

Dielectric Relaxation Properties Of Aqueous Solution Of L-Phenylalanine At Microwave Frequencies

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Abstract

Dielectric relaxation properties for aqueous solution of L-phenylalanine were carried out using time domain reflectometry (TDR) technique at 25^oC, 20^oC, 15^oC and 10^oC in the frequency range from 10 MHz to 50 GHz. Aqueous solutions of L-phenylalanine are prepared for five different molar concentrations of the respective amino acid. The relaxation behaviour of aqueous solutions of L-phenylalanine has been illustrated by using Cole-Davidson model. The static dielectric constant (ϵ_0), dielectric constant at high frequency (ϵ_∞), relaxation time (τ) and relaxation time distribution parameter (β) extracted from the complex permittivity spectra using least squares fit method. Activation enthalpy (ΔH) and entropy (ΔS) show endothermic interaction. Also observed hydrogen bonding interactions for aqueous solution of L-phenylalanine through determination of Kirkwood correlation factor (g^{eff}).

Keywords: Dielectric properties, Kirkwood correlation factor, Thermodynamics

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I. INTRODUCTION

Many natural phenomenon is occurring due to the interaction between matter and energy. In these phenomenon, aqueous solution of L-phenylalanine give very effective information about molecular interactions. Therefore, the study of aqueous solution of L-phenylalanine having great importance in the field of molecular physics.

Dielectric relaxation studies have emerged as a powerful tool in the field of physical chemistry, providing valuable insights into the behaviour of molecules and their interactions in solution. Among the numerous compounds investigated, L-phenylalanine, an essential amino acid with a pivotal role in the biosynthesis of proteins, has garnered considerable attention. When dissolved in water, L-phenylalanine exhibits intriguing dielectric relaxation properties, which offer a unique window into its structural and dynamic characteristics. This study delves into the dielectric relaxation of aqueous solutions of L-phenylalanine, shedding light on the intricate interplay between this biomolecule and its surrounding solvent. By unravelling the dielectric behaviour of L-phenylalanine, we aim to enhance our understanding of its solution properties, ultimately contributing to broader insights into the behaviour of biomolecules in aqueous environments. The dielectric relaxation study of amino acids in aqueous media has received considerable attention [1,2].

Amino acids are very small biomolecules and are the principal building blocks of proteins and enzymes. Chaudhari et al [3] have studied the dielectric relaxation properties and activation enthalpy and entropy for aqueous solution of amino acids. The chemical properties of the amino acids of proteins determine the biological activity of the protein. Proteins not only catalyse all (or most) the reactions in living cells, but also control virtually all cellular processes. The amino acid exists in solution mainly in the zwitterion form, where positive and negative charges exist in different parts of the molecule. The nature of interaction that exists between the $-C=O$, $-OH$ and $-NH$ groups in water plays an important role in the biological systems and drug synthesis [4]. Baylay[5] has studied the dependence of dielectric constant on concentrations of amino acids. Jones,[6] Nolory,[7] and Wyman,[8,9] have studied aqueous solutions of amino acids. The temperature dependent dielectric relaxation study of aqueous solutions of Glycine and Valine have been reported by Lokhande et al.[2] using the TDR technique in a frequency range of 10 MHz-10 GHz. Using the same TDR technique Talware et.al.[10] also studied dielectric relaxation study of glycine–water mixtures in the frequency range of 10 MHz to 30 GHz. This work reveals that water structure is modified due to hydrogen bond by the glycine so as to produce an increase in relaxation time and dielectric permittivity in the mixture. Dielectric properties of lysine aqueous solutions have been investigated by Liao et. al.[11] using cavity perturbation technique. Amino acids in aqueous mixed solvents have also been studied by many authors.[12-20]

The aim of this study were to understand the temperature dependent structural changes of aqueous solution of L-phenylalanine and modification of hydrogen bonding in this mixture. The present work deals with the comparative dielectric relaxation study of aqueous solutions of L-phenylalanine using pico-second Time Domain Reflectometry (TDR) technique in the frequency range 10 MHz to 50 GHz at 25^oC, 20^oC, 15^oC and 10^oC. From the complex permittivity spectra, the static dielectric constant (ϵ_0), relaxation time (τ) and asymmetric relaxation distribution parameter (β) were obtained by least square fit method. Kirkwood correlation factor and thermodynamics parameters were also determined to study the heterogeneous interactions through hydrogen bonding.

II. MATERIALS AND METHODS

L-phenylalanine in powder form were obtained commercially from S. D. Fine Chemical Limited, India and was used without further purification. Water was carefully purified by deionization and double distillation and was used for the measurement immediately after the purification. The solutions were prepared at room temperature for different mole fraction water. The dielectric measurements were carried out using TDR.[21,22].

The complex permittivity spectra were studied using TDR technique [23]. The Tektronix model no. DSA8300 Digital Serial Analyzer sampling mainframe along with the sampling module 8E10B has been used for the dielectric measurement using TDR technique. A repetitive fast rising voltage pulse was fed through coaxial line system of impedance of 50 Ω . All measurements are carried out in open load condition.

Sampling oscilloscope monitors the 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 5 ns and digitized in 2000 points in the memory of the oscilloscope and transferred to the computer for further analysis. The selection of proper time window, sampling rate and bilinear calibration method suggested by Cole et al. were useful to measure the accurate complex permittivity at higher frequencies [24]. The smaller time window causes loss of signal while larger time window includes unwanted reflections. Thus selection of proper time window is important to minimize these effects. Further the Fourier transformation of the pulses and data analysis were done earlier to determine complex permittivity spectra using nonlinear least squares fit method [24, 25].

III. RESULT AND DISCUSSION

The dielectric permittivity $\epsilon'(\omega)$ and dielectric loss $\epsilon''(\omega)$ of aqueous solution of L- phenylalanine at 25^oC, were measured using TDR technique as shown in Fig. 1. It is observed that at the relaxation frequency of the real part $\epsilon'(\omega)$ of complex permittivity spectrum of aqueous solution of L- phenylalanine decreases with increase in the frequency. It is due to the less effect of applied field which has been cancelled by the dipoles.

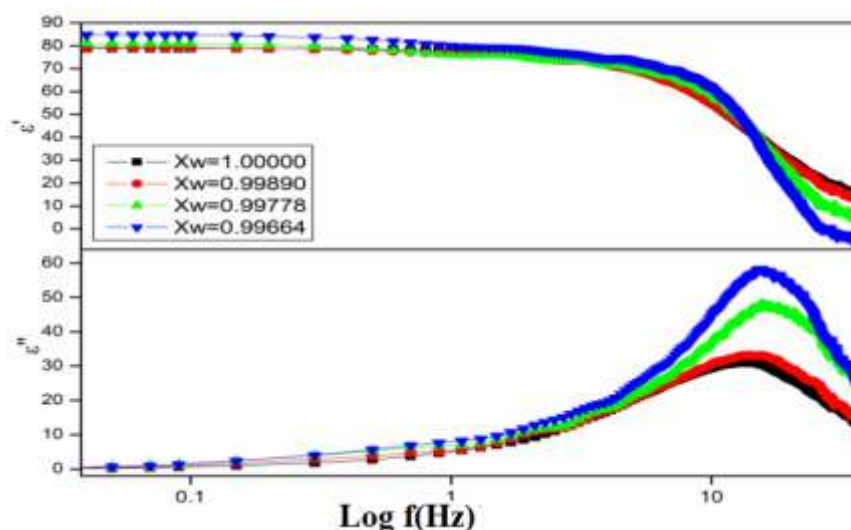


Figure 1. Frequency dependant dielectric permittivity (ϵ') and dielectric loss (ϵ'') for aqueous solution of L-phenylalanine with different mole fraction of water (X_w) at 25 °C.

The complex permittivity $\epsilon^*(\omega)$ data were fitted by the non-linear least squares method to the Cole-Davidson model [26].

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

where, ϵ_0 is the static dielectric constant, ϵ_∞ is the permittivity at high frequency, τ is the relaxation time in pico-second. The exponents α and β describes the irregularity and broadness of the corresponding spectra, β are empirical parameters for distribution of relaxation times with values between 0 and 1. In this study the aqueous solution of L- phenylalanine shows Cole–Davidson type dispersion. Therefore the complex permittivity spectra $\epsilon^*(\omega)$ of the L- phenylalanine-water mixtures were fitted in CD model using non-linear least squares fit method to determine the dielectric relaxation parameters. The real part (ϵ') of complex permittivity will decrease when the relaxation frequency is reached since less of the applied field is cancelled by the dipoles as the frequency is increased. In an imaginary part (ϵ'') of the complex permittivity spectra the peak value occurs at this frequency since most of the energy lost at that point[27]. The Cole-Cole plot shows dielectric loss $\epsilon''(\omega)$ for aqueous solutions of L- phenylalanine at different mole fraction of water as a function of dielectric dispersion $\epsilon'(\omega)$ in Fig. 2. The plot is asymmetric in nature and exhibits Cole-Davidson type behavior.

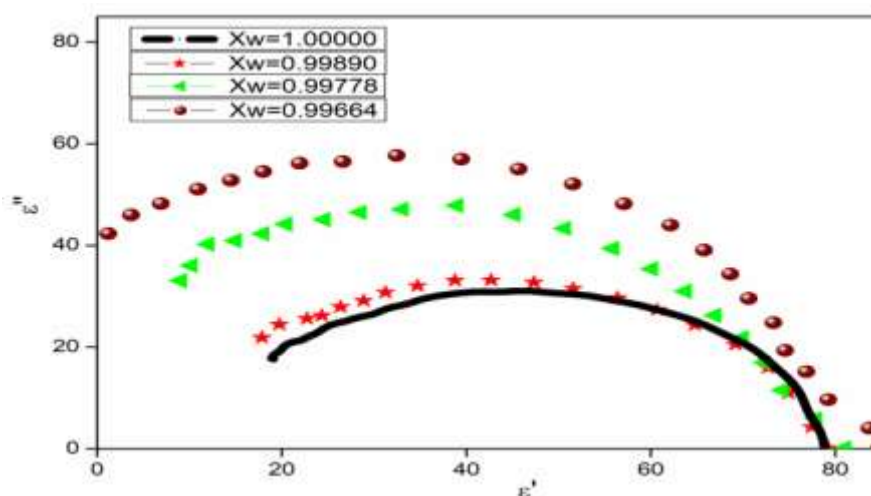


Figure 2. Cole-Cole plot for aqueous solutions of L-phenylalanine.

Dielectric constant and Relaxation time

The values of dielectric parameters (ϵ_0 , ϵ_∞ , τ and β) for aqueous solution of L-phenylalanine at 25^oC, 20^oC, 15^oC and 10^oC with different mole fraction of water(X_w) have been reported in Table 1.

Table 1. Dielectric Relaxation Parameter For Aqueous Solutions of L-Phenylalanine at Different Mole Fraction Of Water (X_w) and Temperature.

25 ^o C				
X_w	ϵ_0	ϵ_∞	τ (ps)	β
0.9966	85.38(10)	2.48(11)	9.54(53)	0.721(1)
0.9978	81.92(11)	2.45(12)	8.09(55)	0.692(1)
0.9989	79.61(7)	1.87(7)	5.65(33)	0.728(1)
1.0000	78.78(3)	2.04(3)	8.43(6)	0.931(2)
20 ^o C				
X_w	ϵ_0	ϵ_∞	τ (ps)	β
0.9966	85.32(4)	1.98(6)	10.65(29)	0.817(1)
0.9978	81.96(8)	2.99(9)	8.09(32)	0.725(1)
0.9989	80.97(6)	1.77(7)	5.95(32)	0.743(1)
1.0000	79.74(8)	2.89(6)	9.62(3)	0.939(1)
15 ^o C				
X_w	ϵ_0	ϵ_∞	τ (ps)	β
0.9966	86.70(4)	1.97(6)	11.25(30)	0.824(6)
0.9978	83.34(4)	1.77(5)	9.50(27)	0.816(6)
0.9989	82.11(3)	1.80(5)	7.32(25)	0.828(7)
1.0000	80.88(10)	3.30(7)	10.27(4)	0.946(2)

10°C				
X_w	ϵ_0	ϵ''	τ (ps)	β
0.9966	90.00(5)	1.94(6)	12.15(31)	0.830(6)
0.9978	87.84(3)	1.10(4)	11.12(24)	0.862(5)
0.9989	84.73(3)	1.61(4)	8.62(24)	0.860(6)
1.0000	82.89(3)	5.72(2)	11.32(1)	0.993(7)

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 water 78.78(3) means 78 ± 0.03 . The decrease in dielectric constant of the solution with increasing mole fraction of water (X_w) and systematic change in the dielectric parameters of the solution can be explained on the basis of molecular interactions.

The plot of ϵ_0 , vs. mole fraction of water in Fig. 3 of aqueous solution of L-phenylalanine shows the linear behaviour in all concentrations and around in the lower molar solution the non-linearity is exhibited, which is attributed to the large breaking of the homogeneous structures due to the formation of higher order heterogeneous species [28].

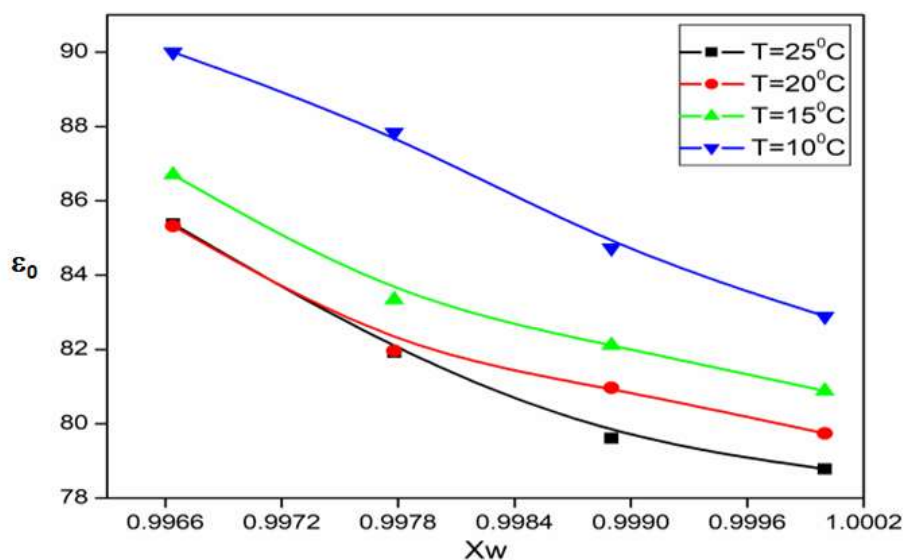


Figure 3. Static dielectric constant (ϵ_0) of vs. mole fraction of water (X_w) for aqueous solutions of L-phenylalanine at different temperature.

The strong electrostatic interactions between amino acid dipolar ions and the solvent polar molecules can be expected, this is may be because the dipole moment for the amino acid dipolar ion is much greater than that of ordinary polar molecules. According to Debye theory, the large dipole moment of such a biomolecule should have large permittivity values for this solution. This is confirmed by the present work where amino acids produce remarkable permittivity increments in aqueous solutions of polar solvents. The values of static dielectric constant and relaxation time decrease with an increase in temperature. This may be due to a decrease in orientational correlation of dipole moments with an increase in temperature [3]. The decrease in the dielectric constant as the concentration of water increases in the L-phenylalanine+water mixtures suggests that the polarizing effect of water, its molecular structure, and its concentration dominate the dielectric behaviour of the mixture, leading to a lower dielectric constant when water solvent is the dominant component.

From Fig. 4, the decrease in τ values with increasing mole fraction of water indicates that number of dipoles decreases in the solution, the intermediate structure formed rotates faster there by giving the decrease in values of τ in the solution. The dielectric properties will also get affected by temperature. 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 [28], this is due to there may be hydrogen bonding and other interactions between molecules. As temperature increases, these interactions can be weakened, allowing molecules to move more freely and reducing the time required for the system to relax.

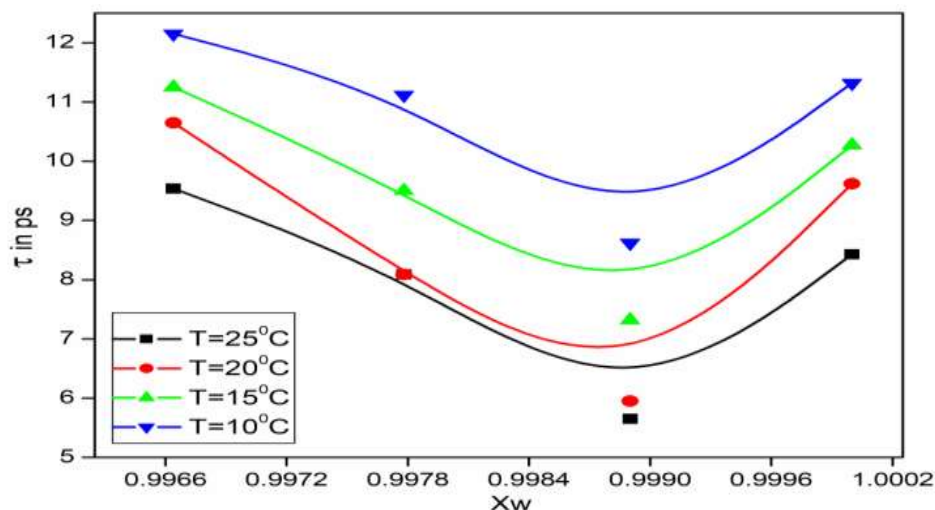


Figure 4. Relaxation time (τ) vs. mole fraction (X_w) of aqueous solution of L-phenylalanine at different temperature.

Kirkwood correlation factor

To understand the significance of association effect due to the hydrogen bonding, it is very useful to compute the values of Kirkwood correlation factor g for these binary mixtures using following expression [29,30]

$$\frac{(\epsilon_0 - \epsilon_\infty)(2\epsilon_0 + \epsilon_\infty)}{\epsilon_0(\epsilon_\infty + 2)^2} = g\mu^2 \frac{4\pi N\rho}{9\kappa TM} \tag{2}$$

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

For binary mixture, the static dielectric permittivity needs to be considered as the dipole orientation correlation factor (g^{eff}). The modified form of Eq. (3) is used to study the orientation of the electric dipoles in the binary mixtures as follows[29,30].

$$\frac{4\pi N}{9kT} \left[\frac{\mu_x^2 \rho_x X_x}{M_x} + \frac{\mu_A^2 \rho_A (1 - X_x)}{M_A} \right] \times g^{eff} = \frac{(\epsilon_{0m} - \epsilon_{\infty m})(2\epsilon_{0m} + \epsilon_{\infty m})}{\epsilon_{0m}(\epsilon_{\infty m} + 2)^2} \tag{3}$$

where M_x and M_A are molecular weight of water and L-phenylalanine respectively. ρ_x and ρ_A are corresponding densities, X_x is mole fraction of water. ϵ_{0m} and $\epsilon_{\infty m}$ are the static dielectric constant and dielectric constant at high frequency of the mixtures. To calculate the values of g^{eff} , we have taken $\mu_A = 2.42D$ [31] and $\mu_x = 1.85D$ [32] for L-phenylalanine and water respectively. The values of ϵ_∞ are taken from the fitting data.

The values of g^{eff} for aqueous solution of L-phenylalanine at different temperature are reported in Table 2. It illustrates that g^{eff} values for all the concentrations greater than unity and reveals parallel orientation of electric dipole among molecules. The g^{eff} values of aqueous solution of L-phenylalanine at different temperature shown in Fig. 5. The g^{eff} values are decreasing with increasing the concentration of water indicates that there is stronger hydrogen bonded parallel dipolar ordering in the mixtures as compared to the g^{eff} values for pure water molecules.

Table 2. Kirkwood Correlation Factor (g^{eff}) For Aqueous Solution of L-Phenylalanine at Different Temperature.

X_w	g^{eff}			
	25 ^o c	20 ^o c	15 ^o c	10 ^o c
0.9966	3.07	3.62	3.02	3.08
0.9977	2.94	2.9	2.9	3
0.9989	2.86	2.86	2.85	2.89
1.0000	2.83	2.81	2.81	2.83

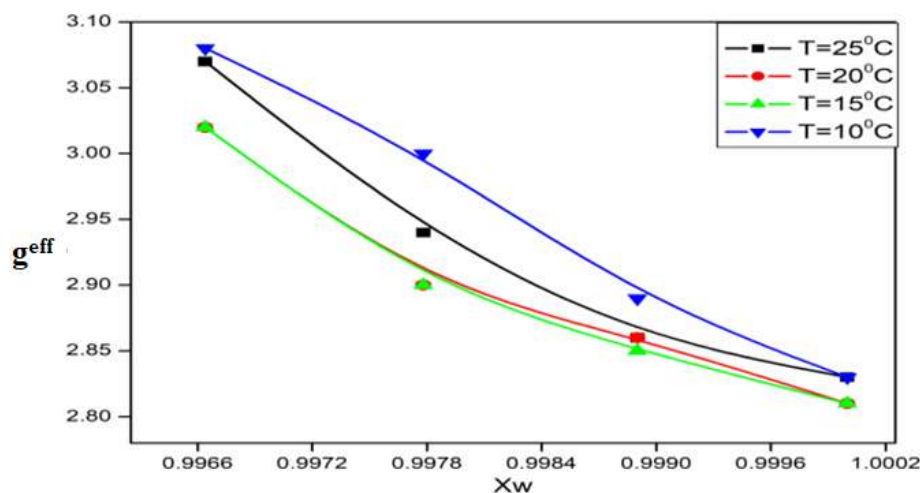


Figure 5. Kirkwood correlation factor (g^{eff}) vs. Mole fraction water for aqueous solution of L-phenylalanine.

Thermodynamics parameters

The Eyring equation is used to describe the relationship between reaction rate and temperature. It is analogous to the Arrhenius equation, which also describes the temperature dependence of reaction rates. However, whereas Arrhenius equation can be applied only to gas-phase kinetics, the Eyring equation is helpful in the study of gas, condensed, and mixed-phase reactions [33]

The Eyring equation gives a more precise calculation of rate constants and provides approaching into how a reaction progresses at the molecular level [33]. The thermodynamic parameters evaluated using Eyring equation is as follows [34]

$$\tau = \frac{h}{kT} \exp\left(\frac{\Delta H}{RT}\right) \exp\left(\frac{-\Delta S}{R}\right) \tag{4}$$

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), h is the Planck's constant and R is the gas constant. The results of activation energies are obtained by least square fit method and are reported in Table 3. ΔH for water is 10.88 kJ/mol that is energy required to break single hydrogen bond [35]. However, it occurs high for $X_w = 0.9989$ and 0.9978 concentration for aqueous solution of L-phenylalanine. This reveals that the aqueous solutions of L-phenylalanine requires more energy for rotation of molecules as well as to break hydrogen bonding than pure water. Also it suggests the hetero molecular association of L-phenylalanine-water molecules. Meanwhile, for $X_w = 0.9966$ concentrations $\Delta H < 10.88$ kJ/mole indicates that requires less energy for rotation of molecules as well as to break hydrogen bonding.

Table 3. Activation Enthalpy ΔH (KJ/mol) and Entropy ΔS (J/mol K) Of Aqueous Solution of L-Phenylalanine For Different Mole Fraction of Water.

X_w	ΔH (kJ/mol)	ΔS (J/mol k)
0.9966	8.51	0.224
0.9978	13.29	0.242
0.9989	18.31	0.261
1.0000	10.88	0.233

VI. CONCLUSION

The temperature dependent complex permittivity spectra of L-phenylalanine in aqueous solution have been studied using TDR technique in the frequency range 10 MHz–50 GHz. Using Cole-Davidson model, microwave dielectric properties of aqueous solution of L-phenylalanine have been carried out. Also investigating how the dielectric constant (ϵ_0), relaxation time (τ) are sensitive to the variations in mixture constituents of aqueous solutions of L-phenylalanine. The observed shifts in dielectric relaxation times with changing temperatures suggest the presence of dynamic processes within the system. The Kirkwood correlation factor is greater than unity reveals parallel ordering of the electric dipole. Activation enthalpy confirms strong interaction takes place among aqueous solution of L-phenylalanine. Overall, this study contributes to the understanding of L-phenylalanine behavior in aqueous solutions and provides a foundation for future research in this domain.

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