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Thermodynamics Properties of Amino Acid with Water Mixture using Time Domain Reflectometry Technique

Ravindra Talware
Department of Physics, K. J. Somaiya College of Arts, Commerce and Science, Kopargaon - 423601, Dist. Ahmednagar, Maharashtra, India

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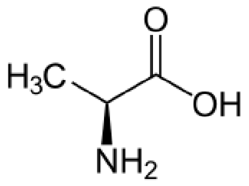
ABSTRACT

In this paper we have reported the thermodynamics properties of the amino acids (L-alanine) in water solution were carried out using time domain reflectometry at 250C to -50C 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 dielectric relaxation parameters increase with an increase in concentration (mM) of amino acid due to the structure of hydrogen bond groups by the amino acid molecules in the aqueous solution. The relaxation peak shifted to lower frequency with an increase in molar concentration of amino acid.

Keywords : Thermodynamics Properties, Amino Acid, Time Domain Reflectometry.

I. INTRODUCTION

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 [1]. 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 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 [2] have explained the dielectric dispersion of unclear of amino acids, peptides and proteins. They found that adsorbed water improved the dielectric constant precisely.

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) ie. 0 to 1 M/liter H_2O. We deliberate the dielectric relaxation spectra for these solutions at 25^0C to -5^0C using time domain reflectometry [3-4] 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

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 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 $R_1(t)$ and with sample $R_X(t)$ were recorded in a time window of 5ns and digitized over 2000 points.

Data Analysis

The step pulses recorded without sample $R_1(t)$ and with sample $R_X(t)$ were subtracted and added to get

$$p(t) = [R_1(t) - R_X(t)] \qquad (1)$$

$$q(t) = [R_1(t) + R_X(t)] \qquad (2)$$

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:

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

Where p(ω) and q(ω) 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, ε*(ω), were obtained from the reflection coefficient spectra ρ*(ω) by applying the bilinear calibration method suggested by Cole [5].

III.Result and Discussion

The general form of the relaxation equation is given by the Havriliak-Negami equation [6].

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

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 (α=0 and β = 1) implies a single relaxation time while the Cole-Cole model (0≤α≤1 and β=1) and Cole-Davidson model (α=0 and 0≤β≤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 α=0 and 0≤β≤1 and experimental values of ε*(ω) were fitted to the Cole-Davidson equation as,

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

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. 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. 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.

Thermodynamics Properties

The dielectric relaxation can be treated as a rate process involving a path over a potential barrier [7]. The energy of activation of the dielectric relaxation process can be calculated from the dielectric relaxation time spectrum by using the Erying equation. The thermodynamic parameters, like molar energy of activation, ΔH, and molar entropy of activation, ΔS, are determined from the Eryings rate equation [8].

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

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 (τT) vs 1000/T, is shown in Fig. 1 for aqueous L-alanine in water. The values of ΔH and ΔS obtained from the Erying equation are displayed in table 1 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 [9]. 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.

Table 1. 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)

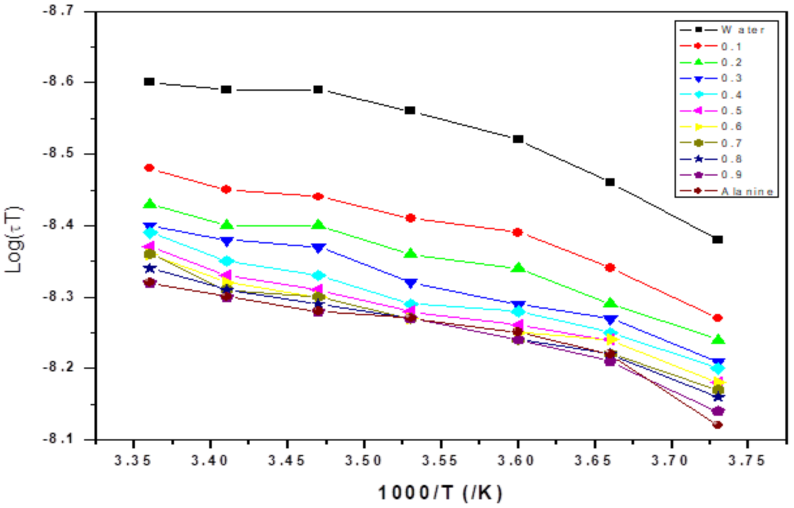


Fig.1 Log (τT) vs. reciprocal of temperature (1000/T) at various concentrations -5 ^{0}C to 25^{0}C.

IV. 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 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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