INTERNATIONAL JOURNAL OF PHARMACEUTICAL, CHEMICAL AND BIOLOGICAL SCIENCES

Available online at www.ijpcbs.com

Research Article

ACOUSTICAL AND THERMODYNAMICAL STUDIES OF MOLECULAR INTERACTIONS IN AQUEOUS ETHYLENE GLYCOL AT 303.15, 308.15 AND 313.15K

S. Thirumaran[1]*, Gene George[2], S. Vijay[2] and N. Prakash[1]

[1]Department of Physics (DDE), Annamalai University, Annamalai Nagar-608 002,
Tamil Nadu, India.
[2]Department of Physics, T.B.M.L College, Poraiyar, Tamil Nadu, India.

ABSTRACT
The ultrasonic velocity, density and viscosity have been measured for the ternary liquid mixtures of (i) water + ethylene glycol + Tetrahydrofuran (THF), (ii) water + ethylene glycol + dimethyl formamide (DMF), and (iii) water + ethylene glycol + dimethyl sulphoxide (DMSO) have been measured as a function of the composition of 303.15, 308.15 and 313.15K. The fixed binary solvent mixture (water + ethylene glycol) has been prepared under the constant ratio of 4:1 respectively. The experimental data have been used to calculate some excess parameters namely, adiabatic compressibility (β^E), intermolecular free length ($L_f{}^E$), free volume (V_f^E), internal pressure ($\pi_i{}^E$), viscosity ($\acute{\eta}^E$) and Gibb's free energy (ΔG^{*E}). The results are discussed and interpreted in terms of structural and specific interactions that predominated by hydrogen bonding.

Keywords: adiabatic compressibility, Intermolecular free length, hydrogen bonding.

1 INTRODUCTION

In recent years, the measurement of ultrasonic velocity has been adequately employed in understanding the nature of molecular interactions in pure liquids and liquid mixtures. The ultrasonic velocity measurements are highly sensitive to molecular interactions and can be used to provide qualitative information about the physical nature and strength of molecular interaction in the liquid mixtures[1-2] Ultrasonic velocity of a liquid is fundamentally related to the binding forces between the atoms or the molecules and has been adequately employed in understanding the nature of molecular interaction in pure liquids [3-5]. The variation of ultrasonic velocity and related parameters throw much light upon the structural changes associated with the liquid mixtures having weakly interacting components[6-8]as well as strongly interacting components. Ultrasonic studies of aqueous mixed solvent systems are of importance because of their extensive use in textile, leather and pharmaceutical industries. Organic solvents whose miscibility with water is unlimited usually from H-bonds in aqueous solutions. Some solvents also present auto-association by hydrogen bonds in pure state but others do not. The functional group of organic solvent can form H-bonds with water due to hydrophilic effects, which the hydrocarbon part of the organic solvents is responsible for hydrophobic effects.

The calculated excess quantities from experimental acoustical data have been interpreted in terms of the differences in the size of the molecules as well as the strength of specific and non-specific interactions between the components of the mixtures. Further, the measurement of excess thermodynamic properties are found to be greatly significant in studying the structural changes associated with the liquids. They also provide important information about molecular packing, molecular motion and various type of intermolecular interactions and their strength influenced by the size, shape and chemical nature of component molecules[9].This in turn helps in bringing out the facts which can have positive implementation for both industry as well as the theory building process. A thorough knowledge of thermodynamic and transport properties of ternary liquid systems is essential in many industrial such as design calculations, heat transfer, mass transfer, fluid flow and so on.The present chapter deals with the study of excess thermodynamic and transport properties of some aqueous mixed solvent system at different temperatures. The liquids under investigation have been chosen on the basis of their industrial applications. These applications have greatly simulated the need for extensive information on the thermodynamic, acoustic and transport properties of these solvents and their mixtures[10].

The increasing use of Tetrahydofuran (THF), Dimethyl formamide (DMF) and Dimethylsulphoxide (DMSO) and their aqueous mixtures in many industrial process such as battery, pharmaceutical and cosmetics have greatly stimulated the need for extensive informations on their various properties. Tetrahydrofuran (THF) commercially known as cello solves and is a good industrial solvent. It figures prominently in the high energy battery industry and have founded application in the organic synthesis as manifested from physic-chemical studies in this medium. The most important use of dimethylformamide (DMF) as a dipolar, aprotic solvent for polymer in the preparation of polyacrylonitrile solutions for the manufacture of fibrous poly acrylonitride. DMF used in the production of acrylic fibres and plastics. It is also used in peptide coupling for pharmaceuticals in the development and production of pesticides and in the manufacture of adhesives, synthetic leather, fibres, films and surface coatings. Dimethylsulphoxide (DMSO) is an aprotic polar solvent strongly associated due to a high polar S=O group in the molecule and large dipole moment (3.96D). Due to its polar nature, it can interact with water through H-bonding. DMSO is called super solvent due to its wide range of applicability as solvent in chemical, biological process and chemical intermediates. The study of DMSO is important because of its utilisation in a broad range of application in medicine. Ethylene Glycol (EG) is the simplest with dielectric constant (€=38.66 at T= 293.15K) and dipole moment (μ = 2020 D)[11]. It is self associated in the pure state creating a net of hydrogen bonds which are dependent on the temperature and the presence of electrolytes. In aqueous solutions, EG gives rise to two or three dimensional networks through hydrogen bonds with the consequence that the mixture display negative deviation from ideality. Owing to the characteristics and physical nature of above constituent chemicals had motivated the authors to carry out the molecular interactions of ternary liquids mixtures of THF, DMF and DMSO with binary solvent mixtures of water + ethylene glycol taken at a ratio of 4:1 respectively at 303.15, 308.15 and 313.15K.

System –I	THF	water	ethyleneglycol
System –II	DMF	water	ethyleneglycol
System – III	DMSO	water	ethylene glycol

2 MATERIALS AND METHODS

All the chemicals which have been used, are analytical reagent (AR) and spectroscopic reagent (SR) grades of minimum assay of 99.9% obtained from E-Merk, Germany and Sd fine chemicals, India. The purities of the above chemicals were checked by the density determination at 303.15, 308.15 and 313.15K at an accuracy of 0.0001g. The solvent binary mixture containing water and ethylene glycol were prepared in the fixed ratio of 4:1 on mole fraction basis and the solutes such as tetrahydofuran(THF), dimethyl formamide (DMF) and dimethyl sulphoxide(DMSO) were added to this binary solvent mixture on mole fraction basis. For this purpose, binary solvent mixture (water + ethylene glycol) with fixed mole ratios X_2/X_3 = 4:1 was prepared by mass and used on that day itself. The ternary liquid mixtures of different known compositions were prepared in stopper measuring flasks. The chemicals were weighed in an electronic digital balance (SHIMADZU AX-200, Japan Make) with a least count of 0.0001g. The density was determined using a specific gravity bottle by relative measurement method with an accuracy of ±0.01kgm^{-3}. An Ostwald's viscometer of 10ml capacity was used for the viscosity measurement. Efflux time was determined using a digital chronometer within ±0.01s. An Ultrasonic Interferometer having the fixed frequency of 2MHz (Mittal Enterprises, New Delhi-Model: F-81) with an overall accuracy of 2ms^{-1} has been used for velocity measurement. An electronically digital operated constant temperature bath (RAAGA Industries, Chennai) has been used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at desired temperature, whose accuracy is maintained at ± 0.1K.

3 RESULTS AND DISCUSSION

The experimentally determined values of density (ρ), viscosity (η) and ultrasonic velocity (U) of thee liquid systems at 303.15,308.15 and

313.15K are presented in Table 1. The excess values of adiabatic compressibility (β^E), free length (L_f^E), free volume (V_f^E), internal pressure (π^E_i) Gibbs Free Energy(ΔG^E) and viscosity (η^E) are reported in Tables 2 and 3.

It is observed from the Table 1, that the value s of density ,viscosity and ultrasonic velocity decrease with increase in mole fractions of Tetrahydofuran (THF), Dimethyl formamide (DMF) and Dimethylsulphoxide (DMSO) with aqueous ethylene glycol in all the three liquid systems as well as rise of temperature. The variation of ultrasonic velocity in a mixture depends upon the increase (or) decrease of intermolecular free length after mixing the components. On the basis of a model, for sound propagation proposed by Eyring and Kincaid[13], ultrasonic velocity should decrease, if the intermolecular free length increase and vice-versa. This is in fact observed in the present investigation for all the four liquid systems.

The thermodynamic excess properties are found to be more sensitive towards intermolecular interaction between the component molecules of liquid mixtures. The sign and magnitude of deviation of excess properties depend on strength of interaction between unlike molecules. In order to understand the nature of molecular interactions between the components of the liquid mixtures, it is of interest to discuss the same in term of excess parameter rather than actual values. Non-ideal liquid mixtures show considerable deviation from linearity in their physical behaviour with respect to concentration and these have been interpreted as arising from the presence of strong or weak interactions [14].

The Table 2 exhibits the values of excess adiabatic compressibility (β^E) for all the three liquid systems. The negative values of β^E is associated with a structure-forming tendency, while positive values are an indication of structure-breaking tendency due to hetero-molecular interaction between the component molecules of the mixtures. The positive values of excess adiabatic compressibility which indicates the loosely packed molecules in the mixtures resulting due to shape and size. From the present study, it is evident that the excess adiabatic compressibility are negative in all the liquid systems, (except in System-I, where positive deviations are found) and it increases with molar concentrations of solutes such as THF, DMF and DMSO in respective systems with aqueous ethylene glycol as well as with elevation of temperature. In the present work, the negative values of compressibility for ternary liquid mixtures may be attributed to the formation of hydrogen bonds between the oxygen atom of tetrahydrofuran (THF), dimethy lformamide (DMF) anddimehtylsulphoxide (DM SO) and hydrogen atom of water and ethylene glycol.

The perusal of Table 2 shows the values of excess free length (L_f^E) for all the three ternary liquid systems. It is noticed that the L_f^E values are negative in all the systems (except in System-I, where positive deviations are noticed at higher mole fraction range) and found to be increased with molar concentration of solutes. Further, it is noticed that the values of excess free length increases with increase with rise of temperature in all the three liquid systems. According to Kannappan *et al.* [15], the negative values of L_f^E indicate that sound waves cover long distances due to decrease in intermolecular free length describing the dominant nature of hydrogen bond interaction between unlike molecules. Fort and Moore [16] indicated that the positive excess values of free length should be attributed to the dispersive forces and negative excess values of should be due to charge transfer and hydrogen bond formation. In the present investigation, one can notice that the increasing trend of negative excess values of intermolecular free length (L_f^E) with the increasing concentration of solutes such as THF, DMF and DMSO may be attributed to increase in or enhancement of molecular interactions between the unlike molecules influenced by hydrogen bonding.

From the present investigation, one can notice that a qualitative picture of excess free volume (V_f^E) values for all the three ternary liquid systems. The present parameter indicates the extent of deviation from ideal with the mole fraction of the mixtures. The present study shows that the excess values of free volume for all the three ternary liquid systems found to be negative in all the three liquid systems studied. Similarly, the values of excess free volume show almost an increasing trend over the increase of molar concentration of solutes and decreases with elevation of temperature. The results can be explained in terms of molecular interaction, structural effect and interstitial accommodation along with the changes in free volume. The sign of the V_f^E depends on the relative strength between the contractive forces and expansive forces. The factors responsible for volume contraction are (i) specific interactions between the component molecules and (ii) weak physical forces, such as dipole-dipole or dipole-induced dipole interactions or Vanderwaal's forces. The factors that cause expansion in volume are dispersive forces, steric hindrance of component molecules, unfavourable geometric fitting and electrostatic repulsion. In the present study, the increasing trend of negative values of excess free volume contribute the presence of greater interaction in the liquid mixtures. Thirumaranet.al[17]., have also reported a similar observation, which supports the present study.

In the study of liquid mixtures, the variation of internal pressure may give some suitable information regarding the nature and strength of the forces existing between the molecules. In fact, the internal pressure is a broader concept and it is a measure of the totality of forces of the dispersion, ionic and dipolar interaction that contribute to be overall cohesion of the liquid systems. The present study shows that the excess internal pressure values (π^E_i) are negative in all the three liquid systems studied and almost decrease with increasing molar concentration of solutes, (where it exhibits an increasing trend in System-III.) and increase with elevation of temperature. Such a decreasing trend of excess internal pressure values depicts (Table3) the strengthening of cohesive forces results in due to making up of the structure of the solvent which advocates a strong molecular interaction in the present study of liquid mixtures.

One should observe that the values of variation of excess Gibbs energy ΔG^E for the three ternary liquid systems. The values of ΔG^E are all positive in all the three liquid systems concerned and decrease with molar concentration of solutes and non-linear with the rise of temperature. However, System-II exhibits an increasing trend with elevation of mole fraction of solutes.[From Table 3]. According to Read *et al*[18], the positive values of excess Gibbs energy values may be attributed to specific interactions like hydrogen bonding and charge transfer, while negative ΔG^E values may be ascribed to the dominance of dispersion forces[19].

In the present study, the observed behaviour of excess Gibb's free energy show that the formation of H-bond heterogeneous interactions between the components of unlike molecules. DMF, DMSO and THF molecules exist in self-associated structures through H-bonds with parallel alignment in their pure liquid State [20]. Self-associated depends not only on the steric arrangement of the respective groups, but is also sensitive to the size and shape of the polar molecules. The Ethylene Glycol(EG) has at both ends hydroxyl groups with a gauche confirmation, which results in intra molecular H-bonding, and hence probably only –OH group of EG molecules can interact with neighbouring molecules through H-bond[21]. In the present investigation, our close observation suggest that the increasing positive values of ΔG^E indicates a strong molecular interaction in the liquid mixtures.

According to Fort *et al.*[16] the variation of excess viscosity (η^E) gives the strength of molecular interaction between the molecules. For systems, where dispersion, induction, and dipolar forces which are operated by the values of excess viscosity are found to be negative, whereas the existence of specific interactions leading to the formation of complexes in liquid mixtures tends to make excess viscosity positive. It is reported from the present Table 2, the excess viscosities are positive in System-III and negative in System I and II and increase with the further addition of solutes as well as rise of temperature. Such an increasing trend of these positive values of η^E further suggests that the dominance of strong hydrogen bond formations between the solvent (water + ethylene glycol) and solutes (THF, DMF and DMSO), which leads to a strong interaction in the present system of liquid mixtures. Further, the increasing trend of temperature enhances the strength of molecular interaction in the component mixtures.

From the magnitudes of excess parameters such as, excess internal pressure (πi^E), excess free volume(V_f^E) and excess viscosity (η^E), it can be concluded that the strength of interaction is in the order: System-III> System-II>System-I.

4 CONCLUSION

It is very obvious that this present study that has there exist a molecular interaction (strong hydrogen bonding) between the solvent (water + ethylene glycol) and solutes (THF, DMF and DMSO).The strength of the molecular interactions gets strengthened on further addition of solutes. The present study finds no formation of donor-acceptor complexes in the component mixtures.The elevation of temperature plays a vital role in enhancement of molecular interactions in the present systems of liquid mixtures.It can be concluded that the strength of interaction among the liquid systems is in the order: System-III> System-II>System-I.

Table 1: Values of Density (ρ), Viscosity (η) and Ultrasonic velocity (U) for

Mole fraction (X_1)	ρ (kg.m^{-3})			η (× 10^{-3} NSm^{-2})			U (ms^{-1})		
	Temperature (K)								
	303.15	308.15	313.15	303.15	308.15	313.15	303.15	308.15	313.15
SYSTEM I: THF (X_1) + WATER (X_2) + ETHYLENE GLYCOL(X_3) [X_2/X_3 = 4:1]									
0.0000	1054.32	1052.39	1050.57	2.4371	2.1296	1.8003	1646.78	1645.30	1640.23
0.0999	1023.31	1021.38	1017.74	2.5906	2.2408	1.8101	1607.64	1599.35	1591.82
0.3005	968.58	963.02	955.73	1.7058	1.5049	1.3457	1423.21	1422.58	1408.60
0.5002	944.87	915.60	911.95	1.0022	0.8989	0.7771	1344.06	1330.66	1313.70
0.7004	886.50	882.15	880.95	0.6297	0.5925	0.5147	1290.92	1283.24	1263.74
0.9005	877.38	875.47	864.53	0.5011	0.4788	0.4192	1273.25	1253.53	1231.54
SYSTEM II: DMF (X_1) + WATER (X_2) + ETHYLENE GLYCOL (X_3) [X_2/X_3 = 4:1]									
0.0000	1056.14	1054.21	1050.57	2.4937	2.1333	1.8003	1650.30	1648.76	1640.23
0.1000	1034.25	1032.33	1030.51	2.8046	2.2338	1.9760	1644.58	1636.18	1623.73
0.3002	1008.71	1006.79	1003.15	2.5537	2.2491	1.8214	1588.10	1588.75	1570.99
0.5006	988.64	983.08	975.79	1.7708	1.5855	1.3197	1548.77	1539.80	1523.41
0.7007	957.64	955.72	953.90	1.1115	1.0435	0.9013	1492.26	1485.71	1468.13
0.9004	950.34	945.63	941.14	0.8083	0.7862	0.6802	1459.49	1442.49	1424.85
SYSTEM III: DMSO (X_1) +WATER (X_2) + ETHYLENE GLYCOL (X_3) [X_2/X_3 = 4:1]									
0.0000	1056.14	1054.21	1050.57	2.3356	2.1296	1.8003	1655.24	1647.30	1640.23
0.0999	1074.38	1072.45	1070.63	3.0640	2.6644	2.1521	1657.76	1652.61	1623.77
0.3001	1096.2	1092.52	1085.22	3.0162	2.5173	2.0407	1632.20	1625.32	1611.82
0.5000	1101.74	1097.99	1092.52	2.3151	2.2329	1.9937	1573.65	1567.69	1553.94
0.7006	1099.92	1094.34	1090.70	2.2783	2.2254	1.9399	1517.44	1514.73	1499.47
0.9009	1098.09	1096.16	1090.70	2.0203	1.8778	1.5862	1492.26	1476.28	1460.66

Table 2: Excess values of Viscosity (η^E), Adiabatic compressibility (β^E) and Intermolecular free length (L_f^E) for

Mole fraction (X_1)	η^E(× 10^{-3} NSm^{-2})			β^E / (× 10^{-10}m^{2}N^1)				L_f^E/ × 10^{-10}m	
	Temperature (K)								
	303.15	308.15	313.15	303.15	308.15	313.15	303.15	308.15	313.15
SYSTEM I: THF (X_1) + WATER (X_2) + ETHYLENEGLYCOL (X_3) [X_2/X_3 = 4:1]									
0.0000	-.8685	-.6435	-0.527	-.7112	-.6739	-.6257	-.0354	-.0340	-.0319
0.0999	-.4291	-.2977	-.3215	-.7434	-.6866	-.6386	-.0339	-.0348	-.0351
0.3005	-.7295	-0.554	-.3861	-.0624	-.0780	-.5772	0.0018	0.0055	0.0068
0.5002	-.8777	-.7042	-.5742	0.0703	0.2837	0.2494	0.0079	0.0282	0.0298
0.7004	-.6809	-.5434	-.4475	0.3566	0.3141	0.4094	0.0178	0.0255	0.0208
0.9005	-0.239	-.1889	-.1519	0.0212	0.0175	0.2010	0.0008	0.0140	0.0095
SYSTEM II: DMF (X_1) + WATER (X_2) + ETHYLENEGLYCOL (X_3) [X_2/X_3 = 4:1]									
0.0000	-0.810	-.6378	-.5253	-.7334	-.6961	-0.6158	-0366	-.0352	-0.0314
0.1000	-.2454	-.3322	-.1831	-.7280	-.6779	-0.5889	-0357	-.0335	-0.0332
0.3002	-.0696	-.0317	-.0008	-.5591	-.5614	-0.6015	-0262	-.0264	-0.0387

0.5006	-.2566	-.1514	-.1670	-.4636	-.4148	-0.3205	-0209	-.0187	-0.0141
0.7007	-.4039	-.2784	-.2478	-0.180	-.1738	-0.1064	-0075	-.0062	-0.0004
0.9004	-.1938	-.1195	-.1310	-.1198	-.0406	-0.0146	-0005	-.0476	-0.0045

SYSTEM III : DMSO (X1) +WATER (X2) + ETHYLENEGLYCOL (X3) [X2/X3 = 4:1]

0.0000	-0.9675	- 0.6415	- 0.5253	- 0.7541	- 0.6887	- 0.6158	- 0.0377	- 0.0348	- 0.0314
0.0999	- 0.0858	- 0.0835	- 0.0828	- 0.8246	- 0.7796	- 0.6323	- 0.0451	- 0.0397	- 0.0322
0.3001	0.9463	0.8565	0.5941	- 0.8802	- 0.7487	- 0.6709	- 0.0399	- 0.0380	- 0.0342
0.5000	0.5819	0.5849	0.4312	- 0.5758	- 0.4685	- 0.4509	- 0.0286	- 0.0264	- 0.0236
0.7006	0.0625	0.2592	0.2595	- 0.2773	- 0.2709	- 0.2264	- 0.0134	- 0.0132	- 0.0107
0.9009	0.1154	0.1405	0.0892	- 0.1352	- 0.0876	- 0.0497	- 0.0068	- 0.0042	- 0.0023

Table 3: Excess values of Free volume (V_f^E),Internal pressure (π_i^E) and Gibb's free energy (ΔG^{*E}) for

Mole fraction (X_1)	V_f^E / × $10^{-7} m^3 mol^{-1}$			π_i^E / × $10^6 Nm^{-2}$			ΔG^{*E}/ × $10^{20} KJmol^{-1}$		
	Temperature (K)								
	303.15	**308.15**	**313.15**	**303.15**	**308.15**	**313.15**	**303.15**	**308.15**	**313.15**
SYSTEM I : THF (X_1) + WATER (X_2) + ETHYLENEGLYCOL (X_3) [X_2/X_3 = 4:1]									
0.0000	-0.0965	-.1117	-0.1181	240.9894	219.2931	150.1993	0.1572	0.1583	0.1669
0.0999	-0.3765	-.4023	-0.4641	43.8823	24.7591	-75.5407	0.2386	0.2356	0.2273
0.3005	-0.8331	-.8634	-1.0639	20.8696	-424.8748	399.5682	0.2375	0.2295	0.2696
0.5002	-1.0217	-.0273	-1.2543	-578.5523	-544.859	-543.4342	0.116	0.0862	0.148
0.7004	-0.7271	-.7301	-0.9145	-470.5965	-441.1447	-441.5298	0.0284	0.0316	0.0546
0.9005	-0.2422	-.2903	-0.4490	-173.7417	-160.0439	-151.3128	0.0033	0.0015	0.033
SYSTEM II: DMF (X_1) + WATER (X_2) + ETHYLENEGLYCOL (X_3) [X_2/X_3 = 4:1]									
0.0000	-0.0992	-.1117	-0.1182	273.0382	222.019	149.7174	0.1641	0.1563	0.167
0.1000	-0.2623	-.2761	-0.3107	112.7146	-4.6626	-2.7147	0.2426	0.2048	0.2342
0.3002	-0.5433	-.5947	-0.6098	-193.2933	-198.080	-253.4228	0.2779	0.2729	0.2592
0.5006	-0.4232	-.7523	-0.7837	-383.3653	-364.2943	-354.2445	0.0174	0.2391	0.4387
0.7007	-0.5977	-.6681	-0.6685	-367.7154	-339.0063	-333.0554	0.8424	0.8639	0.8722
0.9004	-0.1455	-.2752	-0.1568	-152.0374	-129.6718	-135.0434	0.7655	0.8022	0.7989

SYSTEM III: DMSO (X_1) +WATER (X_2) + ETHYLENEGLYCOL (X_3) [X_2/X_3 = 4:1]

0.0000	-0.0901	-0.1115	-0.1182	246.1718	220.7384	150.1574	0.1346	0.1568	0.1676
0.1000	-0.1442	-0.1905	-0.2129	456.607	333.3791	270.1558	0.2299	0.3181	0.3219
0.3002	-0.1856	-0.1929	-0.2056	105.9029	81.8674	-11.5502	0.3034	0.2987	0.2979

0.5006	-0.1515	-0.1921	-0.2422	-119.6326	-129.5502	-159.2287	0.2272	0.2312	0.2413
0.7007	-0.1707	-0.2184	-0.2695	-211.2934	-160.4462	-154.5854	0.1111	0.1414	0.1766
0.9004	-0.1117	-0.1331	-0.1414	-65.075	-51.2596	-48.9909	0.0554	0.0647	0.1424

REFERENCES

1. Mehta, S.K. and Chauhan, R.K., *J. Solution Chem.,*26 (1996) 295.
2. Dewan, R.K., Mehta, S.K., Parashar, R. and Bala, K., *J. Chem. Soc. Faraday*, Trans, 87 (1991)1561.
3. Tabhane, V.A., *Acoust Lett. (G.B),*6 (1983) 120.
4. Srinivasalu, U. and Ramachandra Naidu, P., *Ind. J. Pure & Appli Physics,*29 (1991) 576.
5. Kannappan, AN. and Rajendran, V., *Indi. J. Pure &Appli. Phys.,* 29 (1991) 465.
6. S.Thirumaran and J.Ramesh, Rasayan. J.chem 2009, 2(3), 733.
7. S.Thirumaran and J.Jayakumar, Ind. J.Pure and Appl. Phys. 2009, 47, 265.
8. S.Thirumaran andS.Sarathadevi, Archives Appl. Sci. Res. 2009, 1(2),128.
9. S.Thirumaran, R.Mathammal and P.Thenmozhi, Chem. Sci.Trans, 2012, 1(3),674.
10. S.Thirumaran, J.EarnestJayakumar and B.HubertDhanasundaram, E-J. Chem.2010, 7(2), 465.
11. S.Thirumaran andK.Sathish, Res. J.Chem.Sci. 2011,1(8),63.
12. Oswel S.L, and Desai, H.S, 2001, Fluid Phase Equilibria, 186, 81.
13. Erying H.J, and Kincaid J.F.(1928) J.Chem.Phys,(USA).6,620.
14. Moham Y., Liew C.N. and Mathur A.E. (2002) *J. Sol.Chem.,* 31,743-756.
15. Kannappan AN. and Palani R. (1996) *Ind. J. Phys.,*70B, 59-65.
16. Fort R.J. and Moore W.R. (1965) *Trans. Farad. Soc.,*61, 2102.
17. S.Thirumaran, N.Karthikeyan, Int. Journ. Chem. Res. 3(3), (2011) 83
18. Reed T.M. and Taylor T.E. (1959) *J. Phys. Chem.,*63,58-63.
19. Qin A.W., Haffmann D.E. and Munk P. (1992) *J. Chem. Eng. Data.,* 37, 66-70.
20. Bottcher, C.J.F 1973,The Theory of Electric Polarisation, Elsevier,Amsterdam, Vol-1.
21. Sengwa, R.J, Sankhla, S 2007 J.Mol. Liq. 130, 119-131.