Dielectric Relaxation Studies of Cellulose-Water Mixtures Using Time and Frequency Domain Technique

S H Saknure[a], N P Garad[a], A G Gubre[a], Y S Joshi[b] & A C Kumbharkhane[a]*

[a]School of Physical Sciences, Swami Ramanand Teerth Marathwada University, Nanded, 431 606, India
[b]Department of Physics, Lal Bahadur Shastri Mahavidyalaya, Dharmabad, 431 802, India

The complex dielectric permittivity of hydroxypropyl methyl cellulose (HPMC)-water mixture was measured by using Time Domain Reflectometry (TDR) and Frequency Domain (LCR) Technique at 25 °C. The complex dielectric permittivity $\varepsilon^*(\omega)$, complex electrical modulus $M^*(\omega)$, complex electrical conductivity $\sigma^*(\omega)$, loss tangent (tanδ), static dielectric constant (ε_0) and relaxation time (τ) have been determined for the cellulose-water system.

1 Introduction

Over the last two decades a significant advancement in the experimental dielectric spectroscopy technique developed in the frequency range from 10^{-6} to 10^{12} Hz[1]. Dielectric dispersion and absorption spectra of binary liquid mixtures provides information on molecular interaction in the liquid mixture via hydrogen bonding[2]. Therefore, systems like aqueous or alcoholic mixtures where hydrogen bonding is important are frequently studied using dielectric relaxation spectroscopy (DRS)[3]. In recent years polysaccharides have been the topic of several experimental and theoretical researches. There have been attempts to link the characteristics of different polysaccharides to their chemical structure and conformation. On the subject of how polysaccharides interact with a solvent, several publications have been published[4-6]. Numerous studies have also been done on the mechanical and dielectric relaxation of cellulose and its derivatives[7-9]. The present investigation is carried out on cellulose water mixture. Cellulose belongs to the category of polysaccharides andis made up of glucose subunits. Hydroxypropyl methyl cellulose (HPMC) is a cellulose derivative generated from the structure of natural cellulose by changing the -OH group with the -OR group (R is the substituent) cellulose residue group as shown in Fig. 1.

In the present paper complex permittivity spectra for hydroxypropyl methyl cellulose (HPMC15cps and HPMC50cps) in water solutions have been investigated using Time Domain Reflectometry (TDR)10MHz to 30GHz and frequency domain technique in the frequency range 20Hz to 2MHzat 25 °C. The values of static dielectric constant, relaxation time, complex dielectric permittivity $\varepsilon^*(\omega)$, complex electrical modulus $M^*(\omega)$, complex electrical conductivity $\sigma^*(\omega)$ and loss tangent (tan δ), have been determined using the least squares fit method for the aqueous HPMC. An attempt has been made to understand the molecular interaction in the HPMC-water mixture by means of dielectric parameters using TDR and frequency domain techniques. However, the literature survey reveals that no study was reported using Time Domain Technique which is expected to give better results.

2 Experimental

2.1 Materials

The hydroxypropyl methylcellulose 15cPs LR (HPMC 15 cPs) and hydroxylpropyl methyl cellulose 50 cPsLR (HPMC 50 cPs) were used from S. d. Fine-Chemical Limited, whereas water was used after deionization. The mili molar solution of HPMCs were prepared in water and further volume fraction were made with pure water.

2.2 Measurements

Two different techniques were used to evaluate the dielectric properties of the system. The first technique is Time domain Reflectometry. The dielectric dispersion of

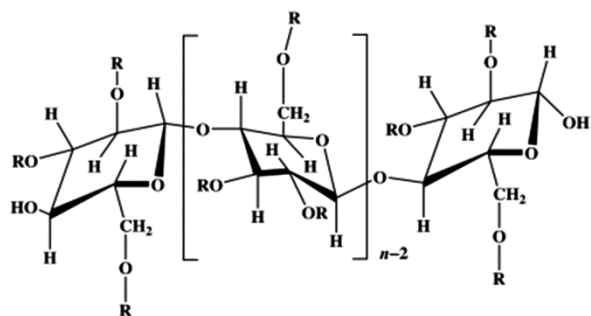*Corresponding author: (E-mail: akumbharkhane@yahoo.co.in)

Fig. 1 — Structure of HPMC where R is H, CH$_3$, or CH$_3$CH (OH)CH$_2$.
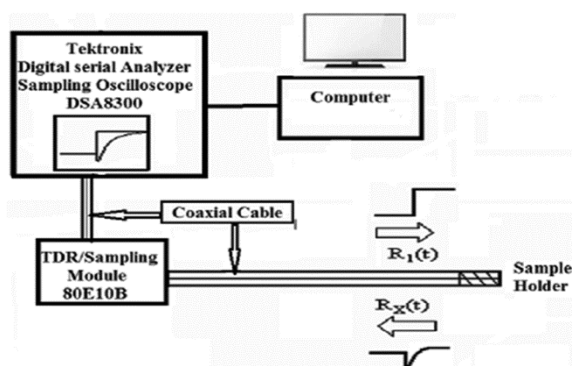

Fig. 3 — TDR Waveform: Reflected pulses with & without Sample.

Fig. 2 — Block Diagram of Time Domain Reflectometry (TDR).
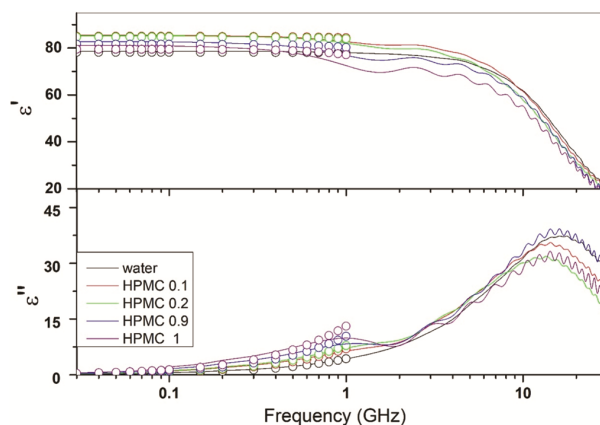
Fig. 4 — Complex permittivity spectra for HPMC 15cPs-water mixture at 25 °C using TDR.

aqueous cellulose was studied using the TDR technique in between the frequency range 10MHz to 30GHz. These measurements were made for different concentrations at 25 °C. The Tektronix Digital Signal Analyzer DSA8300 sampling main frame oscilloscope with the dual channel sampling module 80E10B has been used. The block diagram of TDR is shown in Fig. 2.

The sampling module provides a 12ps incident and 15ps reflected rise time pulse. These pulses are reflected pulse without sample $R_1(t)$ and with sample, $R_x(t)$ were recorded in a time window of 5ns and digitized in 2000 points. Coaxial cable used to feed the pulse which has 50-ohm impedance, inner diameter of 0.28 mm and outer diameter of 1.19 mm.

The addition $[q(t) = R_1(t) + R_x(t)]$ and subtraction $[p(t) = R_1(t) - R_x(t)]$ of these pulses are done in oscilloscope memory and are shown in Fig. 3

These subtracted and added pulses are transferred to computer for further analysis. The Fourier transformation of the pulse and data analysis were done to study complex permittivity spectra $\varepsilon^*(\omega)$ using the nonlinear least squares fit method[10-11].

The second technique has been used to study complex permittivity using an Agilent E 4980A precision LCR meter which can measure capacitance and resistance with a four terminal liquid dielectric
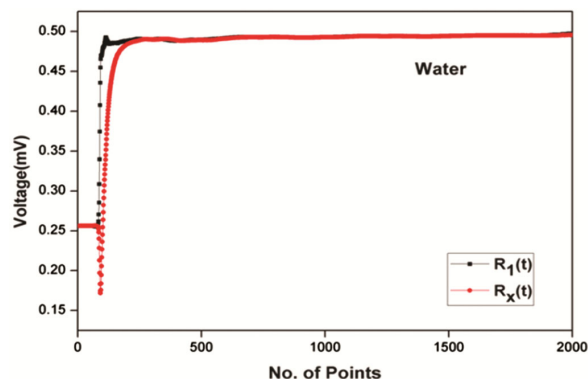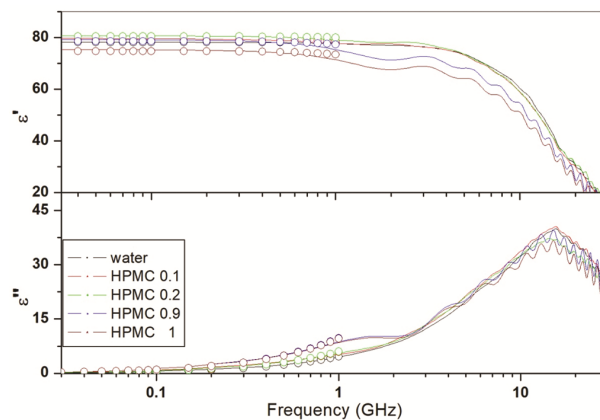
Fig. 5 — Complex permittivity spectra for HPMC 50cPs-water mixture at 25 °C using TDR.

test fixture (Agilent 16452A) in the frequency range 20 Hz to 2 MHz[12].

3 Results and Discussion
3.1 Complex Permittivity Spectra
Figures 4 & 5 represents the complex permittivity spectra obtained by the time domain reflectometry
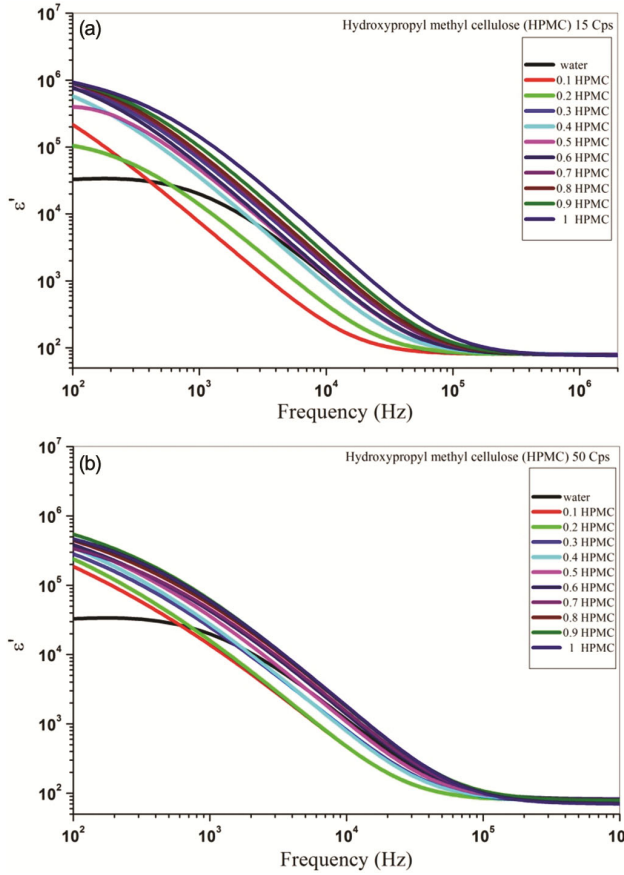
Fig. 6 — (a) and (b) shows the frequency dependent spectra of the real part ε′ of the relative dielectric function ε*(ω) for HPMC 15 Cps-water and HPMC 50 Cps-water binary mixture.

technique (TDR) in the frequency range from 10 MHz to 30 GHz at 25 °C for binary mixtures of HPMCs in water at various concentrations. From Fig. 4 & 5 it is observed that the dielectric permittivity goes on decreasing as the frequency increases this indicates the dielectric dispersion. The dielectric losses are shifted towards higher frequency and exhibit the Debye type dispersion.

Figures 6 (a) and (b) depict the variation of ε′(ω) with frequency for various concentrations of HPMC in water at 25 °C which is obtained by an LCR meter in the frequency range from 100Hz to 2MHz. It is seen that for all concentrations, ε′(ω) remains constant above the frequency 10^5Hz. On the other hand, it is observed that ε′(ω) increases with decreasing frequency in the lower frequency range (*i.e.*, < 10^5 Hz). This is due to the electrode polarization (EP) effect that occurs in a mixture[13]. This effect is a result of the development of long-distance ion and free-charge drift, which results in the creation of an electric double layer (EDL).
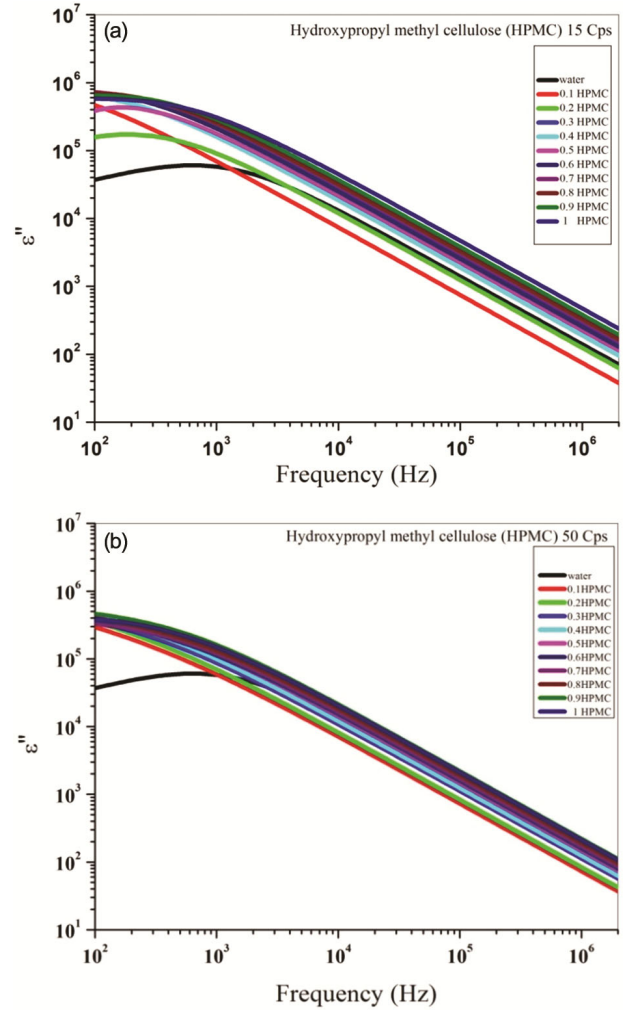

Fig. 7 — Spectra of the imaginary part ε″(ω) of the relative dielectric function ε*(ω) for (a) HPMC 15 Cps-water and (b) HPMC 50 Cps-water binary mixtures.

The capacitance at the interface between the dielectric material and metallic electrode surfaces in plane geometry[14]. When the electric field is applied in the form of a direct current ion is spread in a double layer, and charges are trapped at the interface between an electrode and bulk material surfaces.

The complex permittivity loss spectra for HPMC 15 Cps-water and HPMC 50 Cps-water as shown in Fig. 7 (a,b). In both the systems, dielectric loss value is very high. Also, the value of ε″ is higher for the samples with higher concentrations of both HPMCs and the dielectric loss ε″ is rapidly falls for both HPMC systems (above 10^3 Hz). This is because both HPMC systems are highly polar, and polar liquids absorb ionic contaminants throughout the manufacturing process. The larger values of ε″ are caused by the ionic impurity's conduction loss at lower frequencies[15,16].

Table 1 — Dielectric relaxation parameters for an aqueous solution of HPMC 50 Cps-water at 25 °C and different concentrations.

Molar (M) conc.Of HPMC (10^{-2})	25 °c		
	ε_0(TDR)	ε_0(LCR)	τ (ps)
0	78.18(1)	78.35	9.94(8)
0.1	79.27(9)	78.92	12.57(44)
0.2	80.48(6)	78.57	12.52(30)
0.3	83.33(5)	76.51	12.66(25)
0.4	83.49(7)	79.60	13.08(34)
0.5	84.29(10)	79.81	15.33(47)
0.6	83.74(38)	81.81	16.40(1)
0.7	84.41(22)	79.62	21.53(99)
0.8	85.35(33)	76.70	25.59(1)
0.9	78.63(14)	78.42	21.07(68)
1	74.73(14)	69.75	21.93(74)

The number in bracket indicates errors obtained by least squares fit method *e.g.*, 78.18(1) means 78.18$\pm$0.01

3.2 Static Dielectric Constant

The complex dielectric permittivity $\varepsilon^*(\omega) = (\varepsilon' - j\varepsilon'')$ was fitted with the Havirliak-Negami expression:[17]

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)}{[1 + (i\omega\tau)^{1-\alpha}]^\beta} \qquad \ldots(1)$$

where, ε_0, ε_∞, τ, α and β as fitting parameters. ε_0 is the static dielectric constant, ε_∞ is the limiting high-frequency permittivity and assumed to be 2.0 as a fitting parameter for all concentrations, τ is the relaxation time, α and β are the distribution parameters, and ω is the angular frequency. The Havriliak-Negami expression includes the cole-cole (β=1) Davidson-cole (α=0) and Debye (β=1, α=0) relaxation models. A non-linear least squares fit method was used to determine the values of the dielectric parameters. The values of different dielectric parameters for aqueous cellulose solutions obtained by the Havriliak-Negami equation are represented in Table 1.

The following points can be observed from the dielectric relaxation data (Table 1).

i) It is observed that the dielectric relaxation in these mixtures can be represented by the Debye relaxation behavior (α=0,β=1)

ii) The variation of dielectric constant (ε_0) of solute in water may be due to the large value of dipole moment of the HPMC-50 Cps molecule. This suggested that hydroxypropyl methyl cellulose bonds with water alter its structure, increasing the mixture's relaxation time and dielectric permittivity.

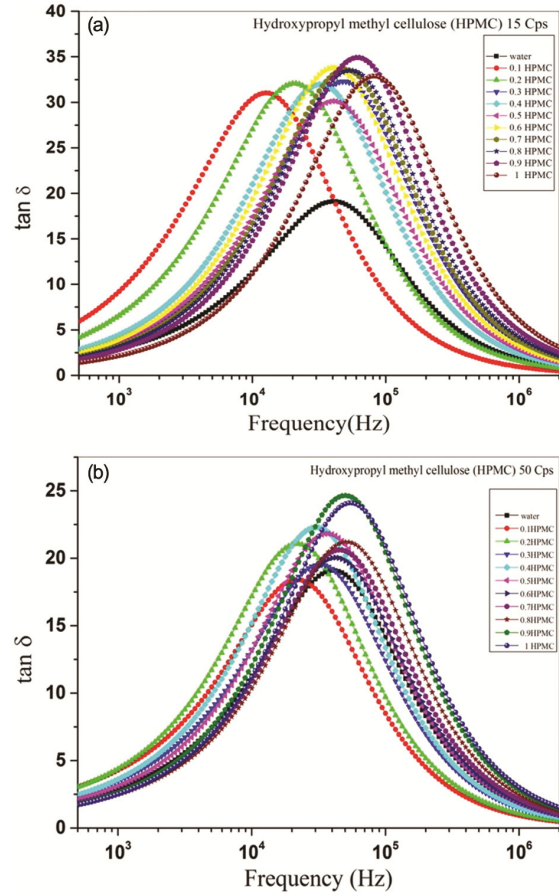iii) Cellulose's dielectric relaxation time is more than water's corresponding values. This further

Fig. 8 — (a, b) spectra of dielectric loss tan δ for HPMC 15 Cps-water and HPMC 50 Cps-water binary mixture.

confirms that the cellulose system breaks the hydrogen bonding in water.

Figure 8 (a,b) shows the frequency-dependent loss tangent tan δ ($=\varepsilon''/\varepsilon'$) spectra for HPMC 15 Cps + water and HPMC 50 Cps + water. However, the conductivity effect is suppressed and a relaxation peak is seen in the 10^4 Hz to 10^5Hz frequency range.

Using the loss peak, electrode polarization (EP) relaxation time can be calculated as[18].

$$\tau_{EP} = (1/2\pi f_{EP}) \qquad \ldots(2)$$

The real part (M$'$) of the electric modulus (M*) for HPMC 15 Cps + water and HPMC 50 Cps+waterare shown in Fig. 9 (a,b) which is dielectric permittivity inverse for all concentrations at 25 °C.

The Fig. 9 shows that M$'$ tends to be very low, at lower frequencies; due to the EP effects at lower frequencies. The values of M$'(\omega)$ rise as the frequency rises with a few exceptions; these are maximum for the water and minimum for both HPMCs[18]. This demonstrates that the two HPMCs systems contained
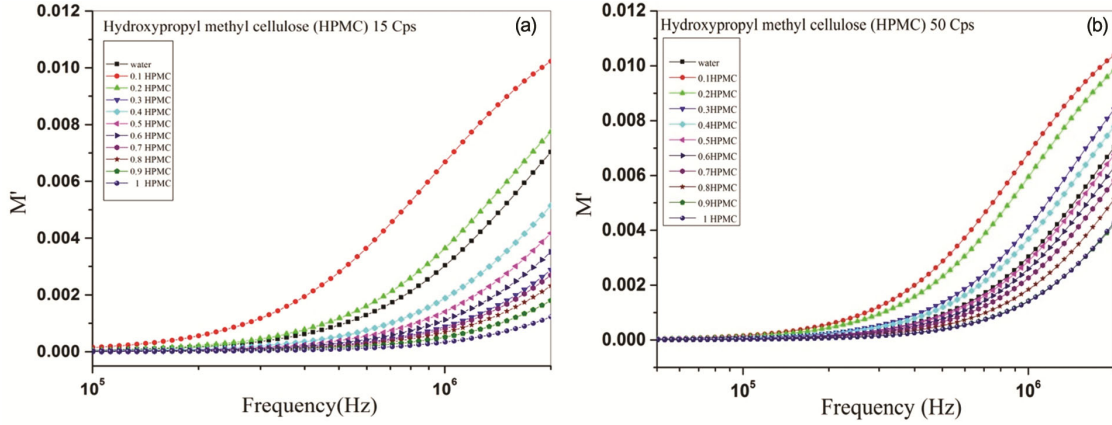
Fig. 9 — Spectra of the real part M′(ω) of the complex electric modulus M*(ω)for (a) HPMC 15 Cps water and (b) HPMC 50 Cps water binary mixture.
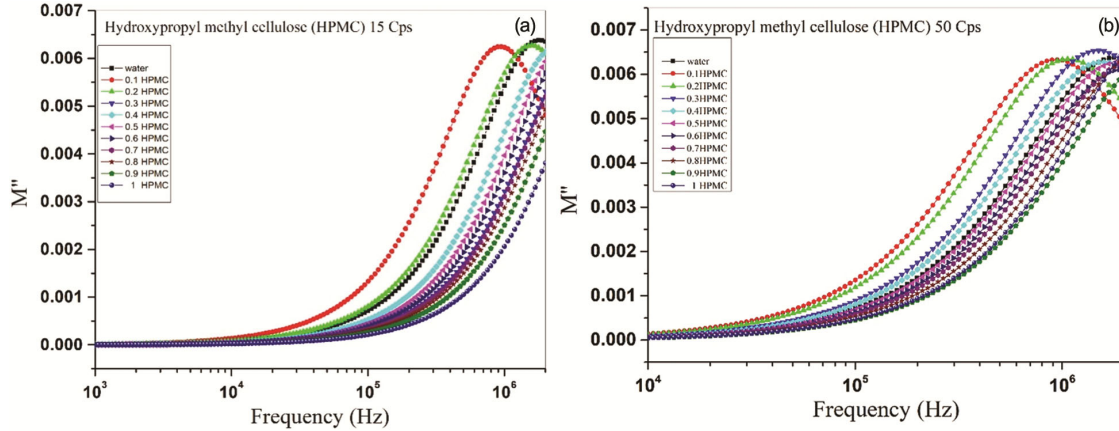

Fig. 10 — (a,b) Frequency dependent electric modulus spectra for binary mixture HPMC 15 Cps – water and HPMC 50 Cps – water at 25 °C.
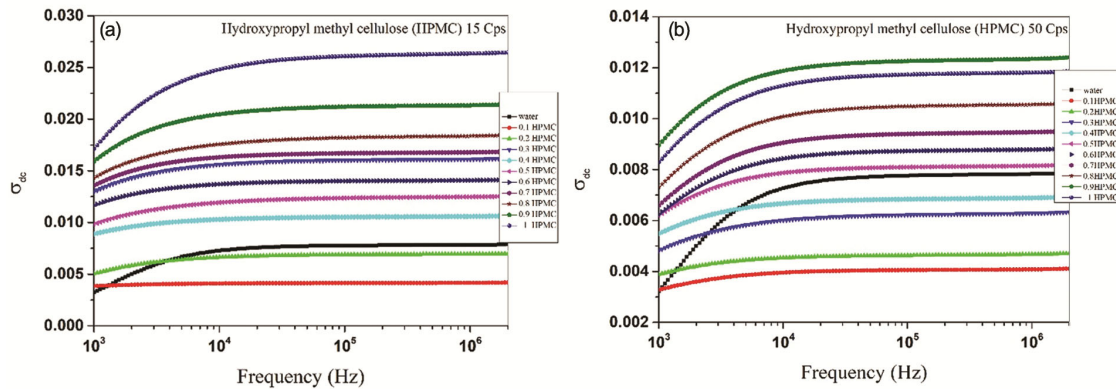

Fig. 11 — (a, b) The ac conductivity spectra for HPMC 15 Cps-water and HPMC 50 Cps-water binary mixture.

less ionic contaminants than water. Ionic conductivity relaxation causes a continuous dispersion in the ionic conduction region above f_{EP} for both systems examined here[18].

Figure 10 (a,b) displays the spectra of the imaginary portion M″(ω) of M*(ω) (a, b). All of the samples examined in this study had the peaks at high frequency. With an increase in HPMC concentration, M″(ω) peaks move towards higher frequency. We can calculate the ionic conductivity relaxation time by using the frequency $\tau_\sigma = (1/2\pi f_\sigma)$ that corresponds to the peak value of M″[18].

Figure 11(a,b) shows the real portion of the AC conductivity spectra for the binary mixture of water and

both the HPMCs at different concentrations. The ionic or dc electrical conductivity correlates to the frequency-independent peak. The dc electrical conductivity is high in areas with a lot of HPMC as compared to water, but it decreases as the concentration of HPMC decreases. As a result, HPMC has more mobile charge carriers compared to water.

4 Conclusions

In this paper, the dielectric properties of an HPMC-water mixture have been studied in the frequency range, 100Hz to 2MHz (LCR) and 10MHz to 30GHz (TDR) at 25 °C. The complex permittivity spectra have been studied and fitted to the Debye model to calculate the dielectric parameters. By using LCR method low-frequency region electrode polarization phenomenon is observed. When ionic impurities are present in the liquid at lower frequencies the dielectric loss is very high. Using the dielectric relaxation parameter, one can get quantitative information about HPMCs-water strong molecular interaction in the mixture. It is difficult to interpret the data in terms of the molecular structure due to the complexity of the systems. However, the data provide information about the charge distribution interaction in the mixtures.

Acknowledgment

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