STUDY OF MOLECULAR INTERACTIONS PRESENT IN BINARY LIQUID MIXTURES OF ANISOLE, PHENETOLE AND BENZYL ETHER WITH 2-PENTANOL AT DIFFERENT TEMPERATURES

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Abstract

The objective of present work under study, is to concentrate on the interpretations of viscosity, density and ultrasonic velocity and their deviations of binary liquid mixtures ofAnisole, Phenetole and Benzyl ether with 2 Pentanol at temperature 303.15K.and 313.15K.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.

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

1. INTRODUCTION

Excess properties and their deviations play a crucial role in providing information regarding molecular interactions and their applications in the industry in binary liquid mixtures of 2-pentanol with anisole, phenetole and benzyl ether. Volumetric and acoustic properties variation with molecular size, shape, chain length and extent of molecular association for binary liquid mixtures of primary alcohol with aliphatic hydrocarbons have been reported [1-3]. The investigation of these properties are found rare in case of primary alcohol with aromatic hydrocarbon [4-6].Anisole is from class aromatic ethers, is practically associated with number of applications such as dyes, pigments and perfumery and acts as a starting material to prepare different derivatives. Thus to look into the physical properties of binary mixture with anisole has immense interest in the literature. [23-28]

Pentanol has all the properties necessary to replace gasoline as an internal combustion fuel. Pentanol can be prepared by fractional distillation of fuel oil. To reduce the use of fossil fuels, research is underway to develop cost-effective methods of producing (chemically identical) bio-pentanol with fermentation.2-pentanol is used as a solvent and an intermediate in the manufacture of other chemicals. 2-Pentanol is a component of many mixtures of amyl alcohols sold industrially. It has been detected in fresh bananas by gas chromatography–mass spectrometry, at an abundance of 14.26±2.63 ppm.

II. EXPERIMENTAL

Anisole, Phenetole and Benzyl ether were from Alfa Aesar while 2- Pentanol from Aldrich chemicals. 2-Pentanol has been used without any purification while Anisole, Phenetole and Benzyl ether (purity stated to be 99%) have been used after purification. The purities of Anisole, Phenetole and Benzyl ether were 99.7% respectively. 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 for the preparation binary liquid mixtures. The error in mole fraction is around 0.0002. Digital densitometer model number DMA 35-84138 made 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, ethanol and benzene. The measured values of densities, viscosities and ultrasonic velocities have been compared with reference values [7-21] and all values are disclosed in table1.

III.RESULT AND DISCUSSION

Table 1.-Experimental and literature values of density, viscosity and ultrasonic velocity of 2-Pentanol, Anisole, Phenetole and Di-benzyl ether at 303.15K and 313.15K

Sr. No	Chemical	Temp/ K	Density		Viscosity		Ultrasonic velocity	
			Expt	lit	Expt	lit	Expt	lit
1.	2-Pentanol	303.15	0.8012	0.8009[7]	2.494	2.78[8]	1197	-
		313.15	0.7941	0.7936[9]	2.115	-	1179	1178[10]
2.	Anisole	303.15	0.9845	0.9846[11]	0.928	0.929[12]	1387	1387[13]
		313.15	0.9750	0.9750[14]	0.780	0.781[14]	1346	1346[15]
3.	Phenetole	303.15	0.9556	0.9555[16]	1.037	1.036[16]	1343	-
		313.15	0.9464	0.9465[17]	0.893	0.894[16]	1302	-
4.	Benzyl ether	303.15	1.0370	1.0370[18]	4.077	4.071[19]	1102	1102[20]
		313.15	1.0315	-	3.205	3.209[21]	1065	1065[21]

Table-2.Density (p), viscosity (η), excess molar volume (V^E) deviations in viscosity (Δη), isentropic compressibility (ΔKs) for 2- Pentanol + Anisole

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}
303.15K	0.0000	0.9844	0.928	1385	0.000	0.000	0.000
	0.1002	0.9673	0.767	1366	-0.146	-0.356	-7.300
	0.2007	0.9503	0.718	1347	-0.314	-0.600	-12.700
	0.2993	0.9334	0.730	1328	-0.458	-0.780	-16.600
	0.3997	0.9156	0.736	1309	-0.539	-0.969	-18.700
	0.4950	0.8986	0.773	1293	-0.606	-1.117	-20.000
	0.5998	0.8790	0.890	1274	-0.569	-1.204	-18.500
	0.6996	0.8600	1.076	1259	-0.489	-1.212	-16.500
	0.7950	0.8415	1.400	1244	-0.365	-1.073	-13.000
	0.8999	0.8208	1.877	1229	-0.172	-0.800	-7.700

ISSN (PRINT): 2393-8374, (ONLINE): 2394-0697, VOLUME-11, ISSUE-9, 2024
DOI: 10.21276/ijcesr.2024.11.9.28

	1.0000	0.8012	2.872	1215	0.000	0.000	0.000
313.15K	0.0000	0.9750	0.786	1342	0.000	0.000	0.000
	0.1002	0.9576	0.712	1326	-0.086	-0.207	-9.010
	0.2007	0.9406	0.720	1309	-0.228	-0.333	-16.220
	0.2993	0.9239	0.754	1291	-0.369	-0.430	-20.680
	0.3997	0.9065	0.777	1273	-0.470	-0.540	-23.660
	0.4950	0.8896	0.843	1258	-0.522	-0.601	-25.420
	0.5998	0.8702	0.929	1240	-0.477	-0.654	-24.170
	0.6996	0.8515	1.016	1225	-0.403	-0.700	-22.150
	0.795	0.8332	1.273	1210	-0.272	-0.570	-17.240
	0.8999	0.8129	1.604	1194	-0.096	-0.378	-9.630
	1.0000	0.7941	2.115	1179	0.000	0.000	0.000

Table-3. Density (p), viscosity (η), excess molar volume (V^E), deviations in viscosity (Δη) and isentropic compressibility (ΔKs) for 2- Pentanol + Phenetole

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}
303.15K	0.0000	0.9556	1.036	1347	0.000	0.000	0.000
	0.1008	0.9433	0.776	1335	-0.172	-0.445	-8.700
	0.2008	0.9309	0.662	1322	-0.367	-0.743	-16.200
	0.3005	0.9177	0.566	1308	-0.504	-1.022	-21.000
	0.4004	0.9038	0.479	1294	-0.607	-1.292	-24.000
	0.5010	0.8888	0.404	1281	-0.638	-1.552	-26.000
	0.6002	0.8730	0.456	1267	-0.595	-1.682	-25.000
	0.6994	0.8562	0.600	1254	-0.481	-1.720	-21.700
	0.8006	0.8385	1.031	1241	-0.358	-1.475	-17.000
	0.9000	0.8202	1.631	1227	-0.183	-1.057	-8.900
	1.0000	0.8012	2.872	1215	0.000	0.000	0.000
313.15K	0.0000	0.9464	0.892	1305	0.000	0.000	0.000
	0.1008	0.9339	0.708	1296	-0.121	-0.307	-11.580
	0.2008	0.9214	0.618	1287	-0.280	-0.520	-22.630
	0.3005	0.9084	0.509	1275	-0.420	-0.751	-29.390
	0.4004	0.8946	0.438	1264	-0.511	-0.944	-34.810
	0.5010	0.8798	0.367	1251	-0.541	-1.138	-36.840
	0.6002	0.8642	0.361	1237	-0.495	-1.265	-35.160
	0.6994	0.8477	0.460	1222	-0.391	-1.287	-30.380
	0.8006	0.8303	0.719	1208	-0.275	-1.152	-22.970
	0.9000	0.8124	1.203	1192	-0.121	-0.790	-11.650
	1.0000	0.7941	2.115	1179	0.000	0.000	0.000

Table-4.Density (p), viscosity (η), excess molar volume (V^E), deviations in viscosity (Δη) and isentropic compressibility (ΔKs) for 2- Pentanol + Benzyl 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}
303.15K	0.0000	1.0360	4.073	1528	0.000	0.000	0.000
	0.0989	1.0213	3.537	1445	0.137	-0.417	12.600
	0.2000	1.0052	3.192	1384	0.225	-0.641	19.600
	0.2997	0.9880	2.769	1335	0.277	-0.944	25.200
	0.3997	0.9692	2.422	1296	0.295	-1.171	28.300

ISSN (PRINT): 2393-8374, (ONLINE): 2394-0697, VOLUME-11, ISSUE-9, 2024
DOI: 10.21276/ijcesr.2024.11.9.28

	0.5005	0.9482	2.061	1265	0.314	-1.411	29.100
	0.6000	0.9254	1.831	1242	0.289	-1.521	28.100
	0.7009	0.8995	1.706	1225	0.259	-1.525	24.100
	0.7999	0.8710	1.756	1214	0.201	-1.356	20.400
	0.8990	0.8386	2.046	1210	0.139	-0.947	12.400
	1.0000	0.8012	2.872	1215	0.000	0.000	0.000
313.15K	0.0000	1.0311	3.204	1499	0.000	0.000	0.000
	0.0989	1.0159	2.780	1412	0.195	-0.316	15.500
	0.2000	0.9996	2.485	1346	0.283	-0.501	25.960
	0.2997	0.9821	2.191	1294	0.350	-0.687	33.880
	0.3997	0.9630	1.904	1255	0.381	-0.865	38.160
	0.5005	0.9419	1.651	1224	0.377	-1.008	40.060
	0.6000	0.9188	1.470	1201	0.361	-1.081	38.380
	0.7009	0.8926	1.328	1186	0.338	-1.113	32.530
	0.7999	0.8639	1.382	1176	0.272	-0.951	26.290
	0.8990	0.8314	1.574	1174	0.188	-0.651	15.090
	1.0000	0.7941	2.115	1179	0.000	0.000	0.000

Table:-5 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
Anisole	303.15	-2.995	0.03	-3.015	0.03	-0.553	0.240
	313.15	-1.813	0.02	-1.829	0.02	0.116	0.080
Phenetole	303.15	-5.187	0.15	-5.196	0.15	-1.373	0.500
	313.15	-4.923	0.13	-4.927	0.13	-0.965	0.310
Benzyl ether	303.15	-2.182	0.17	-2.021	0.17	0.461	0.150
	313.15	-2.000	0.10	-1.839	0.10	0.485	0.080

Table:-6- 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					
Anisole + 2-Pentanol	12.8037	0.9685	-3.0604	-	-	0.0138
Phenetole + 2-pentanol	19.0050	1.9552	-2.2686	-	-	0.0094
Benzyl ether + 2-Pentanol	49.1283	16.6654	4.8494	1.4854	-	0.0108
Viscosity						
Anisole + 2-Pentanol	-779.8965	-6.7803	-175.8302	-	-	5.1581
Phenetole + 2-pentanol	-1679.7187	-760.9098	1170.4517	871.8868	-1185.3683	2.4627
Benzyl ether + 2-Pentanol	-589.4665	-648.0381	-256.8082	157.3763	-87.4866	0.4879
Ultrasonic Velocity						
Anisole + 2-Pentanol	-4.4025	-2.1457	3.7607	-	-	0.0674

ISSN (PRINT): 2393-8374, (ONLINE): 2394-0697, VOLUME-11, ISSUE-9, 2024
DOI: 10.21276/ijcesr.2024.11.9.28

Phenetole + 2-Pentanol	3.5895	-3.0908	0.6704	-0.6570	-3.2822	0.1095
Benzyl ether + 2-Pentanol	-92.2811	10.1022	-6.9430	2.1439	-11.2890	0.1356

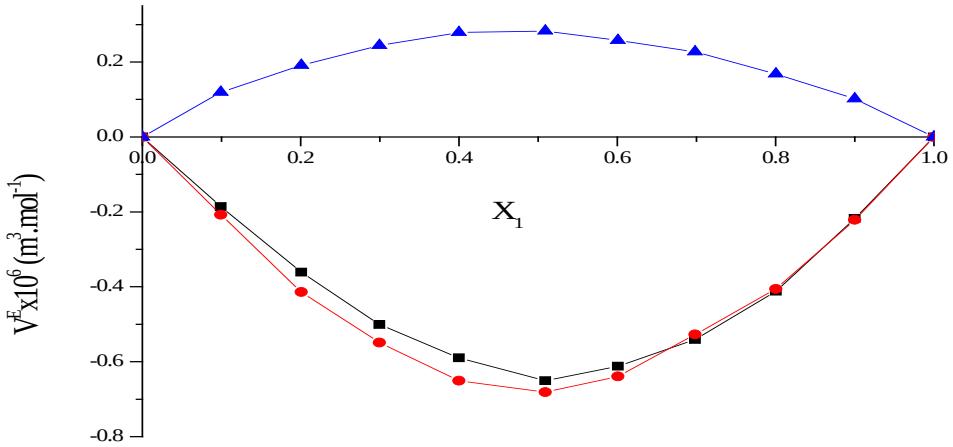

Figure:-1 Plot of excess molar volume against mole fractions of 2-pentanol (X_1) with (1-X_1) mole fractions of anisole (■), phenetole (●) and benzyl ether (▲) at 303.15K.

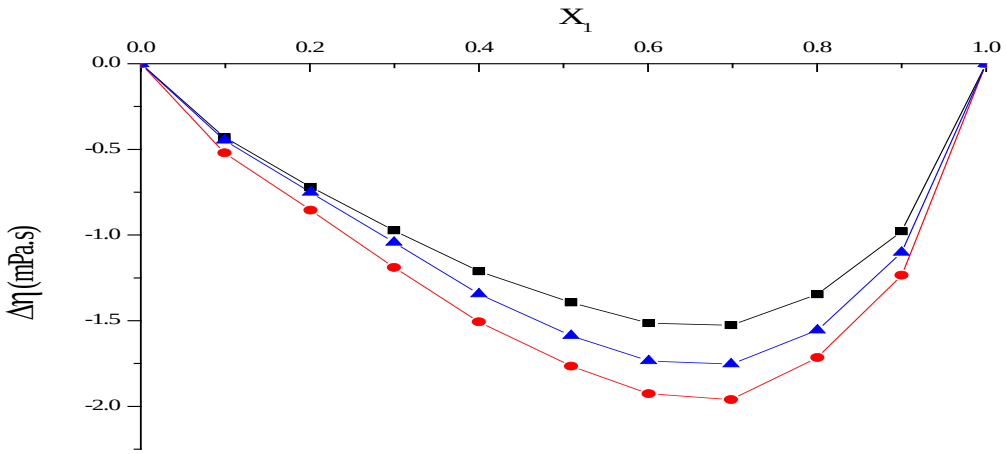

Figure:-2 Plot of deviation in viscosity against mole fractions of 2-pentanol (X_1) with (1-X_1) mole fractions of anisole (■), phenetole (●) and benzyl ether (▲)) at 303.15K.

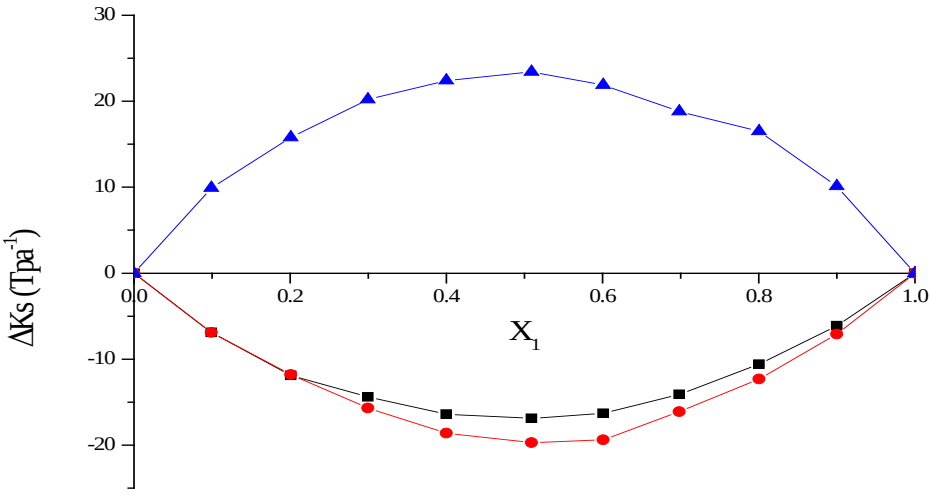

Figure:-3 Plot of deviation in compressibility against mole fractions of 2-pentanol (x_1) with (1-x_1) mole fractions of anisole (■), phenetole (●) and benzyl ether (▲) at 303.15K.

The values of density, viscosity and ultrasonic velocity as a function of mole fractions obtained from an experiment at temperature 303.15 and 313.15K are clearly tabulated. The values of density are exercised to compute the excess molar volumes V^E adopting the equation,

$V^E/ (cm^3.mole^{-1}) = (x_1M_1 + x_2M_2)/ p_{12} - (x_1M_1/p_1) - (x_2M_2/p_2)$ …… (1)

Where p_{12} is the density of the mixture, x_1, M_1, p_1 and x_2, M_2, p_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,

$\Delta\eta = \eta_{12} - x_1\eta_1 - x_2\eta_2$ ..... (2)

Where η_{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,

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

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

$\Delta Ks = Ks_{(12)} - x_1 Ks_1 - x_2 Ks_2$…….. (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,

$$Y = x_1x_2 \sum_i^n a_i(x_1 - x_2)^i \text{……} (5)$$

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 numbers of coefficients are determined from the examination of variation in standard deviation (σ) and it was estimated by adopting the equation,

$\sigma(Y)=[\sum(Y_{expt}-Y_{cal})^2]^{1/2}/N-n$ ……(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 etal.offered an equation for the viscosity of binary liquid mixtures as,

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

Katti and Chaudhari suggested following equation;

$\log(\eta_m V_m) = x_1\log(\eta_1V_1) + x_2\log(\eta_2V_2) + x_1x_2[Wvis/(RT)]$ …….(8)

whereWvis 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,

ISSN (PRINT): 2393-8374, (ONLINE): 2394-0697, VOLUME-11, ISSUE-9, 2024
DOI: 10.21276/ijcesr.2024.11.9.28

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

$APD=(100/N)\sum[(y_{expt}-y_{calc})/y_{expt}]$ ……. (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 variation (disparity) and deviation in compressibility factor with mole fraction x_1 of 2-Pentanol with anisole, phenetole and benzyl ether at 303.15K and 313.15K is clearly shown in fig 1, 2, 3. From experimental values, excess volume, deviation in viscosity and deviation in compressibility factor for binary liquid systems containing 2-pentanol with anisole, phenetole and benzyl ether have been computed at temperature 303.15 and 313.15K and shown in table 2-4. Experimental data shows negative deviation for excess volume and deviation in compressibility factor for the system 2-pentanol with anisole and phenetole whereas shows positive deviation for 2- pentanol with benzyl ether system over the entire range of composition of mole fractions. The maxima and minima in the graph are observed at composition 0.5 mole fraction.It is found that the excess volume increases with increase in temperature but increase is notable in case of anisole and phenetole but it is somewhat less in benzyl ether. Literature [26] gives excess volume variation of anisole and phenetole with propylene carbonate at 303.15K, 313.15K but no data has been reported for anisole and phenetole with 2- pentanol. C_6H_5 group is more electron donating than CH_3, the oxygen atom of phenetole has a more negative charge than that of anisole and hence stronger interactions are observed in phenetole molecules [28]. The factors such as hydrogen bonding, dipole-dipole interactions and molecular size and shape are responsible for such trends. The trend of excess volume is, 2-pentanol + benzyl ether > 2-pentanol + anisole > 2 -pentanol + phenetole. It has been also predicted that excess volume increases with increase in temperature for 2-pentanol + anisole > 2 -pentanol + phenetole and 2- pentanol + benzyl ether binary systems.

Deviation in viscosity is negative for all systems at given temperatures in figure (2). It has been also observed that deviation in viscosity increases with temperature for 2-pentanol + anisole, phenetole and benzyl ether with 2- pentanol system. The factors such as hydrogen bonding, dipole-dipole interactions and molecular size and shape are responsible for such trends. Figure.2 specifies the variation of viscosity deviation with the mole fractions x_1 of 2-pentanol. It has been observed that Δη are negative for all systems with minima at 0.7 mole fractions, showing the weak interactions present in the binary mixtures under consideration. Δη values slightly increase with increase in temperature. Deviation in compressibility factor is also disclosed in the table1, 2, and 3 for anisole, phenetole and benzyl ether with 2- pentanol. It shows negative trend for anisole and phenetole while positive for benzyl ether with 2- pentanolwhich is graphically disclosed in figure 3.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 values of density, viscosity and speed of sound.

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.

Conflict of Interest:-The authorspronounce no conflict of interest.

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ISSN (PRINT): 2393-8374, (ONLINE): 2394-0697, VOLUME-11, ISSUE-9, 2024
DOI: 10.21276/ijcesr.2024.11.9.28