Study of Molecular Interactions present in Binary Liquid Mixtures of Di-ethyl ether, Isopropyl Ether and n-Di-butyl Ether with 2-Pentanol at Different Temperatures

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ABSTRACT

The aim of present work is to concentrate on the interpretations of viscosity, density and ultrasonic velocity and their deviation of binary liquid mixtures of Di-ethyl ether, Isopropyl Ether and Di-butyl Ether with 2 Pentanol at temperature 298.15K and 303.15K.The composition of liquid mixtures is taken in terms of mole fraction from 0.1 to 1.0. From these data, excess molar volume, deviation in viscosity and isentropic compressibility have been calculated. These calculated values have been used in Redlich-Kister equation to get the coefficients and standard errors. These parameters for the given liquid mixtures have been used to study the molecular interactions.

KEYWORDS: Excess molar volume, Deviation in viscosity, Molecular interactions, Isentropic compressibility and Mole fraction.

INTRODUCTION

Ethers find an extensive applications in various fields. Di-isopropyl ether, being a crucial additives of fuel, many researchers have directed their attention to the ethers. [1-4] They are non-toxic and non-polluting chemicals and widely used octane enhancing additives in gasoline production process to improve combustion and reducing emissions and contaminant agents of automobile catalysts and alternative oxygenated stabilizers in unleaded gasoline.[5-6] Wypych et al.[7] disclosed that Di-n-butyl ether (DBE) is an important solvent and an excellent extracting agent for the use with aqueous system due to its very low solubility in water. Calculations of density, viscosity and ultrasonic velocity find an extensive applications in making characterization the thermodynamic and physico- chemical aspects of binary liquid mixtures. The molecular size and shape play a crucial role in determining the thermodynamic behaviour of the mixture. Focus on thermodynamic and transport properties of binary liquid mixtures give an important information on the kind of interactions in the constituent binaries. Literature provides an extensive data on density, viscosity and ultrasonic velocities of liquid mixtures but a collective study of density, viscosity and IR is quite scarce. The effect of molecular size, shape, chain length and chain branching of ethers on solute-solvent interactions has been predicted.

EXPERIMENTAL

The solvent used was 2-Pentanol and imported from Sigma Germany having purity 99%.The solutes are Di-isopropyl Ether (Qualigens) and Di-n-Butyl Ether (Acros Organics)having purity 99% were used after first distillation.

Experimental values of density, viscosity and ultrasonic velocities of pure liquids are compared at 308.15K, 313.15K, and these values are showing good agreement with literature values published in journals.[8-16] Specially designed stoppered bottles were used to prepare mixtures in terms of mole fractions. All the mixtures were used on same day for the measurements of above said parameters. Electronic balance of Adair Dutt with an accuracy of 0.0001 mg. was used to prepare the mixtures. Digital densitometer model number DMA 35-84138 manufactured by Anton Par with an accuracy of 0.001 gm/cm^3, reproducility of 0.0007 gm/cm^3 having capacity 2 ml, was used to measure the densities of pure liquids and their binary mixtures. Digital viscometer model number LVDVII+Pro manufactured by Brookfield Engineering Laboratories, Middleboro INC [USA], calibrated with tripled distilled water with an accuracy ± 1% of full scale of range and viscosity repeatability ± 2% was used to measure the viscosities of pure liquid and their binary liquid mixtures. Variable path single crystal interferometer from Mittal Enterprises F-05(SI No.1415071) model, New Delhi having frequency 2

MHz (with precision of ± 0.8 meter per second) was used to measure ultrasonic velocities of pure liquids and its binaries. Calibration of interferometer was done by using triply distilled water, methanol and benzene.

Table 1.0-Experimental and literature values of density, viscosity and ultrasonic velocity of 2-Pentanol, Di-ethyl ether Isopropyl Ether and Di-Butyl ether at 298.15K and 303.15K

Sr. No	Chemical	Temp/ K	Density(gm.cm^{-3})		Viscosity(mPas)		Ultrasonic velocity(ms^{-1})	
			Expt	lit	Expt	lit	Expt	lit
1.	2-Pentanol	298.15	0.8050	0.8054[8,9,10]	3.273	3.47[8,9,10]	1232	1232[11]
		303.15	0.8012	0.8009[11]	2.494	2.78[12]	1215	-
2.	Di-ethyl ether	298.15	0.7076	0.7076[13]	0.245	0.224[15]	1032	1036[16]
		303.05	0.7020	0.7020[14]	0.210	-	1018	-
3.	Isopropyl ether	298.15	0.7642	0.7542[17]	0.355	0.379[19]	997	998.2[18]
		303.15	0.7597	0.7597[18]	0.315	0.301[19]	995	975[20]
4.	Di-Butyl ether	298.15	0.7642	0.7642[21]	0.648	0.647[23]	1163	1162[24]
		303.15	0.7597	0.9597[22]	0.606	0.607[23]	1142	1142[25]

Table:-2.Density (ρ), viscosity (η), excess molar volume (V^E) deviations in viscosity (Δη), isentropic compressibility (ΔKs) for 2- Pentanol + Di-ethyl Ether

Temp/K	x_1	ρ x10^{-3} Kg.m^{-3}	η mPa.s	U m/s	V^Ex10^6 m^3.mol^{-1}	Δη mPa.s	ΔKs Tpa^{-1}
298.15K	0.0000	0.7079	0.242	1038	0.000	0.000	0.000
	0.0998	0.7165	0.350	1050	0.218	-0.194	3.100
	0.1973	0.7255	0.480	1063	0.328	-0.360	6.200
	0.2990	0.7349	0.665	1078	0.425	-0.483	8.300
	0.3994	0.7444	0.875	1093	0.476	-0.578	9.800
	0.5001	0.7541	1.105	1111	0.488	-0.653	10.500
	0.6009	0.7640	1.373	1130	0.462	-0.690	10.200
	0.7000	0.7738	1.708	1152	0.414	-0.656	8.100
	0.8005	0.7839	2.118	1176	0.333	-0.550	5.600
	0.9006	0.7942	2.622	1203	0.210	-0.350	3.000
	1.0000	0.8050	3.273	1232	0.000	0.000	0.000
303.15K	0.0000	0.7026	0.220	1018	0.000	0.000	0.000
	0.0998	0.7112	0.337	1030	0.241	-0.148	4.700
	0.1973	0.7202	0.433	1043	0.371	-0.310	8.400
	0.2990	0.7298	0.568	1057	0.461	-0.445	11.100
	0.3994	0.7394	0.728	1073	0.518	-0.551	12.700
	0.5001	0.7492	0.928	1090	0.537	-0.618	13.200
	0.6009	0.7592	1.163	1110	0.517	-0.651	12.700
	0.7000	0.7692	1.447	1132	0.463	-0.629	10.800
	0.8005	0.7795	1.828	1157	0.375	-0.515	8.200
	0.9006	0.7899	2.314	1184	0.258	-0.294	4.600
	1.0000	0.8012	2.872	1215	0.000	0.000	0.000

Table: - 3-Density (ρ), viscosity (η), excess molar volume (V^E) deviations in viscosity (Δη), isentropic compressibility (ΔKs) for 2- Pentanol + Isopropyl Ether

Temp/K	x_1	ρ x10^{-3} Kg.m^{-3}	η mPa.s	U m/s	V^Ex10^6 m^3.mol^{-1}	Δη mPa.s	ΔKs Tpa^{-1}
298.15K	0.0000	0.7183	0.378	997	0.000	0.000	0.000
	0.0990	0.7235	0.380	1012	0.300	-0.285	7.100
	0.2006	0.7298	0.459	1029	0.472	-0.500	11.300
	0.3002	0.7366	0.607	1046	0.579	-0.640	14.300
	0.3999	0.7440	0.776	1066	0.642	-0.760	16.400
	0.5003	0.7521	0.979	1087	0.659	-0.847	16.900
	0.6008	0.7610	1.225	1110	0.618	-0.892	16.400
	0.7003	0.7707	1.551	1135	0.514	-0.854	14.400
	0.7997	0.7811	1.992	1164	0.389	-0.701	11.300
	0.9006	0.7925	2.545	1196	0.232	-0.440	6.100
	1.0000	0.8050	3.273	1232	0.000	0.000	0.000
303.15K	0.0000	0.7130	0.305	978	0.000	0.000	0.000
	0.0990	0.7181	0.301	993	0.349	-0.258	7.500
	0.2006	0.7244	0.359	1010	0.542	-0.461	12.800
	0.3002	0.7314	0.491	1027	0.634	-0.585	16.600
	0.3999	0.7390	0.631	1046	0.681	-0.701	18.800
	0.5003	0.7473	0.818	1067	0.686	-0.771	19.700
	0.6008	0.7563	1.036	1091	0.652	-0.811	18.600
	0.7003	0.7661	1.339	1116	0.555	-0.764	16.500
	0.7997	0.7766	1.725	1145	0.438	-0.633	13.100
	0.9006	0.7883	2.226	1178	0.261	-0.391	7.700
	1.0000	0.8012	2.872	1215	0.000	0.000	0.000

Table:- 4 Density (ρ), viscosity (η), excess molar volume (V^E), deviations in viscosity (Δη) and isentropic compressibility (ΔKs) for 2- Pentanol + Di-Butyl Ether

Temp/K	x_1	ρx10^{-3} Kg.m^{-3}	η mPa.s	U m/s	V^Ex10^6 m^3.mol^{-1}	Δη mPa.s	ΔKs Tpa^{-1}
298.15K	0.0000	0.7647	0.645	1163	0.000	0.000	0.000
	0.1002	0.7661	0.658	1168	0.277	-0.250	5.100
	0.2061	0.7684	0.755	1173	0.424	-0.432	8.900
	0.3000	0.7709	0.871	1179	0.494	-0.562	11.800
	0.4008	0.7739	1.018	1185	0.551	-0.680	12.800
	0.4995	0.7774	1.212	1191	0.549	-0.746	13.500
	0.5994	0.7814	1.436	1199	0.524	-0.784	13.400
	0.6993	0.7860	1.728	1207	0.463	-0.755	11.300
	0.7920	0.7910	2.093	1214	0.357	-0.633	9.000
	0.9007	0.7976	2.599	1223	0.218	-0.413	5.200
	1.0000	0.8050	3.273	1232	0.000	0.000	0.000
303.15K	0.0000	0.7597	0.609	1143	0.000	0.000	0.000
	0.1002	0.7610	0.603	1148	0.319	-0.233	6.100
	0.2061	0.7634	0.670	1153	0.463	-0.405	10.600
	0.3000	0.7659	0.760	1159	0.550	-0.528	13.800
	0.4008	0.7690	0.885	1165	0.604	-0.631	15.700
	0.4995	0.7726	1.041	1172	0.602	-0.698	16.300
	0.5994	0.7767	1.225	1179	0.577	-0.740	15.500
	0.6993	0.7815	1.485	1187	0.502	-0.707	14.000
	0.7920	0.7865	1.811	1195	0.414	-0.590	11.000
	0.9007	0.7935	2.287	1205	0.237	-0.360	6.000
	1.0000	0.8012	2.872	1215	0.000	0.000	0.000

Table: -5. Parameters of Jouyban-Acree model and average percentage deviation for Density, Viscosity and Ultrasonic velocity.

System	A_0	A_1	A_2	A_3	A_4	APD
	Density					
2-Pentanol + Di-ethyl Ether	4.3604	-4.1540	0.4856	-42.0994	-53.7933	0.2642
2-Pentanol + Isopropyl Ether	-14.1392	-0.6948	-3.0328	0.0878	-	0.0230
2-Pentanol + Di-butyl Ether	-12.0876	-1.9665	-2.8154	-0.1759	-	0.0201
Viscosity						
2-Pentanol + Di-ethyl Ether	-508.0310	-655.7677	29.0232	176.3356	315.6348	1.3094
2-Pentanol + Isopropyl Ether	-204.6023	123.1041	-336.7226	311.5733	89.1882	1.2543
2-Pentanol + Di-butyl Ether	-349.5808	30.3324	125.9274	227.2982	-321.2197	1.6688
Ultrasonic Velocity						
2-Pentanol + Di-ethyl Ether	-23.6410	-39.4753	33.1050	-252.0239	-	1.3848
2-Pentanol + Isopropyl Ether	-27.4254	-7.2361	-2.9708	-0.4734	1.7057	0.0675
2-Pentanol + Di-butyl Ether	-7.6305	-0.7617	0.5255	0.7129	1.0126	0.0331

Table:-6 Interaction parameter for the binary system.

System- 2-Pentanol +	Temp/K	d	σ	W_{visc}/RT (kj.mol^{-1})	σ	H_{12} mPa.s	σ
Di-ethyl ether	298.15	-0.695	0.04	-0.695	0.04	0.375	0.08
	303.15	-0.942	0.04	-0.942	0.04	0.265	0.08
Isopropyl Ether	298.15	-0.695	0.04	-0.695	0.04	0.375	0.08
	303.15	-0.942	0.04	-0.942	0.04	0.265	0.08
Di-Butyl Ether	298.15	-0.695	0.04	-0.695	0.04	0.375	0.08
	303.15	-0.942	0.04	-0.942	0.04	0.265	0.08

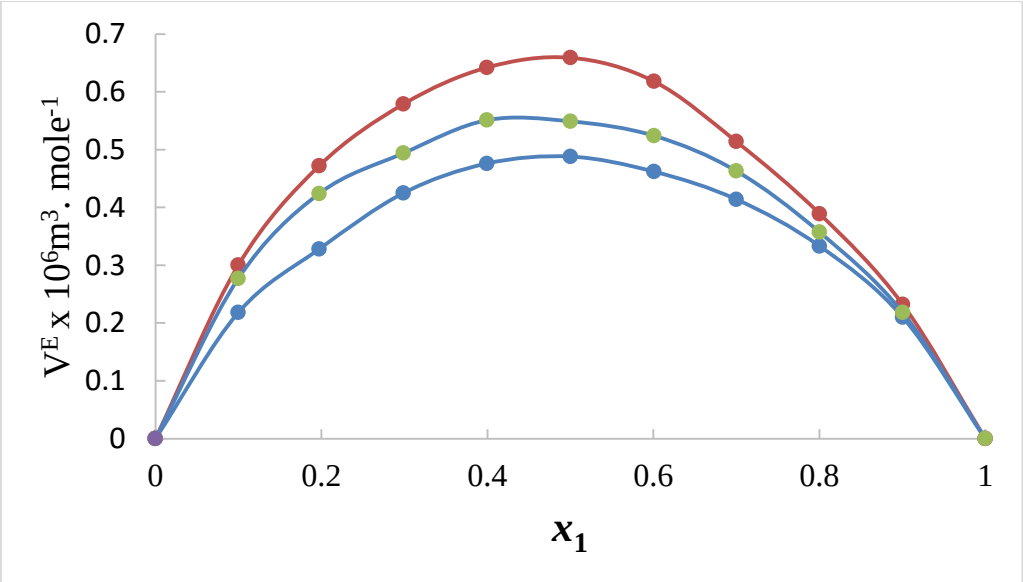

Figure 1:-Plot of excess molar volume against mole fraction of 2- Pentanol (x_1) with (1-x_1) mole fractions of Diethyl ether (●), Isopropyl Ether (●) and Di-butyl Ether (●) at 298.15K.

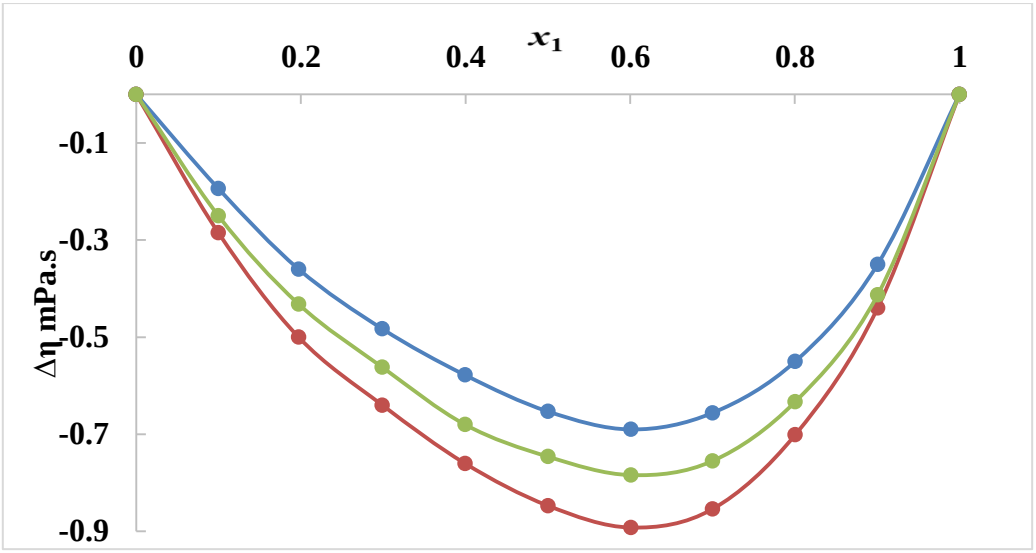

Figure 2:-Plot of deviation in viscosity against mole fraction of 2- Pentanol (x_1) with (1-x_1) mole fractions of Diethyl ether (●), Isopropyl Ether (●) and Dibutyl Ether (●)at 298.15K.

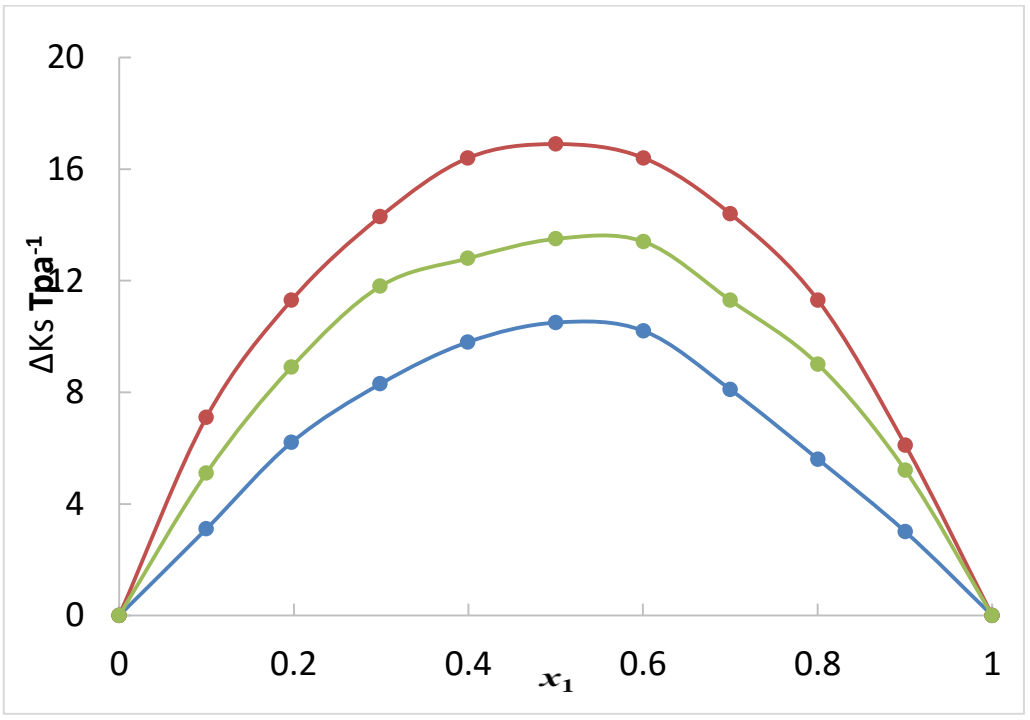

Figure:-3. Plot of deviation in compressibility factor against mole fraction of 2- pentanol (x_1) with (1-x_1) mole fractions of Diethyl ether (●), Isopropyl Ether (●) and Dibutyl Ether (●) at 298.15K.

RESULT AND DISCUSSION

The values of density, viscosity and ultrasonic velocity as a function of mole fractions obtained from an experiment at temperature 308.15 and 313.15K are clearly tabulated. The values of density are exercised to compute the excess molar volumes V^E by employing the equation,

$$V^E/ (cm^3.mole^{-1}) = (x_1M_1 + x_2M_2)/ \rho_{12} - (x_1M_1/\rho_1) - (x_2M_2/\rho_2) \quad (1)$$

Where ρ_{12} is the density of the mixture, x_1, M_1, ρ_1 and x_2, M_2, ρ_2 are the mole fractions, molecular weights and densities of pure components 1 and 2 respectively.

The deviations in viscosities Δη were estimated by employing the relation,

$$\Delta\eta = \eta_{12} - x1\eta_1 - x_2\eta_2 \quad (2)$$

Whereη_{12} is the viscosity of the mixture, x_1,x_2 and η_1, η_2 are the mole fractions and viscosities of the pure components 1 and 2 respectively.

The excess isentropic compressibilities (Ks) were computated by employing the relation,

$$Ks = 1/u^2p \quad (3)$$

And the deviation in isentropic compressibilitis (ΔKs) were estimated by using the relation,

$$\Delta Ks = Ks_{(12)} - x_1 Ks_1 - x_2 Ks_2 \quad (4)$$

Where $Ks_{(12)}$ is the compressibilities of the mixture, x_1,x_2 and, Ks_1, Ks_2 are the mole fractions and isentropic compressebilities of the pure components 1 and 2 respectively.

The excess molar volumes, deviation in viscosities and isentropic compressibilitis were put into Redlich Kister equation of following type,

$$Y = x_1 x_2 \sum_i^n a_i (x_1 - x_2)^i \quad (5)$$

Where Y is either, $V^{E,}$ Δη, or ΔKs and n is the degree of polynomial. Coefficients a_i were sought by applying equation 5 to experimental results using a least-squares regression methods. In each case, the number of coefficients are determined from the examination of variation in standard deviation (σ) and it was estimated by adopting the equation,

$$\sigma(Y) = [\sum (Y_{expt} - Y_{cal})^2]^{1/2} / N\text{-}n \quad (6)$$

Where N is the number of data points and n is the number of coefficients. The computated values of the coefficients (a_i) along with the standard deviations (σ) are displayed in the table 6.

Hind et. al.offered an equation for the viscosity of binary liquid mixtures as,

$$\eta = x_1^2.\ln\eta_1 + x_1^2.\ln\eta_2 + 2x_1x_2\, H_{12} \quad (7)$$

Katti and Chaudhari suggested following equation;

$$\log(\eta mVm) = x_1 \log(\eta_1 V_1) + x2\log(\eta 2V2) + x_1x_2[Wvis/(RT)] \quad (8)$$

where Wvis is defined as interaction energy for the activation of flow. The Jouyban and Acree proposed a model for correlating the density and viscosity of liquid mixtures at various temperatures. The equation is,

$$ln y_{m,T} = f_1 \ln y_{1,T} + f_2 \ln y_{2,T} + f_1 f_2 \sum [A_j (f_1 - f_2)^{j/} T] \quad (9)$$

Where $y_{m,T}$, y_1, T and y_2,T is density or viscosity of the mixture and solvent 1 and 2 respectively at given temperature T and f_1, f_2 are the mole fractions and A_j are model constants.

Jouyban – Acree model is applied to the density, viscosity and speed of sound of data and the correlating ability of this model was tested by calculating the average percent deviation (APD) between the experimental and calculated density, viscosity and speed of sound as

$$APD = (100/N) \sum [(y_{expt} - y_{calc}) / y_{expt}] \quad (10)$$

Where N is the number of data points in each set. The optimum number of constants Aj and in each case they were determined from the examination of APD values.

The excess volume of binary liquid mixture of 2-Pentanol with Di-ethyl ether, Isopropyl Ether and Di-butyl Ether shows positive deviation with maxima observed at mole fraction 0.5. It has also been observed that excess volume increases with increase in temperature. Same trend is observed for deviation in compressibility factor for above said binary liquid system with maxima at mole fraction 0.5.indiacting maximum interactions at this composition.

The deviation in viscosities is showing negative deviation for the given system. The minima is observed at mole fraction composition 0.6 for the given system. It has been also observed that deviation in viscosities increases with increase in temperature. This increase is somewhat greater for di-ethyl ether, Isopropyl Ether than Dibutyl Ether. Jouyban-Acree model is applied to these systems to calculate the values of average percentage values and these values are found to be within the limit. The interacting parameters along with standard deviations are also calculated from Nissan and Grunberg, Katti- Choudhari and Hind et al equations. The values of standard deviations are in the fraction showing an accuracy in the results.

ACKNOWLEDGEMENT

Authors are thankful to the Principal, Head of Chemistry Department, LVH College of Arts, Commerce and Science College, Panchavati, Nashik-3, for extending their cooperation and facilities provided.

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