

AGAROSE BIOPOLYMER ELECTROLYTES: ION CONDUCTION MECHANISM AND DIELECTRIC STUDIES

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The paper describes the fabrication and characterization of biopolymer gel electrolyte films based on agarose. The gel electrolyte solution, comprising agarose, potassium iodide and ionic liquid (1-ethyl-3-methylimidazolium dicyanamide), was dissolved in three different solvents, *i.e.* double distilled water (DI), dimethyl sulfoxide (DMSO) and dimethylformamide (DMF). The electrical and dielectric properties, as well as the ion conduction mechanism, are presented in detail. Complex impedance spectroscopy showed an enhancement in ionic conductivity by salt doping, which correlated well with the dielectric parameters. The dielectric measurements further affirm that conduction in these biopolymer gel electrolytes is primarily governed by ions.

Keywords: biopolymer, ionic conductivity, dielectric constant, ionic conductivity

INTRODUCTION

Biopolymer gel electrolytes have attracted much attention in the search for an alternative, low-cost and stable energy source. It is an open field and offers many opportunities in industries, for medical, food, cosmetics, and pharmaceutical applications. Our focus is to synthesize a stable and high ionic conducting biopolymer electrolyte that can be used in fabricating highly efficient electrochemical devices.¹ Agarose is generally obtained from the purification of agar. The agarose biopolymer is composed of repeating molecules of galactopyranose. The functional groups are extended from the galactopyranose and are arranged in such a way that two adjacent chains are connected with each other to form a helix. The solvent get strapped inside the helix of the biopolymer chain, and this leads to the formation of a cross-linked, three-dimensional network.² For achieving a biopolymer electrolyte, polysaccharides will be mostly chosen as host polymer and different alkali halides will be used

as dispersoids. These materials are in demand since they possess high ionic conductivity, which is essential for electrochemical devices (such as fuel cells,⁴ supercapacitors, batteries,⁵ dye-sensitized solar cells⁶ *etc.*).

Dye-sensitized solar cells (DSSCs) based on a biopolymer electrolyte will be the next big step in the development of electrochemical systems. DSSC was first introduced by Prof. Grätzel in 1991.⁶ Over 13% efficiency has been reached with the use of liquid electrolytes and around 7% using gel biopolymer electrolytes.⁷⁻⁹ Solid polymer electrolytes (SPE) have been proposed as solid electrolytes in which ionic charges are formed by dissolving salts in polymers with high molecular weight. They can also be prepared by an economical and reliable process in semisolid or solid form.¹¹⁻¹⁵ In recent years, biopolymer materials, such as chitosan, agarose, agar, and phytigel, have been frequently used as electrolytes in developing good electrochemical

devices.¹⁶⁻²¹ One of the prime parameters for device application is electrical conductivity. For efficient devices, conductivity must lie in between 10^{-4} and 10^{-2} Scm^{-1} .^{16,17,19} Apart from high electrical conductivity, good mechanical stability and thermal properties are beneficial parameters.

In the present study, we have synthesized an agarose based polymer electrolyte, by the solution cast method using potassium iodide (KI) and ionic liquid (1-ethyl-3-methylimidazolium dicyanamide) as dopants in three different solvents, namely double distilled water (DI, in figures mentioned as H_2O), dimethyl sulfoxide (DMSO), dimethylformamide (DMF). The electrical and dielectric parameters, as well as ion conduction behavior, are presented in detail.

EXPERIMENTAL

Preparation of biopolymer gel electrolyte

The chemicals used in the present study were purified before use in the laboratory. Agarose with average molecular weight ($M_w = 5000$ g/mol) was purchased from HI-MEDIA, Mumbai, India. Other chemicals, such as potassium iodide (KI) and iodine (I_2), were obtained from Sigma Aldrich, USA. Ionic liquid (1-ethyl-3-methylimidazolium dicyanamide), double distilled water (DI), dimethyl sulfoxide (DMSO), dimethylformamide (DMF) were received from Fisher Scientific and used as solvents. As in the most common preparation method of gel polymer electrolytes (GPE), a fixed amount of agarose powder (0.175 g) was dissolved in the solvent (20 ml) in a beaker under continuous stirring and constant heating at 70°C . The same ratio of the stock solution was used for the overall experiment (written here as B1). Stoichiometric ratios of potassium iodide (KI) were then dissolved in the solvents in a separate beaker (written here as B2). Adding B2 to B1 dropwise resulted in a clear transparent GPE. The ionic liquid was then added to B1 (DMSO and DMF only) dropwise, using a pipette under continuous stirring for 30 minutes. Following the procedure mentioned above, we prepared three samples. The first sample was prepared by dissolving agarose biopolymer and KI in DI. The second and third samples were prepared by dissolving agarose, KI and IL in DMF and DMSO respectively.

RESULTS AND DISCUSSION

Electrical analysis

Ionic conductivity

The ionic conductivity measurement of the agarose-KI based biopolymer electrolyte films obtained in various solvents, such as DMSO, DMF and DI, was carried out using a CH instrument workstation (model 604D, USA) over the frequency range from 100 Hz to 1 MHz. To

measure ionic conductivity, we sandwiched free standing biopolymer electrolyte films between two stainless steel electrodes and the electrical conductivity was evaluated using the formula:

$$\sigma = \frac{1}{R_b} \left(\frac{l}{A} \right) \quad (1)$$

where σ is ionic conductivity, R_b is bulk resistance, where the Nyquist plot intercepts with the real axis, l is the thickness of the sample, A is the area of a given sample.

The ionic conductivity values with respect to the KI of the three samples dissolved in DI, DMSO and DMF were evaluated using Equation 1 and plotted in Figure 1. It is clear that the addition of KI in the agarose matrix enhances the ionic conductivity values. Initially, the conductivity enhanced to attain a maximum at ~ 40 wt% KI concentration and then decreased (Fig. 1 a, b, c). This conductivity behavior could be explained in terms of ions provided by the dissociated KI salt. Further decrease in the conductivity values after a certain concentration could be explained by the formation of ion multiples.¹¹⁻¹⁴ It is also clear that the DMF-based GPE is more stable than the other two solvents and also it has the highest ionic conductivity, of $\sim 10^{-2}$ (Fig. 1d).

Ionic conductivity (σ), in the case of the electrolyte system, is given as:

$$\sigma = n \cdot q \cdot \mu \quad (2)$$

where n is the charge carrier density, q is the charge of the carrier, μ is the mobility of the carriers. Therefore, any increase in either of the parameters, n or q , will certainly affect the value of ionic conductivity. To further justify the overall contribution of the number of free charge carriers to the total conductivity, the dielectric constant (ϵ) of the film was calculated. Figure 1 shows the change in dielectric constant with increasing the amount of KI in the biopolymer electrolyte at 82520 Hz frequency. It is clear that the conductivity data match well with the dielectric data. The addition of KI results in a change in the dielectric constant of the matrix, which leads to a change in the number of free charge carriers and thereby in the conductivity. Therefore, a high dielectric constant helps in ion dissociation, which overall assists in ionic conductivity.

Ion dissociation factor measurement

According to the electrolyte dissociation theory given by Barker,²¹ the concentration of charge carriers can be expressed as:

$$n = n_0 \exp\left\{\frac{-U}{2\varepsilon kT}\right\} \quad (3)$$

where U = dissociation energy of the salt, k = Boltzmann constant, ε = dielectric constant of the system, and T = temperature of the sample.

The dissociation energy of KI is 3.33 eV, and the change in the relative number of charge carriers (n/n_0) with the increasing salt (KI) concentration is shown in Figure 2. To further clarify the role of the charge carriers in the

biopolymer electrolyte matrix, we have evaluated the room temperature dissociation factor (n/n_0) for two samples. It may be observed that at the maximum doping limit (40 wt% KI), the n/n_0 reaches a maximum value and then shows a decreasing trend. It follows the same trend observed earlier for conductivity and dielectric measurements.

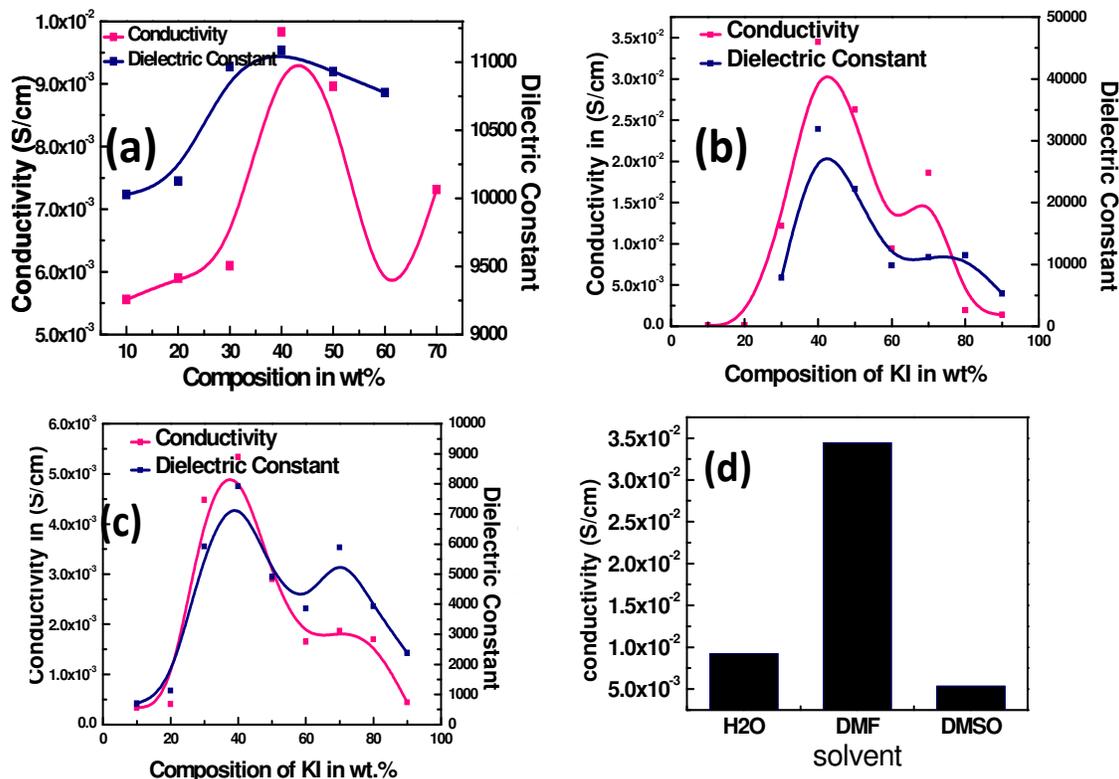


Figure 1: Ionic conductivity and dielectric constant data of (a) Agarose with KI in DI water (H₂O); (b) Agarose with KI and IL in DMF; (c) Agarose with KI in DMSO and (d) conductivity stability data with varying solvents

The conductivity in the biopolymer KI matrix is, therefore, predominantly governed by the number of charge carriers. We can understand the effect of salt concentration with the help of fractional dissociation (n/n_0) of salt, as shown in Figure 2, which affirms that mobile ion concentration data follow the conductivity trend. Hence, the ion pair formation and re-dissociation theory, applicable to polymer-salt complexes, can be applied in the present system. Minimum conductivity is due to the decreased dissociation. Increased ion association (*i.e.* decreased

dissociation) and triplet ion formation both contribute to decreasing mobility.²⁰⁻²²

Dielectric studies

Dielectric properties

Different molecular motion and relaxation processes are well connected with the dielectric studies. Dielectric measurements are extremely sensitive to small changes in material properties (molecular relaxation of the order of only a few nanometers involves dipole changes that can be observed by a dielectric study).

To analyze the experimental observation for explaining the ion transport mechanism, transition behavior, and dielectric properties, we have calculated the permittivity and electrical modulus using complex impedance spectroscopy data. These data provide an insight into the dielectric properties of the biopolymer electrolyte, and are very helpful in the study of the ionic conductivity behavior of biopolymer electrolytes:

$$\epsilon^* = \epsilon' + \epsilon'' \quad (4)$$

where ϵ' and ϵ'' are the real and imaginary parts of dielectric permittivity or the dielectric constant of

a system, and are calculated from the following equations:

$$\epsilon' = \frac{-Z'}{(Z'^2 + Z''^2)\omega C}; \quad \epsilon'' = \frac{Z''}{(Z'^2 + Z''^2)\omega C} \quad (5)$$

$$C = \frac{\epsilon_0 A}{l} \quad (6)$$

where Z' and Z'' are the real and imaginary parts of impedance spectroscopy, ω is angular frequency, C is the capacitance of an empty measuring cell of electrode area A , ϵ_0 is the dielectric constant, and l is the thickness of the biopolymer film.

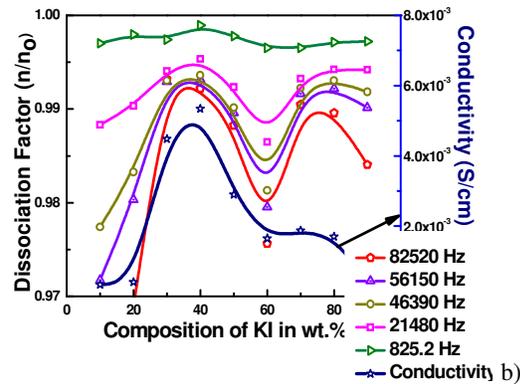
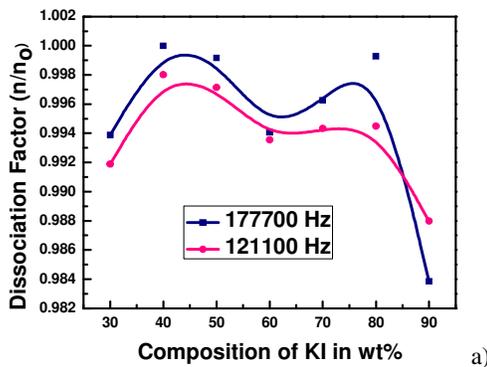


Figure 2: Evolution of fractional number of dissociated mobile charge carrier with varying amount of KI in the agarose biopolymer matrix. (a) Sample prepared in DMF and IL, (b) Sample prepared in DMSO and IL

The dielectric loss tangent ($\tan\delta$) is the ratio of dielectric loss and dielectric permittivity, which is the measure of the electrical energy lost to the electrical energy stored in the periodic field. The loss tangent is calculated using the following equation:

$$\tan \delta = \frac{\epsilon''}{\epsilon'} \quad (7)$$

where ϵ' and ϵ'' are the real and imaginary parts of the dielectric constant of the biopolymer electrolyte.

The complex electric modulus (M^*) is used to investigate the conductivity relaxation phenomena. It suppresses the effects of electrode polarization, resulting in a better picture of existing electrical relaxation. M^* can be estimated from the impedance data as given below:

$$M^* = M' + M'' = \frac{1}{\epsilon^*}, \quad M' = \frac{\epsilon'}{\epsilon'^2 + \epsilon''^2}, \quad M'' = \frac{\epsilon''}{\epsilon'^2 + \epsilon''^2} \quad (8)$$

In biopolymer electrolytes, it is observed that dielectric relaxation generally depends on the solvent and dispersoids used. At low salt concentration, ionic motion and biopolymer

segmental motion are decoupled, the latter giving rise to a dielectric loss. In the case of the DMSO- and H₂O-based solvent, where strong coupling occurs and consequently polymer segmental motion no longer shows up as a loss in the dielectric spectrum, the observed dielectric loss arises from ion-pair formation.

The frequency dependence of the real (ϵ') and imaginary (ϵ'') parts of the dielectric relaxation curves are shown, respectively, in Figure 3a and b. It is clear that, at low frequencies, both the real (ϵ') and imaginary (ϵ'') parts of the dielectric constants rise rapidly, but the rise is slowed down at higher frequencies. The rise of the slope at low frequencies is the result of electrode polarization effects and space charge effects are normally observed in ionic glasses. To explain the ion conduction properties of the dielectrics, polarization should be considered. At high frequencies, the reversal of the electric field occurs rapidly and periodically, so that there is no excess ion diffusion in the direction of the field. The polarization due to the charge accumulation

decreases and, hence, a drop in the values of ϵ' and ϵ'' is observed.¹⁷⁻²⁰ The frequency dependence of the real M' and imaginary M'' parts of the modulus is shown in Figure 3c, d. M' and M'' increase towards high frequencies. The presence of the peaks in the modulus formalism at higher frequencies for all the biopolymer complexes and compositions suggests that the polymer electrolyte films are ionic conductors. The sharply increasing curve at higher frequencies may be the result of the bulk effect.

The height of the peaks decreases with an increase in temperature, suggesting multiple relaxation mechanisms. M' and M'' decrease towards low frequencies, proving the fact that the electrode polarization phenomena have a negligible contribution. The plots also show long tails at lower frequencies. The long tail is probably the result of the large capacitance associated with the electrodes.^{16,17,20,22}

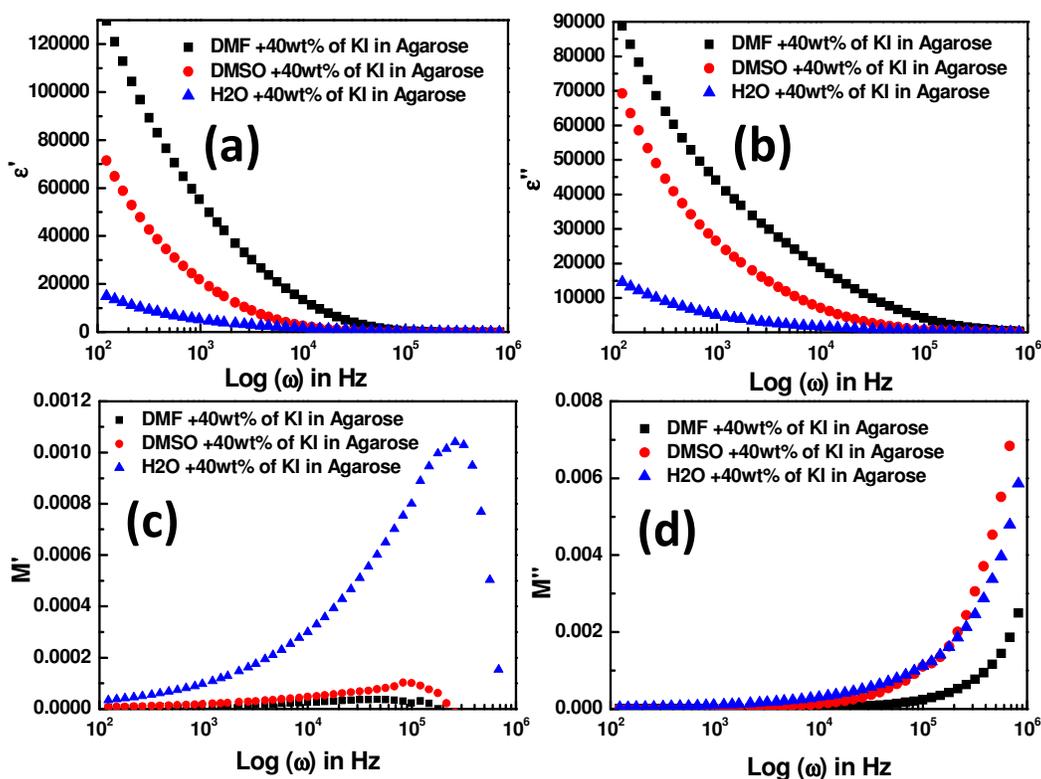


Figure 3: Frequency dependent dielectric constant (ϵ') and dielectric loss (ϵ'') of agarose with KI in H₂O, DMF and DMSO (a, b); Frequency dependence of real M' and imaginary M'' parts of the modulus of agarose with KI in H₂O, DMF and DMSO (c, d)

Dielectric loss tangent

The plot of the dielectric loss angle, $\tan \delta$ versus $\log \omega$, for varying solvents for the sample and with IL is shown in Figure 4. With the increase in frequency, $\tan \delta$ increases. Generally, it has been found to approach the maximum in some ranges of frequencies and then starts decreasing. However, in our case, due to the limitation of the frequency ranges, the drop is not visible. It is clearly observed that by varying the solvent and dispersoids, the dispersion shifts to higher frequencies and the maximum of the loss

tangent is found to be increasing towards higher frequencies.

The presence of relaxing dipoles is observed in all the samples, which is confirmed by the peaks appearing with varying frequencies. The characteristic property of dipolar relaxation controls the strength and frequency of relaxation. The tangent loss peak shifts towards the high frequency side when varying the solvent. With addition of IL, there is an increase in the amorphous content in the materials. It is observed by the shifting of the peak towards the higher frequency side. This will reduce the relaxation

time and, as a result, the immobile ions get energized. An increment in the speed of segmental motion coupled with mobile ions

enhances the transport properties in various solvents.

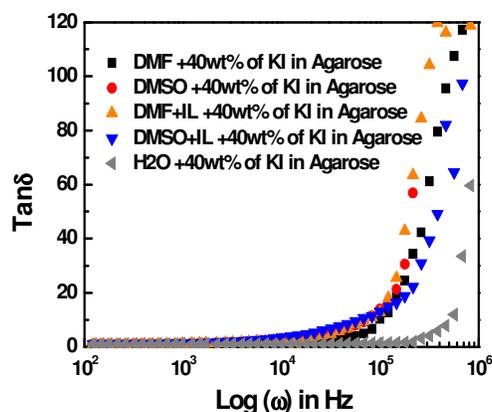


Figure 4: Frequency dependent dielectric tangent loss of agarose with KI in DI, DMF and DMSO solvents

CONCLUSION

We have successfully prepared biopolymer electrolytes showing reasonably good ionic conductivity. Complex impedance spectroscopy indicated a significant enhancement in ionic conductivity by ionic salt doping, which is due to more dissociated ions provided by the salt. The dielectric studies further affirmed that conduction in biopolymer electrolytes is primarily due to ions. The dielectric data matched well with the conductivity data, and the ion transport behavior is well explained using the dissociation factor and dielectric loss tangent data. Further, such high conductivity and good ion transport confirm that the developed biopolymer electrolyte could be applied in electrochemical devices.

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