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Evaluation of excess internal pressure and excess enthalpy of binary mixtures containing of 1,3-dioxolane and monoalkanols at 298.15K.

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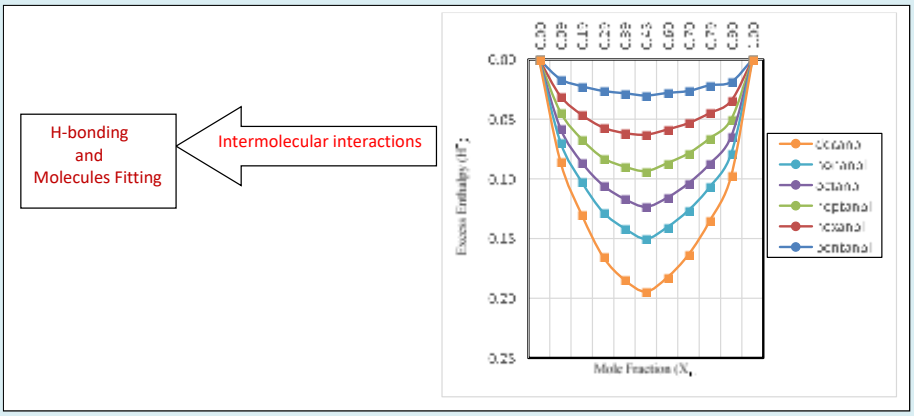
Abstract

An internal pressures and enthalpy of six binary liquid mixtures 1,3-dioxolane with mono alkanols have been computed at 298.15K. Values of excess internal pressure (p_i^E) and excess enthalpy (H^E) have also been evaluated from the data of pure components. The values of excess functions provide an in-depth understanding of the intermolecular interactions between the components. The results have been compared with experimental values and good agreement has been found.

Keywords: *Binary mixtures, Density, Sound velocity, viscosity, enthalpy, internal pressure, hydrogen bonding, molecular interaction.*

Graphical abstract



1. Introduction

The role of internal pressure in solution thermodynamic was recognized by many workers[1-4], since it is highly useful in understanding the intermolecular interaction, internal structure and clustering phenomenon. Several investigations [5-10] have been carried out to evaluate internal pressure in liquid mixtures. Moreover, numerous studies have explored and is still in progress to study molecular interactions in liquid mixtures in the light of excess internal pressure. The internal pressure, and hence enthalpy of mixing are explored using both measurable experimental parameters like density, Sound velocity, viscosity etc. and the thermodynamic data such as coefficient of volume expansion, isothermal compressibility, etc, Suryanaryana have given an indirect method of evaluating the internal pressure. From the known values of density, sound velocity, and viscosity, internal pressure was evaluated to understand the intermolecular interactions within the mixture. The excess enthalpy of binary mixtures was successfully evaluated on the basis of internal pressure data. Flory theory was applied by several workers [10-12], to estimate excess enthalpies in binary liquid mixtures. The present investigation aim to evaluate theoretically internal pressure of six binary liquid mixtures through one approach. Excess enthalpies of systems under consideration are also estimated using computed values of internal pressure through one method, and results are compared with those obtained from Flory theory. An interaction study in the mixtures is discussed in the light

of excess internal pressure. The binary mixtures under the present investigation are:

System I- 1,3-dioxolane + Pentanol
System II- 1,3-dioxolane + Hexanol
System III- 1,3-dioxolane + Heptanol
System IV- 1,3-dioxolane + Octanol
System V - 1,3-dioxolane + Nonanol
System VI- 1,3-dioxolane + Decanol

In the present study, the sound velocity (u), density (ρ) and viscosity (η) of six binary liquid mixtures have been investigated at 298.15 K over the entire range of mole fractions. From these experimental values, enthalpy (H), internal pressure (P_i) and their deviations excess enthalpy (H^E), and excess internal pressure (P_i^E) was evaluated and analyzed to gain insight into the nature of molecular interactions between the constituents of the binary liquid mixtures. We know that excess thermodynamic properties such as excess enthalpy (H^E) and excess internal pressure(p_i^E) good information provide a understanding the inter molecular interaction between component molecules of the liquid mixtures. This work is the first to report a combined an investigation into the sound velocity (u), density (ρ), and viscosity (η) of six binary liquid mixturesof practical importance in soaps, detergents, cosmetics and perfumes.

2. Experimental Section

2.1 Chemicals 1,3-dioxolane (CDH New Delhi) was supplied with purity ≥ 99.7 %, pentanol(CDH New Delhi) with ≥ 99.7 %, hexanol(CDH New Delhi) with ≥ 99.5 %, heptanol(CDH New Delhi) with ≥ 99 %, octanol (CDH New Delhi) with ≥ 99.7 %, nonanol(CDH New Delhi) with ≥ 99 %, decanol(CDH New Delhi) with ≥ 99 %, respectively with corresponding literature values [13-24]. Since the agreement with the literature values is very good.

Table 1. Ultrasonic velocity (u), density (ρ) and viscosity (η) of pure Compounds at 298.15K.

Compound	ρ (g.cm^{-3})		u (m.s^{-1})		η (mPa s)	
	Observed	Review of Literature	Observed	Review of Literature	Observed	Review of Literature
1,3-Dioxolane	1.0616	1.0577[17]	1340	1338[17]	0.5885	0.5878[17]
		1.0586[17]		1338[18]		0.5873[17]
Pentanol	0.8124	0.8108[13]	1198	1197[16]	3.3978	3.5411[13]
		0.8107[13]		1268[22]		3.5424[13]
Hexanol	0.8176	0.8187[13]	1306	1304[15]	4.6091	4.5924[23]
		0.8152[15]		1303[15]		4.5932[20]
Heptanol	0.8196	0.8187[13]	1325	1327[15]	5.9066	5.9443[13]
		0.8197[19]		1327[24]		5.9443[24]
Octanol	0.8236	0.8216[13]	1350	1348[14]	7.1508	7.6605[13]
		0.8218[13]		1347[22]		7.5981[13]
Nonanol	0.8248	0.8244[15]	1366	1365[15]	8.9258	9.0230[21]
		0.8242[15]		1364[24]		9.0200[24]
Decanol	0.8292	0.8267[15]	1378	1380[15]	11.8027	11.825[15]
		0.8264[19]		1379[24]		11.829[15]

2.2 Methods All binary liquid mixtures were prepared by accurately weighing the required amounts of pure liquids using an electronic balance (Citizen Scale (I) Pvt. Ltd., Mumbai, India) with a precision of ±0.1 mg. The uncertainty in the determination of mole fractions was within ±0.0005 for all mixtures. The binary mixtures were prepared gravimetrically and stored in air-tight, stoppered volumetric flasks. For each experimental session, four to five samples were prepared and their density, viscosity, and ultrasonic velocity were measured on the same day to minimize experimental error. The density of each sample was measured using a 25 ml specific gravity bottle, which was immersed in a thermostatic water bath maintained at the experimental temperature (298.15 ± 0.1 K). To ensure accuracy, the volume of the specific gravity bottle at the experimental temperature (298.15 K) was determined by filling it with distilled water and calculating the volume based on its known density. The ultrasonic velocity was measured using a multi-frequency interferometer (Model F-80D, Mittal Enterprises, New Delhi, India) operating at a298.15K. A fixed frequency generator working at 3 MHz. its resonant frequency, the crystal undergoes rapid mechanical oscillations, generating ultrasonic waves. These waves can propagate through the liquid in the vessel, creating effects like cavitation, acoustic streaming, or enhanced mixing. An experimental setup for measuring the viscosity by Ostwald viscometer. Prior to measurements, the viscometer was calibrated with distilled water at 298.15 K to ensure accuracy. And multiple measurements (five repetitions) were taken for each

sample to ensure accuracy. The viscosity measurements were associated with an uncertainty of ±0.000005 mPa.s, reflecting the high precision of the experimental method.

3. Results and Discussion

Table 2 presents the experimentally measured values of density (ρ), sound velocity (u), and viscosity (η) for the binary mixtures of 1,3-dioxolane with various 1-alkanols at 298.15 K. From these values, we have computed enthalpy (H) and internal pressure (P_i) are presented in table 2.

Table 2. Density (ρ), ultrasonic velocity (u), and viscosity (η), Internal pressure (P_i) and Free Volume (V_f) of binary mixture of 1,3-dioxolane (1) + 1-alkanol (2) at 298.15K and frequency 3 MHz.

Mole fraction 1,3-Dioxolane (x_1)	Density (ρ) / g.cm^{-3}	Sound velocity (u) / ms^{-1}	Viscosity (η) / mPas.	Internal pressure (P_i) × 10^9/ N m^{-2}	Enthalpy (H) × 10^6
1,3-Dioxolane + Pentanol					
0.0000	0.8124	1198	3.3978	2.9099	0.3156
0.0939	0.8276	1284	2.3973	3.2892	0.3450
0.1942	0.8436	1290	1.8970	3.3763	0.3468
0.2941	0.8640	1296	1.4437	3.4821	0.3384
0.3942	0.8836	1300	1.1866	3.5776	0.3341
0.4787	0.9068	1304	1.0904	3.6885	0.33.8
0.5999	0.9316	1310	0.9311	3.8155	0.3262
0.6972	0.9596	1318	0.7717	3.9663	0.3236
0.7928	0.9876	1324	0.7171	4.1099	0.3201
0.9035	1.0260	1332	0.6489	4.3085	0.3166
1.0000	1.0616	1340	0.5885	4.4982	0.3135
1,3-Dioxolane + Hexanol					
24.74130	0.8176	1306	4.6091	3.3333	0.4163
0.0912	0.8252	1317	3.3826	3.4069	0.4112
0.1955	0.8432	1320	2.3306	3.4931	0.4003
0.2923	0.8584	1322	1.9839	3.5642	0.3899
0.3982	0.8792	1325	1.5720	3.6629	0.3787
0.4942	0.8992	1327	1.3059	3.7548	0.3683
0.6059	0.9264	1330	1.0343	3.8815	0.3567
0.6976	0.9508	1332	0.9131	3.9927	0.465
0.8018	0.9836	1335	0.7680	4.1444	0.3352
0.8914	1.0168	1337	0.7304	4.2939	0.3254
1.0000	1.0616	1340	0.5885	4.4982	0.3135
1,3-Dioxolane + Heptanol					
0.0000	0.8196	1325	5.9066	3.4147	0.4838
0.0928	0.8304	1334	4.3181	3.4949	0.4725
0.1905	0.8412	1334	3.2577	3.5404	0.4552
0.2939	0.8592	1335	2.5895	3.6202	0.4373
0.3894	0.8740	1335	1.9926	3.6826	0.4201
0.4818	0.8916	1336	1.5315	3.7609	0.4042
0.6021	0.9184	1337	1.2190	3.8784	0.3835
0.6952	0.9420	1337	1.0959	3.9780	0.3667
0.7892	0.9756	1338	0.9903	4.1245	0.3505
0.9006	1.0156	1339	0.7057	4.2985	0.3309
1.0000	1.0616	1340	0.5885	4.4982	0.3135
1,3-Dioxolane + Octanol					
0.0000	0.8296	1350	7.1508	3.5546	0.5619
0.0885	0.8296	1350	5.6095	3.5585	0.5363
0.1967	0.8464	1349	3.9321	3.6225	0.5100

0.2998	0.8560	1348	3.2616	3.6596	0.4845
0.3902	0.8712	1348	2.4284	3.7245	0.4629
0.4963	0.8876	1348	1.9058	3.7947	0.4375
0.6008	0.9140	1347	1.3631	3.9032	0.4117
0.6925	0.9340	1348	1.1376	3.9930	0.3905
0.7975	0.9676	1348	0.9141	4.1367	0.3652
0.8940	1.0104	1348	0.7652	4.3197	0.3421
1.0000	1.0616	1340	0.5885	4.4982	0.3135
	1,3-Dioxolane + Nonanol				
0.0000	0.8248	1366	8.9258	3.5970	0.6291
0.0876	0.8336	1366	6.8601	3.6354	0.6020
0.1913	0.8404	1363	5.8531	3.6530	0.5684
0.2942	0.8504	1359	4.4022	3.6802	0.5347
0.3963	0.8692	1355	3.1558	3.7449	0.5014
0.4959	0.8844	1352	2.3340	3.7978	0.4697
0.6050	0.9092	1349	1.7321	3.8913	0.4354
0.6947	0.9332	1346	1.3334	3.9807	0.4072
0.7993	0.9648	1343	0.9642	4.1018	0.3744
0.9013	1.0084	1340	0.8031	4.2372	0.3402
1.0000	1.0616	1340	0.5885	4.4982	0.3135
	1,3-Dioxolane + Decanol				
0.0000	0.8292	1378	11.8027	3.6639	0.6990
0.0881	0.8364	1374	8.5615	3.6797	0.6634
0.191	0.8396	1370	7.8207	3.6977	0.6226
0.2921	0.8560	1366	5.5340	3.7331	0.5827
0.3937	0.8672	1362	4.2319	3.7654	0.5429
0.4956	0.8824	1358	3.4173	3.8145	0.5035
0.604	0.9076	1353	2.5370	3.9018	0.4615
0.7129	0.9308	1348	1.5262	3.9793	0.4198
0.7983	0.9616	1344	1.1637	4.0927	0.3871
0.8971	1.0040	1340	0.8623	4.2541	0.3505
1.0000	1.0616	1340	0.5885	4.4982	0.3135

Suryanarayana proposed a method for the evaluation of excess internal pressure (P_i^E) based on the measured values of density (ρ), sound velocity (u), and viscosity (η). The proposed relation is expressed as:

$$p_i = \text{bRT}\left(\frac{k\eta}{u}\right)^{\frac{1}{2}} \frac{\rho^{\frac{2}{3}}}{M_{eff}^{\frac{7}{6}}} \qquad \ldots(1)$$

Here, *b* denotes the packing factor, taken as 2 for all liquids and binary mixtures in the present study, as commonly assumed in the literature, k is a dimensionless constant, having a value of 4.28×10^9. This constant is independent of the nature of the liquid and temperature, M is molecular weight.

In the present work enthalpy (H) has also been estimated by molar volume and internal pressure values

$$H = V_m \times P_i \qquad \ldots(2)$$

$$Y^E = Y_{exp} - (X_1Y_1 + X_2Y_2 \qquad \ldots(3)$$

Y^E refer to (H^E) and (p_i^E)whereas Y_{exp}represents the experimentally measured property of the binary mixture, while Y_1 and Y_2 are the values of the corresponding property for pure components 1 and 2, respectively. X_1 and X_2 denote the mole fractions of components 1 and 2.

An examination of Table 2 shows the variation of density, sound velocity, and viscosity with composition for the binary mixtures under study. Mole fraction (X_1) of 1,3-

Dioxolaneincreases, density and ultrasonic velocity increase, while viscosity decreases. This trend can be explained by molecular interactions in the system [25]. When 1,3-Dioxolane is added, it likely leads to closer packing of molecules due to molecular interactions, such as dipole-induced dipole forces.

The internal pressures of binary mixtures under consideration is computed through the relation proposed by Suryanaryana, vide equation (1) and are depicted in table-2. Excess internal pressure(p_i^E) has been obtained with the help of equation (3). An excess internal pressure (p_i^E) has been obtained with the help of equation 1 & 3 and is incorporated in figure-1. In system I to VI, the excess internal pressure comes out to be negative from equation 1 & 3. Furthermore, A non-linear trend is observed in the excess internal pressure (P_i^E), which first decreases with increasing mole fraction of component 1 (X_1), attains a minimum, and subsequently increases at higher. It has been observed that excess internal pressure (p_i^E) vary with the composition of the mixture and also on going from one to other. Thus, it can be taken as useful tool for predicting the intermolecular interactions in liquid mixtures. The molecular interaction between molecules is influenced by structure, stearic hindrance and longer chain length of C_5 to C_{10} respectively effects significantly the interaction with other components.

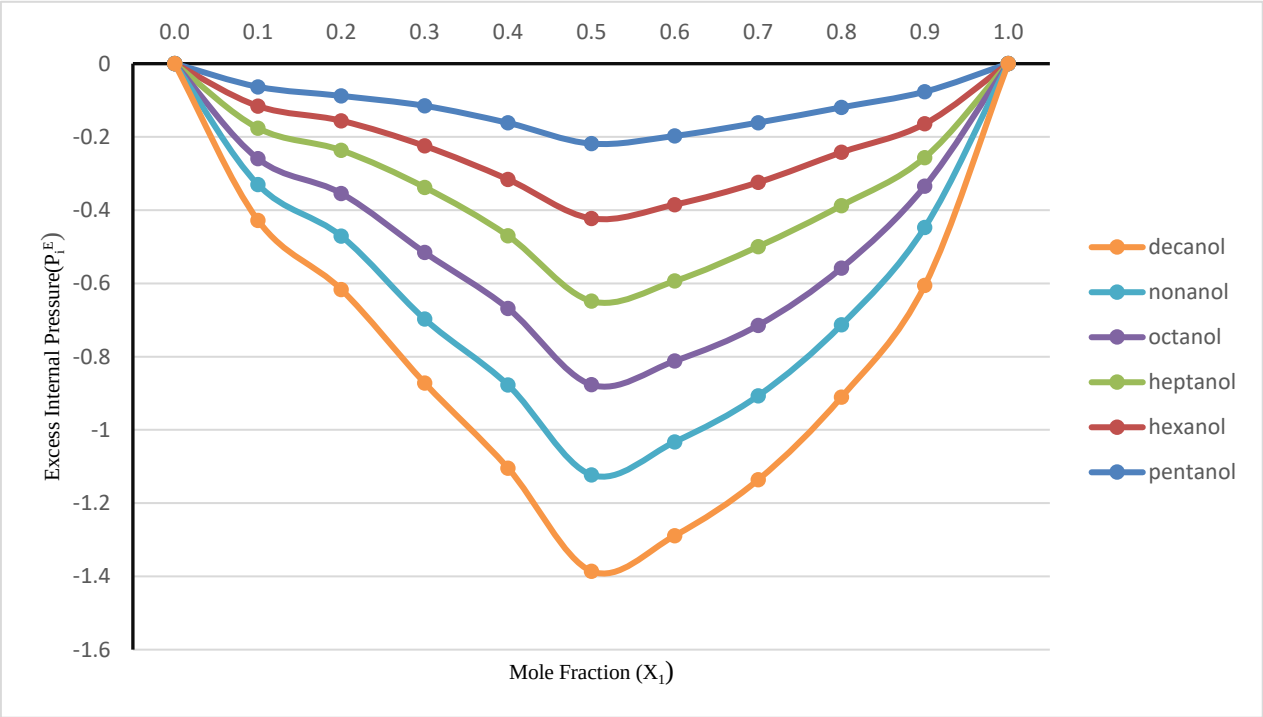


Figure 1. Variation of excess internal pressure (p_i^E) with mole fraction (x_1) of 1,3-dioxolane with 1-alkanols at 298.15K.

Excess enthalpy (H^E) has been obtained with the help of equation (2). The observed behavior is consistent across all six binary systems and is illustrated in the plots presented in Figure 2. An excess internal pressure has been obtained with the help of equation 2 & 3 and is incorporated in figure-2. In system I to VI, the excess enthalpies (H^E) comes out to be negative from equation 2 & 3. The calculated values of enthalpy for six binary liquid mixtures vide equation (2) are presented in table-2. The values of excess enthalpies (H^E) have been evaluated from equation (3), using the computed values of internal pressure vides equation (1) and (3). All these results are presented in figure-2. The values of excess enthalpies (H^E) for these binary systems are negative at all compositions of mixture at all the six systems. The negative magnitude first decrease and then increases all the six binary liquid mixtures. The sign and magnitude of excess enthalpy (H^E) provide insight into the nature of intermolecular interactions within the binary systems. A negative value of H^E indicates the presence of strong attractive forces between unlike molecules, suggesting favorable mixing behavior. [26].

The present study also reveals that, as the size of the alcohol molecules increases, both the internal pressure and the enthalpy decreases, i.e. an increase in the size of the alcohol molecules leads to a decrease in intermolecular interactions, primarily due to the reduction in hydrogen bonding strength with increasing alkyl chain length. Thus, the interaction order may be represented as: Pentanol > Hexanol > Heptanol > Octanol > Nonanol > Decanol

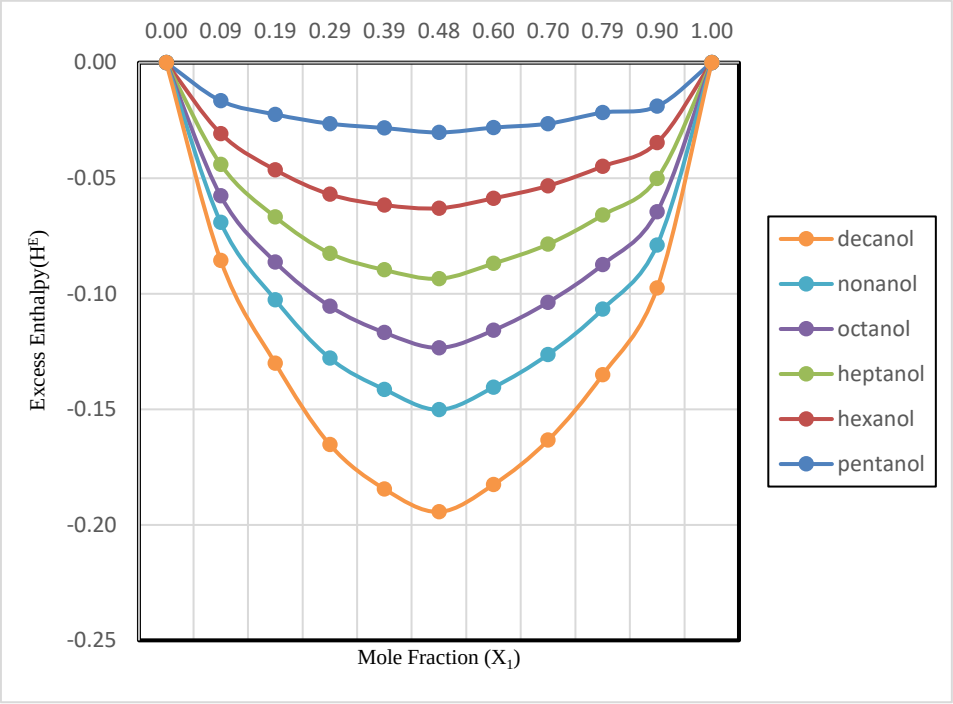


Figure 2- Variation of excess enthalpy (H^E) with mole fraction (x_1) of 1,3-dioxolane with 1-alkanols at 298.15K.

Conclusion

We have determined the sound velocity, density and viscosity of 1,3-dioxolane with 1-alkanols experimentally at 298.15K. The calculated thermodynamic parameters enthalpy (H), excess enthalpy (H^E), internal pressure (P_i), and excess internal pressure (P_i^E) provide strong evidence for significant intermolecular interactions between the unlike components, predominantly governed by hydrogen bonding. In addition, the negative values of excess enthalpy (H^E) and excess internal pressure (P_i^E) further corroborate the existence of significant intermolecular interactions between the components of the binary mixtures.

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REFERENCES

1. Gorden, J.E. (1965). J. Amer. Chem. Soc., 87 : 4347.
2. Irving, H.M.H. and Smith, J.S. (1969). J. Inorg. Nuclear Chem., 31: 3163.
3. Longester, G.F. and Walker, E.E. (1953). Trans. Faraday Soc., 49: 228.
4. Eyring, H. andKinacid, J.F. (1938). Free volume and free angles ratios of molecules in liquids. J. Chem. Phys., 6: 220-229.
5. 5. Dewan, R.K., Gupta, C .M. and Mehta, S.K. (1988). Ultrasonic study of ethyl benzene +n-alkanols, Acoustica., 65: 245.
6. Suryanarayana, C.V. (1972). Ind.J.Chem., 10: 713 .
7. Palaniappan, L. and Karthikeyan, V. (2005). Indian J. Phys., 79(2): 155.
8. Nithiyanantham, S. and Palaniappan, L. (2006). Acta. ciencaIndica., 37(3): 382-392.
9. Nithiyanantham, S. and Palaniappan, L. (2005). Acta. ciencaIndica., 36(4): 533-538
10. Nithya, R., Mullainathan, S. Nithiyanantham, S. and Rajesekaran, R. E. (2009).Journal of chemistry.,6(1): 138.
11. Hildebrand , J.H. and Scott, R.L. (1950). Solubility of Non-electrolytes, IIIrdEdn., Reinhold Publ. Corpn., Newyork, p.121.
12. Hildebrand , J.H. and Scott, R.L. (1962). Regular solutions, PrenticeHall, Englewood Cliffs, New Jersy.

13. Zainab, A.H. Al-Dulaimy, T.A. Dhafir, Al-Heetim, Husam Saleem Khalaf and Abbas, Ahmed Mohammed. (2018). Excess molar quantities of binary mixture of dipropyl amine with aliphatic alcohols at 298.15 K. *Oriential Journal of Chemistry*, 34(4): 2074-208**.**

14. Dubey, G.P. and Sharma, Monika. (2008). Excess volumes, densities, speed of sound and viscosities for the binary systems of 1-Octanol with hexadecane and squalane at (298.15,303.15 and 308.15)K. *Int. J Thermo phys.* 24**:** 1361-1375**.**

15. Al-Kandary, J.A. Al-Jimaz, A. S. and Abdul-Latif, A.H.M. (2009). Densities, viscosities, speeds of sound and refractive indices of binary mixtures of tetra hydro furan with 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol, 1-decanol at 298.15, 303.15, and 313.15 K. *Physics and Chemistry of Liquids*,47(2): 210-224.

16. Indumati, M. Meenakshi, G. Priyadharshini, V.J. Kayalvizhi, R. andThiyagaraj, S. (2013). Theoretical evaluation of ultrasonic velocity and excess parameters in binary liquid mixtures of bromobenzene with alkanols. *Research Journal of Pharmaceutical, Biological and Chemical Science*, 4(2): 1332-1384.

17. Chanda, R. Banerjee, A. and Mahendra, R. N. (2010). Studies of viscous antagonism, excess molar volumes, viscosity deviation and isentropic compressibility of ternary mixtures containing N,N-di methyl formamide, benzene and some ethers at 298.15 K. *Journal of Serbian Chemical Society*,75(12): 1721-1732.

18. Giner, I. Haro, M. Gascon, I. and Lafuente, C. (2007). Thermodynamic properties of binary mixtures formed by cyclic ethers and chloro alkanes. *Journal of Thermal Analysis and Calorimetry*, 2: 587-595.

19. Kumar, A. and Srinivasu, C. (2014). Speeds of Sound and Excess molar volume for binary mixture of 1,4-Dioxane with 1-Heptanol at five Temperatures. *Advance in Chemistry*, 1-7**.**

20. Bhatia Subhash, C. Rani, R. Sangwan, J. and Bhatia, R.(2011). Densities, viscosities, speed of sound, refractive indices of binary mixtures of 1-Decanol with Isomeric Chloro toluene. *Int. J Thermophys*, 32: 1163-1174**.**

21. Banipal, P.K. Singh, V. Kaur, N. Sharma, R. Thakur, S. Kaur , M. and Banipal, T.S. (2017). Physico-Chemical studies on binary mixtures of 1,4-Dioxane and Alkan-1-ols at 298.15K, *Acad. Sci. India. Sec. A Phys. Sci*.88(4): 479-490**.**

22. Venkatalakshmi, V. Gowrisankar, M. Venkateswarlu, P. and Reddy, K.S.(2013). Density, Ultrasonic velocity and their excess parameters of the binary mixtures of 2-Methyl-aniline with 1-Alkanols (C_3-C_8) at different temperatures, *International Journal of Physics and Research*, 3(5): 33-44**.**

23. Zainab, A.H. Al-Dulaimy, T.A. Dhafir, Al-Heetimiand, Husen Saleem Khalaf and Abbas, A. M. (2018). Excess molar quantities of binary mixture of Di propyl amine with Aliphatic Alcohols at 298.15K". *Oriental Journal of Chemistry*, 34 (4): 2074-2082**.**

24. Santhi, N. andMadhumitha, J. (2014). Molecular interaction studies in binary liquid mixture through ultrasonic measurememts at 303.15K, International Journal of Advanced Chemistry, 2(1): 12-16**.**

25. Pandey, J.D. Rai, R.D. Shukla, R.K. Shukla, A.K. and Mishra, N. (1993). Ultrasonic and Thermodynamic Properties Of Quaternary Liquid System At 298.15 K, Indian J. Pure Appl. Phys. 31: 84-90.

26. Nomoto, O. (1958). Empirical Formula for Sound Velocity In Binary Liquid Mixtures, J. Phys. Soc. (Japan.), 13: 1528-1532.