



# Effect of ethylene carbonate plasticizer on agar-agar: $\text{NH}_4\text{Br}$ -based solid polymer electrolytes

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## Abstract

Proton-conducting polymer electrolytes based on biopolymer, agar-agar as the polymer host, ammonium bromide ( $\text{NH}_4\text{Br}$ ) as the salt and ethylene carbonate (EC) as the plasticizer have been prepared by solution casting technique with dimethylformamide as solvent. Addition of  $\text{NH}_4\text{Br}$  and EC with the biopolymer resulted in an increase in the ionic conductivity of polymer electrolyte. EC was added to increase the degree of salt dissociation and also ionic mobility. The highest ionic conductivity achieved at room temperature was for 50 wt% agar/50 wt%  $\text{NH}_4\text{Br}$ /0.3% EC with the conductivity  $3.73 \times 10^{-4} \text{ S cm}^{-1}$ . The conductivity of the polymer electrolyte increases with the increase in amount of plasticizer. The frequency-dependent conductivity, dielectric permittivity ( $\epsilon'$ ) and modulus ( $M'$ ) studies were carried out.

**Keywords** Biopolymer · Plasticizer · AC impedance spectroscopy

## Introduction

Fenton and Wright in 1973 were the pioneers of solid polymer electrolytes (SPEs) who worked with polyethylene oxide (PEO) and alkali metal salts. Since then, the field of solid polymer electrolytes gained a great deal of attention of the researchers. The main reason behind this was the advantages of using SPEs in solid-state devices like batteries, fuel cells, sensors, electrochromic displays and solar cells [1–3]. Other advantages of SPEs over conventional liquid electrolytes are

flexibility, molded to desired shape, mechanical strength, leak-proof and has good electrode-electrolyte contact. Previously, researchers' interests were towards the development of solid polymer electrolytes based on synthetic polymers like PVA [4], PVP [5], PAN [6], PMMA [7] and PVC [8] which exhibited good conductivity values. But currently, this has been adversely swapped with the biodegradable type through the employment of natural polymers. This effort has been undertaken to make the inventions go greener with the environment. Natural or biopolymers possess some outstanding criteria: (i) found in abundance, (ii) sustainable owing to its renewable nature that does not deplete as the petrochemical source, (iii) cheap in cost since it is a naturally occurring polymer and (iv) biodegradable nature that makes it more environmental friendly [9]. Several renewable resource-based biopolymers are suitable to be used as host polymer in the polymer electrolytes, such as starch [10], cellulose [11, 12], chitosan [13], carrageenan [14] and agar [15, 16].

Among all the biopolymers, agar-agar has gained a great attention due to its best film-forming capability. Agar is an unbranched polysaccharide, which is extracted from the family of seaweeds (Rhodophyceae) having the structure of 1,4-linked-3,6-anhydro- $\alpha$ -L-galactopyranose. Agar forms a slightly viscous solution on dissolving in hot water and then becomes a thermoreversible gel when the temperature is brought down. It is widely used in the food industry, in cosmetics and for microbiology. Applications include use as a

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thickener, gelling agent, binding agent, suspension agent and as a stabilizer. It could be an alternative source for biodegradable films since it shows high mechanical strength with water resistance [17]. Agar has been used in the synthesis of agar chemical hydrogel which is used as electrode binder in fuel-electrolyte-fed fuel cells [18]. The suitability of agar gel as an alternative immobilized electrolyte media and as a polymer electrolyte for electrochemical studies has been explored by Kasem K. Kasem [19]. Dalal Jaber Suliman Abdullah Audeh et al. [20] has reported the influence of the NiO nanoparticles on the ionic conductivity of the agar-based electrolyte in which the conductivity value is of the order of  $10^{-5}$  S  $\text{cm}^{-1}$ . Nwanya et al. [15] has reported that the values of the ion conductivity obtained for the agar-based polymer films are  $6.54 \times 10^{-8}$ ,  $9.12 \times 10^{-8}$ ,  $3.53 \times 10^{-8}$  and  $2.24 \times 10^{-8}$  S  $\text{cm}^{-1}$  for the agar/acetic acid, agar/lactic acid, agar/LiClO<sub>4</sub> and agar/KClO<sub>4</sub> polymer films, respectively. Ammonium salts are termed as proton donors as they facilitate the number of protons in the polymer matrix and hence the conductivity. Selvalakshmi et al. [21] has reported the conductivity of agar with NH<sub>4</sub>SCN as  $1.03 \times 10^{-3}$  S  $\text{cm}^{-1}$  and  $1.17 \times 10^{-4}$  S  $\text{cm}^{-1}$  for agar with NH<sub>4</sub>I [22], and Boopathi et al. [16] has reported  $6.57 \times 10^{-4}$  S  $\text{cm}^{-1}$  for agar with NH<sub>4</sub>NO<sub>3</sub>. Conductivity value of  $1.12 \times 10^{-4}$  S  $\text{cm}^{-1}$  has been reported for carboxy methylcellulose doped with NH<sub>4</sub>Br [23]. Sit et al. [24] has reported conductivity value of  $3.61 \times 10^{-4}$  S  $\text{cm}^{-1}$  for hydroxyethyl cellulose with NH<sub>4</sub>Br. The abovementioned authors have prepared their polymer electrolytes with distilled water as solvent. Cornstarch-based electrolytes doped with ammonium bromide (NH<sub>4</sub>Br) in acetic acid exhibited conductivity value of the order of  $10^{-5}$  S  $\text{cm}^{-1}$  [25]. The conductivity value of the polymer electrolytes can be enhanced by the addition of plasticizers like ethylene carbonate [8, 26] and propylene carbonate [27]. Plasticizing enhances the polymer material in terms of its original physical properties like film formation, higher elasticity and more softness and enables it for diversified applications. The present work aims to develop a new biopolymer electrolyte with agar doped with NH<sub>4</sub>Br and plasticized with ethylene carbonate in dimethylformamide (DMF) solvent. The developed polymer is then subjected to Fourier transform infrared spectroscopic analysis and AC impedance spectroscopic analysis.

## Materials and method

### Materials

Agar of average molecular weight 120,000 (manufactured by Condo-Forja, 9 Madrid, Spain, sold by Colloids Impex Pvt. Ltd., India) and NH<sub>4</sub>Br (spectrum) were used in the present work. Ethylene carbonate (EC) was obtained from Himedia, and dimethylformamide (DMF) was purchased from Merck.

## Preparation of electrolyte

The total weight of the polymer and salt was fixed to be 1 g. Different weight percentages of agar and NH<sub>4</sub>Br such as 90 mol% agar/10 mol% NH<sub>4</sub>Br, 80 mol% agar/20 mol% NH<sub>4</sub>Br, 70 mol% agar/30 mol% NH<sub>4</sub>Br, 60 mol% agar/40 mol% NH<sub>4</sub>Br, 50 mol% agar/50 mol% NH<sub>4</sub>Br and 40 mol% agar/60 mol% NH<sub>4</sub>Br are estimated. Agar was dissolved in 40 ml of DMF at 60 °C. After that, the known ratio of NH<sub>4</sub>Br was dissolved in the agar solution and stirred continuously for 2 h. The stirred solution was casted in the clean glass petri dish and allowed to evaporate in a hot air oven at 50 °C. After 48 h, free standing films were obtained. The system was optimized, and it was found that 50 wt% agar/50 wt% NH<sub>4</sub>Br exhibited highest conductivity of value  $7.24 \times 10^{-5}$  S  $\text{cm}^{-1}$ . In the present work, the weight% of agar and NH<sub>4</sub>Br corresponding to 50 mol% agar/50 mol% NH<sub>4</sub>Br composition is taken and ethylene carbonate (EC) is added to it in different compositions as 0.1, 0.2, 0.3 and 0.4 mol% of EC. A similar procedure is applied for the preparation of polymer electrolyte using EC as plasticizer. The prepared electrolyte films are subjected to vibrational and electrical characterizations. FTIR spectra were recorded for the proton-conducting polymer electrolyte films in the range of 400–4000  $\text{cm}^{-1}$  at room temperature using a SHIMADZU-IR Affinity-1 Spectrometer with resolution 1  $\text{cm}^{-1}$ . Electrical measurements were performed on the polymer electrolyte films in the frequency range 42 Hz–1 MHz, over the temperature range 303–373 K by sandwiching them between aluminum blocking electrodes using HIOKI 3532 LCZ meter interfaced with a computer. Though the vibrational and impedance characterizations have been done for pure agar in DMF electrolyte, agar doped with different compositions of NH<sub>4</sub>Br (such as 90:10, 80:20, 70:30, 60:40, 50:50 and 40:60) and 50 mol% agar/50 mol% NH<sub>4</sub>Br/*x* mol% EC (where *x* = 0.1, 0.2, 0.3, 0.4%), the plots of pure agar in DMF, 50 mol% agar/50 mol% NH<sub>4</sub>Br and 50 mol% agar/50 mol% NH<sub>4</sub>Br/0.3 mol% EC polymer electrolytes have been projected.

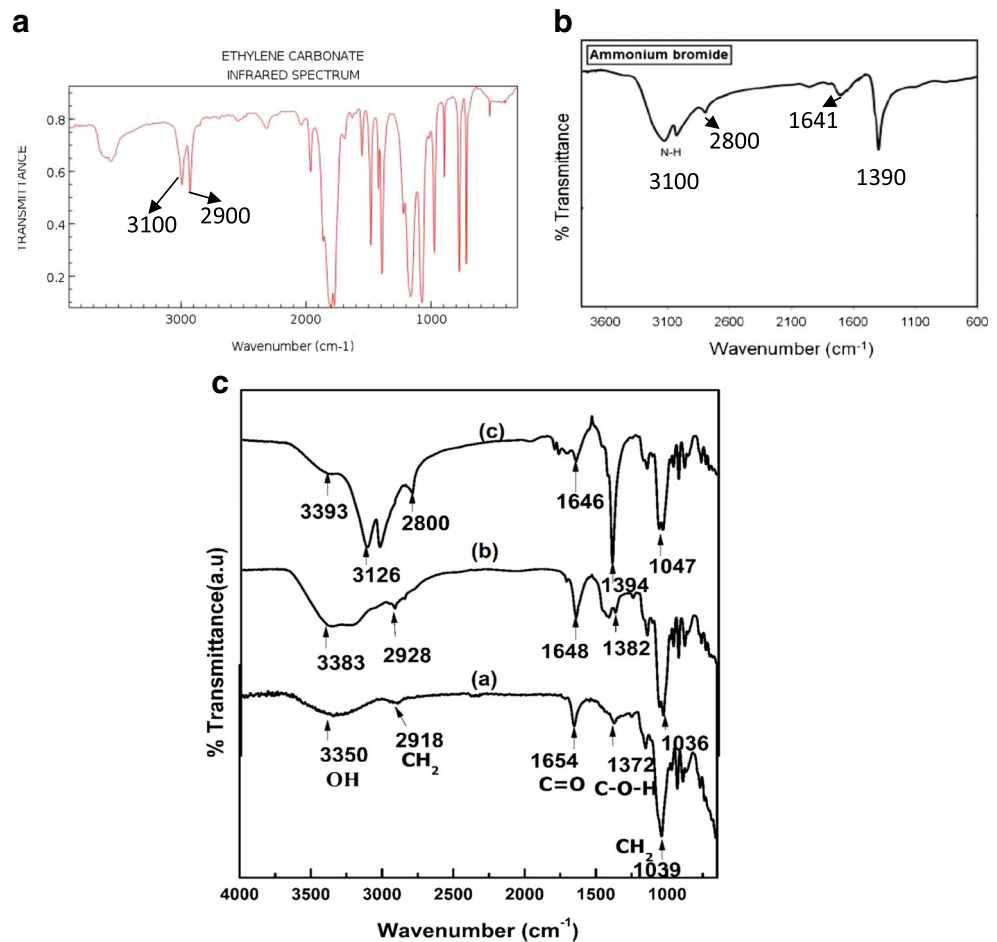
## Results and discussion

### Fourier transform infrared analysis

The FTIR analysis has wide applicability in investigating the structure of materials synthesized chemically or obtained naturally. FTIR is also used to study the interaction between cations, anions, solvents and polymers. The FTIR spectra for pure agar in DMF, 50 wt% agar doped with 50 wt% NH<sub>4</sub>Br and 0.3% EC plasticized with 50 wt% agar/50 wt% NH<sub>4</sub>Br are shown in Fig. 1.

It is clear from the plot that there is a significant change in the FTIR spectra of agar with the addition of NH<sub>4</sub>Br and EC.

**Fig. 1** **a** FTIR spectra of ethylene carbonate (EC). **b** FTIR spectra of ammonium bromide (NH<sub>4</sub>Br). **c** FTIR spectra of (a) pure agar in DMF, (b) 50 mol% agar doped with 50 mol% of NH<sub>4</sub>Br and (c) 50 mol% agar doped with 50 mol% of NH<sub>4</sub>Br plasticized with 0.3% EC



The characteristic peak of pure agar at  $1654\text{ cm}^{-1}$  assigned to C=O stretching is shifted to  $1648$  and  $1646\text{ cm}^{-1}$  in 50 mol% agar doped with 50 mol% NH<sub>4</sub>Br and 0.3% EC plasticized with 50 mol% agar/50 mol% NH<sub>4</sub>Br, respectively. Esam et al. [28] has reported that a peak at  $1654\text{ cm}^{-1}$  is due to stretching vibration of the conjugated peptide bond formed by amine (NH) and acetone (CO) groups. The carbonyl stretch of the 50 mol% agar/50 mol% NH<sub>4</sub>Br polymer complex located at  $1648\text{ cm}^{-1}$  is shifted to lower frequency side ( $1645\text{ cm}^{-1}$ ) with the addition of 0.3 wt% EC. The vibrational band of C=O stretching evolved between  $1648$  and  $1645\text{ cm}^{-1}$  is due to Fermi resonance of skeletal breathing in EC [29]. This C=O band seems to be broadened in the plasticized polymer-salt complex, which indicates the interaction of plasticizer with the polymer. The perturbation in the carbonyl band due to the presence of NH<sub>4</sub>Br salt arises from interaction of H<sup>+</sup> ion with the carbonyl oxygen. It is clear that the basicity of carbonyl group of agar is increased with addition of EC, implying that the C=O group is able to act as a strong electron donor to interact with H<sup>+</sup> ion. Similar reports of Li<sup>+</sup> and Na<sup>+</sup> ion interactions with the carbonyl oxygen of polymers have already been reported in the literature [30, 31]. The vibrational frequencies observed in the FTIR spectra of pure agar in DMF,

50 wt% agar doped with 50 wt% NH<sub>4</sub>Br and 0.3% EC plasticized with 50 wt% agar/50 wt% NH<sub>4</sub>Br polymer electrolytes are given in Table 1.

A characteristic peak of pure agar at  $928\text{ cm}^{-1}$  corresponding to 3,6-anhydrogalactose bridges [32] is found in salt-doped agar sample with a slight shift. The intense band observed at  $1038\text{ cm}^{-1}$ , common to all polysaccharides, is mainly due to the coupling of the C-O or the C-C stretching modes with the C-O-H bending modes. The modes due to the C-O-C bridge of the 3,6 anhydro units may also contribute at this frequency, but the strong absorbance at  $930\text{ cm}^{-1}$  is the one attributed to the vibration of the C-O-C bridge of 3,6-anhydrogalactose. The absorption band at  $1382\text{ cm}^{-1}$  is due to the vibration mode of sulfate groups [33]. The band at  $1149\text{ cm}^{-1}$  is due to vibration mode of ester-sulfate link vibrations and C-N stretching. The broad band at  $3350\text{ cm}^{-1}$  corresponds to the stretching of O-H hydroxyl group of agar that participates in inter- and intra-molecular hydrogen bond formation and has been shifted to  $3383$  and  $3393\text{ cm}^{-1}$  in 50 mol% agar/50 mol% NH<sub>4</sub>Br and EC doped 50 mol% agar/50 mol% NH<sub>4</sub>Br, respectively. It has already been reported that stretching hydroxyl group occurs between  $3570$  and  $3200\text{ cm}^{-1}$  [34]. The shifts in these bands were due to the

**Table 1** Absorption peaks for agar in DMF, 50% agar/50% NH<sub>4</sub>Br and 50% agar/50% NH<sub>4</sub>Br/0.3% EC polymer electrolytes

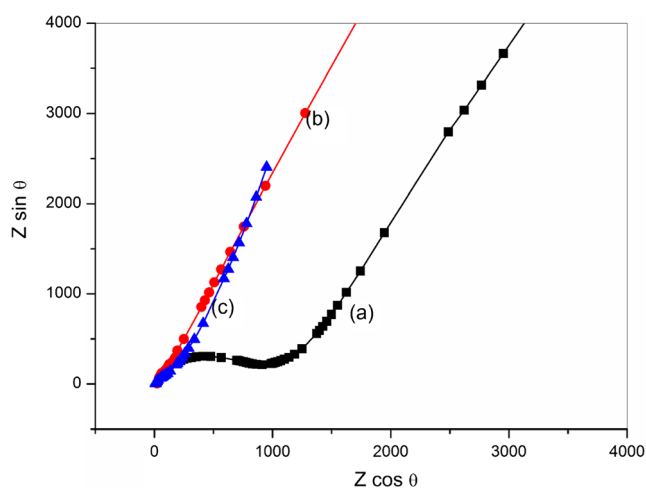
Pure agar in DMF	50% agar/50% NH <sub>4</sub> Br	50% agar/50% NH <sub>4</sub> Br/0.3% EC	Assignment
3350	3383	3393	O-H stretching
–	3197	3126	N-H stretching
2918	2928	2918	CH <sub>2</sub> stretching
–	–	2799	N-H stretching
–	–	1801	C=O stretching
–	–	1772	C=O stretching
–	1716	1718	C=O (H-bonded)
1654	1648	1646	C=O stretching
C=C stretching			
1382	1372	1394	CH <sub>2</sub> bending
C-O-H bending			
1149	1144	1144	C-N stretching
1039	1036	1047	CH <sub>2</sub> scissoring
928	931	931	Ester sulfate link vibration

interaction of the salt with the polymer matrix. The above result confirms the complex formation between the polymer, salt and the plasticizer.

### AC impedance spectroscopic analysis

Electrical properties of all the prepared agar-based polymer electrolyte has been analysed using AC impedance spectroscopy technique. Figure 2 shows the complex impedance plots of pure agar in DMF, 50 mol% agar/50 mol% NH<sub>4</sub>Br and 50 mol% agar/50 mol% NH<sub>4</sub>Br/0.3% EC polymer electrolytes at 303 K.

The plot for pure agar in DMF consists of a high-frequency depressed semicircle, and a low-frequency spike and the semicircle disappear in the plots for other compositions with addition of NH<sub>4</sub>Br and EC. The high-frequency semicircle is



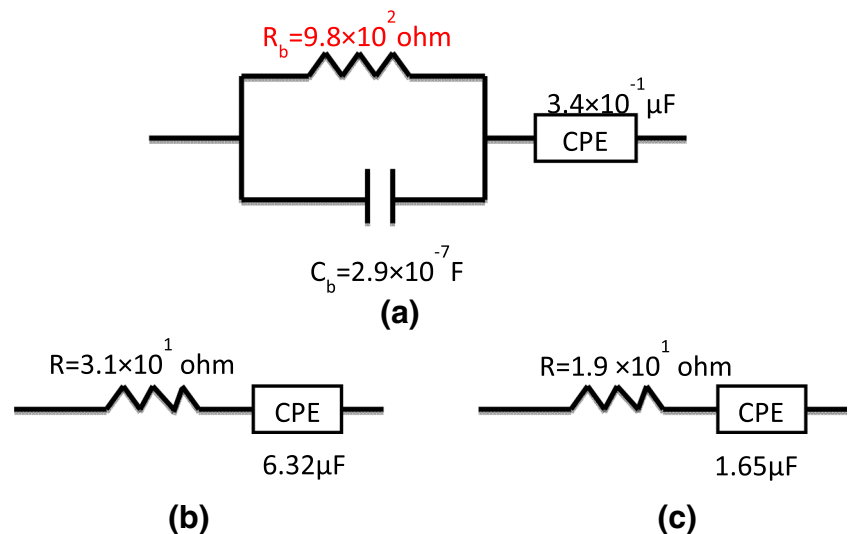
**Fig. 2** Impedance plot of **a** pure agar in DMF, **b** 50 mol% agar doped with 50 mol% of NH<sub>4</sub>Br and **c** 50 mol% agar doped with 50 mol% of NH<sub>4</sub>Br plasticized with 0.3% EC

related to the parallel combination of a resistor ( $R_b$ ) and a capacitor ( $C_b$ ), and the low-frequency spike represents the formation of double layer capacitance (CPE) at the electrode–electrolyte interface due to migration of ions at low frequency. The equivalent electrical circuit representing the behaviour of pure agar in DMF is given as Scheme 1a. The hopping of ions occurs through the free volume of polymer matrix, and it is represented by a resistor ( $R_b$ ). The polymer chains get polarized due to the alternating field and become immobile which is represented by a capacitor ( $C_b$ ). The values of bulk resistance and bulk capacitance of pure agar was found to be  $9.8 \times 10^2 \Omega$  and  $2.9 \times 10^{-7} \text{ F}$ , respectively. The equivalent electrical circuit corresponding to 50 mol% agar/50 mol% NH<sub>4</sub>Br and 0.3% EC in 50 mol% agar/50 mol% NH<sub>4</sub>Br are given as Scheme 1b and Scheme 1c, respectively. The low-frequency response appearing as an inclined spike at an angle less than  $90^\circ$  to the real axis indicates the inhomogeneous nature of the electrode–electrolyte interface, and it is represented as constant phase element (CPE) in the equivalent circuit. The bulk resistance of the polymer electrolytes is obtained either by the intersection of semicircle or the spike with the real axis [5] or by Boukamp's EQ software. The various factors that influence ionic conductivity are the number of charge carriers, ionic mobility and the availability of a connecting polar domain as the conduction pathway [35]. Ionic conductivity of the solid polymer electrolyte was calculated from the measured bulk resistance, area and thickness of the polymer film using the following formula.

$$\sigma = l / (R_b \times A) \quad (1)$$

where  $l$  is the thickness of the polymer electrolyte (cm),  $A$  is the area of the blocking electrode (cm<sup>2</sup>) and  $R_b$  is the bulk resistance of polymer electrolyte.

**Scheme 1** **a** Equivalent circuit for pure agar in DMF. **b** Equivalent circuit for 50 mol% agar doped with 50 mol% of NH<sub>4</sub>Br. **c** Equivalent circuit for 50 mol% agar doped with 50 mol% of NH<sub>4</sub>Br plasticized with 0.3% EC



The conductivity value of 100% agar in DMF was  $3.30 \times 10^{-8} \text{ S cm}^{-1}$ . The conductivity values of 90 mol% agar/10 mol% NH<sub>4</sub>Br, 80 mol% agar/20 mol% NH<sub>4</sub>Br, 70 mol% agar/30 mol% NH<sub>4</sub>Br, 60 mol% agar/40 mol% NH<sub>4</sub>Br, 50 mol% agar/50 mol% NH<sub>4</sub>Br and 40 mol% agar/60 mol% NH<sub>4</sub>Br are  $5.30 \times 10^{-8}$ ,  $7.86 \times 10^{-6}$ ,  $1.08 \times 10^{-5}$ ,  $3.85 \times 10^{-5}$ ,  $7.24 \times 10^{-5}$  and  $9.16 \times 10^{-8} \text{ S cm}^{-1}$ , respectively. The maximum conductivity of  $7.24 \times 10^{-5} \text{ S cm}^{-1}$  was achieved for sample with composition of 50 mol% agar/50 mol% NH<sub>4</sub>Br. Similarly, the conductivity values of 0.1, 0.2, 0.3 and 0.4% EC plasticized in the highest conductivity sample of agar/NH<sub>4</sub>Br system (i.e., 50 mol% agar/50 mol% NH<sub>4</sub>Br) are  $9.08 \times 10^{-5}$ ,  $1.15 \times 10^{-4}$ ,  $3.73 \times 10^{-4}$  and  $9.16 \times 10^{-5} \text{ S cm}^{-1}$ , respectively. Conductivity value of  $2.38 \times 10^{-5} \text{ S cm}^{-1}$  has been obtained for pure agar membrane using distilled water as solvent [21, 22]. In the present work, the conductivity of pure agar membrane prepared using DMF as solvent is  $3.30 \times 10^{-8} \text{ S cm}^{-1}$ . The membrane with composition 50 mol% agar/50 mol% NH<sub>4</sub>Br (in DMF solvent) shows a conductivity value of  $7.24 \times 10^{-5} \text{ S cm}^{-1}$ . So to increase the conductivity, the plasticizer EC has been used. However, by the addition of 0.3% ethylene carbonate (EC) as plasticizer in 50 mol% agar/50 mol% NH<sub>4</sub>Br, the conductivity value increased by one order and the calculated value of ionic conductivity is  $3.73 \times 10^{-4} \text{ S cm}^{-1}$ . In this present work, the increase in conductivity could be attributed to the increment of charge carriers and hopping of the mobile ions. The higher dielectric constant of EC ( $\epsilon_r = 85.1$ ) may allow greater dissolution of the salt resulting in increased number of charge carriers and hence the conductivity. The major role of a plasticizer in a host polymer is to decrease viscosity of the electrolyte and assist in the dissociation of the salt thereby increasing the number of charge carriers [36].

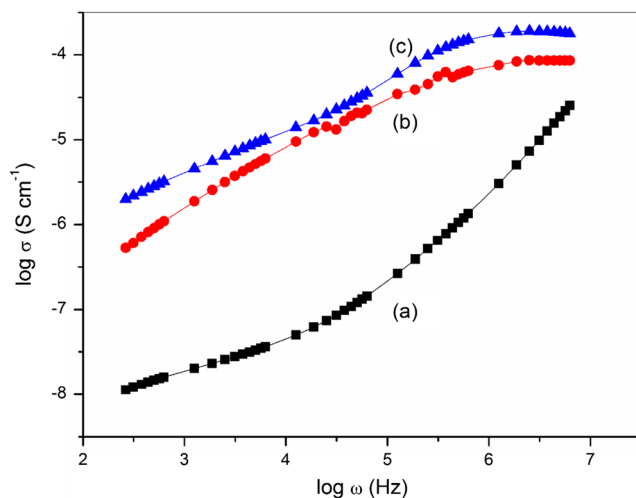
**Conductance spectra analysis**

The conductance spectra for the prepared biopolymer electrolytes at room temperature have been shown in Fig. 3. The conductance spectra of 50 mol% agar/50 mol% NH<sub>4</sub>Br and 50 mol% agar/50 mol% NH<sub>4</sub>Br/0.3% EC exhibit two distinct regions. At lower frequencies, the conductivity is found to increase which is due to the interfacial dispersion or the space charge polarization. A frequency-independent conductivity plateau is observed in the mid-frequency region. The plateau region characterizes the conduction, which is caused due to the hopping of the mobile ions, and extrapolations determine the dc value of conductivity and are tabulated in Table 2. The conductance spectra of pure agar in DMF exhibit a plateau region and a high-frequency dispersion region. The high-frequency dispersion region is attributed to the relaxation of the mobile ion hopping which is due to the Coulomb interactions of the charge carriers and the disorder within the structure [37].

The highest dc conductivity value has been obtained for the biopolymer electrolyte 50 mol% agar/50 mol% NH<sub>4</sub>Br/0.3% EC. The dc conductivity increases with increase of temperature due to the free volume created around the polymer chain which provides migration pathway for the mobile ions and polymer segments [38].

**Dielectric spectra analysis**

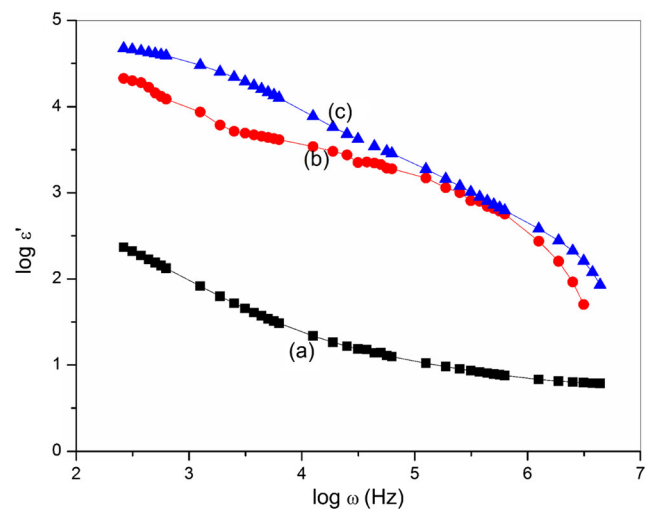
Dielectric relaxation study is a vital tool to reveal the relaxation of dipoles in polymer electrolytes. Dielectric constant is ascribed to the charge stored in a material, while dielectric loss is a measure of energy losses to move ions when the polarity of electric field reverses rapidly [39, 40]. The frequency dependence of  $\epsilon'$  and  $\epsilon''$  for 50 mol% agar/50 mol% NH<sub>4</sub>Br and



**Fig. 3** Conductance spectra of **a** pure agar in DMF, **b** 50 mol% agar doped with 50 mol% of  $\text{NH}_4\text{Br}$  and **c** 50 mol% agar doped with 50 mol% of  $\text{NH}_4\text{Br}$  plasticized with 0.3% EC at room temperature

50 mol% agar/50 mol%  $\text{NH}_4\text{Br}$ /0.3% EC at 303 K is shown in Figs. 4 and 5, respectively.

The higher  $\epsilon'$  and  $\epsilon''$  values obtained by 50 mol% agar/50 mol%  $\text{NH}_4\text{Br}$ /0.3% EC at low-frequency region indicates that the existence of plasticizer may result in more localization of charge carriers along with mobile ions causing higher ionic conductivity [41]. The decreasing  $\epsilon'$  and  $\epsilon''$  with increasing frequency is attributed to the tendency of the dipoles in the polymer chains to orient themselves in the direction of the applied electric field [42]. At higher frequencies, the fast periodic reversal of the electric field occurs; hence, the polarization due to charge accumulation decreases at the electrode–electrolyte interface, which in turn contributes to the decrease in  $\epsilon'$  and  $\epsilon''$  [43]. The frequency dependence of  $\epsilon''$  for 50 mol% agar/50 mol%  $\text{NH}_4\text{Br}$ /0.3% EC clearly shows the high-frequency  $\beta$  relaxation peak which may be caused by the dipolar type of relaxation caused by the presence of carboxyl side group in the system [44] and low-frequency  $\alpha$  relaxation which may be due to the movement of main segments of the polymer chain. Dielectric results imply that the



**Fig. 4** Dielectric constant spectra of **a** pure agar in DMF, **b** 50 mol% agar doped with 50 mol% of  $\text{NH}_4\text{Br}$  and **c** 50 mol% agar doped with 50 mol% of  $\text{NH}_4\text{Br}$  plasticized with 0.3% EC

electrolyte systems in the present work confirm the non-Debye behavior.

### Loss tangent spectra

The dielectric relaxation parameter of the polymer electrolytes can be obtained from the study of  $\tan \delta$  as a function of frequency. The dielectric loss tangent,  $\tan \delta$  can be defined by the equation

$$\tan \delta = \epsilon'' / \epsilon' \quad (2)$$

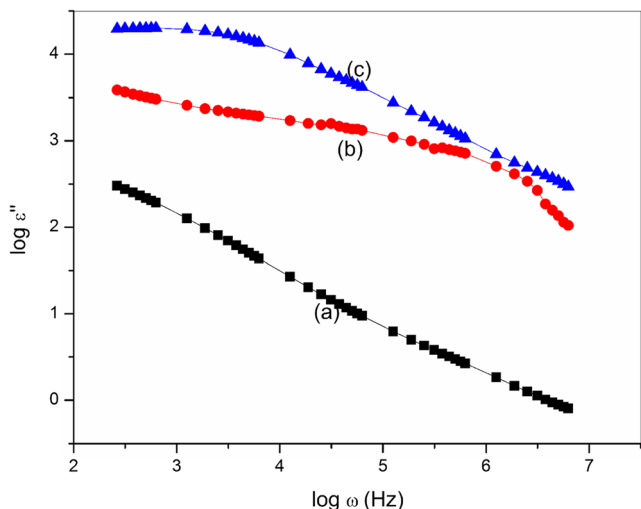
The variation of  $\tan \delta$  with frequency for all the prepared polymer complexes at 303 K is presented in Fig. 6. It has been observed that  $\tan \delta$  increases with increasing frequency and reaches a maximum. Then, it decreases for further increase of frequency.

For maximum dielectric loss ( $\tan \delta$ ) at a particular frequency, the absorption peak is described by

$$\tau \omega = 1 \quad (3)$$

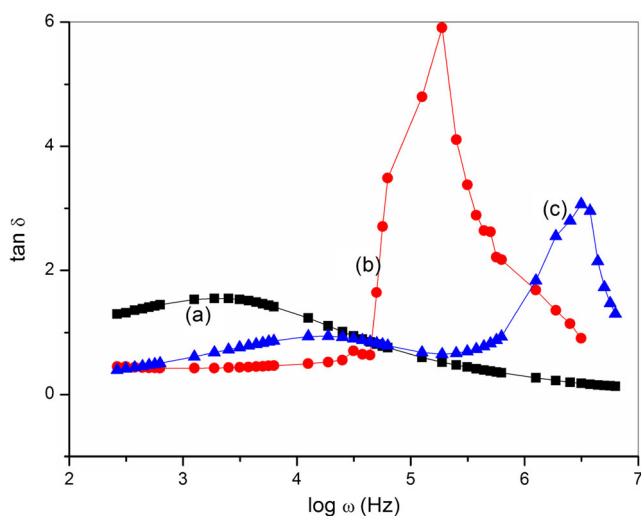
**Table 2** DC conductivity values of agar-based biopolymer electrolytes at different temperatures

Composition of agar-based electrolytes	DC conductivity ( $\sigma_{dc}$ ) (S $\text{cm}^{-1}$ ) for prepared agar-based electrolytes								Relaxation frequency $\omega$ (Hz)	Relaxation time $\tau$ (s)
	303 K	313 K	323 K	333 K	343 K	353 K	363 K	373 K		
Pure agar-agar in DMF	$3.30 \times 10^{-8}$	$4.38 \times 10^{-8}$	$1.53 \times 10^{-7}$	$1.35 \times 10^{-6}$	$2.73 \times 10^{-6}$	$6.84 \times 10^{-6}$	$8.62 \times 10^{-6}$	$1.01 \times 10^{-5}$	$5.02 \times 10^3$	$1.99 \times 10^{-4}$
50 mol% agar/50 mol% $\text{NH}_4\text{Br}$	$7.24 \times 10^{-5}$	$9.91 \times 10^{-5}$	$2.10 \times 10^{-4}$	$2.40 \times 10^{-4}$	$2.46 \times 10^{-4}$	$2.67 \times 10^{-4}$	$2.94 \times 10^{-4}$	$3.12 \times 10^{-4}$	$1.88 \times 10^5$	$1.14 \times 10^{-5}$
50 mol% agar/50 mol% $\text{NH}_4\text{Br}$ /0.3% EC	$3.73 \times 10^{-4}$	$3.98 \times 10^{-4}$	$4.21 \times 10^{-4}$	$4.98 \times 10^{-4}$	$5.13 \times 10^{-4}$	$1.46 \times 10^{-3}$	$1.69 \times 10^{-3}$	$1.84 \times 10^{-3}$	$4.96 \times 10^5$	$2.02 \times 10^{-6}$

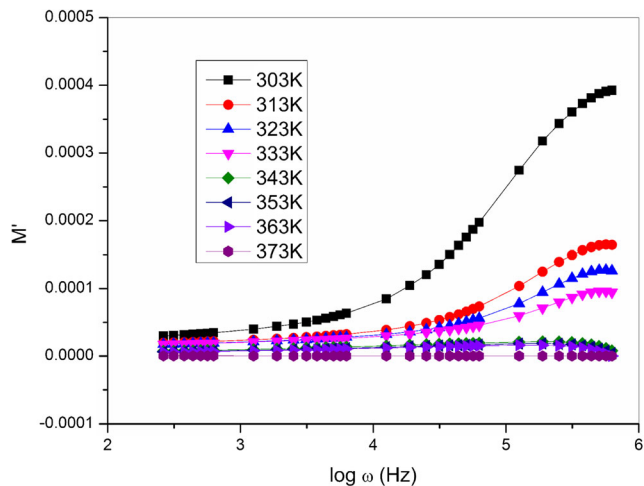


**Fig. 5** Dielectric loss spectra of **a** pure agar in DMF, **b** 50 mol% agar doped with 50 mol% of  $\text{NH}_4\text{Br}$  and **c** 50 mol% agar doped with 50 mol% of  $\text{NH}_4\text{Br}$  plasticized with 0.3% EC

Here,  $\tau$  is the relaxation time,  $\omega$  is the angular velocity with  $\omega = 2\pi f$ , and  $f$  is the frequency value corresponding to maximum  $\tan \delta$  in Hz. Relaxation time occurs when ionic charges carriers within the polymer follow the change in the direction of the applied field. When polarization does not follow the AC field, dielectric constant decreases ( $\epsilon'$ ) with frequency, and so,  $\tan \delta$  is maximum for 50 mol% agar/50 mol%  $\text{NH}_4\text{Br}$ . With the addition of EC, there is a significant increase in the values of dielectric constant ( $\epsilon'$ ) and dielectric loss ( $\epsilon''$ ). Hence, the value of  $\tan \delta$  becomes less compared to that of 50 mol% agar/50 mol%  $\text{NH}_4\text{Br}$ . It is observed from Fig. 6 that the peak frequency shifted towards higher frequency with the addition of  $\text{NH}_4\text{Br}$  and EC. The shift of the peak towards higher frequency leads to very small relaxation time. This in turn leads to increase in ionic conductivity which may also be



**Fig. 6** Loss tangent spectra of **a** pure agar in DMF, **b** 50 mol% agar doped with 50 mol% of  $\text{NH}_4\text{Br}$  and **c** 50 mol% agar doped with 50 mol% of  $\text{NH}_4\text{Br}$  plasticized with 0.3% EC



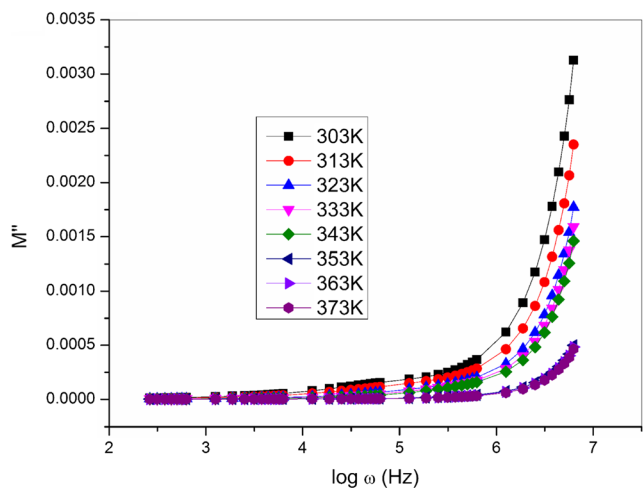
**Fig. 7** Real part of modulus  $M'$  vs  $\log \omega$  for 50 mol% agar doped with 50 mol% of  $\text{NH}_4\text{Br}$  plasticized with 0.3% EC at different temperatures

due to the enhancement in number of charge carriers (mobile ions). The enhancement of charge carriers may be attributed to the plasticizing effect of EC. Thus, the relatively fast segmental motion coupled with mobile ions enhances the transport properties of the sample which explains the decrease in relaxation time with conductivity.

The relaxation time is calculated for all the prepared bio-polymer electrolytes at 303 K and tabulated in Table 2. A low relaxation time of  $2.02 \times 10^{-6}$  s has been obtained for 0.3% EC salt-doped polymer electrolyte which is consistent with the conductivity analysis.

**Electrical modulus studies**

Figures 7a and 8 show the frequency dependence of the real,  $M'$  and imaginary,  $M''$  parts of the modulus formalism of 50 mol% agar doped with 50 mol% of  $\text{NH}_4\text{Br}$  plasticized with



**Fig. 8** Imaginary part of modulus  $M''$  vs  $\log \omega$  for 50 mol% agar doped with 50 mol% of  $\text{NH}_4\text{Br}$  plasticized with 0.3% EC at different temperatures

0.3% EC at different temperatures, respectively. According to Ramesh and Arof [37], the presence of peaks in the modulus formalism at higher frequencies for the polymer system at different temperatures is an indicator that the polymer electrolyte films are ionic conductors. However, in this study, the peaks are visibly absent in  $M''$  and are present in  $M'$  vs log frequency. The values of  $M'$  and  $M''$  approach zero at low frequencies which indicates that electrode polarization is negligible. The appearance of a long tail at low frequencies indicates that there might be a large capacitance associated with the electrodes used in electrochemical impedance spectroscopy which further confirms non-Debye behavior in the sample [45].

## Conclusion

The agar-based ion-conducting polymer electrolytes containing EC and  $\text{NH}_4\text{Br}$  have been prepared by solution casting technique with DMF as solvent and studied by AC impedance spectroscopy. The complexation behaviour between the polymer, the salt and the plasticizer has been confirmed by FTIR studies. The maximum conductivity of value  $3.73 \times 10^{-4} \text{ S cm}^{-1}$  has been obtained for the film 50 wt% agar/50 wt%  $\text{NH}_4\text{Br}$ /0.3% EC. Ionic conductivity of the electrolyte increases by one order of magnitude with the addition of 0.3% of EC. This may be due to the lowering of viscosity of the electrolyte with the addition of plasticizer. The dielectric loss spectrum of the polymer electrolyte plasticized with 0.3% of EC exhibits  $\alpha$  and  $\beta$  relaxations. The relaxation parameters of the electrolytes have been obtained by the study of  $\tan \delta$  as a function of frequency. From the conductance and modulus spectra, it may be concluded that the charge carriers responsible for both conductivity and relaxation are the same. Modulus analysis shows the non-Debye nature of the electrolyte films. All these preliminary results suggest that such agar-based biopolymer film has a good potential for applications as conducting biopolymer electrolytes.

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