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Preparation and Characterization of Biopolymer Electrolytes based on I - Carrageenan

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Abstract

Solid Polymer electrolytes based on I-Carrageenan with sodium nitrate was synthesized via solution casting technique. Distilled water was used as a solvent. AC impedance measurements were carried out in the frequency range of 42Hz to 1MHz. Maximum ionic conductivity 1.0915×10-5 Scm-1 was obtained for 0.4wt% of sodium nitrate at room temperature. From AC impedance data, dielectric parameters were obtained and the same was analyzed.

Keywords: Solid polymer electrolyte, I-Carrageenan, AC Impedance technique, Sodium nitrate, Dielectrics.

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I.INTRODUCTION

Over the years, biopolymer electrolytes play a vital role in the field of various electrochemical energy devices. For the past few years, interest in the naturally available polymers such as polysaccharides (eg., carrageenan, pectin etc.,)[1] has been increasing rapidly, because it is a renewable resource with an extensive uses in nature, functioning as energy storage, transport, signaling, and structural components. Due to these attractive features, I – Carrageenan (iota carrageenan) is used for the present work as a biopolymer. Carrageenan can be obtained from the red seaweeds of the class rhodophyceae. It is a group of linear galactan with ester sulfate content of 15 – 40% (w/w) and containing (1-3)-α-D and (1-4)-β-D-galactopyranosyl (or 3,6-anhydro-α-D-galactopyranosyl) linkages in an alternate manner. Most of the works of carrageenan were based on lithium salts. [2 – 4] But, due to the high cost of lithium salts and its less abundance in nature, it couldn't be used for widespread applications.In recent past, sodium ion based polymer electrolyte system have attained a better interest, because the performance capabilities showed by them are similar to that of lithium based system. [5 – 7] Also, the development of biopolymer electrolytes using sodium salts are very rare. Due to these facts, sodium nitrate (NaNO3) is chosen as an electrolyte.

In the current work, an effort has been made to prepare a series of I – carrageenan/ sodium nitrate samples which has not been reported so far. The properties like ionic conductivity and dielectrics of the prepared samples are also examined.

2 Materials and Methods

For the present work, I – carrageenan and sodium nitrate (both obtained from Merck) were used. The biopolymer I – carrageenan and sodium nitrate was varied as (0.9:0.1, 0.8:0.2, 0.7:0.3 and 0.6:0.4 wt%) respectively. The samples were synthesized by employing solution casting technique. Double distilled water was used as a solvent. At first, I – carrageenan and sodium nitrate were dissolved separatelyin distilled water. It was stirred for 10 hours. Now, the solutions were mixed together and again magnetically stirred until a homogenous solution was attained. Then the solution was poured into petri dish, moved into a vacuum oven and kept at a temperature of 60oC for one day. After this process, a flexible and free standing biopolymer electrolyte films were harvested. The obtained films were subjected to AC impedance spectroscopy. AC impedance was carried out using HIOKI LCR instrument over a frequency range of 42 Hz – 1 MHz.

3 Results and Discussion

3.1 AC Impedance Spectroscopy

Impedance spectra for prepared I-Carrageenan-NaNO3 system are presented in Figure1. It possess a semicircle in the higher frequency side, arises because of the bulk effect of the electrolyte and a linear spike in the lower frequency range, ascribed to the effect of the blocking electrodes. The ionic conductivity (σ) of prepared biopolymer electrolyte system is calculated with the help of following equation.

$$\sigma = l/(AR_B) \quad .... (1)$$

where l is the thickness of the sample, A is area of electrode (SS) and RB is the bulk resistance. The calculated values of ionic conductivity is given in Table 1. The values of ionic conductivity of the prepared systems are estimated using equation (1) and they are listed in Table 1. For pure I-Carrageenan system, ionic conductivity value is to be 2.1800×10^{-8} Scm^{-1} at room temperature. [8] This value increased gradually when a different concentrations of $NaNO_3$ was incorporated to the I-Carrageenan system. Maximum ionic conductivity of 1.0915×10^{-5} Scm^{-1} is attained for the addition of 0.4wt% $NaNO_3$. This increase in the value of ionic conductivity is due to the fact, that there exists a stronger interaction between NaNO3and polymer chains, which results in the establishment of amorphous region. [9]

3.2 Dielectric Analysis

Figures 2a and 2b show the frequency response of the dielectric constants ε’ and ε” for different concentrations of I-Carrageenan-$NaNO_3$ corroborates the variation trend of ionic conductivity.

From these figures, it is observed that the magnitudes of dielectric constant (ε’) and dielectric loss (ε”) are found to be large in the lower frequency region. However, these values get decreased with increase of frequency and reaches saturation in the higher frequency region. This is because, in the lower frequency region, dipoles in the I-Carrageenan may align more easily in a faster manner towards the applied field’s direction. This event do not happen in the higher frequency side as there is no enough time for the dipoles to get align along the direction of the field applied: hence ε’ and ε” values are low.

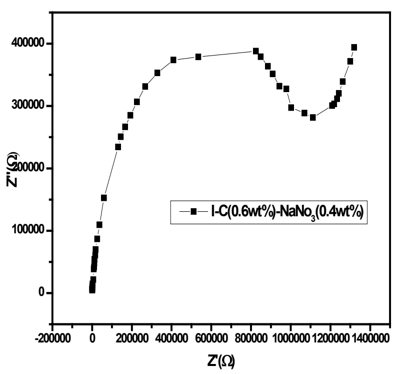
As observed in ionic conductivity, the values of ε’ and ε” is seen to be high for 0.4wt% $NaNO_3$ added I – Carrageenan system while compared with other concentrations, which implies there exist only a small electrostatic attraction between the mobile ions and hence the probability of mobile ions in the free states becomes greater. [10]

3.3 Modulus Analysis

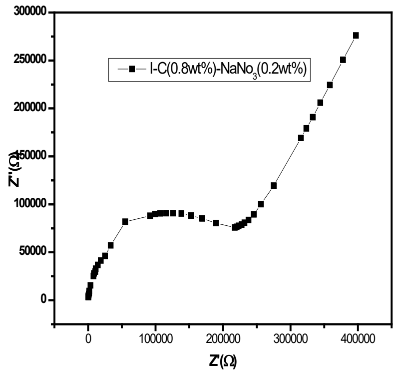
Figures (3a) and (3b) indicates the variation of M’ and M” versus logω for I-Carrageenan-$NaNO_3$ systemIn these plots, at low frequency side, a long tail is observed. It is due to the presence of large capacitance which is accompanied with the electrodes. This substantiate that the materials is of non-Debye type. It is seen from these figures that the spectrum shape is found to be same for all the systems prepared. But, the position of the peak is shifted to higher frequency side for the addition of 0.4wt% of NaNO3 system, whereas the position of the peak is found to be in lower frequency side for the other concentration of NaNO3. It assures that the charge carrier hopping is higher for the said NaNO3 concentration than any other concentrations. [11]

3.4 Loss Tangent Studies

Loss tangent spectra for I-Carrageenan-$NaNO_3$ system are given in Figure 4. These spectra show a broad peak at a distinctive frequency, confirms the prevalencerelaxation of dipole in the prepared system. The peak maxima of loss tangent for 0.4wt% of $NaNO_3$ added system exhibited a small shift towards the higher frequency, whereas the others in the low frequency side. Such a shifting of peak towards the high frequency side is a result of fast segmental motion of the mobile ions, whereas the peak shift towards low frequency side is a result of constrained segmental



(a)



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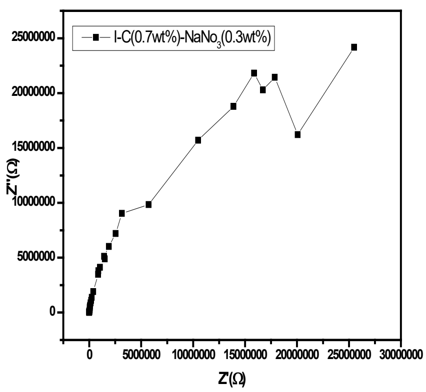

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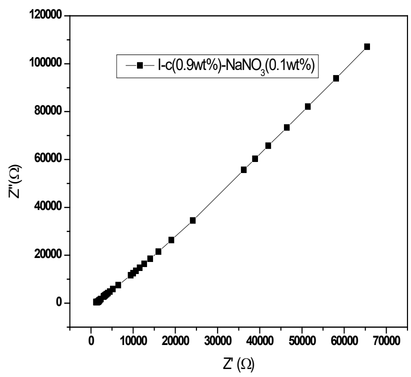

(d)

Figure 1AC Impedance plot of I- carrageenan and NaNO3 system

motion coupled with the ion. [12]

4. Conclusions

Biopolymer electrolytes comprising of I-Carrageenan and NaNO3 have been prepared by solution casting technique using distilled water as solvent.From the AC impedance analysis, the highest conductivity have been found to be 1.0915×10^{-5} Scm^{-1} for 0.6wt% of I-carrageenan and 0.4 wt% of sodium nitrate system. The magnitude of dielectric constant was found to be high for 0.4 wt% of NaNO3added system.The peak maxima of loss tangent peak has been shifted to high frequency side for the sample which possessed the highest ionic conductivity.

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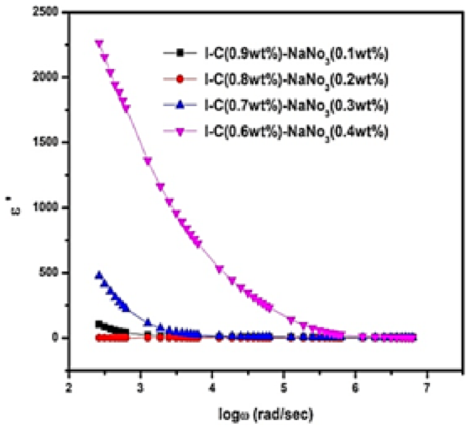
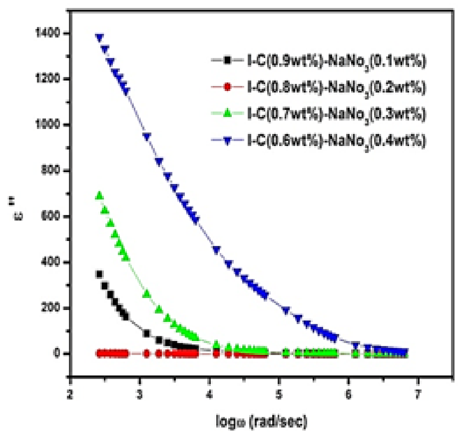
Table 1 Calculated values of ionic conductivity for I-carrageenan/sodium nitrate system

I - Carrageenan:NaNO3 (wt%)	Ionic conductivity (Scm^{-1})
Pure I – Carrageenan	2.1800x10^{-8} [8]
0.9:0.1	8.4213x10^{-7}
0.8:0.2	1.3795x10^{-6}
0.7:0.3	0.5146x10^{-6}
0.6:0.4	1.0915x10^{-5}

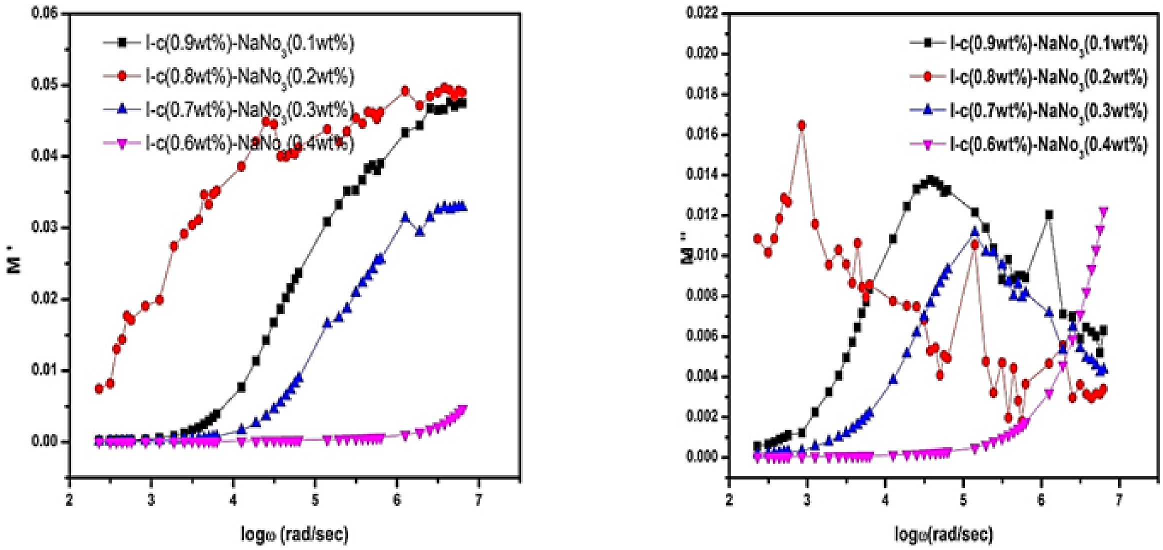


(a)



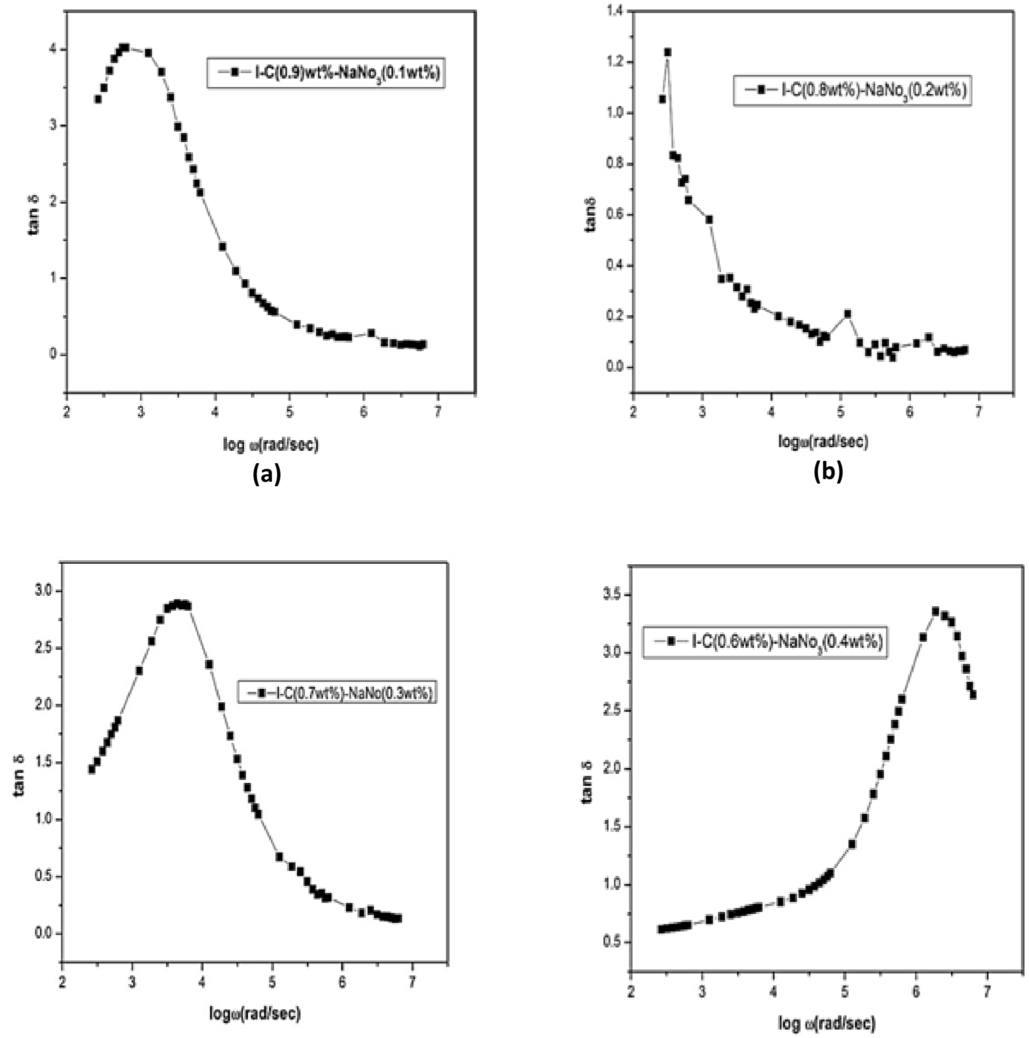
(b)

Figure 2 Variations of the (a) dielectric permittivity, ε' and (b) dielectric loss,ε'' versus log ω for I – Carrageenan – sodium nitrate system



(a) **(b)**

Figure 3 Variations of the (a) real part of electric modulus,M'and (b) imaginary part of electric modulus, M'' versus log ω for I – Carrageenan – sodium nitrate system



(a) **(b)**

(c) **(d)**

Figure 4 Variation of loss tangent spectra for prepared systems at room temperature

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