



DIELECTRIC RECREATION STUDY OF AMINO ACID WITH WATER MIXTURE USING TIME DOMAIN REFLECTOMETRY TECHNIQUE

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Abstract: Dielectric relaxation measurements of amino acid (L-alanine) in water solution were carried out using time domain reflectometry at 25°C to -5°C in the frequency range between 10 MHz to 30 GHz. The dielectric parameters i.e. static dielectric constant and relaxation time, were obtained from the complex permittivity spectra using a nonlinear least square fit method. From the values of the relaxation time, the thermodynamic parameters are determined. The Kirkwood correlation factor was calculated from the static permittivity. The dielectric relaxation parameters increase with an increase in concentration (mM) of amino acid (L-alanine) due to the structure of hydrogen bond groups by the amino acid (L-alanine) molecules in the aqueous solution. The relaxation peak shifted to lower frequency with an increase in molar concentration of amino acid.

Keywords: Dielectric relaxation, Amino acid, Time Domain Reflectometry.

I. INTRODUCTION

Water is the most significant biomolecules and is the principle element of all existing organisms. It also plays a key role in biological science and industrial technology. A significant solvent for all kinds of biomolecules most existing species contain a large amount of water, varying from 97% to less than 50%. It plays a vital role in many biological processes, such as molecular transport, folding and aggregation of biopolymers, enzyme-substrate, binding and catalysis [1]. One of the most interesting aspects of water mixture with other material is the effect of the supplementary component on the structure of the water. An objects when dissolved in water may either split the water structure or conserve the water structure through the interactions between them. The stability between the molecules of normal water (non bonded water) is disturbed because of the addition of solute. Thus, solutes of dissimilar types can be classified as water structure breakers and water structure makers [2]. On the other hand, water is also one of the substances with peculiar properties: such as contraction on melting, with the density and dielectric constant greatest in the liquid phase at 4°C [3].

Amino acids participate numerous significant roles in existing systems. The relations between the solvent and the various basic groups of protein, such as the amino acid side chains and the backbone peptide groups, play an elementary role in the structure and function of proteins in aqueous solutions. The complexity of these relations in the integral macromolecule, one approach to characterize the thermodynamic and hydration behavior of the various element groups of proteins is to revise low molar mass compounds preferred to specific structural facial appearance of a protein. Amino acids are very small biomolecules and the estimation of building blocks of proteins and enzymes [4]. These compounds are referred to as representation compounds. This approach has received a lot of consideration in recent years.

The dielectric relaxation study of amino acid (L-alanine) in water mixture would be expected to reveal information about its communications with water. Mostly all there are free amino acids in cells are dissolved in the aqueous region of the cell. Takashima and Schwan [5] have explained the dielectric dispersion of unclear of amino acids, peptides and proteins. They found that adsorbed water improved the dielectric constant precisely. Kumazaki and Sugai [6] measured the dielectric distribution of electrolytic poly- α -amino acids and their various salts in aqueous solutions in a frequency range of 1 kHz to 3 kHz. They studied the solution belief of the relaxation time on the molecular weight. Baylay [7] studied the belief of the dielectric constant on the concentrations of various amino acids in water. Jones [8], Nolarity [9], Wyman [10-11] and Kirkwood [12] have studied aqueous solutions of amino acids. Bateman et al. [13] studied aqueous amino acid solutions at higher frequency ranges up to 70 GHz and 20 °C [14.] The TDR technique in a frequency range 10 MHz to 10 GHz. Shankarwar [15] studied the effect of the addition of amino acids in aliphatic alcohols-water mixtures on their dielectric parameters at various temperatures and pointed out that the static dielectric constant relaxation time values of glycine were less than that of dyglycine in both solvent media was due to differences in molecular size of these two solutes [16-24].

In this article we considered the dielectric relaxation in L-alanine and water mixtures using time domain reflectometry (TDR) technique. The solution were prepared at room temperature for various molar concentrations of amino acid (L-alanine) i.e. 0 to 1

M/liter H₂O. We deliberate the dielectric relaxation spectra for these solutions at 25^oC to -5^oC using time domain reflectometry [25-26] in the frequency range between 10 MHz-30 GHz. The relaxation performance of these mixtures is explained by the Cole-Davidson model.

II. RESEARCH METHODOLOGY

Amino acid (L-alanine) (Merck Chemicals) was obtained commercially and used without further purification. The aqueous solutions were prepared at room temperature for ten different molar concentrations of amino acid in the HPLC grade distilled water. The dielectric dimensions were carried out using time domain reflectometry. The complex permittivity spectra were studied using the Time Domain Reflectometry (TDR) method [25, 26, 27-31]. The basic TDR setup consists of a broadband sampling oscilloscope, TDR module and coaxial transmission line. A Tektronix DSA8200 sampling oscilloscope with 30 GHz bandwidth and TDR module 80E08 with step generator unit was used. A 200mV step pulse with 18 ps incident pulse and 20 ps reflected pulse times and 200 KHz repetition rate passes through the coaxial 50 Ω lines. The sample was placed at the end of a coaxial line in the coaxial cable with 0.09 mm effective pin length. All measurements were carried out in open load conditions. The change in the pulse after reflection from the sample placed in the sample holder was monitored by the sampling oscilloscope. The reflected pulse without sample R₁(t) and with sample R_x(t) were recorded in a time window of 5ns and digitized over 2000 points.

A temperature control system was used to maintain the temperature at -5^oC to 25^oC with an accuracy of ±1^oC. The temperature at the sample holder was checked by using an electronic thermometer.

III. DATA ANALYSIS

The step pulses recorded without sample R₁(t) and with sample R_x(t) were subtracted and added to get

$$p(t) = [R_1(t) - R_x(t)] \quad (1)$$

$$q(t) = [R_1(t) + R_x(t)] \quad (2)$$

These recorded pulses were as shown in Fig. 1. The processing of the data was carried out to give the complex reflection coefficient $\rho^*(\omega)$ over a frequency range of 10 MHz to 30 GHz determined as follows:

$$\rho^*(\omega) = \frac{c}{j\omega d} \frac{p(\omega)}{q(\omega)} \quad (3)$$

Where $p(\omega)$ and $q(\omega)$ are the Fourier transforms of $p(t)$ and $q(t)$ obtained using the summation and Samulon methods [32], respectively. c is the velocity of light, ω is the angular frequency and d is the effective pin length (0.09 mm). The complex permittivity spectra, $\epsilon^*(\omega)$, were obtained from the reflection coefficient spectra $\rho^*(\omega)$ by applying the bilinear calibration method suggested by Cole [33]. A typical complex permittivity spectra $\epsilon^*(\omega)$ for L-alanine + water is shown in Fig. 2.

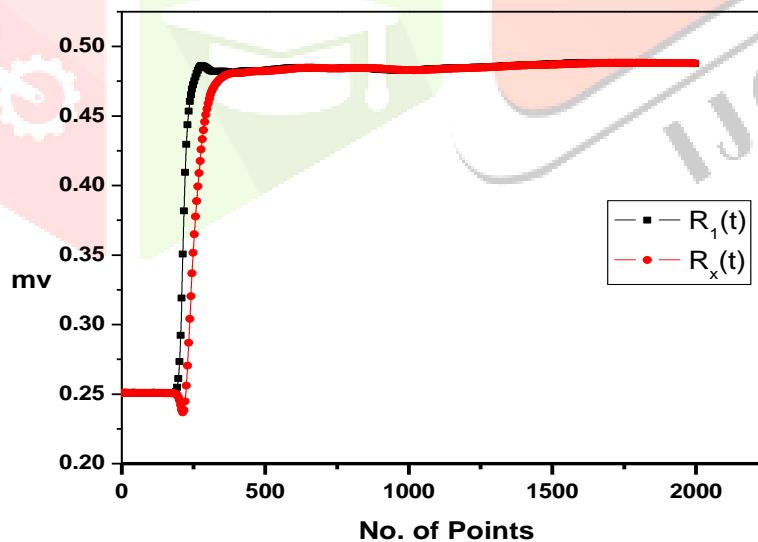


Fig.1 Reflected pulse without sample R₁(t) and with sample R_x (t)

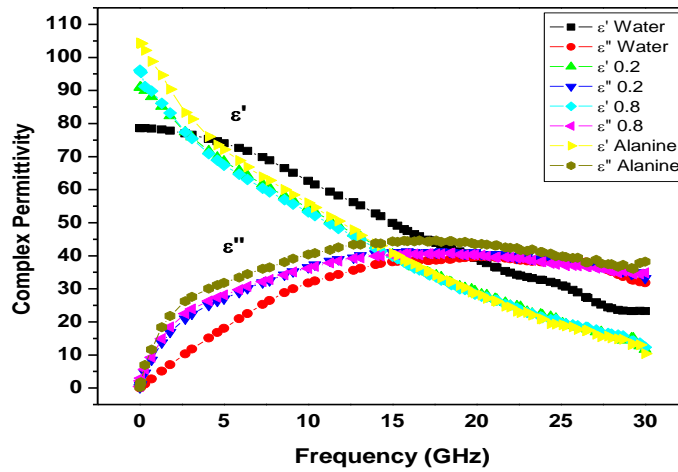


Fig.2 Frequency dependence complex permittivity spectra $\rho^*(\omega)$ for L-Alanine & water mixture at various concentrations of -5 °C to 25°C.

The values of dielectric permittivity and dielectric loss are reported in table 2.

Table 2. Dielectric relaxation parameters for aqueous solutions of L-Alanine at different temperatures and molar concentrations of Alanine.

| L-Alanine Molar Conc. | ϵ_0 | τ (ps) | ϵ_{∞} | β |
|-----------------------|--------------|-------------|---------------------|------------|
| 25°C | | | | |
| 0.0 | 78.27(3) | 8.32(1) | 3.27(4) | 1.00(0.12) |
| 0.1 | 83.80(9) | 11.24(6) | 3.81(6) | 0.82(0.23) |
| 0.2 | 89.51(7) | 12.55(8) | 1.79(5) | 0.80(0.23) |
| 0.3 | 91.66(9) | 13.34(10) | 1.93(7) | 0.79(0.27) |
| 0.4 | 93.09(9) | 13.79(10) | 2.32(7) | 0.78(0.26) |
| 0.5 | 94.21(9) | 14.25(9) | 2.03(6) | 0.76(0.24) |
| 0.6 | 95.09(9) | 14.50(9) | 1.21(6) | 0.75(0.23) |
| 0.7 | 96.52(9) | 14.76(9) | 1.21(6) | 0.75(0.23) |
| 0.8 | 97.96(10) | 15.20(10) | 1.20(7) | 0.76(0.26) |
| 0.9 | 100.39(15) | 15.88(12) | 2.03(10) | 0.75(0.32) |
| 1.0 | 105.35(13) | 16.08(13) | 2.74(9) | 0.75(0.28) |
| 20°C | | | | |
| 0.0 | 79.04(7) | 8.71(1) | 3.92(3) | 1.00(0.11) |
| 0.1 | 85.55(12) | 12.13(13) | 3.67(9) | 0.81(0.33) |
| 0.2 | 91.17(12) | 13.47(12) | 3.21(9) | 0.78(0.33) |
| 0.3 | 93.23(13) | 14.33(15) | 3.65(10) | 0.79(0.38) |
| 0.4 | 96.74(9) | 15.34(10) | 2.32(7) | 0.78(0.26) |
| 0.5 | 102.62(29) | 15.98(25) | 3.46(21) | 0.80(0.63) |
| 0.6 | 103.94(10) | 16.44(11) | 2.68(7) | 0.75(0.24) |
| 0.7 | 105.26(18) | 16.61(18) | 3.43(13) | 0.78(0.39) |
| 0.8 | 104.17(16) | 16.79(16) | 3.39(11) | 0.78(0.36) |
| 0.9 | 105.03(16) | 16.94(19) | 2.78(12) | 0.77(0.42) |
| 1.0 | 105.89(15) | 17.11(12) | 2.91(9) | 0.74(0.27) |
| 15°C | | | | |
| 0.0 | 80.23(5) | 9.04(1) | 2.32(3) | 1.00(0.09) |
| 0.1 | 88.68(11) | 12.47(15) | 1.61(9) | 0.79(0.41) |
| 0.2 | 94.56(12) | 13.82(15) | 2.62(9) | 0.79(0.38) |
| 0.3 | 97.27(14) | 14.81(15) | 1.25(10) | 0.76(0.37) |
| 0.4 | 99.32(11) | 16.09(14) | 1.63(8) | 0.73(0.29) |
| 0.5 | 106.72(21) | 16.97(19) | 2.52(15) | 0.78(0.44) |
| 0.6 | 107.47(16) | 17.27(11) | 4.75(9) | 0.80(0.27) |
| 0.7 | 108.22(21) | 17.58(19) | 2.91(15) | 0.78(0.42) |
| 0.8 | 105.87(19) | 17.82(18) | 3.07(13) | 0.78(0.41) |
| 0.9 | 105.93(15) | 17.82(18) | 2.85(11) | 0.78(0.37) |
| 1.0 | 108.87(14) | 18.05(13) | 2.21(9) | 0.74(0.28) |

| 10°C | | | | |
|------|------------|-----------|----------|------------|
| 0.0 | 82.36(7) | 9.90(1) | 0.93(3) | 1.00(0.08) |
| 0.1 | 91.09(11) | 13.59(13) | 3.76(9) | 0.82(0.36) |
| 0.2 | 97.21(12) | 15.34(17) | 3.88(9) | 0.79(0.38) |
| 0.3 | 98.65(12) | 17.09(15) | 3.71(9) | 0.78(0.34) |
| 0.4 | 102.16(12) | 17.99(14) | 1.49(8) | 0.73(0.29) |
| 0.5 | 110.03(20) | 18.40(21) | 3.61(15) | 0.79(0.43) |
| 0.6 | 110.62(14) | 18.79(20) | 1.77(10) | 0.71(0.36) |
| 0.7 | 111.21(23) | 18.80(23) | 2.24(16) | 0.78(0.47) |
| 0.8 | 109.73(19) | 18.81(20) | 3.22(14) | 0.78(0.41) |
| 0.9 | 109.70(15) | 19.05(17) | 2.54(11) | 0.77(0.33) |
| 1.0 | 111.11(13) | 18.84(13) | 2.14(9) | 0.74(0.26) |
| 5°C | | | | |
| 0.0 | 84.07(9) | 10.76(3) | - | 1.00(0.13) |
| 0.1 | 93.52(10) | 14.79(12) | 3.84(8) | 0.84(0.32) |
| 0.2 | 99.63(11) | 16.54(17) | 4.55(9) | 0.80(0.35) |
| 0.3 | 101.21(12) | 18.30(16) | 4.29(9) | 0.79(0.33) |
| 0.4 | 104.78(13) | 18.87(16) | 1.80(9) | 0.75(0.31) |
| 0.5 | 111.66(31) | 19.55(24) | 1.42(21) | 0.80(0.55) |
| 0.6 | 112.46(23) | 20.09(24) | 1.81(15) | 0.72(0.45) |
| 0.7 | 113.25(28) | 20.63(24) | 2.38(19) | 0.79(0.50) |
| 0.8 | 111.63(25) | 20.58(29) | 3.78(18) | 0.79(0.54) |
| 0.9 | 111.64(21) | 20.54(25) | 3.38(15) | 0.79(0.45) |
| 1.0 | 113.44(13) | 20.04(13) | 1.59(9) | 0.75(0.25) |
| 0°C | | | | |
| 0.0 | 87.57(17) | 12.56(3) | - | 1.00(0.19) |
| 0.1 | 97.36(10) | 16.77(12) | 2.90(8) | 0.85(0.30) |
| 0.2 | 102.25(10) | 18.83(20) | 5.01(8) | 0.82(0.35) |
| 0.3 | 104.05(18) | 19.88(22) | 3.79(13) | 0.80(0.42) |
| 0.4 | 106.09(24) | 20.41(24) | 2.32(17) | 0.78(0.47) |
| 0.5 | 114.82(28) | 20.95(25) | 2.24(20) | 0.80(0.51) |
| 0.6 | 115.09(24) | 21.32(25) | 1.86(16) | 0.76(0.45) |
| 0.7 | 115.36(31) | 21.98(28) | 2.15(21) | 0.81(0.54) |
| 0.8 | 114.70(31) | 22.24(35) | 3.11(22) | 0.79(0.60) |
| 0.9 | 114.98(25) | 22.51(29) | 3.07(18) | 0.78(0.49) |
| 1.0 | 115.58(26) | 22.04(20) | 1.14(16) | 0.77(0.40) |
| -5°C | | | | |
| 0.0 | 92.75(21) | 15.46(4) | - | 1.00(0.10) |
| 0.1 | 101.54(17) | 20.03(18) | 3.61(13) | 0.87(0.39) |
| 0.2 | 105.14(28) | 21.31(23) | 1.66(19) | 0.83(0.51) |
| 0.3 | 108.39(21) | 22.81(25) | 1.17(15) | 0.80(0.42) |
| 0.4 | 111.95(25) | 23.70(31) | 2.61(17) | 0.77(0.47) |
| 0.5 | 118.88(36) | 24.59(32) | 2.06(24) | 0.80(0.58) |
| 0.6 | 119.15(30) | 24.91(33) | 2.30(19) | 0.77(0.50) |
| 0.7 | 119.09(40) | 25.24(37) | 2.01(27) | 0.80(0.64) |
| 0.8 | 119.43(35) | 25.72(33) | 1.85(24) | 0.79(0.56) |
| 0.9 | 118.69(32) | 27.10(30) | 1.65(21) | 0.79(0.51) |
| 1.0 | 121.88(18) | 28.48(27) | 3.61(13) | 0.74(0.35) |

The number in bracket indicates error. For e.g. 78.09(8) means 78.09±0.08

IV. RESULT AND DISCUSSION

The general form of the relaxation equation is given by the Havriliak-Negami equation [34].

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)}{[1 + (j\omega\tau)^{(1-\alpha)}]^\beta} \quad (4)$$

Where ε_0 is the static permittivity, ε_∞ is the permittivity at high frequency, τ is the relaxation time and α and β are empirical parameters for the distribution of relaxation times with values between 0 and 1. The Havriliak-Negami equation includes three relaxation models as limiting forms. The Debye model ($\alpha=0$ and $\beta=1$) implies a single relaxation time while the Cole-Cole model ($0 \leq \alpha \leq 1$ and $\beta=1$) and Cole-Davidson model ($\alpha=0$ and $0 \leq \beta \leq 1$) both suggest a distribution of relaxation times. The magnitudes of α and β indicate the width of the distribution. The relative to the aqueous solutions of the L-alanine at all molar concentrations of L-alanine they fit Cole-Davidson type dispersion. Therefore, here $\alpha=0$ and $0 \leq \beta \leq 1$ and experimental values of $\varepsilon^*(\omega)$ were fitted to the Cole-Davidson equation as,

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{(1 + j\omega\tau)^\beta} \quad (5)$$

The values of ϵ_0 , τ & ϵ_∞ are fitting parameter. A non-linear least squares fit method was used to determine the values of the dielectric parameters. The temperature dependent dielectric relaxation parameters for aqueous solutions of L-alanine are listed in Table 1.

Table 1. Values of Dielectric permittivity and Dielectric loss of L-Alanine in various concentrations and temperatures.

| Temp | 25°C | | 15°C | | 5°C | | -5°C | |
|------------------------------|-------------|--------------|-------------|--------------|-------------|--------------|-------------|--------------|
| X_A = 0.1 M | | | | | | | | |
| Freq (GHz) | ϵ' | ϵ'' | ϵ' | ϵ'' | ϵ' | ϵ'' | ϵ' | ϵ'' |
| 0.01 | 92.29 | 0.10 | 88.81 | 0.20 | 93.45 | 0.17 | 100.91 | 0.14 |
| 0.1 | 92.26 | 1.22 | 88.42 | 2.40 | 93.22 | 2.07 | 100.97 | 1.85 |
| 0.5 | 91.80 | 4.87 | 85.16 | 6.49 | 91.11 | 6.72 | 100.39 | 8.59 |
| 1.0 | 90.52 | 9.33 | 83.89 | 8.48 | 89.21 | 10.94 | 96.21 | 15.84 |
| 5.0 | 75.46 | 27.36 | 69.16 | 26.69 | 71.92 | 30.97 | 70.56 | 40.12 |
| 8.0 | 66.62 | 35.15 | 60.02 | 34.60 | 60.88 | 40.76 | 53.11 | 48.17 |
| 10.0 | 59.98 | 39.70 | 53.68 | 38.76 | 52.86 | 45.50 | 42.64 | 49.69 |
| 15.0 | 44.39 | 45.97 | 37.58 | 43.22 | 32.71 | 48.98 | 23.48 | 47.03 |
| 20.0 | 29.73 | 45.21 | 25.01 | 42.48 | 17.99 | 45.63 | 11.37 | 40.86 |
| 25.0 | 20.46 | 42.84 | 15.70 | 38.78 | 8.05 | 40.46 | 2.97 | 34.67 |
| X_A = 0.2 M | | | | | | | | |
| 0.01 | 89.00 | 0.15 | 94.15 | 0.20 | 99.00 | 0.20 | 105.16 | 0.22 |
| 0.1 | 88.83 | 1.80 | 93.83 | 2.42 | 98.73 | 2.51 | 105.05 | 2.77 |
| 0.5 | 87.12 | 6.09 | 90.96 | 7.25 | 96.11 | 8.26 | 102.86 | 11.08 |
| 1.0 | 85.19 | 10.09 | 89.09 | 11.19 | 93.35 | 13.38 | 97.18 | 18.66 |
| 5.0 | 68.84 | 26.00 | 70.35 | 28.91 | 71.98 | 32.96 | 68.13 | 40.52 |
| 8.0 | 60.74 | 32.43 | 60.87 | 36.22 | 60.49 | 41.81 | 51.06 | 47.18 |
| 10.0 | 55.48 | 36.03 | 54.55 | 40.16 | 52.48 | 46.00 | 41.25 | 48.32 |
| 15.0 | 41.14 | 41.44 | 38.19 | 44.77 | 33.00 | 49.30 | 22.81 | 45.19 |
| 20.0 | 28.91 | 41.47 | 24.89 | 43.28 | 18.48 | 45.77 | 11.65 | 39.33 |
| 25.0 | 20.72 | 39.62 | 16.34 | 40.15 | 8.43 | 41.32 | 5.27 | 33.67 |
| X_A = 0.3 M | | | | | | | | |
| 0.01 | 90.93 | 0.16 | 96.87 | 0.24 | 100.34 | 0.22 | 107.09 | 0.24 |
| 0.1 | 90.75 | 1.94 | 96.41 | 2.97 | 100.07 | 2.67 | 106.99 | 3.01 |
| 0.5 | 88.97 | 6.63 | 92.47 | 8.33 | 97.35 | 9.01 | 104.57 | 12.26 |
| 1.0 | 86.75 | 11.16 | 90.23 | 12.16 | 93.99 | 14.73 | 97.80 | 20.47 |
| 5.0 | 68.54 | 27.04 | 70.08 | 29.60 | 70.40 | 33.62 | 66.15 | 41.46 |
| 8.0 | 59.92 | 33.09 | 60.35 | 36.35 | 58.33 | 41.47 | 48.51 | 46.61 |
| 10.0 | 54.55 | 36.47 | 54.01 | 40.02 | 50.30 | 44.93 | 38.91 | 46.96 |
| 15.0 | 40.43 | 41.07 | 38.14 | 44.04 | 31.67 | 46.79 | 21.84 | 42.95 |
| 20.0 | 28.95 | 40.92 | 24.82 | 42.88 | 18.58 | 43.15 | 12.06 | 37.09 |
| 25.0 | 19.93 | 39.29 | 16.52 | 39.68 | 9.92 | 39.01 | 6.34 | 32.47 |
| X_A = 0.4 M | | | | | | | | |
| 0.01 | 92.39 | 0.18 | 98.76 | 0.28 | 103.80 | 0.28 | 110.82 | 0.32 |
| 0.1 | 92.16 | 2.18 | 98.22 | 3.40 | 103.37 | 3.41 | 110.49 | 3.99 |
| 0.5 | 89.87 | 7.09 | 93.56 | 9.45 | 99.25 | 10.68 | 106.08 | 14.40 |
| 1.0 | 87.51 | 11.45 | 90.65 | 13.60 | 94.99 | 16.44 | 98.14 | 22.23 |
| 5.0 | 68.58 | 27.34 | 69.08 | 29.86 | 70.08 | 34.16 | 65.31 | 41.75 |
| 8.0 | 59.77 | 33.02 | 59.11 | 36.21 | 57.88 | 41.95 | 47.77 | 46.53 |
| 10.0 | 54.53 | 36.23 | 52.81 | 39.45 | 49.92 | 45.34 | 38.23 | 46.49 |
| 15.0 | 40.73 | 40.77 | 37.27 | 42.81 | 31.29 | 47.34 | 21.78 | 42.50 |
| 20.0 | 28.91 | 40.97 | 25.09 | 41.24 | 17.91 | 43.20 | 12.11 | 36.99 |
| 25.0 | 20.76 | 38.17 | 16.50 | 37.71 | 9.50 | 38.72 | 6.52 | 32.59 |
| X_A = 0.5 M | | | | | | | | |
| 0.01 | 93.59 | 0.20 | 105.16 | 0.18 | 110.84 | 0.21 | 117.68 | 0.27 |
| 0.1 | 93.28 | 2.42 | 105.06 | 2.23 | 110.72 | 2.60 | 117.50 | 3.44 |
| 0.5 | 90.50 | 7.50 | 103.64 | 8.70 | 108.98 | 10.15 | 114.88 | 13.31 |
| 1.0 | 88.08 | 11.71 | 100.05 | 15.83 | 104.53 | 18.35 | 108.30 | 23.55 |
| 5.0 | 68.62 | 27.58 | 74.61 | 33.39 | 76.12 | 37.76 | 72.23 | 44.49 |
| 8.0 | 59.92 | 33.21 | 63.37 | 41.20 | 62.86 | 47.54 | 54.05 | 52.38 |
| 10.0 | 54.49 | 36.49 | 55.89 | 44.44 | 53.38 | 51.01 | 42.75 | 52.69 |
| 15.0 | 40.95 | 40.95 | 38.34 | 47.89 | 32.06 | 53.40 | 22.71 | 49.25 |
| 20.0 | 28.88 | 41.20 | 24.97 | 45.76 | 16.28 | 48.83 | 10.56 | 42.70 |
| 25.0 | 20.61 | 39.02 | 15.61 | 42.08 | 6.79 | 42.35 | 2.41 | 36.69 |
| X_A = 0.6 M | | | | | | | | |
| 0.01 | 94.52 | 0.22 | 95.25 | 0.10 | 104.70 | 0.53 | 111.67 | 0.34 |
| 0.1 | 94.16 | 2.68 | 95.53 | 1.41 | 102.77 | 5.92 | 111.31 | 4.30 |
| 0.5 | 90.81 | 8.08 | 95.21 | 8.31 | 96.47 | 10.55 | 106.32 | 15.47 |

| | | | | | | | | |
|------------------------------|--------|-------|--------|-------|--------|-------|--------|-------|
| 1.0 | 88.18 | 12.04 | 91.48 | 15.13 | 91.48 | 17.32 | 97.48 | 23.23 |
| 5.0 | 68.36 | 27.88 | 63.45 | 31.73 | 66.25 | 33.85 | 63.40 | 41.88 |
| 8.0 | 59.48 | 33.28 | 51.15 | 33.61 | 53.95 | 40.67 | 45.86 | 45.58 |
| 10.0 | 54.14 | 36.40 | 44.38 | 33.94 | 46.18 | 43.31 | 36.64 | 45.13 |
| 15.0 | 40.65 | 40.72 | 30.99 | 30.79 | 28.93 | 44.07 | 21.40 | 40.80 |
| 20.0 | 29.12 | 40.79 | 22.97 | 26.25 | 16.99 | 40.37 | 12.56 | 35.61 |
| 25.0 | 21.06 | 38.85 | 17.53 | 22.06 | 9.12 | 36.86 | 6.85 | 31.54 |
| X_A = 0.7 M | | | | | | | | |
| 0.01 | 95.14 | 0.27 | 106.63 | 0.20 | 112.07 | 0.22 | 118.22 | 0.28 |
| 0.1 | 94.41 | 3.11 | 106.52 | 2.46 | 111.93 | 2.79 | 118.03 | 3.55 |
| 0.5 | 91.27 | 7.03 | 104.82 | 9.58 | 109.96 | 10.86 | 115.27 | 13.73 |
| 1.0 | 88.93 | 12.69 | 100.55 | 17.22 | 104.95 | 19.49 | 108.33 | 24.23 |
| 5.0 | 68.40 | 28.29 | 72.96 | 34.08 | 74.78 | 38.56 | 71.17 | 44.59 |
| 8.0 | 59.49 | 33.77 | 61.21 | 41.25 | 61.96 | 47.80 | 53.71 | 51.94 |
| 10.0 | 54.20 | 36.81 | 54.49 | 44.03 | 51.81 | 51.14 | 42.09 | 52.14 |
| 15.0 | 40.41 | 40.95 | 37.53 | 47.05 | 30.77 | 52.69 | 22.78 | 48.49 |
| 20.0 | 28.95 | 40.82 | 24.17 | 44.53 | 15.92 | 48.08 | 10.91 | 42.41 |
| 25.0 | 20.24 | 39.24 | 14.95 | 40.81 | 5.75 | 42.41 | 2.46 | 36.34 |
| X_A = 0.8 M | | | | | | | | |
| 0.01 | 96.15 | 0.45 | 104.63 | 0.21 | 110.04 | 0.22 | 117.26 | 0.28 |
| 0.1 | 94.03 | 4.54 | 104.39 | 2.60 | 109.91 | 2.72 | 117.14 | 3.56 |
| 0.5 | 90.66 | 7.27 | 101.98 | 8.88 | 107.89 | 10.51 | 114.17 | 14.55 |
| 1.0 | 88.12 | 12.70 | 99.15 | 15.21 | 103.34 | 18.57 | 105.80 | 24.21 |
| 5.0 | 67.41 | 28.12 | 73.34 | 33.37 | 74.27 | 37.91 | 70.01 | 44.74 |
| 8.0 | 58.62 | 33.28 | 62.25 | 39.92 | 60.78 | 46.17 | 51.50 | 50.66 |
| 10.0 | 53.25 | 36.16 | 55.30 | 43.33 | 51.87 | 49.70 | 40.95 | 51.26 |
| 15.0 | 39.87 | 40.17 | 38.44 | 46.71 | 31.17 | 51.46 | 21.89 | 47.20 |
| 20.0 | 28.25 | 40.10 | 25.17 | 44.65 | 16.64 | 46.88 | 10.64 | 40.69 |
| 25.0 | 19.89 | 38.04 | 15.46 | 40.91 | 6.98 | 40.07 | 3.40 | 34.12 |
| X_A = 0.9 M | | | | | | | | |
| 0.01 | 97.69 | 0.52 | 105.48 | 0.34 | 110.15 | 0.23 | 117.80 | 0.33 |
| 0.1 | 95.01 | 4.65 | 104.36 | 3.77 | 109.96 | 2.92 | 117.47 | 4.13 |
| 0.5 | 92.05 | 7.44 | 101.43 | 8.74 | 107.52 | 10.88 | 113.23 | 15.01 |
| 1.0 | 89.60 | 13.04 | 98.17 | 15.22 | 102.56 | 18.69 | 105.07 | 24.06 |
| 5.0 | 68.46 | 28.66 | 73.31 | 33.73 | 73.94 | 38.50 | 69.39 | 45.12 |
| 8.0 | 59.37 | 33.96 | 61.95 | 40.15 | 59.86 | 46.52 | 50.23 | 50.49 |
| 10.0 | 53.95 | 37.04 | 54.67 | 43.81 | 50.52 | 50.09 | 39.69 | 50.89 |
| 15.0 | 39.99 | 41.29 | 37.37 | 47.24 | 29.93 | 51.43 | 21.11 | 46.00 |
| 20.0 | 27.83 | 40.71 | 24.24 | 44.82 | 15.56 | 46.47 | 10.88 | 39.68 |
| 25.0 | 20.41 | 38.77 | 15.15 | 41.97 | 5.72 | 41.82 | 3.49 | 34.36 |
| X_A = 1.0 M | | | | | | | | |
| 0.01 | 104.34 | 0.25 | 107.85 | 0.27 | 112.09 | 0.27 | 119.84 | 0.35 |
| 0.1 | 103.93 | 3.10 | 107.41 | 3.35 | 111.80 | 3.30 | 119.54 | 4.35 |
| 0.5 | 100.29 | 9.52 | 103.55 | 10.25 | 108.60 | 11.53 | 115.02 | 16.29 |
| 1.0 | 97.06 | 14.96 | 100.44 | 16.50 | 103.88 | 19.37 | 105.80 | 25.73 |
| 5.0 | 72.12 | 31.79 | 72.67 | 34.13 | 73.45 | 37.64 | 68.82 | 44.40 |
| 8.0 | 61.99 | 37.23 | 61.42 | 40.23 | 60.49 | 45.19 | 50.64 | 49.85 |
| 10.0 | 55.96 | 40.35 | 54.48 | 43.60 | 52.01 | 48.61 | 40.36 | 50.25 |
| 15.0 | 40.70 | 44.35 | 37.30 | 46.81 | 32.03 | 50.38 | 21.98 | 46.25 |
| 20.0 | 28.60 | 43.44 | 24.60 | 44.20 | 18.03 | 46.41 | 11.33 | 39.91 |
| 25.0 | 19.21 | 39.80 | 15.48 | 39.94 | 8.84 | 40.44 | 4.61 | 33.46 |

For the aqueous solutions of L-alanine, the static permittivity and relaxation time both increased with an increase in molar concentration of L-alanine and also increased with a decrease in temperature they are shown in Fig. 3. It should be noted that the relaxation time varied from 8 ps with in temperature range studied. The errors in the last significant digits are also reported. The dielectric constant (ϵ_0) for aqueous solution of L-alanine increased with increase in L-alanine content. This may be due to the larger value of the dipole moment of L-alanine molecules. This suggested that the water structure was modified due to the hydrogen bonds with the L-alanine so as to produce an increase in relaxation time and dielectric permittivity in the mixture with increase.

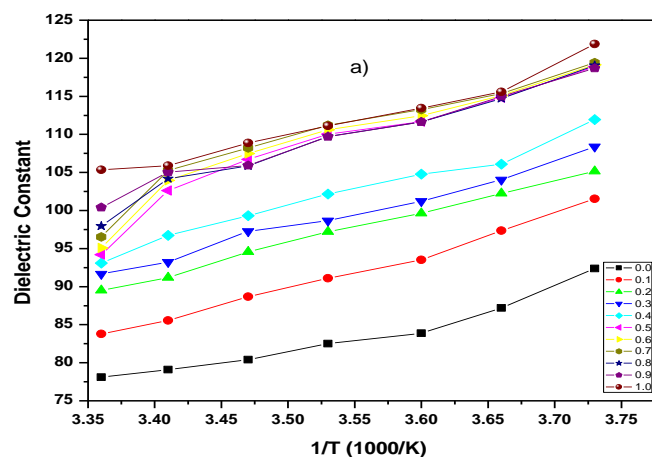


Fig.3 Variation of a) static dielectric constant and b) relaxation time with reciprocal of temperature at various concentrations of -5 °C to 25°C.

V. THERMODYNAMIC PROPERTIES

The dielectric relaxation can be treated as a rate process involving a path over a potential barrier [35]. The energy of activation of the dielectric relaxation process can be calculated from the dielectric relaxation time spectrum by using the Eyring equation. The thermodynamic parameters, like molar energy of activation, ΔH , and molar entropy of activation, ΔS , are determined from the Eyrings rate equation [36].

$$\tau = \frac{h}{kT} \exp(\Delta H - T\Delta S) / RT \quad (6)$$

Here, h is the Planck constant, k is the Boltzmann constant, T is the absolute temperature, τ is the relaxation time and R is the gas constant. The temperature dependence of the relaxation time, described by the Arrhenius plot of $\log(\tau T)$ vs $1000/T$, is shown in Fig. 4 for aqueous L-alanine in water. The values of ΔH and ΔS obtained from the Eyring equation are displayed in table 3 as a function of mixture composition. The activation enthalpy (ΔH) and entropy (ΔS) for pure water were calculated to be 12.39 kJ/mol and 0.23 J/mol K respectively. These values are in good agreement with data in the literature [37]. When an amount of L-alanine is added to water, ΔH and ΔS of the L-alanine-water mixtures decreased from the value of pure water to a minimum at a molar concentration of L-alanine $X_A = 0.8$. The decrease of thermodynamic parameter in the mixtures can be attributed to changes in the hydrogen bond strength and a decrease in the average number of hydrogen bonds. The molar entropy of activation and molar enthalpy of activation were determined using least square fit method.

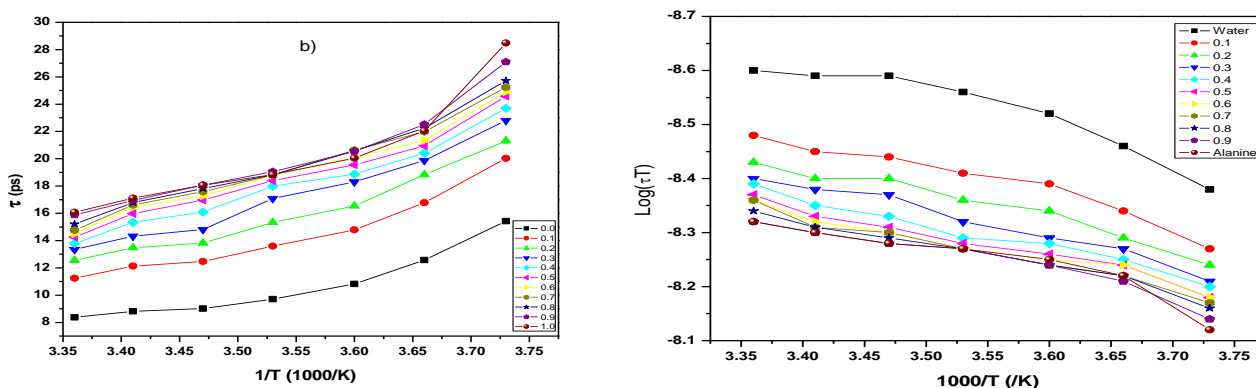


Fig.4 Log (τT) vs. reciprocal of temperature ($1000/T$) at various concentrations -5 °C to 25°C.

Table 3. Thermodynamics parameters for aqueous solution of L-Alanine.

| Molar conc. of L-Alanine | Molar Enthalpy (ΔH) in kJ/mole | Molar Entropy (ΔS) in J/mole K |
|--------------------------|--|--|
| 0 | 10.68(0.23) | 1.69(6) |
| 0.1 | 9.83(1.15) | 0.22(4) |
| 0.2 | 9.27(0.82) | 0.22(2) |
| 0.3 | 8.93(0.94) | 0.22(3) |
| 0.4 | 8.83(0.61) | 0.22(2) |
| 0.5 | 8.67(0.67) | 0.22(2) |
| 0.6 | 8.54(0.68) | 0.22(2) |
| 0.7 | 8.71(0.52) | 0.22(1) |
| 0.8 | 8.52(0.61) | 0.22(2) |
| 0.9 | 8.62(1.01) | 0.22(3) |
| 1 | 8.78(1.70) | 0.22(6) |

VI. KIRKWOOD CORRELATION FACTOR

The Kirkwood correlation factor, determined from the dielectric constant gives information on the collective orientation correlation between the molecules in the sample. The deviation of the Kirkwood correlation factor from unity is a measure of the extent of intermolecular hydrogen bonding. The dipole correlation expressed by the Kirkwood correlation factor 'g' for pure water can be calculated according to the Kirkwood-Froehlich equation [38-40].

$$\frac{4\pi N\mu^2 \rho}{9kTM} g = \frac{(\epsilon_0 - \epsilon_\infty)(2\epsilon_0 + \epsilon_\infty)}{\epsilon_0(\epsilon_\infty + 2)^2} \quad (7)$$

Where μ , ρ and M correspond to the dipole moment in gas phase, density and molecular weight of k is the Boltzmann constant and N is the Avogadro's number.

To calculate the values of 'g' we look $\mu_w = 1.85$ D for water [35, 41] and $\mu_A = 13$ D for L-alanine [42]. The refractive index $\epsilon_\infty = 2.74$ was taken by fitting the value of L-alanine at 25°C. The values of 'g' are listed in Table 4. The observed g was 2.82 for pure water. The high values of 'g' indicate parallel orientation of the electric dipoles in a molecule [35]. It can be seen from Fig. 5 that as water was added in the L-alanine, the value of 'g' increased negligibly in the solution. The decrease of correlation factor in the L-alanine-water mixture may be due to association effects. As molar concentration of L-alanine increase in an aqueous medium there is a decrease in the number of self-associated groups formed by the hydrogen bonds.

Table 4. Kirkwood correlation factor 'g' of L-Alanine in H₂O at 25°C at various concentrations.

| Wt. % of L-Alanine | g |
|--------------------|------|
| 0 | 2.82 |
| 0.89 | 2.69 |
| 1.78 | 2.59 |
| 2.67 | 2.41 |
| 3.56 | 2.24 |
| 4.45 | 2.09 |
| 5.35 | 1.96 |
| 6.24 | 1.83 |
| 7.13 | 1.76 |
| 8.02 | 1.69 |
| 8.91 | 1.67 |

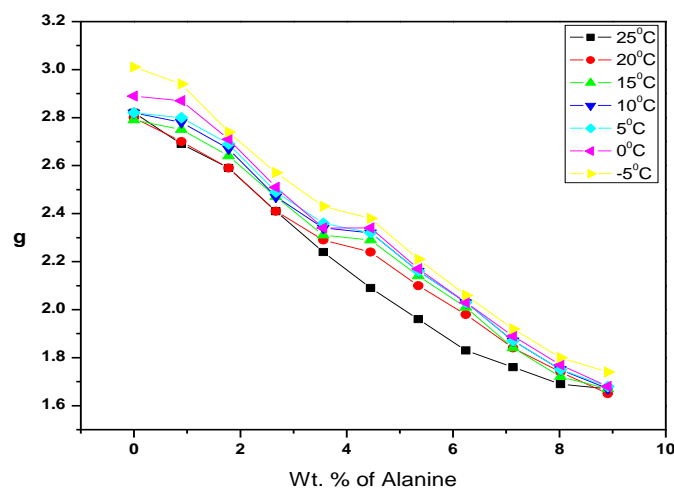


Fig.5 Plot of g respect to wt. % of Alanine at various temperatures.

VII. CONCLUSION

We have studied the dielectric relaxation in aqueous solution of amino acid (L-alanine). The values of static dielectric constant, relaxation time, thermodynamic parameters and Kirkwood correlation factor of amino acid (L-alanine) and water mixtures for various temperatures are reported. The experimental dielectric relaxation data contains valuable information regarding water and amino acid (L-alanine) mixture.

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