



# Research Journal of Pharmaceutical, Biological and Chemical Sciences

## Ultrasonic velocity, density and viscosity studies in the mixtures of bromobenzene and '2-methoxy ethanol + n-butanol'-Molecular interactions

J Glory<sup>1</sup>, N Jayamadhuri<sup>1</sup>, PS Naidu<sup>2\*</sup>, K Ravindra Prasad<sup>3</sup>

<sup>1</sup> Dept of Physics, VSUPG Centre, Kavali (A.P.)

<sup>2</sup> Dept of Physics, JBDegree & PG College, Kavali (A.P.)

<sup>3</sup> Dept of Physics, SVUniversity, Tirupati (A.P.)

### ABSTRACT

Ultrasonic velocity, density and viscosity have been measured in the mixture: bromobenzene + (2 methoxy ethanol + n butanol) at three temperatures 30, 40 and 50 °C. From the excess thermodynamic parameters computed, intermolecular interactions have been suggested to be strong between the component bromobenzene and the binary system at different compositions besides dipole – dipole interactions. The nature of chemical reaction is exothermic at all temperatures. Addition of bromobenzene to the binary system transforms weaker interactions already existing in the binary at low concentrations to strong interactions at all temperatures. Among all the seven theories applied for evaluation of velocities theoretically, Jouyban-Acree model seems to be best suited.

**Keywords:** Ultrasonic velocity, 2 methoxy ethanol, n butanol, bromobenzene, molecular interactions.

*\*corresponding author*

## INTRODUCTION

In order to understand intermolecular interactions in the binary/ternary liquid mixtures, ultrasonic techniques have been found to be more compatible and comparable to other techniques. Several researchers have studied ultrasonically many binary/ternary liquid systems in general and systems involving alkanol + alkoxyalkanols in particular [1-11]. In the present investigation, an attempt has been made to study the binary system: '2-methoxy ethanol + n-butanol' and also the ternary system with bromobenzene as the third component at three temperatures 30, 40 and 50°C. 2-methoxy ethanol is used as a solvent for varnishes, dyes and resins and is toxic to the bone marrow and testicles. n butanol is an ingredient in processed and artificial flavoring. Also used in pharmaceuticals and polymers. Bromobenzene is used in the preparation of Grignard reagent and also in phenocyclidine. Ultrasonic velocity, density and viscosity have been measured experimentally in the binary and ternary at 30, 40 and 50°C. Thermodynamic and other related parameters like adiabatic compressibility, free length, internal pressure, enthalpy, activation energy etc. are computed and the intermolecular interactions in the mixed system are suggested in the light of the excess parameters. Seven theories –Free Length Theory due to Jacobson (FLT), Collision Factor Theory due to Schaaffs (CFT), theories due to NOMOTO, VANDAEL, JUNJIE, KUDRIAVTSEV and JOUYBAN-ACREE have been applied successfully to evaluate velocities theoretically. JOUYBAN-ACREE model is found to be best suited in this context.

## MATERIALS AND METHODS

### EXPERIMENTAL

Ultrasonic velocity, density and viscosity have been measured experimentally with an accuracy of  $\pm 0.05\%$ , 2 parts in  $10^5$  and  $\pm 0.1\%$ , employing a single crystal variable path ultrasonic interferometer (Mittal Enterprises, New Delhi), a double stem capillary type pycnometer and Ostwald viscometer respectively. Triply distilled water has been used as reference liquid and for maintaining temperature stability ( $\pm 0.01$  K), constant temperature water bath is employed. All chemicals are of analar grade and are further purified by standard methods [12].

### THEORETICAL

The thermodynamic/acoustic and other related parameters can be computed from the following relations.

$$\text{Adiabatic Compressibility} \quad \beta = \frac{1}{U_{\text{exp}}^2 \rho_{\text{exp}}} \quad (1)$$

$$\text{Internal pressure} \quad \pi = bRT [K\eta/U]^{3/2} \rho^{2/3} / M^{7/6} \quad (2)$$

$$\text{Free volume} \quad V_f = (M_{\text{eff}} U / K \eta)^{3/2} \quad (3)$$

$$\text{Enthalpy} \quad H = \pi V_M \quad (4)$$

$$\text{Activation Energy} \quad G = RT [ \ln \eta V_M ] \quad (5)$$

Employing the standard theories FLT due to JACOBSON, CFT due to SCHAAFFS, NOMOTO, VANDAEL, JUNJIE, KUDRIAVTSEV and JOUYBAN-ACREE, ultrasonic velocity can be evaluated theoretically.

$$U_{FLT} = \frac{K}{L_f \rho_{mix}^{1/2}} \quad (6)$$

$$U_{CFT} = \frac{U_{\infty} S_{mix} B_{mix}}{V_T^M} \quad (7)$$

$$U_{NOMOTO} = \left(\frac{R}{V}\right)^3 = \left[\frac{(X_A R_A + X_B R_B)}{(X_A V_A + X_B V_B)}\right]^3 \quad (8)$$

$$U_{VANDAEL} = \frac{1}{\left[(X_A M_A + X_B M_B) \left(\frac{X_A}{M_A U_A^2} + \frac{X_B}{M_B U_B^2}\right)\right]^{1/2}} \quad (9)$$

$$U_{JUNJIE} = \frac{\frac{X_A M_A}{\rho_A} + \frac{X_B M_B}{\rho_B}}{\left[(X_A M_A + X_B M_B) \left(\frac{X_A M_A}{V_A^2 \rho_A} + \frac{X_B M_B}{V_B^2 \rho_B}\right)\right]^{1/2}} \quad (10)$$

$$U_{KT}^2 = U_{mix}^2 = X_A(M_B/M) U_A^2 + X_B(M_B/M) U_B^2 + 5.5 \times 10^8 L \quad (11)$$

Where L is the heat capacity of the mixture in cal/g K, M is the effective molecular weight.

Velocity in mixture due to JOUYBAN – ACREE is given by

$$\ln U_{JA} = X_A \ln U_A + X_B \ln U_B + (X_A X_B / T) [A_0 + A_1(X_A - X_B) + A_2(X_A - X_B)^2] \quad (12)$$

All the excess parameters are fitted to Redlich- Kister polynomial of 3<sup>rd</sup> order. All the quantities used in the above equations have their usual meaning [13, 14].

## RESULTS AND DISCUSSION

At first, the three parameters ultrasonic velocity, density and viscosity have been measured in the binary system: 2-methoxy ethanol + n-butanol over the entire composition range of n-butanol at three temperatures 30, 40 and 50<sup>o</sup>C and are presented in Table 1. It can be observed that ultrasonic velocity decreases from 2-methoxy ethanol to n-butanol though not regularly and decreases with temperature at all concentrations. A comparison of experimental velocities with theoretical values evaluated reveals that except FLT and KUDRIAVTSEV, all the other theories agree well with the experiment as portrayed in Fig.1. Based on the knowledge of the derived thermodynamic parameters and the excess values computed it has been indicated that at higher concentrations of n-butanol at all temperatures

strong interactions between the two constituents besides dipole-dipole interactions and at low concentrations weak interactions and dispersive forces dominate. Exothermic reactions at 30 and 40°C at all concentrations and also at higher concentrations at 50°C have been suggested in the binary system. The effect of addition of the third component, bromobenzene to the binary is studied by repeating the above three measurements at various compositions of bromobenzene. Seven ternaries I- VII ( bromobenzene + binary (2 methoxy ethanol+n butanol at different mole fractions - 0.1561, 0.2379, 0.3223, 0.4095, 0.4977, 0.5929 and 0.6894 of n butanol ) have been prepared and studied in the direction of assessing molecular interactions. In all the ternaries, velocity decreases with the concentration of bromobenzene at all temperatures. Density increases with concentration and decreases with temperature while viscosity records decrease with both concentration and temperature. Here is presented the total picture of the three ternaries – I (rich binary),V( equi molar ) and VII(rich bromobenzene ) for convenience (Tables 2(a)-2(c)). Experimental velocities are shown in Figs. 2(a)-2(c) along with the theoretical ones. Except JOUYBAN – ACREE, all the other theories show 3 to 4 % maximum deviations. In all the three ternaries, the thermodynamic and other related parameters --  $\beta$ ,  $L_f$ ,  $V_m$ ,  $\pi$ ,  $H$ ,  $G$  calculated are presented in Tables 3 (a)- 3(c). Except molar volume, all the others decrease with concentration of bromobenzene whereas  $\beta$ ,  $L_f$  and  $V_m$  increase with temperature.

To ascertain the nature of molecular interactions in the mixed state, excess parameters computed are shown in Figs. 3(a)- 3(f) to 5(a)-5(f).  $\beta^E$  is positive in the ternaries I & V at all concentrations and temperatures and in the third ternary negative up to 0.4 m and positive thereafter at 30 and 40°C while mostly positive at 50°C.  $L_f^E$  is negative at 40°C and positive at 30 and 50°C in the system I, mostly positive at 30°C, negative at 40 & 50°C at higher concentrations in the second ternary while negative up to 0.7 m and positive thereafter at all temperatures in the system rich with binary i.e., ternary VII. As cohesive forces play an important role in estimating intermolecular interactions,  $\pi^E$  and  $H^E$  are considered to be more useful.  $\pi^E$  is negative throughout the concentration range at all temperatures. Mostly less negative in I & VII at 50°C. Similar behavior is noticed in  $H^E$  in all the ternaries. Excess activation energy is negative throughout in all the ternaries, being less negative at 50°C. Similar trend is shown out in  $\eta^E$  also. All the excess parameters are fitted to Redlich- Kister polynomial of 2<sup>nd</sup> order and the constants at 30°C are presented in Table 4.

From  $\beta^E$  variation in I& V systems, at all compositions of bromobenzene intrermolecular interactions appear to be weak, still weaker at low concentrations at high temperatures while in the ternary VII at lower concentrations strong interactions which transform into weak with increase of bromobenzene are observed. But from  $\pi^E$  and  $H^E$  (negative) strong AB interactions beside dipole-dipole type interactions are indicated in all the ternaries, the strength of interaction decreasing with temperature.  $G^E$  and  $\eta^E$ , being negative suggest exothermic reactions, slightly varying with temperature in all the systems. An overall examination of the above parameters indicates mostly strong AB interactions and exothermic type of reactions in all the three ternaries. Similar behavior is noticed in other ternaries also.

**Table1. Variation of ultrasonic velocity, density and viscosity with the mole fraction of n-butanol in the binary mixture of 2-methoxy ethanol and n-butanol.**

Mole fraction of n-butanol	Velocity (ms <sup>-1</sup> )	Density (gcm <sup>-3</sup> )	Viscosity (cP)
30 <sup>o</sup> C			
0.0000	1329.6	0.96379	1.55732
0.1561	1299.6	0.92674	1.52188
0.2379	1297.5	0.91656	1.51748
0.3223	1306.3	0.90110	1.50252
0.4095	1269.3	0.88772	1.57208
0.4997	1264.3	0.87398	1.58109
0.5929	1248.8	0.86138	1.62390
0.6894	1243.2	0.83838	1.75587
1.0000	1225.2	0.80150	2.23845
40 <sup>o</sup> C			
0.0000	1298.8	0.95283	1.20472
0.1561	1266.2	0.91827	1.25270
0.2379	1264.8	0.90822	1.18015
0.3223	1262.6	0.89726	1.27598
0.4095	1237.6	0.88008	1.25261
0.4997	1233.0	0.86720	1.09245
0.5929	1211.1	0.85809	1.41167
0.6894	1214.9	0.83120	1.33570
1.0000	1178.5	0.79425	1.72995
50 <sup>o</sup> C			
0.0000	1270.0	0.94284	0.72928
0.1561	1239.7	0.91137	0.84171
0.2379	1227.7	0.89634	0.93775
0.3223	1235.7	0.88981	1.01119
0.4095	1215.5	0.87215	1.00555
0.4997	1204.3	0.85974	1.01941
0.5929	1199.3	0.84988	1.13192
0.6894	1192.6	0.82305	1.01679
1.0000	1149.9	0.78578	1.38788

**Table 2(a). Experimental data of Velocity (U), density (ρ) and viscosity (η) as a function mole fraction of bromobenzene at the concentration of 0.1561 m of n-butanol and 2-methoxy ethanol at three different temperatures.**

Mole fraction of bromobenzene	Velocity (ms <sup>-1</sup> )	Density (gcm <sup>-3</sup> )	Viscosity (cP)
30 <sup>o</sup> C			
0.0000	1299.6	0.92674	1.52188
0.0787	1272.5	1.00156	1.42159
0.1612	1252.4	1.05056	1.35816
0.2477	1227.9	1.10543	1.28659
0.3387	1208.2	1.15139	1.21001
0.4345	1186.4	1.20320	1.15069
0.5355	1171.0	1.26321	1.10253

0.6420	1156.0	1.31431	1.04552
0.7545	1148.1	1.36978	1.00250
0.8737	1144.0	1.41304	1.00965
1.0000	1138.5	1.48344	1.02154
40 <sup>o</sup> C			
0.0000	1266.2	0.91827	1.25270
0.0787	1246.3	0.98680	1.12195
0.1612	1224.5	1.03954	1.07598
0.2477	1198.3	1.09431	1.04132
0.3387	1177.4	1.13985	1.00841
0.4345	1160.3	1.19206	0.97329
0.5355	1145.5	1.24643	0.94689
0.6420	1133.9	1.30297	0.93220
0.7545	1118.1	1.35936	0.91291
0.8737	1108.3	1.40115	0.90152
1.0000	1089.9	1.47102	0.90762
50 <sup>o</sup> C			
0.0000	1239.7	0.91137	0.94171
0.0787	1220.7	0.95281	0.92728
0.1612	1194.3	0.99807	0.90684
0.2477	1174.6	1.05913	0.88065
0.3387	1149.4	1.11400	0.85806
0.4345	1133.1	1.18072	0.83246
0.5355	1117.3	1.23631	0.80561
0.6420	1100.4	1.29028	0.78752
0.7545	1085.6	1.35195	0.78208
0.8737	1073.9	1.38832	0.78001
1.0000	1067.2	1.45427	0.78984

**Table 2(b). Experimental data of Velocity (U), density ( $\rho$ ) and viscosity ( $\eta$ ) as a function mole fraction of bromobenzene at the concentration of 0.4977 m of n-butanol and 2-methoxy ethanol at three different temperatures.**

Mole fraction of Bromobenzene	Velocity (ms <sup>-1</sup> )	Density (gcm <sup>-3</sup> )	Viscosity (cP)
30 <sup>o</sup> C			
0.0000	1264.3	0.87398	1.58109
0.0896	1234.2	0.94489	1.41536
0.1812	1212.1	1.00342	1.34264
0.2751	1193.2	1.06692	1.27299
0.3712	1177.7	1.12235	1.1961
0.4695	1163.9	1.18000	1.13044
0.5705	1150.0	1.23762	1.07739
0.6739	1139.0	1.29456	1.02999
0.7798	1131.9	1.35442	1.01536
0.8885	1131.2	1.41357	1.00588
1.0000	1138.5	1.48344	1.02154
40 <sup>o</sup> C			
0.0000	1233.0		
0.0896	1210.3	0.86720	1.09245

0.1812	1185.0	0.93533	1.11420
0.2751	1166.7	1.00165	1.07782
0.3712	1153.4	1.05557	1.03795
0.4695	1139.4	1.11069	0.99229
0.5705	1125.6	1.16907	0.95532
0.6739	1116.5	1.23238	0.93009
0.7798	1107.1	1.29043	0.90322
0.8885	1096.8	1.35222	0.88946
1.0000	1089.9	1.41337	0.88545
		1.47102	0.90762
50 <sup>o</sup> C			
0.0000	1204.3	0.85975	1.01941
0.0896	1163.1	0.92670	0.93695
0.1812	1168.6	0.99088	0.90234
0.2751	1133.5	1.04371	0.87346
0.3712	1120.5	1.09894	0.84126
0.4695	1108.1	1.16196	0.81738
0.5705	1098.7	1.21658	0.80000
0.6739	1088.0	1.27341	0.78252
0.7798	1077.9	1.32891	0.77284
0.8885	1070.9	1.38254	0.77514
1.0000	1067.2	1.45427	0.78984

**Table 2(c). Experimental data of Velocity (U), density ( $\rho$ ) and viscosity ( $\eta$ ) as a function mole fraction of bromobenzene at the concentration of 0.6894 m of n-butanol and 2-methoxy ethanol at three different temperatures.**

Mole fraction of Bromobenzene	Velocity (ms <sup>-1</sup> )	Density (gcm <sup>-3</sup> )	Viscosity (cP)
30 <sup>o</sup> C			
0.0000	1243.2	0.83838	1.75587
0.0586	1228.9	0.92108	1.62696
0.1745	1210.9	0.98353	1.50343
0.2660	1194.2	1.05491	1.39769
0.3605	1180.7	1.10917	1.32890
0.4582	1165.6	1.16881	1.25909
0.5591	1150.7	1.22325	1.17785
0.6631	1136.6	1.28637	1.08801
0.7718	1128.7	1.35447	1.03988
0.8839	1125.5	1.43382	1.02070
1.0000	1138.5	1.48344	1.02154
40 <sup>o</sup> C			
0.0000	1214.9	0.83120	1.33550
0.0586	1198.1	0.91260	1.28063
0.1745	1179.1	0.97179	1.19989
0.2660	1167.0	1.02804	1.13323
0.3605	1147.6	1.09774	1.07979
0.4582	1127.7	1.15113	1.01161
0.5591	1116.1	1.21134	0.95326
0.6631	1108.1	1.27150	0.90921

0.7718	1100.0	1.33551	0.88768
0.8839	1092.6	1.39392	0.87978
1.0000	1089.9	1.47102	0.90762
50°C			
0.0000	1192.6	0.82305	1.01679
0.0586	1169.9	0.90226	1.00865
0.1745	1145.5	0.97253	0.95256
0.2660	1128.2	1.02418	0.90644
0.3605	1113.9	1.08626	0.85360
0.4582	1101.1	1.14699	0.81346
0.5591	1092.4	1.20086	0.78423
0.6631	1081.9	1.26887	0.75334
0.7718	1074.0	1.32480	0.74282
0.8839	1059.2	1.38230	0.74281
1.0000	1067.2	1.45427	0.78984

**Table 3(a).** Various thermodynamic parameters of enthalpy, internal pressure, free length, free volume, molar volume, adiabatic compressibility, activation energy as a function of mole fraction chlorobenzene at three temperatures in the concentration 0.1561 mole fraction of n-butanol.

Mole fraction of chlorobenzene	Adiabatic compressibility ( $10^{-11}$ dyne $^{-1}$ cm $^2$ )	Internal pressure (atms)	Molar volume (cm $^3$ )	Free length (Å)	Enthalpy (J.mole $^{-1}$ )	Activation energy (RT units)
30°C						
0.0000	6.39	6043	81.78	0.50436	494214	4.82
0.0787	6.17	5656	82.05	0.49549	464074	4.76
0.1612	6.07	5250	84.61	0.49156	444164	4.74
0.2477	6.00	4885	86.76	0.48877	423839	4.71
0.3387	5.95	4500	89.72	0.48672	403754	4.69
0.4345	5.90	4190	92.32	0.48487	386836	4.66
0.5355	5.77	3924	94.43	0.47944	370575	4.64
0.6420	5.69	3639	97.34	0.47613	354273	4.62
0.7545	5.54	3392	100.07	0.46960	339410	4.61
0.8737	5.41	3215	103.86	0.46401	333890	4.65
1.0000	5.20	3094	105.85	0.45505	327539	4.68
40°C						
0.0000	6.79	5521	82.53	0.52005	455650	4.64
0.0787	6.52	5027	83.28	0.50967	418652	4.54
0.1612	6.41	4692	85.50	0.50542	401226	4.52
0.2477	6.36	4419	87.64	0.50338	387289	4.51
0.3387	6.33	4134	90.63	0.50197	374633	4.51
0.4345	6.23	3872	93.19	0.49809	360865	4.51
0.5355	6.11	3644	95.70	0.49340	348777	4.51
0.6420	5.97	3450	98.19	0.48751	338745	4.52
0.7545	5.88	3263	100.84	0.48404	329042	4.52
0.8737	5.81	3069	104.74	0.48098	321450	4.55
1.0000	5.72	2964	106.74	0.47735	316430	4.57
50°C						
0.0000	7.14	4813	83.16	0.53317	400268	4.36
0.0787	7.04	4511	86.25	0.52956	389092	4.38
0.1612	7.02	4245	89.06	0.52885	378067	4.39



0.2477	6.84	4016	90.56	0.52199	363675	4.38
0.3387	6.79	3801	92.73	0.52013	352447	4.38
0.4345	6.60	3601	94.08	0.51249	338798	4.36
0.5355	6.48	3385	96.49	0.50792	326628	4.35
0.6420	6.40	3198	99.16	0.50482	317086	4.36
0.7545	6.28	3054	101.39	0.49989	309642	4.37
0.8737	6.24	2882	105.71	0.49868	304687	4.41
1.0000	6.04	2773	107.97	0.4903	299449	4.44

**Table 3(b). Various thermodynamic parameters of enthalpy, internal pressure, free length, free volume, molar volume, adiabatic compressibility, activation energy as a function of mole fraction bromobenzene at three temperatures in the concentration 0.4977 mole fraction of bromobenzene.**

Mole fraction of bromobenzene	Adiabatic compressibility ( $10^{11}$ dyne <sup>-1</sup> cm <sup>2</sup> )	Internal pressure (atms)	Molar volume (cm <sup>3</sup> )	Free length (Å)	Enthalpy (J.mole <sup>-1</sup> )	Activation energy (RT units)
<b>30°C</b>						
0.0000	7.16	6069	85.94	0.53386	521580	4.91
0.0896	6.95	5491	87.26	0.52596	479145	4.82
0.1812	6.78	5075	89.64	0.51970	454917	4.79
0.2751	6.58	4714	91.52	0.51198	431475	4.76
0.3712	6.42	4346	94.01	0.50574	408623	4.72
0.4695	6.25	4033	96.24	0.49908	388193	4.69
0.5705	6.11	3767	98.45	0.49322	370875	4.66
0.6739	5.95	3526	100.66	0.48690	354952	4.64
0.7798	5.76	3357	102.61	0.47901	344518	4.65
0.8885	5.53	3199	104.62	0.46917	334678	4.66
1.0000	5.20	3094	105.85	0.45505	327539	4.68
<b>40°C</b>						
0.0000	7.58	5082	86.61	0.54955	440164	4.55
0.0896	7.30	4887	88.15	0.53908	430758	4.59
0.1812	7.11	4593	89.80	0.53205	412469	4.57
0.2751	6.96	4275	92.50	0.52641	395418	4.56
0.3712	6.77	3973	95.00	0.51910	377396	4.55
0.4695	6.59	3724	97.14	0.51219	361797	4.53
0.5705	6.40	3528	98.86	0.50498	348799	4.52
0.6739	6.22	3328	100.98	0.49751	336081	4.51
0.7798	6.03	3174	102.78	0.49014	326220	4.51
0.8885	5.88	3048	104.63	0.48392	318906	4.53
1.0000	5.72	2964	106.74	0.47735	316430	4.57
<b>50°C</b>						
0.0000	8.02	4939	87.36	0.56508	431472	4.49
0.0896	7.98	4543	88.97	0.56356	404194	4.42
0.1812	7.65	4238	90.78	0.55189	384718	4.40
0.2751	7.46	3948	93.55	0.54490	369398	4.40
0.3712	7.25	3685	96.01	0.53719	353807	4.39
0.4695	7.01	3479	97.74	0.52827	340044	4.38
0.5705	6.81	3283	100.15	0.52069	328835	4.38
0.6739	6.63	3110	102.33	0.51394	318297	4.38
0.7798	6.48	2964	104.58	0.50781	309966	4.39
0.8885	6.31	2844	106.97	0.50112	304195	4.42
1.0000	6.04	2773	107.97	0.49030	299449	4.44

**Table 3(c). Various thermodynamic parameters of enthalpy, internal pressure, free length, free volume, molar volume, adiabatic compressibility, activation energy as a function of mole fraction bromobenzene at three temperatures in the concentration 0.6894 mole fraction of n butanol.**

Mole fraction of bromobenzene	Adiabatic compressibility ( $10^{-11} \text{ dyne}^{-1} \text{ cm}^2$ )	Internal pressure (atms)	Molar volume ( $\text{cm}^3$ )	Free length ( $\text{A}^0$ )	Enthalpy ( $\text{J.mole}^{-1}$ )	Activation energy (RT units)
<b>30°C</b>						
0.0000	7.72	6410	87.95	0.55433	563762	5.04
0.0586	7.19	6131	85.36	0.53501	523341	4.93
0.1745	6.93	5419	89.75	0.52544	486375	4.90
0.2660	6.65	5005	90.90	0.51445	455004	4.84
0.3605	6.47	4629	93.55	0.50745	433067	4.82
0.4582	6.30	4300	95.74	0.50073	411705	4.79
0.5591	6.17	3965	98.35	0.49580	390000	4.75
0.6631	6.02	3655	100.29	0.48948	366581	4.69
0.7718	5.79	3430	101.90	0.48036	349550	4.66
0.8839	5.50	3275	102.77	0.46821	336592	4.65
1.0000	5.20	3094	105.85	0.45505	327539	4.68
<b>40°C</b>						
0.0000	8.15	5623	88.71	0.56969	498826	4.77
0.0586	7.63	5475	86.15	0.55131	471701	4.70
0.1745	7.40	4867	90.83	0.54287	442098	4.69
0.2660	7.15	4483	93.28	0.53373	418209	4.66
0.3605	6.92	4203	94.52	0.52479	397331	4.62
0.4582	6.83	3879	97.21	0.52152	377093	4.59
0.5591	6.63	3599	99.31	0.51368	357414	4.55
0.6631	6.40	3358	101.46	0.50500	740708	4.52
0.7718	6.19	3180	103.34	0.49638	328684	4.52
0.8839	6.01	3029	105.71	0.48916	320162	4.53
1.0000	5.72	2964	106.74	0.47735	316430	4.57
<b>50°C</b>						
0.0000	8.54	4919	89.59	0.58320	440717	4.51
0.0586	8.09	4880	87.14	0.56782	425253	4.47
0.1745	7.84	4402	90.76	0.55858	399541	4.46
0.2660	7.67	4066	93.63	0.55266	380719	4.44
0.3605	7.42	3767	95.52	0.54352	345835	4.40
0.4582	7.19	3512	97.56	0.53509	342622	4.37
0.5591	6.98	3280	100.18	0.52711	328629	4.36
0.6631	6.73	3089	101.67	0.51777	314081	4.34
0.7718	6.54	2929	104.18	0.51045	305107	4.35
0.8839	6.45	2811	106.60	0.50670	299623	4.37
1.0000	6.03	2773	107.97	0.49030	299449	4.44

**Table 4. Redlich-Kister polynomial constants at 30°C.**

Excess parameter	$A_0$	$A_1$	$A_2$
	I		
$\beta^E$	5.433	-3.51	-7.06
$L_f^E$	0.0057	0.0217	-0.0490
$\pi^E$	-595	1136	-474

$H^E$	-29007	95767	-96319
$G^E$	-0.0713	0.2657	0.316
$\eta^E$	-0.113	42230.	-0.4177
V			
$\beta^E$	4.826	-1.409	-10
$L_f^E$	.0018	.0318	.0608
$\pi^E$	-402	1650	-1832
$H^E$	-18455	134127	-185730
$G^E$	-.0354	.46723	.7235
$\eta^E$	-.0471	.4915.	-.7343-
VII			
$\beta^E$	4.445	-10.676	6.939
$L_f^E$	.0057	.02173	-.011
$\pi^E$	-385	889	-767
$H^E$	-19120	24389	2527
$G^E$	-.0552	-.0602	.2127
$\eta^E$	-.0664	.0505	.0787

Table 5. Correlation studies at 30 °C JOUYBAN –ACREE MODEL % DEVIATIONS

Mole fraction of Bromobenzene	I	V	VII
density			
0.0000	0.00	0.00	0.00
0.0896	-2.09	-1.27	-2.48
0.1812	-1.58	-1.07	-2.70
0.2751	-1.49	-1.24	-3.41
0.3712	-0.44	-0.56	-1.98
0.4695	0.27	-0.01	-0.49
0.5705	0.42	0.55	1.83
0.6739	1.28	1.11	3.41
0.7798	1.55	1.29	3.96
0.8885	2.18	1.23	2.20
1.0000	0.00	0.00	0.00
Surface tension			
0.0000	0.000	0.000	0.000
0.0896	-0.652	-	-0.652
0.1812	-0.303	0.196	-0.303
0.2751	-0.178	0.186	-0.178
0.3712	-0.178	-	-0.178
0.3712	0.281	0.055	0.281
0.4695	0.281	0.055	0.281
0.5705	0.848	0.360	0.848
0.5705	0.451	0.700	0.451
0.6739	1.241	1.425	1.241
0.7798	1.147	2.171	1.147
0.8885	1.560	2.450	1.560
1.0000	0.000	2.103	0.000
viscosity			
0.0000	0.00	0.00	0.00
0.0896	0.51	0.97	0.57
0.1812	-0.76		-1.69

0.2751	-0.82	-1.33	-0.31
0.3712	0.08	-1.89	-0.57
0.4695	0.07	-0.60	-0.55
0.5705	-0.43	0.60	0.33
0.6739	0.59	1.16	2.18
0.7798	1.49	1.71	0.98
0.8885	-0.692	-0.05	-0.88
1.0000	0.00	-0.51	0.00
		0.00	

The recently developed JOUYBAN – ACREE model has been successful in accounting for viscosities, densities and surface tension besides ultrasonic velocities in the binary/ternary systems based on the values measured experimentally in the pure components. As this is the only theory which can explain all the above parameters, correlation studies of the same with concentration are made and the percentage deviations are presented in Table 5 for the three ternaries. For viscosity and velocity mole fraction and for density and surface tension, volume fraction have been considered. It can be seen from the tables that JOUYBAN – ACREE model has a sharp edge in accounting for all the parameters in the mixed state with higher accuracy in a single attempt. Velocity correlation has already been incorporated in the figures concerned.

It is appropriate to refer to the contribution of other researchers to have comparison and conformity. In the mixtures of 2-methoxy ethanol (1) + 2-ethoxy ethanol (or) 2-butoxy ethanol or 2-(2-methoxy ethoxy) ethanol and 2-propoxy ethanol + dibutyl ether systems,  $H^E$ ,  $V^E$ ,  $C_v^E$ ,  $\Delta\alpha$ ,  $\Delta K_s$  are all calculated. In DBE systems,  $H^E$  and  $V^E$  decrease with the size of the 2-alkoxy ethanol and in 2-methoxy ethanol + alkoxy ethanol mixtures, these increase with the size of the second component[1]. In the ternary system 1-alkanols + NN'DMF + cyclohexanone at 30°C [2],  $V^E$  are more positive for 1-propanol + cyclohexanone + DMF suggesting the strength of the hydrogen bonds formed follow the order 1-pentanol > 1-butanol > 1-hexanol > 1-propanol. With temperature, rupture of hydrogen bonds increases.  $\Delta G$  is positive and excess internal pressures are negative. For the ternary system 1-alkanols (pentanol, butanol and propanol) + chlorobenzene + toluene, Thirumaran and Thenmozhi [3] have observed negative  $\pi^E$  and negative  $\beta^E$ , negative  $L_f^E$ , positive  $Z^E$  have suggested strong molecular interactions among the component molecules in the mixture and the order followed is 1-propanol > 1-butanol > 1-pentanol. The systems of alkoxy ethanols and amines in cyclohexanone show that the order of strength of interactions is primary amines > secondary amines and weak molecular interactions are observed in alkoxy ethanol mixtures [4]. In the mixtures of methyl acetate and toluene with 1-pentanol, 1-hexanol and 1-octanol,  $\beta^E$  and  $L_f^E$  are negative while  $\pi^E$ ,  $\eta^E$ ,  $U^E$  are all positive revealing the presence of weak molecular interactions and dipolar and dispersive interactions in the systems. CFT shows better agreement with the experimental velocity [5]. The deviations in the parameters i.e.,  $V^E$ ,  $\beta^E$  and  $\eta^E$  are positive and negative respectively, Redlich-Kister polynomial is employed to calculate the thermodynamic parameters [6] of the systems ethanol(1) + methanol(2) + 2-methoxy 2-methyl propane or 2-methoxy-2-methylbutane(3). Palani et al. [7] from their ultrasonic studies of the system of 1-alkanols + tetrahydrofuran (THF) + 1-chlorobutane, have found negative  $\pi^E$ , negative  $G^E$  and negative  $d$ , positive  $\beta^E$ , positive  $L_f^E$ . Weak molecular interactions exist between the mixing components. Glory et al. [9]

in the ternary 2-methoxy ethanol + 1-butanol + nitrobenzene have observed that strong molecular interactions between the constituent components (nitrobenzene and the binary (2-Methoxy ethanol + n-butanol at three concentrations) besides dipole-dipole type interactions dominate. The exothermic nature of chemical reaction gets strengthened from 0.2473 to 0.7003 mole fraction of n-butanol. In both the mixtures of nitro benzene in the binary (2 butoxy ethanol + n propanol) [10] and chloro benzene in the binary (2-Methoxy ethanol + n-butanol ) [11], strong AB interactions and exothermic and endothermic reactions (respectively) are suggested from the variation of majority of the excess parameters.

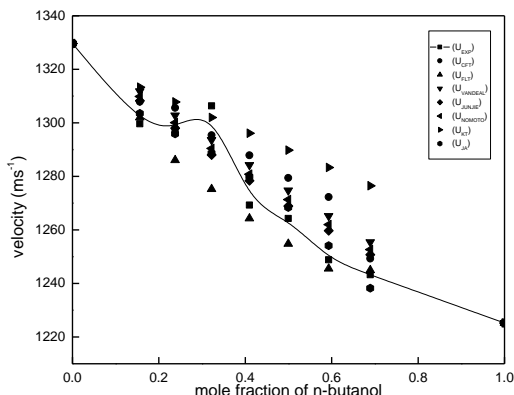


Fig.1(i). Variation of ultrasonic velocity with mole fraction of n-butanol at 30°C in the binary: 2 methoxy ethanol + n butanol

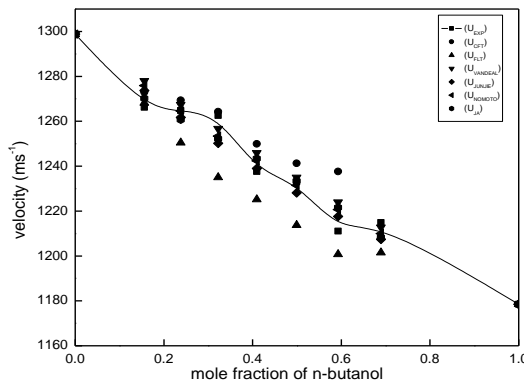


Fig.1(ii). Variation of ultrasonic velocity with mole fraction of n-butanol at 40°C in the binary: 2 methoxy ethanol + n butanol

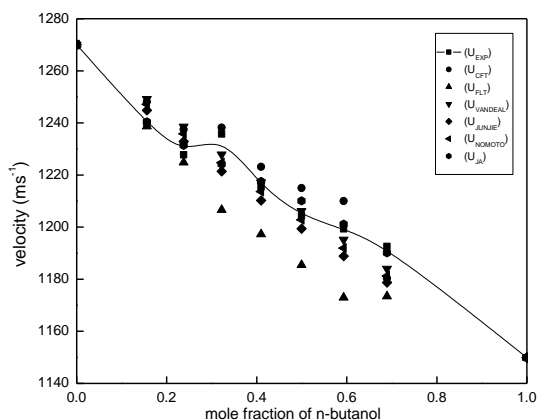


Fig.1(iii). Variation of ultrasonic velocity with mole fraction of n-butanol at 50°C in the binary: 2 methoxy ethanol + n butanol

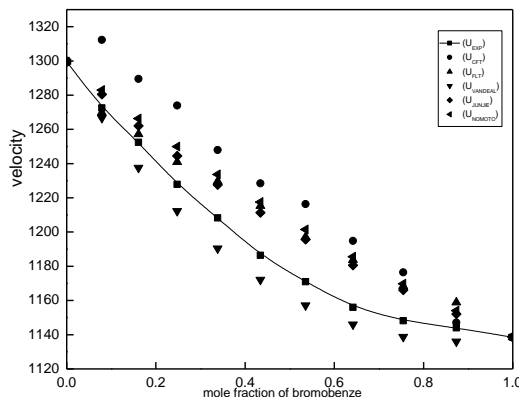


Fig.2(a). Variation of velocity with mole fraction of bromobenzene at 30°C in the mixture: (2 methoxy ethanol + n-butanol) + bromobenzene

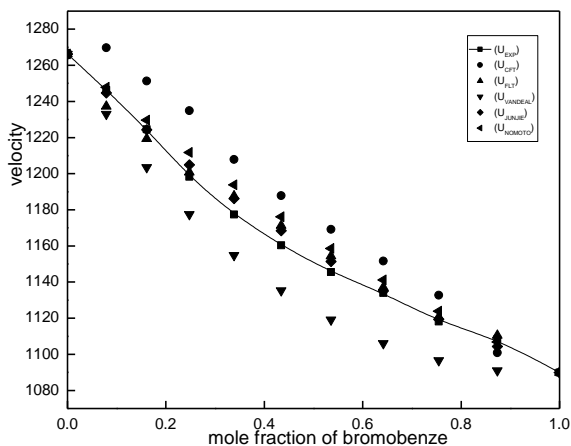


Fig.2(a)ii Variation of velocity with mole fraction of bromobenzene at 40°C in the mixture: I (2 methoxy ethanol + n-butanol) + bromobenzene

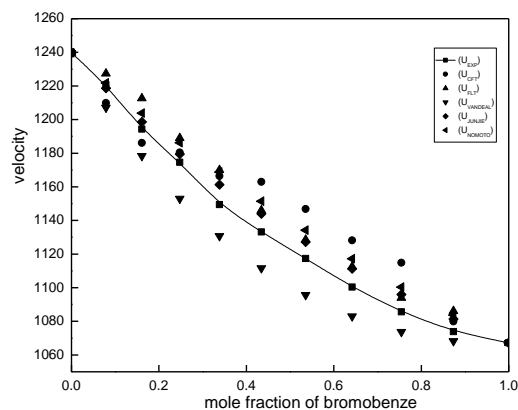


Fig.2(a)iii Variation of velocity with mole fraction of bromobenzene at 50°C in the mixture: I (2 methoxy ethanol + n-butanol) + bromobenzene

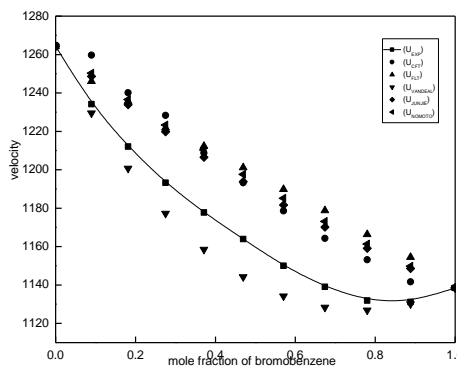


Fig.2(b)i Variation of velocity with mole fraction of bromobenzene at 30°C in the mixture: V (2 methoxy ethanol + n-butanol) + bromobenzene

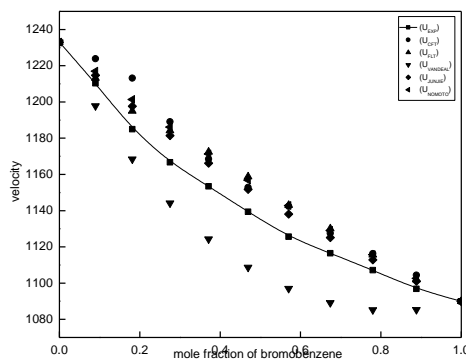


Fig.2(b)ii Variation of velocity with mole fraction of bromobenzene at 40°C in the mixture: V (2 methoxy ethanol + n-butanol) + bromobenzene

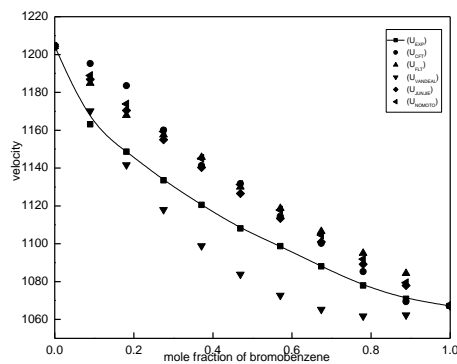


Fig.2(b)iii Variation of velocity with mole fraction of bromobenzene at 50°C in the mixture: V (2 methoxy ethanol + n-butanol) + bromobenzene

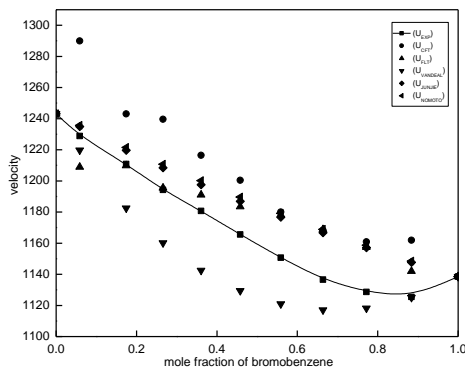


Fig.2(c)i Variation of velocity with mole fraction of bromobenzene at 30°C in the mixture: VII (2 methoxy ethanol + n-butanol) + bromobenzene

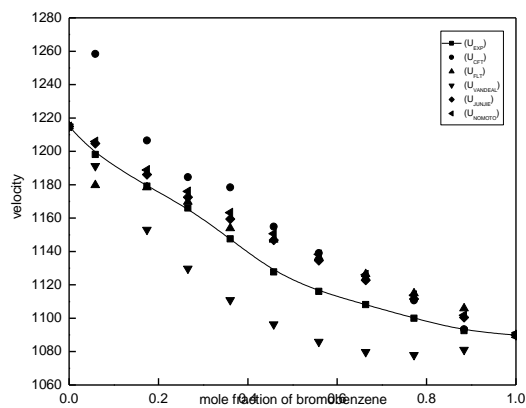


Fig.2(c)ii Variation of velocity with mole fraction of bromobenzene at 40°C in the mixture :VII (2 methoxy ethanol + n-butanol)+bromobenzene

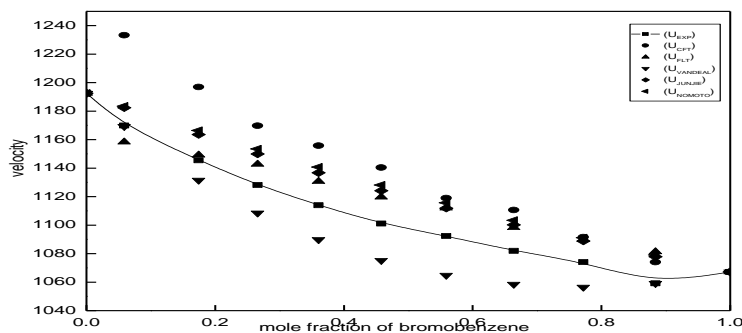


Fig.2(c)iii Variation of velocity with mole fraction of bromobenzene at 50°C in the mixture :VII (2 methoxy ethanol + n-butanol)+bromobenzene

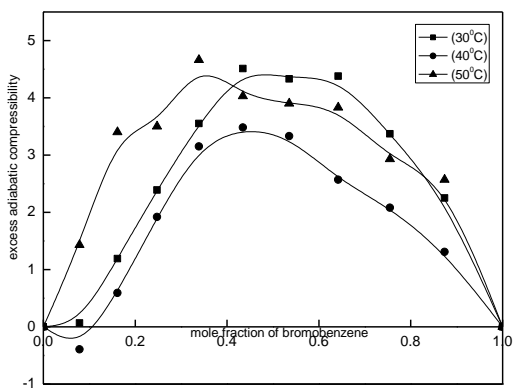


Fig.3(i) Variation of excess adiabatic compressibility with mole fraction of bromobenzene at three different temperatures in the mixture :I (2 methoxy ethanol + n-butanol) + bromobenzene

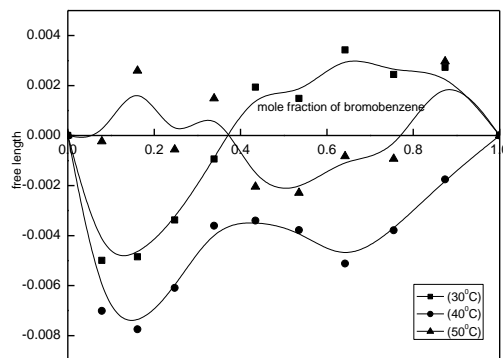


Fig.3(ii) Variation of excess free length with mole fraction of bromobenzene at three different temperatures in the mixture :I (2 methoxy ethanol + n-butanol) + bromobenzene

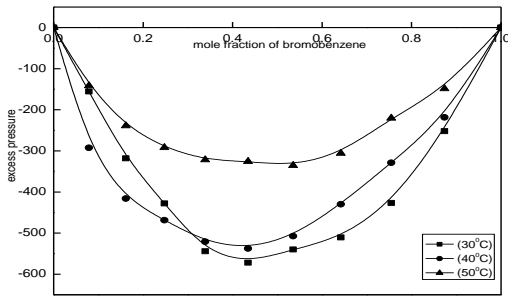


Fig.3(iii) Variation of excess internal pressure with mole fraction of bromobenzene at three different temperatures in the mixture :I (2 methoxy ethanol + n-butanol) + bromobenzene

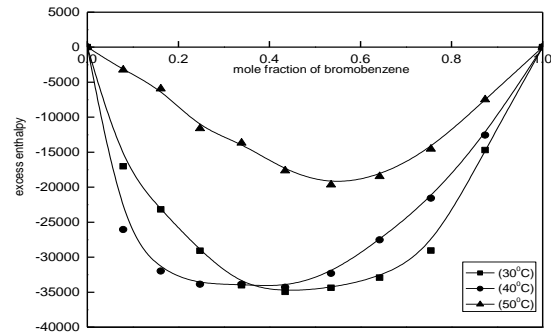


Fig.3(iv) Variation of excess enthalpy with mole fraction of bromobenzene at three different temperatures in the mixture :I (2 methoxy ethanol + n-butanol) + bromobenzene

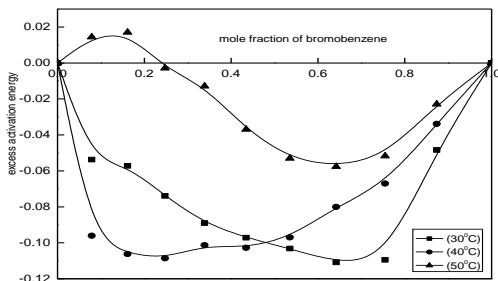


Fig.3(v) Variation of excess free length with mole fraction of bromobenzene at three different temperatures in the mixture :I (2 methoxy ethanol + n-butanol) + bromobenzene

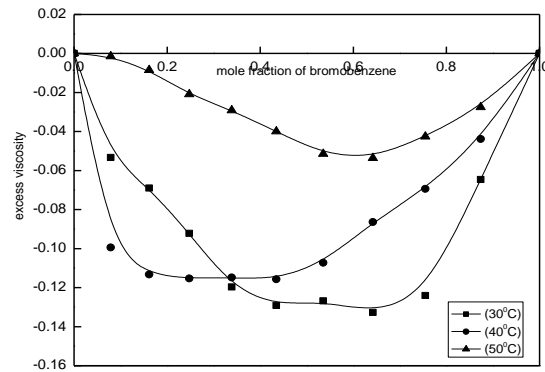


Fig.3(vi) Variation of excess viscosity with mole fraction of bromobenzene at three different temperatures in the mixture :I (2 methoxy ethanol + n-butanol) + bromobenzene

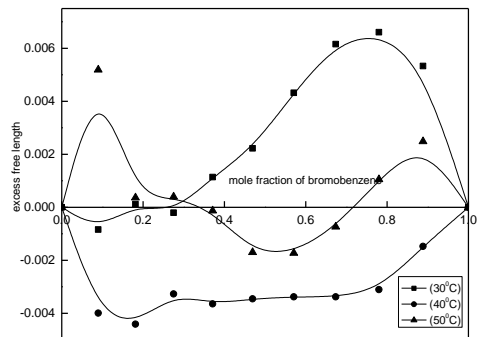


Fig.4(b) Variation of excess free length with mole fraction of bromobenzene at three different temperatures in the mixture :V (2 methoxy ethanol + n-butanol) + bromobenzene

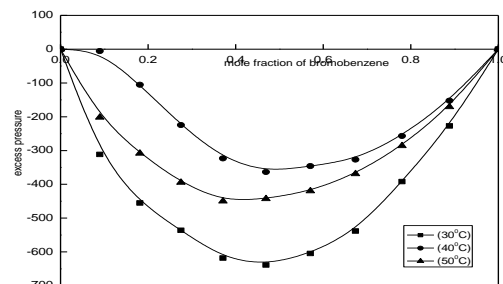


Fig.4(c) Variation of excess internal pressure with mole fraction of bromobenzene at three different temperatures in the mixture :V (2 methoxy ethanol + n-butanol) + bromobenzene



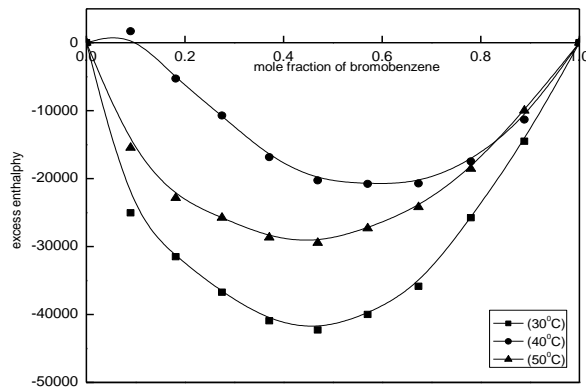


Fig.4(d)(Variation of excess enthalpy with mole fraction of bromobenzene at three different temperatures in the mixture : (2 methoxy ethanol + n-butanol)+bromobenzene)

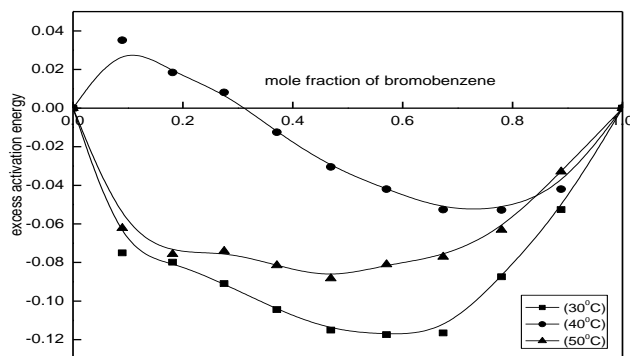


Fig.4(e)(Variation of excess activation energy with mole fraction of bromobenzene at three different temperatures in the mixture :V (2 methoxy ethanol + n-butanol)+bromobenzene)

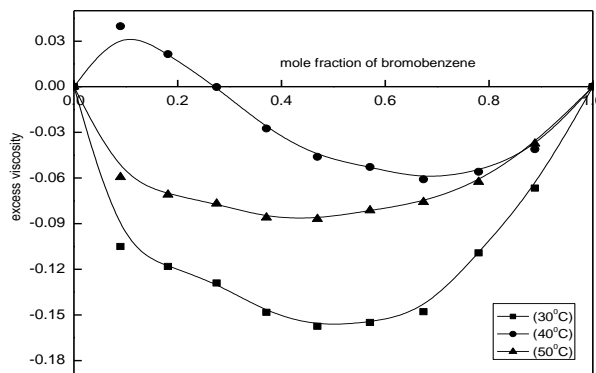


Fig.4(f)(Variation of excess viscosity with mole fraction of bromobenzene at three different temperatures in the mixture :V(2 methoxy ethanol + n-butanol)+bromobenzene)

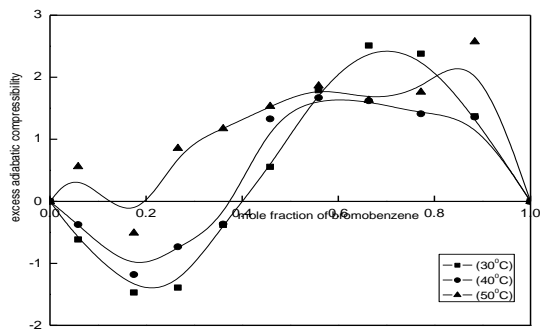


Fig. 5(a) Variation of excess adiabatic compressibility with mole fraction of bromobenzene at three different temperatures in the mixture :VII(2 methoxy ethanol + n-butanol)+bromobenzene

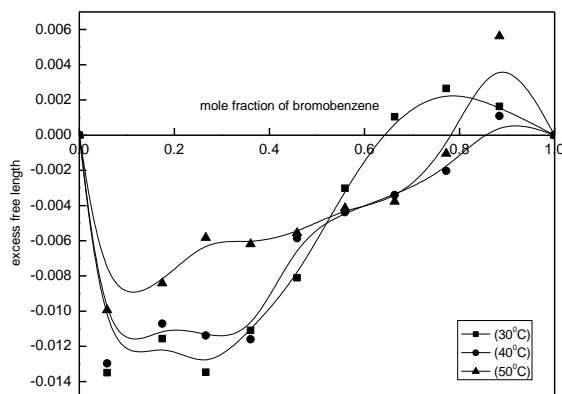


Fig. 5(b) Variation of excess free length with mole fraction of bromobenzene at three different temperatures in the mixture :VII(2 methoxy ethanol + n-butanol)+bromobenzene

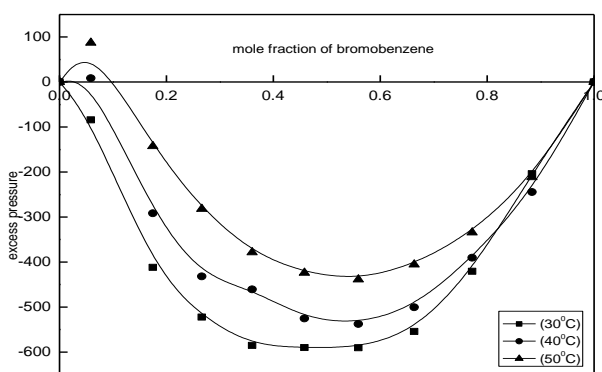


Fig. 5(c) Variation of excess internal pressure with mole fraction of bromobenzene at three different temperatures in the mixture :VII(2 methoxy ethanol + n-butanol)+bromobenzene

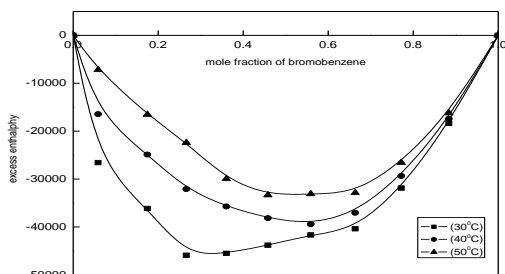


Fig. 5(d) Variation of excess enthalpy with mole fraction of bromobenzene at three different temperatures in the mixture :VII(2 methoxy ethanol + n-butanol)+bromobenzene

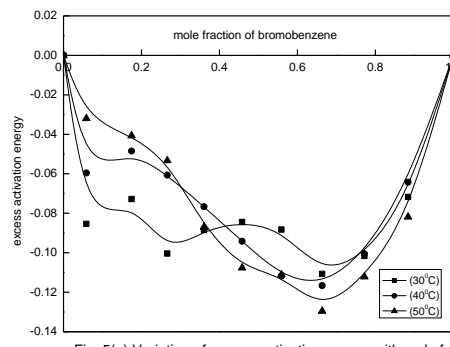


Fig. 5(e) Variation of excess activation energy with mole fraction of bromobenzene at three different temperatures in the mixture :VII(2 methoxy ethanol + n-butanol)+bromobenzene

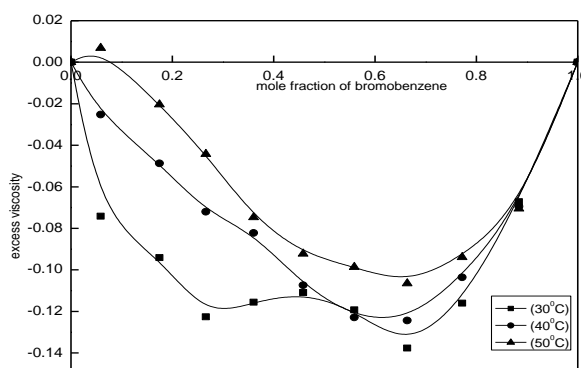


Fig. 5(f) Variation of excess viscosity with mole fraction of bromobenzene at three different temperatures in the mixture :VII(2 methoxy ethanol + n-butanol)+bromobenzene

In the ternary mixture of 1-alkanols + di-isopropyl ether and 2,2,2, trifluoro ethanol [8], all the excess parameters are negative indicating strong molecular interactions which may be due to the dominance of hydrogen bonding and charge transfer. The strength of interactions is in the order 1-pentanol > 1-butanol > 1-propanol. With rise in the temperature, it tends to be weaker. Referring to the conclusions of the above researchers, our results and conclusions are in conformity.

Comparison of the interactions in the binary and ternaries yields interesting results. In the ternaries I, V&VII, totally strong interactions are observed at all temperatures and concentrations of bromobenzene. From  $\pi^E$  and  $H^E$ , the strong interactions at 30 and 40°C and strong at concentrations (up to  $\sim 0.6m$ ) at 50°C which are observed in the binary (2 methoxy ethanol + n butanol) are totally strong at all temperatures and concentrations of bromobenzene.

Finally it may be concluded that JOUYBAN – ACREE model suits well to all the parameters in the mixed state and the excess parameters yield the nature of intermolecular interactions in the mixed state quite satisfactorily.



## ACKNOWLEDGEMENTS

The authors are thankful to the authorities of S.V. University P.G. Centre, Kavali for providing facilities to carry out this work in the department of Physics. One of the authors (J. Glory) acknowledges the financial support from the University Grants Commission as RGNF (senior).

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