film which does not have interaction with each other. The phenomena are linked to important merit of such schemes, which is as follows. The direction of the electricity formed double layers of the interfaces (as well called ‘ charge’) is possessively formed by the sustaining electrolyte, whereas the interfacial charge transfer (process or ion exchange) is brought in by electro- dynamic parts of the original films. It's because of the result of such transfer the effect of charge on the impedance is found to be remarked by the double-layer capacitance which is in accordance with the Faradaic branch [7].

A physical property that is the dielectric constant is acted upon by intermolecular as well as inter- atomic attractions. For separating the electrolytes into their ions the measurement of solvent's efficiency is used. A complete dissociation of the electrolytes is encouraged by the solvent with high dielectric constant, whereas considerable ion pairing occurs in the solvents of low dielectric constant [8]. The behaviour of electrolytes in the solutions is strongly moved by the dielectric constant of the medium and this characteristic is widely employed as a prognostic tool in exercise.

The evidential resources that are available naturally or eventually for the processing of composite material, such as that of bacteria, and fungi, plays a significant and key element in the rectification of toxic metals generally by the diminution in the metal ions [9]. Composite materials are biologically synthesized from the organized and synthesized microbes especially by Gram positive and Gram negative bacteria. Intra as well as extracellular methods is actively used for composite material synthesis, where the extra cellular method of biosynthetically formed nanoparticles is mostly preferable because of its underlying properties such as specificity, simplicity, large-scale synthesis and easier downstream processing [10].

By keeping in view, the present study focussed to introduce Polystyrene based biomaterial to serve as impedance with antibacterial properties. Hereby, now we report the impedance, dielectric constant and electric double layer capacitance of the PS-Ti-As membrane which is followed by their *in vitro* antibacterial screening against three different and prominent bacterial cultures.

2 EXPERIMENTAL

2.1 Synthesis of composite polystyrene-titanium-arsenate membranes

The chemical supplies and the synthesis procedure to obtain PS-Ti-As composite had been described in our previous publications [11,12]. Let us yield a brief information that the first prepared Ti-As composite was mixing by 0.2M titanium (III) chloride and 0.2M sodium arsenate solutions at a constant pH of 1.0 by using dilute HCl and the resulting precipitate was kept it for 24 h at room temperature ($25\pm 0.2^\circ\text{C}$). Following the period of reaction, the precipitate was obtained by vacuum filtration which was washed with Milli-Q water (Millipore, Inc.), dried the residue at $80\pm 0.2^\circ\text{C}$ in a vacuum oven (Binder VD25), ground to a fine powder using a ball mill (Crescent, Wig-L-Bug), and the resulted free flowing powder which was finally sieved using a $75\mu\text{m}$ sieve.

In the upcoming step, Polystyrene was dropped into the Ti-As composite by the mixture of Polystyrene granules that is less than 200 mesh size and at a 200

°C temperature and it was urged with a pressure of 5 tons/cm² respectively. The obtained mixture was embedded in an oven at a specific temperature of 25±0.1°C for about 30 min and kept into cast die of 15.83mm diameter, for bringing the reacted mixture at equilibrium and the membranes was found to be prepared by employing a hydraulic press (Carver Hydraulic Unit Model 3912, Wabash, USA) and compressing the composite into the pellets.

2.2 Measurements of membrane resistance and capacitance

The membrane which has been prepared freshly was cemented at the centre of the cell which is to be assessed, which consists of two parts, each consisting a platinum electrode, for measuring the membrane resistance and the capacity. The volume of each container was approximately 30 cm³. The membrane area was 2.12 cm². A digital multimeter (T48 Electronic Digital Multimeter, HellermannTyton) was utilized to assess the resistance/ $\Omega \pm 0.5$ and capacitance/ $\mu\text{F} \pm 0.5$. Aqueous solutions of BaCl₂ and CaCl₂ were used as electrolytes for the measurements. Both the solutions of BaCl₂ and CaCl₂ were stored in special safety airtight bottles to prevent from air contamination and drying up. The solutions were prepared from ultra-pure distilled water analytical grade reagents (AR grade) and the pH of the solutions was maintained in a range of 5.5-6. At the tail end of each half-cell, a magnetic stirrer was placed which minimizes the concentration-polarization at the membrane surfaces of the membrane and further the calculation as well as estimation were carried away at a stirring rate of 500 RPM that can be controlled externally [13]. The membrane resistance and the capacitance were carried out indiscriminately in the oscillator frequency range of 1-5 kHz at isothermal conditions of constant temperature that is 25±0.1°C, which was subsequently held by water thermostat (Julabo F12-ED). For each system, the experiment was repeated three times.

2.3 Measurement of Antibacterial activity

The antibacterial activity of the PS-Ti-As composite was studied well and significantly by employing the method of agar well-diffusion. The material was tested at a concentration of 0.5 mg mL⁻¹ in dimethyl sulfoxide (DMSO) and compared with the well-known antibiotic that is Tetracycline. Three different bacterial strains (*Escherichia coli*, *Bacillus thuringiensis* and *Pseudomonas aeruginosa*) were taken into account for the study and were tested at material concentrations of 0, 50, 75 and 100 $\mu\text{g mL}^{-1}$. A 100 μL culture broth of about 10⁵ c.f.u. mL⁻¹ of test organism in the log phase, the culture of each recommended strain was inoculated separately in flasks with a dilution of 18 to 48 hours, which was containing the nutrient in broth medium amended with diverse concentrations of the PS-Ti-As material. The flask that was inoculated were placed at the

temperature of 37±1°C on a shaker with the speed of 200 RPM and the growth and development was monitored visually and spectrophotometrically. Later on the specific growth rate and development of bacterial strains was calculated by Stanier *et al.* [14].

3 RESULTS AND DISCUSSION

Our previous work with PS-Ti-As composite primarily deals with the synthesis ofand in depth characterization by various instrumental techniques and methods that enormously includes thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), transmission electron microscopy (TEM), scanning electron microscopy (SEM), x-ray diffraction (XRD), porosity, chemical stability, water uptake, studies with the H9c2 cardiomyoblast cells and also the conductivity measurements under diverse conditions of time, temperature as well as electrolytes respectively [11,12]. In the present study, the measurements of impedance using the PS-Ti-As membrane were carried out under various conditions of the antibacterial efficacy. We therefore presents the results and discussions as in the manners as followed.

Here we are looking at a specific membrane that is usually inserted between the two isothermal media, which is setting aside a mass transfer between them in a sequential order. The permanent flow of charge along with matter is noticed all around it, when the interface is pressed from its rate of equilibrium an external energy source. It is optimistically attained because of the existence of electrochemical reactions which is allowing for the transfer of charge gradients of chemical along with electric potentials, and causes all possible translocation of the reacting species. Although such system is generally considered as non-linear, they are always regarded in a linear regime for each and every small external perturbation [15].

The dielectric constant, ϵ of the membrane was measured at 1 kHz of oscillator frequency and different values of ϵ at various temperatures were evaluated using the relation given below [16].

$$\epsilon = \frac{11.3C_x t}{A} \quad (1)$$

where C_x is the capacitance in μF , t is the thickness of the membrane in cm and A is the surface area in cm² respectively. The thickness of the membrane was taken as 0.075 cm [11].

As the result of experiment, the dielectric constant of the synthesized membrane increases vulnerably with the increase of temperature in the entire range as seen in Fig.1. It is also observed and inferred that; low value dielectric constant can be achieved due to the electronic contribution, ionic jumping orientation and also because of the absence of significant and specific number of space charge polarization [17].

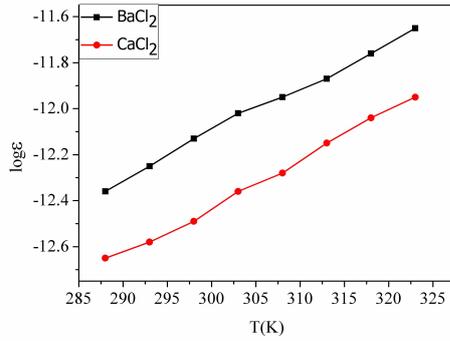


Fig. 1 Plot of dielectric constant versus temperature for the PS-Ti-As composite membrane under 0.1 M of 1:1 electrolyte concentration and 1 kHz oscillator frequency

The differentiation of electrical resistance against the electrolyte concentration for the PS-Ti-As composite membrane is shown in the Fig.2 which will give a clear concept. From the results, the electrical resistance is investigated to be decreased with the increase in the electrolytic concentration for both of the electrolytes. This is due to the well-known fact that the increase in concentration of the electrolyte is responsible to make a progressive accumulation of ionic species that rest inside the membrane. As a result of which, the membrane gain a capability to increasing the conducting ability for the respective ions and therefore, it accounts for a diminution in the values of resistance [18].

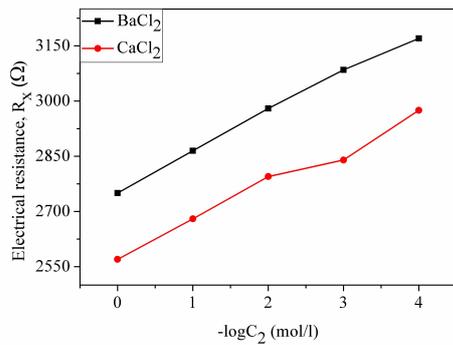


Fig. 2 Plot of electrical resistances versus $-\log C_2$ for the PS-Ti-As composite membrane using 1:1 electrolytes at 1 kHz oscillator frequency

The variation of capacitance against different electrolyte concentration for the PS-Ti-As composite membrane is equally shown in the Fig.3 and it seems from the results that the capacitance is increasing with an increase in the electrolyte concentration. Wandlowski *et al* [19] investigated the influence of an electrolyte concentration on the scale of capacitance and he revealed the fact that the capacitance is enhanced by the increase in electrolyte concentration which is basically because of the changes that have been produced in the dielectric constant (ϵ) and the effective thickness (d) of the membrane-electrolyte interface. This is chosen in agreement with the equation for a parallel plate capacitor that is $C_X = \epsilon/36 \times 10^4 d$. So, as visualized according

to the enlargement in the dielectric constant and reduction of the effective thickness of the membrane electrolyte interface, the capacitance is always found to be increased. In a general sense, increase of the electrolyte concentration is resulting in an agglomeration of ions lying inside the membrane that causes an aptitude decrease in the effective thickness of the membrane that is pertaining to squeeze the water molecules outside the membrane framework by the ions that are entering inside. Therefore, capacitance increases with the addition of electrolyte concentration which enhances the operation. The double layer theory is said to be utilized in understanding the change produced in the extent of capacitance in agreement with the modification of electrolyte concentration [20].

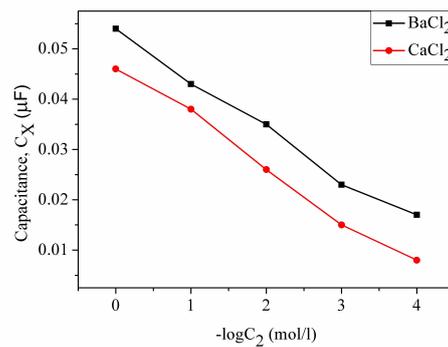


Fig. 3 Plot of capacitances versus $-\log C_2$ for the PS-Ti-As composite membrane using 1:1 electrolytes at 1 kHz frequency

The variations occurring in electric resistance and capacitance of the electrolytes as the effective function of oscillatory frequency were also investigated which are as shown in Figs. 4 and 5, respectively. From the graphs, it is clearly observed that the electric resistance and capacitance of the electrolytes (both BaCl₂ and CaCl₂) decreases with an increase of the oscillatory frequency, hence these are considered to be oscillatory frequency dependent. At a low frequency, the resistance and capacitance were found to be high, whilst up on with the increase of frequency of electrolytes further, both the parameters are found to be decreased. Thus, for the PS-Ti-As composite, the electric resistance and capacitance is depended in the frequency range of 1-5 kHz [21].

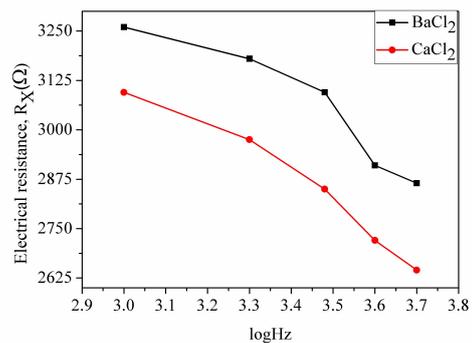


Fig. 4 Plot of electrical resistance versus oscillator frequency for the PS-Ti-As composite membrane under 0.1 M of 1:1 electrolyte solutions

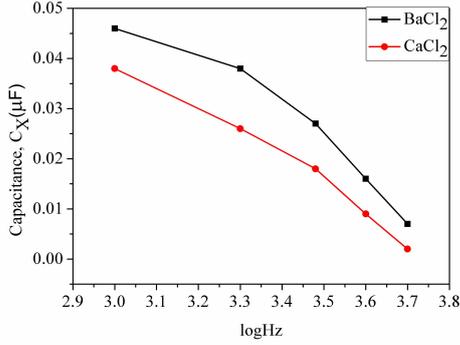


Fig.5 Plots of capacitance versus oscillator frequency for the PS-Ti-As composite membrane when tested under 0.1 M of 1:1 electrolyte solutions

A scheme which is composed of two indistinguishable electrolyte solutions that are disintegrated by the membrane is taken as one dimensional [22]. The assumptions made were as: (a) a membrane bulk also electro-neutral, (b) the two interracial Donnan layers (c) two electro-neutral solutions perfectly stirred and (d) the two electro-neutral layer of diffusion on each and every side of the membrane.

More often than not, the last two interfacial electrical double layers are in equilibrium which are really thin (EDL) and their thickness follows the units of Debye order [23]. In that location is space electric charge within these layers, while beyond these layers, the result is considered as locally electro-neutral. The theory of ionic transfer in electrochemical systems as well as the deflection from the local electro-neutrality is taken into a report by using the Poisson equation [24] by allowing the evaluation of the heaviness of the charged regions respectively.

For examining the mechanism of the flow of ions with the help of the membrane, the impedance that is Z along with the membrane resistance, R_M and membrane capacitance, C_M have been evaluated generally by utilizing the equation which was suggested by Lakshminarayanaiah and Shanes [25].

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

$$X_X = \frac{1}{\omega C_X} \quad (3)$$

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

Impedance of the membrane can be written in the form as given below

$$|Z| = \sqrt{R_X^2 + X_X^2} \quad (5)$$

Z is the vector quantity with phase angle, θ as

$$\theta = -\tan^{-1} \left(\frac{X_X}{R_X} \right) \quad (6)$$

$$X_X = -R_X \tan \theta \quad (7)$$

$$|Z| = \sqrt{R_X^2 + R_X^2 \tan^2 \theta} = R_X \sec \theta \quad (8)$$

We get the two rectangular coordinate values as such which is given below

$$\text{Re}(Z) = R_X = |Z| \cos \theta \quad (9)$$

$$\text{Im}(Z) = X_X = |Z| \sin \theta \quad (10)$$

where X_X is capacitive reactance, C_X is capacitance, θ is the phase angle, R_X is electrical resistance, $\omega = 2\pi f$ and f is frequency that has been used for measuring R_X and C_X , Z is the impedance of the membrane. The values of R_M , C_M and Z were calculated by using Eq. (2)-(5) as a synthesized function of an electrolyte concentration and the practical oscillatory frequency for the respective membrane resistance, which is as shown in Figs. 7, 8 and 9.

From the graphs, it is clear that the membrane resistance values of the electrolytes are higher at the lower electrolyte concentrations (Fig. 6a) and the oscillatory frequency (Fig. 6b). Thus, membrane resistance values were illustrated to increase with the decrease in concentrations and frequency [26].

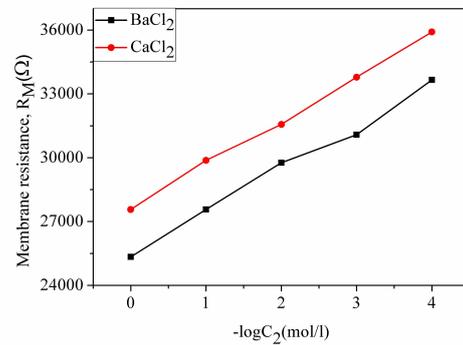


Fig. 6(a) Plot of membrane resistance versus electrolyte concentration for the PS-Ti-As composite membrane when used 1:1 electrolytes at 1 kHz oscillator frequency

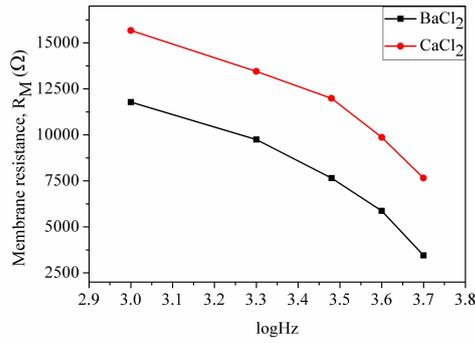


Fig. 6(b) Plot of membrane resistance versus oscillator frequency for the PS-Ti-As composite membrane under 0.1M of 1:1 electrolyte solution

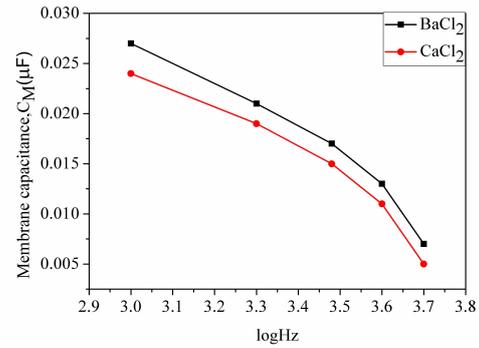


Fig. 7(b) Plot of membrane capacitance versus oscillator frequency for the PS-Ti-As composite membrane under 0.1 M of 1:1 electrolyte solution

Similarly, the variation of membrane capacitance with electrolyte concentration is depicted very apprehensively in Fig. 7a. The increase in the membrane capacitance values that is generally when the electrolyte concentrations is increased mainly because of the concentration which is dependent of an electrolyte [27].

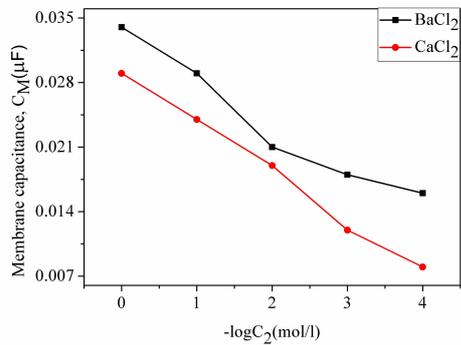


Fig. 7(a) Plot of membrane capacitance versus electrolyte concentration for the PS-Ti-As composite membrane under 1:1 electrolyte solution at 1 kHz oscillator frequency

As shown in Fig. 7b, at the lower frequency region, the capacitance value is increased because of the interface state which is accumulated by the alternating current. If the accumulation of the alternating current is not there the higher frequency become constant which concludes that the contribution of interface-state capacitance is lacking or even ignored completely [28]. By the trapping of responding signal the capacitance is increasing with the decrease in frequency.

A close look at Fig. 8a reveals that as the impedance decreases electrolyte concentration also decrease which enhances the flow of ions around the membrane. Figure 8b is representing the variation of the impedance vs. frequency utilising a logarithmic scale. From Fig.8b it is clear that the impedance decreases slowly in the frequency range and continuously with an increase in frequency.

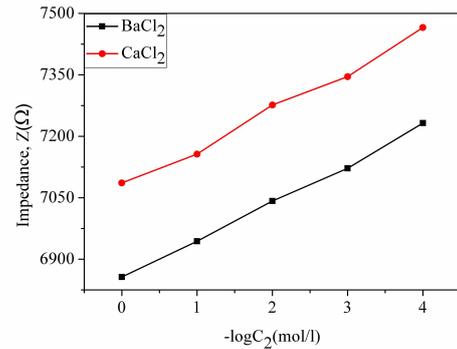


Fig. 8(a) Plot of impedance versus electrolyte concentration for the PS-Ti-As composite membrane under 1:1 electrolytes at 1 kHz frequency

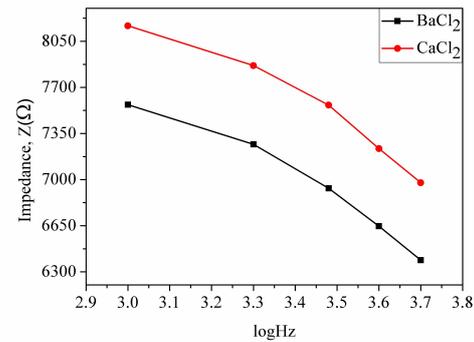


Fig. 8(b) plot of impedance versus oscillator frequency for the PS-Ti-As composite membrane under 0.1 M of 1:1 electrolytes

For a system, the equivalent circuits consist of two divisions: (a) the membrane and (b) the electrolyte solution placed between the electrodes of corresponding electrolyte and the surface of the membrane. Disintegration is impossible in the matter of porous membrane where the framing of unique electric contribution is developing. As a result of which, an equivalent electric circuit for complete membrane system is noticed [29].

The basic concept of the membrane is the impedance which is more specific than resistance. Impedance is separated into real and imaginary parts by algebraic rules as it is also a complex number ($Z = R_x + jX_x$), where j is the imaginary unit. But in the present context, j is used in place of i for

avoiding the confusion regarding the symbol. The real part is electrical resistance (R_X) and the imaginary part is the capacitive reactance (X_X) of the impedance. The equation for Z can be depicted in the polar form such as

$$Z(\omega) = |Z| \exp(j\omega) \quad (11)$$

where

$$\exp(j\omega) = \cos(\theta) + j \sin(\theta) \quad (12)$$

In the general concept of impedance, Z is dependent on frequency. Impedance is the estimation of $Z(\omega)$ on the large range of frequency. It is the structure of $Z(\omega)$ versus ω which delivers the data regarding the electrical properties of the material in the electrolytic system.

The obtained results had demonstrated capacitance reactance and the electrical resistance plot is completely dependent on the membrane materials in the system as shown in Fig.9. The rapid shifting of electrical resistance in both the cases is because of the increase of capacitance reactance [30]. So, we can conclude from the above that high-frequency behaviour is perturbed due to exchange in interfacial electron [31]. The plot very clearly shows that there is an inclined straight line in the very low frequency region.

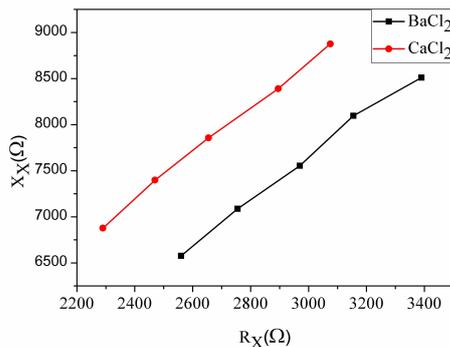


Fig. 9 Plot of capacitance reactance versus resistance for the PS-Ti-As composite membrane using 1:1 electrolytes at 1 kHz oscillator frequency

The capacitance reactance against the oscillator frequency for the PS-Ti-As composite membrane in the occurrence of two electrolytes that are in effective form as shown in Fig. 10. From the given graph, it is clear that the value of the capacitance reactance is at the rate of decreasing randomly with an increasing oscillator frequency that is due to the number of electrons in the form of electrical charge acting on the capacitor plates and passes from one plate to the other very rapidly with respect to the varying frequency. As the frequency increases, the capacitor passes more amount of charge across the plates in a given time resulting in a faster current flow through the capacitor appearing as if the internal resistance of the capacitor had decreased. Therefore, a capacitor which is

connected to a circuit that changes over the given range of frequencies can be said to be "Frequency Dependant". At the zero frequency, the capacitor has an infinite reactance looking more or less like an "open-circuit" between the plates and results in blocking any flow of current through it.

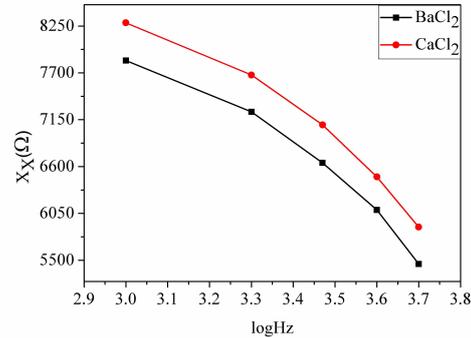


Fig. 10 Plot of capacitance reactances versus oscillator frequency for the PS-Ti-As composite membrane using 0.1 M of 1:1 electrolytes

Fig.11 in general shows that, in this specific region of the capacitance reactance and resistance plots in the graph [32], the phase angle move towards the trend of infinity since 69.9° to 56.7° for BaCl₂ and from 61.4° to 72.7° for CaCl₂. For both of the electrolytes, the phase angle decreases as the highest attainable frequency (5 kHz). A unique and effective relaxation mechanism was noticed at the rapid rate for both the electrolyte-membrane-electrolyte systems, which was also reported elsewhere [33].

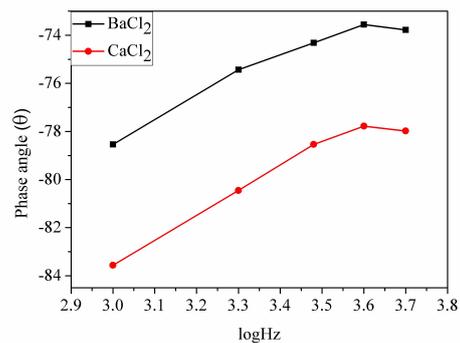


Fig. 11 Plot of phase angle versus oscillator frequency for the PS-Ti-As composite membrane in the presence of 0.1 M of 1:1 electrolytes

To understand the behaviour of membrane in the mechanism, the electrical double layer was assessed according to many other practical studies at the outer surface of the membrane and its solution [34]. All the membrane capacitance is playing a significant role by affecting the polarization charge in the form of diffused doubled layer on the geometric capacitor [35]. The proposed equivalent circuit for membrane-electrolyte interface is calculated [36] by applying the electrical double layer capacitance in the equation (13) given below

$$\frac{R_M}{1 + j\omega C_M R_M} = \frac{R_T}{1 + j\omega C_D R_T} + \frac{R_B}{1 + j\omega C_G R_B} \quad (13)$$

where R_B is the bulk resistance of the membrane, C_G the specific geometric capacitance, C_D the interfacial double layer capacitance, and R_T the charge transfer resistance between the membrane-electrolyte interface and which is assumed as the transfer of single step process. The real and imaginary parts of eq. (13) are given below

$$\frac{R_M}{1 + \omega^2 C_M^2 R_M^2} = \frac{R_T}{1 + \omega^2 C_D^2 R_T^2} + \frac{R_B}{1 + \omega^2 C_G^2 R_B^2} \quad (14)$$

$$\frac{C_M R_M^2}{1 + \omega^2 C_M^2 R_M^2} = \frac{C_D R_T^2}{1 + \omega^2 C_D^2 R_T^2} + \frac{C_G R_B^2}{1 + \omega^2 C_G^2 R_B^2} \quad (15)$$

Eq. (16) now becomes as such when it is at a higher frequency

$$\frac{1}{C_M} = \frac{1}{C_G} + \frac{1}{C_D} \quad (16)$$

The equation (16) shows that it is the addition of two capacitors in a logical series. The capacitor is sandwich between two double layers interface in a very possessive manner [36]. For dilute solutions [37], the capacity of the diffuse layer C_G is more or less small as compared to C_D contribution, which resembles as $C_M \approx C_G$. When the diffused layer becomes more compact and its capacity is large compared to that of the C_D , then the latter contribution should be dominated. It is clear that the potential has a zero charge. There are two concepts which are as follows for the capacitor: (1) the potential of zero total charge is defined as the potential where the electronic charge on the metal place is limited [38], hence it is becoming zero; (2) if the potential do not have a charge in the diffuse double layer it is known as Gouy–Chapman capacity where the value is minimized. This relation is often known as the zero free charge potential.

The comprehensive form of the double-layer capacitance is dependent on the fixed charge (σ_s) and the potential of membrane (V_M). If $\sigma_s=0$, then [39]

$$C_D = \frac{\epsilon_0 \epsilon_w \sinh \alpha}{(1/\kappa)\alpha} \quad (17)$$

where ϵ_w is the dielectric coefficient of water, $\epsilon_0 = 8.85 \times 10^{-14} \text{ F/m}$, α is a constant which is taken into account for the structural details

of membrane polymer, F is Faraday constant, and $(1/\kappa)$ is the Debye-Huckle length and is given by eq. (18)

$$\frac{1}{\kappa} = \left(\frac{4.31 \times 10^{-8}}{\sqrt{2\mu}} \right) \quad (18)$$

where μ is the ionic strength of electrolyte solution. α can be estimated by utilizing the transcendental equation as given below in eq. (19)

$$\left[\frac{\epsilon_0 \epsilon_w}{(1/\kappa) C_G} \cdot \sinh \alpha + 2 \right] = \frac{V_M}{2(RT/F)} \quad (19)$$

Alternatively it can be obtained from eq. (20)

$$C_M V_M = \sigma \rho = 4FC(1/\kappa) \sinh \alpha \quad (20)$$

where $\sigma \rho$ is taken as the polarization charge on the capacitor.

Eq. (17) can be modified to eq. (21) as given below in the following form

$$C_D = \frac{\epsilon_0 \epsilon_w}{(1/\kappa)} \quad (21)$$

If $V_M \ll RT/F$, so that $(\sinh \alpha = \alpha)$. C_D is calculated from Eq. (21) for the aqueous electrolyte solutions which is as given in Table 1. The information depicts that C_D is increasing with an increase in the electrolyte concentration. The magnitude of interfacial double layer capacitance is more high concentration [40] for both the electrolytes in the order of $\text{BaCl}_2 > \text{CaCl}_2$. The distinction in the magnitude of C_D excavated from Eqs. (16) and (21) attributes to the upcoming of charge of polarization and various structural and functional brief matrix of membrane [41].

Table 1: Calculated vales of Interfacial double layer capacitance (C_D) for the PS-Ti-As composite membrane equilibrated with different concentration of BaCl_2 and CaCl_2 at 1 kHz (temp = $25 \pm 0.1^\circ\text{C}$)

Electrolyte Conc (M/L)	C_D from eq. (16) (μF)		C_D from eq. (21) (μF)	
	BaCl_2	CaCl_2	BaCl_2	CaCl_2
0.0001	0.048	0.034	1.765	1.456
0.001	0.053	0.042	8.786	7.908
0.01	0.124	0.098	20.765	18.865
0.1	0.169	0.127	45.753	36.876
1.0	0.197	0.176	97.765	75.980

Later on, investigation on the membrane appears to possess that the charge is positive which is derived from the PS polymer and associated with the counter ions forming the double layer which is due to electrolytes at the membrane's surface. The increase in electrolyte concentration is pertaining to lead the forming of double layer counter ions that is inserted into the membrane which is resulting to decrease the

effective thickness and also increase the charge of ions inside the membrane. It is also found that the charge is an accumulating for the counter ion, which finally increases the conductance of ion channel because it is recommended for “concentration mechanism” in the different notes of biophysics. It is due to such characteristics that the membrane achieves conductance at high levels of the incoming ion by supporting the activity of membrane which is still under discussion.

The PS-Ti-As composite was also screened for its antibacterial efficacy for the three bacterial strains *Escherichia coli*, *Bacillus thuringiensis* and *Pseudomonas aeruginosa* in vitro. The material was analysed at a specific concentration of 0.5 mg mL⁻¹ in dimethyl sulfoxide (DMSO) and it was then matched up with the renowned antibiotic that is tetracycline which is of the same concentration. The study assessed by utilizing the method of agar well-diffusion and the experimental process were carried out thrice where the zone of inhibition was experimentally visualized after 18 h of incubation period at 37±1°C [42] and the observed values was tabulated in Table 2. It can be concluded from the results that the PS-Ti-As composite shows excellent inhibitory activity against all the three bacterial strains. The diameter of the zone of inhibition (mm) was efficiently used to compare the antibacterial efficiency of material with that of the commercial drug (tetracycline as reference). Since the zones of inhibition (mm) were used as one of the genuine reasons for as a certainty the biological activity. On the basis of the criterion, 20 mm inhibition zone represents a very certain process at 10-12 mm inhibition activity was good, and at 7-9 mm the activity was comparatively less and the zone of inhibition below 7 mm represented the non-significant activity which was an exceptional case [9]. The observed inhibition zones form all of the bacterial strains due to the PS-Ti-As composite was found very significant (i.e. >20 mm). It was also found that nutrient broth with the amended material was inhibitory for *Escherichia coli*, *Bacillus thuringiensis* and *Pseudomonas aeruginosa*. It is shown in Fig.12 that there is a development in the function of PS-Ti-As concentration for all the strains, which was later attaining the decrease in the bacterial culture on an increase in the concentration. The minimum inhibition concentration (MIC) of such composite for all the three bacterial strains was near about 100 µg mL⁻¹. The reason for such antibacterial activity of the PS-Ti-As composite membrane is described on the basis of the effects of titanium metallic ion in terms of disrupting the normal cell physiology. Reduction in the polarity of ion by the incomplete sharing of positive metal ion charge is due to the coordination of the donor group along with the process of π electron delocalization inside the system [43]. So, it can be concluded that the lipophilic characteristic of the

metal atom is improved, which on the other hand gives rise with higher capability to move into inside the micro organism through the individual layer of plasma membrane and disrupts the normal physiological processes which is associated for the survival of those organisms [44]. It was analyzed significant increase in the permeability of the membrane is due to the disruption of the synthesized membrane physiology that leads the plasma membrane to lose control of the transport system which results in cell death [45].

Table 2: Mean zone of inhibition (Antibacterial assay)

Bacteria	Polystyrene-Titanium-arsenate membrane	Tetracycline
<i>Escherichia Coli</i> (mm ± sd)	22.1 ± 0.35	16.6 ± 0.20
<i>Bacillus thuringiensis</i> (mm ± sd)	24.6 ± 0.15	18.9 ± 0.6
<i>Pseudomonas aeruginosa</i> (mm ± sd)	26.2 ± 0.4	21.5 ± 0.10

^a mm ± sd: (millimetre ± standard deviation)

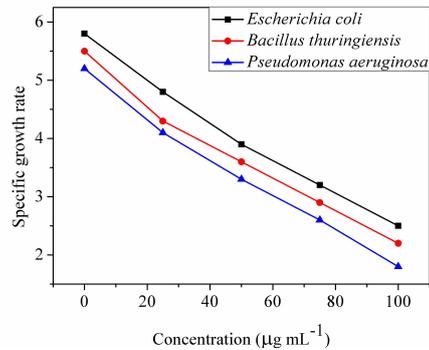


Fig. 12 Plot of specific growth rate versus concentration for the PS-Ti-As composite membrane.

The minimum inhibition concentration (MIC) of the composite is approximately 100 µg mL⁻¹ for all bacterial strains.

4 CONCLUSION

The impedance characteristics of the PS-Ti-As composite membrane were analysed for better understanding and the ability to develop the process of diffusion of ion with the help of the membrane. The observed and inference magnitude of capacitance and resistance of membrane was found to be highly dependent on the electrolyte concentration and the oscillator frequency. The values of capacitance across the membrane were designated to be the last one which evaluate to the formal compact structure of the specific membrane. The magnitude of electrical resistance through such membrane had confirmed this viewpoint in general. The significance of electrical

double layer also refers it is dependent on the concentration of electrolyte. For all the temperature variation, the dielectric constant increases with an increase in temperature. Also, the increasing electrolyte concentration has led to an advance enlargement of the ion inside the PS-Ti-As membrane which makes the membrane to be more conductive to the specific ions (Ba^{2+} and Ca^{2+}), which accounted for a decrease in the value of resistance. It is also because of such assumption that increase in the frequency has led to the rapid exchange of the polarity among the ions and materials of the membrane. The synthesized membranes show potential antibacterial activity and biological activity against pathogenic bacteria such as *Escherichia coli*, *Bacillus thuringiensis* and *Pseudomonas aeruginosa* using the well diffusion method. Finally, the material has exerted an important inhibitory activity for the growth and development of all the bacterial strains that have been tested using the diffusion method and information expose clearly about material that it has good impact of antibacterial efficiency. Such study will finally result in easiness of producing as well as synthesizing membrane along with various additional advantages such as consuming less time in comparison to the other ones, it is eco-friendly, simplicity, versatility and less expensive. Thus, this material can be used for medical, biomaterial applications and clinical aspect also.

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