Ultrasonic Velocity Study of Binary Liquid Mixtures of Ethylene Glycol (EG) With Different Amines at 308.15kψ

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Abstract : The Ultrasonic velocity studies on intermolecular interactions of binary liquid mixtures of Ethylene Glycols (EG) + n-butylamine (NBA), + sec-butylamine (SBA) + tert-butylamine (TBA), + n-hexylamine (NHA), + n-octylamine (NOA) and + cyclohexylamine (CHA) have been measured at 308.15K. From the experimental results the excess molar volume (V^E), excess viscosities (η^E), and excess molar Gibbs free energy of activation of viscous flow (G^{*E}) have been computed as a function of composition. The parameter d^1 of the Grunberg and Nissan expression has been computed. The values of V^E are negative whereas the values of η^E, G^{*E} and d^1 are positive. Deviations from the ideal behavior are discussed from the point of view of the molecular interactions present between the unlike molecules. The strength of these interactions is related with the chain length of the amines. The results are discussed in terms of the theories of non-electrolyte solutions.

***IndexTerms* - viscous flow , binary liquid mixtures , molar Gibbs.**

I. INTRODUCTION

Ultrasonic technique is a versatile tool for investigating the physical properties of matter-solids, liquids and gases. Ultrasonic velocity measurements have proved that they are useful in dealing with the problems of liquid structure and molecular interactions in liquid mixtures. This method has been applied both to pure liquids and to electrolyte solutions. For four and a half decade, extensively ultrasonic velocity measurements have been carried out for a large number of liquid mixtures. Ultrasonic propagation parameters yield valuable information regarding behaviour of binary liquid systems because intramolecular and intermolecular association, dipolar interactions, complex formation and related structural changes affect the compressibility of the system which in turn produces corresponding variations in the ultrasonic velocity.

It may be mentioned here that the sound velocity is not a primary thermodynamic parameter and there is no single agreed view regarding the method of evaluation of sound velocity in an ideal mixture. Even though the sound velocity in an ideal mixture can be expressed as an additive on the mole fraction basis[1,2] or weight fraction basis[3], the excess sound velocity so obtained does not properly characterize the deviations of the acoustic properties of the mixture from ideality. However, the attempts made by Ernst and Glinski[4] and Kiyohara *et al.*[5,6] indicate that sound velocities evaluated making use of thermodynamically valid expressions may be utilized to obtain excess sound velocities which are useful in understanding the solute-solvent interactions. It is worthwhile to note here that Kudriavtsev[7] derived expressions for evaluating theoretically the velocity of sound in pure liquids and liquid mixtures based on thermodynamically valid equations for internal energy in liquids and liquid mixtures and found that the expressions yield velocity data in good agreement with the experimental data for binary mixtures.

In many industrial applications, liquid mixtures are mostly used in processing and product formulations rather than single component liquid systems. Thermodynamic and transport properties[8-10] of liquid mixtures have been extensively used to study the deviation of real liquid mixtures from ideality. In addition, these properties have been widely used to study the intermolecular interactions between the various species present in the liquid mixtures[8-10]. Ultrasonic velocity and related data of liquid mixtures are also found to be the most powerful tool in testing the theories of liquid state. In addition, ultrasonic velocity data can be utilized to deduce some useful properties of liquid mixtures which are not easily accessible by other means.

The high precision of ultrasonic velocity measurements make it possible to calculate many other reliable parameters which gives information regarding deviations of the system from ideality. Molecular association in solution and some important correlations with various parameters, e.g. ratio of heat capacities, isentropic compressibilities, free volume, intermolecular free-length, available volume, internal pressure, energy of vaporisation, solubility parameter, non-linearity parameter, thermoacoustical parameters etc. can be very well studied through ultrasonic velocity measurements in liquid mixtures.

It has been pointed out by several workers that excess thermodynamic functions sensitively depend not only on the differences in intermolecular forces, but also on the differences in size of molecules. It is obvious that the study of excess compressibility and other excess acoustical parameters provide important information on the intermolecular forces existing in the liquid mixtures. Through the statistical theory of solutions, using the ultrasonic velocity and density data, it is also possible to investigate the solute-solvent interactions.

II. EXPERIMENTAL

An ultrasonic interferometer is a simple and direct device to determine the ultrasonic velocity in liquids with a high degree of accuracy.

The principle used in the measurement of velocity (u) is based on the accurate determination of the wavelength (□) in the medium. Ultrasonic waves of known frequency (f) (2 MHz in the present study) are produced by a quartz plate fixed at the bottom of the cell. The waves are reflected by a movable metallic plate (reflector) kept parallel to the quartz plate. If the separation between these two plates is exactly equal to the multiples of the sound wavelength, standing waves are formed in the medium. The acoustic resonance gives rise to an electrical reaction on the generator driving the quartz plate, and the anode current of the generator becomes maximum.

III. Results and Discussions

The density (ρ) and the ultrasonic velocity (u) have been measured over the whole composition range for the binary liquid mixtures of EG + NBA, + SBA, + TBA, + NHA, + NOA and + CHA at 308.15 K. The acoustical parameters like acoustic impedance (Z), isentropic compressibility (K_s), intermolecular free-length (L_f) and relative association (R_A) have been calculated from the measured density (ρ) and ultrasonic velocity (u) values using the relations given in Section 1. The results are given in Tables 1 to 6.

From the Tables 1 to 6, it is observed that the values of u, z, K_s, L_f and R_A with the mole fraction of EG (X_{EG}) varied non-linearly. This indicates the presence of interactions between the components in these binary liquid mixtures. The variation of ultrasonic velocity (u) with mole fraction of EG for all the mixtures is shown in Fig. 1 as a typical graph. Fig.1 shows that the speed of sound for these mixtures increases monotonically with an increase in the ethylene glycol content of the mixtures and it is observed that the ultrasonic velocity value for EG is high. Normally when the medium is thick the higher values of ultrasonic velocity is expected. In the present study the higher ultrasonic velocity values are observed in the EG rich region of the mixtures which indicate the presence of strong intermolecular interactions between the ethylene glycol and amine molecules. This further confirms the formation of complex between the unlike molecules. This complex formation is responsible for thickening of the media in the ethylene glycol rich region which might be responsible for higher ultrasonic velocity values.

Table .1: Values of Density (ρ), Ultrasonic velocity (u), Excess ultrasonic velocity (u^E), Acoustic impedance (Z), Excess acoustic impedance (Z^E), Isentropic compressibility (K_S), Excess isentropic compressibility (K_S^E), Intermolecular free-length (L_f), Excess intermolecular free-length (L_f^E) and Relative association (R_A) for the binary liquid mixture of Ethylene Glycol (EG) + n-butylamine (NBA) at 308.15 K.

Mole fraction of EG X_{EG}	$\rho \times 10^{-3}$ Kg m^{-3}	u m s^{-1}	u^E m s^{-1}	$Z \times 10^{-6}$ Kg $m^{-2} s^{-1}$	$Z^E \times 10^{-4}$ Kg $m^{-2} s^{-1}$	$K_S \times 10^{11}$ $m^2 N^{-1}$	$K_S^E \times 10^{11}$ $m^2 N^{-1}$	$L_f \times 10^{11}$ m	$L_f^E \times 10^{12}$ m	R_A
0.0000	0.7239	1221.5	0.0000	0.8842	0.0000	92.58	0.0000	6.3725	0.0000	1.0000
0.1666	0.7749	1317.0	27.6105	1.0205	-1.3432	74.40	-8.4453	5.7126	-2.4293	1.0439
0.3109	0.8251	1397.0	48.8083	1.1527	-1.5694	62.10	-12.3124	5.2191	-3.7531	1.0899
0.4353	0.8693	1456.0	57.1153	1.2657	-1.6340	54.26	-12.8798	4.8786	-4.0441	1.1326
0.5453	0.9084	1505.0	61.2903	1.3671	-1.5422	48.60	-12.1130	4.6171	-3.9064	1.1705
0.6427	0.9443	1543.0	59.5998	1.4571	-1.3436	44.48	-10.5428	4.4169	-3.4700	1.2067
0.7296	0.9764	1573.0	54.1880	1.5359	-1.0544	41.39	-8.5516	4.2609	-2.8556	1.2398
0.8076	1.0089	1596.0	45.4030	1.6102	-0.5655	38.91	-6.4726	4.1313	-2.1994	1.2748
0.8780	1.0414	1612.0	32.7150	1.6787	-0.2494	36.95	-4.3172	4.0259	-1.4908	1.3115
0.9418	1.0738	1624.0	18.7165	1.7439	-0.1053	35.31	-2.2312	3.9354	-0.7990	1.3490
1.0000	1.1038	1629.0	0.0000	1.7981	0.0000	34.14	0.0000	3.8697	0.0000	1.3853

Table : ¯ ¯.2: Values of Density (ρ), Ultrasonic velocity (u), Excess ultrasonic velocity (u^E), Acoustic impedance (Z), Excess acoustic impedance (Z^E), Isentropic compressibility (K_S), Excess isentropic compressibility (K_S^E), Intermolecular free-length (L_f), Excess intermolecular free-length (L_f^E) and Relative association (R_A) for the binary liquid mixture of Ethylene Glycol (EG) + sec-butylamine(SBA) at 308.15 K.

Mole fraction of EG X_{EG}	$\rho \times 10^{-3}$ Kg m^{-3}	u m s^{-1}	u^E m s^{-1}	$Z \times 10^{-6}$ Kg m^{-2} s^{-1}	Z^E X 10^{-4} Kg m^{-2} s^{-1}	$K_S \times 10^{11}$ m^2 N^{-1}	$K_S^E \times 10^{11}$ m^2 N^{-1}	$L_f \times 10^{11}$ m	$L_f^E \times 10^{12}$ m	R_A
0.0000	0.7078	1145.0	0.0000	0.8104	0.0000	107.77	0.0000	6.8751	0.0000	1.0000
0.1700	0.7641	1261.0	33.7200	0.9635	-1.5525	82.30	-12.9452	6.0083	-3.5591	1.0454
0.3155	0.8154	1353.0	55.2980	1.1032	-1.8801	66.99	-17.5429	5.4207	-5.0617	1.0897
0.4413	0.8610	1425.0	66.4108	1.2269	-1.9360	57.20	-18.0783	5.0087	-5.4012	1.1309
0.5513	0.9027	1480.0	68.1708	1.3360	-1.8932	50.57	-16.6011	4.7099	-5.0836	1.1708
0.6483	0.9418	1526.0	67.2228	1.4372	-1.6316	45.60	-14.4376	4.4721	-4.5464	1.2091
0.7344	0.9767	1562.0	61.5504	1.5256	-1.2476	41.96	-11.7311	4.2902	-3.7770	1.2442
0.8114	1.0099	1588.0	50.2824	1.6037	-0.8096	39.27	-8.7596	4.1500	-2.8647	1.2794
0.8806	1.0418	1608.0	36.7896	1.6752	-0.4949	37.12	-5.8081	4.0352	-1.9335	1.3144
0.9432	1.0717	1622.0	20.4912	1.7383	-0.3694	35.47	-2.8552	3.9442	-0.9624	1.3482
1.0000	1.1038	1629.0	0.0000	1.7981	0.0000	34.14	0.0000	3.8697	0.0000	1.3866

Table: .3: Values of Density (ρ), Ultrasonic velocity (u), Excess ultrasonic velocity (u^E), Acoustic impedance (Z), Excess acoustic impedance (Z^E), Isentropic compressibility (K_S), Excess isentropic compressibility (K_S^E), Intermolecular free-length (L_f), Excess intermolecular free-length (L_f^E) and Relative association (R_A) for the binary liquid mixture of Ethylene Glycol (EG) + tert-butylamine (TBA) at 308.15 K.

Mole fraction of EG X_{EG}	$\rho \times 10^{-3}$ Kg m^{-3}	u m s^{-1}	u^E m s^{-1}	$Z \times 10^{-6}$ Kg m^{-2} s^{-1}	Z^E X 10^{-4} Kg m^{-2} s^{-1}	$K_S \times 10^{11}$ m^2 N^{-1}	$K_S^E \times 10^{11}$ m^2 N^{-1}	$L_f \times 10^{11}$ m	$L_f^E \times 10^{12}$ m	R_A
0.0000	0.6787	1039.8	0.0000	0.7057	0.0000	136.28	0.0000	7.7313	0.0000	1.0000
0.1760	0.7411	1188.0	44.5008	0.8804	-2.1215	95.61	-22.6938	6.4757	-5.7596	1.0445
0.3246	0.7944	1297.0	65.9457	1.0303	-2.9961	74.83	-28.2925	5.7290	-7.4878	1.0873
0.4517	0.8434	1381.0	75.0584	1.1647	-3.3294	62.17	-27.9721	5.2219	-7.6508	1.1305
0.5748	0.8961	1455.0	76.5278	1.3038	-2.9786	52.71	-24.8558	4.8084	-7.0325	1.1804
0.6578	0.9336	1501.0	73.6242	1.4013	-2.6174	47.54	-21.5494	4.5665	-6.2466	1.2171
0.7425	0.9720	1544.0	66.7190	1.5008	-1.9615	43.16	-17.2847	4.3507	-5.1333	1.2553
0.8177	1.0067	1579.0	57.4112	1.5896	-1.2494	39.84	-12.9183	4.1803	-3.9334	1.2905
0.8849	1.0406	1604.0	42.8169	1.6691	-0.6967	37.35	-8.5448	4.0476	-2.6658	1.3269
0.9454	1.0722	1621.5	24.6703	1.7386	0.0126	35.47	-4.2446	3.9445	-1.3607	1.3623
1.0000	1.1038	1629.0	0.0000	1.7981	0.0000	34.14	0.0000	3.8697	0.0000	1.4003

Table 4: Values of Density (ρ), Ultrasonic velocity (u), Excess ultrasonic velocity (u^E), Acoustic impedance (Z), Excess acoustic impedance (Z^E), Isentropic compressibility (K_S), Excess isentropic compressibility (K_S^E), Intermolecular free-length (L_f), Excess intermolecular free-length (L_f^E) and Relative association (R_A) for the binary liquid mixture of Ethylene Glycol (EG) + n-hexylamine (NHA) at 308.15 K.

Mole fraction of EG X_{EG}	$\rho \times 10^{-3}$ Kg m^{-3}	u m s^{-1}	u^E m s^{-1}	$Z \times 10^{-6}$ Kg m^{-2} s^{-1}	$Z^E \times 10^{-4}$ Kg m^{-2} s^{-1}	$K_S \times 10^{11}$ m^2 N^{-1}	$K_S^E \times 10^{11}$ m^2 N^{-1}	$L_f \times 10^{11}$ m	$L_f^E \times 10^{12}$ m	R_A
0.0000	0.7507	1314.5	0.0000	0.9868	0.0000	77.09	0.0000	5.8150	0.0000	1.0000
0.2108	0.7982	1410.8	30.0034	1.1261	-1.2515	62.94	-5.0938	5.2544	-1.5054	1.0385
0.3754	0.8422	1480.0	47.4367	1.2465	-1.5128	54.21	-6.7605	4.8761	-2.0862	1.0784
0.5075	0.8804	1524.6	50.4913	1.3423	-1.4767	48.87	-6.4281	4.6296	-1.9812	1.1162
0.6158	0.9148	1557.0	48.8309	1.4243	-1.3164	45.09	-5.5509	4.4472	-1.6983	1.1517
0.7063	0.9468	1579.0	42.3687	1.4950	-1.0597	42.36	-4.3933	4.3105	-1.3049	1.1865
0.7829	0.9785	1595.0	34.2780	1.5607	-0.6892	40.17	-3.2938	4.1976	-0.9441	1.2221
0.8487	1.0099	1603.8	22.3838	1.6197	-0.2885	38.50	-2.1425	4.1092	-0.5485	1.2590
0.9058	1.0417	1617.0	17.6259	1.6844	-0.0805	36.71	-1.4719	4.0129	-0.4001	1.2951
0.9558	1.0712	1626.7	11.6009	1.7425	0.0227	35.28	-0.7599	3.9337	-0.2199	1.3291
1.0000	1.1038	1629.0	0.0000	1.7981	0.0000	34.14	0.0000	3.8697	0.0000	1.3689

Table : .5: Values of Density (ρ), Ultrasonic velocity (u), Excess ultrasonic velocity (u^E), Acoustic impedance (Z), Excess acoustic impedance (Z^E), Isentropic compressibility (K_S), Excess isentropic compressibility (K_S^E), Intermolecular free-length (L_f), Excess intermolecular free-length (L_f^E) and Relative association (R_A) for the binary liquid mixture of Ethylene Glycol (EG) + n-octylamine (NOA) at 308.15 K.

Mole fraction of EG X_{EG}	$\rho \times 10^{-3}$ Kg m^{-3}	u m s^{-1}	u^E m s^{-1}	$Z \times 10^{-6}$ Kg m^{-2} s^{-1}	Z^E X 10^{-4} Kg m^{-2} s^{-1}	$K_S \times 10^{11}$ m^2 N^{-1}	$K_S^E \times 10^{11}$ m^2 N^{-1}	$L_f \times 10^{11}$ m	$L_f^E \times 10^{12}$ m	R_A
0.0000	0.7702	1375.5	0.0000	1.0594	0.0000	68.62	0.0000	5.4863	0.0000	1.0000
0.2496	0.8141	1469.6	30.8264	1.1964	-1.1823	56.88	-3.1414	4.9946	-0.8816	1.0339
0.4280	0.8536	1527.0	43.0020	1.3034	-1.3952	50.24	-3.6228	4.6943	-1.0004	1.0703
0.5620	0.8886	1562.3	44.3330	1.3883	-1.3460	46.11	-3.1373	4.4970	-0.8075	1.1058
0.6662	0.9199	1584.6	40.2183	1.4577	-1.0876	43.29	-2.3577	4.3576	-0.5167	1.1393
0.7496	0.9508	1598.7	33.1764	1.5200	-0.7549	41.15	-1.6243	4.2484	-0.2604	1.1741
0.8179	0.9808	1607.2	24.3624	1.5763	-0.3325	39.47	-0.9486	4.1608	-0.0322	1.2090
0.8957	1.0239	1616.9	14.3401	1.6555	-0.0429	37.36	-0.3796	4.0479	0.0960	1.2596
0.9229	1.0438	1620.5	11.0448	1.6915	0.0648	36.48	-0.3165	4.0002	0.0590	1.2832
0.9642	1.0738	1626.3	6.3753	1.7463	0.0514	35.21	-0.1641	3.9299	0.0232	1.3185
1.0000	1.1038	1629.0	0.0000	1.7981	0.0000	34.14	0.0000	3.8697	0.0000	1.3546

Table .6: Values of Density (ρ), Ultrasonic velocity (u), Excess ultrasonic velocity (u^E), Acoustic impedance (Z), Excess acoustic impedance (Z^E), Isentropic compressibility (K_S), Excess isentropic compressibility (K_S^E), Intermolecular free-length (L_f), Excess intermolecular free-length (L_f^E) and Relative association (R_A) for the binary liquid mixture of Ethylene Glycol (EG) + cyclohexylamine (CHA) at 308.15 K.

Mole fraction of EG X_{EG}	$\rho \times 10^{-3}$ Kg m^{-3}	u m s^{-1}	u^E m s^{-1}	Z x 10^{-6} Kg m^{-2} s^{-1}	Z^E X 10^{-4} Kg m^{-2} s^{-1}	K_S x 10^{11} m^2 N^{-1}	K_S^E x 10^{11} m^2 N^{-1}	L_f x 10^{11} m	L_f^E x 10^{12} m	R_A
0.0000	0.8527	1276.5	0.0000	1.0885	0.0000	71.97	0.0000	5.6185	0.0000	1.0000
0.1870	0.8883	1363.0	20.5825	1.2108	-0.8145	60.60	-1.8664	5.1554	-0.5399	1.0192
0.3411	0.9218	1430.0	33.2622	1.3182	-1.2348	53.05	-2.9276	4.8238	-0.8415	1.0409
0.4702	0.9507	1480.5	38.2545	1.4075	-1.2862	47.99	-2.8534	4.5879	-0.6999	1.0612
0.5799	0.9750	1517.5	36.5853	1.4796	-1.1885	44.54	-2.3577	4.4199	-0.5754	1.0794
0.6743	0.9973	1547.0	32.8093	1.5428	-0.9676	41.90	-1.5334	4.2868	-0.2987	1.0970
0.7565	1.0183	1569.0	25.8338	1.5977	-0.5836	39.89	-0.7776	4.1829	-0.0498	1.1148
0.8285	1.0388	1587.0	18.4537	1.6486	-0.1675	38.22	-0.3060	4.0945	0.2497	1.1330
0.8923	1.0597	1602.5	11.4643	1.6982	0.0564	36.75	0.2725	4.0147	0.3234	1.1520
0.9491	1.0825	1615.5	4.4423	1.7488	0.1536	35.40	0.2448	3.9402	0.2262	1.1736
1.0000	1.1038	1629.0	0.0000	1.7981	0.0000	34.14	0.0000	3.8697	0.0000	1.1934

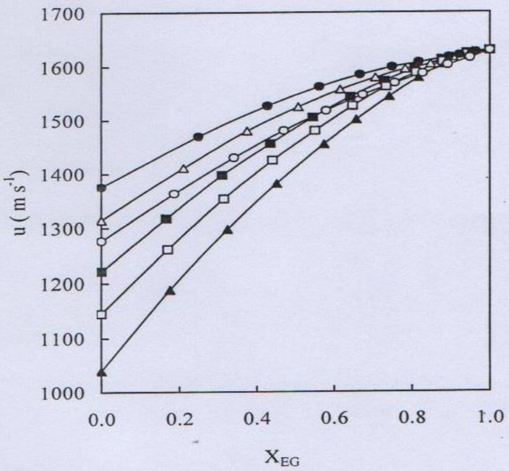

Fig. .1. Plots of ultrasonic velocity (u) vs mole fraction of Ethylene Glycol (X_{EG}) at 308.15 K for the binary mixtures of EG with NBA (■), SBA (□), TBA (▲), NHA (△), NOA (●) and CHA (○).

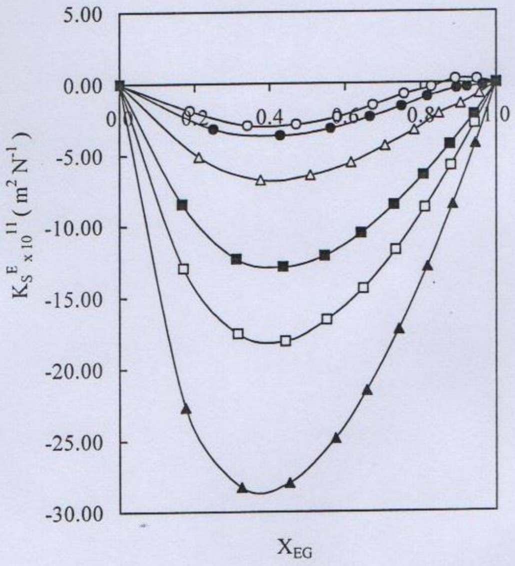

Fig. .2. Plots of excess isentropic compressibility (K_S^E) vs mole fraction of Ethylene Glycol (X_{EG}) at 308.15 K for the binary mixtures of EG with NBA (■), SBA (□),TBA (▲), NHA (△), NOA (●) and CHA (○).

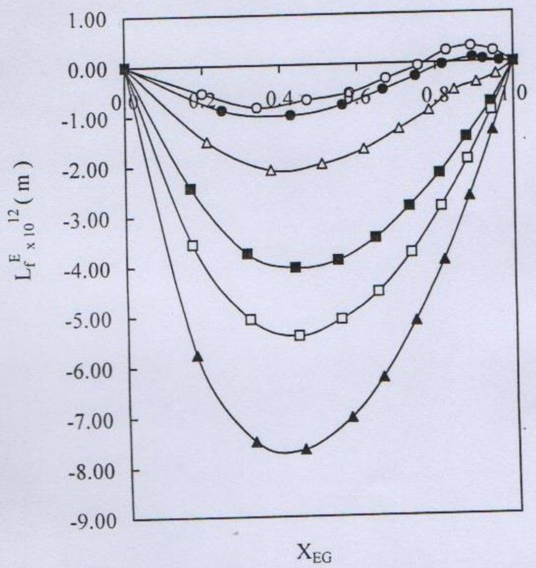

Fig. 3. Plots of excess intermolecular free-length (L_f^E) vs mole fraction of Ethylene Glycol (X_{EG}) at 308.15 K for the binary mixtures of EG with NBA (■), SBA (□), TBA (▲), NHA (△), NOA (●) and CHA (○).

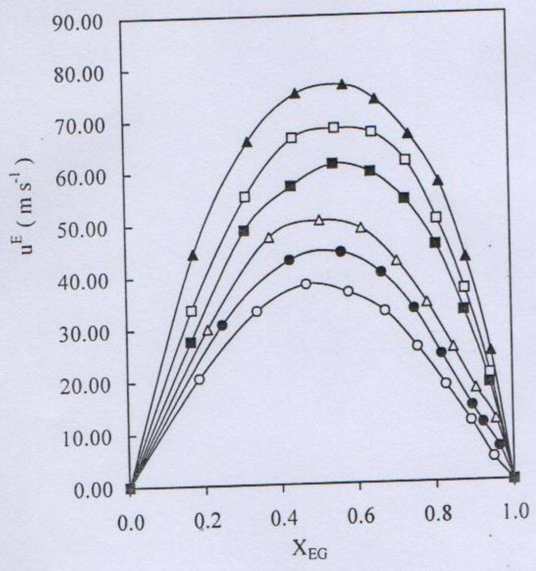

Fig. .4. Plots of excess utlrasonic velocity (u^E) vs mole fraction of Ethylene Glycol (X_{EG}) at 308.15 K for the binary mixtures of EG with NBA (■), SBA (□),TBA (▲), NHA (△),NOA (●) and CHA (○).

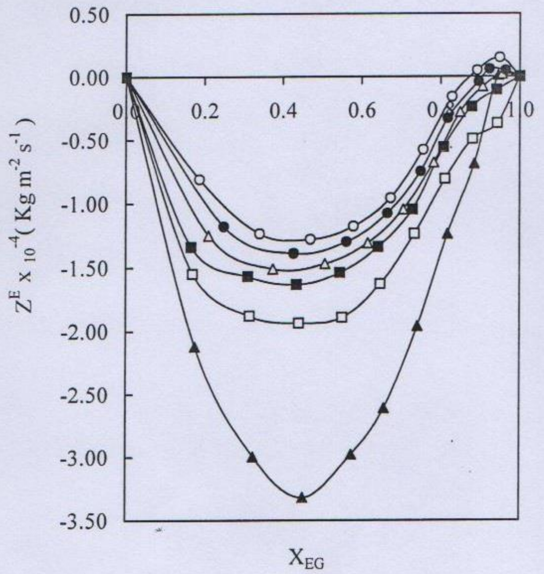

Fig. .5. Plots of excess acoustic impedance (Z^E) vs mole fraction of Ethylene Glycol (X_{EG}) at 308.15 K for the binary mixtures of EG with NBA (■), SBA (□),TBA (▲), NHA (△), NOA (●) and CHA (○).

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