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THERMOPHYSICAL PROPERTIES OF BINARY LIQUID MIXTURES OF TETRAHYDROFURAN WITH BENZENE AND SUBSTITUTED BENZENES AT 308.15 K

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ABSTRACT

Densities ( $\rho$ ) and viscosities ( $\eta$ ) have been measured at 308.15 K over the entire composition range of binary mixtures of Tetrahydrofuran (THF) with benzene (B), methyl benzene (MB), ethyl benzene (EB), chloro benzene (CB), bromo benzene (BB) and nitro benzene (NB). This measured data have been utilized to calculate excess molar volume ( $V^E$ ), excess viscosity ( $\eta^E$ ) and excess gibbs free energy for activation of viscous flow ( $G^{*E}$ ) and Grunberg-Nissan interaction parameter ( $d^1$ ). The values of these excess functions are fitted to the Redlich Kister equation. The results were discussed in terms of the existence of intermolecular interactions between the components in the liquid mixtures under study.

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INTRODUCTION

Thermo-physical properties of liquid mixtures are used to understand different kinds of association, molecular packing, molecular motion and various types of intermolecular interactions present between unlike molecules in mixtures. These properties are generally convenient parameters for interpreting solvent-solvent, solute-solvent and solute-solute interaction in solution phase. The experimental values of thermo-physical properties allow us in establishing new predicting interactions and information about the molecular level structure of the mixtures to determine the properties that are necessary for the industries in a fast reliable and economic way. Therefore a deep knowledge of thermo-physical properties of liquid mixtures containing industrially important organic liquids are essentially required for scientific community. Tetrahydrofuran is a heterocyclic organic compound with low viscosity and with a smell similar to diethyl ether but is a much less potent anesthetic than diethyl ether. It is one of the most polar ethers (dipole moment,

$\mu = 1.75$  D at 298.15 K) (chemical reactivity-2010). THF is the fully hydrogenated analogue of the aromatic compound furan. It is a moderately polar, aprotic solvent with a dielectric constant of 7.58 and unassociated liquid (chemical reactivity-2010) that dissolves a wide range of non-polar and polar compounds. It is often used as a precursor to polymers in polymer science. The most widely used industrial application of THF is, its use in chemical process which involves the acid-catalysed dehydration of 1,4-butanediols, derived from condensation of acetylene with formaldehyde followed by hydrogenation (Herbert Miller, 2002). THF has innumerable industrial applications. Thus, a study of physico-chemical property data on the binary liquid mixtures containing THF has attracted considerable interest in the literature (Prausnitz *et al.*, 1986, Rowlinson *et al.*, 1982, Acree, 1984). Thermodynamic and transport properties of liquid mixtures of THF and benzene and substituted benzenes were not yet completely explored to study the departure of a real mixture from ideality. Benzene and substituted benzenes are quite important organic solvents due to their favorable physico-chemical properties such as the blood temperature range corresponding to their liquid state, relatively higher relative permittivity, and good donor and acceptor properties. These

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**Table 1. Comparison of experimental density and viscosity of pure liquids with literature values at 308.15 K**

Liquid	$\rho \times 10^{-3} \text{ (Kg m}^{-3}\text{)}$		$\eta \times 10^3 \text{ (Kg m}^{-1} \text{ s}^{-1}\text{)}$	
	Exptl.	Lit.	Exptl.	Lit.
benzene	0.8629	0.8629 (Abeer, 2011)	0.6298	0.6160 (Shah et al., 1988)
methyl benzene	0.8526	0.8529 (Abeer, 2011)	0.6066	0.5842 (Ranjith kumar et al., 2009)
ethyl benzene	0.8387	0.8390 (Parthasarathi et al., 2011)	0.5632	0.5631 (Parthasarathi et al., 2011)
chloro benzene	1.0890	1.0907 (Manapragada et al., 2008)	0.6632	0.6637 (Parthasarathi et al., 2011)
bromo benzene	1.4739	1.4748 (Manapragada et al., 2008)	0.9262	0.9260 (Parthasarathi et al., 2011)
Nitro benzene	1.1881	1.1885 (Manapragada et al., 2008)	1.5547	1.5430 (Thirumaran et al., 2011)
Tetrahydrofuran	0.8714	0.8701 (Palani et al., 2009)	0.4742	0.4740 (Selvakumar et al., 2008)

aromatic hydrocarbon molecules possess large quadrupole moments (Patterson, 1994), causing an orientation order in these liquids. The present work is a continuation of our earlier studies (Subha *et al.*, 1988, Subha *et al.*, 1988, Subha *et al.*, 2004, Vijaya Lakshmi *et al.*, 2014 and Vijaya Lakshmi *et al.*, 2014) of thermodynamic and physico-chemical properties of non-aqueous binary liquid mixtures. A survey of literature reveals that the thermo-physical properties of pure molecules of THF, benzene and substituted benzenes have been reported extensively because of their importance from both fundamental and industrial point of view. However, the thermo-physical properties of liquid mixtures of benzene and substituted benzene with THF have not been explored in a systematical way. Our aim is to explore the thermo-physical properties such as density, viscosity and their excess properties for the mixed solvents of these binary mixtures to expand the basic needs for scientific research. This study intends to draw molecular level information from macroscopic properties on the molecular interactions between benzenes and THF.

## Experimental Work

## MATERIALS AND METHODS

THF, benzene (B), methyl benzene (MB), ethyl benzene (EB), chloro benzene (CB), bromo benzene (BB) and nitro benzene (NB) were purchased from Merck (> 98% of purity) and used as purchased. Clear binary Mixtures were prepared by mixing weighed amounts of the pure liquids adopting the method of closed system. The weighing was done by using Mettler balance with the precision of  $\pm 0.1$  mg. The uncertainty in the mole function was estimated to be less than  $\pm 1 \times 10^{-4}$ . Mixtures were allowed to stand for some time before every measurement so as to avoid air bubbles. The densities of pure liquids and their binary mixtures were measured by using a single-capillary pycnometer (made of Borosil glass) having a bulb capacity of  $\approx 10$  ml. The capillary, with graduated marks, had a uniform bore and could be closed by a well-fitting glass cap. The marks on the capillary were calibrated by using triply distilled water. The uncertainty in density measurements was within  $\pm 2 \times 10^{-5} \text{ g cm}^{-3}$ . Viscosity measurements were carried out with a precision of  $\pm 0.2\%$  using calibrated Schott-Gerate AVS 400 viscometer, whose flow time for doubly distilled water was found to be 375 seconds at  $25^\circ\text{C}$ . The temperature of the test liquids during the measurements was maintained

within an uncertainty of  $\pm 0.01$  K in an electronically controlled thermostatic water bath. The measurements were made with proper care in an AC room to avoid evaporation loss. The purities of the liquids were checked by comparing the values of densities and viscosities with literature data (Table 1) and are found good in general.

## RESULTS AND DISCUSSION

The experimental results of measurement of densities and viscosities of binary mixtures are presented in Table 2. The molar volume ( $V$ ), excess volume ( $V^E$ ), excess viscosity ( $\eta^E$ ), excess Gibbs energy of activation of viscous flow ( $G^{*E}$ ) and Grunberg-Nissan interaction parameter ( $d^1$ ) were calculated from the measured data using the following equations 1 to 5 respectively.

$$V = (X_1 M_1 + X_2 M_2) / \rho \quad \dots (1)$$

$$V^E = V - (X_1 V_1 + X_2 V_2) \quad \dots (2)$$

$$\eta^E = \eta - (X_1 \eta_1 + X_2 \eta_2) \quad \dots (3)$$

$$G^{*E} = RT [\ln \eta V - (X_1 \ln \eta_1 V_1 + X_2 \ln \eta_2 V_2)] \quad \dots (4)$$

$$d^1 = \ln \eta / [X_1 \ln \eta_1 + X_2 \ln \eta_2 + X_1 X_2] \quad \dots (5)$$

Where  $\rho$ ,  $\eta$  and  $V$  are the density, viscosity and molar volume of the mixture,  $M_1$  and  $M_2$  are the molar masses,  $\eta_1$  and  $\eta_2$  are the viscosities,  $V_1$  and  $V_2$  are the molar volumes of the benzenes and THF respectively  $d^1$  is a constant (Grunberg *et al.*, 2008 and Grunberg, 1954) and  $x$  is the mole fraction of XTHF and suffixes 1 & 2 denotes the components 1 & 2 in binary mixtures and the values are given in Table 2. The dependence of  $\eta^E$ ,  $V^E$  and  $G^{*E}$  on the mole fraction of methyl acrylate ( $X_{MA}$ ) for all the six systems were fitted to the following Redlich-Kister equation by the least-squares method and the values are given in Table 3.

$$Y^E = x(1-X) \sum_i A_i (2x-1)^i \quad \dots (6)$$

Where  $Y^E$  is  $\eta^E$ ,  $V^E$  and  $G^{*E}$  parameters.

**Table 2. Values of density ( $\rho$ ), viscosity ( $\eta$ ), excess viscosity ( $\eta^E$ ), molar volume ( $V$ ), excess volume ( $V^E$ ) and excess gibbs free energy of activation of viscous flow ( $G^{*E}$ ) for the binary liquid mixtures of Tetrahydrofuran (THF) with benzenes at 308.15 K**

Mole fraction of THF ( $X_{\text{THF}}$ )	$\rho \times 10^{-3}$ (Kg m <sup>-3</sup> )	$\eta \times 10^3$ (Kg m <sup>-1</sup> s <sup>-1</sup> )	$\eta^E \times 10^3$ (Kg m <sup>-1</sup> s <sup>-1</sup> )	$V^E \times 10^6$ (m <sup>3</sup> mol <sup>-1</sup> )	$V^E \times 10^6$ (m <sup>3</sup> mol <sup>-1</sup> )	$G^{*E} \times 10^3$ (N mol <sup>-1</sup> )
<b>Tetrahydrofuran (THF) + Benzene (B)</b>						
0.0000	0.8629	0.6298	0.0000	90.5203	0.0000	0.0000
0.1084	0.8638	0.6142	0.0013	89.6741	-0.0041	3.7228
0.2157	0.8647	0.5983	0.0021	88.8379	-0.0068	6.4264
0.3162	0.8655	0.5831	0.0025	88.0543	-0.0096	8.2507
0.4163	0.8664	0.5678	0.0028	87.2747	-0.0116	9.3962
0.5165	0.8672	0.5523	0.0029	86.4953	-0.0126	9.8718
0.6173	0.8681	0.5364	0.0027	85.7125	-0.0123	9.5171
0.7154	0.8689	0.5209	0.0024	84.9518	-0.0110	8.4701
0.8103	0.8698	0.5053	0.0016	84.2170	-0.0086	6.2833
0.9012	0.8706	0.4898	0.0002	83.5136	-0.0058	2.7852
1.0000	0.8714	0.4742	0.0000	82.7519	0.0000	0.0000
<b>Tetrahydrofuran (THF) + Methyl benzene (MB)</b>						
0.0000	0.8526	0.6066	0.0000	108.0732	0.0000	0.0000
0.1185	0.8546	0.5934	0.0025	105.0441	-0.0253	6.3790
0.2408	0.8568	0.5789	0.0042	101.9159	-0.0570	11.1500
0.3508	0.8588	0.5659	0.0057	99.1074	-0.0806	14.6977
0.4611	0.8609	0.5519	0.0063	96.3002	-0.0953	16.4234
0.5765	0.8632	0.5371	0.0068	93.3668	-0.1071	17.0984
0.6579	0.8648	0.5259	0.0064	91.3122	-0.1008	16.1479
0.7432	0.8664	0.5136	0.0054	89.1694	-0.0840	13.9185
0.8090	0.8676	0.5039	0.0044	87.5229	-0.0647	11.5064
0.9186	0.8697	0.4871	0.0021	84.7845	-0.0283	5.7167
1.0000	0.8714	0.4742	0.0000	82.7519	0.0000	0.0000
<b>Tetrahydrofuran (THF) + Ethyl benzene (EB)</b>						
0.0000	0.8387	0.5632	0.0000	126.5768	0.0000	0.0000
0.1394	0.8430	0.5553	0.0045	120.3059	-0.1617	11.1988
0.2709	0.8471	0.5467	0.0076	114.4337	-0.2710	19.0727
0.3862	0.8507	0.5383	0.0095	109.3290	-0.3227	23.7991
0.4945	0.8544	0.5300	0.0108	104.5402	-0.3652	26.4492
0.5969	0.8580	0.5212	0.0111	100.0403	-0.3775	26.6892
0.6881	0.8611	0.5122	0.0102	96.0726	-0.3483	24.5819
0.7727	0.8642	0.5029	0.0085	92.3978	-0.3155	20.4067
0.8540	0.8670	0.4931	0.0059	88.9107	-0.2396	14.5186
0.9062	0.8687	0.4869	0.0044	86.6840	-0.1786	10.3219
1.0000	0.8714	0.4742	0.0000	82.7519	0.0000	0.0000
<b>Tetrahydrofuran (THF) + Chloro benzene (CB)</b>						
0.0000	1.0890	0.6632	0.0000	103.3580	0.0000	0.0000
0.1311	1.0686	0.6477	0.0093	100.3713	-0.2877	12.3303
0.2765	1.0438	0.6264	0.0155	97.1242	-0.5383	21.3844
0.3985	1.0215	0.6075	0.0196	94.4124	-0.7358	26.9581
0.5081	0.9998	0.5896	0.0224	92.0263	-0.8631	30.4075
0.6082	0.9781	0.5708	0.0225	89.9250	-0.9015	30.6122
0.7021	0.9557	0.5508	0.0203	88.0615	-0.8298	28.0233
0.7837	0.9347	0.5319	0.0168	86.5090	-0.7006	23.6226
0.8595	0.9139	0.5130	0.0122	85.1188	-0.5287	17.4388
0.9211	0.8960	0.4970	0.0079	84.0419	-0.3361	11.2794
1.0000	0.8714	0.4742	0.0000	82.7519	0.0000	0.0000
<b>Tetrahydrofuran (THF) + Bromo benzene (BB)</b>						
0.0000	1.4739	0.9262	0.0000	106.5344	0.0000	0.0000
0.1953	1.4027	0.881	0.0431	100.1184	-1.7707	41.6115
0.3530	1.3362	0.8358	0.0692	95.0820	-3.0567	66.8018
0.4809	1.2759	0.7906	0.0818	91.0595	-4.0376	78.5056
0.5903	1.2163	0.7454	0.0860	87.8847	-4.6106	82.4967
0.6838	1.1569	0.7002	0.0831	85.5371	-4.7346	80.4044
0.7646	1.0968	0.655	0.0744	83.9712	-4.3789	73.8493
0.8345	1.0360	0.6098	0.0608	83.1656	-3.5221	63.6266
0.8989	0.9733	0.5646	0.0447	82.9065	-2.2497	50.9163
0.9500	0.9208	0.5194	0.0226	82.9203	-1.0207	28.7702
1.0000	0.8714	0.4742	0.0000	82.7519	0.0000	0.0000

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Tetrahydrofuran (THF) + Nitro benzene (NB)						
0.0000	1.1881	1.5547	0.0000	103.6227	0.0000	0.0000
0.1592	1.1688	1.4467	0.0640	98.3840	-1.9132	61.8338
0.2966	1.1492	1.3386	0.1044	93.9607	-3.4693	104.9639
0.4190	1.1261	1.2306	0.1286	90.3489	-4.5269	135.2827
0.5294	1.0998	1.1225	0.1398	87.3862	-5.1858	154.0683
0.6298	1.0715	1.0145	0.1402	84.9217	-5.5553	161.4017
0.7188	1.0413	0.9064	0.1284	83.0211	-5.5987	155.5449
0.7989	1.0078	0.7984	0.1069	81.7268	-5.2215	137.4637
0.8697	0.9704	0.6903	0.0753	81.1541	-4.3169	105.3311
0.9376	0.9237	0.5823	0.0406	81.5153	-2.5387	62.5253
1.0000	0.8714	0.4742	0.0000	82.7519	0.0000	0.0000

Table 3. Parameters of Eq. (6) and Standard deviations

Excess Property	A <sub>0</sub>	A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>	A <sub>4</sub>	σ
Tetrahydrofuran (THF) + Benzene (B)						
$\eta^E \times 10^3$ (Kg m <sup>-1</sup> s <sup>-1</sup> )	0.00008	0.01030	-0.00253	-0.01824	0.01022	0.00027
$V^E \times 10^6$ (m <sup>3</sup> mol <sup>-1</sup> )	0.04826	-1.75600	34.88000	-62.27000	4.47900	0.14750
$G^{*E} \times 10^3$ (N mol <sup>-1</sup> )	0.09725	33.89688	-16.54769	-29.70081	12.01873	0.33162
Tetrahydrofuran (THF) + Methyl benzene (MB)						
$\eta^E \times 10^3$ (Kg m <sup>-1</sup> s <sup>-1</sup> )	0.00006	0.01953	-0.00192	-0.02526	0.00754	0.00015
$V^E \times 10^6$ (m <sup>3</sup> mol <sup>-1</sup> )	-0.00073	-0.12943	-0.72776	1.45475	-0.59549	0.00278
$G^{*E} \times 10^3$ (N mol <sup>-1</sup> )	0.06059	56.06462	-33.57642	-21.92641	-0.66217	0.15050
Tetrahydrofuran (THF) + Ethyl benzene (EB)						
$\eta^E \times 10^3$ (Kg m <sup>-1</sup> s <sup>-1</sup> )	0.00007	0.03180	-0.00628	-0.03097	0.00533	0.00022
$V^E \times 10^6$ (m <sup>3</sup> mol <sup>-1</sup> )	0.00051	-1.44400	2.19200	-2.29100	1.54100	0.00545
$G^{*E} \times 10^3$ (N mol <sup>-1</sup> )	8.08580	84.08227	-36.62176	-54.99100	7.37014	0.25586
Tetrahydrofuran (THF) + Chloro benzene (CB)						
$\eta^E \times 10^3$ (Kg m <sup>-1</sup> s <sup>-1</sup> )	0.00022	0.06934	-0.03915	-0.01894	-0.01154	0.00051
$V^E \times 10^6$ (m <sup>3</sup> mol <sup>-1</sup> )	-0.00592	-1.91610	-1.09620	3.17109	-0.15188	0.01434
$G^{*E} \times 10^3$ (N mol <sup>-1</sup> )	0.16228	99.03888	-78.54513	19.80037	-40.48205	0.39935
Tetrahydrofuran (THF) + Bromo benzene (BB)						
$\eta^E \times 10^3$ (Kg m <sup>-1</sup> s <sup>-1</sup> )	-0.00012	0.26794	-0.2624	0.23954	-0.24488	0.00097
$V^E \times 10^6$ (m <sup>3</sup> mol <sup>-1</sup> )	-0.02484	-7.07707	-8.59975	7.5924	8.30216	0.16550
$G^{*E} \times 10^3$ (N mol <sup>-1</sup> )	-0.47300	308.9909	-550.96387	747.05323	-502.149	2.69262
Tetrahydrofuran (THF) + Nitro benzene (NB)						
$\eta^E \times 10^3$ (Kg m <sup>-1</sup> s <sup>-1</sup> )	0.00029	0.44129	-0.29180	0.00581	-0.15659	0.00148
$V^E \times 10^6$ (m <sup>3</sup> mol <sup>-1</sup> )	0.04826	-17.5551	34.87483	-62.26177	44.79236	0.14749
$G^{*E} \times 10^3$ (N mol <sup>-1</sup> )	-0.24441	467.11987	-564.40673	823.00245	-724.27156	1.25965

The parameters A<sub>i</sub>, obtained by a non-linear least squares polynomial fitting procedure, are also given in Table 3 together with the standard deviations (σ) values. The variation of the parameters V<sup>E</sup>, η<sup>E</sup> and G<sup>\*E</sup> with mole fraction of Tetrahydrofuran (X<sub>THF</sub>) for the systems under study are shown graphically in Fig. 1 to 3 respectively. It is clear from the Fig. 1 that the negative V<sup>E</sup> values are obtained over the entire composition range for all these systems which indicates the presence of strong molecular interactions between the unlike components of the mixtures. It is also observed from Fig. 1 and Tables 2 that the negative values fall in the sequence.

$$THF + NB > THF + BB > THF + CB > THF + EB > THF + MB > THF + B$$

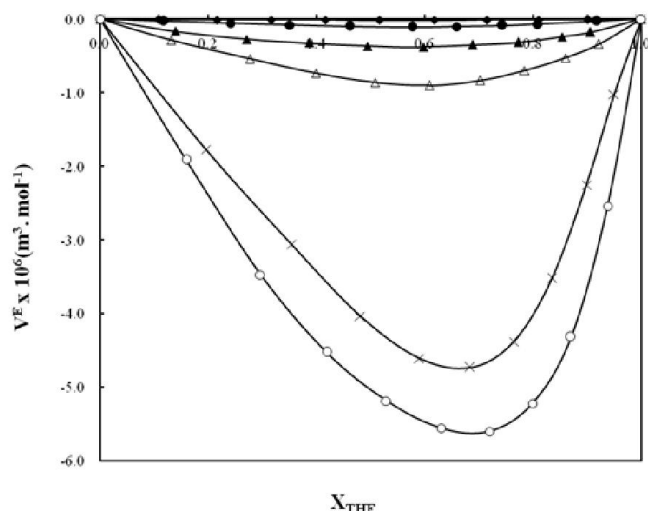
From Fig. 1, it is further observed that the negative V<sup>E</sup> Vs X<sub>THF</sub> plots were found to be large and symmetrical showing a maximum between 0.5 to 0.6 mole fractions of THF (X<sub>THF</sub>). According to Subha et al., (Subha et al., 2004) several effects may contribute to the sign and values of V<sup>E</sup> and the following three effects may be considered as being important.

1. Break up of hydrogen bonds and dipolar interactions in THF and intermolecular interactions in benzenes.
2. The possible intermolecular interactions like hydrogen bonding or electron donor-acceptor interactions between unlike molecules.
3. Interstitial accommodation of one component molecules into the other unlike Component molecules due to their differences in size and shape.

The actual volume change would, therefore, depend on the relative strength of these three opposing effects. Parthasarathi and workers (Parthasarathi et al., 2011) have reported negative excess volumes for the mixtures of THF with polar components; this observation is supported by the present work where V<sup>E</sup> values are negative for all the benzenes with THF. The negative excess volumes reported by Subha et al., (Subha et al., 1999) for propionic acid and alcohol binary liquid mixtures has concluded that this is due to the interaction between the oxygen atom of propionic acid and hydrogen atom of alcohols.

In the present study, the interactions between THF and benzenes may be due to the presence of strong electron donor-acceptor interactions which are responsible for the negative excess volumes. The negative excess volumes of THF + benzenes over the whole range of composition suggest that the 2<sup>nd</sup> and 3<sup>rd</sup> factors are responsible for this situation i.e. formation of electron donor-acceptor interaction between >C=O group of THF with n-π electron density present in the aromatic rings of benzenes and substituted benzenes and the accommodation of smaller size THF molecules in the bigger size benzene and substituted benzene molecules i.e. interstitial accommodation. These two factors lead the negative V<sup>E</sup> values. And also these two effects over weigh the 1<sup>st</sup> effect. Contraction which accompanies the formation of strong electron donor-acceptor interactions is sufficient to compensate the physical effect caused during mixing. A

similar observation was reported earlier by Zachariassen, 1935; Mecke, 1950; Dannhauser, 1964 and Dacre, 1938. From Fig. 1, it is also clear that the negative excess volumes increase in magnitude as the methyl, halo and nitro groups of the benzenes change which inturn become large and they fall in the following order.



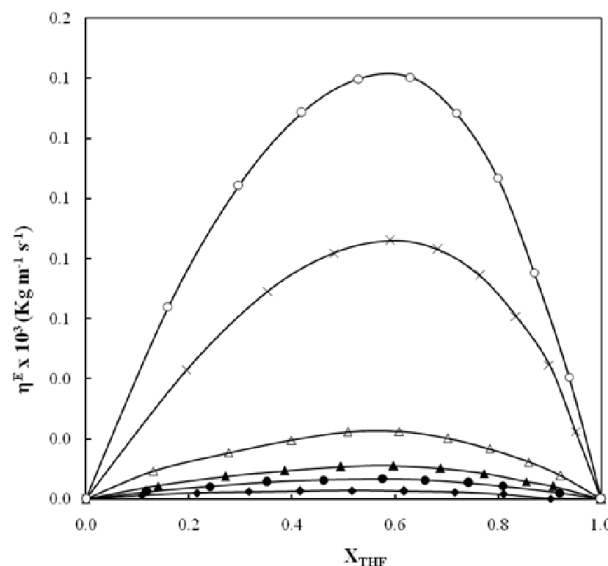
**Fig. 1.** Plots of excess volume ( $V^E$ ) vs mole fraction of Tetrahydrofuran ( $X_{THF}$ ) for binary mixtures of Tetra hydrofuran (THF) with Benzene (B,  $-\diamond-$ ), Methyl benzene (MB,  $-\bullet-$ ), Ethyl benzene (EB,  $-\blacktriangle-$ ), Chloro benzene (CB,  $-\triangle-$ ), Bromo benzene (BB,  $-\times-$ ) and Nitro benzene (NB,  $-\circ-$ ) at 308.15 K

THF + NB > THF + BB > THF + CB > THF + EB > THF + MB > THF + B

The effect of interaction between the two components becomes more and more predominant as the halo and nitro group of the benzenes becomes more due to their electron withdrawing ability. And also the size of benzene molecule increases from benzene, methyl benzene, ethyl benzene, chloro benzene, bromo benzene and nitro benzene, this in turn makes a larger difference in size of THF and benzene molecules. This gives more possibilities for the more interstitial accommodation resulting in negative  $V^E$  to conform the negative excess volumes of these systems for which the explanation can also be considered as reasonable one.

The difference between molar volumes of THF with benzenes [benzene (B), methyl benzene (MB), ethyl benzene (EB), chloro benzene (CB), bromo benzene (BB) and nitro benzene (NB)] at 308.15K are more pronounced. Such difference in molar volumes and, as a consequence, in the free volumes between different species could facilitate the penetration of one component into the other. Therefore, the bigger the differences between the free volumes of the two species are, the more negative the contribution to the  $V^E$  should be. The experimental evidence of the above scheme seems to confirm these conjectures. A similar observation was reported earlier by Metteo Manfredini *et al.*, (Metteo Manfredini *et al.*, 2002). Thus, in the present study the negative  $V^E$  values for THF + benzenes indicate the predominance of the formation of hydrogen bonding and interstitial accommodation between them over the other effect. Fig. 2 shows that  $\eta^E$  values are positive for the whole composition range for all the systems under study. A correlation between signs of  $\eta^E$  and  $V^E$  has been observed for a number of binary solvent systems (pal *et*

*al.*, 1996, Gill, 1983),  $\eta^E$  being positive where  $V^E$  is negative or vice-versa. In general for systems, where dispersion and dipolar interactions are operating  $\eta^E$  values are found to be negative, whereas charge transfer and hydrogen bonding interactions lead to the formation of complex species between unlike molecules there by resulting in positive  $\eta^E$  values.



**Fig. 2.** Plots of excess viscosity ( $\eta^E$ ) vs mole fraction of Tetrahydrofuran ( $X_{THF}$ ) for binary mixtures of Tetra hydrofuran (THF) with Benzene (B,  $-\diamond-$ ), Methyl benzene (MB,  $-\bullet-$ ), Ethyl benzene (EB,  $-\blacktriangle-$ ), Chloro benzene (CB,  $-\triangle-$ ), Bromo benzene (BB,  $-\times-$ ) and Nitro benzene (NB,  $-\circ-$ ) at 308.15 K

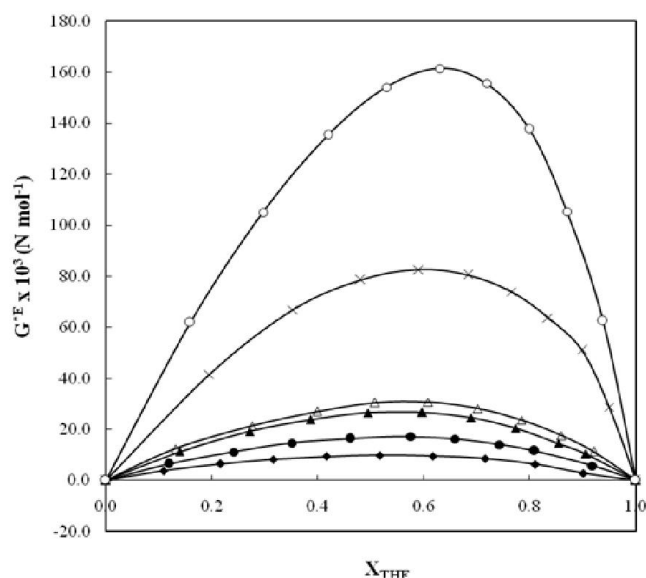
The algebraic values of  $\eta^E$  for all the mixtures of THF + benzenes fall in the order.

THF + NB > THF + BB > THF + CB > THF + EB > THF + MB > THF + B

This order suggests that the presence of charge transfer and hydrogen bonding between unlike molecules increase with increase in electron withdrawing ability in benzenes. A similar observation was reported by Manapragada *et al.*, (Manapragada *et al.*, 2008) from their viscosity study of binary liquid mixtures. The variation of excess gibbs free energy of activation of viscous flow ( $G^{*E}$ ) with  $X_{MA}$  for all the systems under study are shown graphically in Fig. 3. Reed and Taylor (Reed and Taylor, 1959) and Meyer *et al.*, (Meyer *et al.*, 1971) reported that  $G^{*E}$  parameter can be considered as a reliable criterion to detect or exclude the presence of interactions between unlike molecules. According to these authors, the magnitude of the positive values is an excellent indicator of the strength of specific interactions.  $G^{*E}$  values for the systems under study suggest the following order.

THF + NB > THF + BB > THF + CB > THF + B

The above order is in accordance with the viscosity results of these mixtures explained above. Similar behavior was reported by Manapragada *et al.*, (Manapragada *et al.*, 2008) in case of  $G^{*E}$  values for mixtures of methyl formate, ethyl formate, propyl formate and benzyl acetate with bromo-, chloro-, nitro benzenes at 303.15, 308.15 and 313.15 K. Fort and Moore (Fort and Moore, 1966) and Ramamoorthy (Ramamoorthy, 1973) reported that for any binary liquid mixture, the positive



**Fig. 3.** Plots of excess Gibbs free energy of activation of viscous flow ( $G^{*E}$ ) vs mole fraction of Tetrahydrofuran ( $X_{THF}$ ) for binary mixtures of Tetrahydrofuran (THF) with Benzene (B,  $-\blacklozenge-$ ), Methyl benzene (MB,  $-\bullet-$ ), Ethyl benzene (EB,  $-\blacktriangle-$ ), Chloro benzene (CB,  $-\Delta-$ ), Bromo benzene (BB,  $-x-$ ) and Nitro benzene (NB,  $-o-$ ) at 308.15 K

value of  $d^1$  indicates the presence of strong interactions and the negative value of  $d^1$  indicates the presence of weak interactions between the components. It may be conformed that the observed variation of the properties of the mixtures studied support the view that the interactions between unlike molecules is predominant and characterized by the negative  $V^E$  and positive  $\eta^E$ ,  $G^{*E}$  and  $d^1$  values.

## Conclusions

The densities and viscosities for tetrahydrofuran with benzene and substituted benzenes of binary mixtures have been measured and the values of  $V^E$ ,  $\eta^E$ ,  $G^{*E}$  and  $d^1$  were calculated. The  $V^E$  values were found negative for all the mixtures where as  $\eta^E$ ,  $G^{*E}$  and  $d^1$  values were found positive for the presence of specific interactions between tetrahydrofuran with benzene and substituted benzenes. The magnitude of the interactions are shown in the following order

THF + NB > THF + BB > THF + CB > THF + EB > THF + MB > THF + B

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