Excess Free Volume in Binary Liquid Mixtures of 1, 3-Dioxolane and 1-Alkanols at 298.15K and 3 MHz

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Abstract: ***In the present study density (ρ), viscosity (η) and sound velocity (u) have been measured at 3 MHz in the binary mixtures of 1, 3-dioxolane + 1-alkanols at T= 298.15 K using ultrasonic interferometer technique. From the measured data of density (ρ), viscosity (η) and sound velocity (u), thermodynamic property free volume (V_f) excess free volume (V_f^E) have been estimated using standard relations. Thermodynamic property provides important information in understanding the solute-solvent interaction in binary mixtures.***

Keywords: Binary mixtures, density, free volume, viscosity, sound velocity, hydrogen bonding, 1, 3-dioxolane, molecular interaction.

1. Introduction

The study of thermodynamic properties of binary liquid mixtures contributes to an understanding of the behaviour of different liquids and functional groups. Number of studies on the thermodynamic properties of binary liquid mixtures has increased in recent years. In recent years, ultrasonic investigation of binary liquid mixtures has revolutionized the world of medical, petrochemical and pharmaceutical industries to great extent. The excess thermodynamic property of binary liquid mixtures of cyclic diether 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. Ultrasonic investigations of liquid mixtures consisting of polar and non polar components are of considerable importance in understanding intermolecular interactions between the component molecules and find applications in several industrial and technological processes [1-3]. The variation of ultrasonic velocity and other ultrasonic parameters of binary liquid mixtures have been studied by many researchers and they have shed light upon structural changes associated with liquid mixtures of weakly or strongly interacting compounds [4-10]. The study of molecular association in binary mixtures having alcohol as one of the component is of particular interest, since alcohols are strongly self-associated liquids having a three dimensional network of hydrogen bonds and can be associated with any other group having same degree of polar attractions [11-12]. 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 + 1-pentanol, 1, 3-dioxolane + 1-hexanol, 1, 3-dioxolane + 1-heptanol, 1, 3-dioxolane +1-octanol, 1, 3-dioxolane +1-nonanol and 1, 3-dioxolane + 1-decanol, have been studied at 298.15 K over the entire composition range of mole fractions. From these experimental values, free volume (V_f) and excess free volume (V_f^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 free volume (V_f^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 soaps, detergents, cosmetics and perfumes. The study of molecular interaction has attracted the attention of many workers. In recent paper, ultrasonic technique has become a powerful tool in providing valuable information regarding the molecular behavior of liquids. Excess properties are the measure the different type of attractions. The various type of molecular interaction that may operate between molecules of different type are dispersion forces, charge transfer, hydrogen bonding, dipole-dipole and dipole-induced dipole interaction. In any given system more than one type of molecular interaction present. The interaction of 1-alkanols with 1, 3-Dioxolane is interesting due to the acidic nature. The O-H bonds in alcohols are polar and allow the release of hydrogen atom as proton. The order of acidity in alcohols is:

Primary alcohol > Secondary alcohol > Tertiary alcohol Keeping this in view, six binary liquid mixtures 1-pentanol.1-hexanol, 1-heptanol, 1-octanol, 1-nanol and 1-decanol with 1, 3-Dioxolane (Cyclic diether) were selected to study their molecular interactions through their acoustical behavior.

2. Materials and Methods

2.1 Materials

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

Table 1: Density (ρ), sound velocity (u) and viscosity (η) of pure Components at T = 298.15K and frequency 3 MHz.

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]

2.2 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 a analytical single pan balance (Model K-15 Deluxe, K Roy Instruments Pvt. Ltd.) with an accuracy of ± 0.00001×10^{-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. 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 ±0.005 × 10^{-3} mPa. s, indicating high precision.

3. 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 Free Volume (V_f) and excess free volume (V_f^E) are presented in table 2.

Table 2: Density (ρ), ultrasonic velocity (u), and viscosity (η), Free Volume (V_f) and excess free volume (V_f^E) of binary mixture of 1, 3-dioxolane (1) + 1-alkanol (2) at 298.15K and frequency 3 MHz.

Mole fraction 1, 3-Dioxolane (x_1)	Density (ρ) / g. cm^{-3}	Sound velocity (u) / ms^{-1}	Viscosity (η) / mPas.	Free Volume (V_f) × 10^{-7} M^{3}mol^{-1}	Excess Free Volume (V_f^E) × 10^{-8} m^{3}mol^{-1}
1, 3-Dioxolane + Pentanol					
0.0000	0.8124	1198	3.3978	1.9568	-
0.0939	0.8276	1284	2.3973	3.5817	- 0.5145
0.1942	0.8436	1290	1.8970	4.9996	- 0.1381
0.2941	0.8640	1296	1.4437	9.9265	- 0.1268
0.3942	0.8836	1300	1.1866	11.0374	- 2.4698
0.4787	0.9068	1304	1.0904	10.8499	- 2.0138
0.5999	0.9316	1310	0.9311	13.4125	- 2.2127
0.6972	0.9596	1318	0.7717	17.4788	- 0.3633
0.7928	0.9876	1324	0.7171	17.4788	- 0.8781
0.9035	1.0260	1332	0.6489	19.1422	- 0.7801
1.0000	1.0616	1340	0.5885	21.7624	-
	1, 3-Dioxolane + Hexanol				
24.74130	0.8176	1306	4.6091	1.7591	-
0.0912	0.8252	1317	3.3826	2.7275	- 1.1275
0.1955	0.8432	1320	2.3306	4.5760	- 1.6761

0.2923	0.8584	1322	1.9839	5.5951	- 2.8817
0.3982	0.8792	1325	1.5720	7.5845	- 3.3261
0.4942	0.8992	1327	1.3059	9.5968	- 3.5201
0.6059	0.9264	1330	1.0343	12.9396	- 2.7444
0.6976	0.9508	1332	0.9131	14.9307	- 2.8519
0.8018	0.9836	1335	0.7680	18.3980	- 1.788
0.8914	1.0168	1337	0.7304	18.9465	- 3.298
1.0000	1.0616	1340	0.5885	24.7413	-
1, 3-Dioxolane + Heptanol					
0.0000	0.8196	1325	5.9066	1.5030	-
0.0928	0.8304	1334	4.3181	2.3075	- 1.3519
0.1905	0.8412	1334	3.2577	3.3296	- 2.600
0.2939	0.8592	1335	2.5895	4.4224	- 3.9103
0.3894	0.8740	1335	1.9926	6.1746	- 4.3773
0.4818	0.8916	1336	1.5315	8.6425	- 4.0567
0.6021	0.9184	1337	1.2190	11.2315	- 4.2632
0.6952	0.9420	1337	1.0959	12.3322	- 5.3260
0.7892	0.9756	1338	0.9903	13.4017	- 6.4409
0.9006	1.0156	1339	0.7057	20.4381	- 1.9933
1.0000	1.0616	1340	0.5885	24.7413	-
1, 3-Dioxolane + Octanol					
0.0000	0.8296	1350	7.1508	1.3767	-
0.0885	0.8296	1350	5.6095	1.8692	- 1.575.
0.1967	0.8464	1349	3.9321	2.9529	- 3.6097
0.2998	0.8560	1348	3.2616	3.6234	- 4.7580
0.3902	0.8712	1348	2.4284	5.2656	- 5.2279
0.4963	0.8876	1348	1.9058	6.9577	- 6.0149
0.6008	0.9140	1347	1.3631	10.5160	- 4.8981
0.6925	0.9340	1348	1.1376	12.7180	- 4.8387
0.7975	0.9676	1348	0.9141	15.9753	- 4.0346
0.8940	1.0104	1348	0.7652	18.9060	- 3.3586
1.0000	1.0616	1340	0.5885	24.7413	-
1, 3-Dioxolane + Nonanol					
0.0876	0.8336	1366	6.8601	1.6286	- 1.6075
0.1913	0.8404	1363	5.8531	1.899	- 3.781
0.2942	0.8504	1359	4.4022	2.6620	- 5.4436
0.3963	0.8692	1355	3.1558	3.9924	- 6.5197
0.4959	0.8844	1352	2.3340	5.7014	- 7.1582
0.6050	0.9092	1349	1.7321	7.9725	- 7.4586
0.6947	0.9332	1346	1.3334	10.6902	- 6.8552
0.7993	0.9648	1343	0.9642	15.3683	- 4.6424
0.9013	1.0084	1340	0.8031	17.3683	- 4.6685
1.0000	1.0616	1340	0.5885	24.7413	-
1, 3-Dioxolane + Decanol					
0.0000	0.8292	1378	11.8027	0.8971	-
0.0881	0.8364	1374	8.5615	1.3454	- 1.6524
0.191	0.8396	1370	7.8207	1.4040	- 4.0473
0.2921	0.8560	1366	5.5340	2.1400	- 5.7219
0.3937	0.8672	1362	4.2319	2.8863	- 7.3983
0.4956	0.8824	1358	3.4173	3.5598	- 9.1545
0.604	0.9076	1353	2.5370	4.8971	- 10.4018
0.7129	0.9308	1348	1.5262	9.1301	- 8.7655
0.7983	0.9616	1344	1.1637	12.1810	- 7.7509
0.8971	1.0040	1340	0.8623	16.4668	- 5.8209
1.0000	1.0616	1340	0.5885	24.7413	-

The excess parameters such as Free Volume (V_f^E) have been calculated using the following equations.

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

$$Y^E = Y_{exp} - (X_1 Y_1 + X_2 Y_2) \quad \dots (2)$$

Y^E refer to (V_f^E), whereas Y_{exp} is measured property under question. Y_1, Y_2, X_1 and X_2 refer to the properties and mole fractions of pure components 1 and 2 respectively.

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

The 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 1 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: ^{10}-alcohol >^{20}-alcohol >^{30}-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. In the present investigation the negative excess free volume (V_f^E) for binary mixtures of 1, 3-dioxolane with alkanol 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 one component (1-alkanol) into the other (1, 3-dioxolane) due to difference in the free volume between components.

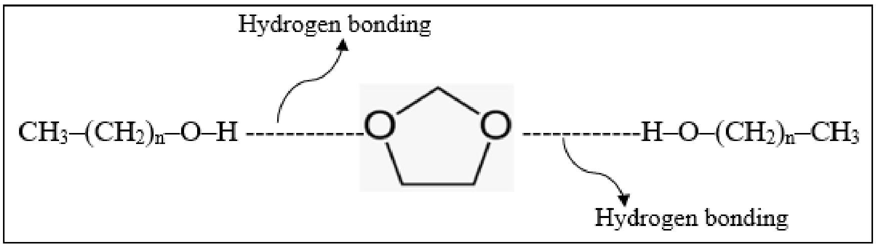

Figure: Hydrogen bonding present in 1, 3-dioxolane – 1-alkanols**.**

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.

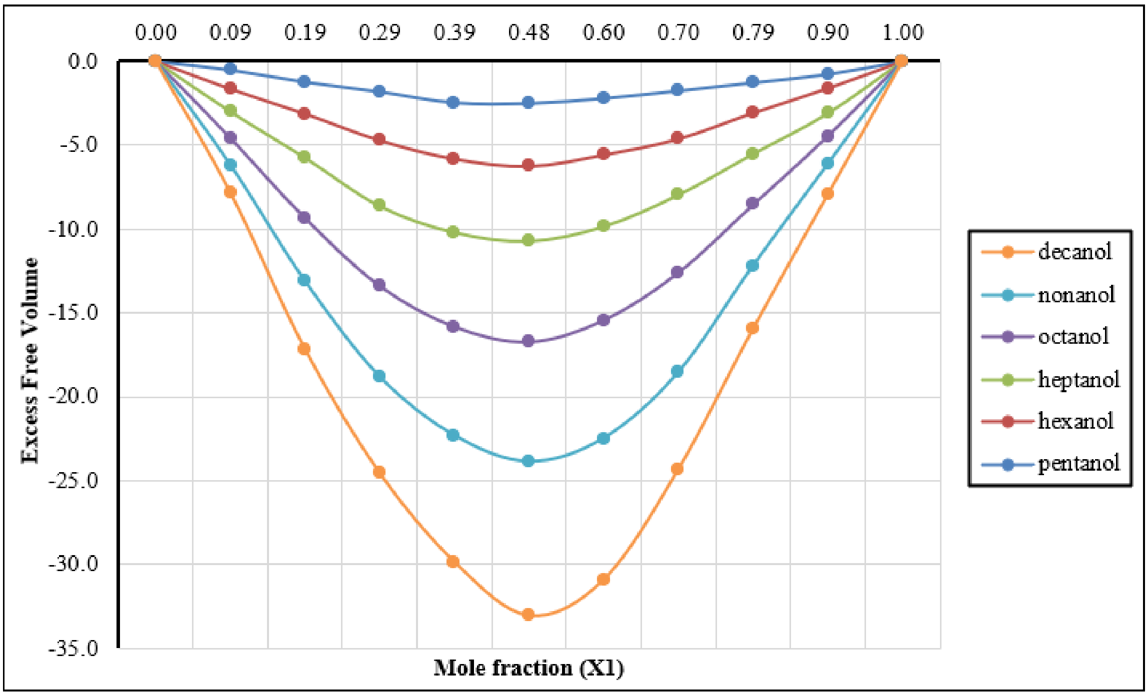

Figure 1: Variation of excess Free Volume (V_f^E), with mole fraction (x_1) of 1, 3-dioxolane with 1-alkanols at 298.15K.

Fort and Moore [25], suggested that the liquids having different molecular sizes and shapes mix well there by reducing the volume which causes the values of excess free volume (V_f^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 free volume (V_f^E), in these mixtures can be associated with a structure forming tendency.

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4. Conclusion

From the observed experimental values of density, viscosity and ultrasonic velocity and related acoustical parameters values for the 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 system at temperatures 298.15K, it is clear that there exists a strong intermolecular association between the component molecules of the liquid mixtures.

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