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Viscosities and excess thermodynamic properties of binary liquid mixtures of cyclic ether with 1-alkanols at 303.15K.

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ABSTRACT
The ultrasonic velocity, density and viscosity were measured experimentally at 303.15 K in six binary liquid mixtures of 1,4-dioxane (cyclic ether) with 1-methanol, 1-ethanol, 1-propanol, 1-butanol, 1-hexanol and 1-octanol. The free volume and internal pressure were calculated for the six binary liquid mixtures of 1,4-dioxane with 1-alkanols at 303.15 K over the entire range of compositions. Excess values of the free volume and internal pressure were calculated for these systems. The results are discussed in light of the existing theories of molecular interactions involved and the chemical composition of the liquid components.
Keywords: *Ultrasonic velocity, density, viscosity, excess free volume, excess internal pressure, binary mixtures, molecular interactions.*

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Nomenclature
ρ Densities of liquid
u, Ultrasonic velocity
u^E, excess ultrasonic velocity
η, Viscosity
η^E, excess viscosity
V_f, Free Volume
$V_f{}^E$, Excess values of free volume
Pi, Internal pressure
Pi^E, Excess internal pressure
X_1, Mole fraction of 1,4-Dioxane
Y^E, Thermodynamic excess function

I. Introduction

During the last three decades, ultrasonic studies of liquid mixtures haves gained much importance for understanding the nature of molecular interactions and for investigating the physico-chemical behavior of such systems. The thermodynamic and transport properties [1-5] of liquid mixtures have been extensively used to study the departure of liquid mixtures from ideality. In addition, these properties have been widely used to study the intermolecular interactions between various species present in liquid mixtures. The excess thermodynamic functions [6-10] are sensitively dependent not only on the differences in intermolecular forces, but also on the difference in the size of the molecules. Internal pressure and free volume are fundamental properties of the liquid state, which were initially studied by Hildebrand and Scott [11,12] and subsequently used to investigate the molecular interactions of binary liquid mixtures. The thermodynamic and transport properties of liquid mixtures have been extensively used to study the departure of real liquid mixture behavior from ideality [13, 14]. Measurements of ultrasonic velocity, viscosity, and density have been adequately employed to understand molecular interactions in liquid mixtures. Measurements of excess thermodynamic properties we are found to be significant in studying the structural changes associated with liquids [15]. The 1,4-dioxane was selected as the solvent in the present study because it has a variety of applications. Alcohols play an important role in many chemical reactions because of their ability to self-associate with their internal structures [16]. 1,4-Dioxane cyclic ether is used as a degreasing agent, component of paints and varnish removers, and wetting and dispersion agent

in the textile industry. 1,4- Dioxane is also used as a solvent in chemical syntheses. Ultrasonic studies of the solution of alcohols with 1,4-dioxane have yielded valuable information regarding the association between the monomers of alcohols and the free oxygen of dioxane through hydrogen bonding.

II. Experimental section

2.1 Material

The chemicals used in the present work were high purity laboratory reagent grade 1,4-dioxane, 1-methanol, 1-ethanol, 1-propanol, 1-butanol, 1-hexanol, and 1-octanol purchased from Merck Chem. Ltd India. All the chemicals were stored in sodium hydroxide pellets for several days. All chemicals were stored in tightly sealed bottles to minimize the absorption of atmospheric moisture.

The purity of the solvent was ascertained by comparing the measured density, dynamic viscosities, and sound velocity of the pure component at 303.15K with those in the available literature [17-28] as shown in Table 1.

2.2 Measurements

Six binary systems namely 1,4-dioxane + 1-methanol, 1,4-dioxane + 1-ethanol, 1,4-dioxane + 1-propanol, 1,4-dioxane + 1-butanol, 1,4-dioxane + 1-hexanol and 1,4-dioxane +1-octanol were studied. Each sample mixture was prepared-, on a mass basis-, by mixing the calculated volume of liquid components in specially designed glass - stoppered bottles. All binary mixtures were prepared by weighing the entire range of the mole fractions. The components of the binary mixtures were injected using a syringe in- to glass vials sealed with a rubber stopper to check for evaporation losses during sample preparation. Mass measurements were carried out using a single pan analytical balance (Model K-15 Deluxe, K Roy Instruments Pvt. Ltd.) with an accuracy of ± 0.00001×10^{-3} kg as described elsewhere [29]. The possible error in the mole fraction was estimated to be less than 1×10^{-4}. Five samples were prepared for each system, and their densities and sound velocities were measured on the same day.

2.2.1 Density

The densities of pure liquids and their binary mixtures were determined using a double-arm pycnometer [30] with a bulb of 25 cm^3 and a capillary with an internal diameter of approximately 1 mm was used to measure the densities (ρ) of pure liquids and binary mixtures. The pycnometer was calibrated using conductive water (having a specific conductance of less than 1×10^6 ohm^{-1}) with densities of 0.9970 and 0.9940 g cm^{-3} at T = 303.15 K, respectively. The pycnometer, filled with air bubble- free liquids, was kept in a thermostate water bath (MSI Goyal Scientific, Meerut, India) controlled with thermal equilibrium. The precision of the density measurements was estimated as ±0.0002 g cm^{-3}. The observed values of densities of pure 1,4-dioxane, 1-methanol, 1-ethanol, 1-propanol, 1-butanol, 1-hexanol and 1-octanol at 303.15K were 1.0108, 0.7840, 0.7720, 0.8070, 0.8040, 0.8128 and 0.8242 $g.cm^{-3}$ which compare well with corresponding literature values of respectively.

2.2.1 Sound velocity

Ultrasonic velocities were measured using a multifrequency ultrasonic interferometer (Model F-80D, Mittal Enterprise, New Delhi, India) operating at 3 M.Hz. The meter was calibrated using water and benzene at 303.15K. The measured values of the ultrasonic velocities of pure 1,4-dioxane, 1-methanol, 1-ethanol, 1-propanol, 1-butanol, 1-hexano, and 1-octanol at 303.15K were 1322.3, 1084, 1141, 1182, 1196, 1298 and 1327 $m.s^{-1}$ respectively, which are in good agreement with the corresponding literature values.

2.2.2 Viscosity

The viscosities of the pure liquids and their binary mixtures were measured using a suspended ubbelohde - type viscometer [31, 32] with a capacity of approximately 15 ml. A capillary with a length of about 90 mm and 0.5 mm internal diameter has been used to measure the flow times of the pure liquids and liquid mixtures, and it was calibrated with triply distilled water, methanol, and benzene at 303.15 K. The details of the methods and techniques have been previously described [33, 34]. The efflux time was measured using an electronic stop watch (Racer) with a time resolution (±0.015), and an average of at least four flow time readings was taken. A glass stopper was placed at the opening of the viscometer to prevent loss owing to evaporation during the measurements. The two bulb reservoirs, one at the top and the other at the bottom of the viscometer linked to each other by U type, facilitate the free flow of liquid at atmospheric pressure. The measured viscosities of pure 1,4-dioxane,1-methanol, 1-ethanol, 1-propanol, 1-butanol, 1-hexanol and 1-octanol at 303.15 K were 1.0303, 0.4949, 1.1399, 1.5477, 2.2045, 4.5642, and 7.8512 C.P., respectively. These values are in good agreement with the corresponding literature values.

Table 1 Physical properties of pure components at 303.15K

component	Density (ρ) g-m^{-3}		Ultrasonic Velocities (u) m.s^{-1}		Viscosity (η) CP	
	Observed	Literature	Observed	Literature	Observed	Literature
1,4-dioxane	1.0108	1.0229 [27]	1348	1322.3 [28]	1.0303	1.0690 [21]
1-Methanol	0.7840	0.7817 [18]	1084	1084.0 [25]	0.4949	0.5040 [19]
1-Ethanol	0.7720	0.7807 [17]	1141	1144.3 [19]	1.1399	1.3560 [17]
1-Propanol	0.8070	0.8003 [24]	1182	1182.6 [19]	1.5477	1.6626 [19]
1-Butanol	0.8040	0.8020 [19]	1196	1196.6 [19]	2.2045	2.2740 [20]
1-Hexanol	0.8128	0.8118 [19]	1298	1282.0 [26]	4.5642	4.5930 [22]
1-Octanol	0.8242	0.8187 [23]	1327	1330.8 [23]	7.8512	7.6630 [22]

III. Theoretical Aspects

3.1 Free volume (V_f)

Liquid viscosity has been treated as a free-volume problem by several researchers. Suryanarayana and Kuppusami derived a formula for the free volume based on one dimensional analysis of the situation. An ultrasonic wave passes through a liquid medium.

$V_f = (M\,U/\,k\,\eta)^{3/2}$

where,- M is the molecular weight, u is the ultrasonic velocity, η is the viscosity, V_f, the free volume in milliliters per mole, and K is a constant, independent of temperature, and it-'s value is 4.28×10^9 for all liquids.

3.2 Internal Pressure (P_i)

Suryanarayana and Kuppuswami [35, 36] suggested a method for evaluating the internal pressure from the knowledge of the ultrasonic velocity, u, density, ρ, and viscosity, η, the relation proposed is expressed as follows:

$p_i = bRT\,(\frac{k\eta}{u})^{\frac{1}{2}}\,\frac{\rho^{2/3}}{M_{eff}^{7/6}}$

where b is the packing factor, which is assumed to be 2 for all liquids and solutions. k is a constant, independent of temperature, and its value is 4.28×10^9 for all liquids, R is the universal gas constant, and T is the absolute temperature.

3.3 Excess Thermodynamic Parameters

The excess thermodynamic function (Y^E) provides a way to directly represent the deviation of a solution from the ideal behavior. The difference between the thermodynamic function of mixing for a real system and the value corresponding to a perfect solution at the same temperature, pressure, and composition is called the thermodynamic excess function,-denoted by Y^E. Excess values for all parameters we are computed using the general formula:

$$Y^E = Y_{exp} - (X_1 Y_1 + X_2\, Y_2)$$

IV. Result and Discussion

The experimental determinate values of density (ρ), viscosity (η), and sound velocity (u) of all the pure liquids at 303.15 K are presented in Table 1, and the same for the six binary systems are listed in Table 2. The excess values of viscosity (η^E), sound velocity (u^E), free volume (V_f^E), and internal pressure (p_i^E) at 303.15 K are listed in Table 3. The results presented in Table 2 show non-linear behavior of viscosity, sound velocity, free volume, and internal pressure, which is further substantial by their excess values (Table 3). All seven organic compounds namely 1,4-dioxane, methanol, ethanol, propanol, butanol, hexanol, and octanol, are polar organic compounds, with dipole moments of 0.45 , 1.70 , 1.69 , 1.68 , 1.66 , 1.60 D, and 1.68 D respectively. Normally, the dipole moment is, the stronger the intermolecular interaction, which results in a decrease in the free space between molecules and an increase in the ultrasonic velocity.

The measured values of density (ρ), viscosity (η), and sound velocity (u) and the evaluated parameters are presented in Table 2. For the binary systemd 1,4-dioxane + methanol, 1,4-dioxane + ethanol, 1,4-dioxane + propanol, 1,4-dioxane + butanol, 1,4-dioxane + hexanol, and 1,4-dioxane + octanol at 303.15 K. From Tables, it can be noticed that, at 303.15 K temperature the values of sound velocity, viscosity, and free volume increase with an increase in the mole fraction of 1,4-dioxane (x_1) but the density (ρ) and internal pressure decrease with an increase in the mole fraction of 1,4-dioxane (x_1). The pronounced increase or decrease in these parameters with the composition of mixtures indicates the presence of interaction between the component molecules in the binary mixtures. This trend indicated specific interactions among the constituents of the mixtures. This behavior can be attributed to intermolecular interaction [37]. The chemical interaction may involve the association due to hydrogen bonding order to dipole-dipole interaction or may be due to the formation of charge-transfer complexes. These processes may lead to strong interaction forces [38].

An analysis of the viscosity values in Table 2 it can be observed that the viscosity decreases with an increase in the mole fraction of 1,4-dioxane. A similar trend was observed for internal pressure values. This type of non-linearity indicates molecular interactions.

For the binary liquid mixtures, the density (ρ) and free volume (V_f) increased with an increase in the concentration of 1,4-dioxane. The increase in density (ρ) and free volume (V_f) in these liquid mixtures suggests molecular interactions among the molecules of components of liquid mixture.

Table 2. Values of density, sound velocity, viscosity, free volume and internal pressure properties for binary liquids mixtures of 1,4-dioxane + 1-methanol, 1,4-dioxane + 1-ethanol, 1,4-dioxane +1- propanol, 1,4-dioxane + 1-butanol, 1,4-dioxane + 1-hexanol and 1,4-dioxane + 1-octanol at 303.15 K

Mole fraction of 1,4-dioxane (X_1)	Density (ρ) g.m^{-3}	Sound velocity (u) m.s^{-1}	Viscosity (η) cp	Free volume (V_f) ml mol^{-1}	Internal pressure ($p_i \times 10^4$) atm.
1,4-Dioxane + 1-Methanol					
0.00000	0.7840	1084.0	0.4949	0.06639	1.85827
0.09770	0.82748	1092.0	0.5704	0.06873	1.55867
0.20043	0.86692	1130.0	0.6005	0.08297	1.29924
0.28674	0.89696	1155.0	0.6339	0.09268	1.13200
0.38010	0.91716	1176.0	0.6703	0.10226	0.98575
0.49857	0.94224	1240.0	0.7168	0.11938	0.83121
0.59198	0.96312	1266.0	0.7802	0.12298	0.75747
0.70860	0.98772	1289.0	0.8441	0.12956	0.67723
0.80020	0.99876	1306.0	0.9426	0.12420	0.63839
0.90362	1.00892	1330.0	1.0244	0.12564	0.58824
1.00000	1.0108	1348.0	1.0303	0.13976	0.52793
1,4-Dioxane + 1-Ethanol					
0.00000	0.7720	1141.0	1.1399	0.03536	1.48567
0.09885	0.80944	1150.0	1.1038	0.04274	1.33256
0.20465	0.8426	1170.0	1.0986	0.05016	1.17588
0.29964	0.8652	1189.0	1.0814	0.05849	1.02250
0.39745	0.8990	1217.0	1.0740	0.06775	0.92291
0.50220	0.92016	1285.0	1.0710	0.08167	0.81416
0.59502	0.94108	1288.0	1.0697	0.08941	0.75046
0.69003	0.9720	1298.0	1.0593	0.09964	0.69393
0.79934	0.98624	1310.0	1.0485	0.11215	0.62849
0.89342	0.99356	1340.0	1.0406	0.12619	0.57388
1.00000	1.0108	1348.0	1.0303	0.13976	0.52793
1,4-Dioxane + 1-Propanol					
0.00000	0.80708	1182.0	1.5477	0.03511	1.12536
0.10006	0.82064	1202.0	1.4964	0.04054	1.02842
0.12264	0.84796	1215.0	1.2610	0.05407	0.94383
0.29821	0.87008	1248.0	1.1498	0.07234	0.79892
0.40573	0.89936	1264.0	1.1319	0.08050	0.74945
0.50439	0.91672	1270.0	1.1274	0.08633	0.70945
0.60251	0.93908	1275.0	1.1097	0.09391	0.67187
0.69410	0.9558	1284.0	1.0881	0.10268	0.63513
0.79626	0.98084	1290.0	1.0711	0.11164	0.60302
0.89926	1.0054	1312.0	1.0534	0.12362	0.56923
1.00000	1.0108	1348.0	1.0303	0.13976	0.52793
1,4-Dioxane + 1-Butanol					
0.00000	0.8040	1196.0	2.2045	0.02879	0.93886
0.09734	0.8136	1203.0	1.7804	0.04113	0.82365
0.19759	0.84252	1209.0	1.4627	0.05720	0.73831
0.30443	0.86264	1221.0	1.3458	0.06771	0.69325
0.40480	0.87696	1268.0	1.1934	0.08813	0.62881
0.49442	0.90224	1282.0	1.1939	0.09166	0.62110
0.59768	0.92744	1287.0	1.1879	0.09539	0.61152
0.68628	0.95028	1297.0	1.1044	0.11009	0.58231
0.79076	0.97392	1315.0	1.0953	0.11678	0.56878
0.89091	0.99836	1334.0	1.0728	0.12616	0.55292
1.00000	1.0108	1348.0	1.0303	0.13976	0.52793
1,4-Dioxane + 1-Hexanol					
0.00000	0.8128	1298.0	4.5642	0.01768	0.76533
0.09108	0.83796	1302.0	3.2904	0.02848	0.67619
0.19485	0.85408	1311.0	2.7369	0.03711	0.63767
0.29842	0.86024	1314.0	2.2727	0.04815	0.59775

0.40439	0.88144	1320.0	1.9013	0.06191	0.56874
0.45430	0.88996	1334.0	1.7643	0.06733	0.55520
0.60286	0.92576	1338.0	1.4365	0.09206	0.53273
0.69974	0.9486	1340.0	1.2914	0.10590	0.53284
0.80182	0.9684	1342.0	1.2103	0.11426	0.52919
0.88834	0.99384	1346.0	1.1144	0.12731	0.52758
1.00000	1.0108	1348.0	1.0303	0.13976	0.52793
1,4-Dioxane + 1-Octanol					
0.00000	0.8242	1327.0	7.8512	0.01166	0.66872
0.09780	0.8284	1329.0	5.1466	0.02098	0.57272
0.20653	0.83708	1330.0	4.6513	0.02313	0.58289
0.29810	0.85292	1332.0	3.2294	0.03818	0.51855
0.40275	0.85956	1334.0	2.5625	0.05113	0.49443
0.49229	0.88528	1336.0	2.3806	0.05439	0.51382
0.60068	0.90304	1338.0	1.8916	0.07220	0.49788
0.69888	0.92664	1339.0	1.4950	0.09686	0.48131
0.79610	0.95648	1341.0	1.3490	0.10643	0.49999
0.89749	0.98596	1345.0	1.1845	0.12142	0.51467
1.00000	1.0108	1348.0	1.0303	0.13976	0.52793

Table 3. Excess values of sound velocity (u^E), viscosity (η^E), free volume(V_f^E) and internal pressure (P_i^E) properties for binary liquids mixtures of 1,4-dioxane + 1-methanol, 1,4-dioxane + 1-ethanol, 1,4-dioxane + 1-propanol, 1,4-dioxane +1- butanol, 1,4-dioxane + 1-hexanol and 1,4-dioxane + 1-octanol at 303.15 K.

Mole fraction of 1,4-dioxane (X_1)	Excess sound velocity (u^E) $m.s^{-1}$	Excess Viscosity (η^E) cp	Excess Free volume (V_f^E) ml mol^{-1}	Excess internal pressure ($p_i^E \times 10^4$) atm.
1,4-Dioxane + 1-Methanol				
0.00000	0	0.0000	0.00000	0.00000
0.09770	17.68	-0.2075	-0.00482	-0.16943
0.20043	16.79	-0.2116	-0.00500	-0.29226
0.28674	14.58	-0.2820	-0.00525	-0.34470
0.38010	13.23	-0.3650	-0.00798	-0.36667
0.49857	12.51	-0.4043	-0.01641	-0.36374
0.59198	11.85	-0.5216	-0.01315	-0.31323
0.70860	11.04	-0.4523	-0.01118	-0.23817
0.80020	10.86	-0.3916	-0.00889	-0.15515
0.90362	7.56	-0.3416	-0.00704	-0.06757
1.00000	0	0.0000	0.00000	0.00000
1,4-Dioxane + 1-Ethanol				
0.00000	0	0.0000	0.00000	0.00000
0.09885	13.43	-0.2160	-0.00294	-0.05836
0.20465	13.3	-0.2215	-0.00656	-0.11371
0.29964	13.05	-0.2298	-0.00814	-0.17610
0.39745	12.96	-0.3115	-0.00910	-0.18209
0.50220	12.54	-0.4160	-0.01010	-0.19038
0.59502	11.78	-0.4965	-0.00806	-0.16522
0.69003	10.58	-0.4510	-0.00775	-0.13077
0.79934	9.76	-0.3920	-0.00666	-0.09162
0.89342	8.54	-0.2361	-0.00244	-0.05613
1.00000	0	0.0000	0.00000	0.00000
1,4-Dioxane +1- Propanol				
0.00000	0	0.0000	0.00000	0.00000
0.10006	12.96	-0.2165	-0.00503	-0.03714
0.12264	12.66	-0.2232	-0.00613	-0.10824
0.29821	12.51	-0.2435	-0.00682	-0.14826
0.40573	11.67	-0.2858	-0.01292	-0.13350
0.50439	11.29	-0.3515	-0.01456	-0.11455
0.60251	10.97	-0.4262	-0.01405	-0.09351
0.69410	10.53	-0.3004	-0.01207	-0.07554
0.79626	9.27	-0.2645	-0.00680	-0.04662
0.89926	8.54	-0.1290	-0.00557	-0.01831
1.00000	0	0.0000	0.00000	0.00000
1,4-Dioxane + 1-Butanol				
0.00000	0	0.0000	0.00000	0.00000
0.09734	11.78	-0.3097	-0.00153	-0.07519
0.19759	11.02	-0.5096	-0.00648	-0.11934

0.30443	10.98	-0.5211	-0.00813	-0.12050
0.40480	10.49	-0.5367	-0.01241	-0.14369
0.49442	10.25	-0.5516	-0.01800	-0.11458
0.59768	9.17	-0.3147	-0.01273	-0.08173
0.68628	8.56	-0.2941	-0.00913	-0.07453
0.79076	8.18	-0.1805	-0.00420	-0.04512
0.89091	7.26	-0.0855	-0.00250	-0.01983
1.00000	0	0.0000	0.00000	0.00000
1,4-Dioxane + 1-Hexanol				
0.00000	0	0.0000	0.0000	0.00000
0.09108	10.54	-0.9518	-0.00032	-0.06751
0.19485	10.28	-1.1385	-0.00435	-0.08139
0.29842	10.1	-1.2368	-0.00596	-0.09673
0.40439	9.85	-1.2397	-0.00614	-0.10058
0.45430	9.36	-1.2943	-0.00881	-0.10227
0.60286	9.25	-1.0971	-0.00780	-0.08947
0.69974	8.72	-0.9999	-0.00279	-0.06636
0.80182	8.52	-0.9825	-0.00130	-0.04578
0.88834	7.23	-0.3103	-0.00117	-0.02685
1.00000	0	0.0000	0.00000	0.00000
1,4-Dioxane + 1-Octanol				
0.00000	0	0.0000	0.00000	0.00000
0.09780	9.04	-2.0374	-0.00320	-0.08222
0.20653	8.92	-2.7911	-0.01498	-0.05674
0.29810	8.86	-2.9833	-0.01526	-0.10819
0.40275	8.54	-3.5414	-0.01863	-0.11758
0.49229	8.26	-3.1126	-0.02033	-0.08558
0.60068	8.1	-2.8623	-0.01641	-0.08626
0.69888	7.66	-1.5891	-0.01433	-0.08901
0.79610	7.27	-1.0720	-0.00722	-0.05664
0.89749	7.12	-0.5448	-0.00522	-0.02768
1.00000	0	0.0000	0.00000	0.00000

4.1 Excess Acoustical and Thermodynamic Parameters

Regarding the nature of the molecular interactions between the components of the liquid mixtures, it is of interest to discuss the same in terms of excess parameters rather than actual values. Non-ideal liquid mixtures exhibit considerable deviation from linearity in their concentrations, which can be interpreted as the presence of strong or weak interactions. The extent of deviation depends on the constituents and compositions of the mixtures. The thermodynamic excess properties were found to be more sensitive to intermolecular interactions among the component molecules of the liquid mixtures. The sign and extent of deviation of the excess parameters depend on the strength of the interaction between different molecules [39]. Therefore, various excess acoustic and thermodynamic parameters were evaluated, and the corresponding graphs are also given.

The sign and magnitude of the excess ultrasonic velocity (u^E) play an important role in describing molecular rearrangement as a result of molecular interactions between the component molecules in the mixtures. The excess ultrasonic velocity (u^E) curves at 303.15 K varying with the mole fraction of 1,4-dioxane, are represented in Figure-1 for the six binary systems. The excess ultrasonic velocity values were positive for all the six binary systems. Generally, the value of the excess function (u^E) depend on several physical and chemical contributions [40, 41]. The physical contribution depends mainly on two factors,

1. The dispersion forces or weak dipole-dipole interaction that leads to positive values.
2. The geometrical effect allowing the fitting of molecules of two different sizes in to each other's structure resulting in negative values

The chemical contributions include the breaking up of the associates present in pure liquids, resulting in a positive u^E. In the present mixture, the graphical representation of the excess sound velocity (u^E) are positive, as shown in Figure 1. The positive values revealed that weak interaction were present in the mixture.

The observed positive trends in excess sound velocity indicate that the effect due to the breaking up of the self-associated structure of the components of the mixtures is dominant over the effect of hydrogen bonding and dipole-dipole interaction between the different molecules. The excess sound velocity values in the sequence 1-methanol < 1-ethanol < 1-propanol < 1-butanol < 1-hexanol < 1-octanol also reflect the decreasing strength of the interaction, unlike the molecule in the mixture.

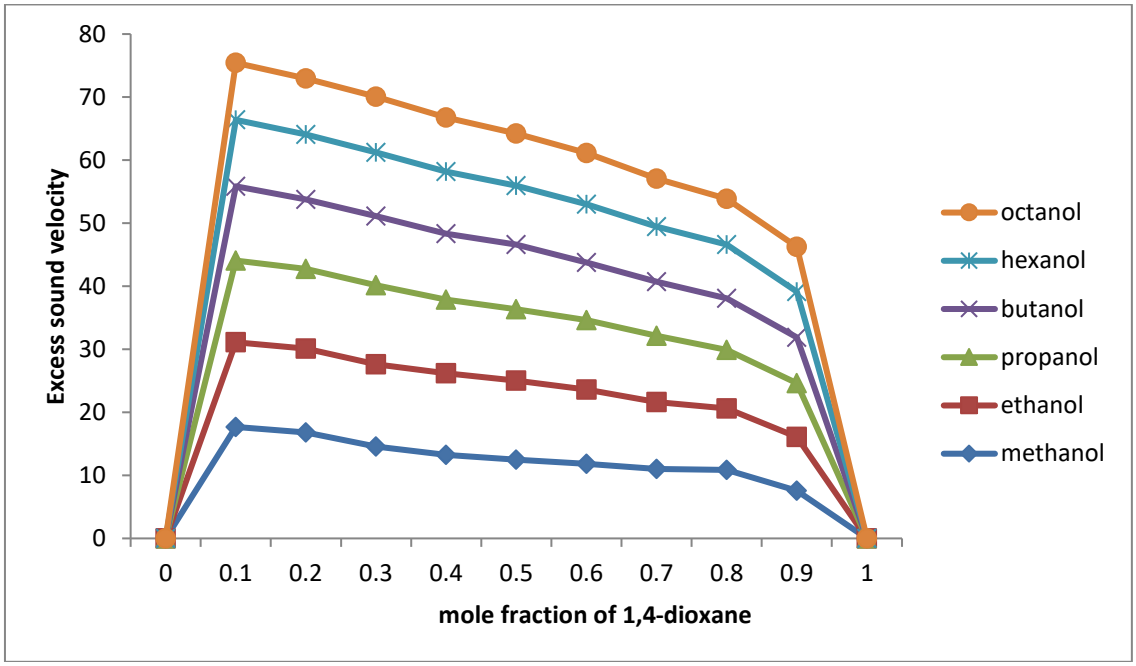

Figure 1. Plots of excess sound velocity versus mole fraction of 1,4-dioxane (x_1) at 303.15 K for binary mixtures of 1,4-dioxane with 1-methanol, 1-ethanol, 1-propanol, 1-butanol, 1-hexanol and 1-octanol at 303.15 K.

The measurement of viscosity in a binary liquid mixture provides reliable information for studying intermolecular interactions. The molecules of one or more components forming the temarise are either polar, associating or accordingly exhibit non-ideal behavior in mixtures. Negative values of η^E in most cases are the consequence of lower viscosity contributions of similar non-specific interactions and hydrogen bonding effects of molecular species in real mixtures rather than those in the corresponding ideal mixtures. In the present study, it is observed that, for the six binary systems the η^E values gradually decrease up to the mole fraction around 0.5 and then begins to increase Figure 2 more over it is observed that the η^E values decrease as the concentration of x_1 increase. Negative values indicate the presence of dispersion forces between the mixing components in the mixtures.

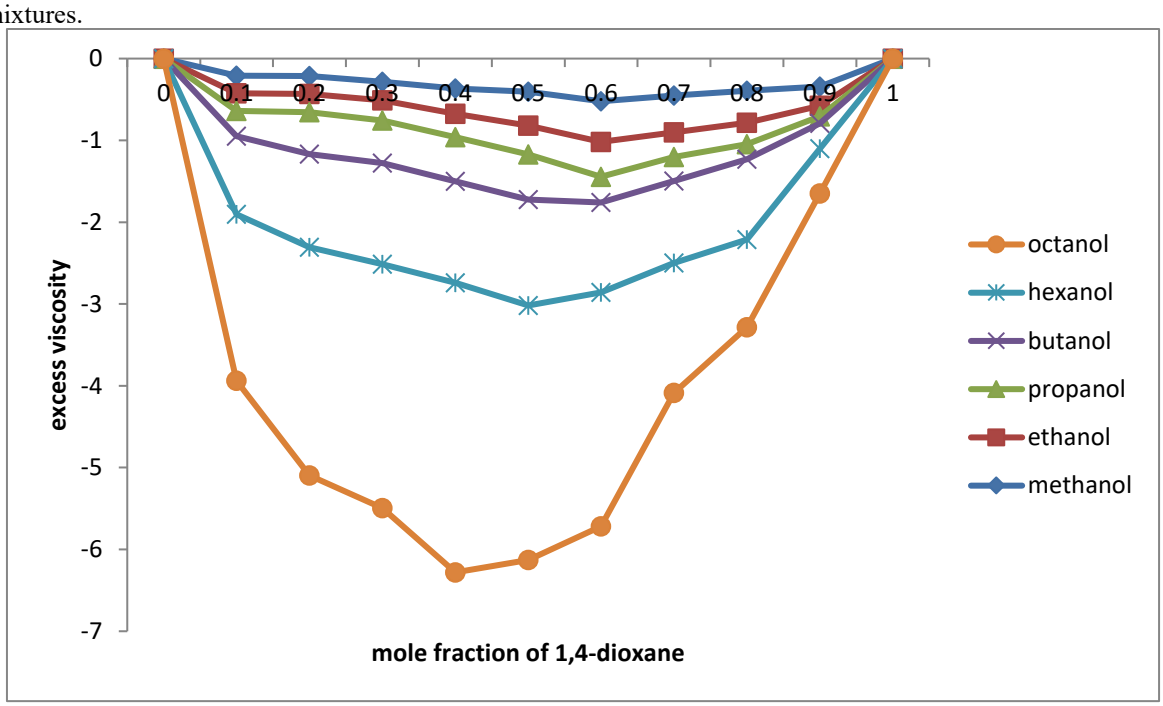

Figure 2. Plots of excess viscosity versus mole fraction of 1,4-dioxane (x_1) at 303.15 K for binary mixtures of 1,4-dioxane with 1-methanol, 1-ethanol, 1-propanol, 1-butanol, 1-hexanol and 1-octanol at 303.15 K.

Excess free volume (V_f^E) is another important parameter that can be used to explain molecular interactions. In the present investigation, the negative excess free volume (V_f^E) for binary mixtures of 1,4-dioxane with alkanols may be attributed to hydrogen bond formation through dipole-dipole interactions between alkanol and 1,4-dioxane molecules or to structural contributions arising from the geometrical fitting of one component (alkanol) to the other (1,4-dioxane) due to the difference in the free volume between the components.

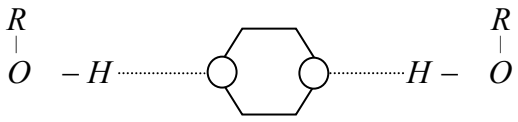

Figure 3. Hydrogen bonding between 1,4-dioxaneand 1- alkanol molecule.

To substantiate the presence of interactions between molecules, it is essential to study excess parameters such as the free volume. The deviation of the physical properties of liquid mixtures from the ideal behavior is a measure of the interaction between the molecules which is attributed to either adhesive or cohesive forces [42]. In the present study, the alkanols were polar and had self - association characteristics in other polar organic solvents.

Figure 4. Self-association of 1-alkanol molecule.

Negative values of excess free volume (V_f^E) indicate the presence of strong molecular interaction [43,44]. We may conclude that alkanols, are is a self – associating polar organic liquids tend to form complexes with 1,4-dioxane, and the increase in their dilution causes disruption of aromatic C – H bond stretching as the self – association of alkanols is disrupted. It is also concluded that the Suryanarayana approach for estimating the free volume of binary liquid mixtures, based on dimensional analysis using thermodynamic considerations, is very well applicable in the present case.

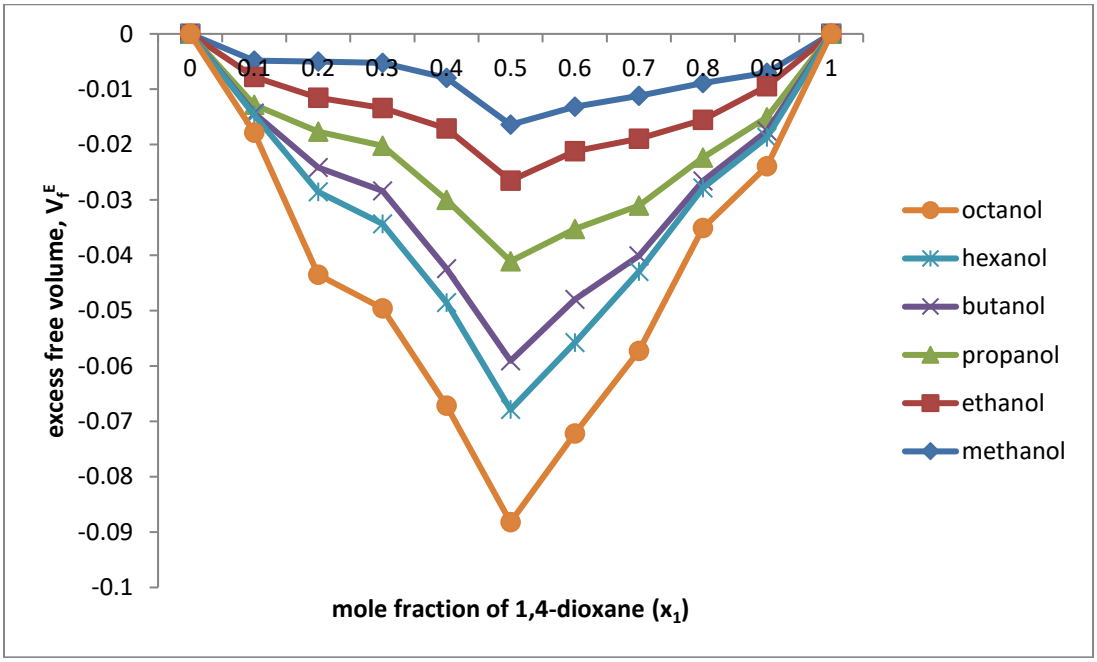

Figure 5. Plots of excess free volume versus mole fraction of 1,4-dioxane (x_1) at 303.15 K for binary mixtures of 1,4-dioxane with 1-methanol, 1-ethanol, 1-propanol, 1-butanol, 1-hexanol and 1-octanol at 303.15 K.

Excess internal pressure (p_i^E) is another important parameter that can be used to explain molecular interactions. In the present investigation of the six binary systems, it was observed that,- as the mole fraction of 1,4-dioxane increased, the p_i^E values decreased. The values of pi are almost negative and gradually decrease and move towards the positive values by the increase of mole fraction of 1,4-dioxane. More over the pi E decrease

with increase in X_1 . This situation is observed for all six binary system under study and can be viewed from plots Figure 6.

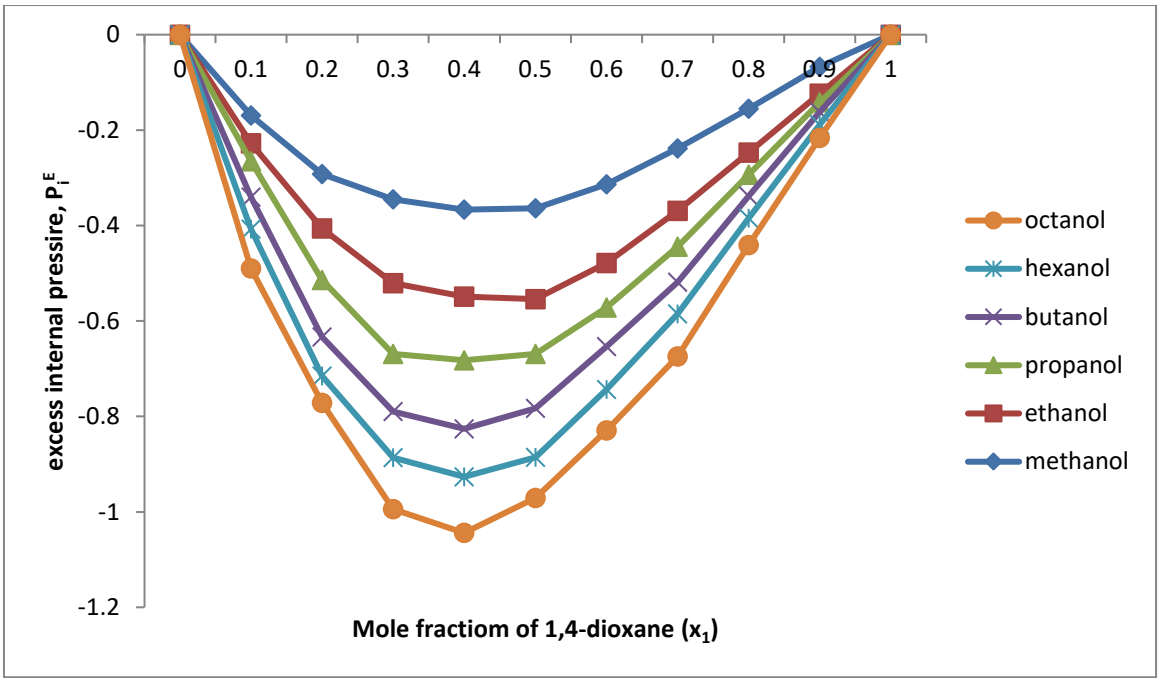

Figure 6. Plots of excess internal pressure versus mole fraction of 1,4-dioxane (x_1) at 303.15 K for binary mixtures of 1,4-dioxane with 1-methanol, 1-ethanol, 1-propanol, 1-butanol, 1-hexanol and 1-octanol at 303.15 K.

This suggests that dipole and dispersion forces operate in these systems,- when the 1,4-dioxane concentration is low. When the concentration of 1,4-dioxane leads to specific interactions, that is, the interactions move from weak to strong which supports the above arguments, is the case for other parameters.

V.Conclusion

From the observed thermo-acoustic and thermodynamic studies of the binary liquid mixtures 1,4-dioxane + methanol, 1,4-dioxane + ethanol, 1,4-dioxane + propanol, 1,4-dioxane + butanol, 1,4-dioxane + hexanol and 1,4-dioxane + octanol at 303.15 K are shown negative values of the excess free volume and excess internal pressure may provide information about the considerable interactions among the molecules of the binary mixtures. Therefore, we may conclude that 1-alkanols, which are self-associating polar organic liquids tend to form complexes with 1,4-dioxane, and the increase in their dilution causes dispersion of aromatic C-H bond stretching as the self-association of 1-alkanols is disrupted. It is also concluded that the Suryanarayana [45] approach for estimating the free volume and internal pressure of binary liquid mixtures, based on dimensional analysis using thermodynamic considerations, is applicable in the present case.

Declarations Conflict of interest

The authors have no competing interests to declare relevant to the content of this article.

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Data availability statement

The authors confirm that data supporting the findings of this study are available within the article.

Author Contribution Statement

Dhirendra Kumar Sharma:-, Research design, investigation, writing-original draft preparation and manuscript correction.

Seema Agarwal, Data Analysis and Mathematical Calculation.

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References

[1] Rama Rao GV. Sama AV. Rambabu C. Indian J Pure & Appl Phys. 2005; 42: 602-608. http://nopr.niscair.res.in/bitstream/123456789/8851/1/IJPAP%2043%288%29%20602-608.pdf
[2] Babu P. Chandrasekhar G. Prabhakara N. Indian J Pure & Appl Phys. 2000; 38: 88 . http://nopr.niscair.res.in/handle/123456789/8851
[3] Nikam PS. Mahale TR. Indian J Pure & Appl Phys. 2001; 39: 561. http://nopr.niscpr.res.in/handle/123456789/26668
[4] Glinski J. Chavepeyer G. Jean Karl P, Chem. Phys. 2001; 272:119. https://doi.org/10.1016/S0301-0104(01)00454-2
[5] Gonzalez Salgado D. Tovar CA,. Cerdeirina CA. Carballo E. Romani L. Fluid Phase Equil. 2002; 199: 121. https://doi.org/10.1016/S0378-3812(01)00796-8
[6] Nikam PS. Mahale TR. Mehdi H. Indian J Pure & Appl. Phys. 2002; 199: 121. http://nopr.niscpr.res.in/handle/123456789/27039
[7] Yasmin Ali A. Nain AK. Indian J Pure & Appl. Phys. 2002; 40: 315. http://nopr.niscpr.res.in/handle/123456789/26133
[8] Rajendra V. Indian J Pure & Appl. Phys. 1996; 34 : 52. https://scholar.google.co.in/scholar?cluster=7334925545348617046&hl=en&as_sdt=0,5&as_vis=1
[9] Rama Rao GV. Sama AV. Rambabu C. Indian J Chem. 2004; 43A : 2518. http://nopr.niscair.res.in/bitstream/123456789/20460/1/IJCA%2043A%2812%29%202518-2528.pdf
[10] Suryanarayana CV. Indian J Pure & Appl. Phys. 1989; 27: 751. https://scholar.google.co.in/scholar?q=C.V.+Suryanarayana,+Indian+J+Pure+%26+Appl+Phys.
[11] Hildebrand JH. Scott RL. Regular solution (Prentice Hall Englewood Cliff New Jersey, USA) 1962. https://www.worldcat.org/title/regular-solutions/oclc/545406
[12] Hildebrand JH. Scott RL. Solubility of non-electrolyte, 3rd Edn, (Reinhold, New York) 1964. https://www.worldcat.org/title/solubility-of-nonelectrolytes/oclc/1137083
[13] Tiyagarajan R. Palaniappan L. Indian J Pure & Appl. Phys. 2008; 46: 852. http://nopr.niscpr.res.in/handle/123456789/3037
[14] Bhandakkar VD. Indian J Pure & Appl. Phys. 2003; 41: 849. http://nopr.niscpr.res.in/handle/123456789/25258
[15] Bedare GR. Bhandakkar VD. Arch. of Appl. Sci. 2011; Res. 3: 323. https://www.researchgate.net/publication/258683238
[16] Palaniappan. Indian J Pure & Appl. Phys. 2002; 40: 828. http://nopr.niscpr.res.in/handle/123456789/26209
[17] Rodriguez A. Canosa J. Tojo J. Journal of Chemical & Engineering Data, 2001; 46: 846. https://doi.org/10.1021/je000180s
[18] Nikam P S. Mahale T R. Hasan M. J. Chem. Eng. Data, 1996; 41: 1055. https://doi.org/10.1021/je960090g
[19] Roy M N. Sinka A. Biswajit S. Journal of Solution Chemistry, 2005; 34:1311. https://link.springer.com/article/10.1007/s10953-005-8022-0%23citeas
[20] Kadam B U. Hiray P A. Sawant BA. Hasan M. Journal of Chemical & Engineering Data, 2006; 51: 60. https://doi.org/10.1021/je050169y
[21] Nayak JN. Aralaguppi MI. Aminabhavi TM. Journal of Chemical & Engineering Data, 2003; 48: 1489. https://doi.org/10.1021/je0301489
[22] Al-Kandary A J. Al-Jimaz A S. Abdul-Latif AM. Physics and Chemistry of Liquid, 2009; 47: 210. https://doi.org/10.1080/00319100802123152
[23] Dubey G P. Sharma M. International Journal of Thermophysics, 2008; 29 : 1361. https://link.springer.com/article/10.1007/s10765-008-0491-0%23citeas
[24] Elangovan S. Mullainathan S. Indian Journal of Physics, 2013; 87: 659. https://link.springer.com/article/10.1007/s12648-013-0288-2%23citeas
[25] Yasmin M. Singh K P. Parveen S. Gupta M. Shukla JP. Acta Physica Polonica A, 2009; 115: 890. http://przyrbwn.icm.edu.pl/APP/PDF/115/a115z508.pdf
[26] Ali A. Hyde SR. Tariq M. Journal of Thermophysics, 2005; 26: 1537. https://link.springer.com/article/10.1007%2Fs10765-005-8102-9%23citeas
[27] Syal VK. Gautam R. Chauhan S. Indian J. Appl. Phys., 1998; 36:108 . http://www.ultrasonicsindia.org/jpau27236169.pdf
[28] Rao TS. Veeraish N. Srinivasa Rao. Ramachandran G. Rambabu D. Indian J. Chem. 2003; 42A: 1876 . **http://nopr.niscpr.res.in/handle/123456789/20712**
[29] Yadava RR. Singh VN. Yadava S. J. Chem. Eng. Data, 1994; 39: 705. : 1988; 33: 402. https://doi.org/10.1021/je00016a014
[30] Sathyanarayan B. Ranjith Kumar B. SavithaJyostna T. Satyanarayan N J. Chem. Thermodyn., 2007; 39:16. https://doi.org/10.1016/j.jct.2006.06.009
[31] Suindells J R. Godfray T B. J. Res. Natd. Bur.Stand., 1952; 48: 1. https://nvlpubs.nist.gov/nistpubs/jres/048/1/V48.N01.A01.pdf
[32] Nikam P S. Shirsat L N. Hasan M. J. Chem. Eng. Data, 1998; 43: 732. https://doi.org/10.1021/je980028e
[33] Roy M N. Jha A. Dey R. J. Chem. Eng. Data, 2001; 46:1327. https://doi.org/10.1021/je010009w
[34] Roy M N. Jha A. Choudhury A. J. Chem. Eng. Data, 2004; 49: 291. https://doi.org/10.1021/je030205y
[35] Kuppusami J. Suryanarayana CV. Indian J Acoustic Soc. India, 1977; 5: 102. https://www.google.com/search?q=J.+Kuppusami%2C+C.V.+Suryanarayana%2C+Indian+J+Acoust+Soc.India%2C++1977.
[36] Suryanarayana CV. Kuppusami J. Indian J Acoustic Soc. India, 1976; 4: 75. https://scholar.google.co.in/scholar?q=C.V.+Suryanarayana,+J.+Kuppusami,+Indian+J+Acoust+Soc.India,
[37] Dean JA. Lange's Handbook of chemistry, 13th Ed. New York: McGraw Hill Int. 1987; 186. https://www.accessengineeringlibrary.com/binary/mheaeworks
[38] Thiyagarajan R. Suhaimi Jaafar M. Palaniappan L. Journal of physical Science, 2007; 18 :81. http://web.usm.my/jps/18-2-07/Article%2018-2-6.pdf
[39] Singh R P. Sinha CP. Das J C. Ghosh P. Journal of Chem. Eng. Data, 1990; 35:93. https://aip.scitation.org/doi/abs/10.1063/1.4926955
[40] Sumathi T. Govindarajan S. International Journal of Biology, Pharmacy and Allied Sciences (IJBPAS) 2012; 1: 1153. https://www.hindawi.com/journals/ac/2014/343012/
[41] Ali A. Nain A K. Sharma VK. Ahmed S. Indian Journal of Physics B, 2001; 75: 519. http://arxiv.iacs.res.in:8080/jspui/bitstream/10821/6364/1/Ultrasonic%20Studies%20in%20Binary%20Liquid%20Mixtures_A%20Ali.pdf
[42] Reddy KC. Subrahmanyan SV. Bhimsenachar J. J. Phys. Soc. Japan, 1964; 19: 59. https://www.sgbaukrc.ac.in/all-theses/science/physics/
[43] Naidu PS. Ravindra Prasad K. Indian J Pure & Appl. Phys., 2002; 40: 264. http://nopr.niscpr.res.in/handle/123456789/25299

[44] Rama Rao GV. Viswanatha Sama A. Ramachandran D. Rambabu C. Indian Journal of Pure & Applied Physics, 2005; 43: 602. http://nopr.niscpr.res.in/handle/123456789/8851
[45] Suryanarayana CV. "The liquid state-A new out look", Indian J Acoustic Soc. India, 1977; 5: 11. .https://www.google.com/search?q="The+liquid+stateA+new+out+look"%2C+Indian+J+Acoust+Soc.India.