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Research Article

TSDC KINETICS IN DIPOLE RELAXATION OF THE L-ASPARAGINE MONOHYDRATE

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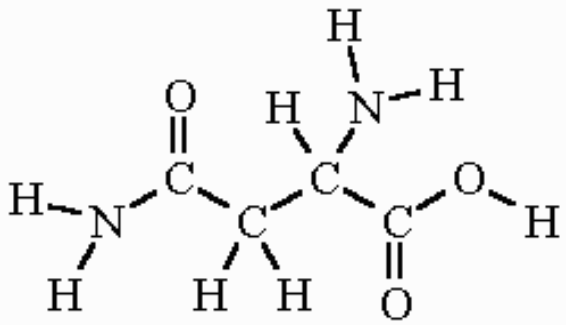
ABSTRACT
In the present paper order of kinetics parameter is evaluated from experimentally reported thermally stimulated depolarization current (TSDC) measurement of L-asparagine monohydrate sample. We report results of our investigation on the effect of heating cooling cycle that the L-asparagine monohydrate sample undergoes while performing the TSDC measurement. Here a new method of analysis has been used to analyze the reported depolarization data. L-asparagine monohydrate is one of the 20 most common natural amino acids in living organism. The TSDC characterization of the L-asparagine monohydrate have shown important results regarding its importance in biology, food, biomedicine and drugs.

Keywords*: Thermally Stimulated Depolarization Current, L-Asparagine Monohydrate, Activation Energy, Relaxation Time, Order Of Kinetics,Amino Acids.*

INTRODUCTION

The building blocks of Proteins are amino acids which are organic in nature. A carboxyl group and a side chain, the various functional groups that comprise the side chain give each amino acid distinct physical properties that influence protein formation and function. Understanding these physical properties, including charge, solubility and pKa aid in designing peptide sequences those are optimized for high synthesis yield and purity. Amino acids are among the simplest organic molecules of biological relevance and they serve as convenient model for studies of biological materials. Asparagine, an amino acid closely related to aspartic acid, and an important component of proteins. First isolated from asparagus, from which its name is derived, asparagine is widely distributed in plant proteins. It is one of several so-called nonessential amino acids in warm-blooded animals: they can synthesize it from aspartic acid. The chemical structure of asparagine is



Asparagine is one of the eleven nonessential amino acids which the body can synthesize for itself and are not essential for human diet. It is very important because it plays a role in metabolic control of some cell functions in nerve and brain tissue and is also used in plants as nitrogen reserve source(Lund 1981)besides this being part of different drug and food. L-asparagine monohydrate (LAM) single crystals have chemical formula $C_4H_8N_2O_3.H_2O$ and orthorhombic in structure(Verbist *et. al.,* 1972).L-asparagine monohydrate for certain properties of importance have studied by several workers (Moreno *et. al.,* 1999, Kripal *et. al.,* 2007, Casado *et. al.,* 1995, Moreno *et. al.,* 1997, Guarini *et. al.,* 1998, Arnold *et. al.,* 2000,

Neacsu *et. al.*, 2008, Bento *et. al.*, 2007, Hutchens *et. al.*, 1963, Close *et. al.*, 1977and Higman *et. al.*, 2004).

In this paper in order to characterize L-asparagine monohydrate we reconsider the experimentally reported thermally stimulated depolarization current (TSDC) data of the material in view of a new proposed method of analysis.

MATERIALS AND METHODS

Method of Analysis:

In reorientation of impurity vacancy dipoles, depolarization current (I) is generally given by the relation (Chen et. Al.1981 and McKeever 1988)

$$I = \frac{Q_0}{\tau_0}\exp[-\frac{E_a}{k\,T} - \frac{1}{b\,\tau_0}\int_{T_0}^{T}\exp\left(-\frac{E_a}{k\,T'}\right)dT'] \quad \ldots (1)$$

and the expression for peak temperature is given by

$$T_m^2 = \frac{b\,E_a\tau_m}{k} \quad \ldots (2)$$

where Q_o is the total charge released during TSDC run, τ_o is the fundamental relaxationtime or the relaxation time at infinite temperature given by Arrhenius relation(Arrhenius 1889) as

$$\tau = \tau_0\exp[\frac{E_a}{kT}] \quad \ldots (3)$$

where τ is the relaxation time at T , k the Boltzmann's constant and E_a the activation energy for the orientation of IV dipole, b is the linear heating rate, T_o is the temperature where from TSDC curve starts to appear, $\acute{T}'$ is any temperature between T_0 to T and τ_m is relaxation time at peak temperature T_m. As per these equations the experimentally reported (Jain et. al. 2010)activation energy and relaxation time of thermally stimulated depolarization spectrum of L-asparagine monohydrate are given in Table.1.The evaluated values of E_a and τ_o by Jain *et. al.*, are expected to satisfy eq.(2). However, it has been observed from column 5 and 6 of Table.1, that evaluated
values of E_a and τ_o do not satisfy eq. (2) in general.

In order to remove this anomaly, Prakash (2013) suggested a model, according to which, the depolarization current is given by equation

$$I = \frac{Q_0}{\ell\,\tau_0}\exp[-\frac{E_a}{k\,T} - \frac{1}{b\,\ell\,\tau_0}\int_{T_0}^{T}\exp(-\frac{E_a}{k\,T'})dT'] \quad \ldots (4)$$

Whereℓ is order of kinetics, and peak temperature relation is modified as

$$T_m^2 = \frac{\ell\,b\,E_a\tau_m}{k} \quad \ldots (5)$$

RESULTS AND DISCUSSION

The TSDC experiments were performed by Jain et. al.(2010) using a TSDC setup designed and developed by them and fabricated locally. In their experiments TSDC spectra were obtained on poly crystalline L-asparagine mono-hydrate pellets of 15mm diameter and 1mm thickness. Global TSDC spectra of L-asparagine monohydrate, as reported experimentally (Jain *et. al.*, 2010) have been taken with polarizing fields E_p = 1x10^5 V/m and 2x10^5 V/m and are shown in Figure 1. The other parameters polarizing temperature T_p = 320 K, polarizing time t_p = 20 min and heating rate b = 5.5 K/min were the same for both the spectra.

They have analyzed the nature of low temperature (LT) peak (217K) in details by taking the TSDC spectrum for temperature range 100 K-300 K with parameter T_p= 250 K, E_p=1-3.5kV/cm, t_p=20 min, b=5.5 K/min as shown in Fig.2. With increase in electric field, polarization increases linearly indicating the dipolar nature of the peak. They also have done thermal windowing TSDC of this peak as shown in

Figure 3. Relaxation parameters for thermal windowing TSDC are also calculated by Jain *et. al.*, (2010) and tabulated in Table 1.

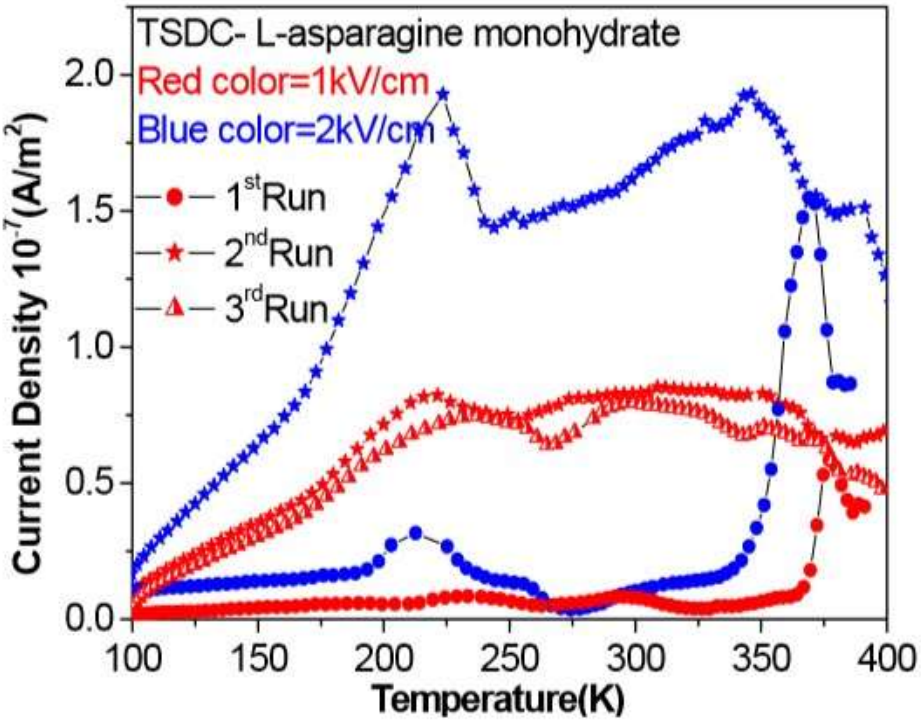


Figure 1: Global TSDC spectra of L-asparagine monohydrate (Jain *et. al.* 2010).

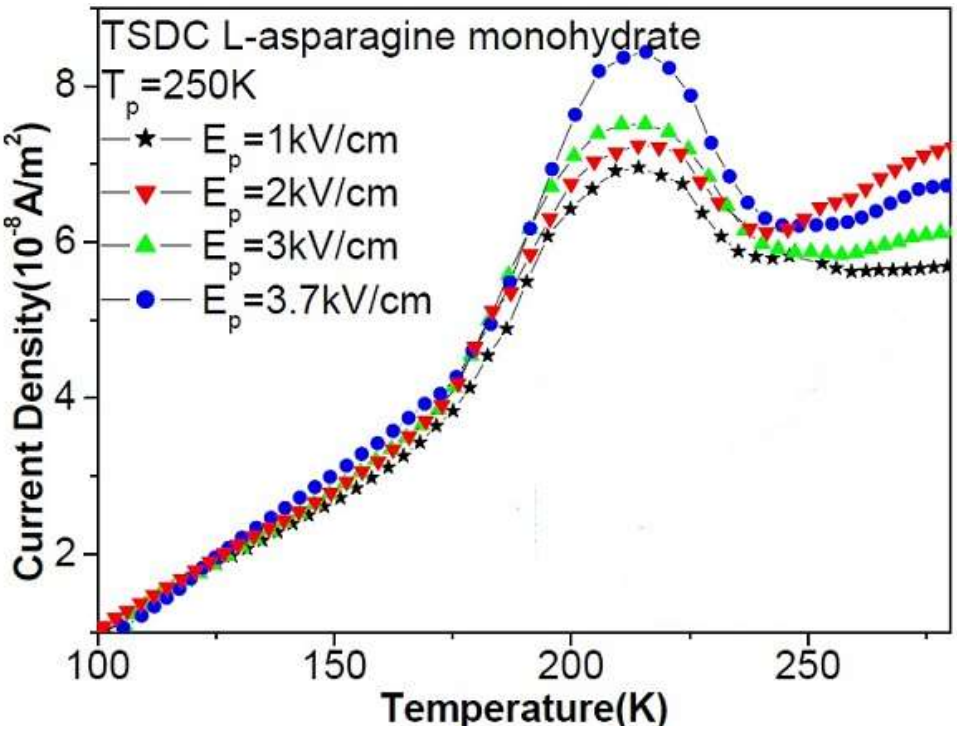


Figure 2: LT peak TSDC spectra at different Ep (Jain et. al.2010).

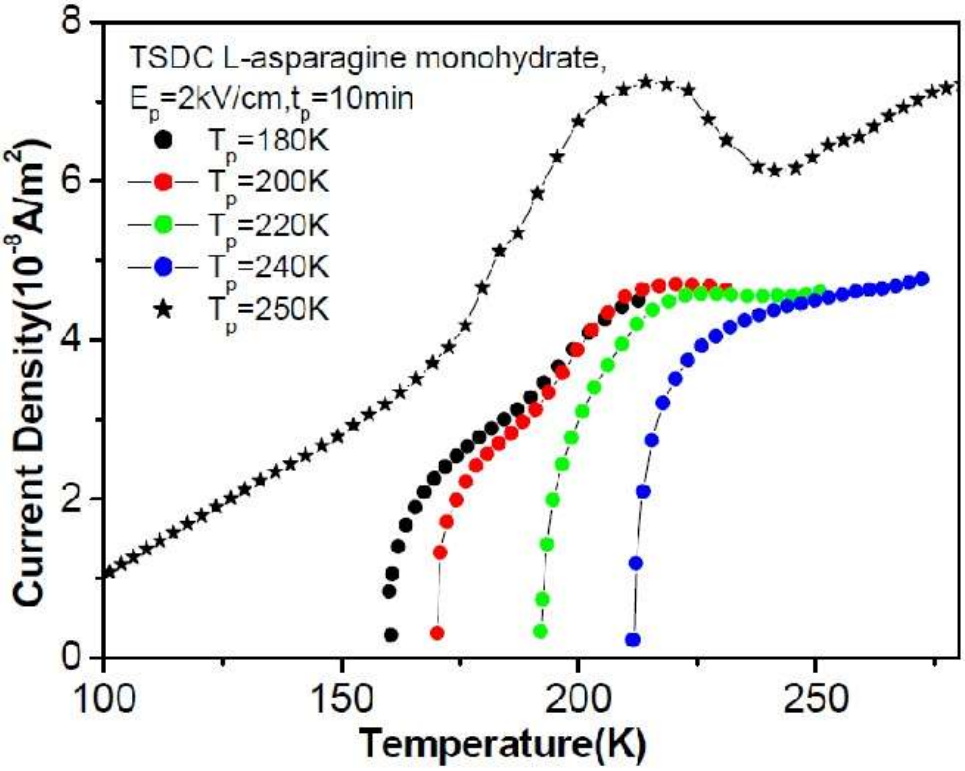


Figure 3: TSDC spectrum of L-asparagine monohydrate after thermal window (Jain et. al.2010).

As per the method of analysis proposed by Prakash, Order of kinetics (**ℓ**) parameter is calculated from reported values of activation energy E_a and relaxation time τ_0 as per equation (5) and is presented in Table.1. Concept of Orders of kinetics parameter came from similarities between TSDC and thermoluminescence (TL) processes as these both processes are studied on same specimen by Bucci *et. al.*, (1966).

Table 1: Experimentally Reported (Jain et. al.2010) values of E_a, τ_0, T_m and evaluated values of order of kinetics ℓ.

L-asparagine monohydrate	**E_a (eV)**	**τ_0 (s)**	**T_m (K)**	**T_m^2 (K^2)**	**$\frac{b\,E_a\tau_m}{k}$ (K^2)**	**ℓ**
LT peak TSDC spectra	0.1	5.00E-03	217	47089	111.5409	422.168
	0.3	4.00E-06	314	98596	83.07503	1186.831
	1.2	3.00E-18	369	136161	92.78096	1467.553
After thermal window TSDC spectra	0.05	3.00E-01	212	44944	246.0677	182.6489
	0.07	1.40E-01	220	48400	417.8303	115.8365
	0.12	1.00E-03	222	49284	67.49119	730.2287
	0.05	2.00E-01	214	45796	159.9036	286.3976

Conclusion

As per the new method of analysis the activation energy and fundamental relaxation time are found as characteristic features of the specimen of the material under consideration, whereas order of kinetic parameter is dependent on experimental conditions like rate of rapid cooling. The experimental conditions of polarization for getting frozen-in polarized dipoles decides the order of kinetics involved. It is because of this reason that different TSDC runs recorded on the same specimen givedifferent values of order of kinetics as can be seen from table. The TSDC studies of the L-asparagine monohydrate have shown important results on an amino acid of importance in biology, food, biomedicine and drugs.The evaluated parameter may be quite helpful in better understanding of the property of the material under consideration.

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REFERENCES

Arnold W D, Sanders L K, McMahon M T, olkov A V, Wu G, Coppens P, Wilson S R, Godbout N and Oldfield E (2000). Experimental, Hartree-Fock, and density functional theory investigations of chargedensity, dipole moment, electrostatic potential and electric field gradients in L-asparagine monohydrate. *Journal of American Chemical Society* **122** 4708-4717.

Arrhenius S (1889). About the reaction rate during the inversion of cane sugar by acids. *Zeitschrift für Physikalische Chemie* 226-248.

Bento I C V, Freire P T C, Melo F E A, Mendes-Filho J, Moreno A J D, Joya M R and Pizani P S (2007). High temperature phase transition in monohydrated L-asparagine crystal. *Solid State Communications* 141 29-32.

Bucci C, Fieschi R and Guidi G (1966). Ionic Thermocurrents in Dielectrics. *Physics Review* 148816-823.

Casado J, Ramirez F J, and Navarrete J T L (1995). Vibrational spectra andassignments of amino acid L-asparagine. *Journal of Molecular Structure* **34** 957-60.

Chen R and Kirsch Y (1981). Analysis of thermally stimulated processes (Pergamon Press, New York).

Close D M, Fouse G W and Bernard W A (1977). ESR and ENDOR study of single crystals of L-asparagine.H2O x-irradiated at room temperature. *Journal of Chemical Physics* **66** 1534-1540.

Guarini G G T and Dei L (1998). Kinetics and mechanism of the thermal dehydration of l. asparagine monohydrate microcrystals and single crystals: Role of aging. *Thermochimica Acta* **311** 129-140.

Higman V A, Boyd J, Smith L J and Redfield C (2004). Asparagine and glutamine side-chain conformation in solution and crystal: A comparison for hen egg-white lysozyme using residual dipolar couplings. *Journal of Biomolecular NMR* **30** 327-346.

Hutchens J O, Cole A G, Robie R A and Stout J W (1963). Heat capacities from 11 to 305 K, entropies and free energies of formation of L-asparagine monohydrate, L-aspartic acid, L-glutamic acid and L-glutamine. *Journal of Biological Chemistry* **238** 2407-2412.

Jain D, Sharath Chandra L S, Bharadwaj S, Anwar S, Ganesan V, Lalla N P, Awasthi A M and Kripal R and Singh P (2007). EPR and optical absorption studies of VO^{2+}ions in L-asparagine and monohydrate Solid State Comm 142 412-416.

Lund P (1981). Nitrogen Metabolism in Mammalian. *Applied Science*, Barking.

McKeever S W S (1988). Thermoluminescence of solids (Cambridge University Press, Cambridge).

Moreno A J D, Freire P T C, Guedes I, Melo F E A, Mendes -Filhoand J.A. Sanjurjo (1999). Raman scattering studies of Monohydrated L-Asparagine. *Brazilian Journal of Physics* 29 380-387.

Moreno A J D, Freire P T C, Melo F E A, Aroujo Silva M A, Guedes I, and Mendes -Filho J (1997). Pressure induced phase transitions in monohydrated l-asparagine amino acid crystals. *Solid State Communications* 103 655-658.

Nath R (2010). Thermally Stimulated Depolarization Current Studies of Relaxation in L-Asparagine Monohydrate. *IEEE Transactions on Dielectrics and Electrical Insulation* **17** 4 1128-1134.

Neacsu A, Contineanu I, Popa V T and Contineanu M (2008). Dehydrationof irradiated and non-irradiated L-α asparagine monohydrate Part I, Isothermal kinetics. *Journal of Thermal Analysis and Calorimetry* **94** 405-410.

Prakash J (2013). A model for the occurrence and analysis of ionic thermocurrent spectrum involving different orders of kinetics. *Pramana Journal of Physics* **80** 1 143-158.

Verbist J J, Lehman M S, Koetza T F and Hamilton W C (1972). Precision neutron diffraction structure determination of protein and nucleic acid components. VI. The crystal and molecular structure of the amino acid L-asparagine monohydrate. *Acta Crystallographica, B* **28** 3006- 3013.