Printed ISSN 1330–0008
Online ISSN 1333–9125
CD ISSN 1333–8390
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ELECTRO-ACTIVITY IN GUM MANGOSTEEN AND ITS COMPLEXES

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Received 4 April 2009; Revised manuscript received 22 September 2009
Accepted 7 October 2009 Online 29 October 2009

Biomaterial has occupied a leading position in material science for its various scientific and technological applications. The present work was carried out with a natural gum extracted from raw fruit of mangosteen - an east Indian tree *Gercinia mangostana*. Solid specimen of the gum was developed following a sol-gel like process. AC and DC electrical analysis on the dried solid specimen of the gum was carried out. It exhibits high electrical conduction, $\sigma \sim 2 \times 10^{-6}$ S/cm at room temperature, of which ionic and electronic contributions are 70% and 30%, respectively. The experimental investigations show that origin of high electrical conductivity is due to the presence of a substantial amount of organic acid unit in its polysaccharide background. In fact the observed σ is about 3 times that observed in gum Arabica - a plant gum. Optical absorption of this new biomaterial was also studied using UV-VIS spectro-photometry. The result shows its high absorption coefficient in UV and blue part of the spectrum. The electrical characterization of the material was also made. It has been observed that the electronic conduction can be enhanced to 70% of the total electrical conductivity by forming complex with iodine or an appropriate organic/inorganic acid, e.g. acetic acid. This high-potential material is being studied for the development in device application.

PACS numbers: 82.35.Pq, 82.35.Cd, 83.80.Mc, 87.68.+z, 82.35.Rs UDC 537.311
Keywords: biopolymer, electro-active, ion-conductive, optical absorption, mixed conduction

1. Introduction

In the recent period, soft matter [1] occupies a leading position in the material science research. The most of the soft matters are derived from living matter. Biomaterials, especially the biopolymers, are playing the most crucial role in soft-matter studies. The mentioned biopolymer/biomaterial systems are mostly dominated by weak, non-covalent interactions, and fluctuations like Brownian motion are also present in them. This highly interdisciplinary research has gained tremendous importance from the viewpoint of material science and modern biology.

During the last few decades it has been found that electro-active polymers (EAP) are high-potential materials for various applications. The conventional EAPs are synthetic organic materials having insoluble, non-degradable and in general toxic nature. The biopolymers are found to have a greater degree of flexibility and functionality over synthetic polymers. Recently, a substantial number of biopolymers/biomaterials have been identified as electro-active biopolymers (EABP). A brief summary and introductory review of EABPs and their functional aspects may be found in a mini-review by Finkenstadt [2]. The known EABPs, like starch, cellulose, chitosan, pectin, plant gums etc., are found to exhibit electrical conduction over a wide range of conductivity (between 10^{-3} and 10^{-14} S/cm). It is also expected that there are many more yet to be investigated. Moreover, they may give rise to organic and inorganic complexes with much more enhanced electro-activity (Pradhan and Sarkar [3]) to meet the demand of modern technologies. The use of these bio-based non-traditional materials may reduce the global dependence on hazardous synthetic materials. The present paper makes an attempt of a comprehensive study of the electro-activity of a new biopolymer/biomaterial.

In earlier studies of Mallick and Sarkar [4] and Mallick et al. [5], it has been found that the plant gum of *Acacia Arabica* exhibits many interesting features of electro-activity from the material-science viewpoint. Plant gums are eco-friendly highly stable and usable materials. They consist of polysaccharides unit, formed by the polymerization of monosacharide with charged groups. These polymers glue together the cellulose micro-fibril to make the composite structure. Most plant gums belong to this class.

The present work was carried out with a natural gum extracted from raw green fruits of *mangosteen*, a tree *Gercinia Mangostana* of east-Indian origin. It is a common fruit tree in most village gardens in south-east Asia, both in the mid and low wet-countries. It is an important natural product widely used [6] for medical and other application. The dried solid specimen of the gum is highly stable at room temperature (RT). The chemical composition of this fruit was well analyzed [7, 8]. The fruit shell contains $7-13\%$ tannin and the seeds contain 3% oil. The rind contains 5.5% of tannin and a resin as well as a yellow crystalline bitter principle, mangostin ($C_{20}H_{22}O_5$) or mangosim. It was reported [9] that the flesh of the fruit (aril) contains saccharose 10.8%, dextrose 1% and kerrelose 1.2% forming the polysaccharide background.

Following an appropriate extraction and purification process, a solid specimen of the gum was developed by a sol-gel like process. Chemical purification of the natural specimen may not be meaningful. The natural composition often varies with geographical location of the plant, moreover, it will make the specimen more expensive. However, purification is desirable for medical application. In the following section, the details of experimental investigations of charge transport and its various aspects are summarized. The experimental probes employed in this study are thermogravimetric analysis (TGA), DC and AC electrical analysis and optical absorption in the UV-VIS region.

2. Experimental

2.1. Material preparation

Raw fruits, collected from mangosteen plant, were cleaned and then their chopped pieces without seeds were allowed to stand in distilled water around 60°C for 5 – 6 hours. The filtrate was allowed to evaporate to obtain a thick viscous gel-like matter. The solid specimens were developed in the pallet form by adequate drying of this gel-like matter. Iodine, acetic acid and ortho-phosphoric acid were added to the viscous gel, and solid specimens of the respective complex were made by sol-gel process, followed by adequate drying. The developed transparent tea-like colored pallet was sandwiched between two highly polished copper electrodes to make the experimental proto-cell for electrical experiments. The chemical structure of mangostin [9], the generic component of gum mangosteen, is shown in Fig. 1.

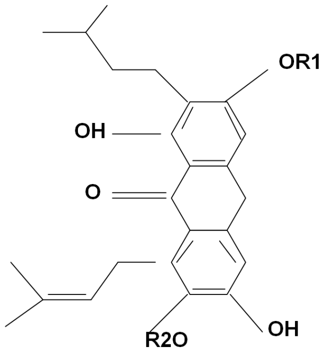

Fig. 1. Chemical structure of mangostin, $R_1 = \mathrm{H}$. $R_2 = \mathrm{CH_3}$.

2.2. Thermal analysis

Thermogravimetric analysis (TGA) of the prepared specimen was carried out using Linseies DTA/TGA unit (Model No. 2045) in the temperature range 2 – 140°C. The TGA is supposed to provide information about thermal stability, phase transformation and glass transition in the specimen.

2.3. Electrical analysis

The prepared specimen of the gum was subjected to electrical analysis to investigate the nature of electrical charge transport in it. DC electrical measurements were carried out (i) to determine its ion-transference number following the Wagner polarization technique [10] and it was carried out using a highly sensitive micro-processor-based set up that was capable to record the variation of transient polarization current with a time resolution of 10^{-3} s. (ii) DC volt ampere (V–I)

characteristics of the specimen were recorded using Keithley (USA) 2400 Sourcemeter.

AC electrical measurements were carried out at room temperature to investigate greater aspect charge transport through the specimen and was recorded using HIOKI (Japan) 3522 LCZ Meter in the frequency range 1 Hz to 100 KHz. The temperature dependence of total electrical conductivity was also measured with same setup and temperature was recorded by Tectronix DTM-900 (USA) thermometer. All measurements were carried out with the two-probe method.

2.4. *Optical experiment*

The physical appearance of the pure gum and its complexes were found to exhibit color, hence their optical absorption characteristics in the UV-VIS region were studied to investigate their optical absorption, absorbance region and photo-charge separation therein. The studies were made using the Systronics (India) 2020 UV-VIS spectrophotometer.

3. *Results*

Figure 2 shows the result of TGA study on prepared mangosteen specimen and the result of it indicates the $\sim 1\%$ free-water content in the mangosteen sample.

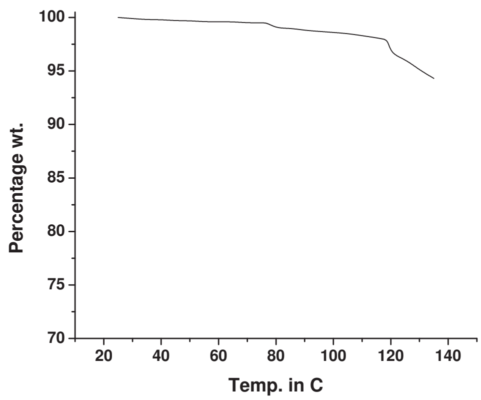

Fig. 2. Percentage loss in weight (w) vs. temperature (t) in deg. centigrade (Sample weight 14.0 mg*). Heating rate* 5°C*/minute.*

The ion transference number (τ) for the specimen was estimated from polarization current data using the following relation

$$\tau = \frac{I_t - I_e}{I_t} \, ,$$

where I_t was the initial transient current and I_e was the final steady electronic current. The τ for the pure specimen was estimated to be 70% and electronic contribution to the total current was about 30%. However, the value of τ obtained for the complexes of the gum were found to be of a lower value. In fact, the results show a clear evidence of a modification of electro-activity of the biopolymer under investigation. The results of ion-transference number measurement on iodine, acetic acid and phosphoric acid complexes of the gum show an enhanced electronic contribution up to 70% of the total contribution. The results obtained are compared with those obtained from DC and AC measurements are summarized in Table 1. The mentioned enhancement was also found to vary with the concentration of the guest in the pure host gum.

TABLE 1. Total electrical and electronic conductivities of experimental specimen at RT.

Samples	Total conductivity from bulk resistance (S/cm)	DC conductivity from V-I characteristics (S/cm)
Pure mangosteen gum	1.78×10^{-6}	8.6×10^{-7}
Acetic acid complex of mangosteen	2.1×10^{-5}	6.6×10^{-6}
Iodine complex of mangosteen	4.91×10^{-4}	1.0×10^{-5}
Orthophosphoric acid complex of mangosteen	1.25×10^{-4}	1.74×10^{-5}

The results of DC V–I characteristics of the pure mangosteen gum and its complexes are shown in Fig. 3. The inset graph in Fig. 3 shows the V–I characteristics

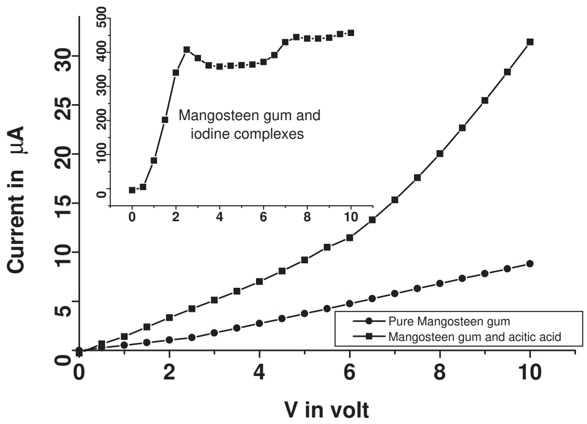

Fig. 3. DC V–I characteristics of pure mangosteen (■) (sample thickness 0.1525 cm, *area 1.76* cm^2*), acetic acid complex of mangosteen (●) (sample thickness 0.1535* cm, *area 1.66* cm^2*). Inset graph: iodine complex of mangosteen (■) (sample thickness 0.15* cm, *area 1.72* cm^2*).*

of the iodine complex of the gum. One can see the presence of a strong non-linearity in the measured V–I characteristics that are due to the formation of gum-complex with iodine. In this regard it is to be mentioned that pure solid iodine at RT does not exhibit any such V–I characteristics. The DC electrical behavior of acetic acid complex of the gum shows that the electronic contribution reduces space-charge effect which is predominant in super-ionic/ionic solids.

The results of AC measurement and frequency characteristics are shown in Fig. 4 and Fig. 5, respectively. Figure 4 is an impedance plot showing the variation

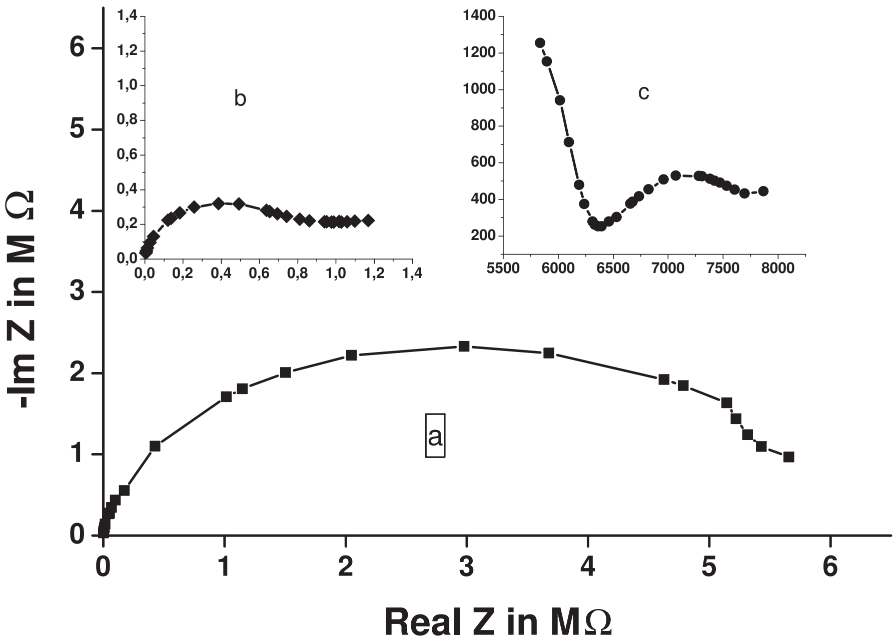

Fig. 4. Impedance plot of (a) pure gum mangosteen, (b) mangosteen gum – acetic acid complex (sample thickness 0.1535 cm*, area 1.66* cm^2*) and (c) mangosteen – orthophosphoric acid complex (sample thickness 0.125* cm*, area 2.54* cm^2*) at RT, applied p.d 1V (sample thickness 0.1525* cm*, area 1.76* cm^2*), Z in* Ω*.*

of real and negative imaginary parts of complex impedances at frequencies of the AC field and it gives the account of the total bulk electric conduction along with the nature of charge transport in the gum specimens. Figure 5 shows the frequency characteristics and variation of AC conductivity with frequency of impressed AC field, as measured for the pure gum and its complexes, respectively.

The temperature dependence of the total electrical conductivity of the mangosteen gum is given by

$$\sigma = \frac{A_0}{T} \exp\left(-\frac{E_a}{kT}\right)$$

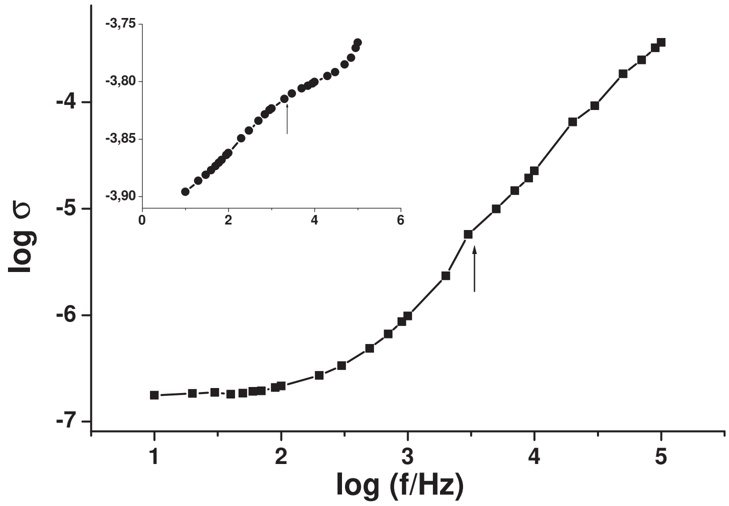

Fig. 5. Conductivity plot of pure mangosteen (■), inset curve for orthophosphoric acid complex of mangosteen (●). Calculated values are at RT.

and is shown by the Arrhenius plot in Fig. 6, in the temperature range 25°C to 50°C. The mentioned temperature range is within the normal stability zone of these biopolymers. The Arrhenius plot was extracted by an AC measurement at 5 kHz at the respective temperatures. The inset graph B in Fig. 6 shows the Arrhenius behavior for the ortho-phosphoric acid complex specimen of the gum. Figure 7 shows an account of the optical absorption of the pure gum in the wavelength range 200 nm to 900 nm.

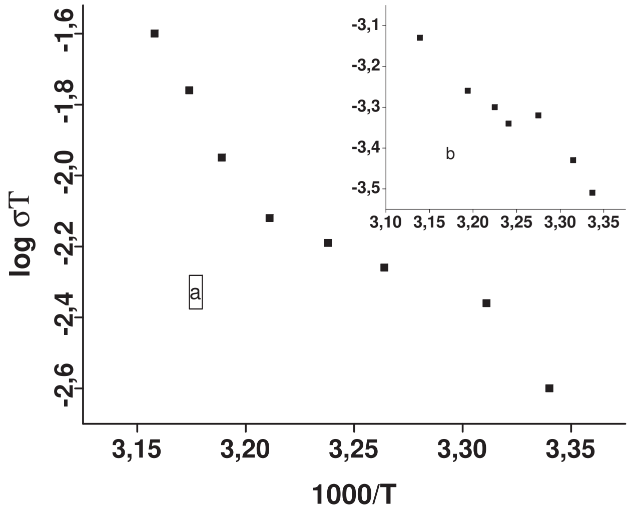

Fig. 6. Arhenius plot for the pure mangosteen (■), inset curve for orthophosphoric acid complex of mangosteen (♦). Applied voltage of 1 V *AC at frequency 5* kHz.

4. Discussion

The TGA result in Fig. 2 shows that it is thermally stable up to the temperature of 80°C where it is devoid of its free water by a reversible change. Above the temperature of 120°C, the near-transparent sample becomes dark grey flake, losses its electrical conduction property and never exhibits any glass transition. This irreversible change of gum mangosteen is the feature of solid protonic conductor (Poulsen [16]) on heating in a water-lean atmosphere and is very similar to that observed in gum *Arabica* [4].

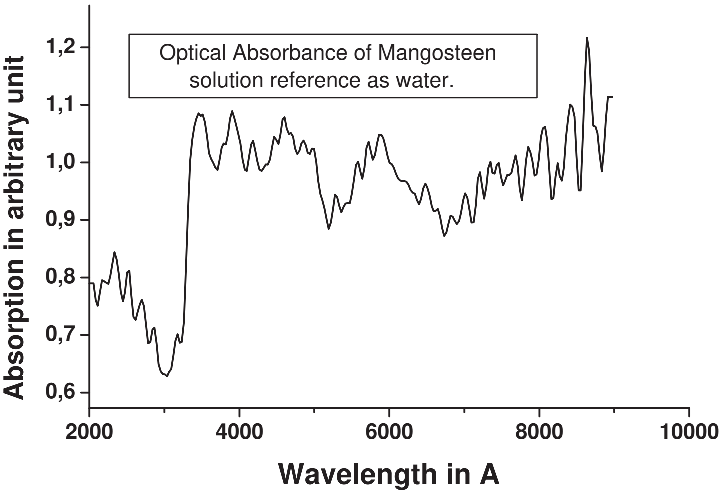

Fig. 7. UV-VIS absorption pattern of mangosteen solution in water at RT, reference water.

The result of ion transference-number measurement shows that the gum has a mixed conduction nature. The electronic conduction in the gum is strongly modified under addition of weak organic/inorganic acid unit in its structure. The inclusions of iodine in the gum perhaps form a complex and are found to behave like n-type doping in the pure gum.

The results of DC V–I characteristics given in Fig. 3 for the pure gum specimen show an electron conduction of nature like that of a n-doped conducting polymer. The effect of electrode reaction was not found to be predominant, but a substantial contact resistance was found. The electronic conductivity for the pure specimen is thus estimated to be 8.6×10^{-7} S/cm. The inset graph in Fig. 3 shows the V–I characteristics of the iodine complex of the gum showing the enhancement of electronic contribution in the total conductivity. The non-linear nature of its V–I characteristics in Fig. 3 shows its material potential for electronic device application. The DC conductivity estimated from the linear part of curve is estimated to be 1.0×10^{-5} S/cm, i.e. an enhancement by ~ 10 times over its pure counterpart.

The gross feature of electro-activity of the material is best understood from the AC measurement. The impedance plot, inset graph a in Fig. 4, for pure mangosteen shows a very clear effect of inhomogenities and heterogeneities present in the natural form of the specimen. Moreover, the nature of the conductivity dispersion of the specimen indicates a high grain boundary effect which probably constitutes an additional conducting path in the specimen. Thus extraction of bulk conductivity becomes an analytical one. Due to the simultaneous occurrence of different types of bonds, the specimen exhibits anisotropy and/or inhomogeneity in its properties. The later gives rise to significant change in the carrier concentration. A possible existence of covalent and ionic bonds may be found in the bio-molecules with ionic/super-ionic character.

The total electrical conductivity of the pure material has been estimated from the data on the bulk resistance of the specimen shown in Fig. 4a and is found to be $\sim 2.0 \times 10^{-6}$ S/cm. This value is very high for a solid biomaterial/biopolymer. The nature of Fig. 4a is also an indicator for enriched electronic contribution in the pure gum specimen. The ratio of contribution of electronic conduction of the specimens estimated from DC experiment to the total electrical conduction obtained from AC experiment is found to be in good agreement with those obtained from ion transference number measurement.

The nature of impedance plot in Fig. 4b for acetic-acid complex of mangosteen gives an impression of superposition of two semicircles. By the inclusion of the acid unit in the gum specimen, additional percolation conducting paths are generated leading to an increase in the bulk conductivity over that of the pure host. This also shows an increase of electronic conductivities in the complex specimen.

The observed nature of the impedance plot of the orthophosphoric acid complex of mangosteen gum is shown in Fig. 4c. It appears like a depressed semi-circle with almost vertical in the left with a dominant constant phase element. The deviation of the overall nature from an ideal one is due to the inhomogeneity and formation of a complex with H_3PO_4 and cross linking [11] of PO_4^{3-} ions with the generic structure shown in Fig. 1. The later is giving rise a strong enhancement of electro-activity over the pure mangosteen host.

The estimated frequency dispersion of electrical conductivity $\sigma(\omega)$ for the specimens is shown in Fig. 5. It was extracted from the AC experimental data and shows a plateau in the near-DC region (low frequency), however, at intermediate frequencies some marked discontinuities are observed. That may be due to the presence of fast internal dynamical or dielectric relaxation processes in the experimental material. The overall nature indicates that both successful and unsuccessful jumps of the carrier ion towards its neighboring site are possible. The nature of the mechanism is an established one for many ionic and mixed conductors [12].

The nature of Arrhenius plot for the pure material in Fig. 6a shows a relatively high negative slope in the upper part of the curve and a probable impurity-dominated smaller negative slope in the lower part. The later is in the vicinity of RT. The estimated electro-thermal activation energy of the pure specimen is thus estimated at 0.81 eV. However, the result for the orthophosphoric acid complex of the mangosteen, shown in Fig. 6b, is estimated to be 0.16 eV. This is again a foot-print of enhancement of electro-activity.

Figure 7 shows the optical absorption of pure mangosteen gum in the wavelength region 190 – 900 nm. It shows a very high absorbance between 350 – 900 nm, i.e., over the entire visible region along with a small region on the either side of VIS region. The absorbance is almost uniform and is probably due to the complex structure and microscopic inhomogeneties resulting from variation of source intensity. In fact, this is a most important characteristic of many biomaterials. The material may be used as light-absorbing layer over planar solar cells. The nature of optical absorption in the specimen indicates that the molecular charge separation occurred in it and leads to a high electrical conduction over its normal ionic conduction. That absorption has been found to be modified greatly due to its complex formation with iodine.

The overall material characteristics investigated so far are very interesting. The presence of organic acid in the molecular structure may provide a high electrical conduction. The presence of photo-absorbing group induces charge separation to provide high carrier concentration. The photo-induced charge separation [13] is observed in many biomaterials and the property has also been used [14] in the development of photo-sensitive biomaterial complex. The inclusion of iodine is found to be more effective than that of natural organic acid. While the former enhances photo-absorption and provides substantial charge carriers, the later requires adequate activation to generate carriers. Using the very fascinating characteristics of the gum and its complex, some electro-chemical and photo-sensitive device applications, e.g. the development of biopolymeric solar cell [15], are in the process of development.

The biopolymer gum mangosteen of this research exhibits electrical charge transport due to the presence of polysaccharide unit along with organic acid unit in it. The ionic conduction in this material is dependent on (i) background polymer matrix including free H_2O molecules, (ii) the concentration of the ion species (H_3O^+) and their mobility and (iii) temperature [16]. The background saccharide unit and organic acid units are get cross-linked with generic mangostin units via -OH radical, leaving hydronium ion as conductive species. Addition of acetic acid unit in the natural specimen favors the formation of cross linkage and leads to an enhanced conducting pathway.

The possible mechanism of the proton conduction may be explained following Poulsen et al. [17] and by the Grotthuus mechanism [18]. The conducting species in solid protonic conductors (SPC) may be proton (H^+), hydronium (H_3O^+), hydroxyl (OH^-), ammonium (NH_4^+) or dihydronium ($H_5O_2^+$) ion. These ion conductions exhibit both bulk and surface conductivity in many SPCs [17]. After a careful experiment by an electrochemical process [17, 19], it was found that the gum mangosteen sample is also a SPC, and conducting ion species in it were hydronium (H_3O^+) ions. The present specimen exhibits high electrical conductivity due to the same and its highly branched structure.

The presence of acid unit, various defects and inhomogeneities in solid gum specimen enhance conductivity pathway which can be attributed to the mobility of ions and electron/holes along with a flexible polymer background leading to chain hopping [20]. The structural nature of this solid gum specimen is amorphous and similar to that obtained from XRD analysis of gum *Arabica* [21]. The amorphous nature of the gum is also important toward the high electro-activity of the material. Due to the inner complexity of bio-molecular structure of this gum, some free electrons are also excited due to the application of electric field leading to generation of free charge carriers and hence the conductivity is influenced by external potentials.

5. Conclusions

The gum mangosteen is a new EABP and this highly conducting biomaterial has a substantial electronic contribution due to the presence of organic acid unit in it. Its electro-activity can be tailored to a great extent through formation of its complex with appropriate organic and inorganic dopant.

Acknowledgements

Authors acknowledge U. G. C., New Delhi, India for support of this research (No. F30-2/2004 SR).

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ELEKTROAKTIVNOST MANGOSTINA I NJEGOVIH KOMPLEKSA

Biološki materijali imaju vodeću ulogu u znanosti o materijalima zbog svojih različitih znanstvenih i tehnoloških primjena. U ovom se radu proučava prirodna smola koja je bila izlučena iz sirovog voća magnostina, ploda istočno-indijske voćke *Gercinia mangostana*. Pripravili smo čvrst uzorak smole sol-gel postupkom. Ispitali smo uzorak izmjeničnom i istosmjernom strujom. Na sobnoj temperaturi našli smo visoku električnu vodljivost, $\sigma \sim 2\times10^{-6}$ S/cm, s ionskim i elektronskim doprinosima od 70% odnosno 30%. Mjerenja pokazuju da je visoka električna vodljivost posljedica poveće količine molekula organske kiseline u polisaharidnoj osnovnoj tvari. Vrijednosti σ su oko tri puta veće nego u biljnoj smoli *Arabica*. Proučavali smo optičku apsorpciju primjenom UV-VIS spektrofotometrije. Ishodi mjerenja pokazuju velik apsorpcijski koeficijent u plavom dijelu spektra. Također smo proučili električne značajke te tvari. Ustanovili smo kako se elektronska vodljivost može povećati na oko 70% ukupne vodljivosti tvorbom kompleksa s jodom ili pogodnom organskom ili anorganskom kiselinom, npr. octenom kiselinom. Ta se tvar velikih mogućnosti proučava radi primjena u raznim napravama.