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Research Article

Molecular Interactions and Thermophysical Properties of 1, 4 Dioxane with Bromo benzene, Ethyl benzene at various Temperatures via Nonlinear Model

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Abstract: Viscosities and densities of 1,4 dioxane with hydrocarbon bromo benzene, ethyl benzene was measured over the entire mole fractions at temperatures ranging from 303.15, 308.15, and 313.15K. From these experimental results, excess molar volume V^E and viscosity deviation $\Delta\eta$ was calculated. The V^E and $\Delta\eta$ exhibited positive and negative values, respectively, over the entire composition range in the order of 1,4 dioxane+ bromo benzene and < 1,4 dioxane +ethyl benzene systems. The outcomes indicated the weak interactions present in the mixtures. It exists mainly because of the number and position of methyl groups in these aromatic hydrocarbons. The molecular dynamics simulation studies for both the mixtures show no phase separation. The volume occupied by 1,4 dioxane + bromo benzene is lesser than 1,4 dioxane + ethyl benzene substantiating the experimental results of V^E and $\Delta\eta$. Standard deviations from the Jouyban–Acree model between the fitting outcomes, and the calculated data are helpful deliberate mixing behavior of the binary mixtures. The molecular interactions existing between the components and comparison of liquid mixtures were also discussed.

Keywords: Viscosity; Density; Molecular interactions; Intermolecular forces; Bond length; Thermodynamics; Correlation.

1. Introduction

The thermodynamic and transport properties of hydrocarbons in binary mixtures are used to study the molecular interactions between the various components of the mixtures. Thermo physical properties such as densities and viscosities play a key role in engineering design involved chemical separations, heat and mass transfer, fluid flows and are important to understand liquid theory and molecular dynamics from both practical and theoretical points of view.[1-3] Thermo physical properties are playing an important role to obtain interpretation data from bio chemical, kinetic, thermo chemical and electro chemical studies.[4] The structural variation and property like interaction between low polarity solvent (1,4 dioxane) with hydrocarbon mixtures are found to be key in industrial application. 1,4 dioxane, a cyclic ether commonly known as aprotic solvent has a zero dipole movement and cyclic ether, that has an electron donor ability towards aromatic rings, which acts as a weak electron acceptor. 1, 4 dioxane is also used as a stabilizer in aluminium containers and solvent in inks and adhesives.[5,6] On other hand, bromo benzene is a good solvent for organic synthesis as well as motor fuel and crystal solvent. Ethyl benzene is commercially important as a precursor to styrene. Recently from our group we have also studied thermophysical properties of 1,4 dioxane with bromo benzene, benzene, ethyl benzene and p-xylene with acetophenone binary mixtures.[7-9] The viscosity values have been fitted to Mc-Allister,[7]Krishnan -Laddha and Grunberg-Nissanmodels.[8] The Jouyban–Acree model[9] has also been extended to density and kinematic viscosity of binary mixtures. The deviation values have been fitted to Redlich-Kister type equation.[10] We reported that the densities (ρ), dynamic viscosity(η), kinematic viscosity (v), excess molar volumes (V^E), viscosity deviation (Δ_η) of pure 1,4 dioxane and binary mixture with bromo benzene and ethyl benzene at different temperatures viz 303.15, 308.15, and 313.15 K and also represents the closed atmospheric condition, which has been obtained from experimental data and molecular interaction between components were well correlated by the nonlinear model.[10]

2. Experimental section

2.1. Chemicals

1, 4 dioxane, bromo benzene and ethyl benzene (analytical grade) were obtained from M/s E. Merck Ltd with 99% purity and were stored over molecular sieves (0.3 nm) were kept in dark bottles, in an inert atmosphere and ultrasonically degassed before a sample preparation. [11,12] In Table 1 the densities and dynamic viscosities of the studied pure substances have been compared with the literature values at several temperatures [27–34]. Densities and viscosities of pure substances and experimental values were compared with literature values are listed in the Table 1.[9,13-17] In most of the cases, the agreement was within the following values: 0.45 kg. m^{-3} for density measurements and 1.6 mPa .s for viscosity measurements. Since these agreements were good, no further purification was performed.

2.2. Apparatus and procedures

Density of pure liquids and their solutions were determined by using bicapillary pycnometer having a stated accuracy of ± $5*10^{-3}$ kg * m^{-3}.The temperature in the cell was regulated (±0.01K) by a built in solid-state thermostat. The apparatus was first calibrated with triple distilled water at a temperature of 303.15 K. To minimize the errors in composition all the mixtures were prepared by mass, with a HR series 300, Japan with a precision of ± 0.1 mg. using the cell and the procedure described previously [35]. The uncertainty in the mole fraction was estimated to be less than $\pm 1\times 10^{-4}$. The uncertainties in density measurements were estimated to be $\pm 1.10^{-2}$ g m^{-3}, while the average uncertainty in excess molar volume is estimated to be 3.10^{-9} m^3. mol^{-1}.

The kinematic viscosities γ of the pure substances and the corresponding binary mixtures were measured using a Ostwald viscometer. The dynamic viscosity η is calculated from the measured kinematic viscosity and density. The stated reproducibility of the dynamic viscosity and density measurements is 0.35% and 0.5 kg.m^{-3} in the temperature interval (303.15 to 313.15) K. The temperature in the cell was regulated to ±0.01 K by a built in solid-state thermostat. The uncertainty in dynamic viscosity measurements was estimated to be within ±3. 10^{-3} mPa.s.

A computational method 25*25*25 cubical system of 0.5 mole fractions 1,4 dioxane + ethyl benzene and 1,4 dioxane + bromo benzene was constructed using experimental density data by pack mol software. The initial configuration of the system was optimized by means of energy minimization 10,000 steps followed by equilibration and relaxation through a 2-ns MD simulation at 300 K in the NVT ensemble. Later production run was done for 250 ps for viscosity determination. All molecular dynamics simulations were performed using the NAMD 2.7 software and the parameters for the ligands were obtained from the Param Chem online server, using the CHARMM General Force Field (CGenFF). Constant temperature was enforced using Langevin dynamics with a damping coefficient of 1 ps^{-1}. Constant pressure (1 atm) was enforced using the Nosé-Andersen Langevin piston method. Short-range electrostatic and Van der waals interactions were truncated smoothly at 12 Å, while long-range electrostatic forces were computed using the particle-mesh Ewald (PME) summation method.

2. Results and Discussion

The experimental data and literature values of densities and viscosities of pure components 1,4 dioxane, bromo benzene, ethyl benzene at temperature of 303.15 K and mixtures 1,4 dioxane with bromo benzene and ethyl benzene at temperatures of (303.15, 308.15, and 313.15 K) are listed in Tables 1-3 respectively.

Table 1 Experimental densities, viscosities and mass fraction purity of pure liquids with literature values at temperature (T) 303.15 K.

component	mass fraction	10^{-3} ρ /(kg. m^{-3})		η/(mpa s)	
		lit	exptl	lit	exptl
1, 4 dioxane	≥0.990	1.0222[9,12]	1.0222	1.0985[9,12,17,16]	1.0984
bromo benzene	≥0.990	1.4815[9,13]	1.4817	0.9850[9,13,]	0.9980
ethyl benzene	≥0.990	0.8645[9,14]	0.8656	0.5980[9,]	0.5957

Table 2 Experimental densities, viscosities and excess molar volume, kinematic viscosities, predictions of jouyban acree nonlinear model for 1, 4 dioxane + bromo benzene at 303.15, 308.15 and 313.15 K.

x_1	γ_{exp}(c.s)	10^{-3} ρ /(kg. m^{-3})	η(mpa.s)	10^6 V^E (m^3 mol^{-1})	$\Delta\eta$(mpa.s)	γ_{pred}(c.s)	10^{-3} ρ /(kg. m^{-3})
{1, 4 dioxane + bromo benzene}							

				303.15K			
0.0000	0.6735	1.4817	0.9980	0.0000	0.0000	0.6735	1.4817
0.1047	0.6992	1.4368	1.0046	0.3608	-0.0039	0.6992	1.4368
0.2083	0.7278	1.3907	1.0122	0.7323	-0.0067	0.7277	1.3910
0.3109	0.7592	1.3443	1.0205	1.0429	-0.0087	0.7597	1.3434
0.4124	0.7930	1.2974	1.0288	1.3054	-0.0106	0.7926	1.2976
0.5128	0.8294	1.2505	1.0372	1.4759	-0.0123	0.8287	1.2520
0.6122	0.8690	1.2071	1.0490	1.2658	-0.0104	0.8696	1.2063
0.7106	0.9122	1.1640	1.0618	0.9089	-0.0075	0.9132	1.1627
0.8080	0.9604	1.1185	1.0742	0.6106	-0.0050	0.9591	1.1199
0.9045	1.0135	1.0717	1.0862	0.2707	-0.0026	1.0139	1.0713
1.0000	1.0745	1.0222	1.0984	0.0000	0.0000	1.0745	1.0222
				308.15			
0.0000	0.6670	1.4723	0.9820	0.0000	0.0000	0.6670	1.4723
0.1047	0.6872	1.4241	0.9786	0.6449	-0.0061	0.6872	1.4241
0.2083	0.7096	1.3787	0.9783	1.0094	-0.0092	0.7094	1.3788
0.3109	0.7341	1.3333	0.9788	1.2928	-0.0114	0.7347	1.3328
0.4124	0.7611	1.2869	0.9794	1.5570	-0.0134	0.7608	1.2869
0.5128	0.7907	1.2399	0.9804	1.7821	-0.0151	0.7899	1.2411
0.6122	0.8223	1.1972	0.9845	1.5591	-0.0136	0.8230	1.1963
0.7106	0.8573	1.1542	0.9895	1.2296	-0.0112	0.8580	1.1536
0.8080	0.8960	1.1101	0.9946	0.8581	-0.0086	0.8950	1.1109
0.9045	0.9402	1.0640	1.0004	0.5014	-0.0054	0.9405	1.0637
1.0000	0.9908	1.0177	1.0083	0.0000	0.0000	0.9908	1.0177
				313.15			
0.0000	0.6549	1.4628	0.9581	0.0000	0.0000	0.6549	1.4628
0.1047	0.6747	1.4121	0.9527	0.8782	-0.0079	0.6747	1.4120
0.2083	0.6964	1.3662	0.9514	1.3249	-0.0117	0.6961	1.3664
0.3109	0.7200	1.3209	0.9510	1.6422	-0.0146	0.7206	1.3208
0.4124	0.7464	1.2751	0.9517	1.9097	-0.0163	0.7463	1.2746
0.5128	0.7756	1.2281	0.9526	2.1832	-0.0179	0.7747	1.2290
0.6122	0.8059	1.1860	0.9558	1.9474	-0.0171	0.8065	1.1855
0.7106	0.8394	1.1437	0.9601	1.6003	-0.0152	0.8400	1.1436
0.8080	0.8768	1.1006	0.9650	1.1891	-0.0126	0.8759	1.1008
0.9045	0.9203	1.0555	0.9714	0.7897	-0.0085	0.9206	1.0554
1.0000	0.9696	1.0130	0.9822	0.0000	0.0000	0.9696	1.0130

Table 3 Experimental densities, viscosities and excess molar volume, kinematic viscosities, predictions of jouyban acree nonlinear model for 1, 4 dioxane + ethyl benzene at 303.15, 308.15 and 313.15 K.

x_1	γ_{exp}(c.s)	$10^{-3}\ \rho$ /(kg m^{-3})	η(mpa.s)	$10^6\ V^E$ (m^3 mol^{-1})	Δη(mpa.s)	γ_{pred}(c.s)	$10^{-3}\ \rho$ /(kg m^{-3})
				{1, 4 dioxane + ethyl benzene}			
				303.15K			
0.0000	0.6882	0.8656	0.5957	0.0000	0.0000	0.6882	0.8656
0.1047	0.7342	0.8755	0.6428	0.2673	-0.0055	0.7339	0.8755

0.2083	0.7775	0.8857	0.6887	0.5578	-0.0118	0.7790	0.8857
0.3109	0.8189	0.8959	0.7337	0.9167	-0.0183	0.8170	0.8961
0.4124	0.8547	0.9066	0.7749	1.2719	-0.0281	0.8540	0.9063
0.5128	0.8900	0.9189	0.8178	1.5027	-0.0357	0.8931	0.9192
0.6122	0.9362	0.9363	0.8765	1.2483	-0.0269	0.9349	0.9360
0.7106	0.9797	0.9547	0.9354	1.0171	-0.0176	0.9781	0.9551
0.8080	1.0162	0.9752	0.9909	0.7138	-0.0109	1.0178	0.9749
0.9045	1.0470	0.9981	1.0450	0.3284	-0.0054	1.0466	0.9981
1.0000	1.0745	1.0222	1.0984	0.0000	0.0000	1.0745	1.0222
				308.15			
0.0000	0.6697	0.8567	0.5737	0.0000	0.0000	0.6697	0.8567
0.1047	0.7093	0.8612	0.6108	0.8613	-0.0084	0.7090	0.8611
0.2083	0.7452	0.8686	0.6473	1.5633	-0.0169	0.7465	0.8688
0.3109	0.7792	0.8780	0.6841	2.0504	-0.0247	0.7777	0.8784
0.4124	0.8095	0.8877	0.7186	2.5458	-0.0343	0.8084	0.8871
0.5128	0.8380	0.9000	0.7542	2.7841	-0.0424	0.8413	0.8997
0.6122	0.8781	0.9182	0.8062	2.4347	-0.0335	0.8767	0.9186
0.7106	0.9151	0.9387	0.8590	1.9797	-0.0236	0.9134	0.9395
0.8080	0.9454	0.9607	0.9082	1.5274	-0.0166	0.9471	0.9596
0.9045	0.9705	0.9859	0.9568	0.9515	-0.0100	0.9701	0.9863
1.0000	0.9908	1.0177	1.0083	0.0000	0.0000	0.9908	1.0177
				313.15			
0.0000	0.6549	0.8453	0.5536	0.0000	0.0000	0.6549	0.8453
0.1047	0.6916	0.8470	0.5858	1.5743	-0.0127	0.6917	0.8468
0.2083	0.7295	0.8522	0.6217	2.6223	-0.0212	0.7294	0.8525
0.3109	0.7630	0.8600	0.6562	3.3353	-0.0306	0.7626	0.8607
0.4124	0.7945	0.8688	0.6902	3.9695	-0.0402	0.7943	0.8676
0.5128	0.8246	0.8802	0.7259	4.3112	-0.0475	0.8266	0.8798
0.6122	0.8623	0.8993	0.7754	3.8136	-0.0405	0.8609	0.9000
0.7106	0.8983	0.9211	0.8274	3.1790	-0.0308	0.8967	0.9225
0.8080	0.9270	0.9461	0.8771	2.4027	-0.0228	0.9292	0.9442
0.9045	0.9510	0.9746	0.9268	1.5134	-0.0145	0.9503	0.9752
1.0000	0.9696	1.0130	0.9822	0.0000	0.0000	0.9696	1.0130

The density values have been used to calculate excess molar volumes V^E using the following equation.

$$V^E= ((x_1M_1+x_2M_2)/ \rho_{mix})–(x_1M_1/ \rho_1) + x_2M_2/ \rho_2) \qquad \text{-----------------(1)}$$

Here, x_1 and x_2 refer to the mole fraction of components 1 and 2. ρ_1, ρ_2, and ρ_m refer to the density of components 1 and 2 is density of the mixture, respectively. The viscosity deviations Δ_η were calculated from the viscosity values by given equation.

$$\Delta_\eta = (\eta) – (x_1\eta_1 + x_2\eta_2) \qquad \text{-------------------- (2)}$$

Where η, η_1, and η_2 are the viscosity of the mixture and the viscosity of pure components 1 and 2, respectively. The uncertainty in the calculation of Δ_η from viscosity measurements was estimated to be ±3. 10^{-3} mPa.s. For binary mixtures (1, 4 dioxane + bromo benzene and 1, 4 dioxane + ethyl benzene), calculated data of kinematic viscosity, density were correlated with the composition data by the jouyban-acree polynomial (equation 2). The predictions of the jouyban–acre model shown in Tables 2 and 3, coefficients A_1 to A_7 of kinematic viscosity and density for all temperatures of binary liquid mixtures as shown in Tables 4 and 5.

Table 4 Kinematic viscosity parameters of study jouyban acree nonlinear model, constants and standard deviations (σ) of 1, 4 dioxane + bromo benzene, 1, 4dioxane + ethyl benzene at 303.15, 308.15 and 313.15 K.

T/K	A_1	A_2	A_3	A_4	A_5	A_6	A_7	σ

				{1, 4 dioxane + bromo benzene}				
				γ				
303.1	180.3	22.36	-	-	32.08	-	-	0.001
308.1	178.7	31.87	-	-	27.54	-	-	0.000
313.1	165.9	36.87	-	-	17.52	-	-	0.000
				{1,4 dioxane + ethyl benzene}				
				γ				
303.1	-	1.182	31.48	-	62.50	3.968	38.87	0.002
308.1	-	-	56.15	-	59.14	8.040	33.46	0.002
313.1	-	-	26.37	39.49	56.25	4.631	39.53	0.001

Table 5 Density parameters of studied jouyban acree nonlinear model, constants and standard deviations (σ) of 1, 4 dioxane + bromo benzene, 1,4 dioxane + ethyl benzene at 303.15, 308.15 and 313.15 K.

T/K	A_1	A_2	A_3	A_4	A_5	A_6	A_7	σ
				{1, 4 dioxane + bromo benzene}				
				ρ				
303.1	-	-	107.3	29.64	-	3.926	26.46	0.001
308.1	-	-	37.63	35.93	6.805	1.845	22.79	0.001
313.1	-	-	-	25.57	18.12	2.505	17.85	0.000
				{1,4 dioxane + ethyl benzene}				
				ρ				
303.1	101.2	15.56	-	-	40.06	- 5.65	-	0.000
308.1	242.7	27.85	-	-	71.70	-	-	0.001
313.1	333.6	45.72	-	-	95.10	-	-	0.002

The densities of mixtures of 1,4 dioxane with bromo benzene and ethyl benzene have been correlated with the model proposed by jouyban–acree model.

$$ln\,\rho_{m,T} = f_1\,ln\,\rho_{1,T} + f_2\,ln\,\rho_{2,T} + f_1 f_2 \sum\left[\frac{A_j(f_1-f_2)^j}{T}\right] \qquad \text{------------------ (3)}$$

Where, ρ_m, ρ_1 and ρ_2 is, density of the mixture and pure components 1 and 2 at temperature T, respectively, f_1 and f_2 are the volume fractions of the pure components and Aj are the model constants.

The kinematic viscosity was obtained from the working equation.

$$\gamma = at - b/t \qquad \text{-------------------- (4)}$$

Where the two constants a and b were obtained by measuring the flow time t of benzene and lab distilled water. The kinematic viscosities of mixtures of 1,4 dioxane with bromo benzene and ethyl benzene have been correlated with the model proposed by jouyban–acree model.

$$ln\,\gamma_{m,T} = f_1\,ln\,\gamma_{1,T} + f_2\,ln\,\gamma_{2,T} + f_1 f_2 \sum\left[\frac{A_j(f_1-f_2)^j}{T}\right] \text{------------------ (5)}$$

Where, γ_m and γ_1 are γ_2 the kinematic viscosity of the mixture and pure solvents 1 and 2 at temperature T, respectively, f_1 and f_2 are the volume fractions of the pure components and A_J is the model constants. In this case, the optimum number of coefficients are ascertained from an examination of the variation in standard deviation was calculated using the relation (equation 6).

$$\sigma(Y) = [\Sigma\,(A_{exp} - A_{cal})^2 / (N-n)^{1/2}] \qquad \text{--------------------------(6)}$$

Where, N is the number of data points and n is the number of coefficients. The calculated values of coefficients along with the standard deviation (σ) are given in Tables 4 and 5. The variation of excess volumes with the mole fraction (x_1) of 1, 4 dioxane with bromo benzene and ethyl benzene at (303.15, 308.15 and 313.15 K) are represented in Fig 1. This shows that the excess molar volumes are always positive for all the studied temperatures. Treszczanowicz et al.[18] and Roux and Desnoyers[19] suggested that V^E is the resultant contribution from several opposing effects. These may be divided arbitrarily into three types, namely chemical, physical and structural.[20-22]

Vektarieneet al.,[23] stated that the Br–Br bond length in dioxane di bromide is 0.231 nm, where as it is 0.228 nm in the Br_2 molecule. Thus, the Br–Br bond in dioxane di bromide is a little elongated and the bromine molecule is slightly polarized. It has also been suggested that when bromine interacts with dioxane forming a dioxane di bromide, the electron density flows from the lone pair of non bonding occupied orbitals of bromine to the unoccupied orbitals on the dioxane unit. The specific interactions between the real species present in the mixture contribute a positive term to V^E in Fig 1. Therefore, the attacking electrophile derived from dioxane is likely to be a slightly polarized neutral bromine molecule with enhanced electro philicity. It is probable that the weak interaction existing in the mixture is due to the loss of intermolecular hydrogen bonding reported by Subratakumar et al.[24]

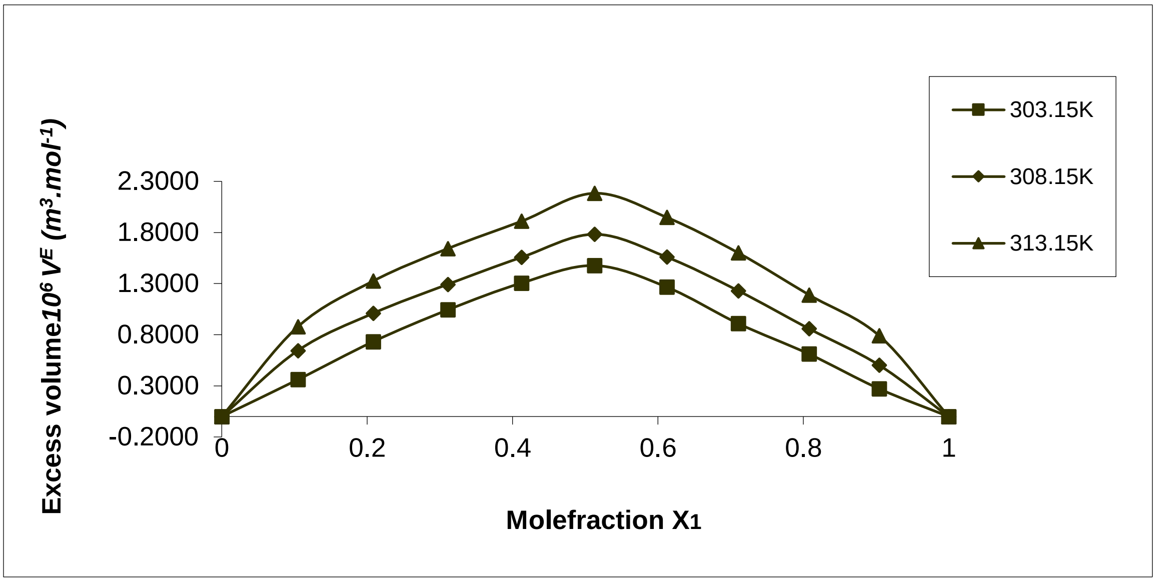

FIGURE 1. Excess molar volume (V^E) for 1, 4 dioxane + bromo benzene at 303.15 K, 308.15 K and 313.15 K.

The positive sign of V^E indicates a weak interaction through london depressive forces in mixture. These magnitudes of the contributions are helpful to form different types of interactions will vary with the composition and components of the mixtures. In this study, all the two mixtures gave positive magnitude of V^E with consistent presence of hetero molecular interactions.[25,26] As proposed the reaction may involve the initial formation of a cyclic bromonium ion and its subsequent conversion to the carbo cationic in the 1,4 dioxane and bromo benzene mixture,[24] it is probable that the weak interaction existing in the mixture is due to the loss of intermolecular hydrogen bonding. The aromatic ring substituted with the electron-donating group in dioxane appeared due to olefinic hydrogen at C_4 having no partner to couple with the hydrogen bonding interaction in the dioxane as shown in Fig 5. The incorporation of bromine at intermediate, depending on its stabilization by alkyl substituents at carbon through an electron-donating inductive effect and hyper conjugation and by the substituents at carbon rendering an electron-donating mesomeric effect as shown in the Fig 5.

In Fig 2 shows the positive excess molar volumes in 1,4 dioxane with ethyl benzene system provides unlike molecular interactions, dispersion forces and dipole induced dipole interactions in mixture. The complex formation of weak hydrogen bonds between unlike molecules with the type of C-H-π electrons leads to positive sign to excess molar volume. This is due to dipolar interaction that involves opposite poles on neighbouring molecules. The dipolar interaction is the sense, that neighbouring molecules of a polar component cause association in the pure state, due to electrostatic interaction and charge transfer complexes in polar components, all of the alkyl benzenes will have roughly the same +I inductive effect (Mulliken and Par, 1951). Where they differ regard to the resonance effect. The alkyl group (ethyl) in ethyl benzenes at are capable of donating electrons into the aromatic ring by hyper conjugation. Ethyl benzene should be the most electron donating of the compounds due to resonance involving hyper conjugation of 1,4 dioxane and ethyl benzene. Inductively, the methyl group releases electron density into the benzene ring. This is because the methyl group, being sp^3 hybridized carbon centers are less electronegative than the sp^2 hybridized aromatic carbon. Hence, one would expect less dipole-dipole and dipole-induced dipole interactions in the mixture compared to pure components, also reported by Rena et al.[27] Ethyl benzene being an electron donor and dioxane being a electron acceptors, there is possibility of forming charge transfer complexes between dioxane and ethyl benzene mixture.[24,25] These two factors may result in expansion in volumes is studied in detail using MD simulation as shown in Table 6.

Table 6. The molecular dynamics viscosity measurement with respect to temperature for 1, 4 dioxane + bromo benzene and 1,4 dioxane + ethyl benzene at 303.15, 308.15 and 313.15 K.

T/K	{1,4 dioxane + ethyl benzene} (mpa.s)	{1,4 dioxane + bromo benzene} (mpa.s)
303.15	0.802	1.101
308.15	0.751	1.014
313.15	0.717	0.985

Viscosity of the simulated system was determined by first calculating Einstein and Smoluchowski relation:

$$D = 1/6 \lim_{t\rightarrow\infty} < [r_i(t) - r_i(0)]^2> \text{ ----------- (7)}$$

Where D the diffusion coefficient with limit of slope of the mean squared displacement (MSD) with respect to time. The computational result of mean squared displacement of 250 ps is plotted using VMD software and analyzed using XMGRACE for linear fit. The slope obtained divided by six gives D. On calculating D then the viscosity is obtained by substituting it in Stokes-Einstein relation[45,46]:

$$\eta = (k_b\, T) / (6\, \pi\, D\, r) \text{ ------------- (8)}$$

Where η is viscosity with respect to molecule of radius r and D diffusion coefficient.

The 2ns long MD simulation shows the factors such as difference in size and shape, loss of dipolar association of dioxane by addition of ethyl benzene has lead to expansion of volume.[28] However, the actual volume change depends on the relative strengths of the two contributions.

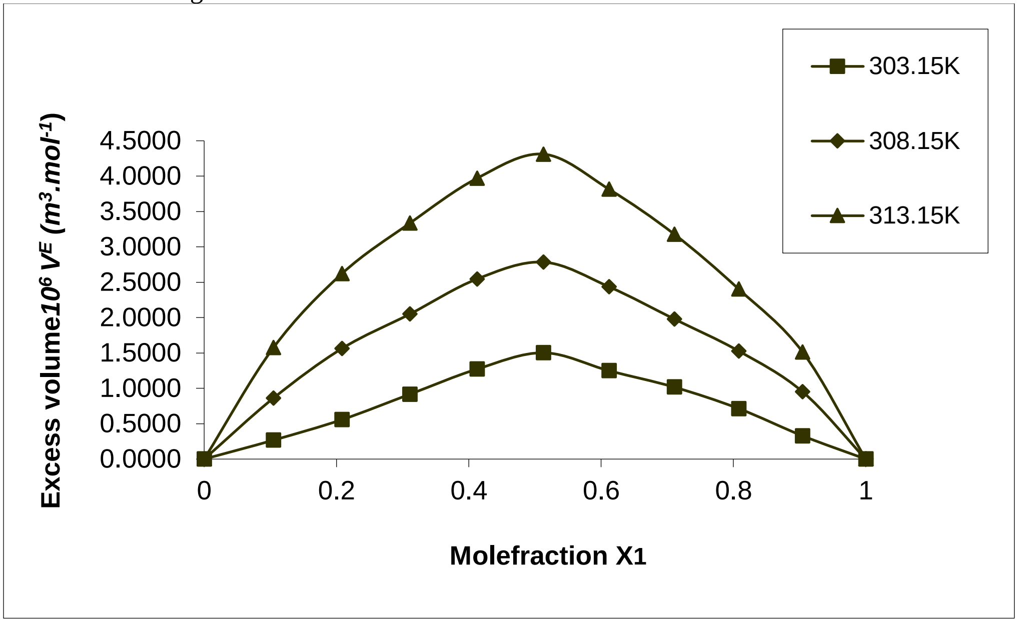

FIGURE 2. Excess molar volume (V^E) for 1, 4 dioxane + ethyl benzene at 303.15, 308.15 and 313.15 K.

The observed positive values in Fig 2 suggest that the dipole-dipole interactions and charge transfer complexes between unlike molecules dominate the volume contraction factor. This effect contributes to the positive values to V^E. The structural contributions are mostly positive and arise from several effects, especially from interstitial accommodation and changes of free volume.

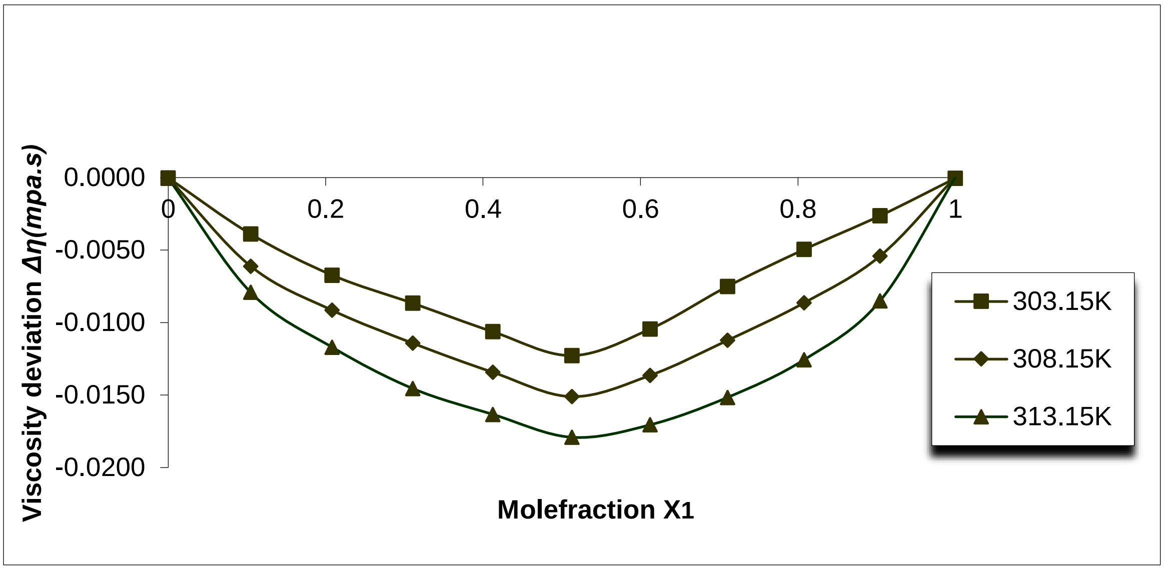

FIGURE 3. Viscosity deviation (Δη) for 1,4 dioxane + bromo benzene at 303.15, 308.15 and 313.15 K.

In other words, structural contributions arising from geometrical fitting of one component into the other due to the differences in the free volume and molar volume between components lead to a positive contribution to V^E. The variation of viscosity deviations, with the mole fraction (x_1) of dioxane with bromo benzene and ethyl benzene at (303.15, 308.15 and 313.15 K) are represented in Fig 4 and Fig. 5. The increase in temperature and the viscosity deviation values become less negative. The negative viscosity deviations[3,30,31] may be attributed to the existence of dispersion and dipolar forces between unlike molecules and related to the difference in size and shape of the unlike molecules. The negative viscosity deviation indicates that the weak interaction in the liquid mixtures as well as interstitial accommodation of bromo benzene molecules in aggregates with dioxane. The negative viscosity deviation found vary with mole fraction may be attributed to the breaking both the hydrogen bond and bipolar interaction in mixture. It can be concluded that negative deviations viscosity in Fig. 3 due to weak molecular interactions in mixtures.[32,33]

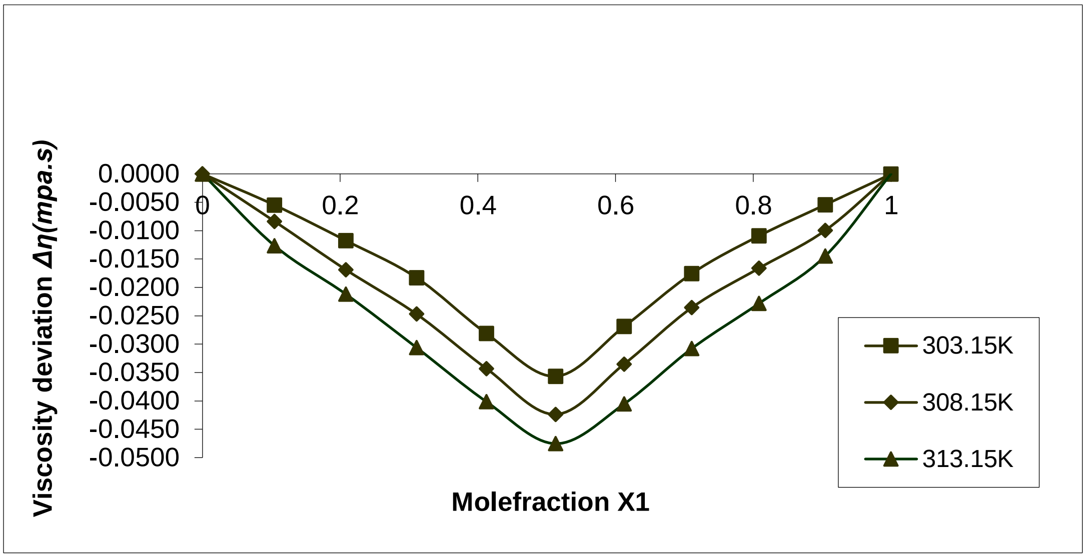

FIGURE 4. Viscosity deviation (Δη) for 1,4 dioxane + ethyl benzene at 303.15, 308.15 and 313.15 K.

The MD simulation force field parameters consist of bonding and non-bonding parameters[46]. The ethyl group in ethyl benzene is electron donating has more electrostatic interaction shield in the mixture of polar-nonpolar mixture (ethyl benzene-dioxane) compared to bromo capped bromo benzene. This brings the ethyl benzene compound to weakly dipolar compound. The positive excess molar volume is due to the formation of dipole-dipole interaction between ethyl benzene and 1, 4 dioxane. In Fig 5, the viscosity deviation (Δ_η) also found to be negative. The viscosity deviation gives the strength of molecular interaction between the interacting molecules. The excess volume depends not only on the difference in molecular forces, but also on the difference in size of the molecule. In these systems, the viscosity of the mixture strongly depends on the entropy of mixture, which is related with liquid's structure and enthalpy.[33,34]

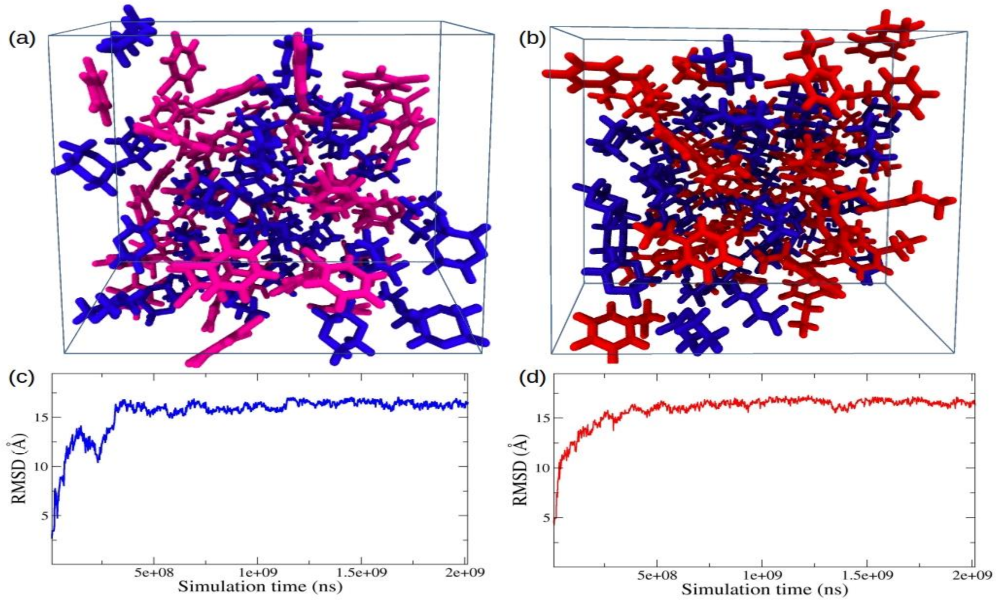

FIGURE 5. 1,4 dioxane-bromo benzene and 1,4 dioxane-ethyl benzene mixture of 0.5 molar mixture simulation box representation of the last frame is shown in (a,b) respectively. Below Figure (c,d) represents root mean square distribution (RMSD) along the time scale of 2 ns total simulation.

Ethyl group becomes slightly positive and dioxane group becomes negative whereas in the case of bromo benzene the bromine withdraws the electron cloud over benzene inducing polar stack among molecules. Therefore, the viscosity deviation depends on molecular interactions as well as on the size and shape of the molecules, where dispersion, induction and dipolar forces are operating, viscosity deviations are found to be negative.[27,35-41]

Conclusion

Densities, viscosities of binary mixtures constant of 1,4 dioxane, bromo benzene and ethyl benzene have been measured and it has been observed that negative deviations for viscosity and positive excess molar volume of the mixtures. In the case of excess molar volumes, viscosity deviations, 1, 4 dioxane is repulse towards the bromine group in bromo benzene and it forms dipole-dipole bond. Inductive effect of ethyl group in ethyl benzene is donating electron, due to this ethyl group becomes slightly positive and at the same time phenyl group becomes negative, this makes the compound to feebly dipolar. In this cases, the force between unlike molecules are lesser than the force between like molecules in both mixtures. It is also clear that the jouyban acree model polynomial equation can represent the kinematic viscosity and density, which is indicated by low standard deviations < 2.50%. It has been concluded that the jouyban-acree model is very well suited for correlating the thermo physical properties of the binary mixtures studied. The computational modelling using molecular dynamics simulation substantiates the experimental properties of change in molecular volume and packing with respect to the excess molar volume parameters.

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