

**Intermolecular Interaction Studies In Aqueous Amino Acid And Glycol Ether System At 298.15 K And At Various Concentrations**A.V. Kachare^{1*}, D.D.Patil¹, S.R.Patil¹, and A.N.Sonar²

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Email: avi.vsnt@gmail.comReceived on 21st July, Revised on 12th August and finalized on 20th August 2013.**ABSTRACT**

The thermo physical parameters such as density (ρ), viscosity (η), and ultrasonic velocity (u) have been measured for aqueous glycine and glycol ether at 0.1 to 1 mole fractions and at 298.15 K temperature. Physical parameters viz acoustical impedance (z), adiabatic compressibility (β), relaxation time (τ), Rao's constant (R), Wada's constant (W), free volume (V_f), viscosity deviation ($\Delta\eta$), excess volume (V^E), intermolecular free length (L_f) have been obtained from experimental data which show intermolecular interaction. The measured and calculated thermodynamic parameters have been discussed in terms of solute-solute or solute-solvent or solvent-solvent interaction.

Keywords: Acoustical impedance, Adiabatic compressibility, Relaxation time, Rao's constant, Wada's constant.

INTRODUCTION

The interactions between aqueous amino acid and other components are evident from their thermodynamic parameters [1-5]. The study of interactions within the system with recent data about physical parameter like viscosity, density, ultrasonic velocity and transport properties of aqueous amino acids electrolytes[6] are very helpful. The various solution properties in recent studies consisting of polar as well as non polar components find applications in industrial and technology processes [1]. The correlation of physical parameters in aqueous amino acid and glycol ether system at various concentration and temperature gives information about intermolecular interaction. In aqueous amino acid as water – protein system interactions give easy guide line about their correlation [7]. The correlation of physical parameter to study aqueous amino acid and organic solvent system it gives essential data about protein unfolding [8-10] and the hydrophobic interactions of non-polar side chains [11]. The aqueous amino acid behave as zwitterions[12-16] at physiological conditions, the two functional groups of amino acid having both positive charge (amino group NH_3^+) and negative charge (Carboxylate group, COO^-)[17]. The recent data about intermolecular interaction in aqueous proteins system have resemblances with those of electrolytes. The aqueous amino acid system in which solute-solvent interactions verify by related thermo physical properties and that interaction decide the fate of that system. Such interactions are responsible for physiological processes in a living cell [18]. Volumetric and thermodynamic properties[19-20] such as

acoustical impedance, adiabatic compressibility, relaxation time, Rao's constant, Wada's constant, free volume, molar volume, intermolecular free length, apparent molar volume, molar hydration no., apparent molar compressibility, free energy, entropy and enthalpy of aqueous amino acid play important role to investigate the interaction between aqueous amino acid and related aqueous systems. Such research proved that some of the novel molecules can stabilize the biochemical part of living beings. The results of such molecules with their structure and functions of proteins in terms of structure making or structure breaking characteristics have been observed by various researchers [17, 21-23].

MATERIALS AND METHODS

All the chemicals are analytical reagent (AR) and spectroscopic reagent (SR) grades from E-Merck, Germany and Sd Fine, AVRA chemicals India. The liquid mixtures of different known compositions are prepared in stoppered volumetric flasks. The density, viscosity and ultrasonic velocity values are measured as a function of composition of the liquid mixture of amino acid with glycol ether at 298.15 K. The density was determined using a Bi-capillary pycnometer. The weight of the sample measured using electronic digital balance with an accuracy of ± 0.1 mg (Model: Shimadzu AX-200). An Ubbelohde viscometer (20ml) is used for the viscosity measurement and efflux time determined with digital clock ± 0.01 s. An ultrasonic interferometer having the frequency of 3 MHz (Mittal Enterprises, New Delhi, Model: F-05) with an overall accuracy of $\pm 0.1\%$ is used for velocity measurement. An electronically digital operating constant temperature bath (RAAGA Industries) is used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desired temperature with an accuracy of ± 0.01 K [24].

Theory and Calculation : From the measured values of density (ρ), ultrasonic velocity (u) and viscosity (η) we can calculate the physical parameter like acoustical impedance (Z), adiabatic compressibility (β), relaxation time (τ), Rao's constant (R), Wada's constant (W), free volume (V_f), viscosity deviation ($\Delta\eta$), excess volume (V^E), intermolecular free length (L_f), calculated by using following standard relation[1,24-28].

- 1) $Z = \rho \cdot u$
- 2) $\beta = 1/u^2 \rho$
- 3) $\tau = 4/3 \eta \beta$
- 4) $R = u^{1/3} v$
- 5) $W = \beta^{1/7} v$
- 6) $V_f = M_{\text{eff}} u / K \eta$ ($K = 4.28 \times 10^9$ is a temperature independent constant)
(M_{eff} —effective molecular wt.of soln. $M_{\text{eff}} = x_1 M_1 + x_2 M_2 + x_3 M_3$. Where $x_1, x_2, x_3, M_1, M_2, M_3$) are mole fractions and molar masses of the pure components 1, 2 and 3.)
- 7) $\Delta\eta = \eta_{12} - x_1 \eta_1 - x_2 \eta_2$
(Where $x_1, x_2, \eta_{12}, \eta_1, \eta_2$ are mole fractions, viscosity of mixture, viscosities components respectively.)
- 8) $V^E = ((x_1 M_1 + x_2 M_2 + x_3 M_3) / \rho) - (x_1 M_1 / \rho_1) - (x_2 M_2 / \rho_2) - (x_3 M_3 / \rho_3)$
(Where $x_1, x_2, x_3, M_1, M_2, M_3, \rho_1, \rho_2, \rho_3$ are mole fractions, molar masses and densities of pure components 1, 2 and 3 respectively.)
- 9) $L_f = K_j \beta^{1/2}$ ($K_j = 6.0816 \times 10^4$)
(K_j is Jacobson's constant which is temperature dependent constant but independent of the nature of the liquid.)

RESULTS AND DISCUSSION

The present work is a system of aqueous glycine with diethylene glycol and aqueous l-proline with diethylene glycol. The investigate the physical properties like density (ρ), ultrasonic velocity (u) and viscosity (η), acoustical impedance (Z), adiabatic compressibility (β), relaxation time (τ), Rao's constant (R), Wada's constant (W), free volume (V_f), viscosity deviation ($\Delta\eta$), excess volume (V^E), intermolecular free length (L_f) gives information about interactions between aqueous amino acids and glycol ether. It is proved by experimental data from tables 1-2 and figures 1-8. These physical properties correlated with various concentrations 0.1 to 1.0 and at 298.15 K.

The present experimental data clearly reveals that as concentration increases the parameter like density, viscosity, ultrasonic velocity, acoustical impedance, Rao's constant, free volume, increases while adiabatic compressibility, relaxation time, Wada's constant, intermolecular free length decreases. As concentration increases the number of molecules in the medium increases making the medium to be denser which leads to increase of density, viscosity, ultrasonic velocity, acoustical impedance, Rao's constant, free volume increases and hence lesser intermolecular free length, adiabatic compressibility, relaxation time, Wada's constant. As the increase in the number of particles that increases the fractional resistance between the layers of medium and that leads to increase the coefficient of viscosity. The present system in which particle-particle frictional resistance leads intermolecular interaction. It shows increasing and decreasing trend of the measured parameters. Density is a parameter giving information about solvent – solvent and ion - solvent interactions [29]. The higher compressibility values predict that the medium is loosely packed whereas the lower compressibility is an indication of maximum interaction. The gradual decrease in adiabatic compressibility in present work suggest that the medium become more and more less compressible. The intermolecular free length (L_f) is again a predominant factor in determining the existing interactions among the components of the mixture. Analyzing the respective table, (L_f) reflects a similar trend as that of (β).

The increasing trend in these parameters suggest the strengthening of interaction among the components. The interaction may be solute-solute or solute-solvent or solvent-solvent type. The molar sound velocity (R) indicates the cube root of sound velocity through one molar volume of solutions called as Rao's constant. It is also a measure of interaction existing in the solution. Further the trend of molar adiabatic compressibility (W) called as Wada's constant which depends on the adiabatic compressibility of one molar volume solutions may be taken as a confirmation for existing interactions. The observed values of molar sound velocity and molar compressibility in the amino acid are of increasing trend with glycol ether indicating that the magnitude of interactions are enhanced. The increasing trend of molar compressibility or molar sound velocity with increasing glycol ether indicates the availability of more number of components in a given region thus leads to a tight packing of the medium and thereby increase the interactions. The acoustic impedance that the specific interactions are of solute-solute and solute-solvent type. The increase in ultrasonic velocity in the aqueous solution of amino acid may be attributed to the cohesion brought by the ionic hydration. The increase in density with molar concentration suggests a solute-solvent interaction exist between water and amino acid [1]. In other words the increase in density may be interpreted to the structure making of the solvent due to H-bonding [30-31]. As concentration increases density increases due to the shrinkage in the volume. It results in increase in density is interpreted to the structure - maker of the solvent.

The decrease in density indicates the decrease in solute - solvent and solvent – solvent interactions which results structure – breaking of the solvent. It reveals that solvent – solvent interactions bring about a bonding, probably hydrogen bonding between them. Thus, size of the resultant molecule increases and there will be decrease in density [32]. The viscosity is an physical property in understanding the structure as well as molecular interaction occurring in the aqueous system. The variations of physical parameter related to aqueous system attributed to structural changes [31]. The values of adiabatic compressibility (β) show decreasing trend with concentration which suggest the making and breaking of H-bonding [1]. The intermolecular free length depends upon the intermolecular attractive and repulsive forces. The values of density and viscosity of any system vary with increase or decrease in

concentration of solutions [32]. Eyring and Kincaid [33] have proposed that (L_f) is a predominating factor in determining the variation of ultrasonic velocity in aqueous system. The values of intermolecular free length listed in the tables show decreasing trend with concentration. The system changes as a result of hydrogen bond formation or dissociation or hydrophobic (structure – breaking) or hydrophilic (structure – forming) nature of solute. Hence hydrogen bond forming or dissociating properties can be correlated with change in density and viscosity [32]. Hence it can be concluded that there is significant interaction of solute-solute or solute-solvent or solvent-solvent type due to which the structural arrangement is also affected. Thus it is clear from the above parameters that there is a strong association between present systems showing hydrophilic nature.

Table-1 (Aqueous Glycine and Diethylene glycol system at 298.15 K)

X_1	X_2	X_3	X	ρ (kg/m^3)	η ($\times 10^{-3}$) (Ns/m^2)	u (m/s^1)	Z ($\times 10^6$) ($\text{kg/ m}^2\text{s}^1$)	β ($\times 10^{-10}$) (m^2/N^1)	τ ($\times 10^{-13}$) (s)
.....	1001.1	0.8920	1499.2	1.5008	4.4443	5.2857
0.9611	0.01870	0.02012	0.1327	1006.0	0.8924	1504.1	1.5131	4.3938	5.2280
0.9377	0.01824	0.04404	0.2241	1010.0	0.8927	1507.0	1.5220	4.3596	5.1890
0.9099	0.01770	0.07234	0.3100	1015.2	0.8932	1511.2	1.5341	4.3132	5.1367
0.8753	0.01702	0.1076	0.4013	1021.0	0.8935	1514.1	1.5458	4.2723	5.0897
0.8303	0.01615	0.1535	0.5253	1024.1	0.8939	1519.0	1.5556	4.2655	5.0438
0.7752	0.01484	0.2099	0.6102	1028.0	0.8943	1523.1	1.5657	4.1932	4.9999
0.6915	0.01331	0.2950	0.7310	1031.2	0.8947	1527.0	1.5746	4.1589	4.9672
0.5707	0.01105	0.4182	0.8221	1033.0	0.8952	1531.1	1.5816	4.1294	4.9288
0.3792	0.00717	0.6136	0.9152	1037.1	0.8956	1534.2	1.5911	4.0965	4.8917
.....	1.0000	1.0124	1041.2	0.8960	1538.1	1.6014	4.0597	4.8499

(Where, mole fraction of water (x_1), mole fraction of glycine (x_2), mole fraction of diethylene glycol (x_3), mole fraction of aqueous glycine and diethylene glycol system (x), density (ρ), viscosity (η), and ultrasonic velocity (u), acoustical impedance (Z), adiabatic compressibility (β), relaxation time (τ))

Table-1 to be continue here...

X_1	X_2	X_3	X	R ($\times 10^3$) (m^3/mol^1)	W (m^3/mol^1)	V_f (m^3/mol^1)	$\Delta\eta$ ($\times 10^{-7}$)	$-V^E$ ($\times 10^4$)	L_f (A°)
.....	2.2797	9.1883	0.4276	1.9907	1.2820
0.9611	0.01870	0.02012	0.1327	2.2822	9.1734	0.4280	3.0100	2.1888	1.2747
0.9377	0.01824	0.04404	0.2241	2.2836	9.1631	0.4282	5.7700	2.4245	1.2698
0.9099	0.01770	0.07234	0.3100	2.2858	9.1491	0.4286	9.5500	2.7033	1.2630
0.8753	0.01702	0.1076	0.4013	2.2872	9.1367	0.4288	0.1158	3.0506	1.2570
0.8303	0.01615	0.1535	0.5253	2.2897	9.1243	0.4292	0.1375	3.5029	1.2510
0.7752	0.01484	0.2099	0.6102	2.2918	9.1123	0.4295	0.1549	4.0561	1.2453
0.6915	0.01331	0.2950	0.7310	2.2937	9.1016	0.4298	0.1519	4.8953	1.2402
0.5707	0.01105	0.4182	0.8221	2.2958	9.0924	0.4301	0.1616	6.1103	1.2358
0.3792	0.00717	0.6136	0.9152	2.2973	9.0820	0.4303	0.1234	8.0340	1.2309
.....	1.0000	1.0124	2.2993	9.0703	0.4306	1.2253

(Rao's constant (R), Wada's constant (W), free volume (V_f), viscosity deviation ($\Delta\eta$), excess volume (V^E), intermolecular free length (L_f)).

The table-1 data shows relative correlation as concentration increases. The parameter like density, viscosity, ultrasonic velocity, acoustical impedance, Rao's constant, free volume, excess volume increases

while apparent molar volume, adiabatic compressibility, relaxation time, Wada's constant, molar volume, intermolecular free length, viscosity deviation decreases.

Table-2 (Aqueous L-Proline and Diethylene glycol system at 298 .15 K)

X ₁	X ₂	X ₃	X	P	η ($\times 10^{-3}$)	u	z ($\times 10^6$)	β ($\times 10^{-10}$)	τ ($\times 10^{-13}$)
.....	kg/m ³	Ns/m ²	m/s ¹	kg/ m ² s ¹	m ² / N ¹	s
0.9800	0.01993	0.0000	1036.0	0.8948	1591.1	1.6483	3.8128	4.5489
0.9602	0.01937	0.01970	0.1251	1039.1	0.8951	1594.0	1.6563	3.7876	4.5204
0.9356	0.01903	0.04528	0.2010	1042.0	0.8954	1597.1	1.6641	3.7624	4.4918
0.9073	0.01836	0.07435	0.3401	1046.0	0.8957	1601.0	1.6746	3.7298	4.4543
0.8710	0.01771	0.1112	0.4214	1050.2	0.8961	1606.0	1.6866	3.6917	4.4108
0.8243	0.01669	0.1590	0.5100	1053.0	0.8964	1609.1	1.6943	3.6677	4.3836
0.7632	0.01552	0.2212	0.6041	1057.1	0.8969	1612.2	1.7042	3.6395	4.3523
0.6829	0.01378	0.3032	0.7210	1060.0	0.8973	1616.1	1.7130	3.6120	4.3213
0.5603	0.01133	0.4283	0.8102	1064.1	0.8976	1619.0	1.7227	3.5852	4.2908
0.3749	0.007137	0.6179	0.9013	1069.1	0.8980	1623.0	1.7351	3.5509	4.2516
.....	1.0000	1.0014	1073.0	0.8983	1627.0	1.7457	3.5206	4.2167

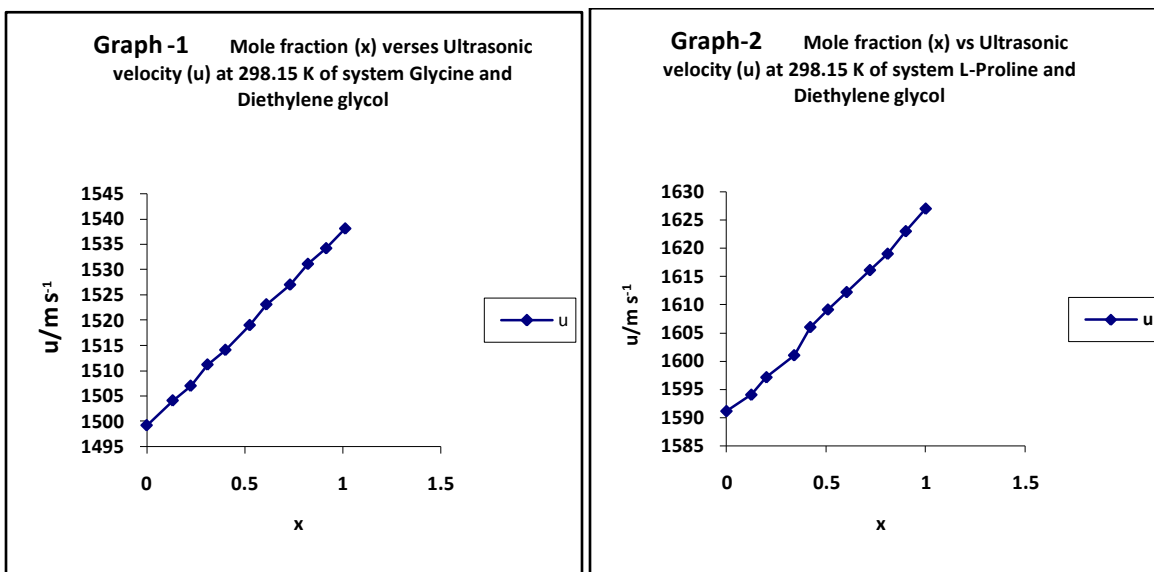
(Where, mole fraction of water (x₁), mole fraction of l-proline (x₂), mole fraction of diethylene glycol (x₃), mole fraction of aqueous l-proline and diethylene glycol system (X), density (ρ), viscosity (η), and ultrasonic velocity (u), acoustical impedance (Z), adiabatic compressibility (β), relaxation time (τ))

Table-2 to be continue here...

X ₁	X ₂	X ₃	X	R ($\times 10^3$)	W	V _f	$\Delta\eta$ ($\times 10^{-7}$)	$-V^E$ ($\times 10^4$)	L _f
.....	m/s ¹ mol ¹	m ³ /mol ¹	m ³ / mol ¹			A ^o
0.9800	0.01993	0.0000	2.7931	10.7973	0.4632	1.7593	1.1875
0.9602	0.01937	0.01970	0.1251	2.7948	10.7871	0.4635	8.5700	1.7240	1.1835
0.9356	0.01903	0.04528	0.2010	2.7966	10.7768	0.4637	5.4800	1.6801	1.1796
0.9073	0.01836	0.07435	0.3401	2.7989	10.7634	0.4640	5.9500	1.6296	1.1745
0.8710	0.01771	0.1112	0.4214	2.8018	10.7476	0.4644	0.1000	1.5649	1.1685
0.8243	0.01669	0.1590	0.5100	2.8036	10.7376	0.4647	0.1132	1.4816	1.1647
0.7632	0.01552	0.2212	0.6041	2.8054	10.7257	0.4649	0.1325	1.3729	1.1602
0.6829	0.01378	0.3032	0.7210	2.8076	10.7141	0.4652	0.1438	1.2297	1.1558
0.5603	0.01133	0.4283	0.8102	2.8093	10.7027	0.4654	0.1211	1.0109	1.1515
0.3749	0.007137	0.6179	0.9013	2.8116	10.6880	0.4657	0.1126	0.6803	1.1460
.....	1.0000	1.0014	2.8139	10.6750	0.4660	1.1411

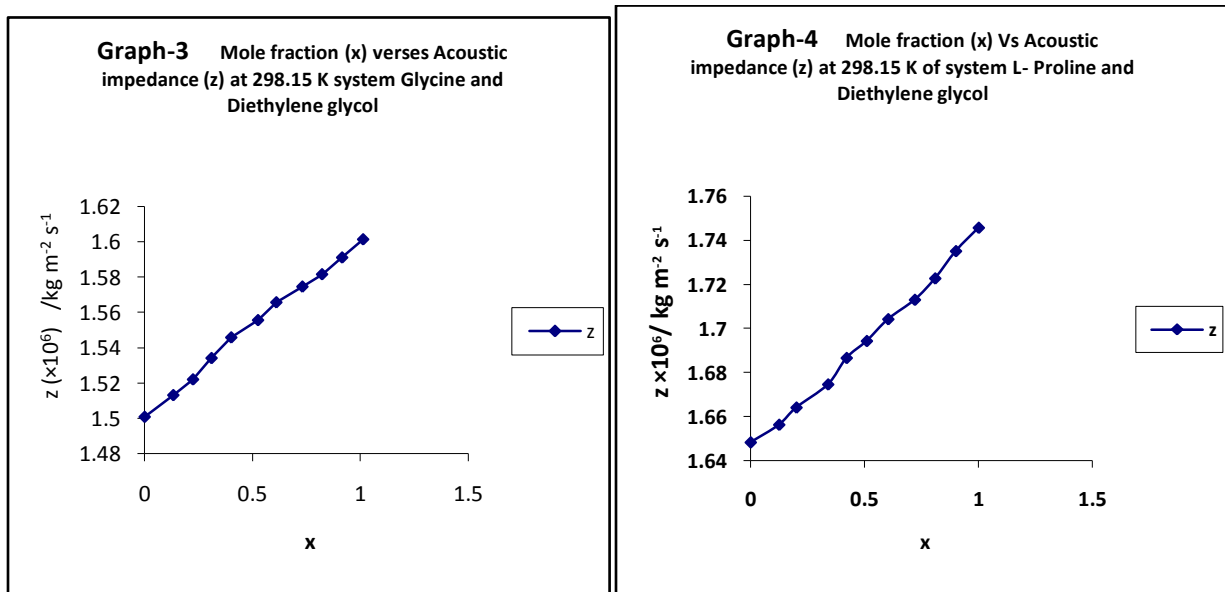
(Rao's constant (R), Wada's constant (W), free volume (V_f), viscosity deviation ($\Delta\eta$), excess volume (V^E), intermolecular free length (L_f).)

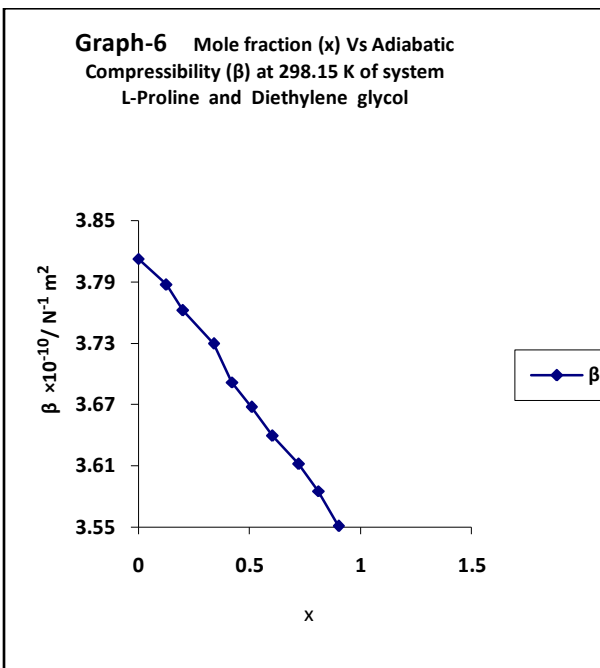
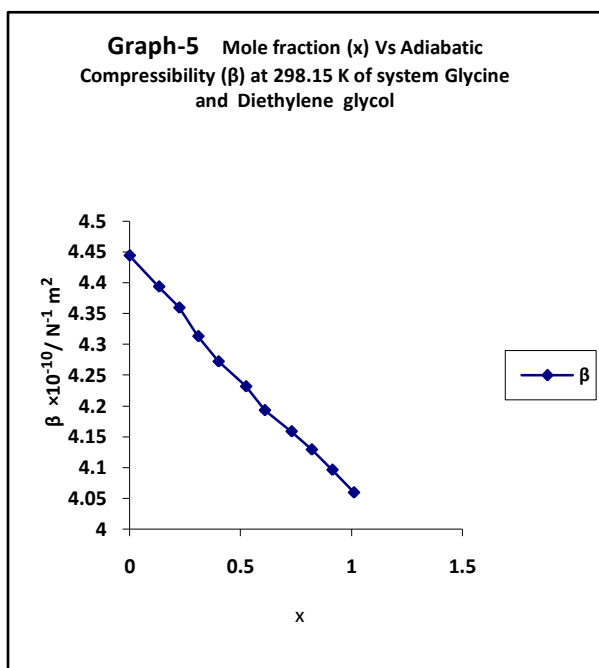
The table-2 data shows that as concentration increases the parameter like density, viscosity, ultrasonic velocity, acoustical impedance, Rao's constant, free volume increases while apparent molar volume, adiabatic compressibility, relaxation time, Wada's constant, molar volume, intermolecular free length, viscosity deviation, excess volume decreases.



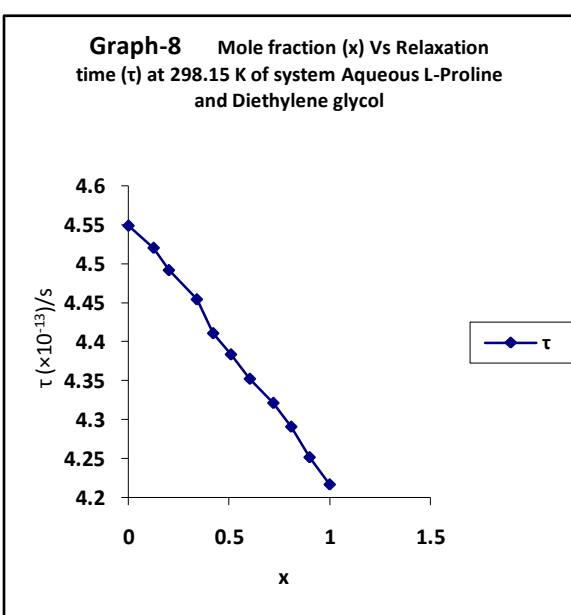
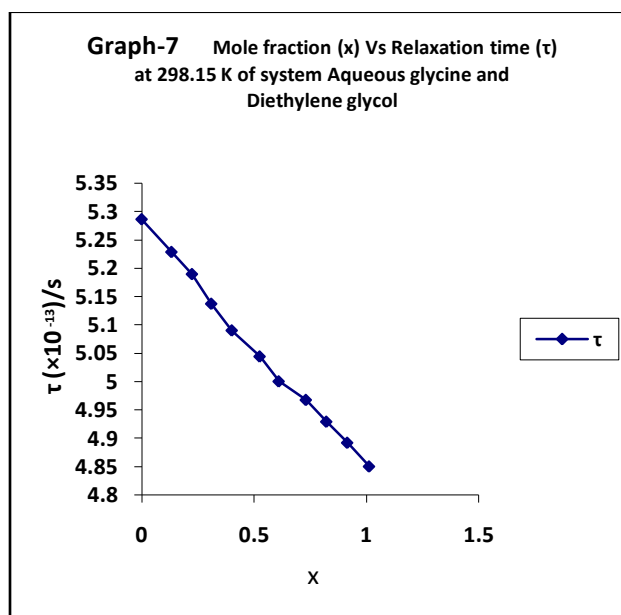
The nature of variation of ultrasonic velocity (u) with mole fraction (x) at 298.15 K is evident from tables 1,2 and graphs 1,2 show the variation which indicates increasing trends in both the systems attributed to the cohesion brought by the ionic hydration it predict the interaction between aqueous glycine with diethylene glycol and aqueous l-proline with diethylene glycol.

The correlation of acoustic impedance (z) with mole fraction (x) at 298.15 K is evident from tables 1,2 and graphs 3,4 show the variation which indicates increasing trends in both the systems. Hence it can be concluded that there is significant interaction between solute and solvent molecules due to which the structural arrangement is also affected. Thus it is clear from the above parameters that there is a strong association between water and amino acid molecules showing hydrophilic nature.





The variation of adiabatic compressibility (β) with mole fraction (x) at 298.15 K is evident from tables 1,2 and graph 5,6 show the variation which indicating decreasing trends in both the systems. It suggests that making and breaking of H-bonding. The higher compressibility values predict that the medium is loosely packed whereas the lower compressibility is an indication of maximum interaction. The gradual decrease in adiabatic compressibility in present work suggest that the medium become more and more less compressible. The intermolecular free length (L_f) is again a predominant factor in determining the existing interactions among the components of the mixture. Analyzing the respective table, (L_f) reflects a similar trend as that of (β). Increasing trend in these parameters suggest the strengthening of interaction among the components. The interaction may be solute-solute or solute-solvent or solvent-solvent type. Further the trend of molar adiabatic compressibility (W) called as Wada's constant which depends on the adiabatic compressibility of one molar volume solutions may be taken as a confirmation for existing interactions.



As concentration increases the number of molecules in the medium increases making the medium to be denser. It leads to increase of density, viscosity, ultrasonic velocity, acoustical impedance, Rao's constant, free volume and hence lesser intermolecular free length, adiabatic compressibility, relaxation time, Wada's constant. The present system in which particle-particle frictional resistance leads to intermolecular interaction shows increasing and decreasing trend of the measured parameters. The interaction may be solute-solute or solute-solvent or solvent-solvent type. Variations of physical parameter related to aqueous system attributed to structural changes[34].

APPLICATIONS

The various solution properties in recent studies consisting of polar as well as non polar components find applications in industrial and technology processes [1]. This research work prove that some of the novel molecules can stabilize the biochemical part of living beings [17,21-23]. The measured and calculated thermodynamic parameters are useful to know the interactions like solute-solute or solute-solvent or solvent-solvent type.

CONCLUSIONS

The experimental data clearly reveals the conclusion of system-1 aqueous glycine and diethylene glycol and system-2 aqueous l-proline and diethylene glycol in which as concentration increases the parameter like density, viscosity, ultrasonic velocity, acoustical impedance, Rao's constant, free volume, increases while adiabatic compressibility, relaxation time, Wada's constant, intermolecular free length decreases. These parameter are related with intermolecular correlation of aqueous amino acid and glycol ether. The system containing aqueous amino acid and glycol ether has strong intermolecular H-bonding. The acoustical parameters proved that H-bonding interaction is very strong at higher concentration. The gradual decreases in adiabatic compressibility with present work suggest that the medium become more and less compressible. The intermolecular free length (L_f) is again a predominant factor in determining the existing interactions among the components of the mixture. Analyzing the respective table, (L_f) reflects a similar trend as that of (β). Increasing trend in these parameters suggest the strengthening of interaction among the components. Thus molecular interactions are confirmed. The interaction may be solute-solute or solute-solvent or solvent-solvent type. As the increase in the number of particles that increases the fractional resistance between the layers of medium leads to increase the coefficient of viscosity. The present system in which particle-particle frictional resistance leads to intermolecular interaction.

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