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DYNAMIC INTERACTIONS: A STUDY OF VISCOSITIES AND EXCESS THERMODYNAMIC PROPERTIES IN CYCLIC ETHER-1-ALKANOL SYSTEMS

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Abstract

Over the past three decades, the ultrasonic study of liquid mixtures has emerged as a pivotal avenue for unraveling molecular interactions and exploring the physicochemical behavior inherent in such systems. This paper delves into the importance of ultrasonic techniques, focusing on their profound role in comprehending molecular interactions and investigating the departure of liquid mixtures from ideality. Thermodynamic and transport properties, widely utilized for studying liquid mixtures, serve as key indicators of the intricate intermolecular forces and size differences within these systems.

The exploration of excess thermodynamic functions forms a cornerstone in understanding the nuanced molecular interactions and structural changes exhibited by binary liquid mixtures. Sensitivity to variations in both intermolecular forces and molecular sizes, excess thermodynamic functions play a crucial role in deciphering deviations from ideal behavior. Fundamental properties like internal pressure and free volume, initially investigated by Hildebrand and Scott, serve as pivotal parameters in studying molecular interactions within liquid mixtures.

Utilizing ultrasonic velocity, viscosity, and density measurements, this study employs a multidimensional approach to unravel the molecular intricacies of liquid mixtures. The insights gained from measuring these properties are not only significant for studying the departure of real liquid mixtures from ideal behavior but also for comprehending the structural changes associated with these dynamic systems. The paper underscores the importance of ultrasonic techniques in providing a comprehensive understanding of liquid mixtures, shedding light on their thermodynamic and transport properties, and facilitating insights into the molecular interactions governing their behavior.

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1. Introduction

During the last three decades, ultrasonic study of liquid mixtures has gained much importance in understanding the nature of molecular interactions and also for investigating the physic-chemical behaviour of such systems. 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 the various species present in the 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 molecules. Internal pressure and free volume are the fundamental properties of the liquid state which have been studied initially by Hildebrand and Scott (11,12) and subsequently used to investigate molecular interactions of binary liquid mixtures. Thermodynamic and transport properties of liquid mixtures have been extensively used to study the departure of a real liquid mixture behaviour from ideality (13,14). The measurements of ultrasonic velocity, viscosity and density have been adequately employed in understanding the molecular interactions in the liquid mixtures. The measurements of excess thermodynamic properties are found to be greatly significant in studying the structural changes associated with the liquids (15).

The 1,4-dioxane is selected as a solvent in the present work since it finds a variety of application. Alcohols play an important role in many chemical reactions due to the ability to undergo self-association with internal structures (16). 1,4-Dioxane cyclic ether is used as a degreasing agent, as a component of paints and varnish removers and as a wetting and dispersion agent in the textile industry. 1,4- Dioxane is also used as a solvent in the chemical synthesis. Ultrasonic studies of the solution of the alcohols with 1,4-dioxane have yielding valuable information regarding the association between the momomers of alcohols and free oxygen of dioxane through hydrogen bonding.

2 Experimental section

2.1 Material

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

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

2.2 Measurements

Six binary system viz. 1,4-dioxane + 1-methanol, 1,4-dioxane + 1-ethanol, 1,4-dioxane + 1-propanol, 1,4dioxane + 1-butanol, 1,4-dioxane + 1-hexanol and 1,4-dioxane +1-octanol were studied. Each sample mixture was prepared, on mass basis, by mixing the calculated volume of liquid components in specially designed glass stoppered bottles. All binary mixtures were prepared by weight covering the entire mole fraction range. The components of binary mixtures were injected by means of syringe in to the glass vials of sealed with rubber stopper in order to check evaporation losses during sample preparation. The mass measurements were carried out using an 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 one system, and their density and sound velocity were measured on the same day.

2.2.1 Density

Densities of pure liquids and their binary mixtures were determined by using a double-arm pycnometer (30) with a bulb of 25 cm^3 and a capillary of an internal diameter of about 1 mm is used to measure the densities (ρ) of pure liquids and binary mixtures. The pycnometer is calibrated by using conductivity water (having specific conductance less than 1×106 ohm^{-1}) with 0.9970 and 0.9940 g cm^{-3} as its densities at T = 303.15 K, respectively. The pycnometer filled with air bubbles free liquids is kept in a thermostate water bath (MSI Goyal Scientific, Meerut, India) controlled with a thermal equilibrium. The precision of the density measurements was estimated to be ±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

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

2.2.2 Viscosity

The viscosity of pure liquids and their binary mixture were measured using suspended ubbelohde type viscometer (31,32) having a capacity of about 15 ml and the capillary having a length of about 90 mm and 0.5 mm internal diameter has been used to measure the flow time of 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 described by researchers (33,34). The efflux time was measured with an electronic stop watch (Racer) with a time resolution (±0.015), and an average of at least four flow time readings was taken. Glass stopper was placed at the opening of the viscometer to prevent the loss due to evaporation during measurements. The two bulbs reservoir, one at the top and other at the bottom of the viscometer linked to each other by U type facilitate the free full of liquid at atmospheric pressure. The measured values of 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. which compare well 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	.6630 [22]

3 Theoretical Aspects

3.1 Free volume (V_f)

Liquid viscosity has been treated as free volume problem by a number of workers. Suryanarayana and Kuppusami derived a formula for the free volume based on one dimensional analysis of the situation. When a 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 is 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 evaluation of internal pressure from the knowledge of ultrasonic velocity, u, density, ρ, and viscosity, η, the relation proposed is expressed as

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

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

3.3 Excess Thermodynamic Parameters

The excess thermodynamic function (Y^E) provide a way to represent directly the deviation of a solution from 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 the parameters are computed using the general formu

$$Y^E = Y_{exp} - (X_1Y_1 + X_2Y_2)$$

4. 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 value of viscosity (η^E), sound velocity (u^E), free volume (V_f^E) and internal pressure (p_i^E) at 303.15 K are reported in Table 3. The result present 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 the seven organic compounds namely 1,4-dioxane, methanol, ethanol, propanol, butanol, hexanol and octanol are a polar organic compounds having dipole moment 0.45 D, 1.70 D, 1.69 D, 1.68 D, 1.66 D, 1.60 D and 1.68 D respectively.

Normally more the dipole moment, stronger is the intermolecular interaction, which result is decreasing of free space between molecules and increase in the ultrasonic velocity.

The measured values density (ρ), viscosity (η) and sound velocity (u) and the evaluated parameters are presented in Table 2. For the binary system 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 the 303.15 K temperature the value of sound velocity, viscosity and free volume increase with increase in mole fraction of 1,4-dioxane (x_1) but the value of density (ρ) and internal pressure decrease with increase in mole fraction of 1,4-dioxane (x_1). It is evident that the pronounced increase or decrease in these parameters with composition of mixtures indicates the presence of interaction between the component molecules in the binary mixtures. This trend indicates 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. All these process may lead to strong interaction forces (38).

An analysis of the viscosity values from the Table 2 it can be observed that the viscosity is in decrease trend with increase in mole fraction of 1,4-dioxane. Similar trend is also observed for the internal pressure values. This kind of non-linearity indicates the presence of molecular interactions.

It is observed that for the binary liquid mixtures, the density (ρ) and free volume (V_f) increase with increase in concentration of 1,4-dioxane. The increases the density (ρ) and free volume (V_f) in these liquid mixtures suggest that molecular interaction among the molecules of the 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 + 1propanol, 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-M ethanol				
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-E thanol				
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

The nature of 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 show considerable deviation from linearity in their concentrations and this can be interpreted as the presence of strong or weak interactions. The extent of deviation depends upon the nature of the constituents and composition of the mixtures. The thermodynamic excess properties are found to be more sensitive towards intermolecular interaction among the component molecules of liquid mixtures. The sign and extent of deviation of excess parameters depend upon on the strength of interaction between unlike molecules (39). So various excess acoustic and thermodynamic parameters have been evaluated and corresponding graphs are also given.

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

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
3. The chemical contributions include breaking up of the associates present in pure liquids, resulting in positive u^E. In the present mixture the graphical representation of excess sound velocity (u^E) are positive, presented in Figure 1. The positive values reveal that there are present weak interactions in the mixture.

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

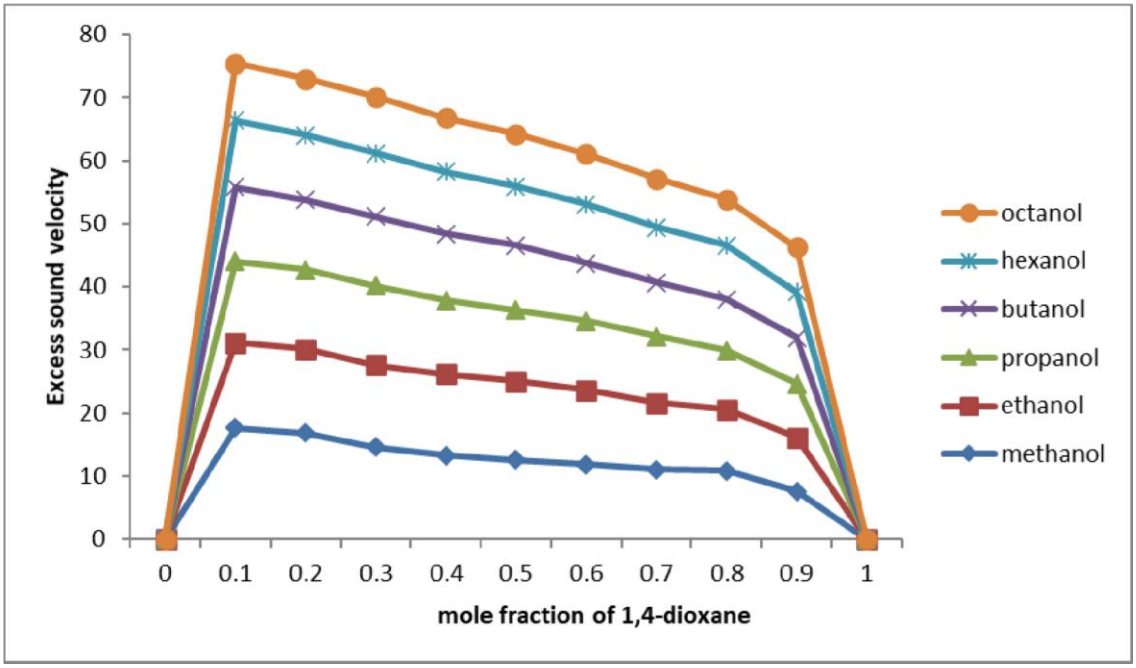

Figure 1. Plots of excess sound velocity versus mole fraction of 1,4 -dioxane (x_1) at 303.15 K for binary mixtures of 1,4-dioxane with 1-methanol, 1-ethanol, 1-propanol, 1-butanol, 1-hexanol and 1-octanol at 303.15 K.

The measurement of viscosity in binary liquid mixture gives some reliable information in the study of intermolecular interaction. The molecules of one or more components forming the temarise are either polar, associating or accordingly show non-ideal behavior's in mixtures. Negative values of η^E in most of the cases are the consequence of lower viscosity contributions of similar non-specific interaction and hydrogen bonding effect 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. The negative values imply the presence of dispersion forces between the mixing components in the mixtures.

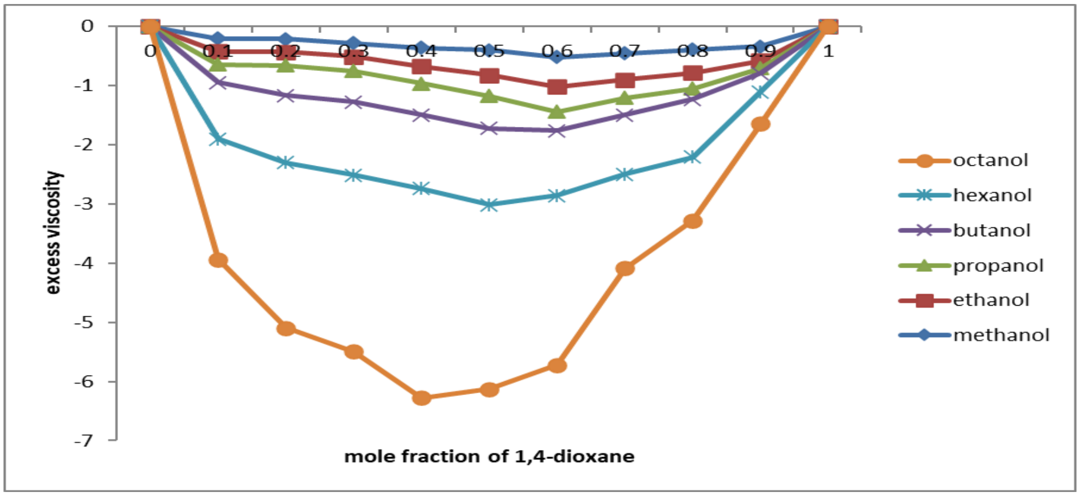

Figure 2. Plots of excess viscosity versus mole fraction of 1,4-dioxane (x_1) at 303.15 K for binarymixtures of 1,4 dioxane with 1-methanol, 1-ethanol, 1-propanol, 1-butanol, 1-hexanol and 1-octanol at 303.15 K.

The excess free volume (V_f^E) is another important parameter through which molecular interactions can be explained. 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 interaction between alkanol and 1,4dioxane molecule or to structural contributions arising from the geometrical fitting of one component (alkanol) into the other (1,4-dioxane) due to difference in the free volume between components.

R R
| |
O □ H H □ *O*

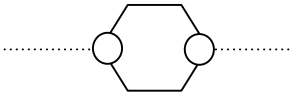

Figure 3. Hydrogen bonding between 1,4-dioxaneand 1- alkanol molecule.

In order to substantiate the presence of interaction between the molecules, it is essential to study the excess parameter such as free volume. The deviation of physical property of the 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, alkanols in a polar and has self - association character in other polar organic solvents.

R *R* *R* *R*
| | | |
.... *O* □ *H* .... *O* □ *H* .... *O* □ *H* .... *O* □ *H* ....

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

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

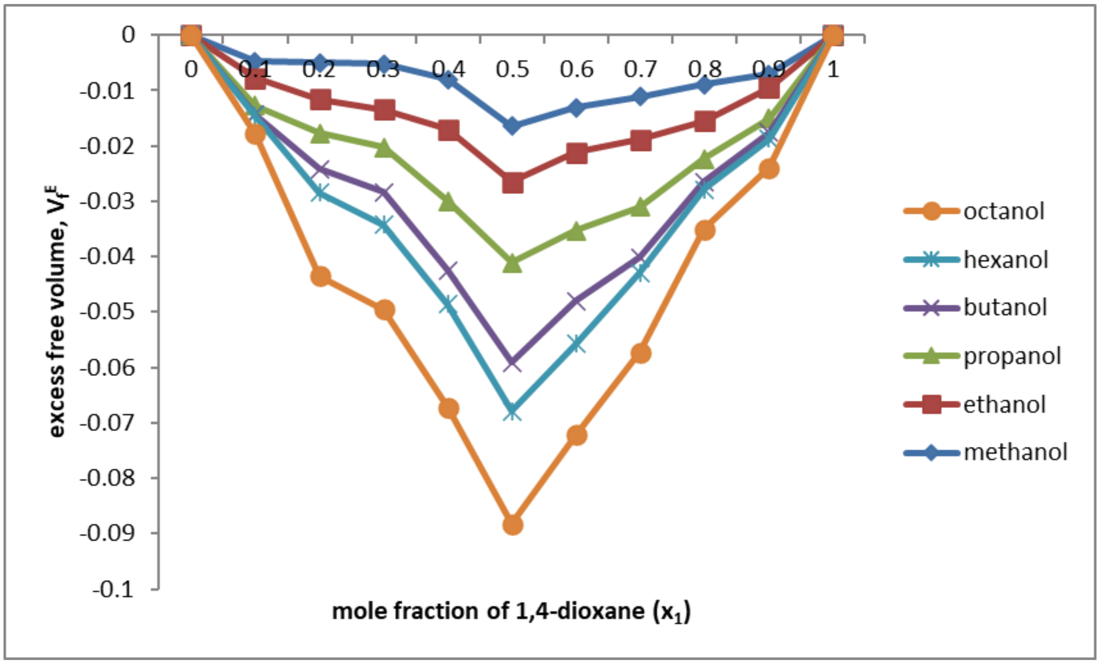

Figure 5. Plots of excess free volume versus mole fraction of 1,4-dioxane (x_1) at 303.15 K for binary mixtures of 1,4 dioxane with 1-methanol, 1-ethanol, 1-propanol, 1-butanol, 1-hexanol and 1-octanol at 303.15 K.

The excess internal pressure (p_i^E) is another important parameter through which molecular interactions can be explained. In the present investigation for the six binary systems it is observed that, as the mole fraction of 1,4 dioxane increase, the p_i^E values decreases. The values of 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 decrease with increase in $_1$. This situation is observed for all six binary system under study and can be viewed from plots Figure 6.

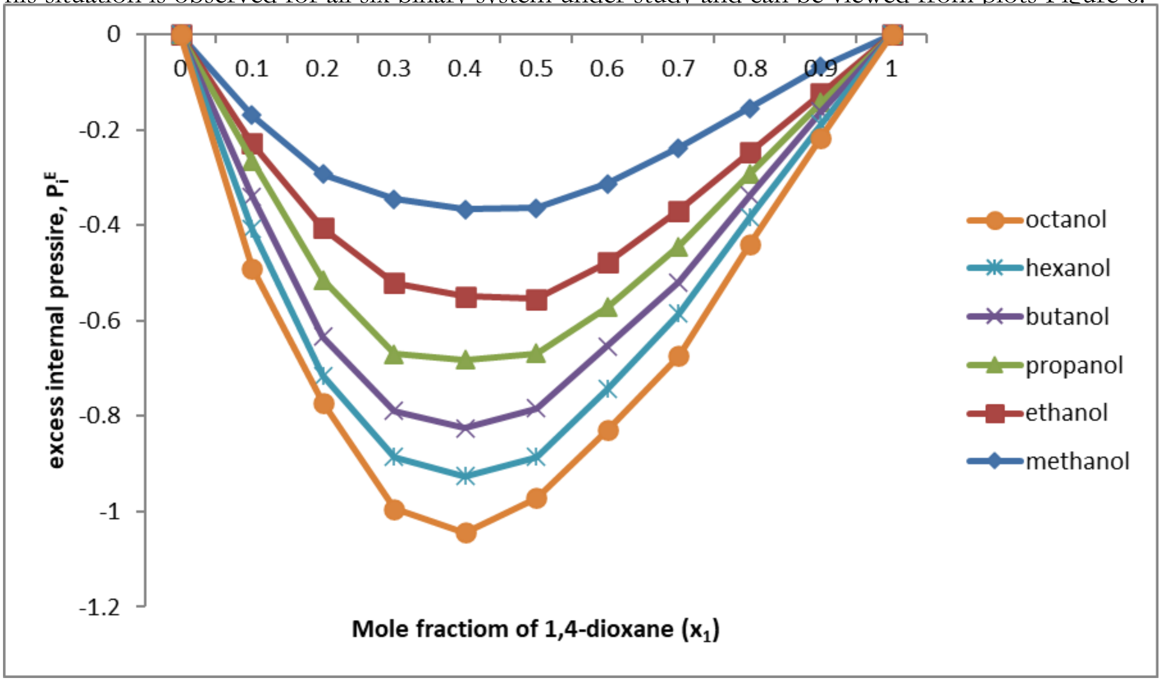

Figure 6. Plots of excess internal pressure versus mole fraction of 1,4-dioxane (x_1) at 303.15 K for binary mixtures of 1,4-dioxane with 1-methanol, 1-ethanol, 1-propanol, 1-butanol, 1-hexanol and 1-octanol at 303.15 K.

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

5. 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 1,4dioxane + octanol at 303.15 K are shown negative values of excess free volume and excess internal pressure may given information about the considerable interactions among the molecules of the between these binary mixtures. So, we may conclude that 1-alkanols which is self-associating polar organic liquid has a tendency to form complexes with 1,4-dioxane and the increase in its dilution causes dispersion of aromatic C-H bond stretching as the self-association of 1-alkanols is disrupted. It is also concluded that Suryanarayana (45) approach for estimating free volume and internal pressure of binary liquid mixtures, based on dimensional analysis using thermodynamic considerations is very well applicable in the present case.

Declarations Conflict of interest

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

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Data availability statement

The authors confirm that the 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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