Asian Journal of Chemistry Vol. 19, No. 1 (2007), 213–218

Electrochemical Kinetic Study of *Calotropis procera*

P.K. SINGH*, RAMA AGRAWAL†, M.U. KHAN†, SUNIL K. NIGAM†
and SHAHNAJ KHAN†
Department of Chemistry, S.G.S. Government College, Sidhi-486 661, India

Electrochemical kinetic study of *Calotropis procera* (verna: *madar*) of the family Asclepiadaceae has been carried out with electrode pair Ag-Zn in three different seasons. The reaction showed first to zero order rate dependence and also indicated complex nature of oscillatory reaction occurring in the system, obeying redox process. Various amino acids were analyzed. The zwitter ions of proteins present in the sap are fully responsible for flow of current due to charge transfer. A plausible mechanism based on rate law was proposed and thermodynamic parameters evaluated.

Key Words: Plausible, Zwitter ions, Electrophytogram, Charge transfer enhance.

INTRODUCTION

Oxidation kinetics of natural products are quite important from technological and synthetic points of view. The present age is aptly the age of electricity. Most of the energy sources are not yet available for exploitation. The reserve of fossil fuel is limited. The xerophytic plants (medicinal and aromatic) as a good source of ionic potential can be used for pharmaceutical, perfumery, cosmetics, flavour, food in agrochemical industries and electrochemistry[1]. The investigation emphasizes on the thermodynamics, kinetics and mechanism of biological electron transfer which are responsible for enhancing activity[2, 3] and giving impetus to social forestry. It enables one to study ionic reactions occurring at an electrode surface. The potential manifested in a biosystem has been studied in three seasons, *viz.*, rainy, winter and summer, in terms of energy of activation. Bose[4] proved experimentally the movements of ions in plants associated with electromagnetic waves. The plants are very sensitive to light showing transport phenomenon of ions. Thus in order to study the secrets of plants and the kinetics of their tissues present in the sap, the authors have taken this task for exploration.

†Department of Chemistry, Government Model Science College, Rewa-486 001, India.

EXPERIMENTAL

Calotropis procera is a wild shrub used in medicinal science in the treatment of dysentery and is also a strong purgative. The fresh leaf is plucked, processed and after removing epidermis, it is cut into the size of 2 cm × 2 cm dimension of electrodes. The bio-emf cell is constructed by sandwiching the injured leaf between two employed electrodes Ag-Zn as shown in the circuit diagram *in vitro* condition (Fig. 1). The pH, conductivity of bio-sap, number of cells were determined by digital pH-meter with highly sophisticated electronic based apparatus and microscope respectively. The pigments, free amino acids, were identified chromatographically. All the electrical measurements have been made through digital panel meter (UNI-T, Model DT 830 B) with an accuracy of ± 0.1% and analyses have been carried out statistically by computer.

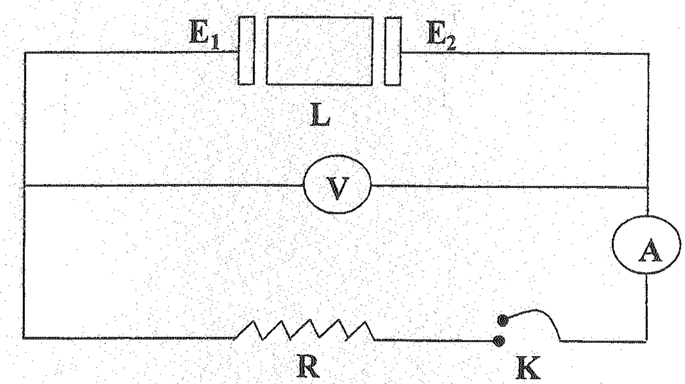

Fig. 1. Circuit diagram of bio-cell *in vitro* condition (E_1 and E_2 = electrodes; R = resistance; K = key; A = ammeter; V = voltmeter; L = leaf piece)

RESULTS AND DISCUSSION

The origin of electrode potential depends upon the availability of ions and permeability of surface cuticle of the leaf, *i.e.*, movement of ions. Although the epidermis of *Calotropis procera* is not stiff and waxy yet it allows ease of movement of ions. The kinetic study has been carried out in summer, rainy and winter seasons at different periods: morning (06.00 am), noon (12.00 am), evening (06.00 pm) and midnight (12.00 pm). The highest potential for *Calotropis procera* was observed during rainy season (1030 mV) and lowest in summer season (620 mV). The fluctuations are due to varying temperature in different seasons. $CuSO_4$ (divalent) acts as deactivator, whereas NaCl, KCl (monovalent) and $C_6H_{12}O_6$ as respirators increase the kinetic rate during the study of the salt effect. This is due to ionic contribution in charge transfer reaction.

The plots of log (a – x) *vs.* time and log a/(a – x) *vs.* time (Table-1, Figs. 2 and 3) clearly indicate that the redox process follows the first order kinetics and as potential goes on decreasing, it behaves as fractional to zero order and becomes very complicated due to the occurrence of oscillatory reactions.

TABLE-1
TYPICAL KINETIC STUDY

Biosystem: *Calotropis procera* Electrode pair: Ag-Zn
Season: Summer Temp.: 308 K

S.No.	Time (s)	OCV (mV)	$k \times 10^{-6}$ (s^{-1})
1.	0	935	
2.	64800	820	1.990
3.	129600	600	3.376
4.	216000	419	3.625
5.	302400	309	3.655
6.	345600	206	4.331

OCV (open circuit voltage); Average $k = 3.395 \times 10^{-6} (s^{-1})$;
Graphical $k = \pm 3.385 \times 10^{-6}$ (s^{-1})

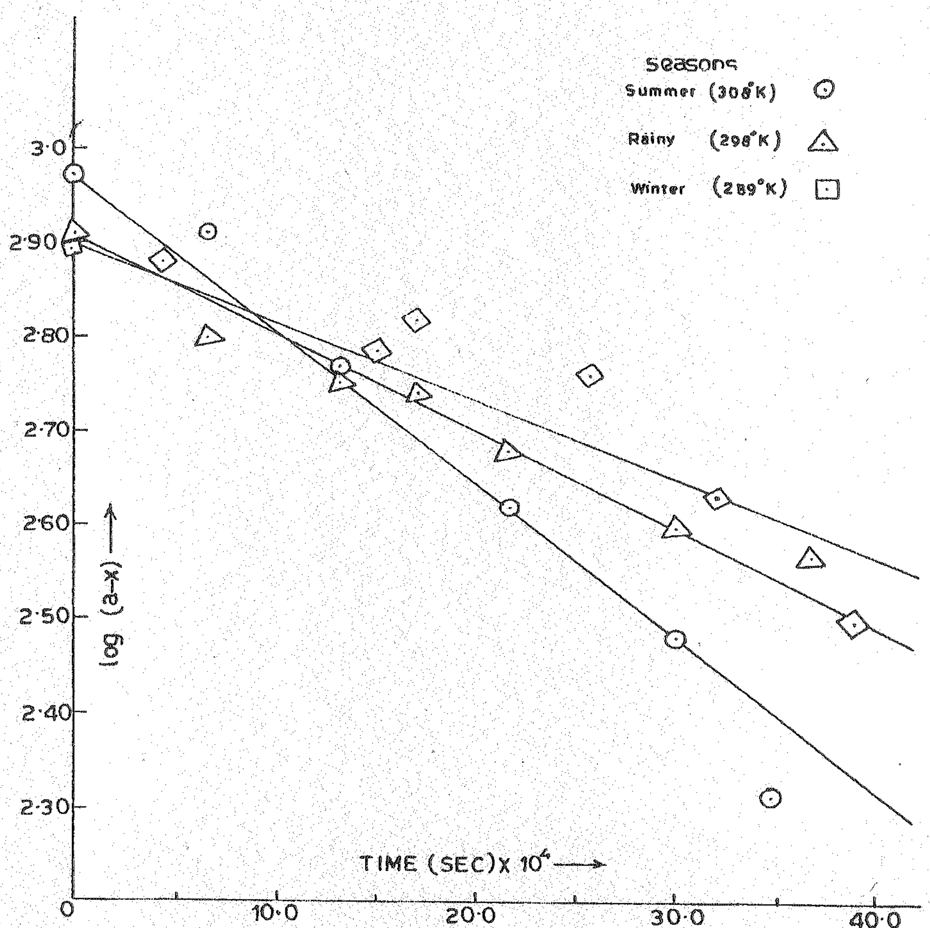

Fig. 2. Dependence of rate on variation of seasons of *Calotropis procera*

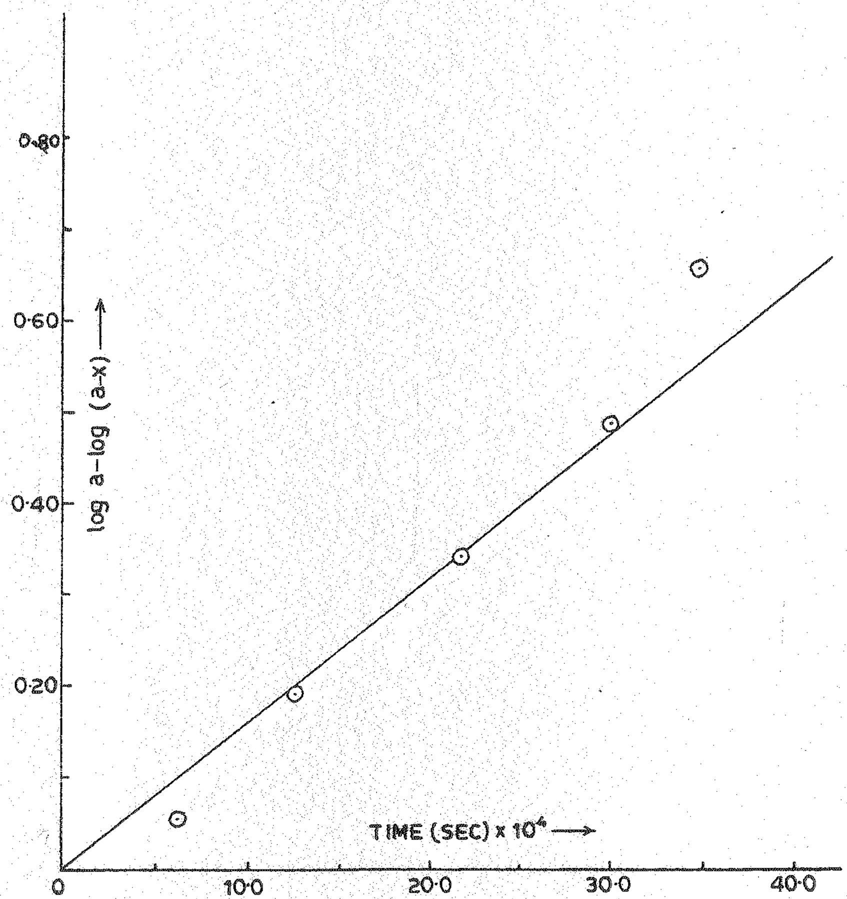

Fig. 3. Showing plot of log a (a – x) *vs.* time of *Calotropis procera* for summer season (Electron-pair: Ag-Zn; Seadon: summer; Temperature: 308 K)

The rate constant has been evaluated graphically and by integration method selecting their peak values. It is observed that when the system is injured, it contains multi-layers of waxy food materials deposited around the sap heavily cutinized showing considerably less water loss; such surface of leaf is shiny and reflects much of solar radiations falling on it, being photosensitive. It is found that rate of healing is equal to rate of injury at equilibrium. The present study shows a higher potential during injury of the system at the site of leaf. There would be rushing of ions towards the site of injury for healing process and thus higher potential is created. This is due to rushing up of trips of tissues during injury forming a contusion in the system where biomass is being collected. This causes rise in peaks as electron is withdrawn by oxidation. It steadily decreases due to reduction, during the lag time, when another trip of tissue reaches there, this process goes an continuously so long as tissues are there in the fuel cells; it stops giving null potential when asymptotically it becomes zero. The authors have revealed that the number of tissues will be proportional to the potential. The presence of humidity makes the ionic transport phenomenon more prolific. The detached leaf loses its supply of water and other required bio-fluid flow from the mother body; on increasing the temperature, the rate becomes faster and slowed down by reducing it. The physical parameters such as pH, conductivity, number of fuel cells, photosynthesis play a very important role during the kinetic study. The rate is highest in the morning, because when the sun rises, the mesophyll cell of leaf gets activated, *i.e.*, movement of Na^+ and K^+ ions becomes very fast as photosynthesis starts.

Mechanism

The chemical reactions which are known to occur during photosynthesis[5] for the growth and building up of damaged tissues are as under :

$$6CO_2 + 6H_2O \xrightarrow{\text{light}} (CH_2O)_6 + 6O_2$$

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 12H^+ + 12e^- + 686 \text{ kcal} + 3O_2$$

$$12H^+ + 3O_2 \longrightarrow 6H_2O$$

According to quantum theory, photon of light is observed by chrollophyll atom in the low energy state and electron is pushed to higher energy state, due to migratory movement of ions from one hole to another; this causes increase in rate during photic excitation[6]. Besides this, swelling and shrinking of chloroplast has also been observed across the membrane[7]. Due to flow of electrons, the synthesis of ATP takes place which is electrochemical in nature. During redox process the amino acids present in the sap of biosystem form dipolar zwitter ions showing transfer of charge responsible for flow of current, forming equally into cations and anions; therefore, the rate expression may be derived as:

$$\text{Amino acid} \xrightleftharpoons{K} \text{Zwitter ion} \quad (1)$$

$$\text{Zwitter ion} \xrightarrow{k_1} \text{Cation} \quad (2)$$

$$\text{Zwitter ion} \xrightarrow{k_2} \text{Anion} \quad (3)$$

$$\text{Rate} = K[\text{Amino acid}](k_1 + k_2) \quad (4)$$

There are so many factors which affect the rate of biosystem. The younger cells increase the rate of permeability for water and ions whereas the older cells hinder the physiological process reducing conductance and ionic potential. The complexity develops in the system due to waves coming from different directions spread over the system in the form of a matrix network. During redox process between electrode and biomass of sap (electrolyte) there is formation of an electrical double layer.

The various physical and thermodynamic parameters have been determined (Tables 2 and 3).

TABLE-2
PHYSICAL PARAMTERS

Biosystem	Weight of leaf before treatment	pH value	Conductivity (μmhos)
Calotropis procera	1.70 g	6.97	4.8×10^{-3}

TABLE-3
THERMODYNAMIC PARAMETERS

Biosystem	E_a (kJ)	A (s^{-1})	$\Delta H^{\#}$ (kJ)	$\Delta G^{\#}$ (kJ)	$-\Delta S^{\#}$ (J K)
Calotropis procera	27.37	1.53×10^{-1}	2454	104.84	64.29

Conclusion

The plants are a good source of low cost energy which may solve not only the energy crisis coming in future, but also will pave the way for social forestry. It will create zeal for knowing the secrets of plants maintaining the environmental and ecological balance on the earth. The study will give a new momentum and dimensions to the electrochemist and the naturophilic environmental chemist.

REFERENCES

1. D.S. Bhakuni, Some Aspects of Aromatic and Medicinal Plants, p. 74 (1977).
2. J. Koryla and J. Dvorak, Principles of Electrochemistry, John Wiley & Sons (1987).
3. V.A. Shepherd, *Curr. Sci. (India)*, **77**, 189 (1999).
4. J.C. Bose, The Nervous Mechanism of Plants, Longmans, Green and Co., London (1926).
5. C.B.Van Niel, The Comparative Biochem. Photosynthesis, in: Frank and Loomis (Eds.), Photosynthesis in Plants, Iowa State College Press, Ames, Iowa, pp. 437, 449 (1949).
6. E.G. Weaver and H. Weaver, Electron Resonance Studies of Photosynthetic Systems, in: Giese (Ed.), Photo Physiology: Current Topics, Academic Press, New York, pp. 1–32 (1972).
7. L. Packer and D.W. Deamer, Studies on the Effect of Light on Chloroplast Structure, in: Giese (Ed.), Photo Physiology: Current Topics, Academic Press, New York, Vol. 3, pp. 99–122 (1968).
8. M.U. Khan, Ph.D. Thesis, A.P.S. University, Rewa, India (2001).

(*Received*: 10 August 2005; *Accepted:* 29 May 2006) AJC-4928