Studies of Acoustic And Thermodynamic Properties of Aqueous Amino Acid And Glycol Ether System At 308.15 K And At Various Concentrations

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Abstract

The thermo physical parameters viz. density (ϱ), viscosity (η), and ultrasonic velocity (u) have been measured for aqueous amino acid and glycol ether system at 0.1 to 1 mole fractions and at 308.15 K. Physical parameters viz. acoustical impedance (z), adiabatic compressibility (β), relaxation time (τ), Rao's constant (R), Wada's constant (W), free volume (V_f), molar volume(V_m), intermolecular free length (L_f) have been obtained from experimental data. The acoustical parameters proved that H-bonding interaction is very strong at higher concentration. The trends in present system suggest the strengthening of interaction among the components and particle-particle frictional resistance leads intermolecular interaction. It shows increasing and decreasing trends of the measured parameters. Thus molecular interactions are confirmed. The interaction may be solute-solute or solute-solvent or solvent-solvent type.

KEYWORDS: - Acoustical impedance, Adiabatic compressibility, Relaxation time.

INTRODUCTION

The study of ultrasonic velocity is found to be useful in measuring no. of physicochemical parameters [1-4]. From a long time researcher interested in studies of solubility and stability of complex molecules like proteins but because of complex nature of molecules, low molecular weight compounds are preferred [5]. Hence the physical properties of amino acids in aqueous solution have been studied to understand solute solvent interaction and their role in the stability of proteins [6]. The random coil, unfolded, forms of denatured proteins these studies in the form of thermodynamic stability of protein [7-8].To studies volumetric and compressibility parameter of amino acids in aqueous salt system show molecular interactions [9-22]. The amino acid like L-Proline shows solute solvent interactions [23]. The data of density of glycine, L-alanine and L-serine in aqueous glucose solutions discussed by Li et al [24]. The data of the ultrasonic velocity of glycine, DL-alanine, diglycine and triglycine in aqueous solution of glucose discussed by Banipal et al [25]. To study of the molecular interactions of ions and proteins is useful in the separation and purification processes and to understand the physiological systems [26-30]. In proteins the amino acids are building blocks compounds; their study provides important information about nature of larger biomolecules. The proteins as amino acids play a important role in metabolism and neurochemical mechanisms such as pain transmission, reflex action, hormones mechanism [31-32]. They have many applications in pharmaceutical industries and also used as food additives. To studies the effect of temperature and concentration of salt on the thermodynamic properties of amino acids have been proved by researcher to useful in elucidating the various interactions [33-41]. The thermo physical parameter show molecular interactions of aqueous glycine. This data useful to understand the nature of biological molecules

[42]. The electrolytes in aqueous solution have been studied under thermo dynamical property [43-44].

EXPERIMENTAL

2.1 SOURCE AND PURITY OF SAMPLE:-

All the chemicals are analytical reagent (AR) and spectroscopic reagent (SR) grades from E-Merck, Germany and Sd Fine, AVRA chemicals India. The purities of the above chemicals were checked by density determination at 308.15 K.

2.2 METHOD:-

The liquid mixtures of different known compositions were prepared in stopper volumetric flasks. The density, viscosity and ultrasonic velocity values were measured as a function of composition of the liquid mixture of amino acid with glycol ether at 308.15 K. The density was determined using a Bi-capillary pyknometer. 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) was used for the viscosity measurement and efflux time determined with digital clock ±0.01s. An ultrasonic interferometer having the frequency of 3 MHz (Mittal Enterprises, New Delhi, Model: F-05) with an overall accuracy of ±0.1% was used for velocity measurement. An electronically digital operating constant temperature bath (RAAGA Industries) was 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 [45].

THEORY AND CALCULATIONS

The measured values viz. density (ρ), ultrasonic velocity (u) and viscosity (η) we obtained the physical parameter viz. acoustical impedance (z), adiabatic compressibility (β), relaxation time (τ), Rao's constant (R),Wada's constant (W), free volume (V_f), molar volume(V_m), intermolecular free length (L_f), calculated by using following standard relation[42,45-49].

1) $\mathbf{z = \rho u}$

2) $\mathbf{\beta = 1/u^2\rho}$

3) $\mathbf{\tau = 4/3\ \eta\ \beta}$

4) $\mathbf{R = u^{1/3}v}$

5) $\mathbf{W = \beta^{1/7}v}$

6) $\mathbf{V_f = M_{eff}\, u/K\eta}$ **(K=4.28×10^9** is a temperature independent constant**)**
(M_{eff} –effective molecular wt. of soln. $M_{eff} = x_1M_1+x_2M_2+x_3M_3$. 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) $\mathbf{V_m = M_{eff} / \rho}$

8) $\mathbf{L_f = K_j\, \beta^{1/2}}$ **(K_j =6.0816×10^4)**
(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. To investigate the physical properties viz. 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), molar volume (V_m), intermolecular free length (L_f) gives information about interactions between aqueous amino acids and glycol ether. It is proved by experimental data from tables and figures. These physical properties correlated with various concentrations 0.1 to 1.0 and at 308.15 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 [50]. 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 suggests 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 trends 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 [42]. In other words the increase in density may be interpreted to the structure making of the solvent due to H-bonding [51-52]. 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 [53].

The viscosity is a 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 [52]. The values of adiabatic compressibility (β) show decreasing trend with concentration which suggest the making and breaking of H-bonding [42]. 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 [53]. Eyring and Kincaid [54] 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 [53]. 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 308.15 K)

X_1	X_2	X_3	X	ρ	η ($\times10^{-3}$)	u	z ($\times10^{6}$)	β ($\times10^{-10}$)	τ ($\times10^{-13}$)
…….	……..	……..	…….	kgm^{-3}	Nsm^{-2}	ms^{-1}	$kg\ m^{-2}s^{-1}$	$N^{-1}\ m^2$	s
……..	…….	……..	0.0000	995.1	0.8914	1507.0	1.4996	4.4249	5.2591
0.9611	0.01870	0.02012	0.1327	997.0	0.8916	1510.1	1.5055	4.3983	5.2287
0.9377	0.01824	0.04404	0.2241	999.1	0.8921	1512.0	1.5106	4.3781	5.2076
0.9099	0.01770	0.07234	0.3100	1003.0	0.8924	1515.0	1.5195	4.3438	5.1685
0.8753	0.01702	0.1076	0.4013	1006.1	0.8927	1518.1	1.5273	4.3127	5.1332
0.8303	0.01615	0.1535	0.5253	1008.1	0.8930	1521.2	1.5335	4.2867	5.1040
0.7752	0.01484	0.2099	0.6102	1011.0	0.8934	1523.0	1.5397	4.2643	5.0796
0.6915	0.01331	0.2950	0.7310	1014.2	0.8939	1528.1	1.5497	4.2225	5.0326
0.5707	0.01105	0.4182	0.8221	1017.0	0.8942	1533.0	1.5590	4.1840	4.9884
0.3792	0.00717	0.6136	0.9152	1019.1	0.8944	1538.0	1.5673	4.1483	4.9469
……	…….	1.0000	1.0124	1021.0	0.8947	1541.0	1.5733	4.1244	4.9201

(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 (continued)

X_1	X_2	X_3	X	R ($\times 10^3$)	W	V_f	Vm	L_f
.....	.....	.....	.....	$ms^{-1}mol^{-1}$	m^3mol^{-1}	m^3mol^{-1}	cm^3mol^{-1}	A^o
.....	.....	.....	0.0000	2.2836	9.1826	0.4285	0.2002	1.2793
0.9611	0.01870	0.02012	0.1327	2.2852	9.1747	0.4287	0.1998	1.2754
0.9377	0.01824	0.04404	0.2241	2.2862	9.1687	0.4288	0.1994	1.2725
0.9099	0.01770	0.07234	0.3100	2.2877	9.1584	0.4291	0.1985	1.2675
0.8753	0.01702	0.1076	0.4013	2.2892	9.1490	0.4293	0.1979	1.2630
0.8303	0.01615	0.1535	0.5253	2.2908	9.1411	0.4295	0.1975	1.2592
0.7752	0.01484	0.2099	0.6102	2.2917	9.1342	0.4296	0.1970	1.2558
0.6915	0.01331	0.2950	0.7310	2.2943	9.1214	0.4300	0.1964	1.2497
0.5707	0.01105	0.4182	0.8221	2.2967	9.1095	0.4305	0.1958	1.2440
0.3792	0.00717	0.6136	0.9152	2.2992	9.0983	0.4309	0.1954	1.2387
.....	.....	1.0000	1.0124	2.3007	9.0908	0.4312	0.1950	1.2350

Rao's constant (R), Wada's constant (W), free volume (V_f), molar volume (V_m), 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 increases while adiabatic compressibility, relaxation time, Wada's constant, molar volume, intermolecular free length decreases.

Table-2 (Aqueous L-Proline and Diethylene glycol system at 308 .15 K)

X_1	X_2	X_3	X	ρ	η $(\times10^{-3})$	u	z $(\times10^{6})$	β $(\times10^{-10})$	τ $(\times10^{-13})$
……..	…….	……..	……	kgm^{-3}	Nsm^{-2}	ms^{-1}	$kg\ m^{-2}s^{-1}$	$N^{-1}\ m^{2}$	s
0.9800	0.01993	…….	0.0000	1028.0	0.8939	1597.0	1.6417	3.8141	4.5459
0.9602	0.01937	0.01970	0.1251	1034.1	0.8943	1600.0	1.6546	3.7774	4.5042
0.9356	0.01903	0.04528	0.2010	1038.0	0.8948	1603.1	1.6640	3.7487	4.4724
0.9073	0.01836	0.07435	0.3401	1040.2	0.8951	1607.0	1.6716	3.7226	4.4428
0.8710	0.01771	0.1112	0.4214	1044.0	0.8954	1611.0	1.6819	3.6906	4.4061
0.8243	0.01669	0.1590	0.5100	1047.1	0.8957	1616.0	1.6921	3.6570	4.3674
0.7632	0.01552	0.2212	0.6041	1051.0	0.8961	1620.0	1.7026	3.6255	4.3317
0.6829	0.01378	0.3032	0.7210	1055.0	0.8966	1623.1	1.7124	3.5980	4.3013
0.5603	0.01133	0.4283	0.8102	1058.1	0.8969	1627.0	1.7215	3.5706	4.2700
0.3749	0.007137	0.6179	0.9013	1062.0	0.8973	1630.2	1.7313	3.5432	4.2391
…….	…….	1.0000	1.0014	1068.0	0.8975	1633.0	1.7440	3.5112	4.2017

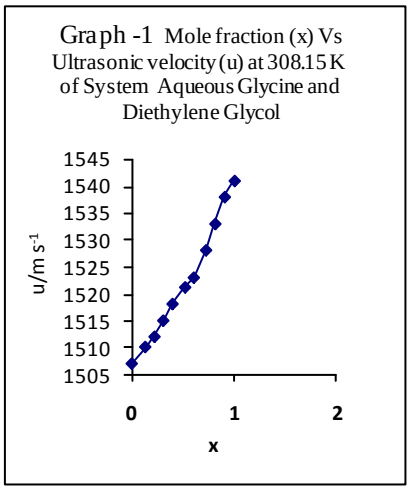
(Where, mole fraction of water (x_1), mole fraction of l-proline (x_2), mole fraction of diethylene glycol (x_3), mole fraction of aqueous l-proline and diethylene glycol system (X), density (ρ), viscosity (η), and ultrasonic velocity (u), acoustical impedance (Z), adiabatic compressibility (β), relaxation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

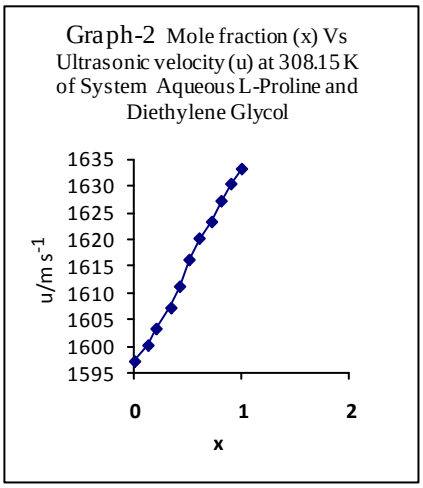
Table-2 (continued)

X_1	X_2	X_3	X	R $(\times10^{3})$	W	V_f	Vm	Lf
……..	…….	……..	……	$ms^{-1}\ mol^{-1}$	m^3mol^{-1}	m^3mol^{-1}	$cm^3\ mol^{-1}$	A^o
0.9800	0.01993	…….	0.0000	2.7965	10.7978	0.4640	0.2327	1.1877
0.9602	0.01937	0.01970	0.1251	2.7983	10.7829	0.4642	0.2314	1.1820
0.9356	0.01903	0.04528	0.2010	2.8001	10.7712	0.4644	0.2305	1.1775
0.9073	0.01836	0.07435	0.3401	2.8024	10.7604	0.4647	0.2300	1.1734
0.8710	0.01771	0.1112	0.4214	2.8047	10.7471	0.4650	0.2292	1.1683
0.8243	0.01669	0.1590	0.5100	2.8076	10.7331	0.4655	0.2285	1.1630
0.7632	0.01552	0.2212	0.6041	2.8099	10.7199	0.4658	0.2276	1.1580
0.6829	0.01378	0.3032	0.7210	2.8117	10.7082	0.4660	0.2268	1.1536
0.5603	0.01133	0.4283	0.8102	2.8139	10.6965	0.4663	0.2261	1.1492
0.3749	0.007137	0.6179	0.9013	2.8158	10.6848	0.4666	0.2253	1.1448
…….	…….	1.0000	1.0014	2.8174	10.6709	0.4668	0.2240	1.1396

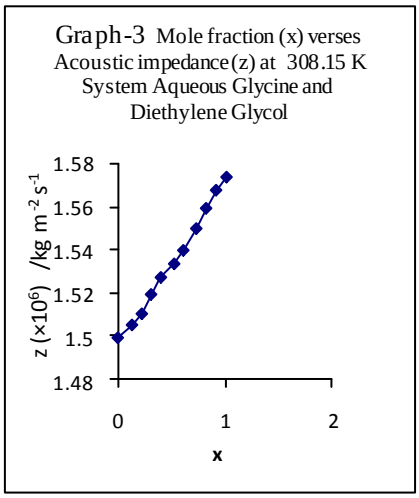
(Rao's constant (R), Wada's constant (W), free volume (V_f), molar volume (V_m), intermolecular free length (L_f).

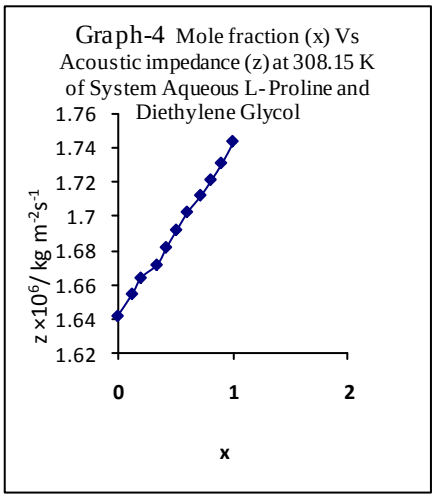
The table-2 data shows that as concentration increases the parameter like density, viscosity, ultrasonic velocity, acoustical impedance, Rao's constant, free volume increases while adiabatic compressibility, relaxation time, Wada's constant, molar volume, intermolecular free length decreases.



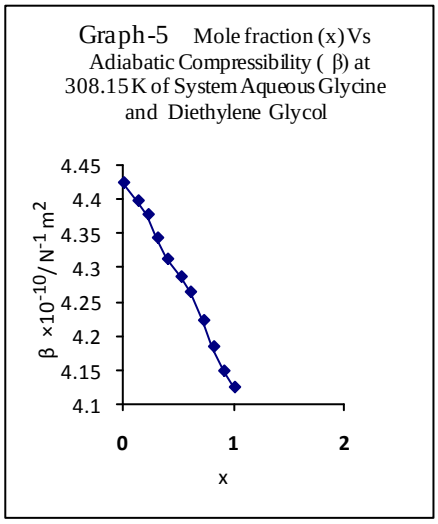


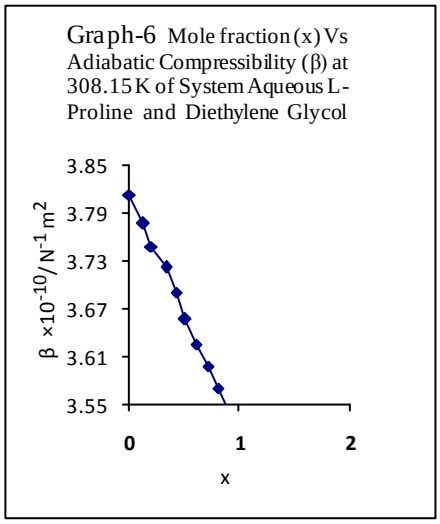
The nature of variation of ultrasonic velocity (u) with mole fraction (x) at 308.15 K is evident from tables 1,2 and figures 1,2 show the variation which indicates increasing trends in both the systems attributed to the cohesion brought by the ionic hydration it predict the interaction between aqueous glycine with diethylene glycol and aqueous l-proline with diethylene glycol.



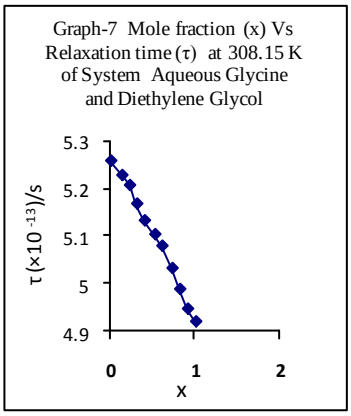


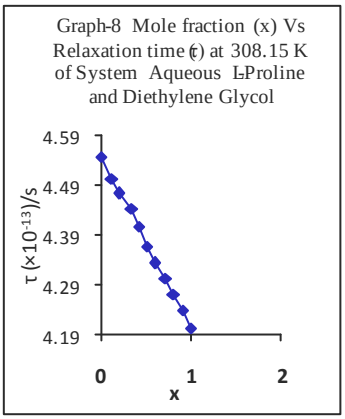
The correlation of acoustic impedance (z) with mole fraction (x) at 308.15 K is evident from tables 1, 2 and figures 3, 4 show the variation which indicates increasing trends in both the systems. Hence it can be concluded that there is significant interaction between solute and solvent molecules due 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 308.15 K is evident from tables 1, 2 and figures 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 suggests 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 [55].

APPLICATIONS

The study of the molecular interactions of ions and proteins are useful in the separation and purification processes and to understand the physiological systems[26-30]. The proteins as amino acids play an important role in metabolism and neuro-chemical mechanisms such as pain transmission, reflex action and hormones mechanism[31-32]. The various solution properties in recent studies consisting of polar as well as non polar components find applications in industrial and technology processes[42]. They have many applications in pharmaceutical industries and also used as food additives. The variations of physical parameter related to aqueous system attributed to structural changes[55]. This research work proved that some of the novel molecules can stabilize the biochemical part of living beings[56-59]. The measured and calculated thermodynamic parameters are useful to know the interactions like solute-solute or solute-solvent or solvent-solvent type.

CONCLUSION

The experimental data clearly revels that 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 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. 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. The values of adiabatic compressibility (β) show decreasing trends with concentration which suggest the making and breaking of H-bonding.

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