Effect of Temperature on Plant Exudates Sandwitched Between Metal Electrodes

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Acacia and Karaya exudates exhibited currents when heated at a constant rate between two metal foils. The magnitude and direction of current depended on the difference in the work function of the electrodes used. These currents are reversible and reproducible during successive heatings. This is denoted as spontaneous current emission. Imbibed water in the molecules of the exudates played an important role in the electrochemical reaction between the exudates and the electrode surface to generate this current. This current is not pyroelectric in nature and is different from thermally stimulated depolarization currents. The latter is destroyed when the sample is heated once.

Some polymers [1] exhibit short circuit currents during heating in contact with two metals. Pillai [2] observed some of the cellulosic materials producing appreciable reversible and reproducible current of this type. Acacia and Karaya plants exude hygroscopic acidic salts of complex polysaccarides (3) containing Ca^{++}, Mg^{++} and K^{+} ions. These exudates also have been found to generate current when sandwitched between foil electrodes. The present study aims at understanding the nature, origin and behaviour of this current.

EXPERIMENTAL

Exudates of Acacia and Karaya plants were collected, purified [4,5] and pellets of 1 mm thick and 1 sq cm area were sandwitched between two metallic foil electrode. One of the metals was connected to the positive terminal of a Keithly electrometer 600 B and the other metal foil to the negative terminal. The entire assembly was heated at a controlled rate using a thermostat. Currents were measured at different heating rates, different electrode materials and different interval between two heatings of the same sample.

RESULTS

Current during first heating

1. When the gums were heated between two copper electrodes, the current observed was of very low order (10^{-12}A) and the direction of the current was uncertain.

2. When gums were heated between two dissimilar electrodes eg. Cu - exudate - Al, the observed current was higher and the direction of the current was definite positive from Cu to Al.

3. Interchange of electrodes resulted in a charge in the direction of the current but the magnitude ramained nearly the same.

4. When Cu/Acacia/Al was heated, at 7°/min., the current attained a peak value of the order of 10^{-8} A at 113°C. When the same was heated at a lower rate -3°/min- the observed current was only of the order of 10^{-10}A and the peak shifted to 82°C (lower temperature) Fig. 1&2.

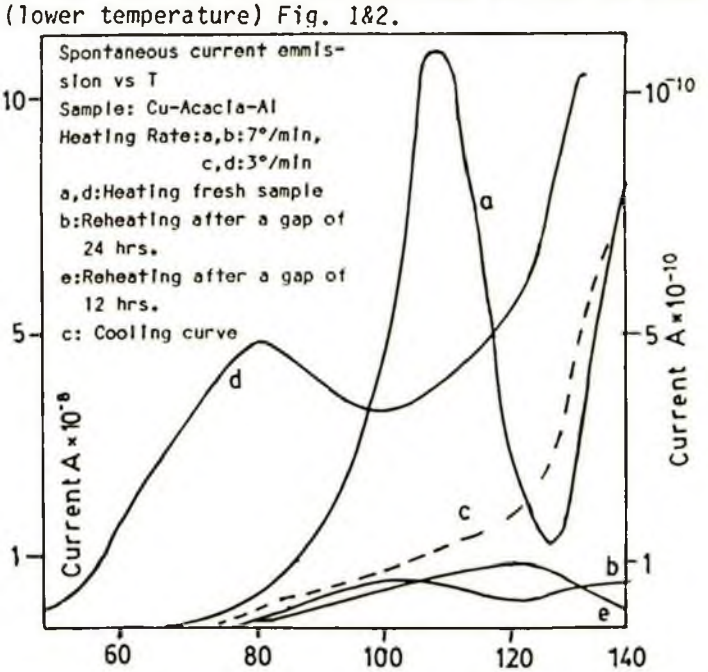


Fig. 1 SCE versus temperature [IN Cu/acacia/Al System]

5. When Cu/Karaya/Al was heated at 7°/min., the current attained a peak value ≈ 10^{-10} A at 104°C. When the same was heated at 3°/min, two peaks (at 38° and 110°C) were observed the currents being of the same order (Fig. 3&2.)

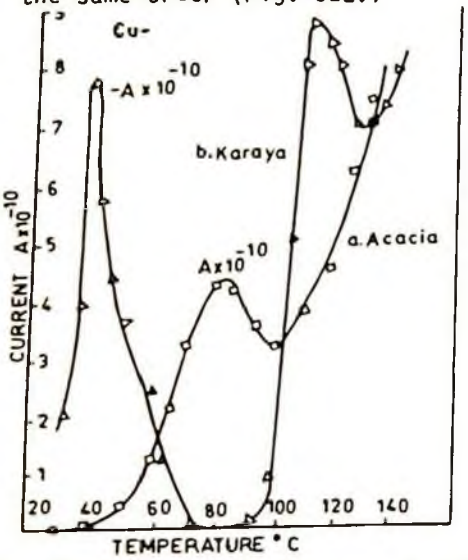
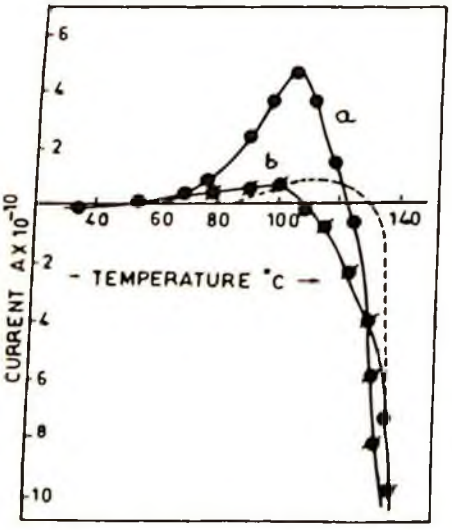


Fig.2 SCE versus temperature Cu/gum/Al heating rate 3°/mt.

6. When the samples were cooled, the current decay was in the same direction in the case of both the gums (dashed curve of Fig. 1&3).



Cu - Karaya - Al
Heating rate 7°/min
a: fresh heating
b: repeated heating
dashed curve cooling

Fig. 3 SCE versus temperature [Karaya] in successive heatings

7. When different metals like Ni, Zn and Pb were used with copper as the electrode material, the currents were found to be positive from copper to the second metal Cu-Acacia-Al gave one peak of 4.5×10^{-10} A at 82° Cu-Karaya-Al gave two peaks of about 8×10^{-10}A at 38° and 9×10^{-10}A at 110°C (Fig.2)

Cu-Acacia-Pb gave two peaks of 9×10^{-8} A at 49° and 9.6×10^{-8} A at 120°. Cu-Karaya-Pb gave 3 peaks of currents of the same order at 49°, 80° and 108° C (Fig. 4)

Cu-Acacia-Zn gave 3 peaks of current in the range $7\text{-}8 \times 10^{-8}$ A at 38°, 54° and 77°. Cu-Karaya-Zn also

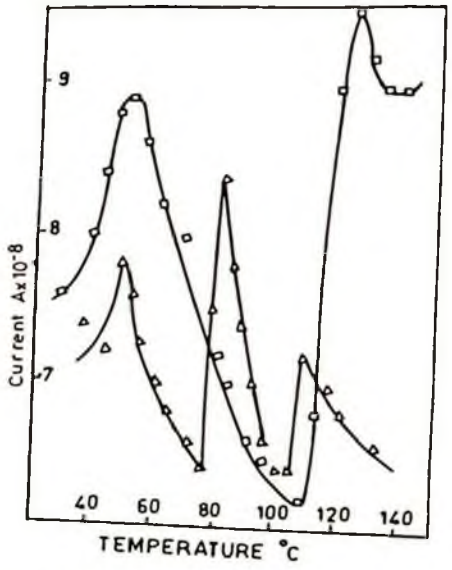


Fig. 4 SCE versus Temperature Cu-gum-Pb

gave 3 peaks of current in the range $8.5\text{-}9 \times 10^{-}$ at 47°, 77° and 103°C (Fig. 5)

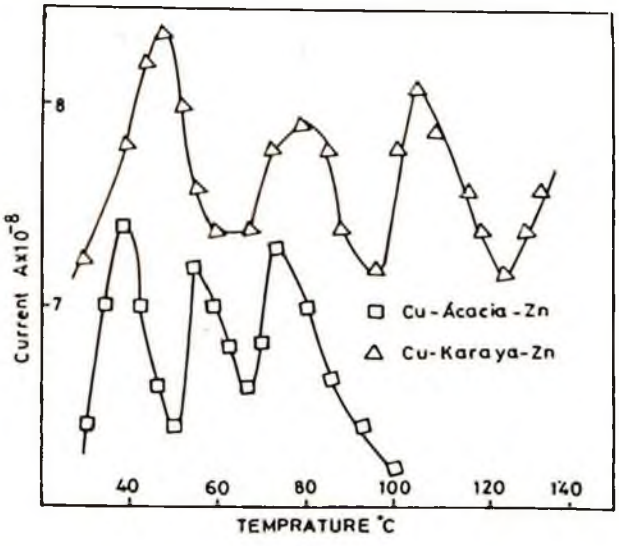


Fig.5 SCE versus temperature, for Cu-gum-Zn

Cu-Acacia-Ni and Cu-Karaya-Ni both gave 4 pea each, with currents of the order of 10^{-8} A (Fig.6

Current during repeated heatings

The current was found to be reproducible when t sample with the same electrodes was heated aga after a long gap of interval after the first hea ing. When this interval was small, the curren were low (Fig.1 & 3). The peaks were obtained both the gums in every heating experiment but th were distinct when the time interval between t successive experiments was large. The peak temp rature after successive heatings either remain unchanged or it changed in an irregular manner.

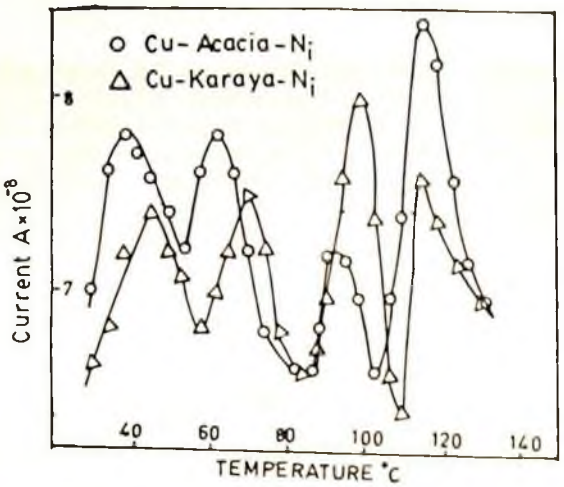


Fig. 6 SCE vs temperature Cu-gum-Ni

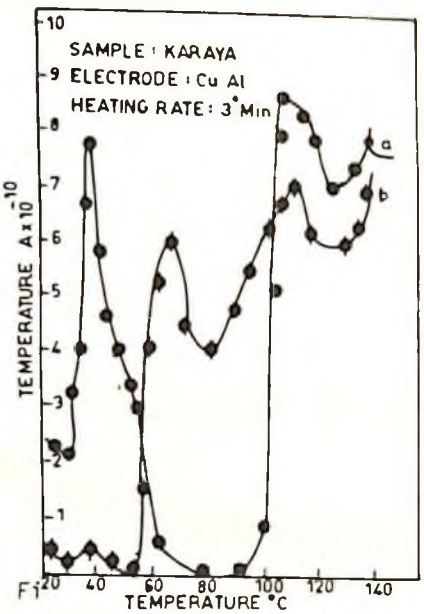


Fig.7 SCE Versus Temperature [Karaya]

a)First heating
b)Heating after 36 hrs.

DISCUSSION

Acacia and Karaya exudates are hygroscopic acidic salts of complex polysaccarides containing Ca^{++}, Mg^{++} and K^{+} ions. These possess irregular flexible chains with carboxyl chains of uronic acids distributed along the chain [3]. During heating, these units come in close contact with the eletrodes of different work functions. A potential difference set up depends on the difference in the work function. The magnitude of current and the peaks thus obtained depend on the number of glycosidal bonds broken and corresponding change in the degree of ionization[7] due to release of absorbed water inside these bonds. In this way the average distance between the charge centres in polymar chain increases, the coulombic repulsion between the charge centres decreases and the polymer chain gets coiled up. This causes an increase or decrease in viscosity of the sample irregularly.

This coiling up of the chain and corresponding breaking of the glycosidal bonds and consequent release of the imbibed water causes different peaks of current with heating. Arabates of Ca^{++}, Mg^{++} and K^{+} present in the gums which migrate towards the electrode and cause irregular change in the molecular arrangements in the gums and hence the peak temperature varied with heating rates.

During rapid heating, the glycosidal bonds have been found to break and release imbibed water. It appears that Ca^{++}, Mg^{++} and K^{+} - play an active role of charge carriers and they orient towards the main chain of carboxylic group; the current is found to increase. Fukuda [6] has found such currents due to rotation of hydroxyl groups in the molecular chains of cellulose. Number of peaks increase as the heating rate decreases.

These current peaks and the shift in the temperature with heating rates resemble the thermally stimulated discharge current. In this case, a current is observed in the external circuit when the polymers are polarized and heated at a uniform rate. This current cannot be reproduced in repeated heating of the same sample.

The spontaneous current emission reported here is not due to the existance of any thermal gradient across the dielectric. This cannot be due to depolarization of any previously existing polarization as in the case in thermal stimulated discharge current because it is found that reversal of the pellet with respect to the electrodes does not change the direction of the current. It is therefore clear that imbibed water (under uniform heating rate) releases Ca^{++}, Mg^{++} and K^{+}as charge carries which come up to the pellet electrode interface to generate an electrochemical reaction. Current growth continues until these orient along the main chain, hence the current peak is observed.

Current was found to be reproducible in successive heatings and peak was obtained where there was longer time interval between two heatings. The magnitude of the current in successive heating too depended on the time interval. Curve of a similar shape in every heating seemed to be due to the absorbed water. Magnitude of the current was found to be very small if the sample was heated soon after one heating was over (i.e. after one or two hours) indicating dependence of the current on water content. After longer gap between two heatings, gum absorbed some moisture from atmosphere thus giving increase in the magnitude of the current. This was verified with a simple experiment. Gum sample was moistened, kept in contact with Cu - Al system of electrodes and current was measured. Steady current of the order of 10^{-5}A was found to decay at a slow rate. After 24 hours, the current diminished to a low value but as soon as a few drops of water were added, nearly the

same magnitude of current decaying with the same rate was observed with a slight change, in both the samples. This proves that the generation of current is based on some chemical reaction between absorbed water, gum material and electrode in contact. Reasons for this may be one or more of the following:-

(a) Water helped in transporting or conducting (nonohmic) charge carriers through the gum polysaccharides.

(b) Water stimulated the electrochemical reaction which produces charge carriers.

(c) Water itself took part in the overall electrochemical reaction and produced charge carriers species.

(d) Arabic acid naturally present in gum, ionised the released imbibed water thus Ca^{++} , Mg^{++} , K^{+} charge carriers generated.

(e) On breaking of the glycosidal bonds, the moistened electrode - interface came in close contact with water molecules, dissolved molecules and hydrogen ions (H^{+}). Thus as described by Reddy [8] the metal surface may acquire a net positive or negative charge due to electron transfer between metal and ions.

(Viz. :- $2H^{+} + 2e \longrightarrow H_2$
and in opposite direction :-
$H_2 \longrightarrow 2H^{+} + 2e$
in the water protective film inside the exudates).

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