Conduction Behaviour of Plant Exudates Under High Electric Stress and Temperature

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Plant exudates like Acacia and Karaya gum polysaccarides have been studied under high field and temperature. Mechanism responsable for charge generation and transportation is examined. Breaking up of glycosidic bonds and coiling up of the polysaccaride chains releases charge carriers like Ca^{++}, Mg^{++} and K^{+}. These accumulate at the gum electrode interface at ordinary conditions and give rise to space change limited currents (SCLC). Simultaneous change in temperature and electric field changes the SCLC and consequently trapping and detrapping take place. Further changes allow the charge carriers (both holes and electrons) to come up to the conduction band as in hopping model, but as the gum miscelles release the ions, breaking the water protective film temperature enhanced field emission takes place. In both gums electrical conductivity was found to be in the region 10^{-13} to 10^{-10} ohm/cm. Band gaps for Acacia and Karaya have been calculated to be 3.15 eV and 8.63 ev respectively.

The mechanism responsible for conduction of any organic solid depends on the generation of charge carriers, their transportation their recombination and trapping. The existance and nature of distribution of traps of Acacia and Karaya plant exudates [1] provide a way to study them in the field of electrical conduction. The present study attempts to achieve this objective.

EXPERIMENTAL

Experimental set up and procedure as regards purification of samples, conductivity cell and current measurements are as described earlier [1,2].

RESULTS AND DISCUSSION

Current voltage characteristics of Acacia and Karaya plant exudates over a wide range of field and temperature showed space charge limited current (SCLC) as suitable mechanism for carrier generation inside these polysaccarides [1]. A plot of log J vs $E^{1/2}$ was found to be linear at higher fields (Fig.1a & b) showing the possibility that carrier generation occurs through Schottky emission [3]. The work function (θ) is calculated using the relationship $J \sim T^2 \exp(-\theta/kT)$ for both the gums from the slope of log (J/T^2) vs $1/T^{-1}$ curves (i.e. by the slope of curves drawn between the zero field values of current obtained by extrapolation of the Schottky plot to zero field value vs inverse of temperature - an Arhenious plot) (Fig. 2a and b) and found to be greater than 1. Further the dielectric constant calculated

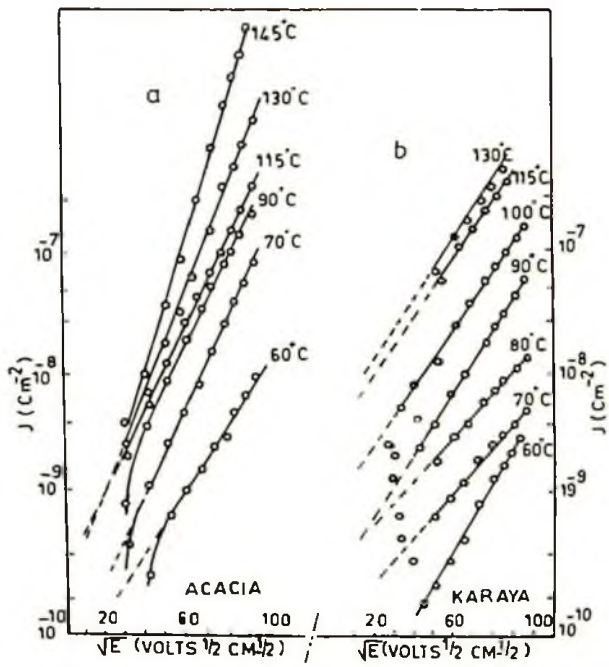


Fig. 1 Schottky plot in the case of Acacia and Karaya

from the Schottky slope

$$\beta_{SR} = \left[\frac{e^2}{4\pi\epsilon}\right]^{1/2} \frac{1}{kT}$$

does not agree with the experimental value [4].

Thus it can not be concluded that Schottky emission occurs in these cases. Similarly pool Frenkel mechanism [5] also gives unsatisfactory results in these gums (Fig. 1a & b).

Fowler Nordheim equation is

$$J = AV^2 \exp(-B/V)$$

Where A and B are temperature independent constants involving barrier height. It may be used to examine the possibility of tunnelling. To satisfy this, the plot of log (J/V^2) vs $1/V$ should be a straight line with negative slope; This was found to be not true in the present case. More over log (J/T^2) vs $(1/T)$ plots for these gums (Fig. 2a & b) show strong temperature dependance

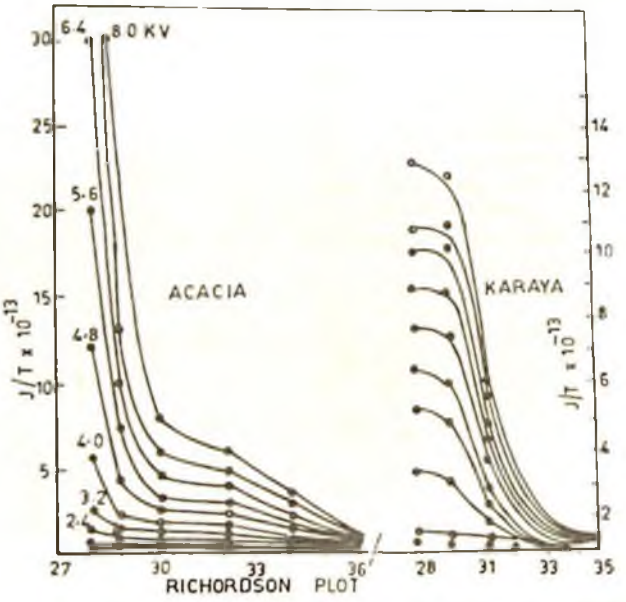


Fig. 2 Richordson plot a) Acacia b) Karaya

whereas Fowler-Nordheim equation shows no temperature dependance. So tunnelling possibility is eliminated.

Earlier observation [2,6] has shown that the carboxyl groups in the glucosidic bonds in Acacia and Karaya gums break at high temperature and thus release sorbed water from the miscelles. The gum chains are disturbed and coil up; the volume of the gums under these conditions increase and decrease according to the release and evaporation of water. The ions Ca^{++}, Mg^{++} and K^{+} may therefore create Schottky defect and/or Frenkel defect and hence the following four cases may arise:

(i) Direct interchange of two atoms: In the case of ionic compounds, the large repulsive forces between the atoms of like charges makes this mechanism requiring relatively large amount of energy and this may be impossible in the present case.

(ii) Migration of an interstitial atom subsequent to formation of a Frenkel defect.

(iii) Atomic displacement into a neighbouring vacancy subsequent to formation of a Schottky defect. This is usually described as a diffusion of vacancies in the opposite direction.

(iv) Diffusion of pairs of vacancies by means of atomic movements into either of two adjecent vancancies. Since the pair moves by the motion of either vacancy provided that the pair is not split up in the process, the energy required to move the pair is actually less than that required to move an isolated vacancy.

The energy required for any of the above processes to operate, i.e. the sum of the energies of defect formation and subsequent migration, is called the activation energy of that process. Activation energies for both the gums have been shown in Table 1. It is clear that at higher

TABLE 1

ACTIVATION ENERGIES FOR ACACIA & KARAYA

ACACIA				KARAYA	
Field	Activation Energy			Field	Activation Energy
KV	>400 °k	400-350 °k	<350 °k	KV	(ev)
0.8	0.23	-	0.3	2.7	0.79
1.6	0.37	-	0.46	3.6	0.83
2.4	0.54	0.14	0.34	4.5	0.84
3.2	0.64	0.10	0.46	5.4	0.87
4.0	0.76	0.15	0.48	6.3	0.99
4.8	1.14	0.10	0.44	7.2	0.99
5.6	1.07	0.14	0.43	8.1	0.86
6.4	1.13	0.13	0.36	9.0	0.81
7.2	0.99	0.19	0.30		
8.0	1.16	0.21	0.23		

temperature, activation energy increases for both the gums and becomes sufficient to create either or both processes (ii) and (iii) depicted above. Ionic conduction may be represented by

$$\sigma_{ionic} = \frac{e^2 N}{kT} D_0 \exp(-\Psi/kT)$$

Where N = gradient of the concentration of atoms, e = electronic charge, k = Boltzman constant. Ψ = activation energy. D_0 = constant for the crystal.

Plots between logσ and inverse of temperature (1/T) have been shown in (Fig. 3a & b) indicating clearly three regions for Acacia and only one main

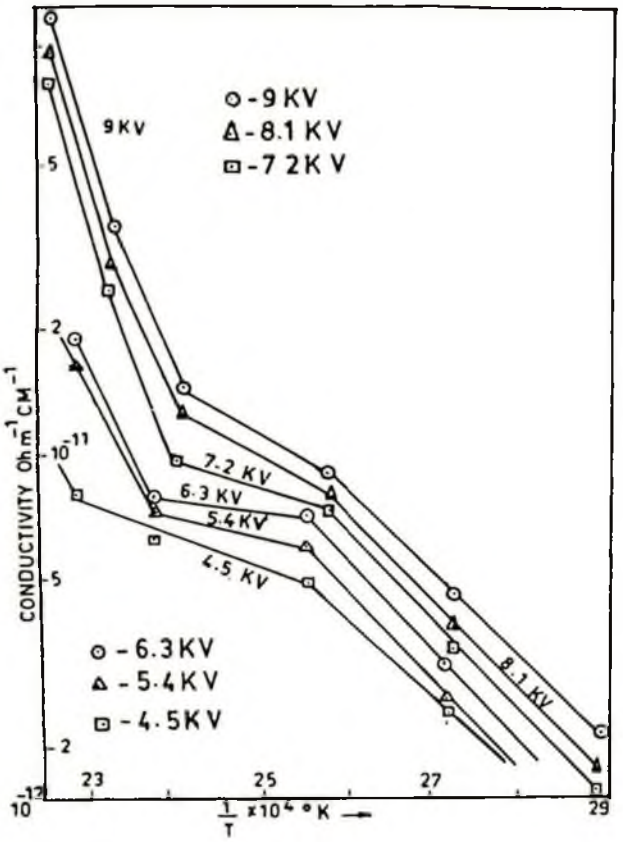


Fig. 3a Variation of conductivity (σ) with T at specified fields.(graph on semi log paper)

region for Karaya (curvature seen on the low and high temperature ends of Karaya plots are not taken into consideration). Thus Acacia plots show, at high temperature the thermal energy to be sufficiently great to create vacancies and the activation energy (Table 1) represents a sum of the energies required for vacancy generation and the motion of ions into the vacancies. At lower temperature the thermal energy is only enough to allow the migration of atoms into vacancies already present in the crystal. These vacancies may be (primarilly) due to the inclusion of divalent atoms Ca^{++} (ionic radii of cations = 0.99A°) Mg^{++} (ionic radii of cations = 0.66A°) (which are naturally present in the Acacia gum) in substitution for the larger monovalant K^{+} (ionic radii = 1.33A°) in the solid structure. For each divalent metal thus incarporated in the crystal, a positive vacancy must be present nearby in order to maintain charge neutrality. Thus at low temperature, conductivity may be treated as in the extrinsic region of a semi conductor. Divalent impurity atoms are required for conduction to occur in this temperature region. On the other hand, the conductivity at higher temperature is characterstic of the gum itself, indicating intrinsic conductivity. Similarly the middle region of lower activation energy may thus be inferred to be due to the conduction through dispersed phase of ionic sorbed water released from the broken glycosidic bonds due to rise in temperature.

In the case of Karaya, cations naturally present in the gum i.e. (Ca^{++} Mg^{++} K^{+}) may be less in quantity than in Acacia. Behaviour at low and very high temperature regions are affected by these ions. Middle region, which is the characterstic of the imbibed water, may be dominating in Karaya gum. Incidentally moisture absorbing capacity of Karaya is greater than that of Acacia. Ionic conduction of this type in some of the organic semiconductors have been reported very recently [7].

Above discussions does not lead to the definite conclusion of ionic conduction in these plant exudates. If we see field dependence of the conductivity (Fig. 4a & b & 5a,b), it is clear

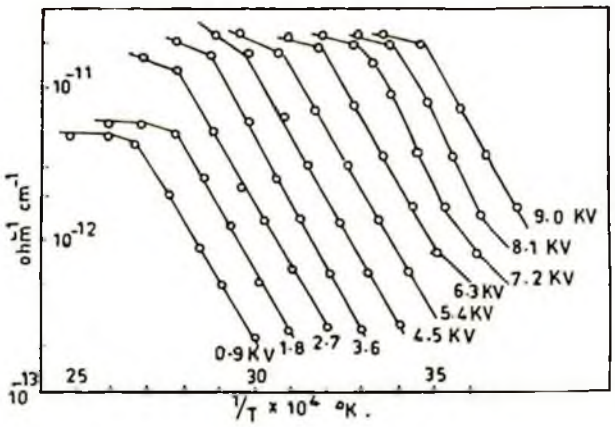


Fig.3b Variation of conductivity (σ) with reciprocal of temperature (T) at specified fields in case of Karaya, each curve is shifted on x-axis by 1 unit

that conductivity depends on both temperature and field. It may therfore be inferred [8,9] that the electronic and ionic currents are super-imposed in this dielectric and there exists no sharp demarcation between the two ranges of temperature. Hence additional investigations were made for obtaining the electronic component by plotting log J vs $E^{1/2}$ (Schottky plots Fig. 1a & b) and log J vs 1/E (field emission plots) graphs. Schottky plots yielded straight lines in this region suggesting Schottky emission to be a suitable mechanism of emission of electrons from the cathode into the dielectric or from dielectric into the anode. However, the slope of the straight lines so obtained was found to be greater than the theoretically calculated slope at least by a factor 6 and Schottky mechanism was eliminated. Fig. 4a, b shows a series of log J vs 1/E characterstics for different temperature in the ranges of temperature and field of interest. The straight lines obtained are almost in the form of

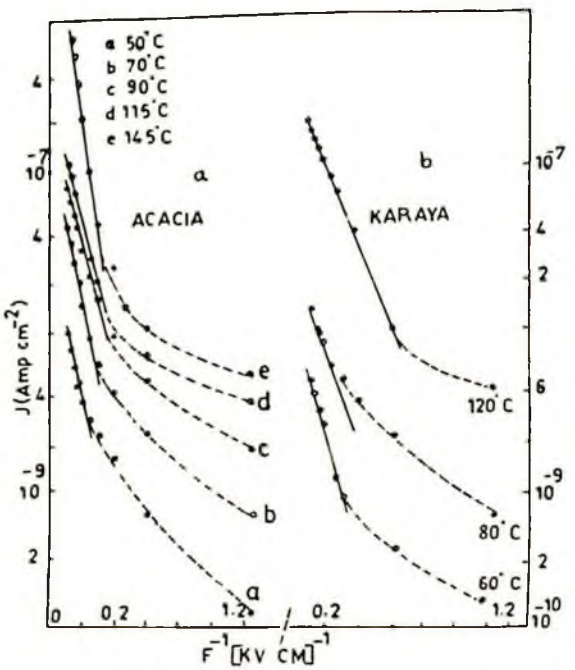


Fig. 4 Variation of J with 1/F of Acacia and Karaya on semi log paper at specified temperature

a fan which is characterstic of field emission currents [8]. They however indicate that field emission current depends greatly on temperature. The nature of this temperature dependence is apparent from Fig. 3a and b.

Stratton [9] described the density of field emission current from a nondegenerate semiconductor (when surface states are neglected) as

$$J = en_{\infty}\left(\frac{kT}{2\pi m}\right)^{1/2} \exp\left(\frac{\Delta R}{kT}\right) \exp\left[\frac{4X}{3F}\psi\theta\left\{\left(\frac{\epsilon-1}{\epsilon+1}\right)^{1/2}\cdot\frac{eF^{1/2}}{\psi}\right\}\right]$$

Where e is electronic change, k = Boltzmann constant, m the effective mass of electron, F the electric field intensity, T the absolute temperature, θ is Nordheims function, ψ external function, ϵ = dielectic constant ΔR is the decrease in the potential energy of an electron on the semiconductor surface layer due to the penetration of the external field.

$$n_{\infty} = \left\{\frac{2(2\pi mkT)^{3/2}}{h^3}\right\} \exp\left(\frac{-\Delta E}{2kT}\right)$$

Where ΔE being the width of the forbidden band, $X = 4\pi^2 m/h^2 \approx 5.16 \times 10^{-7}$ $(ev)^{1/2}$

According to Stration the value of ΔR depends on the field intensity and temperature and is given by

$$\Delta R = 2kT \sinh (F\psi_0/2fkT)$$

Where $\psi_0 = (fkT/8\pi n_{\infty} e^2)^{1/2}$ is the Debye shielding radius.

The penetration of the external field, therefore brings about a bending in the energy bands which results in an increase in the electron concentration on the surface layer as compared to that in the bulk.

It is evident from above theory that the temperature dependence of the field emission current is determined only by the electron concentration in the surface layer given by $n = n_{\infty} \exp \Delta R/kT$ and its temperature dependence. Similar type of thermal field emission is observed by Bhatnagar [10] in the case of Sugar cane wax. Temperature dependence of the field emission can therefore be interpreted both as thermal field emission and as a result of the temperature dependence of electron concentration in the surface layer. For small anode voltages, the field hardly penetrates the gum specimen and practically does not distort the surface band. Under these conditions $\exp(\Delta R/kT) \approx 1$ and the concentration in the surface layer is equal to the concentration in the bulk ie $n = n_{\infty}$. The slope of the lowest curve (3.15 ev) for Acacia and (8.63 ev) for Karaya may therefore be interpreted as band gap. The slope of the low temperture segment should be equal to the activation energy of impurities and the slope of the high temperature segment to the width of the forbidden band (Fig. 3a, b).

Temperature enhanced field emission in these gums may be further varified by temperature versus current density curves Fig. (6a,b). It is clear that Karaya shows saturation at 115°C. Acacia at lower field behaves similar to Karaya up to 90°C, current density increases with field and from 9 °C to 115°C it decreases and again reaches to maximum after 115°C. This behaviour shows that breaking of the glycosidal bonds cause the long chain of sugars and arabic acid with carboxyl groups in gum micelles to coil up. The sorbed water released in this way acts as a charge carrier (mostly Ca^{++} Mg^{++} K^{+} ions). These ions in case of Karaya migrate rapidly but because of decrease in the internal viscosity of Karaya at higher temperature these may get trapped in the available traps thus the saturation after 115°C is observed. (Fig. 6b). Acacia shows anomalous behaviour at higher temperature. In Acacia, viscocity after 115°C was found to increase thus imbibed water helped the charge carriers to migrate at a faster rate. This continues till its decomposition point ie 145°C. It appears that at

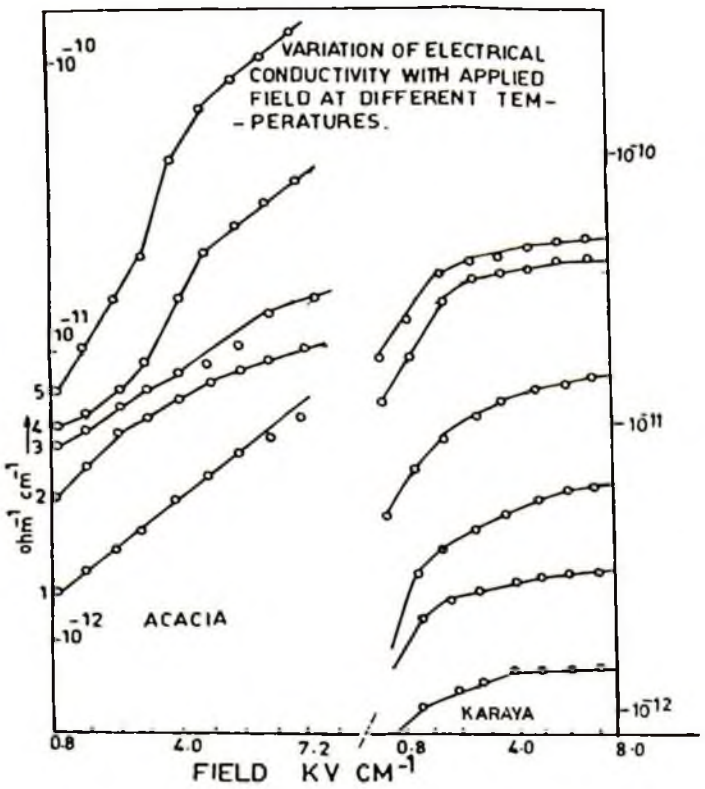


Fig. 5 Variation of Electrical conductivity with applied field at different temperatures.

lower fields, within 90°C to 115°C observed saturation may be due to occurance of the trap filled limit but as soon as further field is increased, the sorbed water released may produce empty holes thus trapping and/or detrapping causing a further increase in the current in Acacia. (Fig. 6a).

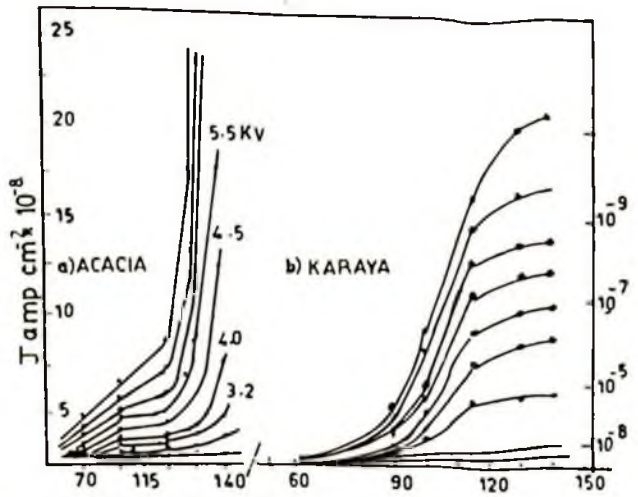


Fig. 6 Variation of current density (J) with temperature at different fields in the case of a) Acacia b) Karaya

CONCLUSION

As is established in the foregoing discussion, not a single mechanism for conduction, charge generation or transportation may be applied to understand the behaviour of both the gums. Because, both the gums are long irregularly chained polysaccharides, their behaviour with electric field and temperature depends on the changes produced on the glycosidal bonds.

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