

Study of Inter Molecular Interaction in Some Binary Liquid Mixtures Through Ultrasonic Measurements at 298.15K

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ABSTRACT

Experimental determined density, viscosity and sound velocity for binary mixtures of 1,3-dioxolane + 1-alkanols at T= 298.15 K, are conducted at atmospheric pressure. From these experimental values, various thermodynamic and excess thermodynamic properties were calculated. The adiabatic compressibility (β_{ad}), excess adiabatic compressibility (β_{ad}^E), inter molecular free length (L_f), excess inter molecular free length (L_f^E), enthalpy (H), excess enthalpy (H^E), free volume (V_f), excess free volume (V_f^E), internal pressure (Pi), excess internal pressure (p_i^E) have been investigated from density (ρ), viscosity (η) and sound velocity (u) measurements of six binary liquid mixtures of 1,3-Dioxolane with pentanol, hexanol, heptanol, octanol, nonanol and decanol over the entire composition range of mole fractions at 298.15K. An excess value of adiabatic compressibility (β_{ad}^E), inter molecular free length (L_f^E), excess enthalpy (H^E), excess free volume (V_f^E) and excess internal pressure (p_i^E) were plotted against the mole fraction of 1,3-dioxolane over the whole composition range. The values of (β_{ad}^E), (L_f^E), (H^E), (V_f^E) and (p_i^E) for six binary liquid mixtures have been found to be negative which suggest the presence of weak molecular interaction in all the six binary mixtures. These mixtures exhibit very strong cross association through hydrogen bonding.

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Abbreviations

ρ : Densities of Liquid

u: Ultrasonic Velocity

η : Viscosity

X_1 : Mole Fraction of 1,3-Dioxolane

T: Temperature

(β_{ad}): Adiabatic Compressibility

(β_{ad}^E): Excess Adiabatic Compressibility

(L_f): Inter Molecular Free Length

(L_f^E): Excess Inter Molecular Free Length

(H): Enthalpy

(H^E): Excess Enthalpy

(V_f): Free Volume

(V_f^E): Excess Free Volume,

(Pi): Internal Pressure

(p_i^E): Excess Internal Pressure

YE: Thermodynamic Excess Function

Introduction

In recent years, many research scholars have discussed thermodynamic and excess thermodynamic properties in liquid mixture and interpreted these properties using the interactions among the molecules [1-7]. Additionally, the study of liquid mixtures involves investigating the acoustic and thermodynamic properties, which provide insights on molecular interactions among different compounds [5].

This study explains the relationship between thermodynamic parameters and the nature of molecular bonds. Therefore, ultrasonic techniques mainly used to explore and understand the characteristics and dynamics of such molecular interactions. The excess thermodynamic property of binary liquid mixtures of 1,3-dioxolane with 1-alkanols is of great importance both from practical and theoretical point of view. We can interpret the interactions and predict the application of the liquid mixture using the thermodynamic and physical properties of liquid and liquid mixtures. The ultrasonic velocity, density and viscosity of liquid mixtures are used to understand the theory of a mixture in liquid state. The intermolecular forces among the molecules in a liquid mixture alter the physical and chemical properties like dipole moment in the heat of mixing [8-12]. The experimental values of sound velocity (u), density (ρ) and viscosity (η) are useful in evaluating thermodynamic properties such as adiabatic compressibility (β_{ad}), inter molecular free length (L_f), enthalpy (H), free volume (V_f), internal pressure (Pi) and several excess parameters which will be very much useful in concerning the nature of intermolecular forces between the component molecules. Over the last four decades, research has been focused on measuring the ultrasonic velocity of liquid system and interpreting their molecular structures. In the present paper, sound velocity (u), density (ρ) and viscosity (η) of six binary liquid mixtures of 1,3-dioxolane + pentanol, 1,3-dioxolane + hexanol, 1,3-dioxolane + heptanol, 1,3-dioxolane + octanol, 1,3-dioxolane + nonanol and 1,3-dioxolane + decanol, have been studied at 298.15 K over the entire composition range of mole fractions. From these experimental values, adiabatic compressibility (β_{ad}), inter molecular free length (L_f), enthalpy (H), free volume (V_f), internal

pressure (P_i) and their deviations excess adiabatic compressibility (β_{ad}^E), excess inter molecular free length (L_f^E), excess enthalpy (H^E), excess free volume (V_f^E) and excess internal pressure (p_i^E) have been calculated and interpreted in term of molecular interaction between the components of the binary liquid mixtures. We know that excess thermodynamic properties such as excess adiabatic compressibility (β_{ad}^E), excess inter molecular free length (L_f^E), excess enthalpy (H^E), excess free volume (V_f^E) and excess internal pressure (p_i^E) good information provide a understanding the intermolecular interaction between component molecules of the liquid mixtures. This work is the first to report a combined study of sound velocity (u), density (ρ) and viscosity (η) of six binary liquid mixtures of practical importance in many industrial processes such as pharmaceutical and cosmetics have greatly stimulated the need for extensive information on the thermodynamic, acoustic

and transport properties of 1,3-dioxolane, 1-alcohols and their mixtures. The 1,3-dioxolane and the 1-alcohols have both a proton donor and a proton acceptor group. It is expected that there will be a significant degree of H-bonding leading to self-association in the pure state in addition to mutual association in their binaries.

Materials and Methods

Materials

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

Table 1: Density (ρ), Sound Velocity (u) and Viscosity (η) of Pure Components at T = 298.15K

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

Methods

Binary liquid mixtures are prepared by mixing appropriate volumes of the liquid components in the specially designed glass bottles with air tight Teflon coated caps and mass measurements performed on an analytical single pan balance (Model K-15 Deluxe, K Roy Instruments Pvt. Ltd.) with an accuracy of $\pm 0.00001 \times 10^{-3}$ kg. 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, viscosity and sound velocity were measured on the same day. We determined the density was determined at the experimental temperature using a 25-mL capacity specific gravity bottle immersed in the thermostatic bath. The volume of the bottle at the experimental temperature viz 298.15K was ascertained using distilled water. Sound velocity determined by the multi-frequency interferometer (Model F-80D, Mittal Enterprise, New Delhi, India) at 3 MHz and 298.15 K, A fixed frequency generator working at 3 MHz. its resonant frequency, the crystal undergoes rapid mechanical oscillations, generating ultrasonic waves. These waves can propagate through the liquid in the vessel, creating effects like cavitation, acoustic streaming, or enhanced mixing. An experimental setup for measuring the viscosity by Ostwald viscometer. The viscometer was calibrated using distilled water at 298.15 K, and multiple measurements (five repetitions) were taken for each sample to ensure accuracy. The uncertainty in viscosity measurement is given as $\pm 0.005 \times 10^{-3}$ mPa·s, indicating high precision.

Results and Discussion

The experimental values of ultrasonic velocity (u), density (ρ) and viscosity (η) of 1,3-dioxolane with 1-alkanol mixtures at 298.15K are listed in Table 2. From these values, we have computed Intermolecular free length (L_f), adiabatic compressibility (β_{ad}), Enthalpy (H), internal pressure (P_i) and Free Volume (V_f) are presented in table 2.

Table 2: Density (ρ), Ultrasonic Velocity (u), and Viscosity (η), Intermolecular Free Length (L_p), Adiabatic Compressibility (β_{ad}), Internal Pressure (P_i) and Free Volume (V_f) of Binary Mixture of 1,3-Dioxolane (1) + 1-Alkanol (2) at 298.15K

Mole fraction 1,3-Dioxolane (x1)	Density (ρ) / g.cm ⁻³	Sound velocity (u) / ms ⁻¹	Viscosity (η) / mPas.	Intermolecular free length (L_p) × 10 ⁻⁴ / m	adiabatic compressibility (β_{ad}) × 10 ⁻⁷ / Pa ⁻¹	Internal pressure (P_i) × 10 ⁹ / N m ⁻²	Free Volume (V_f) × 10 ⁻⁷ M3mol ⁻¹	Enthalpy (H) × 10 ⁶
1,3-Dioxolane + Pentanol								
0.0000	0.8124	1198	3.3978	2.6732	8.5770	2.9099	1.9568	0.3156
0.0939	0.8276	1284	2.3973	2.2842	7.3290	3.2892	3.5817	0.3450
0.1942	0.8436	1290	1.8970	2.2201	7.1233	3.3763	4.9996	0.3468
0.2941	0.8640	1296	1.4437	2.1477	6.8909	3.4821	9.9265	0.3384
0.3942	0.8836	1300	1.1866	2.0872	6.6966	3.5776	11.0374	0.3341
0.4787	0.9068	1304	1.0904	2.0213	6.4853	3.6885	10.8499	0.33.8
0.5999	0.9316	1310	0.9311	1.9495	6.2551	3.8155	13.4125	0.3262
0.6972	0.9596	1318	0.7717	1.8697	5.9991	3.9663	17.4788	0.3236
0.7928	0.9876	1324	0.7171	1.8003	5.7762	4.1099	17.4788	0.3201
0.9035	1.0260	1332	0.6489	1.7121	5.4934	4.3085	19.1422	0.3166
1.0000	1.0616	1340	0.5885	1.6350	5.2460	4.4982	21.7624	0.3135
1,3-Dioxolane + Hexanol								
24.74130	0.8176	1306	4.6091	2.2349	7.1709	3.3333	1.7591	0.4163
0.0912	0.8252	1317	3.3826	2.1775	6.9867	3.4069	2.7275	0.4112
0.1955	0.8432	1320	2.3306	2.1214	6.8065	3.4931	4.5760	0.4003
0.2923	0.8584	1322	1.9839	2.0775	6.6657	3.5642	5.5951	0.3899
0.3982	0.8792	1325	1.5720	2.0192	6.4786	3.6629	7.5845	0.3787
0.4942	0.8992	1327	1.3059	1.9619	6.3154	3.7548	9.5968	0.3683
0.6059	0.9264	1330	1.0343	1.9019	6.1024	3.8815	12.9396	0.3567
0.6976	0.9508	1332	0.9131	1.8475	5.9279	3.9927	14.9307	0.465
0.8018	0.9836	1335	0.7680	1.7779	5.7045	4.1444	18.3980	0.3352
0.8914	1.0168	1337	0.7304	1.7147	5.5018	4.2939	18.9465	0.3254
1.0000	1.0616	1340	0.5885	1.6350	5.2460	4.4982	24.7413	0.3135
1,3-Dioxolane + Heptanol								
0.0000	0.8196	1325	5.9066	2.1660	6.9497	3.4147	1.5030	0.4838
0.0928	0.8304	1334	4.3181	2.1091	6.7671	3.4949	2.3075	0.4725
0.1905	0.8412	1334	3.2577	2.0820	6.6802	3.5404	3.3296	0.4552
0.2939	0.8592	1335	2.5895	2.0353	6.5304	3.6202	4.4224	0.4373
0.3894	0.8740	1335	1.9926	2.0009	6.4199	3.6826	6.1746	0.4201
0.4818	0.8916	1336	1.5315	1.9584	6.2837	3.7609	8.6425	0.4042
0.6021	0.9184	1337	1.2190	1.8984	6.0912	3.8784	11.2315	0.3835
0.6952	0.9420	1337	1.0959	1.8509	5.9387	3.9780	12.3322	0.3667
0.7892	0.9756	1338	0.9903	1.7845	5.7255	4.1245	13.4017	0.3505
0.9006	1.0156	1339	0.7057	1.7116	5.4918	4.2985	20.4381	0.3309
1.0000	1.0616	1340	0.5885	1.6350	5.2460	4.4982	24.7413	0.3135
1,3-Dioxolane + Octanol								
0.0000	0.8296	1350	7.1508	2.0764	6.6622	3.5546	1.3767	0.5619
0.0885	0.8296	1350	5.6095	2.0614	6.6139	3.5585	1.8692	0.5363
0.1967	0.8464	1349	3.9321	2.0235	6.4923	3.6225	2.9529	0.5100
0.2998	0.8560	1348	3.2616	2.0038	6.4291	3.6596	3.6234	0.4845
0.3902	0.8712	1348	2.4284	1.9688	6.3168	3.7245	5.2656	0.4629
0.4963	0.8876	1348	1.9058	1.9324	6.2002	3.7947	6.9577	0.4375
0.6008	0.9140	1347	1.3631	1.8794	6.0301	3.9032	10.5160	0.4117

0.6925	0.9340	1348	1.1376	1.8364	5.8921	3.9930	12.7180	0.3905
0.7975	0.9676	1348	0.9141	1.7726	5.6875	4.1367	15.9753	0.3652
0.8940	1.0104	1348	0.7652	1.6975	5.4466	4.3197	18.9060	0.3421
1.0000	1.0616	1340	0.5885	1.6350	5.2460	4.4982	24.7413	0.3135
1,3-Dioxolane + Nonanol								
0.0000	0.8248	1366	8.9258	2.0251	6.4976	3.5970	1.1714	0.6291
0.0876	0.8336	1366	6.8601	2.0037	6.4289	3.6354	1.6286	0.6020
0.1913	0.8404	1363	5.8531	1.9963	6.4051	3.6530	1.899	0.5684
0.2942	0.8504	1359	4.4022	1.9844	6.3671	3.6802	2.6620	0.5347
0.3963	0.8692	1355	3.1558	1.9529	6.2662	3.7449	3.9924	0.5014
0.4959	0.8844	1352	2.3340	1.9279	6.1859	3.7978	5.7014	0.4697
0.6050	0.9092	1349	1.7321	1.8837	6.0439	3.8913	7.9725	0.4354
0.6947	0.9332	1346	1.3334	1.8434	5.9145	3.9807	10.6902	0.4072
0.7993	0.9648	1343	0.9642	1.7910	5.7466	4.1018	15.3683	0.3744
0.9013	1.0084	1340	0.8031	1.7213	5.5228	4.2372	17.3683	0.3402
1.0000	1.0616	1340	0.5885	1.6350	5.2460	4.4982	24.7413	0.3135
1,3-Dioxolane + Decanol								
0.0000	0.8292	1378	11.8027	1.9794	6.4976	3.6639	0.8971	0.6990
0.0881	0.8364	1374	8.5615	1.9638	6.4289	3.6797	1.3454	0.6634
0.191	0.8396	1370	7.8207	1.9578	6.4051	3.6977	1.4040	0.6226
0.2921	0.8560	1366	5.5340	1.9413	6.3671	3.7331	2.1400	0.5827
0.3937	0.8672	1362	4.2319	1.9374	6.2662	3.7654	2.8863	0.5429
0.4956	0.8824	1358	3.4173	1.9153	6.1859	3.8145	3.5598	0.5035
0.604	0.9076	1353	2.5370	1.8759	6.0439	3.9018	4.8971	0.4615
0.7129	0.9308	1348	1.5262	1.8427	5.9145	3.9793	9.1301	0.4198
0.7983	0.9616	1344	1.1637	1.7943	5.7466	4.0927	12.1810	0.3871
0.8971	1.0040	1340	0.8623	1.7288	5.5228	4.2541	16.4668	0.3505
1.0000	1.0616	1340	0.5885	1.6350	5.246	4.4982	24.7413	0.3135

The excess parameters such as Intermolecular free length (L_f^E), adiabatic compressibility (β_{ad}^E), Enthalpy (H^E), internal pressure (p_i^E) and Free Volume (V_f^E) have been calculated using the following equations.

In the year 1952, Jacobson, suggested an empirical relation for calculating the free length (L_f) of liquids. Intermolecular free length (L_f), can be calculated from the adiabatic compressibility (β_{ad}) by the relation given below

$$L_f = K \beta_{ad}^{1/2} \quad (1)$$

Where K is temperature dependent constant and β_{ad} is the adiabatic compressibility, which is given by the relation.

The adiabatic compressibility (β_{ad}) has been calculated from the ultrasonic velocity (u) and density (ρ) of the medium using the equation as

$$\beta_{ad} = u^{-2} \rho^{-1} \quad (2)$$

The free volumes of the mixtures have been computed using its relationship with the ultrasonic velocity and viscosity is given below

$$V_f = (MU/k\eta)^{3/2} \quad (3)$$

where k is a constant, independent of temperature and its value is 4.28×10^9 for all liquids.

On the basis of dimensional analysis, using free volume concept, the following expression can be used for calculating internal pressure

$$p_i = bRT \left(\frac{k\eta}{u}\right)^{\frac{1}{2}} \frac{\rho^{2/3}}{M_{eff}^{7/6}} \quad (4)$$

here b is packing factor ($b = 2$), 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.

Enthalpy (H) can be calculated by the following equation

$$H = V_m \times P_i \quad (5)$$

The excess values of the above acoustical parameters have been calculated from the following relations.

$$Y^E = Y_{exp} - (X_1 Y_1 + X_2 Y_2) \quad (6)$$

A perusal of table 2 shows the mole fraction (X_1) of 1,3-dioxolane increases, density and ultrasonic velocity increase, while viscosity decreases. This trend can be explained by molecular interactions in the system [25]. When 1,3-Dioxolane is added, it likely leads to closer packing of molecules due to molecular interactions, such as dipole-induced dipole forces.

Figure 1 depicts the variation of the excess intermolecular free length of the chosen system. We clearly see from figure 1 that the non-linear variation of excess intermolecular free length with mole fraction of 1,3-dioxolane. The negative deviation of excess intermolecular free length reaching a minimum at 0.48 mole fraction of 1,3-dioxolane shows the molecular interactions between the molecules. The structural changes take place due to the variation in intermolecular free length (L_f) of the system. The excess intermolecular free length (shown in figure 1) decrease with increase in the composition of 1,3-dioxolane till 0.48 mole fraction, reaches minimum at 0.48 mole fraction and beyond 0.48 mole fraction, it again increases. The existence of minimum free length indicates the squeezing of molecules in the system.

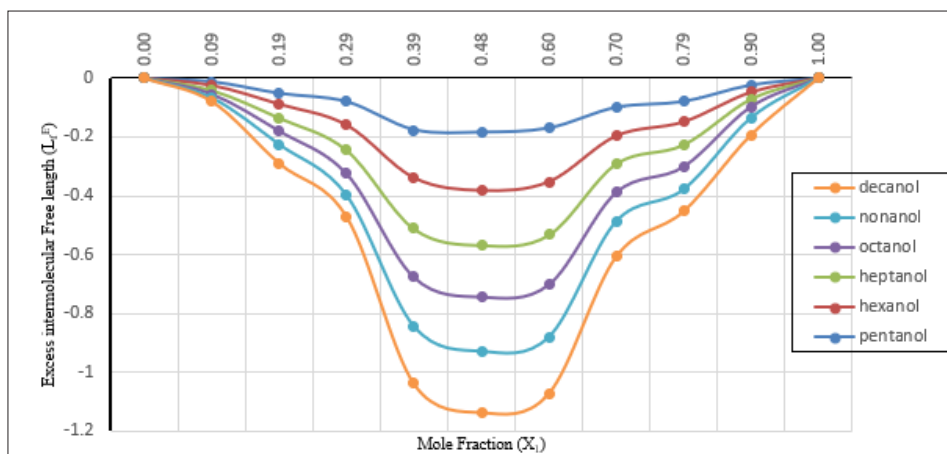


Figure 1: Variation of Excess Intermolecular Free Length (L_f^E) with Mole Fraction (x_1) of 1,3-Dioxolane with 1-Alkanols at 298.15K.

The calculated excess adiabatic compressibility (β_{ad}^E), values for the binary liquid mixture listed in Figure 2. The change of this property has been shown in figure-2. The excess adiabatic compressibility (β_{ad}^E), values are negative over the entire mole fraction range and become more negative with increasing the mole fraction of second component for all binary mixtures. These results can be explained in term of molecular interactions and structured effects.

The variation of excess adiabatic compressibility (β_{ad}^E), with volume fraction of 1,3-dioxolane (x_1) is represent in figure 2. Fort and Moore have suggested that excess adiabatic compressibility (β_{ad}^E), is the result of several opposing effects. Strong molecular interactions occur through charge transfer, dipole- induced dipole and dipole-dipole interaction, interstitial accommodation and orientational ordering all lead to a more compact structure making excess adiabatic compressibility (β_{ad}^E) negative. The negative values of (β_{ad}^E), in these mixtures can be associated with a structure forming tendency [26,27].

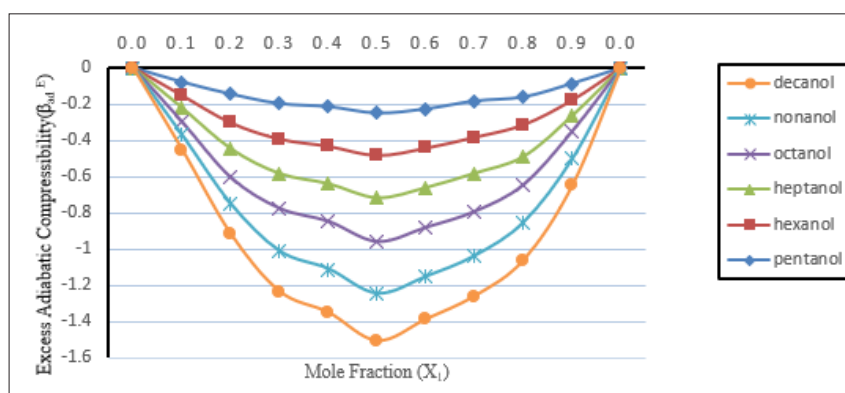


Figure 2: Variation of Excess Adiabatic Compressibility (β_{ad}^E) with Mole Fraction (x_1) of 1,3-Dioxolane with 1-Alkanols at 298.15K.

The concept of free volume is an extension of the idea that each molecule is enclosed by its neighbor in a cell. The free volume per molecules may be regarded as the effective volume accessible to the centers of a molecule in a liquid. It is however, evident from the consideration of the liquid state theories that the concept of free volume varies with the specific model chosen for the liquid. A perusal of Figure 3 shows that the value of excess Free Volume (V_f^E), are negative for the all-binary liquid system 1,3-dioxolane with 1-alkanols at 298.15 K. In the present investigation the negative excess free volume (V_f^E), for binary mixtures of 1,3-dioxolane with 1-alkanols may be attributed to hydrogen bond formation through dipole-dipole interaction between 1-alkanol and 1,3-dioxolane molecule or to structural contributions arising from the geometrical fitting of 1-alkanol into the 1,3-dioxolane due to difference in

the free volume between components. The interactions of alcohols with organic liquids are interesting due to its acetic nature. The O-H bond in alcohols is polar and allows the release of hydrogen atom as proton (H^+). The order of acidity in alcohols is: 1° -alcohol $> 2^{\circ}$ -alcohol $> 3^{\circ}$ -alcohol. This order is due to +I effect while the interacting ability of alcohols is well established no such opinion is suggested from literature with regards to 1,3-dioxolane with 1-alkanols were selected to study their molecular interactions through their acoustical behavior.

Hydrogen bonding

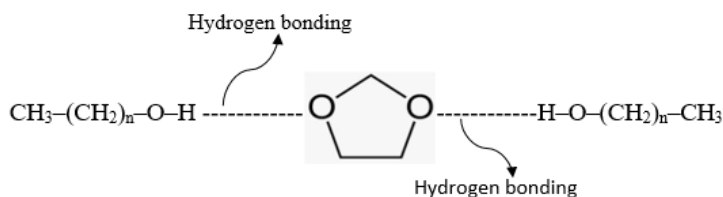


Figure: Hydrogen Bonding Present in 1,3-Dioxolane– n-Alkanols.

The negative values of excess free volume (V_f^E), indicate the presence of strong molecular interaction. We may conclude that 1-alkanols, is disrupted. It is also concluded that Suryanarayana approach for estimating free volume thermodynamic considerations is very well applicable in the present case.

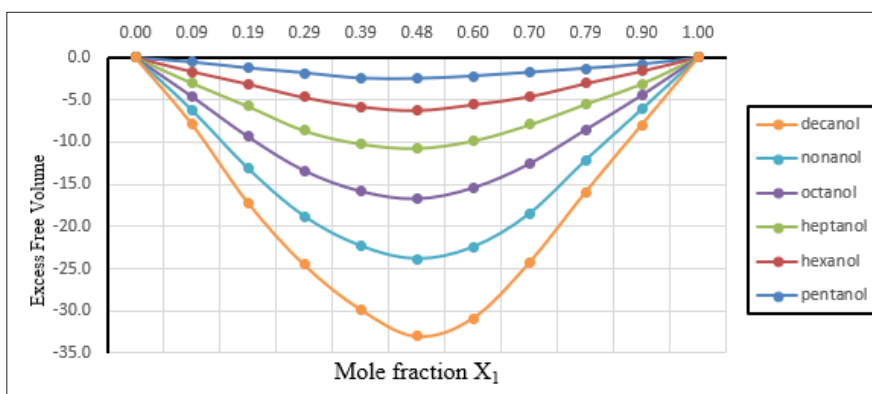


Figure 3: Variation of Excess Free Volume (V_f^E), with Mole Fraction (x_1) of 1,3-Dioxolane with 1-Alkanols at 298.15K

The internal pressure is a cohesive force, which is the result of attractive and repulsive forces between the molecules. The attraction forces mainly consist of hydrogen bonding, dipole-dipole and dispersion interactions. Repulsive forces acting over very small intermolecular distances play a minor role in the cohesion process under normal circumstances. For the binary system 1,3-dioxolane with 1-alkanols, the excess internal pressure values are negative and decreasing with the increase in mole fraction of 1,3-dioxolane up to the mole fraction (0.5) and the increase with increase in mole fraction. Figure 4 shows the variation of excess internal pressure (p_i^E) with mole fraction of 1,3-dioxolane at the temperature 298.15K. This negative trend in excess internal pressure (p_i^E) indicate that only dispersion and dipolar forces operating with complete absence of specific interaction. 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 suggested 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.

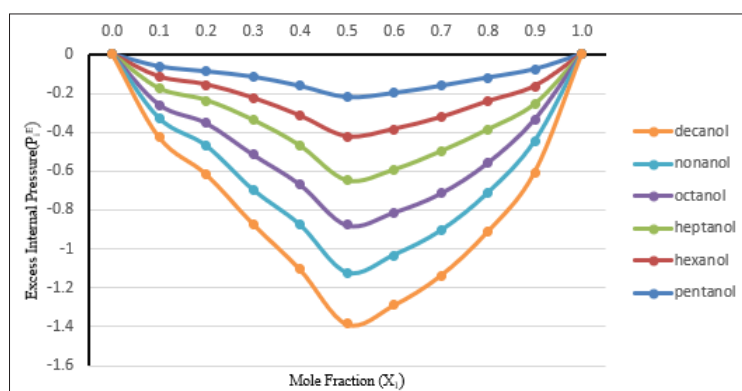


Figure 4: Variation of Excess Internal Pressure (p_i^E) with Mole Fraction (x_1) of 1,3-Dioxolane with 1-Alkanols at 298.15K

Figure 5 shows the variation of excess enthalpy (H^E) with mole fraction of 1,3-dioxolane at the temperature 298.15K. For the binary system 1,3-dioxolane with 1-alkanols, the excess enthalpy (H^E) values are negative and decreasing with the increase in mole fraction of 1,3-dioxolane up to the mole fraction (0.5) and the increase with increase in mole fraction. The excess enthalpy (H^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 1,3-dioxolane increases, the excess enthalpy (H^E) values decrease. This situation is observed for all six binary systems under study and can be viewed from plots Figure 5. This suggests that dipole and dispersive force are operative in these systems, when the 1,3-dioxolane concentration is low. When the concentration of 1,3-dioxolane increases, the corresponding decrease in concentration of 1,3-dioxolane leads to specific interactions i.e., the interactions move from weak to strong which supports the above arguments in case of other parameters. As a result, the free dipoles released from the alkanols in association with 1,3-dioxolane molecules forming strong hydrogen bonds, hence stronger molecular association existing between the 1,3-dioxolane with 1-alkanols molecules through hydrogen bonding [28-31].

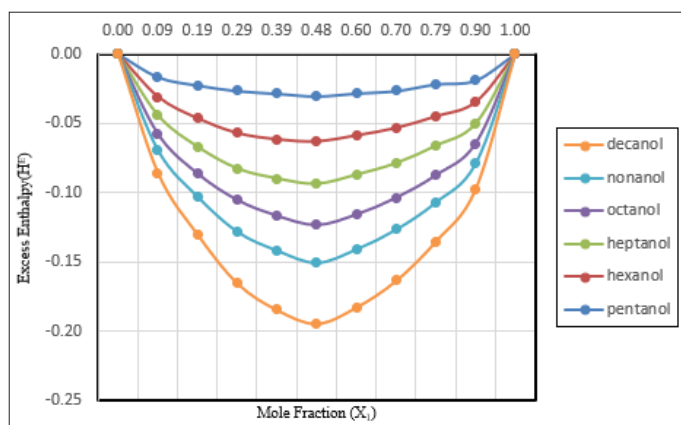


Figure 5: Variation of Excess Enthalpy (H^E) with mole Fraction (x_1) of 1,3-Dioxolane with 1-Alkanols at 298.15K

Conclusion

We measured sound velocity, density and viscosity of 1,3-dioxolane with 1-alkanols experimentally at 298.15K. The calculated intermolecular free length (L_f), excess Intermolecular free length (L_f^E), adiabatic compressibility (β_{ad}), excess adiabatic compressibility (β_{ad}^E), enthalpy (H), excess enthalpy (H^E), internal pressure (P_i), excess internal pressure (p_i^E), Free Volume (V_f) and excess Free Volume (V_f^E) strongly confirm the presence of strong molecular interactions between the unlike molecules through the hydrogen bonding. After a thorough study of the behavior of 1-alkanols and 1,3-dioxolane, we get a clear idea about the type and number of molecular interactions between the components. In addition, molecular interactions are confirmed from the negative values of excess intermolecular free length (L_f^E), excess adiabatic compressibility (β_{ad}^E), excess enthalpy (H^E), excess internal pressure (p_i^E) and excess Free Volume (V_f^E). Hence it is concluded that there exists a molecular interaction between 1,3-dioxolane and 1-alkanols due to Hydrogen bonding.

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