The International Journal Of Engineering And Science (IJES)
|| Volume || 3 || Issue || 3 || Pages || 68-74 || 2014 ||
ISSN (e): 2319 – 1813 ISSN (p): 2319 – 1805

Measurement and Prediction of Thermo Physical Properties of Binary Liquid Mixtures at Various Temperatures Using Mc Allister Model

[1,] R.Ramesh, [2,] A.Hisyam, [3,] K.Ramesh
[1,2,3,]Process Systems Engineering group (PSEG), Faculty of Chemical & Natural Resources Engineering,
Universiti Malaysia Pahang, 26300 Gambang, MALAYSIA

ABSTRACT

The purpose of this study conducted in this research was to measure thermo physical properties like Viscosities, η, and Densities, ρ, of 1,4 Dioxane with two hydrocarbons like Bromobenzene and Ethylebenzene at different mole fractions and various temperatures in the atmospheric pressure condition. From the experimental data excess volumes, V^E, and deviations in viscosities, $\Delta\eta$, of mixtures at infinite dilutions have been obtained. The measured systems exhibited positive values of V^E and negative values of $\Delta\eta$. The binary mixture 1, 4 Dioxane + Bromobenzene show positive V^E and negative $\Delta\eta$ with increasing temperatures. The outcomes clearly indicate that weak interactions present in mixture. It is mainly because of number and position of methyl groups exist in these aromatic hydrocarbons. These measured data tailored to the McAllister model to derive the binary coefficients. Standard deviations obtained from the fitted outcomes and the calculated data is helpful deliberate mixing behavior of the binary mixtures. It can conclude that in our case, the data found with the values correlated by the corresponding model is very well. The molecular interactions existing between the components and comparison of liquid mixtures were also discussed.

KEYWORDS: *Density, Excess molar volume, Oswald-Sprengel Pyknometer, Oswald viscometer, Viscosity and Viscosity deviation.*

Date of Submission: 06 March 2014 Date of Publication: 25 March 2014

I. INTRODUCTION

In chemical design and effective chemical process optimization, the molecular interactions existing in process fluids and thermo physical properties like Densities and viscosities playing key role. These two are essential for engineering designs involving chemical separations, heat transfer, mass transfer, and fluid flow. It is important from practical and theoretical points of view for understanding liquid theory [1]. 1, 4 Dioxane commonly known as excellent aprotic solvent, has a dipole movement is zero. In polymerization and other chemical reactions it was used commercially like cleaning of polymer surfaces and electronic materials. The aromatic hydrocarbon molecules possess a large quadruple moment, which causes an orientational order in these liquids. The orientational order is thought of as a partial alignment of neighboring segments or possibly of whole molecules. Also, binary mixtures containing aromatic hydrocarbons are interesting because they have applications in the study of polymer phase diagrams and the preferential interaction of polymers in mixed solvents. 1, 4 Dioxane is cyclic ether that has electron-donor ability toward the aromatic rings that act like weak electron acceptors. Therefore, the 1, 4 Dioxane + aromatic hydrocarbon mixtures will be interesting because they involve charge-transfer interactions that may be influenced by the presence of alkyl groups on the ring. Other uses of 1, 4 Dioxane include manufacture of adhesives and cements, deodorant fumigants, cosmetics, drugs, cleaning preparations, magnetic tape, plastic, rubber, insecticides, herbicides, and as a chemical intermediate.

As a polymerization catalyst, in the purification of drugs, and 1, 4 Dioxane has low toxicity to aquatic organisms and toxicity values are greater than 100 mg/L. 1, 4 Dioxane is not likely to be acutely toxic. The entire range of composition was studied at T = (303.15to313.15) K. With this data, the excess molar volume and deviation in viscosity have been computed. These results have been fitted to the McAllister's three-body model is used to correlate the kinematic viscosities of these binary mixtures [1]. This analyzed technique to derive the binary coefficients and to estimate the standard deviation (σ) between experimental and calculated data.

II. EXPERIMENTAL SECTION

Materials

1, 4 Dioxane, Bromobenzene, Ethyl benzene this were all supplied by M/s E.Merck Ltd. With stated purities of better than 99 % were stored over molecular sieves (0.3 nm Merck, India). 1, 4 Dioxane with a purity of 99 % was provided by Sigma-Aldrich Chemicals and was used without further purification. To minimize the contact of these reagents with moist air, the products were kept in sealed bottles in a desiccator. The purity of the substances was determined by GLC. Densities and viscosities of pure substances and their comparison with literature values are listed in Table 1.[2–4]

Apparatus and Procedure

Measurements of the density, ρ, and the kinematic viscosity, γ, of pure liquids and their solutions were carried out using an Oswald Sprengel Pycknometer and Oswald Viscometer and two integrated Pt 100 thermometers. The temperature in the cell was regulated to 0.001K with a proportional temperature controller. The apparatus was first calibrated with triple distilled water. The uncertainties in density measurements were estimated to be $2\bullet10^{-3}$ $g\bullet cm^{-3}$ and. Further information about the experimental techniques has been the kinematic viscosities of the pure liquids and their mixtures were measured at (303.15, 308.15, and 313.15) K.

The viscometer was filled with liquid or liquid mixtures, and its limbs were closed with Teflon caps taking due precaution to reduce evaporation losses. An electronic digital stopwatch with a readability of 0.01 s was used for flow time measurements. Experiments were repeated a minimum of four times for all compositions, and the results were averaged. The caps of the limbs were removed during the measurement of flow times. The measured values of kinematic viscosity, γ, were converted to dynamic viscosity,η, after multiplication by the density. The reproducibility of dynamic viscosity was found to be within 0.003 mPa•s. A thermostatically controlled well-stirred water bath whose temperature was controlled to 0.01 K and It was used for all the measurements. Conductivity measurements were carried out in a jacket containing a conductivity cell of cell constant 1.0 cm^{-1}. Water was circulated in the jacket from thermostat, and the temperature was maintained within ± 0.01 K was used for all the measurements. The kinematic viscosity of solution γ is given by

$$\gamma = (at - (b/t)) \qquad (1)$$

Where γ is the kinematic viscosity, t is the flow time, the two constants a, and b are the kinematic viscosities, γ, and densities. The uncer-tainty for the dynamic viscosity determination is estimated to be ± 0.5 %.

III. RESULTS AND DISCUSSION

Densities, ρ, dynamic viscosities, η, of pure liquids are shown in Table 1.

Table-1: Experimental Densities and viscosities of Pure Liquids with Literature Values at 303.15K.

		$\rho/g.cm^{-3}$		$\eta/(mPa).s$	
Component	T/K	Lit	Exptl.	Lit	Exptl.
1, 4-Dioxane	303.15	1.0222[2]	1.0271	1.0985[2]	1.0958
Bromobenzene	303.15	1.4815[3]	1.4817	0.9850[3]	1.0201
Ethyl benzene	303.15	0.8645[4]	0.8662	0.5980[4]	0.6020

Excess molar volumes, V^E, and viscosity deviation, Δη, changes of mixing at various temperatures and atmospheric pressure are reported in Tables 2, and 3 for the Bromobenzene +1, 4 Dioxane and Ethylebenzene + 1, 4 Dioxane. In Table 2,interaction between Bromobenzene +1, 4 Dioxane mixture is weak compared to Table 3 interaction between Ethylebenzene + 1, 4 Dioxane. The experimental values shows clearly Bromine group in bromobenzene and it forms dipole-dipole bond with 1, 4 Dioxane, because of dipole-dipole bond, thermo physical properties decreasing with addition of 1, 4 Dioxane at all temperature reported in Table 2. The correlated values by Mc Allister model are shown in tables 4 and 5. The obtained thermo physical data shows high degree of precision compared with the experimental values. Parameters of McAllister nonlinear model, constants and standard deviations (σ) of Binary liquid mixtures are shown in Table 6.

Table: 2 Experimental Densities and viscosities of 1,4 Dioxane + Bromo Benzene at 303.15, 308.15 and 313.15 K

	T/K=303.15			**T/K=308.15**			**T/K=313.15**		
x1	$^{\rho}/_{g.cm^{-3}}$	$^{\eta}/_{mPa\cdot s}$	$^{V^E}/_{cm^3\cdot mol^{-1}}$	$^{\rho}/_{g.cm^{-3}}$	$^{\eta}/_{mPa\cdot s}$	$^{V^E}/_{cm^3\cdot mol^{-1}}$	$^{\rho}/_{g.cm^{-3}}$	$^{\eta}/_{mPa\cdot s}$	$^{V^E}/_{cm^3\cdot mol^{-1}}$
0.0000	**1.4817**	**1.0201**	**0.0000**	**1.4682**	**0.9815**	**0.0000**	**1.4549**	**0.9550**	**0.0000**
0.1047	**1.4432**	**1.0255**	**0.7354**	**1.4267**	**0.9785**	**0.5469**	**1.4129**	**0.9429**	**0.2930**
0.2083	**1.3962**	**1.0302**	**1.1127**	**1.3819**	**0.9795**	**0.7984**	**1.3698**	**0.9489**	**0.5855**
0.3109	**1.3468**	**1.0333**	**1.5952**	**1.3356**	**0.9886**	**1.2546**	**1.3256**	**0.9480**	**0.8719**
0.4124	**1.2965**	**1.0333**	**2.0647**	**1.2826**	**0.9875**	**1.6914**	**1.2775**	**0.9467**	**1.3704**
0.5128	**1.2496**	**1.0355**	**2.1888**	**1.2373**	**0.9735**	**1.8053**	**1.2308**	**0.9370**	**1.6700**
0.6122	**1.1999**	**1.0450**	**2.4288**	**1.1899**	**0.9555**	**1.9880**	**1.1873**	**0.9162**	**1.7245**
0.7106	**1.1578**	**1.0569**	**1.9581**	**1.1499**	**0.9589**	**1.4459**	**1.1467**	**0.9011**	**1.1760**
0.8080	**1.1125**	**1.0688**	**1.6002**	**1.1036**	**0.9705**	**1.2838**	**1.1026**	**0.9203**	**0.8960**
0.9045	**1.0698**	**1.0800**	**0.8876**	**1.0596**	**0.9717**	**0.7805**	**1.0568**	**0.9145**	**0.6064**
1.0000	**1.0271**	**1.0958**	**0.0000**	**1.0169**	**1.0094**	**0.0000**	**1.0128**	**0.9447**	**0.0000**

Table-3: Experimental Densities and viscosities of 1,4Dioxane +Ethyl Benzene at 303.15, 308.15 and 313.15 K

	T/K=303.15			**T/K=308.15**			**T/K=313.15**		
x1	$^{\rho}/_{g.cm^{-3}}$	$^{\eta}/_{mPa\cdot s}$	$^{V^E}/_{cm^3\cdot mol^{-1}}$	$^{\rho}/_{g.cm^{-3}}$	$^{\eta}/_{mPa\cdot s}$	$^{V^E}/_{cm^3\cdot mol^{-1}}$	$^{\rho}/_{g.cm^{-3}}$	$^{\eta}/_{mPa\cdot s}$	$^{V^E}/_{cm^3\cdot mol^{-1}}$
0.0000	**0.8662**	**0.6020**	**0.0000**	**0.8595**	**0.5893**	**0.0000**	**0.8519**	**0.5699**	**0.0000**
0.1047	**0.9068**	**0.6514**	**0.7737**	**0.8948**	**0.6220**	**0.6049**	**0.8615**	**0.5957**	**0.3975**
0.2083	**0.9135**	**0.6663**	**1.1728**	**0.903**	**0.6399**	**0.8638**	**0.8725**	**0.6161**	**0.6663**
0.3109	**0.9218**	**0.6934**	**1.4122**	**0.9118**	**0.6665**	**1.0935**	**0.8845**	**0.6379**	**0.8803**
0.4124	**0.9301**	**0.7161**	**1.6919**	**0.9207**	**0.6844**	**1.3569**	**0.8974**	**0.6600**	**1.0629**
0.5128	**0.9399**	**0.7489**	**1.8462**	**0.9310**	**0.7073**	**1.5074**	**0.9120**	**0.6808**	**1.1312**
0.6122	**0.9534**	**0.7925**	**1.6595**	**0.9445**	**0.7421**	**1.3707**	**0.9300**	**0.7068**	**0.9261**
0.7106	**0.9687**	**0.839**	**1.3748**	**0.9602**	**0.7874**	**1.0924**	**0.9498**	**0.7379**	**0.6624**
0.8080	**0.9876**	**0.8986**	**0.8473**	**0.9786**	**0.8440**	**0.6535**	**0.9712**	**0.7814**	**0.3894**
0.9045	**1.0069**	**0.9711**	**0.4005**	**0.9976**	**0.8858**	**0.2810**	**0.9935**	**0.8539**	**0.1881**
1.0000	**1.0271**	**1.0958**	**0.0000**	**1.0169**	**1.0095**	**0.0000**	**1.0128**	**0.9446**	**0.0000**

Table: 4 Predicted kinematic viscosities by McAllister nonlinear model for 1,4Dioxane + Bromo Benzene at 303.15, 308.15 and 313.15 K

X_1	γ_{expt} (C.S) 303.15K	γ_{pred} (c.s) Mc-Allister308.15K)	γ_{expt} (C.S) 308.15K	γ_{pred} (c.s) (Mc-Allister308.15K)	γ_{expt} (C.S) 313.15K	γ_{pred} (c.s) (Mc-Allister313.15K)
0.0000	0.6863	0.6863	0.6685	0.6685	0.6564	0.6564
0.1047	0.7106	0.7095	0.6858	0.6859	0.6700	0.6789
0.2083	0.7379	0.7352	0.7088	0.7065	0.6980	0.6988
0.3109	0.7672	0.7636	0.7335	0.7303	0.7182	0.7173
0.4124	0.7919	0.7949	0.7562	0.7572	0.7411	0.7358
0.5128	0.8229	0.8293	0.7808	0.7874	0.7613	0.7555
0.6122	0.8655	0.8674	0.8187	0.8208	0.7746	0.7781
0.7106	0.9129	0.9095	0.8618	0.8577	0.7958	0.8050
0.8080	0.9607	0.9562	0.9011	0.8984	0.8457	0.8382
0.9045	1.0095	1.0083	0.9445	0.9432	0.8757	0.8799
1.0000	1.0669	1.0669	0.9927	0.9927	0.9327	0.9327

Table: 5 Predicted kinematic viscosities by McAllister nonlinear model for 1,4Dioxane +Ethyl Benzene at 303.15, 308.15 and 313.15 K

X_1	γ_{expt} (C.S) 303.15K	γ_{pred} (c.s) Mc-Allister308.15K)	γ_{expt} (C.S) 308.15K	γ_{pred} (c.s) (Mc-Allister308.15K)	γ_{expt} (C.S) 313.15K	γ_{pred} (c.s) (Mc-Allister313.15K)
0.0000	0.7042	0.7042	0.6855	0.6855	0.6690	0.6690
0.1047	0.7193	0.7297	0.6951	0.6945	0.6812	0.6812
0.2083	0.7298	0.7329	0.7086	0.7145	0.6910	0.6903
0.3109	0.7522	0.7496	0.7310	0.7272	0.7100	0.7146
0.4124	0.7689	0.7698	0.7433	0.7414	0.7266	0.7223
0.5128	0.7924	0.7949	0.7597	0.7592	0.7411	0.7365
0.6122	0.8302	0.8400	0.7857	0.7829	0.7607	0.7555
0.7106	0.8677	0.8672	0.8200	0.8149	0.7885	0.7817
0.8080	0.9236	0.9186	0.8625	0.8569	0.8099	0.8097
0.9045	0.9722	0.9840	0.8879	0.8945	0.8455	0.8457
1.0000	1.0669	1.0669	0.9927	0.9927	0.9327	0.9327

Table 6: Parameters of McAllister nonlinear model, constants and standard deviations (σ) of Binary liquid mixtures

McAllister constants and standard deviations (σ) of Binary liquid mixtures			
Temperature (T/K)	A	B	σ
1,4Dioxane +Bromo Benzene			
303.15	0.89527	0.768697	0.0035
308.15	0.85032	0.72892	0.0032
313.15	0.76769	0.74621	0.0025
1,4Dioxane + Ethyl Benzene			
303.15	0.78696	0.75184	0.0066
308.15	0.74530	0.72797	0.0043
313.15	0.73555	0.70144	0.0039

The excess molar volumes, V^E, dynamic viscosity, η, and molar refraction changes of mixing were calculated from experimental values using the following expressions.

$$V^E = V_M - \sum_{i=1}^{n} X_i V_i \qquad (2)$$

Where V_M is the molar volume of the mixture, η is the dynamic viscosity, and V_i, X_i are the Molar volume and mole fractions respectively.

The variation of excess volumes with the mole fraction of Bromobenzene and Ethylebenzene with 1, 4 Dioxane at various temperatures (303 .15, 308.15 and 313.15) K are represented in "Fig. 1 and 2".

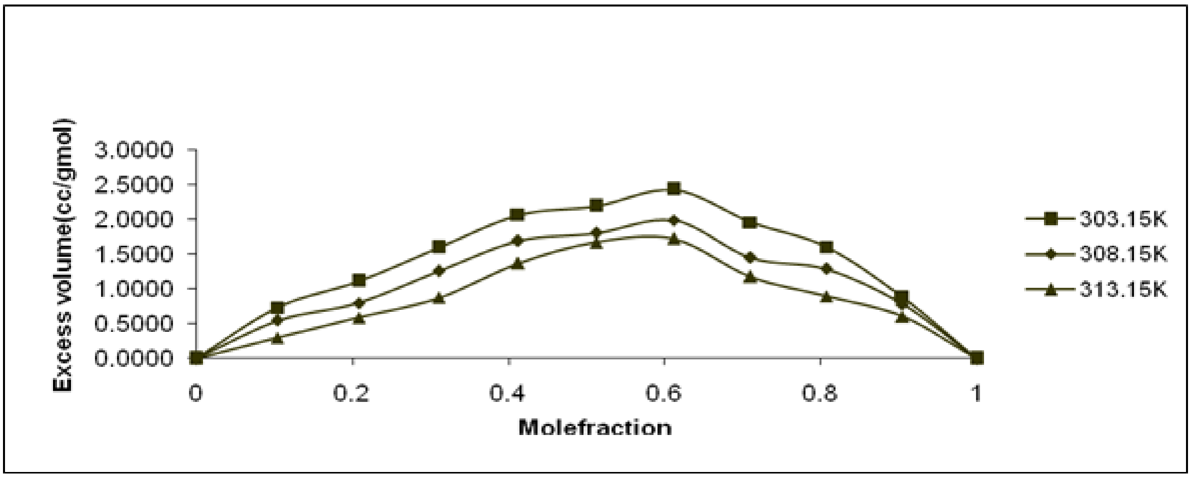

Figure 1: Excess molar volume (V^E) for 1, 4 Dioxane + Bromo benzene at 303.15, 308.15 and 313.15 K

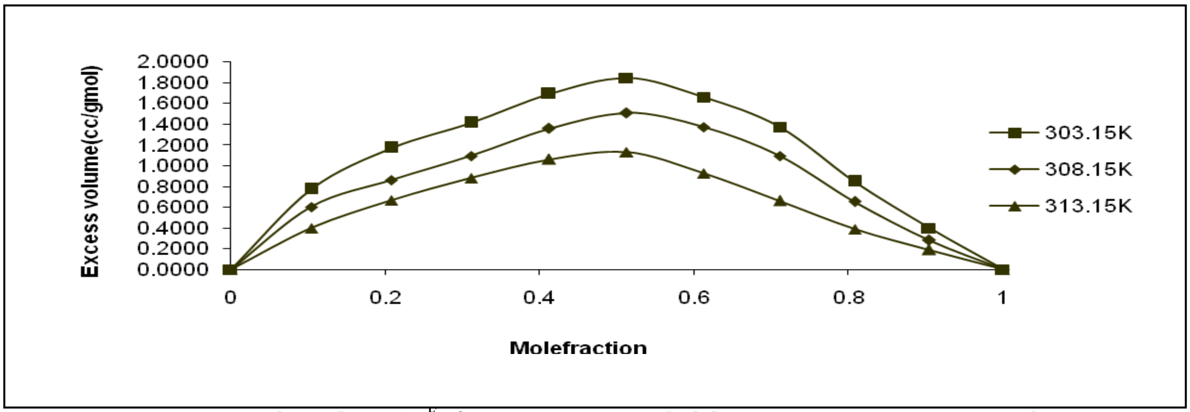

Figure 2: Excess molar volume (V^E) for 1,4Dioxane + Ethylebenzene at 303.15, 308.15 and 313.15 K

The sign of excess volume of a system depends on the relative magnitude of expansion/contraction on mixing of two liquids. If the factors causing expansion dominate the contraction factors, the V^E becomes positive. On the other hand if the contraction factors dominate the expansion factors, then V^E become negative. The factors that are responsible for expansion in volume are as follows, Loss of dipolar association and geometry of molecular structure, which does not allow fitting of one component into other component. The Steric hindrance opposes proximity of the constituent molecules [5]-[10]. The negative V^E values arise due to dominance of the following factors Chemical interaction between constituent chemicals and accommodation of molecules of one component into the interstitials of the molecules of the other component. The Geometry of molecular structure that favors fitting of the component molecules with each other. The negative V^E values in the mixtures under study indicate that interactions between molecules of the mixtures are stronger than interactions between molecules in the pure liquids and that associative force dominate the behaviour of the solution.

$$\Delta\eta = \eta - \sum_{i=1}^{n} X_i \eta_i \qquad (3)$$

Where $\Delta\eta$ is the viscosity deviation and η is the dynamic viscosity.

The results of variation in viscosity deviations of binary systems consisting of Bromobenzene and Ethylebenzene with 1, 4 Dioxane at temperatures of 303.15K, 308.15K, and 313.15K are represented in "Fig. 3 and 4".

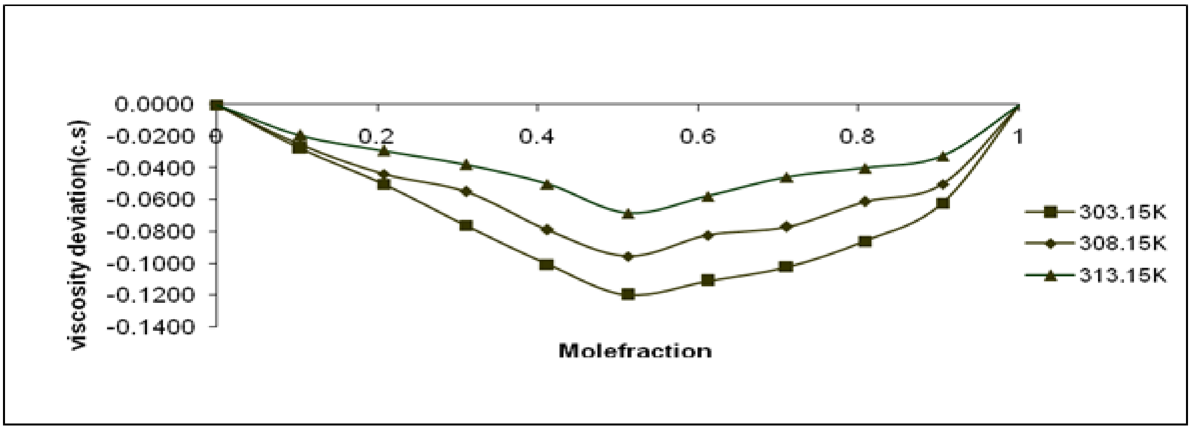

Figure 3: Deviation in viscosity (Δη) for 1,4Dioxane + Bromo benzene at 303.15, 308.15 and 313.15 K

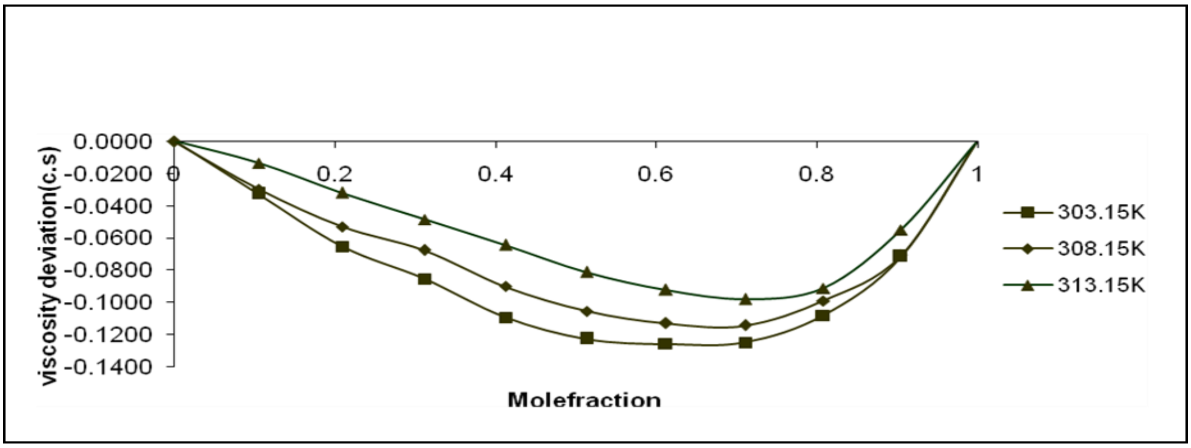

Figure 4: Deviation in viscosity (Δη) for 1,4Dioxane + Ethylebenzene at 303.15, 308.15 and 313.15 K

This result shows negative deviations over the entire range of mole fraction. The viscosity of the mixture strongly depends on the entropy of mixture, which is related with liquid's structure and enthalpy. It will consequently with molecular interactions between the components of the mixtures. Therefore the viscosity deviation depends on molecular interactions as well as on the size and shape of the molecules.

Standard Deviation

It was calculated using the relationship.

$$\sigma = \left(\Sigma(\nu_{exp} - \nu_{calc})^2 / \left(\mathrm{N} - \mathrm{m}\right)^{1/2}\right) \quad (4)$$

Where, N-Number of data points, m – Number of coefficients, the calculated values of coefficients along with the standard deviation (σ) are given in table 6. Interaction parameters and Predicted kinematic viscosities and Excess molar volume of Bromobenzene and Ethylebenzene and 1, 4-dioxane mixture at (303.15, 308.15 and 313.15) K are presented in tables4-5.

3.2. Nonlinear Model

The binary mixture calculated data of V^E, $\Delta\eta$ were correlated with the composition data by the McAllister Model. The size ratio of the 2 molecules should be less than 1.5.

$$\ln\upsilon = x_1^3 \ln\upsilon_1 + 3\,x_1^2 x_2 \ln\upsilon_{12} + 3x_1 x_2^2 \ln\upsilon_{21} + x_2^3 \ln\upsilon_2 - \ln\left(x_1 + x_2 m_2 / m_1\right) + 3x_1^2 x_2 \ln\left(\left(2 + m_2 / m_1\right) / 3\right) + 3x_1 x_2^2 \ln\left(1 + 2\,m_2 / m_1\right) / 3) + x_{-2}^3 \ln\left(m_2 / m_1\right) \qquad (5)$$

This McAllister equation is based on three body model. It contains 2 constants namely υ_{12} and υ_{21}. The constants can be evaluated using least square method.

IV. IV CONCLUSION

From the study, 1, 4 Dioxane is repulse towards the Bromine group in bromobenzene 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 case, the force between unlike molecules is lesser than the force between like molecules in mixtures. It can be concluded that the positive Excess molar volumes and negative deviations viscosity due to weak molecular interactions existing between the binary mixtures of 1, 4 Dioxane + Bromo benzene + Ethylebenzene. Viscosity of the binary mixture and the McAllister three-body model is very well suited for correlating Kinematic viscosity of the binary mixture with minimum standard deviation in present study.

REFERENCES

[1]. Mc-Allister. R.A. 1960. The Viscosity of liquid mixtures, *AICHE Journal.*l6: 427-431.

[2]. Martin Contreras S. 2001 Densities and Viscosities of Binary Mixtures of 1, 4-Dioxane with 1-Propanol and 2-Propanol at (25, 30, 35, and 40) °C *J. Chem. Eng. Data*, 46, 1149 - 1152.

[3]. Riddick, J. A.; Bunger, W. B.; Sakano, T. K. Organic Solvents, Physical Properties and Methods of Purification, 4th ed.; Wiley-Interscience: New York, 1986.

[4]. Changsheng, Y.; Wali, Yu; Peisheng, M. Densities and viscosities of binary mixtures of ethyl benzene + N-methyl 2 pyrillidone, ethyl benzene + sulfolane and styrene + octane from 303.15 to 353.15 K. *J. Chem. Eng. Data* 2005, *50*, 1197–1203.

[5]. S. Senthil Raja and T. R Kubendran, 2004. Viscosities and Densities of Binary Mixtures of 1, 4 Dioxane, Carbon Tetrachloride, and Butanol at 303.15K, 308.15K, and 313.15K *J. Chem. Eng. Data, 49, 421-425.*

[6]. Baskaran.R. and Kubendran.T.R, 2007. Intermolecular Interactions in Binary Liquid Mixtures, Of Anisaldehyde with Nitrobenzene and Ethyl Benzene by Ultrasonic Measurements at (303.15, 313.15 and 313.15) K, *Chemical Physics Research Journal,* 2: 1-14.

[7]. Fabio Comelli, Romolo Francesconi, Adriana Bigi, and Katia Rubini, 2006. Excess Molar Enthalpies, Molar Heat Capacities, Densities, Viscosities, and Refractive Indices of Dimethyl Sulfoxide + Esters of Carbonic Acid at 308.15 K and Atmospheric Pressure *J. Chem. Eng. Data , 51,* 665-670

[8]. Francesconi, R.; Bigi, A.; Rubini, K.; Comelli, F. 2005 Excess enthalpies, heat Capacities, densities, viscosities, and refractive indices of dimethyl sulfoxide + three aryl alcohols at 308.14 K and atmospheric pressure. *J. Chem. Eng. Data, 50,* 1932-1937.

[9]. Hiannie, D.; Suryadi, I. 2005 Density and viscosity of several aldehydes fragrance compounds in their binary mixtures with ethanol at 298.15, 308.15 and 318.15 K. *J. Chem. Eng. Data, 50,* 2003– 2007.

[10]. S. Senthil Raja and T. R Kubendran, 2004. Viscosities and Densities of Binary Mixtures of 1, 4 Dioxane, Carbon Tetrachloride, and Butanol at 303.15K, 308.15K, and 313.15K *J. Chem. Eng. Data, 49, 421-425.*M. Young, *The Techincal Writers Handbook.* Mill Valley, CA: University Science, 1989.