# Relaxation dynamics of L-alanine in water medium investigated by dielectric relaxation spectroscopy

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## ARTICLE INFO

## ABSTRACT

The complex dielectric permittivity of L-alanine in aqueous medium at different concentrations and different temperatures were measured in the microwave ($0.02 < \nu/\text{GHz} < 20$) frequency region by using open-ended co-axial probe technique. From the reflection coefficient and impedance data, the real and imaginary part of the dielectric permittivity values is determined. It is observed that there is a decrease in the real part of the dielectric permittivity up to certain frequency and an increase in the imaginary part of the dielectric permittivity with increase in the molar concentration of L-alanine in water medium. Based on the experimental data the average relaxation time values are calculated and its behavior is analyzed in terms of bound water and free water molecules. The theoretical dipole moment of L-alanine is calculated at gaseous state as well as in aqueous medium by using PCM and IEFPCM model at HF, DFT/B3LYP and MP2 calculations using 6-311G* basis set. Analysis between experimentally determined parameters and computed dipole moments were discussed. The mean molecular polarizability is calculated from the Lippincott δ function potential model and compared with the Le Fèvre method of polarizability values.

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## 1. Introduction

The study of dielectric relaxation behavior of biological liquids is a task of great importance because it provides valuable information on the structural dynamics of molecules. Most of the biological systems contain the hydrogen bonds between molecules [1]. This hydrogen bond plays an important role in the various bio functional activities, metabolic reactions, protein synthesis, drug designing, and electrical properties of the material. Dielectric relaxation spectroscopy (DRS) technique is so sensitive to detect changes in the molecular dynamics, inter molecular bonding between the molecules and orientation of the dipoles. The understanding of intermolecular hydrogen bonding, typical relaxation behavior of proteins solutions attracted many researchers for the study of interest for recent and past [2–14]. The electromagnetic characteristic of basic amino acids in solution and its applications in microwave sterilization as well as mechanism process explained by Chen Meng et al. [15]. Floros et al. [16] analyzed the lysozyme with molecular dynamics simulations in terms of the dielectric function and the results were explained by the hydration shell decomposition approach. Godfrey et al. [17] interpreted the rotational spectra of two conformers of alanine together with molecular orbital calculations using a larger

basis set (6-311G**). Degtyarenko et al. [18] applied the Born-Oppenheimer molecular dynamics simulations of an L-alanine zwitter-ion solvated in water medium by considering the whole system relatively larger in size i.e. the L-alanine amino acid and 50 water molecules have been treated quantum mechanically.

## 2. Experimental and computational details

The chemical sample used in this work such as L-alanine of analytical grade is procured from SRL Pvt. Ltd., Mumbai, India is taken in a different molar concentration levels (0.1 to 1 M) in double distilled water medium with respective maximum solubility. The complex dielectric permittivity ($\varepsilon^* = \varepsilon' - j\varepsilon''$) of these samples is measured in the microwave frequency range 20 MHz-20 GHz using the open-ended coaxial probe method [19,20] between 298 K–323 K. The high frequency dielectric permittivity ($\varepsilon_\infty$) is measured by using Abbe refractometer. The dipole moment of the L-alanine molecule is calculated theoretically at gaseous state as well as in aqueous medium by using IEFPCM and PCM model at the DFT/B3LYP and MP2 using 6-311G* basis set using Gaussian software-03 [21–28]. The difference in energy between aqueous L-alanine and L-alanine (gaseous state) provides the information regarding the strength of the hydrogen bond interaction between L-alanine and water molecules and which is tabulated in the Table 1, respectively. The average dielectric relaxation time is determined from

**Table 1**
Theoretical dipole moment of the L-alanine molecule in gaseous state, aqueous solvent medium and difference in energy is calculated from the different quantum mechanical methods and its molecular polarizability ($\alpha_M$) from the Lippincott delta function model and Lefevre method.

| State | Gaseous state | | | | In water medium | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Model | HF | DFT-B3LYP | MP2 | Exptl. value from literature [17] | IEFPCM | | | PCM | | |
| | | | | | HF | DFT-B3LYP | MP2 | HF | DFT-B3LYP | MP2 |
| Basis sets | 6-311G* | 6-311G* | TZVP | | 6-311G* | 6-311G* | 6-311G* | 6-311G* | 6-311G* | 6-311G* |
| Dipole moment (Debye) | 2.293 | 1.737 | 2.436 | 1.80 | 3.540 | 3.231 | 3.735 | 2.291 | 3.231 | 4.060 |
| Energy (a.u.) | −321.7164 | −323.7360 | −322.9982 | | −321.8122 | −323.7571 | −322.9871 | −321.8061 | −323.7477 | −322.9888 |
| Difference in Energy (kcal/mol) $E = E_{water\ medium} - E_{gas\ state}$ | | | | – | 56.4758 | 13.2410 | 6.9653 | 60.2408 | 6.9025 | 5.8988 |
| Molecular Polarizability ($\alpha_M * 10^{-25}$ cm$^{-3}$) | 82.655 | 83.581 | 82.926 | – | 83.600 | 85.034 | 85.842 | 84.348 | 84.873 | 84.892 |
| Polarizability ($\times 10^{-25}$ cm$^{-3}$) by Lefevre method | 73.29 | 73.29 | 73.29 | – | 73.29 | 73.29 | 73.29 | 73.29 | 73.29 | 73.29 |

the Debye and Cole-Cole plots [29] and the behavior is analyzed in terms of bound water interaction with the amino acid molecule. The mean molecular polarizability ($\alpha_M$) value of L-alanine in gaseous state and aqueous medium is calculated from the Lippincott $\delta$ function potential [30,31] model by considering optimized bond lengths from the minimum energy structure and compared with the Le Fèvre method [32] of polarizability values.

## 3. Results and discussion

The temperature dependent low frequency dielectric constant ($\varepsilon_0$) and high frequency dielectric permittivity ($\varepsilon_\infty = n^2$) values of different molar concentrations of L-alanine in aqueous medium are shown in Figs. 1 and 2. From the Figs. 1 and 2, it is noted that there is an increase in the dielectric constant, high frequency dielectric permittivity value with increase in the molar concentration of L-alanine in water medium and decreasing trend with an increase in temperature. It may be due to the larger value of the dipole moment of L-alanine molecules and also water structure is modified due to hydrogen bond. The nonlinear variation of the graphs indicates that molecular interaction exists between the L-alanine and water mixtures through H-bonding. The complex dielectric permittivity ($\varepsilon^* = \varepsilon' - j\varepsilon''$) for all concentrations of L-alanine with frequency at one of the temperatures 308 K as shown in Fig. 3. It is observed that there is an increase in the real part of dielectric

permittivity value ($\varepsilon'$) with increase in the molar concentration levels of L-alanine in water up to 5GHz and thereafter decreases with increase in frequency and the same is observed for other temperatures. This may due to the rotational diffusion of zwitterionic amino acid molecule. The increase in the dielectric loss ($\varepsilon''$) (From the Fig. 3) with increase in the molar concentration of L-alanine in water medium, it may due to the presence of more number of self-associated groups formed by the hydrogen bonds with water molecules. Further, the dielectric field strength $\Delta\varepsilon = (\varepsilon_0 - \varepsilon_\infty)$ parameter reveals the presence of clusters in the solutions. These clusters are developed in the liquid solution due to the hydrogen bond network linkage or electrostatic attractive forces between the polar groups present in the system. The polarity nature of the L-alanine water system is greater when compared to the individual aqueous system. From Fig. 4, it is noted that the dielectric field strength value increased with increase in L-alanine concentration in water and which indicates the existence of clusters in the solution. These clusters are responsible for increase in the degree of polarization of the dipoles results increase in $\Delta\varepsilon$ values. The water molecules nearer to L-alanine (bound water) play a significant role in the increase of degree of polarization and it causes to rise in the electrical susceptibility and field strength values. The degree of polarization is affected by the increase in temperature which in turn decreases the dielectric relaxation strength values. From the Fig. 4 it is observed that dielectric field strength value decreases with rise in temperature and it is due to breakage of the number of hydrogen bonds between the self-associated
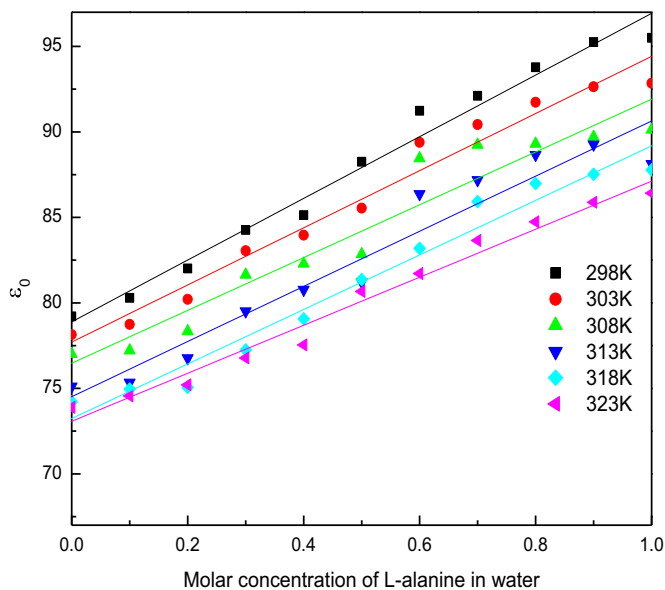


**Fig. 1.** Graph of low frequency dielectric permittivity ($\varepsilon_0$) with respective molar concentration of L-alanine in water at different temperatures.
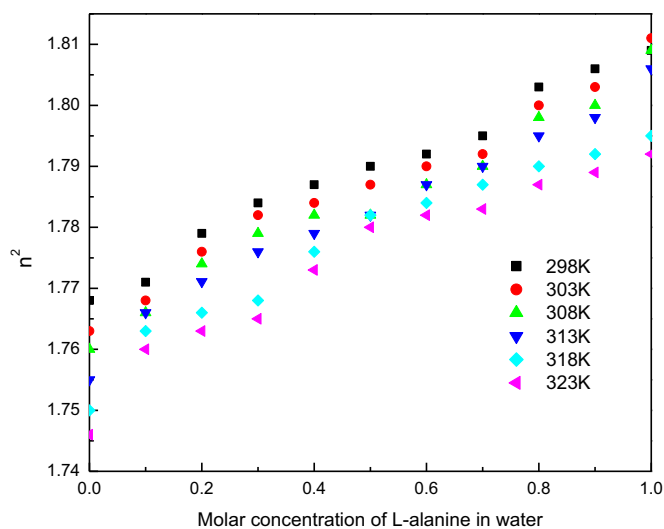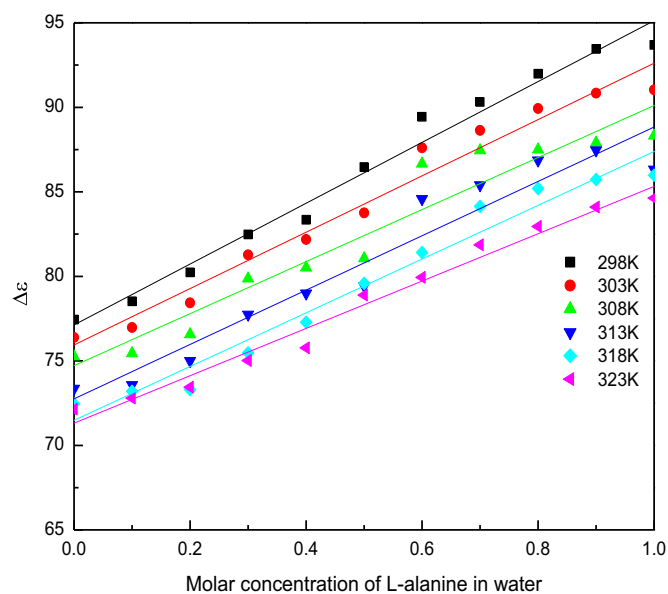


**Fig. 2.** Graph of high frequency dielectric permittivity ($\varepsilon_\infty = n^2$) with respective molar concentration of L-alanine in water at different temperatures.
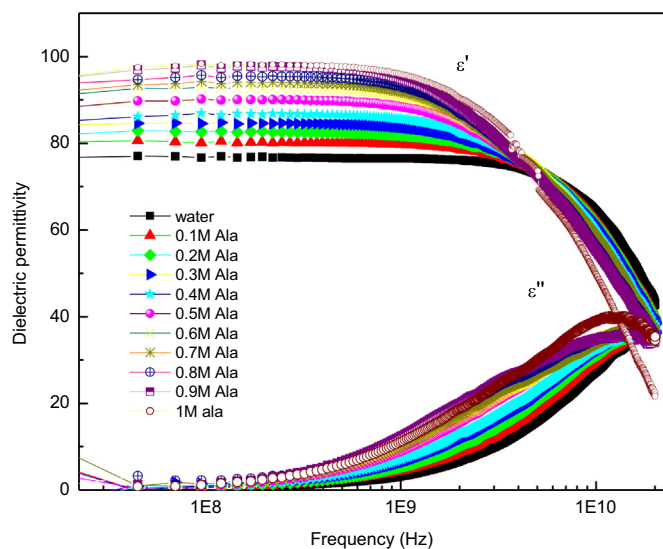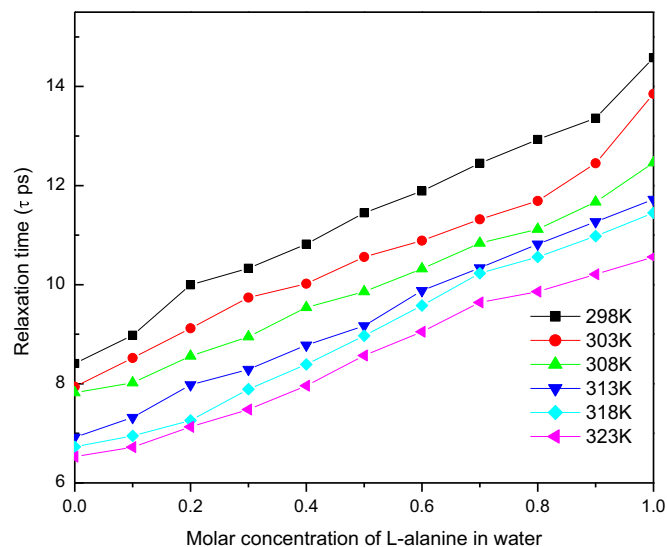
**Fig. 3.** Plot of real ($\varepsilon'$) and imaginary part of dielectric permittivity ($\varepsilon''$) of L-alanine in water at one of the measured temperatures 308 K.



**Fig. 5.** Plot of relaxation time ($\tau$ ps) with respective molar concentration of L-alanine in water at different temperatures.

groups (multimers) and also obstruct the orientational movement of the molecules in the liquid medium.

From the Fig. 5, it is realized that the relaxation time of L-alanine-water mixtures is greater than that of water and it may due to hydrogen bonding between L-alanine to the water molecules. These hydrogen bonds tend to correlate additively causes an increase in the net dipole moment and polarizability values of the system. Further, L-alanine molecule surrounded with water (bound water) relaxes little bit slower and absorb more electromagnetic energy when compared to the non-bound water. Since the relaxation time value of bound water is slightly greater than non-bound water i.e., 8. 47 ps which as shown in the Fig. 5. The rotational moment of the combined system hindered by the nearby molecules causes further slower rotation of the dipoles and it leads to the dominant relaxation process. Thermal energy is sufficient to break the hydrogen-bonded network in the liquid system and effects the degree of polarization, hence decrease in the relaxation time values which are as shown in Fig. 5.
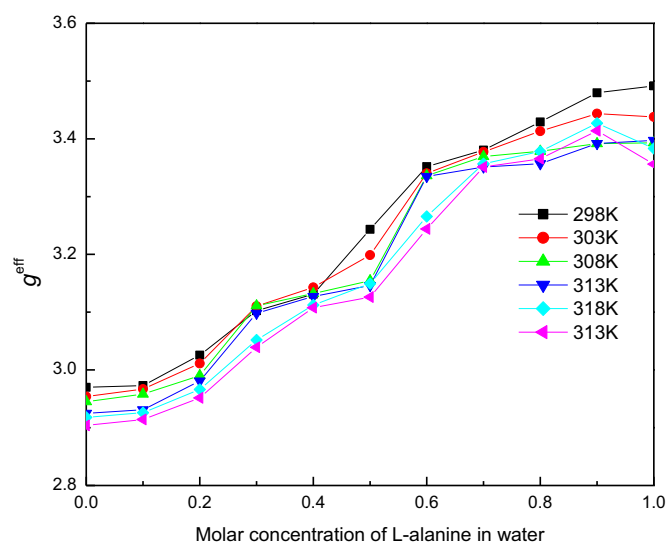
The ordering nature of the dipoles and their interaction is well explained by the Kirkwood correlation $g^{eff}$ factor [33,34]. If the $g^{eff}$ factor is less than one indicates the random orientation of the dipoles whereas if it is greater one indicates ordering nature as well as interaction between the dipoles. In order to calculate the ordering nature of the dipoles ($g^{eff}$ value) we have considered the theoretically derived dipole moments of L-alanine in gaseous state as well as in aqueous medium. From the Fig. 6, it is observed that $g^{eff}$ value increases with increase in molar concentration of L-alanine in water due to increase in the effective dipole-dipole interaction between the self-associated groups and which leads to alignment of the dipoles in the field direction. The interaction as well as ordering nature of the dipoles reduced by raising the temperature. From the Fig. 6, it noted that $g^{eff}$ value decreases with increase in temperature and it is due to breakage of hydrogen bonded network in the liquid system.

The theoretical dipole moment of the L-alanine molecule is calculated at gaseous state as well as aqueous medium by using different solvation models such as Polarizable Continuum Model (PCM), Integral Equation Formalism variant (IEFPCM) with Density Functional Theoretical (DFT-B3LYP), Møller–Plesset perturbation theory (MP2) methods at



**Fig. 4.** Graph of excessive dielectric constant ($\Delta\varepsilon$) with respective molar concentration of L-alanine in water at different temperatures.



**Fig. 6.** Plot of Kirkwood effective ($g^{eff}$) correlation factor with respective molar concentration of L-alanine in water at different temperatures.

6-311G* basis set. In the present paper, we have considered the dipole moment of L-alanine molecule is determined by one of the experimental methods [17,35] and compared with the theoretical dipole moments which are tabulated in Table 1. From the Table 1, it is observed that there is an increase in the net dipole moment and mean molecular polarizability values of aqueous L-alanine when compare to the gaseous state L-alanine. The increase in values indicates the presence of hydrogen-bonded network in the aqueous L-alanine system and which in turn causes changes in the bond length parameters. Further, from the Table 1, it is noticed that the difference in energy between the aqueous L-alanine (Dimer) and L-alanine (monomer) is in the range of 6–53 kcal/mol which reveals the presence of hydrogen bond interaction between the system.

The temperature dependence of $\ln(T\tau)$ vs $1/T$ of different molar concentrations of L-alanine in water as shown in Fig. 7. From this graph, evaluated the thermodynamic parameters such as enthalpy of activation $\Delta H^*$, entropy of activation $\Delta S^*$ by using Eyring's rate equation [36] and which are tabulated in Table 2 respectively. From the Fig. 7 it is observed that $\ln(T\tau)$ varies linearly with increase in molar concentration of L-alanine in water attributes the formation of multimeric structure in the solution. From the Table 2, it is observed that the enthalpy of activation $\Delta H^*$ is a positive value and this value increases with increase in L-alanine concentration in an aqueous medium which indicates the surrounding environment of the system is cooperative and in favor of forming the hydrogen bonding network in the solution. Further, the Gibbs free energy of activation $\Delta G^*$ is positive which indicates the presence of interaction between dipoles in the system. The entropy of activation $\Delta S^*$ indicates the molecularity of the rate-determining step in a reaction that is whether the reactants are bonded to each other, or not. If the $\Delta S^*$ is positive which explains that entropy increases upon achieving the transition state and also activated complex system is loosely bound and about to dissociate whereas negative values for $\Delta S^*$ indicate that entropy decreases on forming the transition state towards associative nature forming single activated complex system. From the Table 2, it is marked that $\Delta S^*$ values are negative for all concentrations which indicate the activated complex system is associative nature forming single activated system by means of hydrogen bonding between L-alanine and water molecules.

The mean molecular polarizability of the L-alanine and aqueous L-alanine is calculated from the Lippincott δ functional model by evaluating a parallel, perpendicular and nonbonding component of the polarizability of the bonds. The value obtained with the Lippincott δ functional model is verified with the Lefevre method of polarizability calculations
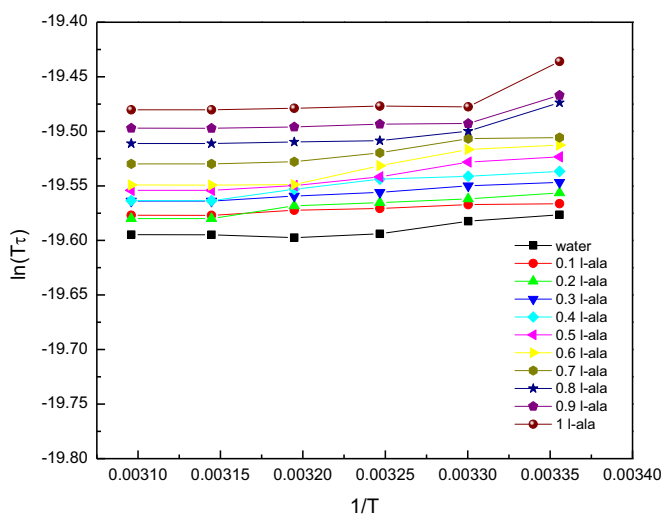


**Fig. 7.** Plot of temperature dependence of $\ln(T\tau)$ vs $1/T$ of different molar concentrations of L-alanine in water.

**Table 2**
Variation of thermodynamical parameters $\Delta G^*$, $\Delta H^*$ and $\Delta S^*$ with respective molar concentration of L-alanine in water at different temperatures.

| Sample | Temperature in K | $\Delta H^*$ kcal/mol | $\Delta G^*$ kcal/mol | $\Delta S^*$ cal/mol/K |
|---|---|---|---|---|
| Water | 298 | 2.834 | 10.284 | −25.00 |
| | 303 | | 10.499 | −25.30 |
| | 308 | | 10.714 | −25.58 |
| | 313 | | 10.873 | −25.68 |
| | 318 | | 11.084 | −25.94 |
| | 323 | | 11.298 | −26.20 |
| 0.1 M ala | 298 | 1.018 | 10.227 | −30.90 |
| | 303 | | 10.440 | −31.10 |
| | 308 | | 10.738 | −31.56 |
| | 313 | | 10.904 | −31.59 |
| | 318 | | 11.088 | −31.67 |
| | 323 | | 11.301 | −31.84 |
| | 308 | | 10.738 | −31.56 |
| 0.2 M ala | 298 | 2.060 | 10.204 | −27.33 |
| | 303 | | 10.417 | −27.58 |
| | 308 | | 10.765 | −28.27 |
| | 313 | | 10.926 | −28.33 |
| | 318 | | 11.110 | −28.46 |
| | 323 | | 11.304 | −28.62 |
| 0.3 M ala | 298 | 1.688 | 10.209 | −28.59 |
| | 303 | | 10.422 | −28.83 |
| | 308 | | 10.790 | −29.55 |
| | 313 | | 10.957 | −29.61 |
| | 318 | | 11.116 | −29.65 |
| | 323 | | 11.309 | −29.79 |
| 0.4 M ala | 298 | 2.522 | 10.220 | −25.83 |
| | 303 | | 10.429 | −26.09 |
| | 308 | | 10.816 | −26.93 |
| | 313 | | 10.980 | −27.02 |
| | 318 | | 11.148 | −27.13 |
| | 323 | | 11.358 | −27.35 |
| 0.5 M ala | 298 | 3.210 | 10.421 | −24.20 |
| | 303 | | 10.591 | −24.36 |
| | 308 | | 10.850 | −24.81 |
| | 313 | | 11.014 | −24.93 |
| | 318 | | 11.154 | −24.98 |
| | 323 | | 11.362 | −25.24 |
| 0.6 M ala | 298 | 4.684 | 10.493 | −19.49 |
| | 303 | | 10.684 | −19.80 |
| | 308 | | 10.878 | −20.11 |
| | 313 | | 11.044 | −20.32 |
| | 318 | | 11.181 | −20.43 |
| | 323 | | 11.391 | −20.76 |
| 0.7 M ala | 298 | 3.059 | 10.375 | −24.55 |
| | 303 | | 10.543 | −24.70 |
| | 308 | | 10.893 | −25.43 |
| | 313 | | 11.072 | −25.60 |
| | 318 | | 11.212 | −25.64 |
| | 323 | | 11.420 | −25.88 |
| 0.8 M ala | 298 | 6.553 | 10.375 | −12.82 |
| | 303 | | 10.543 | −13.17 |
| | 308 | | 10.977 | −14.36 |
| | 313 | | 11.088 | −14.49 |
| | 318 | | 11.242 | −14.74 |
| | 323 | | 11.447 | −15.15 |
| 0.9 M ala | 298 | 0.623 | 10.421 | −32.88 |
| | 303 | | 10.591 | −32.90 |
| | 308 | | 10.995 | −33.68 |
| | 313 | | 11.104 | −33.49 |
| | 318 | | 11.282 | −33.52 |
| | 323 | | 11.479 | −33.61 |
| 1 M ala | 298 | 0.399 | 10.511 | −33.93 |
| | 303 | | 10.661 | −33.87 |
| | 308 | | 11.074 | −34.66 |
| | 313 | | 11.146 | −34.33 |
| | 318 | | 11.299 | −34.28 |
| | 323 | | 11.503 | −34.38 |

and which are mentioned in Table 1. The determined values are in good agreement with each other within the error limit. The mean polarizability of the aqueous L-alanine is higher than the individual L-alanine molecule and it is due to the presence of hydrogen bonding. The formation of hydrogen bonding between L-alanine with water molecules

enhances the polarizabilities, dipole moment, relaxation time values when compared to the individual system.

## 4. Conclusions

The temperature dependence of dielectric relaxation behavior of L-alanine-water mixtures was investigated by using open-ended coaxial probe technique at microwave frequencies. The average relaxation time, dielectric field strength values and Kirkwood correlation factor ($g^{eff}$) increases with increasing molar concentration of L-alanine in water medium due to the presence of hydrogen-bonded network in the system and decreases with increasing temperature. The water molecules bound to L-alanine have higher relaxation times than the relaxation time of free water molecules. There is an increase in the net dipole moment and molecular polarizability values compared to free water molecules due to the changes in the bond length parameters. The dipole moment of the L-alanine molecule is calculated in a gaseous state and in water medium by using theoretical quantum mechanical calculations. The enthalpy of activation $\Delta H^*$ is positive which indicates the environment of the system is favorable for the molecular interactions.

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