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Research Article

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Static dielectric constant and excess properties of amino acids

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ABSTRACT

Amino acids are the basic "building blocks" that combine to form proteins and play an important physiological role in all life-forms. They can be used as models for the examination of the importance of intermolecular bonding in life processes. Dielectric spectroscopy severs to obtained information of the binary solutions on the macroscopic level regarding hydrogen bonding, molecular associations, charge transfer, dipole-dipole and dipole induced dipole interactions. In this paper two amino acids (DL-Alanine & L-Asparagines) with water have been studied by dielectric spectroscopy. The static dielectric constants, their excess dielectric properties, Kirkwood correlation factor and Bruggeman factor of the amino acids - water solutions for different temperatures have been calculated and reported. The static dielectric constants have been achieved by using a sensor which is based on frequency domain reflectometry technique. The behavior of excess dielectric permittivity and Bruggman factor suggest the presence of intermolecular interaction in the binary mixtures. The angular Kirkwood correlation factor confirms the parallel and antiparallel orientation of the electric dipoles in the mixtures.

Keywords: Static dielectric constant; Excess dielectric properties; Kirkwood correlation factor; Bruggeman factor; Amino acids.

INTRODUCTION

Dielectric spectroscopy yields detailed information about the structures, intermolecular interactions, hydrogen bonding, molecular associations, charge transfer and dipole induced dipole interactions. Amino acids are the basic "building blocks" that combine to form proteins. In every species, proteins are constructed from the same set of twenty amino acids. As well as forming proteins, enzymes and other body tissue they are also found throughout the body participating in a wide variety of chemical reactions, and are vital in basic energy production cycles, energy transfer and muscle activity. In the higher organisms including humans, amino acids are classified as either "essential" amino acids (which must be consumed in the diet), or "non-essential" amino acids (which can be made by the body) [1]. While there are many forms of amino acids, all of the important amino acids found in living organisms are alpha amino acids. Alpha-amino acids have the –COOH and $–NH_2$ groups, both attached to the same carbon atom, called the alpha carbon atom. The simplest amino acid, which is the molecule glycine, H_2NCH_2COOH contains no asymmetric carbon atoms (tetrahedral carbon atoms with four different groups attached). All of the other amino acids contain an asymmetric or "chiral" carbon atom and are, therefore, optically active. The general structure of the alpha amino acids is $R–CHNH_2$ (alpha)–COOH, and the optical activity for alpha-amino acids is more complex than glycine is directed by the alpha carbon [2-4].

Macroscopic parameter the dielectric constant has extensively used for explanation of solvents effects. It is an important physicochemical parameter, as it is related to many important physical and biological applications [5-7]. The dielectric constant of a solvent is a relative measure of its polarity and its measurements are often used for evaluation of characteristics of the liquid solutions [8]. This property can also be very useful as a support for efficient design, stimulation of separation processes, sample preparation and chromatography techniques in analytical chemistry [9, 10].

The aim of the present work is to determine the intermolecular interactions and hydrogen bonding between amino acids- water solutions. The behavior of amino acids in aqueous solutions is of a major interest because water is the natural medium for biological molecules. A detailed knowledge of amino acid interactions with water is a primary step in understanding the salvation process of larger systems, such as peptides and proteins. The excess dielectric properties (ε^E), Kirkwood correlation factor (g^{eff}) and Bruggeman factor (f_B) of the amino acids- water solutions have been reported at 288, 298 and 308 K temperatures.

EXPERIMENTAL SECTION

Chemicals

The chemicals used in the present investigation are of spectroscopic grade with 99.9% purity. One mole solutions of the two amino acids were prepared by mixing amino acids with water. The experimental solutions were prepared by mixing solution from one mole stock of amino acids with water at eleven different volume percentage of water as 0 to 100% in steps of 10%. The temperature controller system with water bath has been used to maintain the constant temperature within the accuracy limit of ± 1°C. The sample cell is surrounded by a heat insulating container through which the water of constant temperature using a temperature controller system is circulated**.**

Measurement of dielectric constant

The static dielectric constants of the aqueous solutions of amino acids with water were measured using a sensor, which is based on the principle of frequency domain reflectometry (FDR) technique. When power is applied to the sensor, it creates a 100 MHz frequency signal. This signal is then applied to a pair of stainless steel rods, which transmits an electromagnetic signal into the mixture. The field passes easily through the mixture resulting in stable voltage output that acts as a simple sensitive measure of dielectric constant. Each measurement was repeated at least three times and average value of that reading was taken as a dielectric constant. The accuracy of measurement in the dielectric constant was ± 3.0 %.

Study of excess permittivity

The information related to the excess permittivity of the aqueous solution was obtained from the excess properties [11] of the mixture. The excess permittivity is defined as

$$\varepsilon^{\mathrm{E}} = (\varepsilon_{\mathrm{O}})_m - [(\varepsilon_{\mathrm{A}} \cdot \mathrm{X_A}) + (\varepsilon_{\mathrm{B}}.\mathrm{X_B})] \qquad (3)$$

Where X is volume fraction and suffix m, A, B represents mixture, liquid A (1 mole aqueous solution of amino acid) and liquid B (water) respectively. The excess permittivity provides qualitative information about formation of new structure in the mixture as follows:

i) $\varepsilon^E = 0$: Indicates that solution A and B do not interact.

ii)$\varepsilon^E < 0$: Indicates that solution A and B interact is in such a way that the effective dipole moment gets reduced.

iii) $\varepsilon^E > 0$: Indicates that solution A and B interact in such a way that the effective dipole moment increases.

Study of Kirkwood correlation factor

The Kirkwood correlation factor [12] provides information regarding the orientation of the electric dipoles in polar liquids.

For a pure polar liquid, the Kirkwood correlation factor g may be obtained by the expression

$$\frac{4\pi N\mu^2\rho}{9KTM} g = \frac{(\varepsilon_0 - \varepsilon_\infty)(2\varepsilon_0 + \varepsilon_\infty)}{\varepsilon_0(\varepsilon_\infty + 2)^2} \qquad \textbf{(5)}$$

Where μ is dipole moment, ρ is density at temperature T, M is molecular weight, K is Boltzman constant, N is Avogadro's number, ($\in_s$) is static dielectric permittivity and ε_∞ is the dielectric permittivity at high frequency, often represented by the square of the refractive index.

Modified forms of this equation have been used to study the orientations of electric dipoles in the binary mixtures are given by Kumbharkhane et al [13, 14] two such equations used are as follows:

$$\frac{4\pi N}{9kT}\left(\frac{\mu^2{}_M\rho_M}{M_M}X_M + \frac{\mu^2{}_F\rho_F}{M_F}X_F\right)g^{eff} = \frac{(\varepsilon_{0m} - \varepsilon_{\infty m})(2\varepsilon_{0m} + \varepsilon_{\infty m})}{[\varepsilon_{0m}(\varepsilon_{\infty m} + 2)^2]} \qquad (6)$$

where g^{eff} is the Kirkwood correlation factor for a binary mixture. g^{eff} varies between g_M and g_F.

$$\frac{4\pi N}{9kT}\left(\frac{\mu^2{}_M\rho_M g_M}{M_M}X_M + \frac{\mu^2{}_F\rho_F g_F}{M_F}X_F\right)g^f = \frac{(\varepsilon_{0m} - \varepsilon_{\infty m})(2\varepsilon_{0m} + \varepsilon_{\infty m})}{\varepsilon_{0m}(\varepsilon_{\infty m} + 2)^2} \qquad (7)$$

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g_M and g_F are assumed to be affected by an amount g^f in the mixture. $g^f = 1$ for an ideal mixture and deviation from unity may indicate the interaction between the two components of the mixture.

Study of Bruggeman factor

The static permittivity of two mixture must lie somewhere between two extremes corresponding to static permittivity of two liquids. In order to understand the dipole interaction in the mixture of two liquids a various mixture formula has been proposed [15, 16]

Bruggeman mixture formula [17, 18] can be used as first evidence of molecular interactions in binary mixture. The effective volume of the solute gets modified by solute – solvent interactions and is best illustrated by the non-linearity of Bruggman formula. The static dielectric constant ($\in_s$) of the mixtures is related to the Bruggman mixture formula with volume fraction of solute which indicates the interaction between solvent and solute. This formula states that static dielectric permittivity of binary mixture ($\in_{sm}$), solute ($\in_{sA}$) and solvent ($\in_{sB}$) can be related to volume fraction of solvent (V) which indicates the interaction between solvent and solute in the mixture as;

$$f_B = \left(\frac{\varepsilon sm - \varepsilon sB}{\varepsilon sA - \varepsilon sB}\right)\left(\frac{\varepsilon sA}{\varepsilon sm}\right)^{1/3} = 1 - V$$

According to above equation linear relationship is expected in the Bruggman factor **(**f_B) and (V). Any deviation from this linear relation indicates molecular interaction [19].

RESULTS AND DISCUSSION

The experimental results of static dielectric constants (ε_s) of the amino acids- water solutions of DL- Alanine and L-Asparagines at 288, 298 and 308K are presented in Figure 1 and 2 respectively. It has been observed that the dielectric permittivity of the binary mixture decreases with increase in temperature as well as increase in volume fraction of water. The decrease in permittivity with increase in temperature might be due to rapid fall in orientation polarization, because the increased thermal motion reduces the alignment of the permanent dipoles [20]. The decreases in dielectric permittivity with increase in volume fraction of water may be due to increase in size and shape of the complex molecules after hydrogen bonding interaction. This could be attributed to a decrease in number of dipoles in the complex, which may lead to a decrease in volume of the rotating molecules [21, 22].

Table 1. Variation in excess dielectric constant of DL- alanine with volume fraction of water at different temperatures

Percentage volume of Water in DL-alanine	Excess dielectric constant T=288 K	Excess dielectric constant T=298 K	Excess dielectric constant T=308 K
00	0.0	0.0	0.0
10	1.59	2.01	1.13
20	0.58	2.17	2.24
30	0.27	1.40	1.41
40	1.10	0.93	1.18
50	1.12	-0.46	0.32
60	0.99	0.0	-1.00
70	-0.54	-1.08	-2.35
80	-0.35	-0.62	-2.38
90	-0.007	-0.46	-0.20
100	0.0	0.0	0.0

Table 2. Variation in excess dielectric constant of L-asparagines with volume fraction of water at different temperatures

Percentage volume of Water in L-asparagines	Excess dielectric constant T=288 K	Excess dielectric constant T=298 K	Excess dielectric constant T=308 K
00	0.0	0.0	0.0
10	0.35	-0.52	0.16
20	0.22	-0.70	0.26
30	0.36	-0.97	0.64
40	0.26	-0.54	0.73
50	0.35	-0.55	0.60
60	0.15	-0.38	0.77
70	0.45	-0.02	0.76
80	0.40	0.15	1.11
90	0.08	0.03	0.26
100	0.0	0.0	0.0

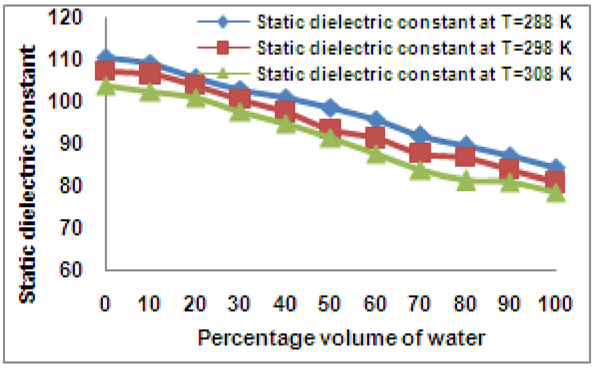

Fig. 1 Variation in static dielectric constant of DL-Alanine with volume fraction of water at different temperatures

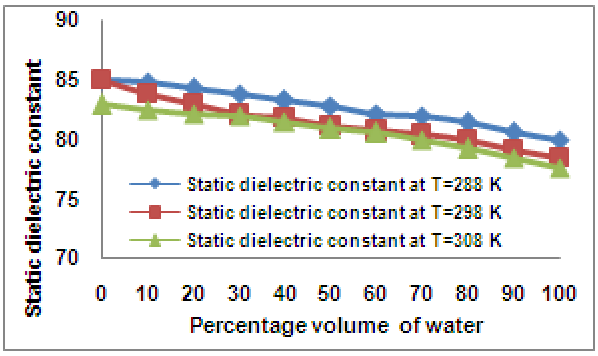

Fig.2 Variation in static dielectric constant of L-Asparagines with volume fraction of water at different temperatures

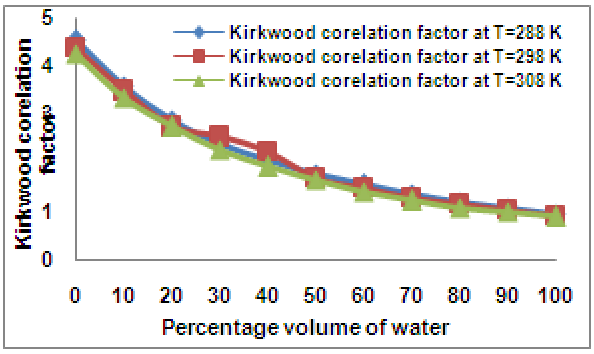

Fig. 3 Variation in Kirkwood correlation factor (g^{eff}) of DL-Alanine with volume fraction of water at different temperatures

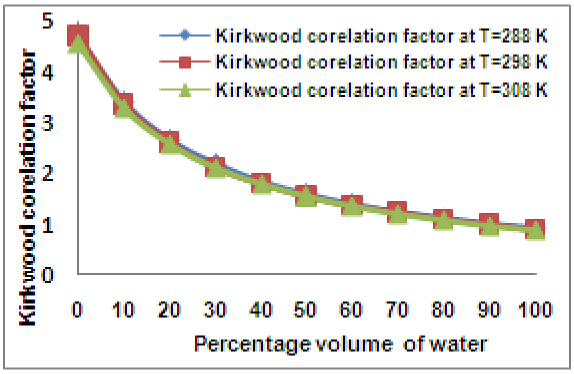

Fig. 4 Variation in Kirkwood correlation factor (g^{eff}) of L-Asparagines with volume fraction of water at different temperatures

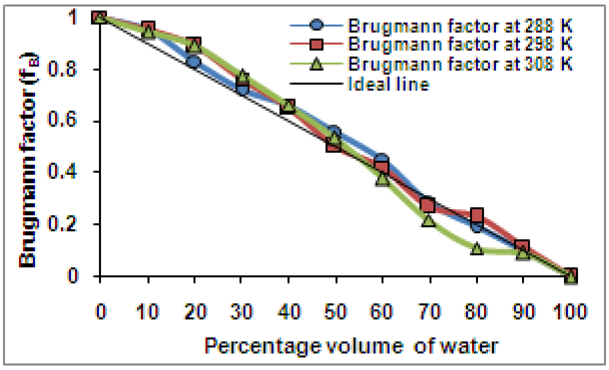

Fig. 5 Variation in Bruggeman factor (f_B) of DL-Alanine with volume fraction of water at different temperatures

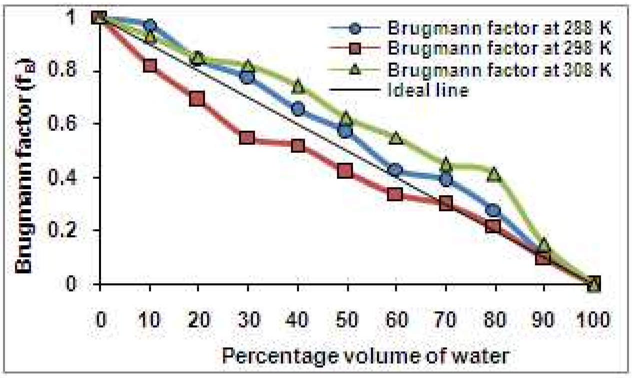

Fig. 6 Variation in Bruggeman factor (f_B) of L-Asparagines with volume fraction of water at different temperatures

The excess permittivity (ε^E) provides significant information regarding interaction between the polar-polar liquid mixtures and it is calculated by using equation (3). The excess permittivity of the amino acid- water solutions of DL-Alanine with water at 288, 298 and 308K is presented in Table 1. The excess permittivity is positive in Dl-Alanine rich region but negative in water rich region at the studied temperatures. The positive excess permittivity (ε^E) indicate that the effective number of dipoles in the mixture might be greater than the corresponding average number in the pure liquids, probably due to the creation of new structure leading to a higher macroscopic permittivity. The negative values of excess permittivity in water rich region are probably due to the creation of less polar structure leading to a lower macroscopic permittivity [23]. From a molecular point of view the negative values of excess permittivity in water-alanine mixtures is the consequence of formation of hydrogen bonds.

The excess permittivity of the amino acid- water solutions of L-Asparagines with water at 288, 298 and 308K is given in Table 2. The excess permittivity is positive nearly for the entire volume fraction ranges and at 288 and 308K temperatures, indicates that the binary mixture interacts in such a way that the effective dipole moment increases.

From Table 2 it is also observed that, at 298K temperature the excess permittivity is negative in L-Asparagines rich region but positive in water rich region. The negative excess permittivity indicates that the two solutions interact in such a way that the effective dipole moment decreases in L-Asparagines rich region but increases in water rich region. The negative values of (ε^E) at this temperature are probably due to the creation of less polar structure leading to a lower macroscopic permittivity and positive values of (ε^E) are probably due to the creation of new structure leading to a higher macroscopic permittivity [23].

The Kirkwood angular correlation factors (g^{eff}) of amino acids- water solutions of DL- Alanine and L- Asparagines were calculated for three different temperatures which is presented in Figure 3 and 4 respectively. $g^{eff} > 1$ in DL-Alanine and L-Asparagines rich region for the studied temperatures, this indicates parallel orientation of electric dipoles in DL-Alanine and L-Asparagines molecules. Whereas for pure water $g^{eff} < 1$ [24, 25]

The Bruggeman factor (f_B) values of amino acids- water solutions of DL- Alanine and L- Asparagines at 288, 298 and 308K temperatures are noted graphically in Figure 5 and 6 respectively. According to the given data there is deviation from the linear relation which gives the evidence of strong molecular interactions between the amino acids- water solutions of DL- Alanine and L- Asparagines.

CONCLUSION

The static dielectric constant of amino acids- water solutions of DL- Alanine and L- Asparagines decreases with increase in temperature and volume fraction of water.

The excess permittivity of the amino acid- water solutions of DL- Alanine is positive at DL-Alanine rich region for the studied temperatures, indicates the effective number of dipoles in the mixture might be greater than the corresponding average number in the pure liquids. The excess permittivity of the binary solutions of DL-Alanine is negative at water rich region for the studied temperatures, shows the presence of certain interaction between unlike molecules.

The excess permittivity of the amino acid- water solutions of L-Asparagines is positive for 288 and 308 K temperatures and negative at 298K temperature for the entire volume fraction range of water.

In the amino acids- water solutions the dipole pairs are formed and orient in parallel direction in amino acids rich region and in antiparallel direction in pure water.

Bruggeman factor shows the deviation from the linear relation which gives the evidence of molecular interactions in amino acids- water solutions.

Such study has potential advantage in qualitative detection of drug binding and to enable semi-quantitative study of the interaction between the drug and its target.

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