

An experimental investigation of electrical conductivities in biopolymers

H MALLICK and A SARKAR*

Physics Department, Bijay Krishna Girls' College, 5/3 M G Road, Howrah 711 101, India

MS received 6 April 1999; revised 29 May 2000

Abstract. Gum arabica obtained from acacia plant is a conducting biopolymer. Experiments are carried out on this natural gum arabica. In the present study TGA, ion transference number, transient ionic current, thermal analysis, frequency and temperature variation of a.c. conductivity, Arrhenius plot and volt-ampere characteristics of specimens are carried out. The total electrical conductivity of these biopolymers are comparable to that of synthetic polymers doped with inorganic salts. The ion transference number of these biopolymers show their superionic nature of electrical conduction. The overall conduction mechanism seems to be protonic in nature rather than electronic one.

Keywords. Biopolymer; protonic; gum arabica; ion transference number; electrical conductivity; solid protonic conductor.

1. Introduction

Many ion-conductive polymers have been reported so far (Chowdari 1996). It is needless to re-emphasize their future application and scope in tomorrow's technology (Chandra 1981; Chowdari 1996). Considerable time has been devoted to investigate the synthetic conducting polymers but only little attention has been paid towards the electrical conductivity of biopolymers (Chandra 1981). Recently Bermudez *et al* (1997) have reported that sulfamide and its derivatives exhibit electrical conductivity ($\sim 10^{-3} \text{ S cm}^{-1}$) at room temperature. The various mechanisms of charge and energy transfer in biopolymers in the part of living biological systems (cellulose, collagen, melanin etc) were studied (Glasser 1975) in detail but a comprehensive study on bioproducts as conducting materials is found to be rare. The studies (Glasser 1975) of course firmly established the proton conductivity in biopolymers. The biopolymers have several advantages in general. They are commercially cheaper and non-toxic compared to that of synthetic polymers. Moreover in many cases the synthetic polymers have toxic effects. Following Hummel (1993), one can say that popularly known synthetic conducting polymer or its many dopants used to improve conductivity are highly toxic.

In the present paper an intensive investigation on the electrical conductivity of gum arabica has been carried out. The preliminary investigation (Sarkar 1997, 1998) shows that gum arabica exhibits electrical conduction properties like superionic conductor.

Gum arabica has been found from different species of *Acacia* e.g. *Acacia arabica*, *Acacia babul* etc. It is an important substance in medicine and bacteriology and its chemistry and structure may be found in literature (Aspinall and Wood 1963, 1965; Aspinall *et al* 1968; Barton and Olis 1979).

The gum arabica specimen under investigation has a complex molecular structure in which chain of L-arabinose (24%), L-galactose (67%) and L-rhamnose (7%) are inter-linked with D-galacturonic acid ($\sim 2\%$) unit. Its melting point is around 160°C .

It is important to mention here that gum arabica produces salt complexes with inorganic materials like FeSO_4 , $[\text{K}_2\text{SO}_4, \text{Al}_2(\text{SO}_4)_3, 24\text{H}_2\text{O}]$, LiClO_4 , iodine etc. The biopolymer in salt exhibits many interesting features of the electrical conduction properties. A comprehensive experimental study on the gum arabica along with some preliminary survey on some other biopolymer are presented in this paper.

2. Experimental

2.1 Preparation of biopolymer specimen

Samples were prepared with *Acacia arabica* powder (supplied by LOBA CHEMICAL, Bombay) of 98% purity grade by pressing it in pellet form. Samples were also prepared using naturally collected raw bio-product from *Acacia* plant. The powdered solid gum sample was cast as an experimental specimen by preparing a thick viscid bubble free water solution and then allowed it to dry for 3 to 5 days depending on specimen thickness (for 1 mm specimen 48 h was sufficient).

*Author for correspondence

Finally the specimen thus obtained was placed in vacuum ($\sim 10^{-2}$ mm of Hg) for at least 4 h. In fact the use of aqueous solution is one of the standard techniques in biopolymer sample preparation e.g. hydrogenuranyl phosphate tetrahydrate (Howe and Shitten 1980). The pellet or specimen thus produced was sandwiched between two uniform polished copper electrodes. Samples of different thickness from 0.5 mm to 2 mm were prepared for different experimental analyses and their comparison.

2.2 Thermal analysis of the specimen

Thermal analysis of the gum arabica sample was carried out to estimate its normal natural water content. The thermogravimetric analysis (TGA) studies were carried out using Linseies DTA/TGA unit (Model No 2045) to investigate the thermal behaviour of the gum arabica specimen in the temperature range 25–150°C. The heating rate was 5°C/min.

2.3 Detection of conducting ion species

The conducting species in solid protonic conductors (SPC) (Poulsen 1989) may be proton (H^+), hydronium (H_3O^+), hydroxyl ion (OH^-), ammonium (NH_4^+) or dihydronium ($H_5O_2^+$). These ion conduction exhibit both bulk and surface conductivity in many SPCs (Poulsen 1989). After a careful experiment by an electrochemical process (Poulsen 1989; Shimura *et al* 1996), it was found that the gum arabica sample was also a SPC and conducting ion species in it were hydronium (H_3O^+) ions. After a long-duration, in d.c. electrolysis of the sample using porous Cu electrodes (which were prepared from thin copper wire in the form of a dense spiral), it was found that no hydrogen gas was detected at the cathode but a loss of the sample weight was recorded. The mentioned loss of weight of the gum arabica specimen was exactly equal to the gain of weight by the anhydrous copper sulphate which was used as a water vapour trap. The experiment was performed in a glass chamber at room temperature for 3 h at an average electric current of 2.1 mA and the observed loss in specimen weight was 5.0 mg. It was also found that the observed loss in weight was in accordance with the Faraday's law of electrolysis with hydronium as conducting species. The weight of the sample (along with the electrodes) used was equal to 1.72 g with cross-sectional area, 5 cm² and applied potential difference being 70 V.

2.4 Ion transference number, transient ionic current, bulk electrical conductivity, volt-ampere characteristics and Arrhenius plot

For electrical measurement polished and clean copper plates were pressed on both surfaces of the biopolymeric

specimen to ensure good electrical contact. The ion transference number of mobile ions (mostly hydronium) in the biopolymer was estimated following blocking electrode method (Chandra 1981) technically known as Wagner's polarization technique (Yamashita and Nicholson 1986). In the present measurement polarization current was recorded as a function of time across a Cu/electrolyte/Cu proto cell and was recorded by a Network 3100 electrometer.

The ionic mobility of mobile species of the gum arabica specimen was determined by using transient ionic current technique. The sample was subjected to a d.c. electric field across Cu/sample/Cu cell to polarize it. The transient ionic current was then recorded as a function of time by reversing the polarizer electric field. The said reversal was however done by very simple setup using a mercury commutator. The current was recorded by a computerized data acquisition system.

The variation of complex impedances and loss angle were also studied for a better information of a.c. conductance of the biopolymer gum arabica. This measurement was done between frequency range 0.05 Hz and 100 KHz by HIOKI 3522 LCR/Z Meter (Japan).

The a.c. conductivities were measured to depict the Arrhenius behaviour of solid specimen with temperature variation setup and HIOKI 3522 LCR/Z Meter by using two-probe method. The temperature variation of a.c. conductivities were recorded by Tektronix DTM 900 Thermometer between temperature range 25°C and 75°C.

The d.c. ionic conductivities were measured to depict the Arrhenius plot of the ionic conductivities from 25°C to 100°C (for 1 : 1 water solution). Network 3100 electrometer was used for the measurement. The steady volt-ampere characteristics of the solid specimen was also measured using the same set-up. The sample cell was prepared in the same manner as used for ionic transference number measurement.

3. Results and discussion

It has been observed that gum arabica from LOBA CHEMICAL, Bombay and that obtained from Acacia plant exhibit almost same character in experiments i.e. natural bio-impurities (if any) do not affect the electrical properties of the biopolymer. Therefore for a better interest one may carry out experiments using samples from LOBA CHEMICAL.

In the thermogravimetric analysis (TGA) of the powdered sample the percentage loss of weight of the sample was recorded by a TGA analyser (CGCRI, CSIR Facilities). Figure 1 shows experimental results of the thermal analysis. It has been estimated from the experimental data that on an average gum arabica contains 2% of free water (H_2O). Thermal analysis results show that gum arabica is thermally stable up to 80°C, TGA measurement restricted to temperature range 25–125°C. The data reported here shows that at 80°C the gum arabica is devoid of its free

water and this is a reversible change. On constant heating above 120°C the transparent sample becomes dark grey in colour and it loses its electrical conduction property. In fact this irreversible change of the gum arabica is a possible feature of SPC (Poulsen 1989) on heating in a water lean atmosphere.

Figure 2 shows the variation of polarization current as a function of time. The ionic transference number of mobile species in the gum arabica has been estimated by Wagner's polarization method (Wagner and Wagner 1957). The total current i consists of both ionic current (i_{ion}) and the electronic current (i_e). The ionic transference number was obtained by using standard (Chandra 1981) formula,

$$\tau_{\text{ion}} = \frac{i_{\text{ion}}}{i} = \frac{i - i_e}{i}. \quad (1)$$

The ionic transference number (τ_{ion}) was found to be 0.96. So one may consider that the observed specimen of gum arabica exhibits ionic character like other solid electrolytes and current occurs mostly due to the motion of the hydronium (H_3O^+). The same has been verified from the mentioned porous electrode experiment on the gum arabica with the passage of electric current. Moreover the observed polarization current characteristics of the solid specimen have been found to be contradictory with earlier results of electrolysis studies (Glasser 1975).

The variation of transient ionic current as a function of time for the gum arabica sample is shown in figure 3. Even this very simplistic measurement exhibits a single clear peak which indicates that the current is due to a single ion species, in this case it is hydronium (H_3O^+)

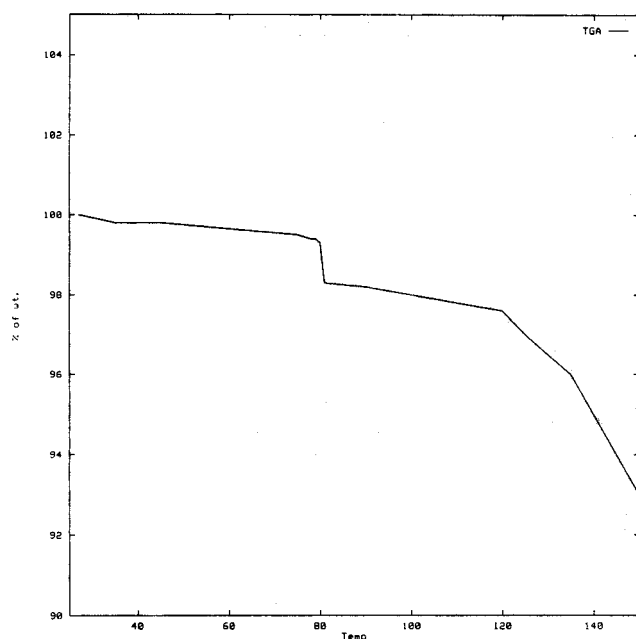


Figure 1. Percentage loss in weight (w) vs temperature (t) in °C (sample weight = 12.9 mg).

and its ionic mobility (μ) is estimated using the standard formula,

$$\mu = \frac{d^2}{\Gamma V}, \quad (2)$$

where d ($= 1$ mm) is the sample thickness, Γ ($= 50$ sec) the time of flight and V ($= 1.5$ V) the applied reverse voltage. The value of the ionic mobility obtained from the measurement using (2) is found to be $\mu_{\text{H}_3\text{O}^+} \sim 1.33 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

Figure 4 shows Cole–Cole plot of the measured impedance spectroscopy data on specimen of gum arabica. It shows that a semi-circular arc with a tail at low frequency range can be assigned to electrode interface roughness effects. The value of extrapolated left cross point of the impedance spectra at the real axis is 310 Ω , from which maximum total conductivity of $1.1 \times 10^{-4} \text{ S cm}^{-1}$ is calculated. The centre of the semi-circle is below the real axis which makes an angle of 18° with real axis. The extrapolated right crossing point to the real axis corresponding to d.c. resistance of 21600 Ω , from which room temperature d.c. conductivity of $1.5 \times 10^{-6} \text{ S cm}^{-1}$ is calculated. The observed single semi-circle in Cole–Cole plot indicates the existence of single relaxation process of this SPC.

Figure 5a shows the variation of a.c. electrical conductivity of solid specimen with applied a.c. frequencies at room temperature. The experimental a.c. conductivities have been calculated from measured admittance data following relation,

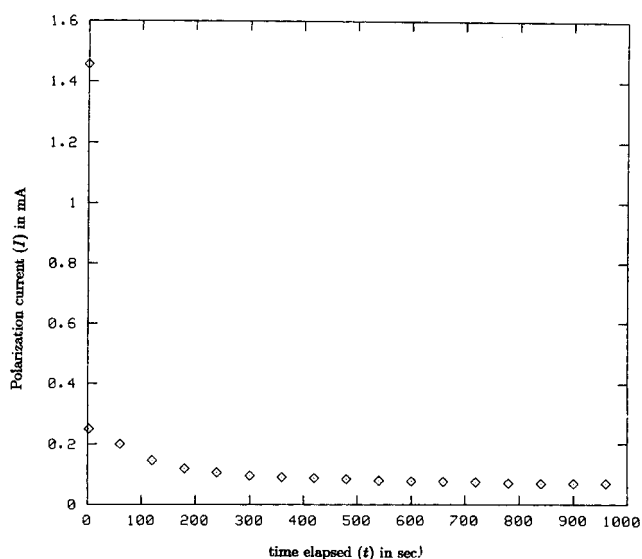


Figure 2. Plot of polarization current (I) in mA vs time elapsed (t) in sec (applied p.d. = 1.9 V, specimen C.S.A. = 2 cm^2 , thickness = 0.5 mm).

$$\sigma_{ac}(\omega) = Y' \frac{d}{A}, \quad (3)$$

where Y' is the real part of the admittance, d the sample thickness and A the cross-sectional area of the electrodes. The variation of a.c. conductivity with frequency ω may be described following the equation given by (Almond and West 1987) and Jonscher's (1977) power law viz.

$$\sigma_{\omega} = \sigma_{dc} + K\omega^n, \quad (4)$$

or,

$$\log(\sigma_{\omega} - \sigma_{dc}) = n \log \omega + \log K, \quad (5)$$

where K and n are temperature dependent frequency independent material parameters and value of n may be directly estimated from the slope of (5). Although the graphical nature of figure 5a is not in complete agreement with (5), however one can account for a reasonable value of exponent from figure 5a which is found to be 0.98 with value of σ_{dc} obtained from extrapolated σ_{ω} to zero frequency and found to be $\sim 1.5 \times 10^{-6} \text{ S cm}^{-1}$. In fact the obtained value of $n = 0.98$ is at around 50 KHz frequency. However at lower frequencies the same reduces to 0.8. The observed high value of exponential index is similar to that observed for *cis*-polyacetylene (Epstien *et al* 1985) [*cis*-(CH)_x] and other conducting polymeric system (Epstien 1986) with $\sigma_{dc} \sim 10^{-9} \text{ S cm}^{-1}$ at 295 K and σ_{ω} was found to follow ω^1 variation. It has also been reported (Epstien 1986) that at low frequency σ_{ω} is slightly larger than σ_{dc} .

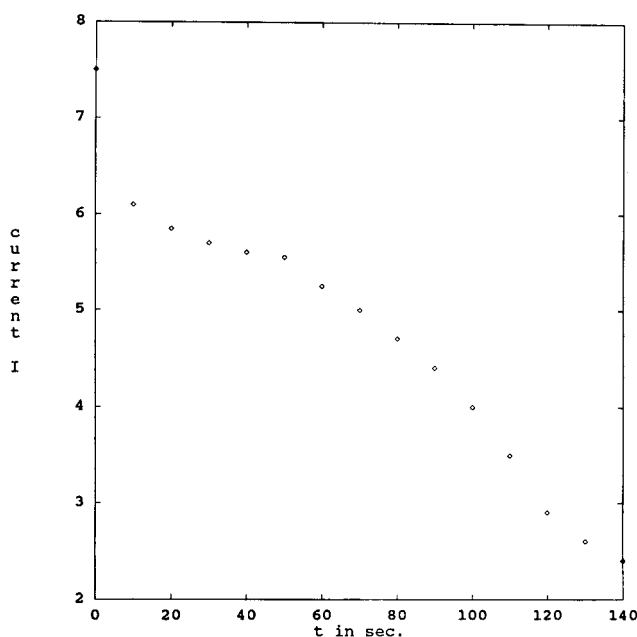


Figure 3. Plot of transient ionic current (I) in μA vs time elapsed (t) in sec (specimen thickness = 1 mm, C.S.A. = 1 cm^2 and applied p.d. = 1.5 V).

Figure 5b shows the variation of a.c. electrical conductivities of solid gum arabica specimen with applied a.c. frequency at various temperatures. The observed nature of variation is similar to that of other synthetic conducting polymers. It was found that results obtained for σ_{dc} from d.c. experiment are higher than that obtained from extrapolated a.c. data which may be due to the polarization effect and standard deficiencies in two-probe method (Chandra 1981).

Figure 6a shows the Arrhenius behaviour of gum arabica that measured with a.c. supply at 1 KHz. Since gum arabica is biopolymer and TGA indicates its stability up to a temperature of 80°C , the temperature variation of total conductivity is recorded and repeated between room temperature and below 80° . The activation energy thus calculated is about 0.17 eV which is comparable to other SPC and biopolymer like HUP (Colomban and Novak 1992). The linear Arrhenius plot in the stable temperature range has also been observed for other SPC like H⁺NYS and H⁺NGS (Yamashita and Nicholson 1986).

Figure 6b shows Arrhenius plot for water solution (1 : 1 by wt.) of the gum arabica specimen between temperature range 25°C and 100°C . There exist three distinct regions between temperature range 25°C and 100°C . Thus the entire variation of electrical conductivity in figure 6b cannot be fitted by an Arrhenius type equation (Poulsen 1989) with same set of parameters, the same equation is in agreement with figure 6a within the stable temperature range and the equation is given by,

$$\sigma = \sigma_0 \exp\left(-\frac{E_0}{k_B T}\right), \quad (6)$$

where, σ_0 is the pre-exponential factor and E_0 an activation energy for conduction.

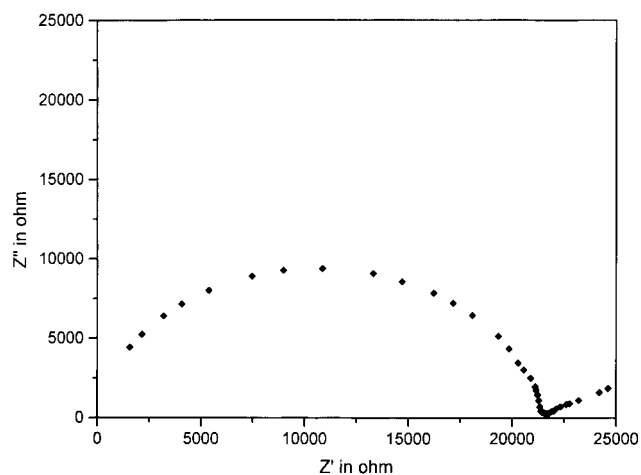


Figure 4. Cole-Cole plot, $Z''(\omega)$ vs $Z'(\omega)$ between frequency range 0.05 Hz and 100 KHz at 25°C (specimen thickness = 1.0 mm, C.S.A. = 3 cm^2).

Figure 7 shows the volt-ampere characteristics of the specimen at room temperature. The final stabilized currents were recorded at various d.c. voltages. Following Wagner and Wagner (1957) one can conclude that the observed stabilized current is due to electronic conductivity. The nature of the graph shown in figure 7 can be explained by Wagner's explanation for the total electronic current and is given by,

$$I_T = I_- + I_+, \tag{7}$$

where I_- is the current due to electrons and I_+ is that due to holes. The experimental nature of saturation of the observed electronic current is also in accordance with

Wagner's analysis (Wagner and Wagner 1957). Since the observed result (figure 7) shows that the measured current tends to assume a saturation value with increasing potential difference, so the observed stabilized current is due to the electronic contribution (I_-).

However during experimental observation it has been observed that gum arabica specimen has a surface electrical conductivity which is very sensitive on local humidity. Moreover it has been observed that the bulk electrical conductivity has a poor dependence on local humidity saving from prolonged exposure of the sample to high humidity environment.

The d.c. polarization experiments show that the ion transference number τ_i for *Acacia catechu* gum (constituents

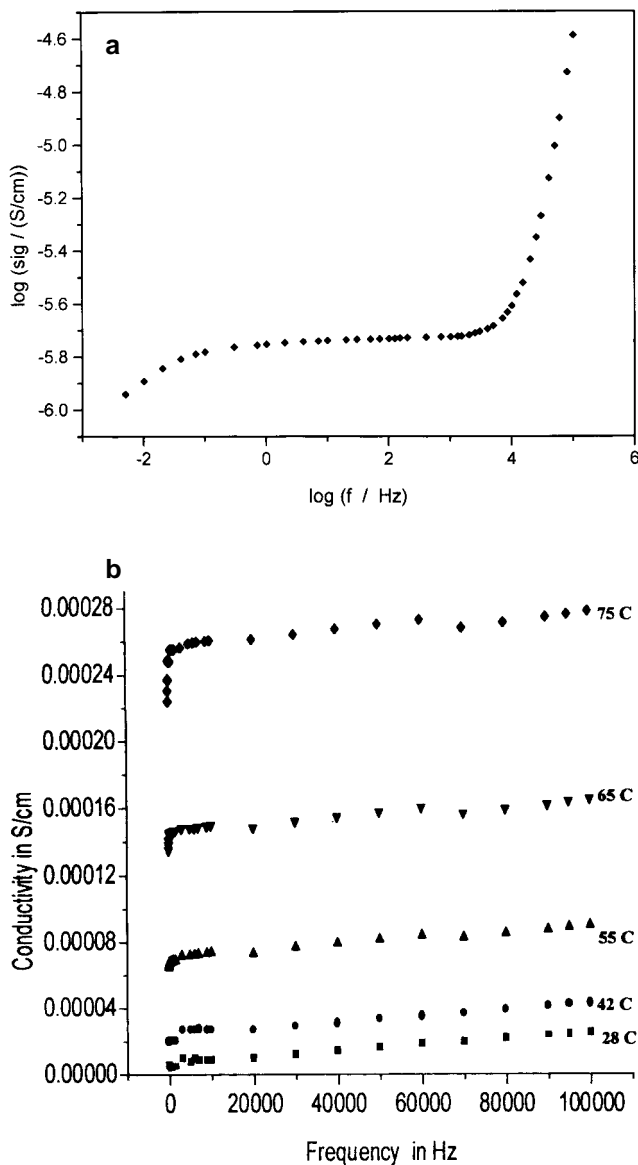


Figure 5. a. Plot of $\log(\sigma_{ac})$ vs $\log(f)$ at 25°C. The specimen thickness = 1 mm, C.S.A. = 3 cm² and b. plot of σ_{ac} vs (f) at marked temperatures. The specimen thickness = 1 mm, C.S.A. = 1 cm².

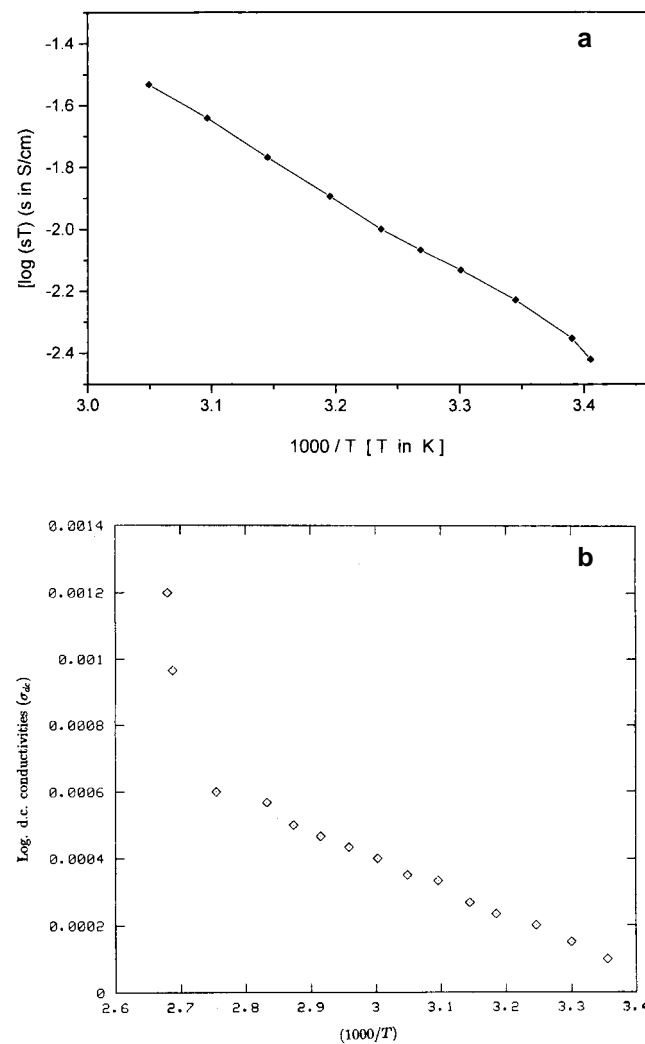


Figure 6. a. Plot of $\log(\sigma_{ac}T)$ (calculated from Cole-Cole analysis) vs $(1000/T)$, where T is the temperature in °K between 25 and 75°C. The specimen thickness = 1.0 mm, C.S.A. = 1 cm². The heating rate was 5°C per min and applied p.d. = 1 V (a.c.) and b. \log d.c. conductivities (σ_{dc}) [for 1 : 1 (by wt.) solution of the specimen] vs $(1000/T)$, where T is the temperature in °K. The electrode separation = 5 cm, C.S.A. = 2 cm². The heating rate was 5°C per min, applied p.d. = 1.5 V.

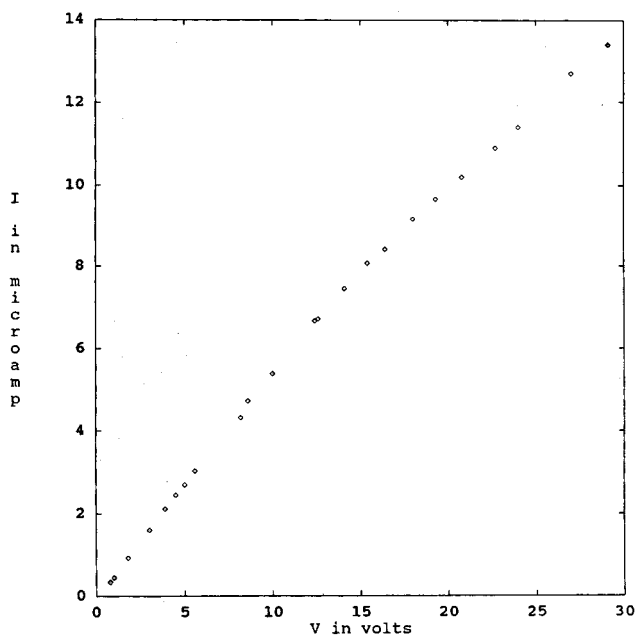


Figure 7. Applied voltage (V) in volts vs electronic current (I) in mA are measured at room temperature. The specimen thickness = 1 mm, C.S.A. = 2 cm².

(Soni and Srivastava 1988, 1992) are orthodihydroxy benzene, D-galactose, L-arabinose, L-rhamnose and D-glucuronic acid), *Asafetida* (constituents are Farniferol (Glasby 1982) A, B and C with molecular formula (C₂₄H₃₀O₄) and arbutin-galactan) and animal gums are 0.89, 0.97 and 0.83, respectively and their respective total d.c. conductivities are found to be $\sim 10^{-4}$, 10^{-4} and 10^{-3} S cm⁻¹. Their detailed studies and chemical characterization are in the process of development.

4. Conclusion

The electrical properties of the conducting biopolymer gum arabica is similar to that of synthetic conducting polymer doped with inorganic salt and seems to be proton conducting in nature. The gum arabica is a stable conducting biopolymer up to a temperature of 80°C. An intensive effort on these materials may reveal many interesting other aspects also. Repetitive experiments show that like other superionic solid these materials are also proton conductors.

Acknowledgements

The authors acknowledge UGC, New Delhi, for financial support (MRP No. F-10-5/98(SR-I)) to this research work and wish to thank the following persons for their active cooperation at various stages of the work: Prof. N Bhattacharyya (retd.), Department of Botany, Presidency College, Calcutta; Prof. D Roy, Dr S Tarafder and Dr D Sen, CMPRC, Physics Department, Jadavpur University and Dr S Saha, IACS, Calcutta.

References

- Almond D P and West A R 1987 *Solid State Ionics* **23** 27
 Aspinall G O and Wood T M 1963 *J. Chem. Soc. (London)* 1696
 Aspinall G O and Wood T M 1965 *J. Chem. Soc. (London)* 3003
 Aspinall G O *et al* 1968 *Carbohydrate Res.* **7** 244
 Barton D and Ollis W O (eds) 1979 *Comprehensive organic chemistry, the synthesis and reaction of organic compound in biological compounds* (Oxford, UK: Pergamon Press) Vol. 5, p. 740
 Bermudez V Z, Poinsignon C and Armand M B 1997 *J. Mater. Chem.* **7** 1677
 Chandra S 1981 *Superionic solids—Principle and application* (Amsterdam: NHPC)
 Chowdari B V R (ed.) 1996 *Solid state ionics, Parts I & II* (Amsterdam: NHPC) **86–88** pp 297–414
 Colomban P and Novak A 1992 *Proton conductors solids, membranes and gels—Materials and devices* (ed.) P Colomban (Cambridge: Cambridge Univ. Press) p. 266
 Epstein A J 1986 *Handbook of conducting polymers* (ed.) T A Skotheim (New York and Basel: Marcel Dekker Inc.) p. 1065
 Epstein A J, Rommelmann H and Gibson H W 1985 *Phys. Rev.* **B31** 2502
 Glasby J S 1982 *Encyclopaedia of the terpenoids* (New York: John Wiley & Sons) p. 971
 Glasser L 1975 *Chem. Rev.* **75** 21
 Howe A T and Shitten M G 1980 *J. Solid State Chem.* **34** 149
 Hummel R E 1993 *Electronic properties of material* (Berlin: Springer-Verlag) 2nd ed., p. 155
 Jonscher A K 1997 *Nature* **267** 23
 Poulsen F W 1989 *Solid ionic conductor—Recent trends and application* (ed.) T Takahasi (Singapore: World Scientific) p. 166
 Sarkar A 1997 *Solid State Phys. (India)* **C40** 409
 Sarkar A 1998 *Tenth nat. conf. on ferro and dielectrics* (Madras: IIT)
 Shimura T, Komori M and Iwahara H 1996 *Solid State Ionics* (ed.) B V R Chowdari (Singapore: World Scientific) **86–88** p. 685
 Soni P L and Srivastava H C 1988 *Indian J. Chem.* **B27** 1093
 Soni P L and Srivastava H C 1992 *Structural polysaccharide chemistry* (Dehra Dun: A Surya Publication) p. 13
 Wagner J B and Wagner C J 1957 *Chem. Rev.* **26** 1597
 Yamashita Y and Nicholson P S 1986 *Solid State Ionics* **20** 147