

Dielectric Relaxation Study of Alkaloid (Caffeine) in Aqueous Solution Using Time Domain Reflectometry Technique

A. R. Lathi¹, S. K. Popalghat²

¹Department of Physics and Electronics, A. E.S. College, Hingoli Maharashtra, India

²Department of Physics and Electronics, J. E.S. College, Jalna Maharashtra, India

Abstract: *The complex permittivity of Caffeine (1,3,7-trimethyl xanthine) in aqueous solution for various temperatures and concentrations have been measured as a function of frequency between 10 MHz to 30 GHz using time domain reflectometry technique. Dielectric parameters, static dielectric constant, relaxation time and thermodynamic parameters i.e. Enthalpy of Activation ΔH , Entropy of activation ΔS were obtained for various concentration of caffeine in water.*

Keywords: Caffeine, Dielectric Relaxation; Time Domain Reflectometry; Thermodynamics

1. Introduction

Caffeine (1,3,7-trimethyl xanthine) [C₈H₁₀N₄O₂] is alkaloid, which is naturally found in coffee, tea, cola etc. Caffeine comes under group of purine alkaloids and nitrogen containing substance [1, 2]. The molecular structure of caffeine is shown in Fig. 1. Caffeine is colourless compound which crystallises in silky needles and it is weak base and forms salts with strong acids which easily decomposed by water. Caffeine used as nerve and heart stimulant as a medicine [3]. Caffeine is extracted from tea with water – saturated solvent [1]. Solubility of caffeine in water is 2.17 gm. / 100ml. Solubility in water is temperature dependant, as temperature increases solubility increases [4]. Analytical and some physical properties of caffeine was studied [5].

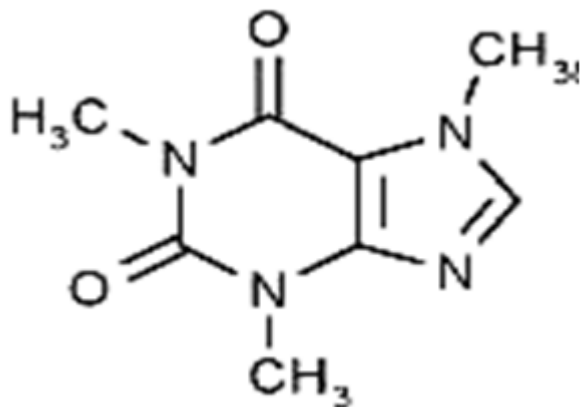


Figure 1

The present paper reports the temperature dependant dielectric relaxation studies of caffeine-water mixture for different molar fraction of caffeine in the frequency range of 10 MHz to 30 GHz using pico-second Time Domain Reflectometry technique. The static dielectric constant, relaxation time, high frequency permittivity has been determined. From dielectric parameters the thermodynamics parameters are obtained. On the basis of these parameters, intermolecular interaction and dynamics of molecules at molecular level are discussed.

2. Experimental

2.1 Material

Caffeine (1,3,7-trimethyl xanthine) was purchased from OTTO Chemie, India. Solution using water as a solvent of different concentration in molar fraction were prepared.

2.2 Measurements

The dielectric spectra were obtained by the time domain reflectometry (TDR) technique [6-11]. The Tektronix model no. DSA8200 Digital Serial Analyzer sampling mainframe along with the sampling module 80E08 has been used for the time domain reflectometry (TDR). A repetitive fast rising voltage pulse with 18ps incident rise time was fed through coaxial line system of impedance 50 ohm. All measurements are carried out in open load condition. Sampling

oscilloscope monitors changes in step pulse after reflection from the end of line. Reflected pulse without sample $R_1(t)$ and with sample $R_x(t)$ were recorded in time window of 5ns and digitized in 2000 points. The Fourier transformation of the pulses and data analysis were done earlier to determine complex permittivity spectra $\epsilon^*(\omega)$ using non linear least squares fit method [9].

2.3 Data Analysis

These recorded pulses are added [$q(t) = R_1(t) + R_x(t)$] and subtracted [$p(t) = R_1(t) - R_x(t)$]. Further the Fourier transformation of $p(t)$ and $q(t)$ was obtained by summation and Samulon [12-13] methods respectively, for the frequency range 10 MHz to 30 GHz. The complex reflection spectra were determined as follows,

$$\rho^*(\omega) = \left(\frac{c}{j\omega d} \right) \left[\frac{p(\omega)}{q(\omega)} \right] \quad (1)$$

where $p(\omega)$ & $q(\omega)$ are Fourier transforms of $p(t)$ and $q(t)$ respectively, c is the speed of light, ω is the angular frequency, d is the effective pin length and $j = \sqrt{-1}$. The Complex permittivity spectra $\epsilon^*(\omega)$ was obtained from reflection coefficient $\rho^*(\omega)$ by applying calibration method as described earlier [9]. The dielectric permittivity ϵ' and dielectric loss ϵ'' for 0.06M, 0.1M and water mixtures at 25°C is shown in Fig.2.

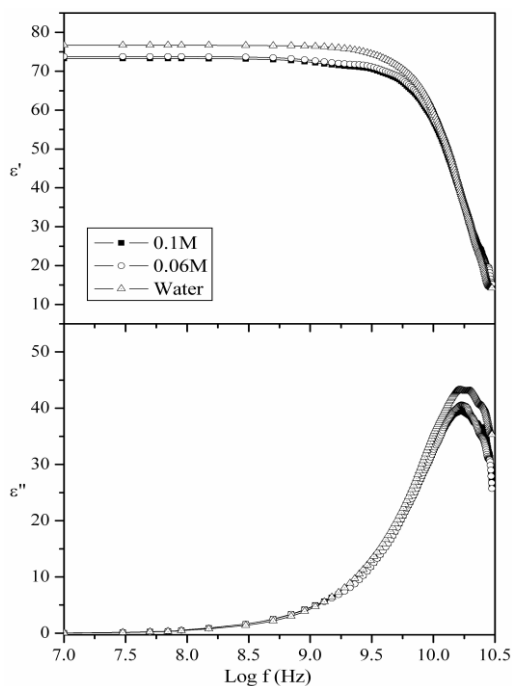


Figure 2

3. Results and Discussion

The complex dielectric permittivity data were fitted to a Havriliak-Negami equation using non linear least squares fit method in order to extract dielectric relaxation parameters with the following expression [14].

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{[1 + (j\omega\tau)^{1-\alpha}]^\beta} \quad (2)$$

where ϵ_0 is the static permittivity, ϵ_∞ is the permittivity at high frequency, τ is the relaxation time in picosecond, α and β are the empirical parameters for the distribution of relaxation times with values between 0 and 1. The HN equation includes three relaxation models. The Debye model [15] ($\alpha = 0$ and $\beta = 1$) shows the single relaxation whereas the Cole-Cole [16] ($0 \leq \alpha \leq 1$ and $\beta = 1$) and Cole-Davidson [17] ($\alpha = 0$ and $0 \leq \beta \leq 1$) models which suggests the symmetric and asymmetric distribution of relaxation times. The complex permittivity spectra $\epsilon^*(\omega)$ of the caffeine-water mixtures were fitted in Debye model using non linear least squares fit method to determine the dielectric parameters (ϵ_0 , ϵ_∞ and τ). The temperature dependent dielectric relaxation parameters for caffeine-water mixtures with molar fraction of caffeine are listed in Table 1. The errors in these parameters have been given in the brackets which shows an uncertainty in the last significant digits e.g. the static dielectric constant of 0.1M 72.70(6) means 72.70 ± 0.06 . The decrease in dielectric constant of the solution with increasing caffeine concentration and systematic change in the dielectric parameters of the solution can be explained on the basis of molecular interactions. The dielectric properties will get affected by temperature for all molar concentration. This is due to the effect of temperature on polarization mechanism and charge mobility. Similar behavior observed from the Table 1, the values of ϵ_0 and τ are decreasing with an increasing temperature.

Table 1

(a) Water

Temp	ϵ_∞	ϵ_0	τ
25°C	2.00	78.32(2)	8.21(2)
20°C	2.04(2)	79.87(5)	9.35
15°C	2.07(2)	82.01(6)	10.56(1)

(b) 0.06 M Sol.

Temp	ϵ_{∞}	ϵ_0	τ
25°C	2.76(8)	73.24(5)	8.77(13)
20°C	2.77(5)	74.09(5)	8.77(13)
15°C	2.79(5)	75.75(3)	9.54(9)

(c) 0.1M Sol.

Temp	ϵ_{∞}	ϵ_0	τ
25°C	2.76(9)	72.70(6)	8.93(14)
20°C	2.77(8)	73.68(5)	9.18(12)
15°C	2.78(6)	75.10(4)	9.61(10)

3.3 Thermodynamic Parameters

The thermodynamic parameters evaluated using Eyring equation is as follows [18, 19]

$$\tau = (h/KT) \exp(\Delta H/RT) \exp(-\Delta S/R) \quad (3)$$

where ΔS is the entropy of activation, ΔH is the activation energy in kJ/mol. τ is the relaxation time in ps and T is the temperature in K and h is the Plank's constant. The result in values of activation energy are obtained by least square fit method are reported in Table 2.

Table 2: Thermodynamic Parameters for caffeine–water mixtures

Molar Conc. of caffeine	$\Delta H(\text{kJ mole}^{-1})$	$\Delta S(\text{Jmole}^{-1}\text{k}^{-1})$
Water	17.62(15)	0.249(1)
.06M	3.60(34)	0.208(1)
0.1M	2.80(70)	0.205(2)

Number in bracket denotes uncertainties in the last significant digits obtained by least square fit method e.g. 17.62 (15) means 17.62 ± 0.15

The temperature dependence of relaxation time described by Arrhenius plot shown in Fig. 3. Activation energy (ΔH) for water, 0.06M and 0.1M is positive. This indicates endothermic reaction in entire concentrations.

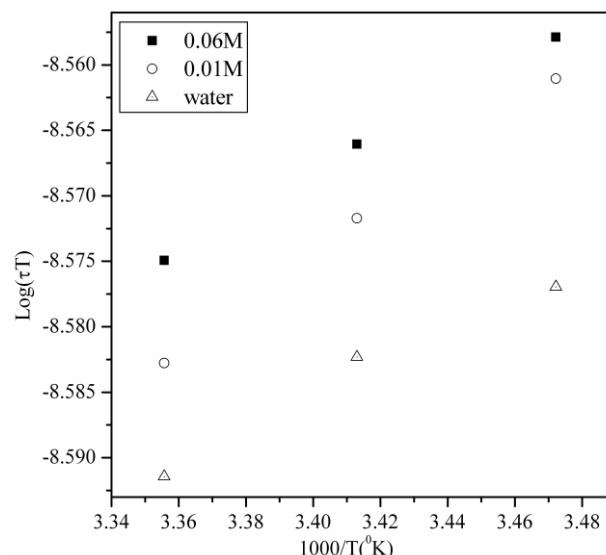


Figure 3

4. Conclusion

The dielectric permittivity spectra of Caffeine (1,3,7-treimethyl xanthine) in aqueous solution have been studied using time domain reflectometry technique in frequency range 10 MHz to 30 GHz at 15°C, 20°C and 25°C. With increase caffeine concentration, the dielectric constant decreases which can be explained on the basis of molecular interaction.

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