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Effect of temperature on the AC impedance of protein and carbohydrate biopolymers

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Abstract. **The influence of temperature on the electrical behaviour of protein biopolymer papain and carbohydrate biopolymers like gum acacia, gum tragacanth and guar gum has been investigated using AC impedance technique. The observed semi-circles represent the material's bulk electrical property that indicate the single relaxation process in the biopolymers. An increase in bulk electrical conductivity in the biopolymers with temperature is due to the hopping of charge carriers between the trapped sites. The depression parameter reveals the electrical equivalent circuit for the biopolymers. The AC electrical conductivity in the biopolymers follows the universal power law. From this, it is observed that the AC conductivity is frequency dependent and the biopolymer papain obeys large polaron tunnelling model, gum acacia and gum guar obey ion or electron tunnelling model, and gum tragacanth obeys the correlated barrier hopping model of conduction mechanisms.**

Keywords. **Biopolymers; AC impedance; bulk electrical conductivity; AC conductivity; depression parameter.**

1. Introduction

The electroactivity of the material is best understood from the AC impedance measurement. When dealing with charge carrier systems, AC impedance approach is used for characterizing the electrical properties of polymeric materials. In this paper, a thorough experimental investigation on the electrical properties of four biopolymers such as papain, gum acacia, gum tragacanth and gum guar has been undertaken.

Papain is an endolytic cysteine protease obtained from the latex of papaya, a milky fluid containing papain that oozes out of green papaya. It is widely used in fields like medical applications, cell isolation, food, detergents, leather, textile, cosmetics and pharmaceutical industry (Sai-Nan Su *et al* 2008). Gum arabic or gum acacia is an edible biopolymer obtained as exudates of mature trees of *Acacia senegal* and *Acacia seyal*. It is a complex mixture of macromolecules of different size and composition mainly carbohydrates and proteins. It is being used in a wide range of industrial sectors such as textiles, ceramics, lithography, cosmetics and pharmaceuticals, encapsulation, food, etc. In the food industry, it is used as a stabilizer, a thickener and an emulsifier (Verbeken *et al* 2003).

Gum tragacanth is a high-arabinose, protein containing, acidic heteropolysaccharide collected from astragalus species. It is approved as a food ingredient by the Food and Drug Administration, USA, under the function of emulsifier, stabilizer and thickener (Phillips and Williams 2009). Gum guar, a galactomannan obtained from the Indian cluster bean *Cyamposis tetragonolobus* is a water soluble polysaccharide. It is an excellent stiffener and the absence of toxicity allows its use in the textile, pharmaceutical, biomedical, cosmetic and food industries (Srivastava and Kapoor 2005). In the present work, the electrical characterization of the biopolymers is studied by AC impedance technique and the effect of temperature on the electrical behaviour of the biopolymers is reported.

2. Experimental

All the biopolymers used were in powder form of analytical grade from S.D. Fine Chem. Ltd. and Merck, Mumbai, India. The samples were pressed in the form of pellets with 13 mm diameter and 2 mm thickness at a constant pressure of 5 metric tons. For AC conductivity study, the pellet was sandwiched between two uniformly polished copper electrodes. The complex impedance spectra were measured in the frequency range of 10 Hz to 100 kHz using a lock-in-amplifier (model SR830 DSP Lock-in Amplifier, Stanford Research Systems, USA). The measurement was taken from room temperature to the temperature nearer to the melting point of the biopolymers. The impedance study was carried out in the range of 28–135 °C for papain, 28–180 °C for gum acacia, 28–100 °C for gum tragacanth and 28–150 °C for gum guar.

3. Results and discussion

3.1 *Bulk electrical conductivity and activation energy*

The impedance plots of the imaginary component of Z'' vs the real part of Z' for various frequencies measured at

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different temperatures for the biopolymers are shown in figures 1 and 2. The observed semi-circles in the Cole–Cole plots represent the material's bulk electrical property which indicates the existence of single relaxation process in these biopolymers. The imaginary component Z'' reaches to zero at low frequency, a behaviour indicating that used copper electrodes are non-blocking type (Lanfredi *et al* 2002; Lanfredi and Rodrigues 1999; Nobre and Lanfredi 2001). A non-blocking interface is generally thermodynamically reversible. The electrical properties of biopolymers can be described as a parallel R_bC_b circuit in series with R_a, where R_b represents the bulk resistance, C_b is the bulk capacitance

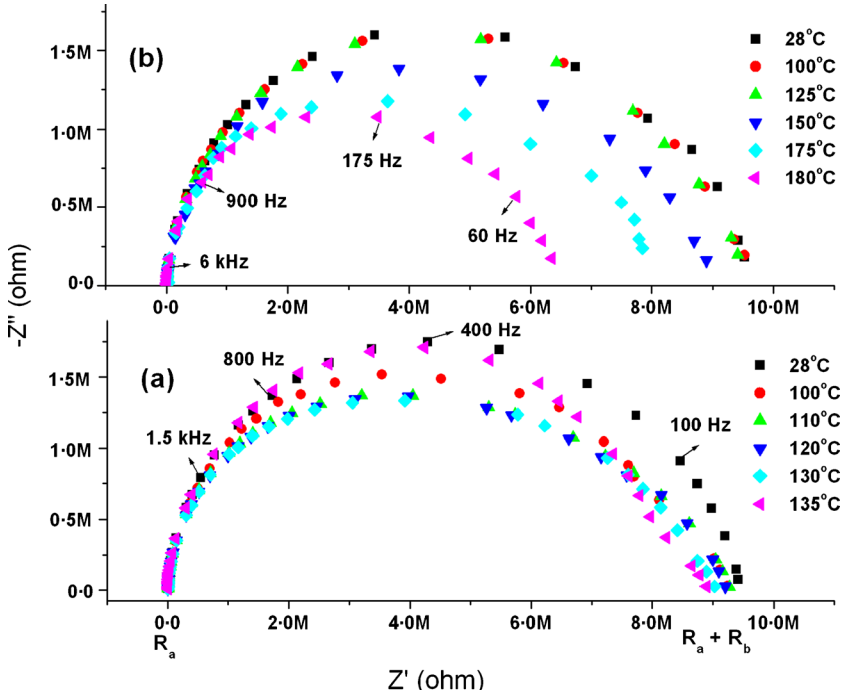

Figure 1. Cole–Cole plots for (**a**) papain and (**b**) gum acacia at different temperatures.

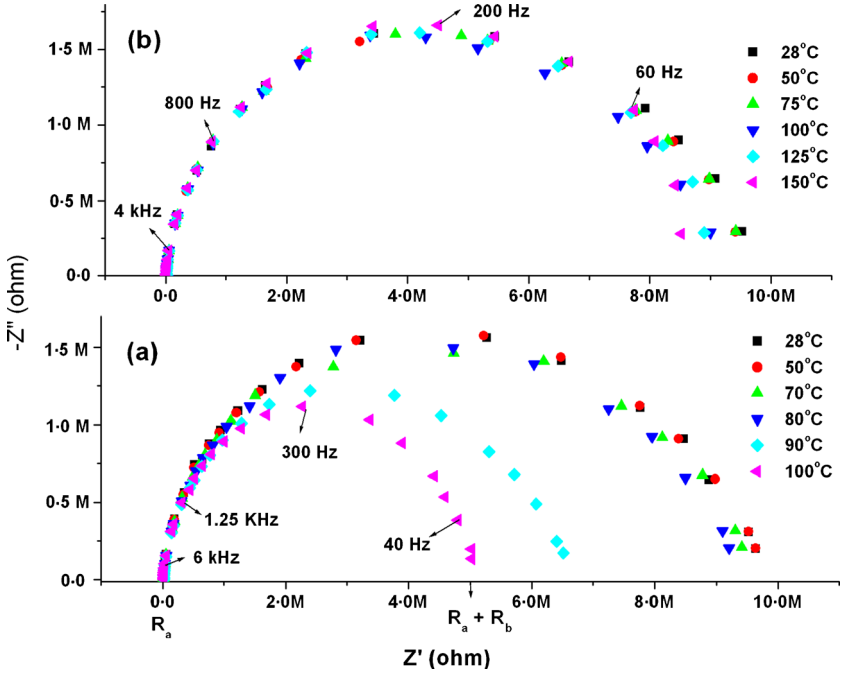

Figure 2. Cole–Cole plots for (**a**) gum tragacanth and (**b**) gum guar at different temperatures.

of the material and R_a is the resistance at infinite or high frequency. The observation of a single semi-circle reflecting the charge transfer system through hopping with the equivalent circuit of element R in series with RC parallel for polyaniline is reported (Hui *et al* 2004).

The conductivity is derived from the resistance value ($R_b = R_o - R_a$) obtained through the semi-circle's diameter on the intercept with the real axis for various temperatures using the equation $\sigma_b = t/R_b A$ where t is the thickness and A is the area of cross-section of the sample. As the temperature rises, a shift in R_o towards the lower resistance is observed in the Cole-Cole plots of biopolymers. It shows that the resistivity of biopolymers decreases with the rise in temperature and hence the bulk electrical conductivity increases. The relaxation frequency or the maximum frequency ω_o is the frequency at which the complex impedance is maximum and this gives the relaxation time $\tau = R_b C_b = 1/\omega_o$. The consistency of R_b, C_b and the relaxation frequency ω_o can be checked from the product $R_b C_b \omega_o$ which is found to be equal to 1 for all temperatures. The bulk dielectric constant ε_b is determined using the formula $\varepsilon_b = C_b t/\varepsilon_o A$ where ε_o is the permittivity of free space. The bulk dielectric constant gets increased with temperature for all the biopolymers which corresponds to high polarization effect in these biopolymers. The AC impedance parameters for papain, gum acacia, gum tragacanth and gum guar are given for four different temperatures in table 1 for comparison.

The conductivity of papain increases from $1{\cdot}65\times10^{-6}$ S/m at room temperature to $1{\cdot}77\times10^{-6}$ S/m at 135 °C. It is found to increase from $1{\cdot}58\times10^{-6}$ to $2{\cdot}38\times10^{-6}$ S/m for gum acacia when the temperature rises from 28 to 180 °C. For gum tragacanth, the conductivity shows a sharp increase from 1·57 to $3{\cdot}01\times10^{-6}$ S/m in the temperature range of 28–100 °C. In the case of gum guar, it rises from 1·59 to $1{\cdot}77\times10^{-6}$ S/m in the increasing temperature range of 28–150 °C. The electrical conductivity in biopolymer originates from motion of either electrons or ions or both. The electrical conductivity of biopolymers is given by $\sigma = \sum q_i n_i \mu_i$ where q_i, n_i and μ_i are the respective charge, concentration and mobility of the i species of conducting carriers. The carrier mobility is the carrier drift velocity in the field direction per unit electric field. Electronic conduction in a biopolymeric system is possible where unsaturated or π type chemical bond exists. The band theory also explains electron and hole conduction in a polymeric system.

In the biopolymers papain, gum acacia, gum tragacanth and gum guar, protonation takes place in the presence of water molecules. When the biopolymers are heated the water loss is followed by an increase in H_3O^+ ion concentration which increases the conductivity of the biopolymers. It is reported that in polyaniline the conduction occurs through hopping of charge carriers by the general process of oxidation. Such protonation can also take place in the presence of water molecules (Shilpa Jain *et al* 2003; Bishop and Gouma 2005). The loss of water molecules during dehydration influences the electrical conductivity of polyaniline and its hybrids (Chithra Lekha *et al* 2009). The spectroscopic results obtained by Mioc *et al* (1991) for polytungstates and polymolybdates at the elevated temperatures show that water loss is followed by an increase in H_3O^+ ion. The results also show that oxonium ion may form dioxonium ion with some of the remaining water molecules and is given by

$$H_5O_2^+ \leftrightarrow H_3O^+ + H_2O \leftrightarrow H^+ + 2H_2O.$$

This process takes place at the electrode-electrolyte interface.

The ionic conductors in which the presence of thermally generated Frenkel or Schottky defect pairs or disorder produces ionic transport, leading to conductivity upto 10^{-5} S/cm (Susheel Kalia and Luc Averous 2011). The DC conductivity of biopolymer gum arabica using AC impedance is found to be $1{\cdot}5\times10^{-6}$ S/cm at room temperature and, from Wagner's

Table 1. AC impedance parameters for the biopolymers at four different temperatures.

Biopolymer	Temperature (°C)	Bulk dielectric constant (ε_b) F/m	Conductivity (σ) × 10^{-6} S/m	Depression parameter (α)	Frequency exponent (s)
Papain	28	71·89	1·649	0·238	1·915
	100	73·95	1·653	0·218	1·825
	130	101·54	1·696	0·171	1·761
	135	102·78	1·769	0·231	2·163
Gum acacia	28	94·98	1·584	0·335	1·774
	150	174·29	1·695	0·366	1·655
	175	197·69	1·923	0·294	1·685
	180	244·29	2·376	0·273	1·600
Gum tragacanth	28	161·09	1·567	0·425	1·610
	80	168·68	1·641	0·362	1·537
	90	238·38	2·318	0·338	1·507
	100	309·50	3·010	0·411	1·504
Gum guar	28	95·06	1·585	0·356	1·651
	100	100·63	1·678	0·342	1·662
	125	101·76	1·697	0·364	1·651
	150	106·26	1·772	0·370	1·658

polarization method, it is reported that gum arabica exhibits ionic character like other solid electrolytes and the current occurs mostly due to the motion of the hydronium (H_3O^+) ions (Mallick and Sarkar 2000). By an electrochemical process (Poulsen 1989; Shimura *et al* 1996), it is also found that gum mangosteen is a solid protonic conductor. From these observations, it can be predicted that, in the biopolymers papain, gum acacia, gum tragacanth and gum guar, ionic conduction contributes more than electronic conduction, though the total electrical conductivity is due to electrons and ions in these biomaterials.

The increase in conductivity of papain, gum acacia and gum tragacanth with temperature is the characteristic of 'thermal activated behaviour' (Kulkarni and Viswanath 2005; McGovern *et al* 2005). The increment in temperature provides an increase in volume and segmental mobility. These two entities permit free charges to hop from one site to another in biopolymers and thereby increase the conductivity. It also indicates that more ions gain kinetic energy via thermally activated hopping of charge carriers between trapped sites which is temperature dependent. Pike (1972) and Elliot (1977) suggest that the charge carrier hops between defect sites $D^+$and D^- over the potential barrier separating them. The increased efficiency of charge transfer between biopolymer chains with the increase in temperature may have caused the increase in conductivity. On heating, there will be molecular rearrangement which is also favourable for charge delocalization. A common feature that makes polymers capable of transporting electrical charge is a conjugated π-electron consisting of alternating single and double bonds along the polymer chain backbone or ring structure (Joel Fried 1999). In the biopolymers, the thermal effect affects the chain alignment, leads to the increase of conjugation length of biopolymer chain which is also responsible for the increase in conductivity.

The catalytic efficiency of enzymes like papain is affected by temperature which in turn increases the rate of chemical reactions. In gums, the increase in temperature decreases the viscosity and improves the emulsifying action. In the literature, it is also reported that the mild UV absorption reduces the solution viscosity of gum acacia which gives improved emulsifying property of the gum (Kuan *et al* 2009). Gum acacia, gum tragacanth and gum guar are widely used natural emulsifiers, thickeners and stabilizers for food, drug and allied industries (Daniel *et al* 1994). Hence the reduction in viscosity due to high temperature in these carbohydrate biopolymers leads to better emulsifying property and it can be correlated with increase in electrical conductivity in gum acacia, gum tragacanth and gum guar with the increase in temperature.

The bulk electrical conductivity increases with the increase of temperature and indicates that it is fitted to Arrhenius exponential law equation

$$\sigma = \sigma_o \exp(-E_A/kT), \tag{1}$$

where σ_o is the high temperature limit of conductivity, E_A is activation energy, k is Boltzmann constant and T is temperature. The linear regression of the Arrhenius plots of log σ vs 1000/T gives the slope of E_A (figure 3). A linear increase in conductivity with temperature is observed from room temperature to 100 °C for papain, 28–125 °C for gum acacia, 28–70 °C for gum tragacanth and 28–75 °C for gum guar in the low temperature region I. In the high temperature

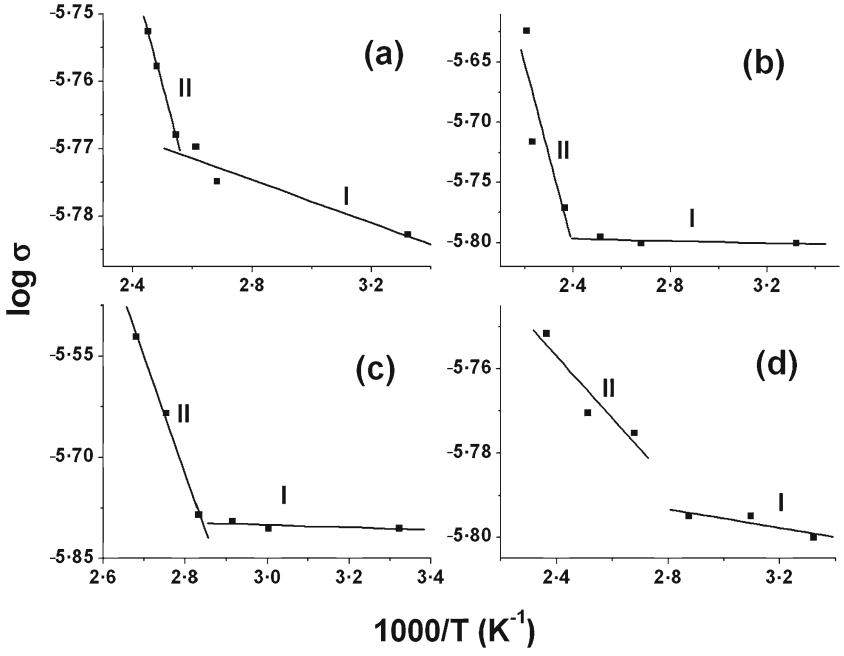

Figure 3. Arrhenius plots of biopolymers (**a**) papain, (**b**) gum acacia, (**c**) gum tragacanth and (**d**) gum guar with low (region I) and high (region II) temperature regions.

Table 2. Activation energy for the biopolymers in the low (region I) and high (region II) temperature regions.

Sample	Activation energy (meV)	
	Region I	Region II
Papain	2·98	30·60
Gum acacia	0·83	142·00
Gum tragacanth	3·39	325·00
Gum guar	2·11	13·77

region II, the conductivity rises fast from 110–135 °C for papain, 150–180 °C for gum acacia, 80–100 °C for gum tragacanth and 100–150 °C for gum guar. The activation energy for the four biopolymers is calculated and reported in table 2. The activation energy for the high temperature region is found to be high compared to the low temperature region for all the biopolymers. The gum tragacanth has higher activation energy of 3·39 meV in region I and 325 meV in region II compared to other three biopolymers.

High conductivity of $2{\cdot}38\times10^{-6}$ S/m and $3{\cdot}01\times10^{-6}$ S/m at maximum temperature of study in gum acacia and gum tragacanth are due to their high molecular weights of $8{\cdot}4\times10^5$ g/mol and $2{\cdot}5\times10^5$ g/mol respectively, and complex structures of polysaccharides are responsible for the increase in the concentration of ionic charge carriers. This results in the rise in the activation energy of 142 and 325 meV for gum acacia and gum tragacanth in the high temperature regions respectively, compared to other biopolymers. That is why gum tragacanth has better emulsifying property than gum acacia. The activation energy in region I shows the variation of carrier concentration with temperature which increases the conductivity in the biopolymers. In region II, a deformation of the polymer chain could have occurred which leads to further increase of charge carriers and this is responsible for increase in activation energy for the biopolymers at this region (Aggour *et al* 2000).

3.2 *Depression parameter α*

The impedance spectra show semicircular arcs whose centres invariably lie below the real axis, and allow easy graphical determination of the impedance parameters. For some biopolymers, however, the impedance spectra display distortions of various shapes because of overlapping time constants. Tsai and Whitmore (1982) proposed a nonlinear curve-fitting technique which allows fast, reliable and accurate elucidation of the basic impedance parameters for cases having overlapping time constants. A depressed semi-circle of papain at room temperature in the complex impedance plot, as shown in figure 4, is described by an expression

$$Z(\omega) = Z_a + (Z_o - Z_a)\,/1 + (j\omega/\omega_o)^{(1-\alpha)}\,, \qquad (2)$$

where $Z(\omega)$ is the complex impedance at the angular frequency ω, Z_a the high frequency intercept of the arc with the real axis, Z_o the low frequency real axis intercept, ω_o the relaxation angular frequency, and α the depression parameter ($0 \leq \alpha \leq \frac{1}{2}$) and $j = \sqrt{-1}$. The limiting case of $\alpha = 0$ represents an equivalent circuit consisting of lumped R–C elements with a zero depression angle, while $\alpha = \frac{1}{2}$ corresponds to a combination of resistors and Warburg impedance with a 45° depression angle. The equivalent circuit corresponding to the impedance spectrum (figure 4) consists of a frequency dependent capacitor and two frequency independent resistors. By rearranging the above equation the relation obtained is,

$$\ln(V/U) = (1-\alpha)\ln\omega - (1-\alpha)\ln\omega_o, \qquad (3)$$

where U and V are the distances of $Z(\omega)$ from Z_a and Z_o, respectively. A plot of ln (V/U) vs ln ω yields a straight line of slope (1- α). The depression parameter α determined from the Cole–Cole plot at various temperatures for biopolymers is given in table 1. The depression parameter α, found between 0 and $\frac{1}{2}$, confirms that the equivalent circuit of a resistor in series with the parallel combination of RC does not change for biopolymers with temperature variation.

3.3 *Frequency dependence of AC conductivity*

Figures 5 and 6 show the variation of AC electrical conductivity of papain, gum acacia, gum tragacanth and gum guar with applied AC frequencies at different temperatures. The frequency dependent conductivity $\sigma_{AC}(\omega)$ is due to the trapped charges which is only active at higher frequency region. The electrical behaviour follows a universal power law which is applicable for polymeric and semiconductor materials. The $\sigma_{AC}(\omega)$ obeys the Almond–West universal power law in the form (Hamzah Harun *et al* 2008)

$$\sigma_{AC}(\omega) = A\omega^s, \qquad (4)$$

where A is the temperature dependent coefficient, ω the angular frequency and s the frequency exponent. The value of s can be determined from the linear slope of log $\sigma_{AC}(\omega)$ vs log ω graph which represents frequency dependent conductivity. In figures 5 and 6, the AC conductivity varies slowly at low frequencies and then increases fast at high frequency region. In the case of papain, acacia and tragacanth, the temperature dependent dispersion occurs in the low frequency region while for gum guar it is not so. It is also observed that the dispersion is more prominent in gum tragacanth. The dependence of AC conductivity is due to the relaxation caused by the motion of electrons or ions, hopping or tunnelling between equilibrium sites (Ammar *et al* 2007). All the curves at different temperatures appear to merge at higher frequencies. This corresponds to the short range hopping of charge carriers through trapped sites separated by energy barriers of varied heights (Rizwana *et al* 2007). The values of s parameter at different temperatures for the biopolymers are given in table 1. The frequency exponent lies between 1 and 2 for all the four biopolymers.

The temperature dependence of s for the polymers in the linear region can be explained by various theoretical

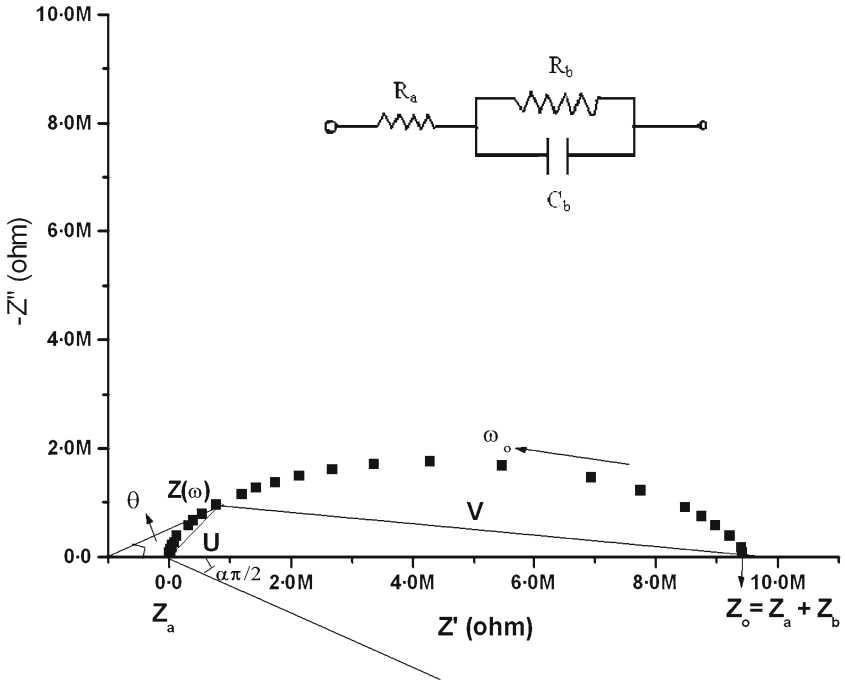

Figure 4. Cole–Cole plot, showing a semi-circle whose centre lies below the real axis for papain at room temperature.

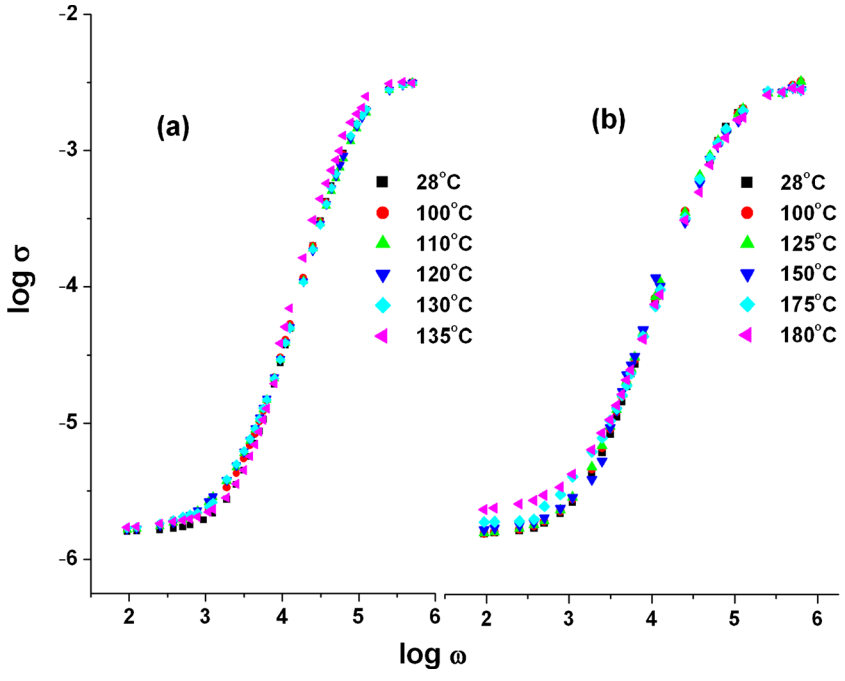

Figure 5. Frequency dependent AC conductivity graphs for (**a**) papain and (**b**) gum acacia at different temperatures.

models for AC conductivity. Temperature and frequency dependent AC conductivity behaviour had been reported for the chemically synthesized polyaniline-polymannuronate nanocomposites (Basavaraja *et al* 2009). The AC conductivity of polyaniline and its hybrids (Chithra Lekha *et al* 2009) had also been reported using these various theories of conduction mechanisms. In the case of small polaron tunnelling, s increases with temperature (Long 1982), whereas for overlapping large polaron tunnelling (OLPT), s decreases upto a certain temperature and then increases with further increase of temperature (Elliot 1987). In papain, the frequency exponent s first decreases with T and then further

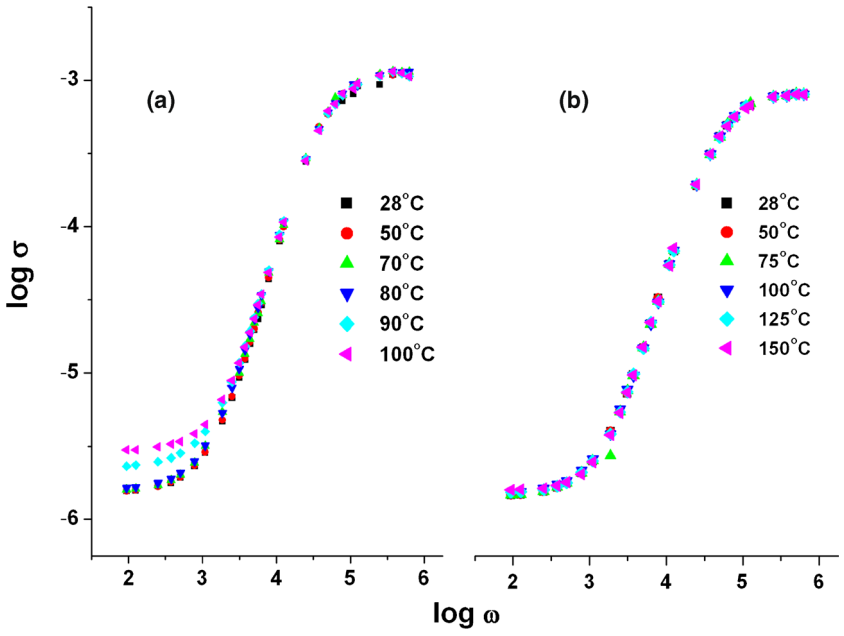

Figure 6. Frequency dependent AC conductivity graphs for (**a**) gum tragacanth and (**b**) gum guar at different temperatures.

increases. This obeys the overlapping large polaron tunnelling model of conduction mechanism. The electron tunnelling model suggests that s is independent of T, but dependent of ω (Dyre 1988). Therefore, s is not linear with T. The table 1 shows the non-linearity of s parameter with temperature T for gum acacia and gum guar which predicts the existence of electron or ion tunnelling model of conduction mechanism in these biopolymers. In the correlated barrier hopping model where s decreases with temperature, the carrier hops between the sites over the potential barrier separating them (Efros 1987). The frequency exponent s for such model is

$$s = 1 - 6kT/\{W - kT \ln[1/(\omega\tau_o)]\}, \quad (5)$$

where W is the effective barrier height and τ_o the relaxation time. It is also observed that the s parameter of gum tragacanth decreases with the increase of temperature. Hence, it is believed to obey the correlated barrier hopping model of conduction mechanism.

4. Conclusions

The AC impedance measurement shows an increase in bulk electrical conductivity of biopolymers papain, gum acacia, gum tragacanth and gum guar with increase in temperature. Loss of water molecules during dehydration influences the electrical conductivity. This is attributed to the thermal induced strain in the biopolymers which enhances the hopping of charge carriers between the trapped sites. The increased activation energy depicts the rise in carrier concentration with the increase in temperature. The depression parameter s confirms the equivalent circuit of biopolymers as a resistor in series with the parallel combination of resistance and capacitance and it does not change due to temperature effect. The universal power law predicts that AC conductivity of the biopolymers is frequency dependent. It is also observed from the theoretical models of AC conductivity that the biopolymer papain obeys overlapping large polaron model, gum acacia and gum guar obey electron or ion tunnelling model, and gum tragacanth obeys correlated barrier hopping model of conduction mechanism.

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