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Research Article

DIELECTRIC RELAXATION KINETICS OF WATER IN BIOMOLECULES

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ABSTRACT
In the present paper we reconsider the already reported experimental study of thermally stimulated depolarization of red oak seeds, having two different water contents, to estimate the order of kinetics involved. The evaluation of order of kinetics follows the new model introduced by Prakash and is depends on experimental conditions. It is evaluated for all the resolved peaks of different thermally stimulated depolarization spectrums. The order of kinetics along with the reported dielectric relaxation parameters help in explaining the biological and physical nature of material under consideration regarding investigation of mode of hydration in biological systems. This study provides information concerning the mobility and rotational freedom of hydration water, hydration sites, and mechanisms.

Keywords: *Thermally Stimulated Depolarization, Dielectric Relaxation Parameters, Orders of Kinetics, Water Content*

INTRODUCTION
Intracellular water, which comprises 80% mass of most living cells, has been the focus of most investigations. The Properties of water in biological systems were studied extensively by means of different physical techniques like isothermal sorption measurement (Schneider and Schneider, 1972; Clegg, 1978; Lusher-Mattli and Ruegg, 1982; Rupley *et al.,* 1983), calorimetric method (Ruegg *et al.,* 1975; Bakradze and Balla, 1983; Vertucci, 1990), infrared and Raman spectroscopy (Careri *et al.,* 1979; Luck, 1985; Cameron *et al.,* 1988), nuclear magnetic resonance (NMR) spectroscopy (Mathur-de Vre R, 1979; Seewaldt *et al.,* 1981; Rorschach and Hazlewood, 1986; Ratkovic, 1987), quasi-elastic neutron-scattering spectroscopy (Lehmann, 1984; Trantham *et al.,* 1984), and dielectric relaxation techniques (Harvey and Hoekstra, 1972; Kamiyoshi and Kudo, 1978; Clegg *et al.,* 1982; Pissis *et al.,* 1987; Bruni and Leopold, 1992; Pissis *et al.,* 1996). With the help of these different techniques of study we are able to explain the complex nature water in biological systems. The various properties and structures of macromolecules and membranes are explored by interfacial water which is close to macromolecules and membranes. As the water molecules are part of biological network interfaces they are dynamically oriented and exhibit restricted motion and consequently the mobility and the ordering of water molecules are very different from those of pure bulk or "free" water. Changes in thermodynamic and motional properties of water at different hydration levels indicate the existence of different fractions of water, which may vary in structures and properties and presumably play different biological roles. Isothermal sorption measurements showed the presence of three hydration regions: a strong water-binding region at low water content (WC), a weak binding region at intermediate WC, and a very loose binding region at high WC (Clegg1978; Vertucci and Leopold 1987). The thermally stimulated depolarization current (TSDC) technique is a powerful tool for investigating the mode of hydration in biological systems. This technique is capable of providing information concerning the mobility and rotational freedom of hydration water, hydration sites, and mechanisms (Mascarenhas 1980; Pissis *et al.,* 1987; Bruni and Leopold, 1992; Pissis *et al.,* 1996). TSDC is based upon the dependence of the micro dynamics of water dielectric relaxation on their surroundings resulting in different dielectric relaxation times for water in different fractions, and on the influence of water on the dielectric relaxation mechanisms of other biomolecules. TSDC is a very sensitive technique and able to detect small amounts of water in different phases, and to measure dipole concentration as low as 0.1 ppm can be measured accurately (Pissis *et al.,*

1991). Sun (2000) in his study investigated the dielectric relaxation properties of water and water-plasticized biomolecules in red oak (*Quercus rubra*) seeds. In present study order of kinetics for already reported TSDC study of red oak material is evaluated which may offers some more valuable information insight into the organization of cellular water, molecular interactions between water and other bio molecules, and relationships between cytoplasmic viscosity, molecular mobility, and desiccation tolerance.

MATERIAL AND METHOD

Red oak (*Quercus rubra*) seeds are collected by Sun (2000) at the natural seed shedding period when WC declined to approximately 45% (i.e. approximately 0.8 g/g dry weight). Acorns are transversely cut into discs with a thickness of approximately 1.5 mm and a diameter of approximately 1.2 cm. Transverse sections are fully hydrated in distilled water, and then dehydrated to various WC by equilibrating over saturated solutions of NaCl (76% RH) and KCl (85% RH) at 5°C. WC of seed tissues decreased to approximately 0.16 g/g dry weight within 6 to 8 d in 76% RH. TSDC measurements were carried out by Wendell Q. Sun (2000) with a sample holder configuration and electrode arrangement that were described previously (Bruni and Leopold, 1992).

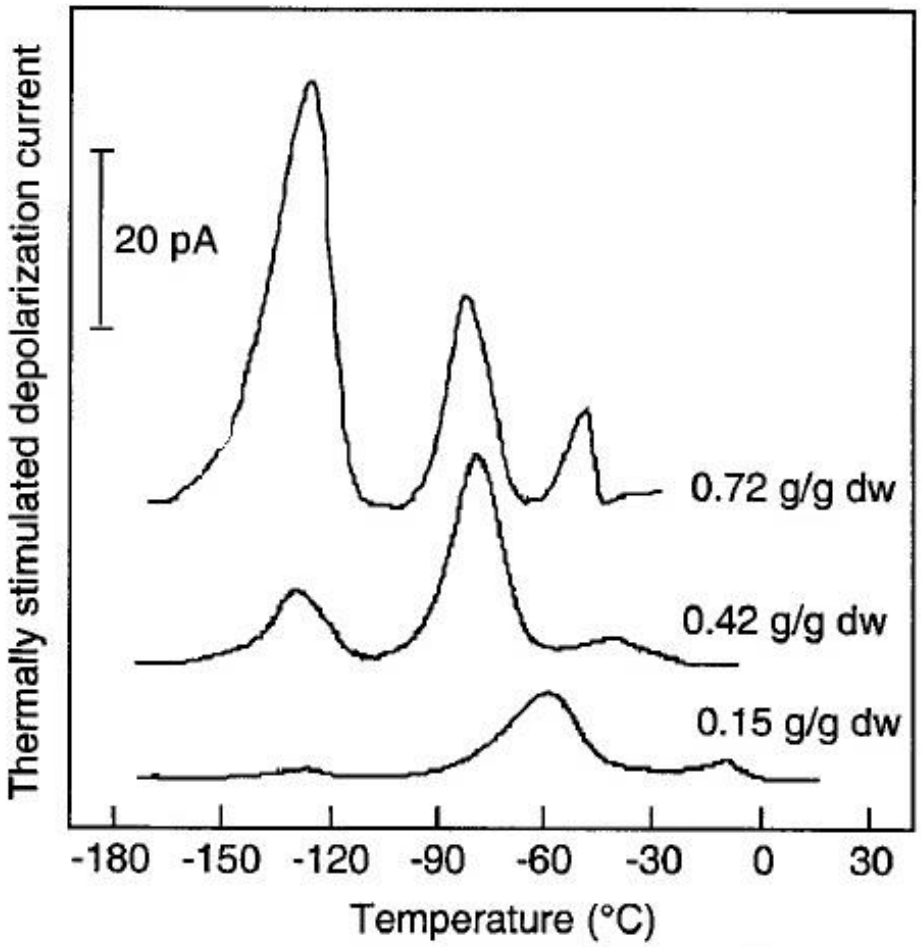

Fig.1 TSDC Spectrum for red oak seeds for different WC (Wendell Q. Sun, 2000).

The arrangement using insulating electrodes excluded the possibility of space charge relaxation of ionic origin (i.e. dc conductivity). For performing experiment, the sample was polarized by a direct electrical field of 3 kV/cm at approximately 22°C for 3 min, and rapidly cooled (>20°C/min) with liquid nitrogen to -180°C while the field was on.

TSDC was measured during warming at a constant rate of 3°C/min. After measurement, the sample was dried at approximately 95°C under vacuum for at least 24 h to determine its WC.
Sun (2000) used analysis method as suggested by Christodoulides *et al.*, (1988) and Bruni and Leopold (1992). In present work we estimate order of kinetics involved in different TSD spectrums of specimen under consideration.

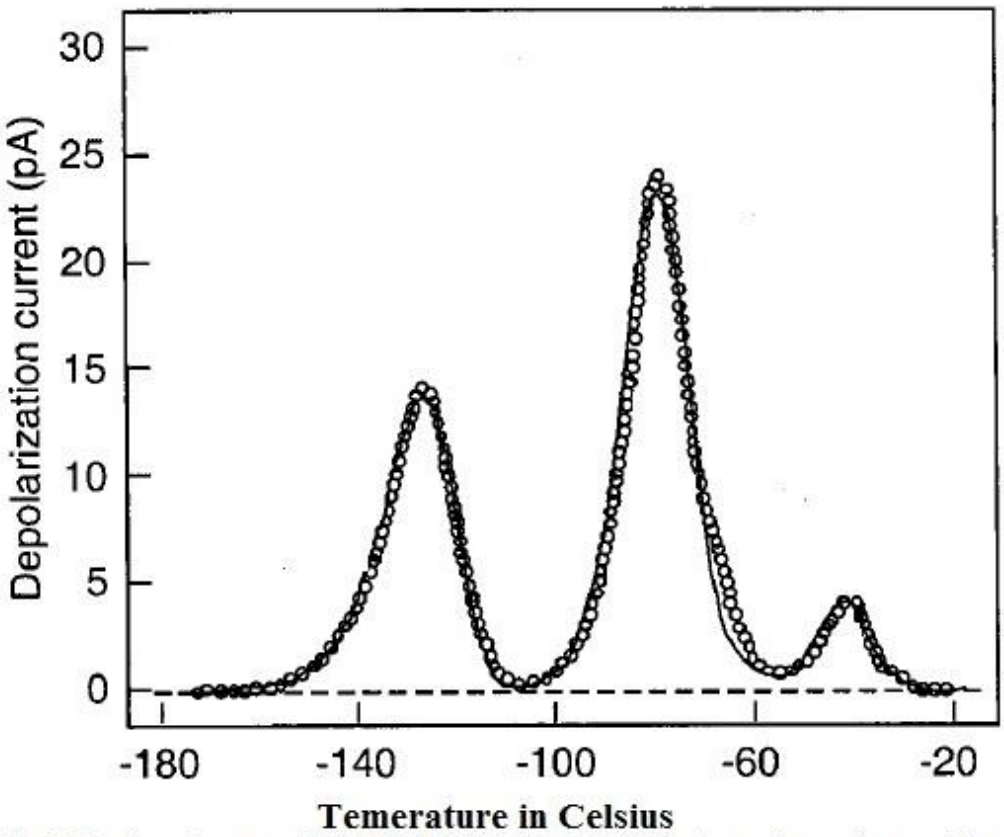

Fig.2 The iterative curve fitting of a TSD spectrum. Symbols are data points and the solid line represents the curve fitting. WC of the sample was 0.37 g/g dry weight (Wendell Q. Sun 2000).

RESULTS AND DISCUSSION

TSDC plots of red oak seeds as reported by Sun (2000) at different WC showed three dielectric dispersions as shown in Figure 1.
Conditions of TSDC experiments are, polarization dc field is 3 kV/cm; polarization temperature is approximately 22°C; polarization time is 3 min; and linear constant heating rate is 3°C/min. Three peaks are due to the dipolar disorientation.
The possibility that their occurrence was due to space charge relaxations of the ionic origin was excluded. The iterative curve fitting of a TSDC spectrum for two different water contents, i.e., 0.37 g/g and 0.10 g/g dry weights, are shown in Figure 2 and Figure 3, respectively. The different peaks of the spectrums are clearly resolved by iterative curve fitting method. Temperature dependence of dipole relaxation follows the Arrhenius equation (1989)

$$\tau(T) = \tau_0 \exp[\frac{E_a}{k\,T}] \qquad (1)$$

Where, τ_0 is the pre-exponential factor also known as fundamental relaxation time, E_a is activation energy for dipole reorientation, and *k* is the Boltzmann constant.

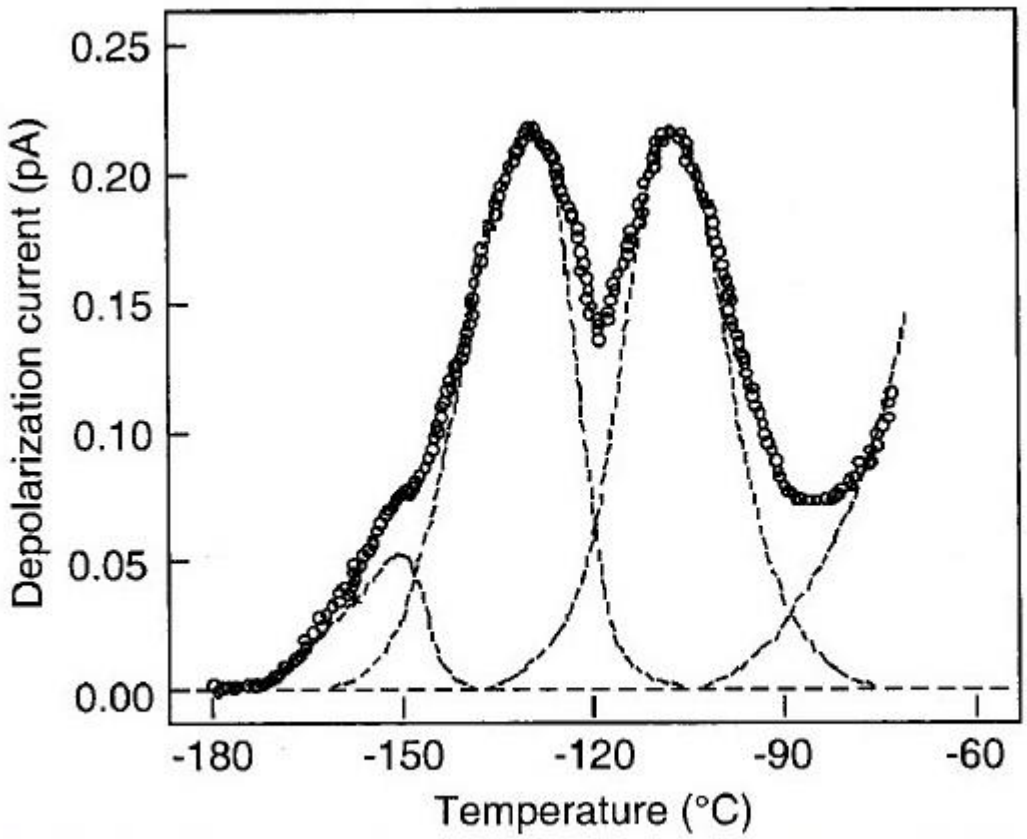

Fig.3 The TSD spectrum at the low-temperature region for a sample with WC 0.10 g/g dry weight. Symbols are data points and the solid line represents the curve fitting (Wendell Q. Sun 2000).

In the case of dipole disorientation with a single relaxation time, the depolarization current, *I*(*T*), is given by the following equation (Chen and Krisch, 1988)

$$I(T) = \frac{Q}{\tau_0}\exp\left(-\frac{E_a}{k\,T}\right)\exp[-\frac{1}{b\,\tau_0}\int_{T_0}^{T}\exp\left(-\frac{E_a}{k\,T'}\right)dT'] \quad (2)$$

Where, *Q* is the initial polarization (relaxation discharge, area under the peak), b is linear heating rate, and T_o is temperature at which depolarization current starts to appear. Dielectric relaxation parameters E_a and τ_0 are determined by mathematical approximation, suggested by Christodoulides *et al.*, (1988) and Bruni and Leopold (1992), implemented on equation (2) as

$$I(T) = \frac{Q}{\tau_0}\exp\{-\frac{E_a}{k\,T} - \left(\frac{T}{T_m}\right)^2\exp\left[\frac{E_a}{k}\left(\frac{T-T_m}{T_m\,T}\right)\right]\} \quad (3)$$

Where, T_m is temperature at which maximum depolarization current occurs in a peak. The iterative curve-fitting analysis of TSDC peaks was performed by Sun (2000) using a procedure that was developed by Dr. F.
Bruni and inserted as a macro into the commercially available software "Igor" (Wave Metrics, Lake Oswego, OR). Reported parameters are given in Table 1.
From reported values of relaxation parameters, order of kinetics for the respective peak is calculated following the new model given by Prakash (2013). According to new model relation for peak temperature of TSDC spectrum is given as

$$T_m^2 = \frac{\ell\, b\, E_a\, \tau_m}{k} \quad (4)$$

Where, ℓ is order of kinetics and τ_m is relaxation time at peak temperature. As per equation (4) order of kinetics is evaluated for different peaks and presented in Table 1.

Table 1

Water Content (g/g dw)	Peak	E_a (eV)	τ_0 (s)	T_m (^{0}K)	ℓ
0.37	I	0.24	2.60E-08	147	35.26213961
	II	0.48	4.90E-12	194	9.343631423
	III	0.84	1.00E-14	232	0.006235974
0.10	II	0.14	3.20E-04	146	12.0493292
	III	0.14	7.60E-04	168	28.84598956

Conclusions

Already reported data of dielectric relaxation parameters of red oak seeds are reconsidered here and order of kinetics for different resolved peaks are evaluated according to new kinetic model proposed by Prakash.

The two TSDC spectrums are for different water contents. From above discussion it is clear that order of kinetics is different for different peaks. Order of kinetics totally dependent on experimental conditions and does not represent characteristic feature of material under consideration. The introduction and estimation of this new parameter might be quite helpful in explaining the biological and physical nature of different relaxation peaks regarding investigation of mode of hydration of red oak seeds. This study provides some more insight information concerning the mobility and rotational freedom of hydration water, hydration sites, and mechanisms.

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REFERENCES

Arrhenius S (1889). On the reaction rate of the inversion of non-refined sugar upon souring. *Zeitschrift für Physikalische Chemie* **4** 226–248.

Bakradze NG and Balla YI (1983). Crystallization of intracellular water in plant tissues. *Biophysics* **28** 125–128.

Bruni F and Leopold AC (1992). Pools of water in an hydro biotic organisms: a thermally stimulated depolarization current study. *Biophysical Journal* **63** 663–672.

Cameron IL, Ord VA and Fullerton GD (1988). Water of hydration in the intra- and extracellular environment of human erythrocyte. *Biochemistry and Cell Biology* **66** 1186–1199.

Careri G, Giansanti A and Gratton E (1979). Lysozyme film hydration events: an IR and gravimetric study. *Biopolymers* **18** 1187–1203.

Chen R and Kirsch Y (1988). *Analysis of Thermally Stimulated Processes*, (Pergamon Press, New York, USA).

Christodoulides C, Apekis L and Pissis P (1988). Peak parameters from peak area to height ratio in thermally stimulated depolarization and termoluminescence. *Journal of Applied Physiology* **64** 1367–1370.

Clegg JS (1978). Hydration-dependent metabolic transitions and the state of cellular water in *Artemia* cysts. *In* JH Crowe, JS Clegg, edition, *Dry Biological Systems*, (Academic Press, New York, USA) 117–153.

Clegg JS, Szwarnowski S, McClean VER, Sheppard RJ and Grant EH (1982). Interrelationships between water and cell metabolism in *Artemia* cysts: X. Microwave dielectric studies. *Biochimica et Biophysica Acta* **721** 458–468.

Harvey SC and Hoekstra P (1972). Dielectric relaxation spectra of water adsorbed on lysozyme. *The Journal of Physical Chemistry* **76** 2981–2994.
Kamiyoshi K and Kudo A (1978). Dielectric relaxation of water contained in plant tissues. *Japanese Journal of Applied Physics* **17** 1531–1536.
Lehmann MS (1984). Probing the protein-bound water with other small molecules using neutron small angle scattering. *Journal de Physique Colloques* **C7** 235–239.
Luck WAP (1985). Spectroscopic attempts to determine the structure of water and of biopolymer hydration phenomena. *Óptica Pura y Aplicada* **18** 71–82.
Lusher-Mattli M and Ruegg M (1982). Thermodynamic function of biopolymer hydration: I. Their determination by vapor pressure studies, discussed in an analysis of the primary hydration process. *Biopolymers* **21** 403–418.
Mascarenhas S (1980). Biolectrets: electrets in biomaterias and biopolymers. *In* GM Sessler, edition, *Electrets*. (Springer-Verlag, Berlin, Germany) 321–346.
Mathur-de Vre R (1979). The NMR studies of water in biological systems. *Progress in Biophysics & Molecular Biology* **35** 103–134.
Pissis P, Anagnostopoulou-Konsta A and Apekis L (1987). A dielectric study of the state of water in plant stems. *Journal of Experimental Botany* **38** 1528–1540.
Pissis P, Anagonostopoulou-Konsta A, Apekis L, Daoukaki-Diamanti D and Christodoulides C (1991). Dielectric effects of water in water-containing systems. *Journal of Non-Crystalline Solids* **131–133** 1174–118.
Pissis P, Konsta AA, Ratkovic S, Todorovic S and Laudat J (1996). Temperature and hydration-dependence of molecular mobility in seeds. *Journal of Thermal Analysis* **47** 1463–1483.
Ratkovic S (1987). Proton NMR of maize seed water: the relationship between spin-lattice relaxation time and water content. *Seed Science and Technology* **15** 147–154.
Rorschach HE and Hazlewood CF (1986). Protein dynamics and the NMR relaxation time T1 of water in biological systems. *Journal of Magnetic Resonance* **70** 79–88.
Ruegg M, Moor U and Blanc BH (1975). Hydration and thermal denaturation of b-lactoglobulin: calorimetric study. *Biochimica et Biophysica Acta* **400** 334–342.
Rupley HA, Gratton E and Careri G (1983). Water and globular proteins. *Trends in Biochemical Sciences* **8** 18–22.
Schneider MJT and Schneider AS (1972). Water in biological membrane: adsorption isotherms and circular dichroism as a function of hydration. *Journal of Membrane Biology* **9** 127–140.
Seewaldt V, Proestley DA, Leopold AC, Feigenson W and Goodsaid-Zalduondo F (1981). Membrane organization in soybean seeds during hydration. *Planta* **52** 19–23.
Sun WQ (2000). Dielectric Relaxation of Water and Water-Plasticized Biomolecules in Relation to Cellular Water Organization, Cytoplasmic Viscosity, and Desiccation Tolerance in Recalcitrant Seed Tissues, *Plant Physiology* **124** 1203–1215.
Trantham EC, Rorschach HE, Clegg JS, Hazlewood CF, Nicklow RM and Wakabayashi N (1984). The diffusive properties of water in *Artemia* cells determined by quasielectron neutron scattering. *Biophysical Journal* **45** 927–938.
Vertucci CW (1990). Calorimetric studies of the state of water in seed tissues. *Biophysical Journal* **58** 1463–1471.
Vertucci CW and Leopold AC (1987). The relationship between water binding and desiccation tolerance in tissues. *Plant Physiology* **85** 232–238.