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Acoustical and excess thermodynamical studies on cyclic ether (1,4-Dioxane) with 1-alkanols at 303.15K

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Abstract
The ultrasonic velocity of liquids and liquid mixtures play very important role in understanding the nature of molecular interaction occurring in the system. In this paper presents experimental values of ultrasonic velocity (u), density (ρ), and viscosity values (η) of pure1,4-dioxane, 1-methanol, 1-ethanol, 1-propanol, 1-butanol, 1-hexanol, 1-octanol and their binary mixtures with 1,4-dioxane as a common component over the whole composition range at 303.15 K. From these data acoustical parameters such as adiabatic compressibility (β_s), free volume (V_f), internal pressure (P_i), molar volume (V_m), and their excess values are evaluated. From the properties of these acoustical parameters, the nature and strength of molecular interactions in these binary systems are discussed. The non-linear variation of these parameters shows the presence of interaction and their excess values is indicative of interaction between the components molecule in all systems.

Keywords: ultrasonic velocity, density, acoustical parameters, binary mixtures, molecular interaction, isentropic compressibility, free volume, free length

Introduction
In recent years the ultrasonic study of properties of liquid mixtures and solvation find direct application in chemical and biochemical industry. Thermodynamic and transport properties of liquid of liquid mixtures have been extensively used to study the departure of a real liquid mixture behavior from ideality. The measurements of ultrasonic velocity, viscosity and density have been adequately employed in understanding the molecular interactions in liquid mixtures. In recent years, ultrasonic investigation of binary liquid mixtures has revolutionized the world of medical, petro chemical and pharmaceutical industries to great extent. Ultrasonic technique has become a powerful tool for studying the molecular behavior of liquid mixtures. This is because of its ability of characterizing physic-chemical behavior of liquid medium. Ultrasonic velocity and isentropic compressibility of liquid mixtures are useful in understanding the solute-solvent interaction and investigation the physico-chemical behavior of liquid mixtures. Excess parameters provide valuable information about the molecular interaction and macroscopic behavior of liquid mixtures and be used to test and improve thermo dynamical models, for calculating and predicting the fluid phase equilibria. The knowledge of excess isentropic compressibility helps in understanding the molecular orientation and study the extent of intermolecular interaction between component molecules of the liquid mixtures. Fundamental thermodynamic and thermo physical properties are essential sources of information necessary for a better understanding of the non-ideal behaviour of complex systems because physical and chemical effects which are caused by molecular interactions, intermolecular forces etc. of unlike molecules. The present paper is part of our ongoing research on the thermodynamic properties of binary liquid mixtures containing cyclic ether with 1-alkanols. Physical properties of binary organic liquid mixtures have been extensively studied in the literature of solution chemistry in view of the importance of such data in many areas of science and engineering. The physical properties of binary mixtures are studied for many reasons, the most important of which is to provide information about molecular interactions present in the liquid studied (Vural *et al*, 2011) [1]. Experimental data of physical properties such as densities, viscosities or sound velocity are required for a full understanding of the thermodynamic properties of liquid mixtures, as well as for practical chemical engineering works. The knowledge of transport and thermodynamic properties of binary liquid mixtures containing cyclic ether are considerable interest from the view point of academic and many industrial processes. Cyclic ethers are excellent solvents of polymers and are used in polymer synthesis (Brandrup, 1989) [2]. Excess thermodynamic functions of mixture of cyclic ethers in polar and non – polar solvent have gained considerable interest because these compounds are good solvent (Banipal,2000) [3]. In recent years the ultrasonic study of properties of liquid mixtures and solvation find direct application in chemical and biochemical industry. Thermodynamic and transport properties of liquid of liquid mixtures have been extensively used to study the departure of a real liquid

mixture behavior from ideality. The measurements of ultrasonic velocity, viscosity and density have been adequately employed in understanding the molecular interactions in liquid mixtures. The 1,4-dioxane is selected as a solvent in the present work since it finds a variety of applications. Alcohols play an important role in many chemical reactions due to the ability to undergo self-association with internal structures (Palaniappan, 2002) [4]. Present study of binary mixture of 1,4- dioxane and alcohols is extension of our research work (Seema *et al*, 2021) [5]. In order to have a clear understanding of intermolecular interaction between the component molecules, densities, viscosities and ultrasonic velocities of a six binary liquid mixtures at 303.15K, over the entire composition range is being reported here. The experimental values of densities, viscosities and sound velocities have been used for computation of isentropic compressibility (β_s), molar volume (V_m), internal pressure (P_i) and free volumes (V_f). These parameters have been found to be sensitive to the interactions between component molecules, which enables used to have a better understanding of behavior of liquid mixture.

Experimental

Material

The chemicals used in the present work were high purity laboratory reagent grade samples of 1,4-dioxane, 1-methanol, 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 and fractionally distilled twice (Perrin, 1988) [6]. All chemicals was purified by the method described by Zhao (Zhao *et al*, 2000) [7] ethyl acetate was dried over K_2CO_3, filtered and distilled were discarded. All the chemicals were stored in dark bottles over freshly activated molecular sieve to minimize adsorption of 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 the available literature (Rodriguez *et al* 2001, Nikam *et al* 1996, Roy *et al* 2005, Kadam *et al* 2006, Nayak *et al* 2003, Baragi *et al* 2005, Al- Kandary *et al* 2009, Dubey *et al* 2008, Elagovan etv al 2013, Yasmin *et al* 2019, Ali *et al* 2005, Koneti *et al* 2014) [8-19] as shown in Table 1. The reported experimental values of density (ρ) and viscosity (η) conform closely to their corresponding literature values.

Measurements

Six binary system *viz.* 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 mass basis, by mixing the calculated volume of liquid components in specially designed glass stoppered bottles. All binary mixture 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 (Yadava *et al*, 1988) [20]. 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.

Density

Densities of pure liquids and their binary mixtures were determined by using a double-arm pycnometer (Satynarayana *et al*, 2007) [21] 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 1×10^6 ohm^{-1}) with 0.9970 and 0.9940 gcm^{-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 $g.m^{-3}$ which compare well with corresponding literature values of respectively.

Sound velocity

The ultrasonic velocities were measured using a multi frequency 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, 1-butanol, 1-hexanol and 1-octanol at 303.15K were 1348, 1084, 1141, 1182, 1196, 1298 and 1327 $m.s^{-1}$ respectively, which compare well with the corresponding literature values.

Viscosity

The viscosity of pure liquids and their binary mixture were measured using suspended ubbelohde type viscometer (Suindells *et al*, 1952, Nikam *et al*, 1988) [22-23] 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 (Roy *et al*, 2001, Choudhury *et al* 2004) [24-25]. 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. Viscosity values (η) of pure liquids and their binary mixtures are calculated using the solution.

$$\frac{\eta}{\rho} = \text{at} - \frac{b}{t}$$

Where t is the efflux time and a & b are viscometric constants.
The measured viscosities have reproducibility within ±0.002 CP. 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 7.8512C.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 [13]	1348	1322.3 [19]	1.0303	1.0690 [12]
1-Methanol	0.7840	0.7817 [9]	1084	1084.0 [17]	0.4949	0.5040 [10]
1-Ethanol	0.7720	0.7807 [8]	1141	1144.3 [10]	1.1399	1.3560 [8]
1-Propanol	0.8070	0.8003 [16]	1182	1182.6 [10]	1.5477	1.6626 [10]
1-Butanol	0.8040	0.8020 [10]	1196	1196.6 [10]	2.2045	2.2740 [11]
1-Hexanol	0.8128	0.8118 [10]	1298	1282.0 [18]	4.5642	4.5930 [14]
1-Octanol	0.8242	0.8187 [15]	1327	1330.8 [15]	7.8512	7.6630 [14]

Theoretical

Free Volume (V_f)

According to Bingham (Bingham, 1922) [26] and Macleod (Macleod, 1945) [27] free volume (V_f) can be calculated from the sound velocity and viscosity by the relation given below

$$V_f = (M\,U/\,k\,\eta)^{3/2} \quad (1)$$

Where M is the molecular weight (gm)
U, is the sound velocity (cm/sec)
η, is the viscosity (CP)
k is the constant, equal to 4.28×10^9, independence of temperature and V_f, the free volume is in milliliters per mole.

Molar volume (V_m)

The molar volume V_m calculated from the measured values of density (ρ), molar volume (V_m) was calculated using the relation

$$V_m = \frac{(X_1M_1 + X_2\,M_2)}{\rho} \quad (2)$$

Where X_1, X_2 and M_1, M_2 are the mole fraction and molecular weight of the component 1 and 2 respectively.

Internal Pressure (P_i)

Suryanarayana 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

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

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.

Isentropic compressibility (β_s)

β_s is the isentropic compressibility, which is given by the relation

$$\beta_s = u^{-2}\,\rho^{-1} \quad (4)$$

Where ρ is the density of liquid.

Excess Thermodynamic Parameters

The excess value of A^E of these thermodynamic parameters have been obtained by substracting the ideal value from the experimental value\

$$A^E = A_{exp.} - (X_1 A_1 + X_2 A_2)$$

Where A represents the parameter such as intermolecular free length, molar volume, available volume, free volume and isentropic compressibility and $X_1 and\ X_2$ are the mole fractions of components whose parameters.

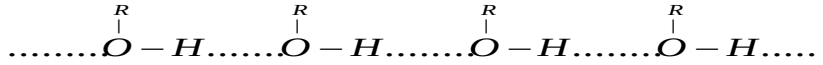
Results and Discussions

The experimentally determined 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 system are listed in Table-2. The excess values of isentropic compressibility (β_s^E), internal pressure (P_i^E), free length (V_f^E) and molar volume (V_m^E) at the 303.15 K are reported in Table -3.

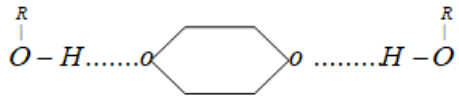
In all the mixtures, the ultrasonic velocity increase with increase in mole fraction of alkanols. It is observed that as the number of hydrocarbon group or chain length of alcohol increases, a gradual increase in sound velocity is noticed. This behavior of such concentration is different from the ideal mixture behavior can be attributed to intermolecular interaction in the system studied (Tiwari *et al*, 1995, Kannappan *et al* 1998) [28-29]. The dissociation of hydrogen bonded structure of 1-alkanols due to mixing of 1,4-dioxane with it may result in increase in ultrasonic velocity.

Alkanols are liquids which are associated through the hydrogen bonding and in the pure state, they exhibit an equilibrium between the monomer and multimer species. Also, they can be associated with any other group having some degree of polar attraction (Thirumaran *et al*, 2009) [30]. Due to polar nature od 1,4-dioxane and alkanols, the dipole-dipole interaction prevail in these mixtures. When the compounds are mixed the changes the occur in association equilibria are evidently repture of the hydrogen bonds (Vankatasu *et al*, 2006) [31] in pure 1,4-dioxane and alkanols, dipole-dipole interactions and the formation of O −H----O hydrogen bonds between the components.

The 1-alkanols are associated through hydrogen bonding.



and 1,4-dioxane – 1-alkanols interactions are due to hydrogen bonding between the oxygen atom of the cyclic ether and the proton of hydrogen group of alkanols.



The result presented in Table-2, show non-linear behavior of isentropic compressibility, internal pressure, molar volume and free volume which is further substantiated by their excess values Table-3. All these organic compounds, namely 1,4-dioxane, 1-methanol, 1-ethanol, 1-propanol, 1-butanol, 1-hexanol and 1-octanol are a polar organic compounds having dipole moments 0.45 D, 1.70 D, 1.69D, 1.68D,1.66D, 1.60D and 1.68D. Normally more the dipole moment, stronger is the intermolecular interaction, which results in decreasing of free space between molecules and increase in the ultrasonic velocity. Similar results have been also reported by Reddy (Reddy *et al*,2000) [32].

It is evident from Table-3 for the system 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 that the excess isentropic compressibility is negative over the entire range of composition and at the 303.15 K. More over its negative values has increased in mole fraction of 1,4-dioxane. These values are indications of stronger molecular interaction in these systems. The value of β_s^E are plotted against the mole fraction of 1,4-dioxane and are shown in Figure 1. The sign of excess isentropic compressibility plays a vital role in assessing the compactness due to molecular interaction in liquid mixtures through charge transfer, dipole-dipole interactions, dipole induced dipole interactions interstitial accommodation and orientational ordering leading to more compact structure making, which enhances excess isentropic compressibility to have negative values. Fort and Moore suggested that the liquids having different molecular sizes and shapes mix well there by reducing the volume which causes the values of β_s^E to be negative. It also suggest that the liquids are less compressible when compared to their ideal mixtures signifying the chemical effects including charge transfer forces, formation of H-bond and other

complex forming interactions (Iloukhani *et al*, 2005) [33]. It can also be said that the molecular interactions are strong in these binary liquid mixtures and that the medium is highly packed. Similar results were obtained by earlier workers (Bhatia, 2011) [34]. The negative values of β_s^E in these mixtures can be associated with a structure forming tendency.

A perusal of Table- 3 shows the value of excess internal pressure (P_i^E) are negative in all systems and increase with increase in the concentration of 1,4-dioxane in its binary mixture at 303.15 K. The value of excess internal pressure (P_i^E) are plotted against the mole fraction of 1,4-dioxane and are shown in Figure 2. Fort and Moore, suggested that the liquids having different molecular sizes and shapes mix well there by reducing the volume which causes the values of excess internal pressure (P_i^E) to be negative. It is also suggest that the liquids are less compressible when compared to their ideal mixtures signifying the chemical effects including charge transfer forces, formation of H-bond and other complex forming interactions. It can also be said that the molecular interactions are strong in these binary liquid mixtures that the medium is highly packed. The negative values of excess internal pressure (P_i^E) in these mixtures can be associated with a structure forming tendency.

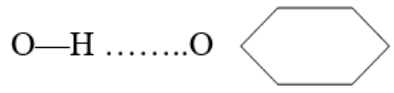
A perusal of Table-3 reveal that value of excess molar volume (V_m^E) are negative in all systems and increase with increase in the concentration of 1,4-dioxane in its binary mixture at 303.15 K. The value of (V_m^E) are plotted against the mole fraction of 1,4-dioxane and are shown in Figure 3. Generally V_m^E can be considered to arise from two type of interaction (Rao GVR *et al*, 2004)[35] between component molecule (i) Physical interaction consisting mainly of dispersion forces or weak dipole-dipole interaction and making a positive contribution (ii) Chemical or Specific interactions, including formation of hydrogen bond, charge transfer and other complex forming interactions, difference in size and shapes of the structure of component molecules which result in negative contribution. When 1,4-dioxane is mixed with alcohols hydrogen bond of alcohols of alcohols polymers are broken and specific intermolecular interaction leading to the bond formation like (−H----O−) take place causing decrease in excess molar volume (V_m^E).

A perusal of Table-3 also reveal that the values of excess free volume V_f^E are negative with the increase in concentration of 1,4-dioxane molecule at 303.15 K. The value of V_f^E are plotted against the mole fraction of 1,4-dioxane and are shown in Figure 4.

The observed values of V_f^E over whole range of composition suggest the weak interaction between component molecules. Similar results have also been found in other binary liquid mixtures (Hari Babu *et al*, 1996) [36]. A perusal of Table -3 shows that the value of excess free volume of the mixture under investigation are negative for all the binary liquid mixture 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. A negative excess free volume value is suggestive of the presence of strong specific interactions like the formation of H-bond, association through weaker physical forces and accommodation of one component molecules into the voids in the network of the other component molecules.

The charge in molar volume, free volume and internal pressure with change in composition in these systems, indicate the variations in cohesive forces of these system (Prakash *et al*, 1976) [37]. A perusal of the sign and magnitude of the excess values of the parameters (β_s^E), (P_i^E), (V_m^E), and (V_f^E) show that the strength of the molecular interaction between the component molecules. The present study point at clearly that in all six binary systems 1,4-dioxane is involved in the charge transfer interaction with alcohols. The oxygen atom of 1,4-dioxane being strongly electronegative would have tendency to attract electropositive hydrogen of alcohols resulting in the formation of new species, showing the negative value of excess thermodynamic properties (Mehra *et al*, 2006) [38].

The negative deviations of high magnitude lead to the unstable complex formation between the hetero molecules of the mixtures. In the present study the negative excess volume indicates the breaking of hydrogen bond of alcohols polymers as alcohol is diluted with 1,4-dioxane and association between unlike molecules causing contraction with increasing concentration of 1,4-dioxane. Therefore it can be concluded that AB type strong specific interaction take place leading to a bonding like (−H---O−) Which results in the formation of a complex of the type



The results reveal that the intermolecular interaction decreases with the increasing size of the alcohol molecules (Prasad *et al*, 2014) [39]. Hydrogen bonding strength also decreases with decreasing dipole moment of the alcohol molecules.

Table 2: Values of density, ultrasonic velocity, isentropic compressibility, internal pressure, molar volume, and free volume 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.

x_1	ρ k.gm^{-3}	U m/s	$\beta_s \times 10^{-8}$ (m^{2}N^{-1})	P$_i$×10^4 (atm.)	$V_m \times 10^6$ (m^{3}mol^{-1})	$V_f \times 10^6$ (m^{3}mol^{-1})
1,4-Dioxane +1- Methanol						
0.00000	784.00	1084.0	108.54	1.85827	40.8673	0.06639
0.09770	827.48	1092.0	101.34	1.55867	45.3365	0.06873
0.20043	866.92	1130.0	90.33	1.29924	49.9160	0.08297
0.28674	896.96	1155.0	83.57	1.13200	53.6390	0.09268
0.38010	917.16	1176.0	78.83	0.98575	58.1676	0.10226
0.49857	942.24	1240.0	69.02	0.83121	63.6649	0.11938
0.59198	96312	1266.0	64.78	0.75747	67.7222	0.12298
0.70860	98772	1289.0	60.93	0.67723	72.6602	0.12956
0.80020	998.76	1306.0	58.70	0.63839	76.9994	0.12420
0.90362	1008.9	1330.0	56.03	0.58824	81.9704	0.12564
1.00000	1010.8	1348.0	54.44	0.52793	87.1685	0.13976
1,4-Dioxane + 1-Ethanol						
0.00000	772.00	1141.0	99.49	1.48567	59.6761	0.03536
0.09885	809.44	1150.0	93.41	1.33256	62.0470	0.04274
0.20465	842.60	1170.0	86.69	1.17588	64.8839	0.05016
0.29964	865.20	1189.0	81.75	1.02250	67.8040	0.05849
0.39745	899.00	1217.0	75.10	0.92291	69.8318	0.06775
0.50220	920.16	1285.0	65.81	0.81416	73.0067	0.08167
0.59502	941.08	1288.0	64.05	0.75046	75.5312	0.08941
0.69003	972.00	1298.0	61.06	0.69393	77.2383	0.09964
0.79934	986.24	1310.0	59.08	0.62849	80.7854	0.11215
0.89342	993.56	1340.0	56.05	0.57388	84.1700	0.12619
1.00000	1010.8	1348.0	54.44	0.52793	87.1685	0.13976
1,4-Dioxane +1-Propanol						
0.00000	807.08	1182.0	88.68	1.12536	74.4563	0.03511
0.10006	820.64	1202.0	84.34	1.02842	76.6390	0.04054
0.12264	847.96	1215.0	79.88	0.94383	77.9160	0.05407
0.29821	870.08	1248.0	73.79	0.79892	78.6654	0.07234
0.40573	899.36	1264.0	69.59	0.74945	79.4542	0.08050
0.50439	916.72	1270.0	67.63	0.70945	80.9651	0.08633
0.60251	939.08	1275.0	65.50	0.67187	81.9650	0.09391
0.69410	955.8	1284.0	67.17	0.63513	82.6892	0.10268
0.79626	980.84	1290.0	61.26	0.60302	84.0102	0.11164
0.89926	1005.4	1312.0	57.78	0.56923	84.8285	0.12362
1.00000	1010.8	1348.0	54.44	0.52793	87.1685	0.13976
1,4-Dioxane +1- Butanol						
0.00000	804.0	1196.0	86.95	0.93886	92.1902	0.02879
0.09734	813.6	1203.0	84.92	0.82365	92.7720	0.04113
0.19759	842.52	1209.0	81.20	0.73831	91.2552	0.05720
0.30443	862.64	1221.0	77.75	0.69325	90.8593	0.06771
0.40480	876.96	1268.0	70.92	0.62881	90.9767	0.08813
0.49442	902.24	1282.0	67.43	0.62110	89.8172	0.09166
0.59768	927.44	1287.0	65.09	0.61152	88.9342	0.09539
0.68628	950.28	1297.0	62.55	0.58231	88.1010	0.11009
0.79076	973.92	1315.0	59.37	0.56878	87.4632	0.11678
0.89091	998.36	1334.0	56.28	0.55292	86.7254	0.12616
1.00000	1010.8	1348.0	54.44	0.52793	87.1685	0.13976
1,4-Dioxane +1-Hexanol						
0.00000	812.8	1298.0	73.02	0.76533	125.691	0.01768
0.09108	837.96	1302.0	70.39	0.67619	120.389	0.02848
0.19485	854.08	1311.0	68.12	0.63767	116.409	0.03711
0.29842	860.24	1314.0	67.32	0.59775	113.884	0.04815
0.40439	881.44	1320.0	65.11	0.56874	109.455	0.06191
0.45430	889.96	1334.0	63.14	0.55520	107.619	0.06733

0.60286	925.76	1338.0	60.33	0.53273	101.202	0.09206
0.69974	948.6	1340.0	58.70	0.53284	97.3310	0.10590
0.80182	968.4	1342.0	57.33	0.52919	93.8597	0.11426
0.88834	993.84	1346.0	55.53	0.52758	90.2338	0.12731
1.00000	1010.8	1348.0	54.44	0.52793	87.1685	0.13976
1,4-Dioxane +1-Octanol						
0.00000	824.2	1327.0	68.90	0.66872	158.005	0.01166
0.09780	828.4	1329.0	68.34	0.57272	152.230	0.02098
0.20653	837.08	1330.0	67.53	0.58289	145.177	0.02313
0.29810	852.92	1332.0	66.08	0.51855	137.962	0.03818
0.40275	859.56	1334.0	65.37	0.49443	131.769	0.05113
0.49229	885.28	1336.0	63.28	0.51382	123.674	0.05439
0.60068	903.04	1338.0	61.85	0.49788	116.193	0.07220
0.69888	926.64	1339.0	60.19	0.48131	108.770	0.09686
0.79610	956.48	1341.0	58.13	0.49999	101.096	0.10643
0.89749	985.96	1345.0	56.06	0.51467	93.7423	0.12142
1.00000	1010.8	1348.0	54.44	0.52793	87.1685	0.13976

Table 3: Excess values of isentropic compressibility(β_s^E), internal pressure(P_i^E), molar volume (V_m^E), and free volume(V_f^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

x_1	$\beta_s^E \times 10^{-7}$ (m^2N^{-1})	P_i^E X 10^4 (atm.)	V_m^E (m^3mol^{-1})	V_f^E (m^3mol^{-1})
1,4-dioxane + 1-Methanol				
0.00000	0.000000	0.00000	0.0000	0.00000
0.09770	-0.19084	-0.16943	-0.05058	-0.00482
0.20043	-0.73591	-0.29226	-0.22597	-0.00500
0.28674	-0.94539	-0.34470	-0.49879	-0.00525
0.38010	-0.91341	-0.36667	-0.59475	-0.00798
0.49857	-1.25438	-0.36374	-0.77944	-0.01641
0.59198	-1.17320	-0.31323	-0.94673	-0.01315
0.70860	-0.92656	-0.23817	-0.81204	-0.01118
0.80020	-0.65418	-0.15515	-0.71401	-0.00889
0.90362	-0.36169	-0.06757	-0.33058	-0.00704
1.00000	0.000000	0.00000	0.0000	0.00000
1,4-Dioxane + 1-Ethanol				
0.00000	0.000000	0.0000	0.0000	0.00000
0.09885	-0.16232	-0.05836	-0.34377	-0.00294
0.20465	-0.35747	-0.11371	-0.41559	-0.00656
0.29964	-0.42357	-0.17610	-0.50631	-0.00814
0.39745	-0.64868	-0.18209	-0.78121	-0.00910
0.50220	-1.10460	-0.19038	-0.97014	-0.01010
0.59502	-0.86285	-0.16522	-0.99867	-0.00806
0.69003	-0.73387	-0.13077	-0.80426	-0.00775
0.79934	-0.44002	-0.09162	-0.76595	-0.00666
0.89342	-0.31936	-0.05613	-0.36686	-0.00244
1.00000	0.000000	0.0000	0.00000	0.00000
1,4-Dioxane + 1-Propanol				
0.00000	0.000000	0.0000	0.00000	0.00000
0.10006	-0.09167	-0.03714	-0.91399	-0.00503
0.12264	-0.45983	-0.10824	-1.09620	-0.00613
0.29821	-0.46806	-0.14826	-1.42088	-0.00682
0.40573	-0.51974	-0.13350	-1.45746	-0.01292
0.50439	-0.37808	-0.11455	-1.99903	-0.01456
0.60251	-0.25484	-0.09351	-2.14871	-0.01405
0.69410	-0.22566	-0.07554	-1.43194	-0.01207
0.79626	-0.17533	-0.04662	-0.56704	-0.00680
0.89926	-0.11109	-0.01831	-0.45833	-0.00557
1.00000	0.000000	0.0000	0.00000	0.00000
1,4-Dioxane +1- Butanol				
0.00000	0.000000	0.0000	0.00000	0.00000

0.09734	-0.114212	-0.07519	-1.07405	-0.00153
0.19759	-0.167370	-0.11934	-1.25808	-0.00648
0.30443	-0.270173	-0.12050	-1.39875	-0.00813
0.40480	-0.287026	-0.14369	-1.82020	-0.01241
0.49442	-0.344147	-0.11458	-2.11069	-0.01800
0.59768	-0.242586	-0.08173	-2.25372	-0.01273
0.68628	-0.208616	-0.07453	-1.64205	-0.00913
0.79076	-0.186772	-0.04512	-0.55516	-0.00420
0.89091	-0.170392	-0.01983	-0.52992	-0.00250
1.00000	0.000000	0.0000	0.00000	0.00000
1,4-Dioxane + 1-Hexanol				
0.00000	0.000000	0.0000	0.00000	0.0000
0.09108	-0.093432	-0.06751	-1.79251	-0.00032
0.19485	-0.127989	-0.08139	-1.87459	-0.00435
0.29842	-0.015190	-0.09673	-2.31017	-0.00596
0.40439	-0.039833	-0.10058	-2.65638	-0.00614
0.45430	-0.144084	-0.10227	-3.56962	-0.00881
0.60286	-0.148480	-0.08947	-2.26339	-0.00780
0.69974	-0.131324	-0.06636	-2.00314	-0.00279
0.80182	-0.078830	-0.04578	-1.94200	-0.00130
0.88834	-0.098008	-0.02685	-1.23491	-0.00117
1.00000	0.000000	0.0000	0.00000	0.00000
1,4-Dioxane +1-Octanol				
0.00000	0.000000	0.0000	0.00000	0.00000
0.09780	-0.085902	-0.08222	-1.15434	-0.00320
0.20653	-0.162049	-0.05674	-1.80656	-0.01498
0.29810	-0.189114	-0.10819	-1.97558	-0.01526
0.40275	-0.229705	-0.11758	-2.29511	-0.01863
0.49229	-0.250224	-0.08558	-2.54289	-0.02033
0.60068	-0.163919	-0.08626	-2.73983	-0.01641
0.69888	-0.139344	-0.08901	-1.27332	-0.01433
0.79610	-0.074727	-0.05664	-1.11434	-0.00722
0.89749	-0.013970	-0.02768	-0.68611	-0.00522
1.00000	0.000000	0.0000	0.00000	0.00000

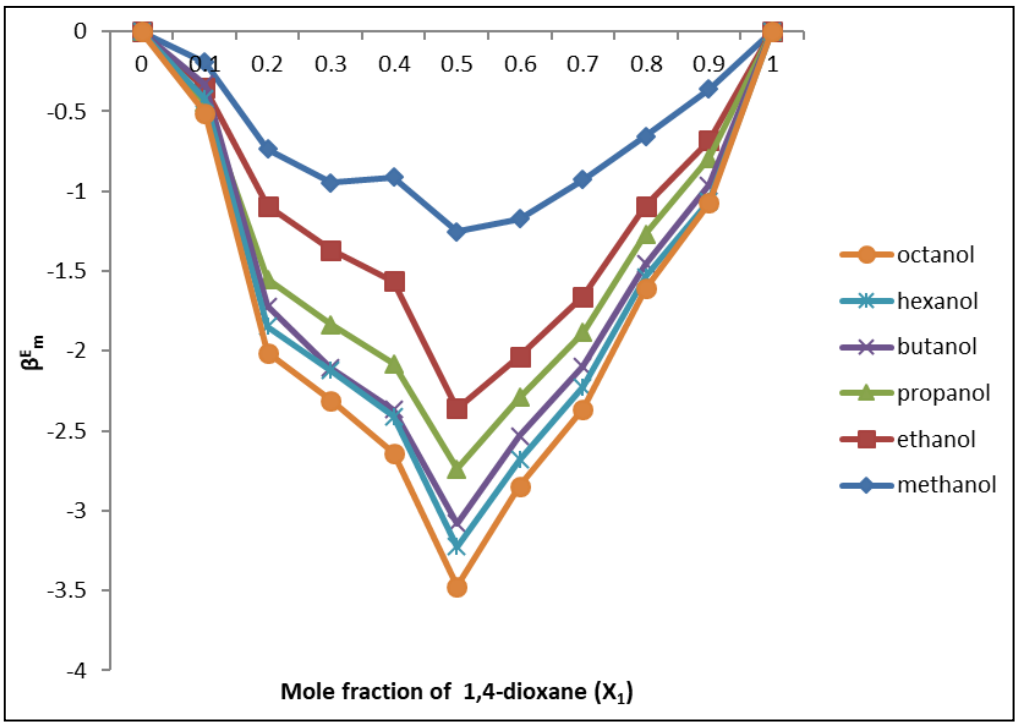


Fig 1: Plots of excess isentropic compressibility β_s^E versus mole fraction of 1,4-dioxane (X_1) at 303.15 K for binary mixtures of 1,4-dioxane with 1-methanol, 1-ethanol,1-propanol, 1-butanol, 1-hexanol and 1-octanol at 303.15 K

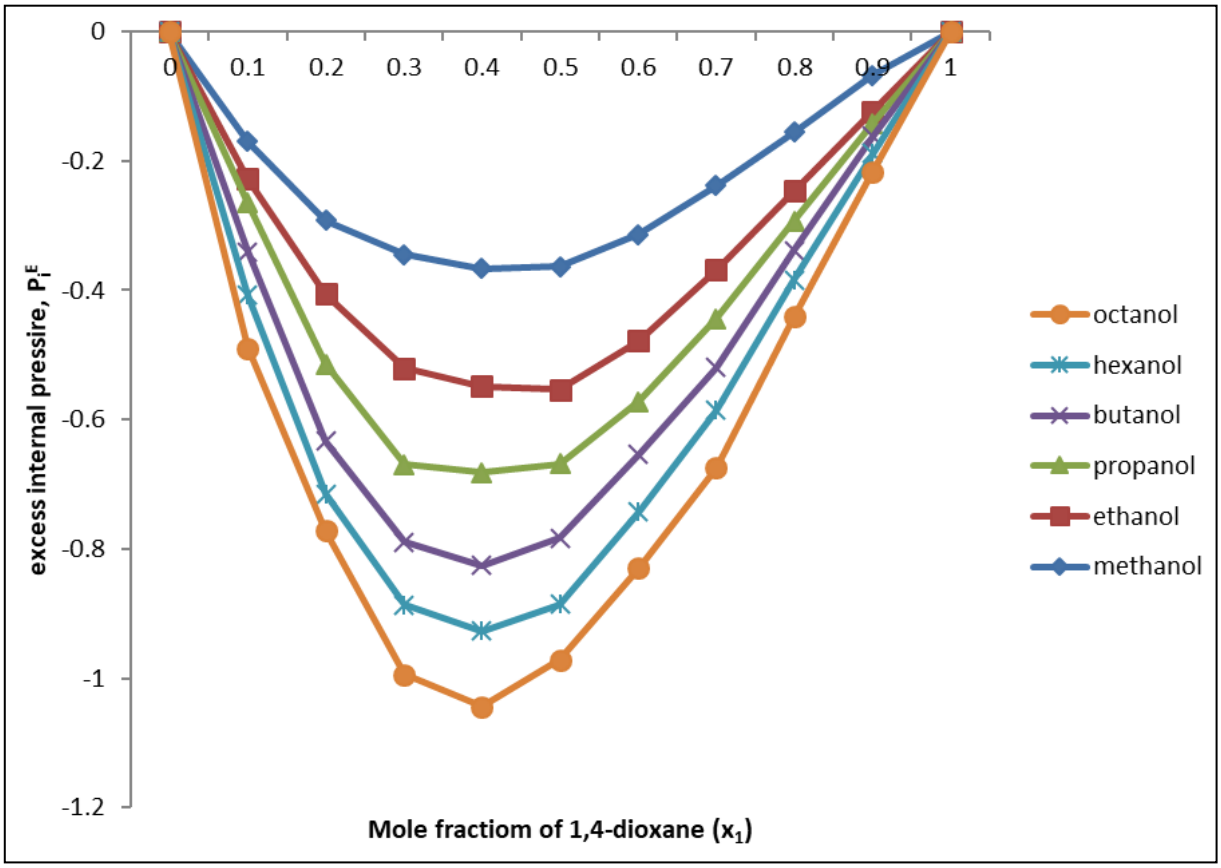


Fig 2: Plots of excess internal pressure versus mole fraction of 1,4-dioxane (X_1) at 303.15 K for binary mixtures of ethyl acetate with 1- methanol, 1-ethanol, 1-propanol, 1-butanol, 1-hexanol and 1-octanol at 303.15 K

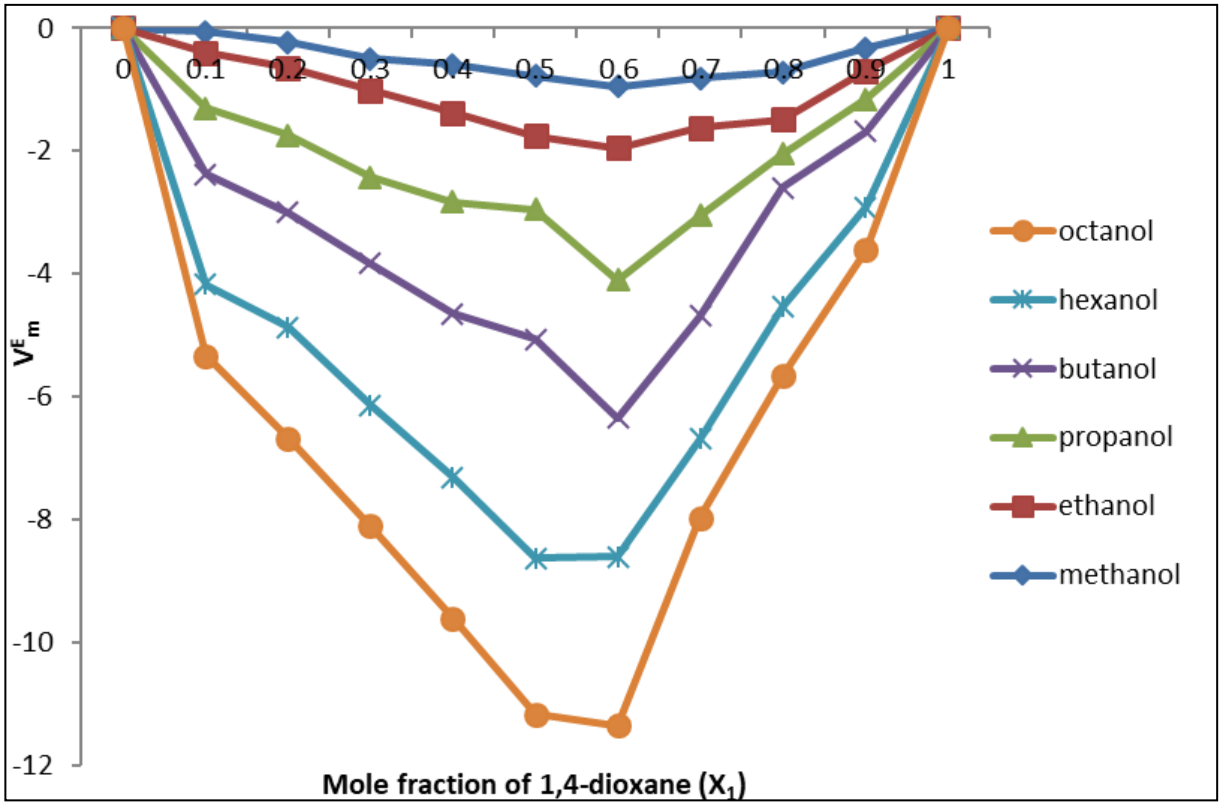


Fig 3: Plots of excess molar volume (V_m^E) versus mole fraction of 1,4-dioxane (X_1) at 303.15 K for binary mixtures of 1,4-dioxane with 1-methanol, 1-ethanol, 1-propanol, 1-butanol, 1-hexanol and 1-octanol at 303.15 K

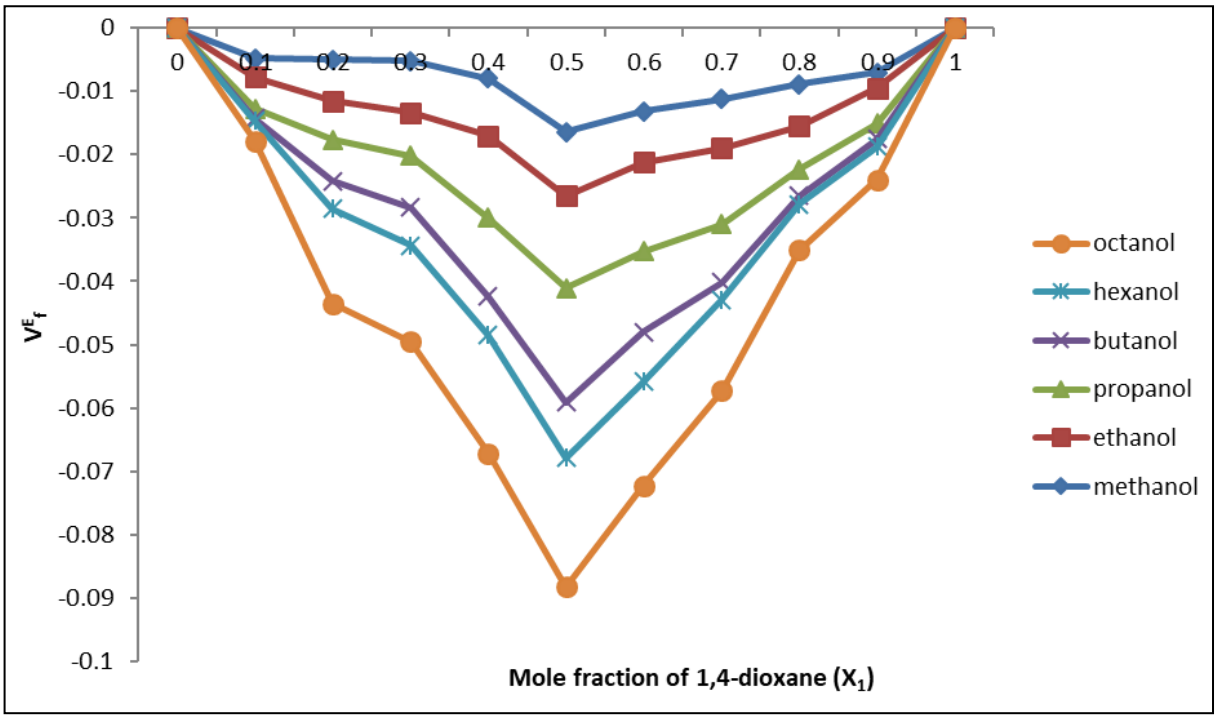


Fig 4: Plots of excess free volume V_f^E versus mole fraction of 1,4-dioxane (X_1) at 303.15 K for binary mixtures of 1,4-dioxane with 1-methanol, 1-ethanol,1-propanol, 1-butanol, 1-hexanol and 1-octanol at 303.15 K

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