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Research paper

Ultrasonic velocities and refractive indies of binary liquid mixtures of 1, 4-dioxane with 1 – alkanols (C3, C4, C6 , C8) at 303.15 K

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Abstract

Density (ρ), ultrasonic velocities (u) and refractive indices (n) of the binary mixture between cyclic ether with 1-propanol, 1-butanol, 1-hexanol, 1-octanol for the entire concentration range have been measured at 303.15K, furthermore, deviation in refractive indies from ideal mixture, molar refraction, deviation in molar refraction from ideal values for these mixture has also been evaluated. The deviations from ideality of the acoustical parameters are explained on the basis of molecular interaction between the component molecules in these binary liquid mixtures. The molecular refraction (Rm), excess molecular refraction ( ) and excess molar volume (VE) were calculated from the experimental data. The results are discussed in term of molecular interactions between the components of the binary mixtures.

Keywords: *Refractive Indices; Density; Ultrasonic Velocity; Molar Volume; Mass Refraction; 1- Alkanol; Molecular Interaction.*

1. Introduction

The ultrasonic velocity (u), density (ρ) and refractive indices (n) represent the thermodynamic properties of a liquid. The study of refractive indices (n) are being increasingly used as tools 1-5 for investigation of the physical properties of pure component and the nature of intermolecular interaction between the liquid mixture constituents. In this paper we are measured ultrasonic velocity (u), density (ρ) and refractive indices (n) of the binary mixtures of 1, 4-Dioxane with 1-propanol, 1-butanol, 1-hexanol, and 1-octanol are performed directly over the entire range of composition at 303.15K. The review of literature 6 on acoustical studies of solution reveals that refraction indies measurement are also used to estimate the different elastic properties of the molecule from which the type of molecular interaction can be very well understood. Pandy et al 7 have made refractive indices measurements in liquid mixtures and have suggested that such studies are very much helpful for understanding of the molecular interaction in the components of the mixture.
The study of molecular interaction has attracted the attention of many workers 8-12 . 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, 4-Dioxane 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, four binary liquid mixtures 1-propanol, 1-butanol, 1-hexanol, 1-octanol with 1, 4-Dioxane (Cyclic ether) were selected to study their molecular interactions through their acoustical behavior.
A relatively new method 13 has been used for the estimation of excess molar volumes of binary mixtures from the known experimental values of refractive indices and densities of pure liquids and refractive indices of their mixtures.

2. Experimental

2.1. Apparatus and procedures

Four binary liquid system viz: 1, 4-Dioxane + 1-propanol, 1, 4-Dioxane + 1-butanol, 1, 4-Dioxane + 1-hexanol and 1, 4-Dioxane + 1-octanol were studied. All chemicals were Merch Chem. Ltd. India. (AR grade, 98-99.5%)
All the chemicals were purified by a method given in the literature 14. The purity of the liquids was also checked by measuring their densities, refractive indices and ultrasonic velocities at 303.15 K and were in agreement with the literature values 15-22 are depicted in Table -I.

Densities of pure liquid and liquid mixtures at experimental temperature were determined using a single capillary pycnometer, made of borosil glass, having a bulb capacity of 30 cm^3. The capillary, with graduated marks, had a uniform pore and could be closed by a well-fitted glass cap. The marks on the capillary were calibrated by using double-distilled water at 303.15 K. The pycnometer was kept for about 30 minute in an electronically controlled thermostate water bath (MSI Goyal Scientific Meerut) 303.15 ± 0.02 K and the position of the liquid level on the capillary was noted. The volume of the pycnometer at each mark was calculated by using the literature 23 value of the density of pure water at 303.15K. The volume these obtained is used to determine the density of the unknown liquid. The observed values of densities of pure 1,4-dioxane,1- propanol, 1-butanol, 1-hexanol and 1-octanol at 303.15 K were 1.0108, 0.8070, 0.8040, 0.8128 and 0.8242 $g\text{-}m^{-3}$which compare well with corresponding literature values of respectively. The ultrasonic velocities were measured using a multi-frequency ultrasonic interferometer, M-80D, (Mittal Enterprise, New Delhi) working at 3 M.Hz. The meter was calibrated with water and benzene at 303.15 K. The measured values of ultrasonic velocities of pure 1,4-dioxane, 1- propanol, 1-butanol, 1-hexanol and 1-octanol at 303.15K were 1348, 1182, 1196, 1298 and 1327 $m.s^{-1}$ respectively, which compare well with the corresponding literature values. Refractive indices of pure liquids and liquid mixtures were measure using white light by an Abbe refractometer (Model R- 8 M/S Mittal Enterprises, New Delhi). Refractometer was calibrated with kept constant at 303.15 ± 0.03 K by circulating water of the thermostate with the help of pump through both the prism boxes of the refractometer. Refractive indices of liquid were measured after attainment of constant temperature. An average five measurements was made for each sample. The measured values of refractive indices of pure 1,4-dioxane, 1-propanol, 1- butanol, 1-hexanol and 1-octanol at 303.15K were 1.421, 1.387, 1.398, 1.412 and 1.429 respectively, which compare well with the corresponding literature values. The mixtures were prepared by mixing known volumes of the pure liquids in air tight stoppered bottles. The weights were taken on a single pan electronic balance (K. Roy Company New Delhi) accurate to 0.01mg.

Table 1: Physical Properties of Pure Components at 303.15 K

Component	Density, ρ ($g\text{-}m^{-3}$)		Refractive index,n		Ultrasonic velocity, u($m\text{-}s^{-1}$)	
	Observed	Literature	Observed	Literature	Observed	Literature
1,4-Dioxane	1.0108	1.0229 [17]	1.4210	1.4164 [16]	1348.0	1322.3 [22]
1-Propanol	0.8070	0.8003[21]	1.3870	1.3810 [19]	1182.0	1182.6 [15]
1-Butanol	0.8040	0.8020 [15]	1.3980	1.3952 [19]	1196.0	1196.6[15]
1-Hexanol	0.8128	0.8118[15]	1.4120	1.4134 [3]	1298.0	1282.0 [3]
1-Octanol	0.8242	0.8187 [20]	1.4290	1.4274 [18]	1327.0	1330.8 [18]

3. Results and discussion

The experimental values of densities (ρ), ultrasonic velocity (u) and refractive indices (n) at 303.15K with mole fraction of second components are reported in table-II.
The derived parameter R_m (using Lorentz – Lorenz equation) were calculated from the following relation.

$$R_m = [(n^2_{mix.} - 1)/ (n^2_{mix.} + 2)]\ V_{mix.}$$

Where, $V_{mix.} = (X_1M_1 + X_2M_2) /\rho)$ is the molar volume of the mixture $_1$ and X_2 are the mole fractions of component 1 (1,4-dioxane) and component 2 (alkanols); and M_1 and M_2 are their molar masses.

Table 2: Experimental Value of Densities (P), Ultrasonic Velocity (U), Refractive Indices (N) , Molar Refraction (R_m) , Excess Molar Refraction(R_m^E) and Excess Molar Volume(V^E) of Mole Fraction X_1 of 1,4-Dioxane for the Binary Mixtures at 303.15 K

Mole fraction 1,4-Dioxane (x_1)	P ($kg.m^{-3}$)	U ($m\text{-}s^{-1}$)	Refractive indices (n)	Molar refraction (R_m) $m^3\ mol^{-1}$	Excess molar refraction (R_m^E) $m^3\ mol^{-1}$	V^E (m^3mole^{-1})
1,4-Dioxane + 1- Propanol						
0.00000	807.08	1182.0	1.387	17.5291	+0.0000	+0.0000
0.10006	820.64	1202.0	1.389	18.1258	+0.1373	+0.9297
0.12264	840.70	1215.0	1.392	18.5539	+0.1865	+0.9139
0.29821	870.08	1248.0	1.394	18.8170	+0.2062	+0.8426
0.40573	889.36	1264.0	1.396	19.3058	+0.2583	+0.7539
0.50439	916.72	1270.0	1.398	19.5411	+0.3456	+0.7333
0.60251	929.08	1275.0	1.399	20.0397	+0.3625	+0.6452
0.69410	955.80	1284.0	1.401	26.8930	+0.3841	+0.5816
0.79626	970.84	1290.0	1.403	20.7121	+0.4737	+0.5088
0.89926	992.40	1312.0	1.406	21.1238	+0.5349	+0.4726
1.00000	1010.8	1348.0	1.421	22.1216	+0.0000	+0.0000
1,4-Dioxane + 1-Butanol						
0.00000	804.00	1196.0	1.398	22.2503	+0.0000	+0.0000
0.09734	813.60	1203.0	1.399	22.4404	+0.1473	+0.7405
0.19759	842.52	1209.0	1.400	22.1224	+0.1852	+0.7216
0.30443	86.264	1221.0	1.401	22.0751	+0.2164	+0.7156
0.40480	876.96	1268.0	1.402	22.1523	+0.2632	+0.6926
0.49442	902.24	1282.0	1.403	21.9180	+0.3325	+0.6452
0.59768	917.44	1287.0	1.404	21.9871	+0.3525	+0.6128
0.68628	940.28	1297.0	1.405	21.8230	+0.4812	+0.5808
0.79076	963.92	1315.0	1.406	21.7066	+0.5426	+0.5426
0.89091	986.36	1334.0	1.407	21.6084	+0.5512	+0.4816
1.00000	1010.8	1348.0	1.421	22.1216	+0.0000	+0.0000
1,4-Dioxane + 1-Hexanol						
0.00000	812.80	1298.0	1.412	31.2751	+0.0000	+0.0000
0.09108	821.96	1302.0	1.413	30.6041	+0.1738	+0.7216
0.19485	840.02	1311.0	1.414	29.5760	+0.1926	+0.7125
0.29842	857.24	1314.0	1.415	28.6182	+0.2154	+0.7026
0.40439	871.44	1320.0	1.416	27.7827	+0.2234	+0.6812

0.45430	879.96	1334.0	1.417	27.3713	+0.2523	+0.6725
0.60286	910.76	1338.0	1.418	25.9237	+0.3216	+0.6512
0.69974	934.60	1340.0	1.418	24.8953	+0.4916	+0.5916
0.80182	958.40	1342.0	1.419	23.9501	+0.5321	+0.5314
0.88834	980.04	1346.0	1.420	23.1563	+0.5628	+0.4926
1.00000	1010.8	1348.0	1.421	22.1216	+0.0000	+0.0000
1,4-Dioxane + 1-Octanol						
0.00000	824.20	1327.0	1.429	40.7338	+0.0000	+0.0000
0.09780	82.804	1329.0	1.428	39.1651	+0.1856	+0.7526
0.20653	837.08	1330.0	1.427	37.2744	+0.2519	+0.7455
0.29810	852.92	1332.0	1.426	35.3417	+0.2780	+0.7234
0.40275	859.56	1334.0	1.425	33.6932	+0.3421	+0.6458
0.49229	885.28	1336.0	1.424	31.5582	+0.3792	+0.6216
0.60068	903.04	1338.0	1.423	29.5880	+0.4052	+0.5813
0.69888	926.64	1339.0	1.423	27.6979	+0.4826	+0.5426
0.79610	946.48	1341.0	1.422	25.9618	+0.5812	+0.5036
0.89749	975'96	1345.0	1.422	24.4083	+0.6125	+0.5001
1.00000	1010.8	1348.0	1.421	22.1216	+0.0000	+0.0000

The dependence of R_m and $V_{mix.}$ on the composition of the mixtures is also included in Table II. The molar refraction (R_m) increases with the chain length in the homologes series from 1-propanol to 1-octanol while it decreases with an increase in 1, 4-dioxane concentration (Table II). The average value of R_m for the -CH_2 group estimated from the data for 1-propanol, 1-butanol, 1-hexanol and 1-octanol comes out to be constant. This is in good agreement with the value of R_m of C and H, moreover, the value of R_m obtained for the – CH_2 group of the present alkanols is in close agreement with the value 4.6440×10^{-6} m^3 mol^{-1} for the alkanols series reported by Sjoblom et.al 24.
The functions, V^E are highly sensitive to intermolecular interactions between the component molecules of the mixture. The value of the functions V^E were computed using the following relation.

$$V^E = \sum_{i=1}^{2} X_i M_i \left(\frac{1}{\rho_1} - \frac{1}{\rho_2}\right)$$

Where M_i is molar masses of the i^{th} component respectively. The curve in Fig. 1 reveals that values of V^E are positive over the entire mole fraction of 1,4-dioxane for the all four systems investigated. Mixing of 1,4-dioxane with alkanols will first lead to the mutual dissociation of 1,4-dioxane – 1,4-dioxane and alkanol - alkanol associates (both are strongly associated due to highly polar group in the former and H-bonding in the latter molecule). The interactions which are expected to operate between 1,4-dioxane and alkanols are (a) dipolar – interaction (b) interstitial accommodation of one component in to the other (c) possible hydrogen bonding interactions between unlike molecules.
The observed positive trends in V^E values 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 H - bonding and dipole – dipole interaction between unlike molecule. The V^E values increase in the sequence 1- propanol < 1- butanol < 1- hexanol< 1- octanol which also reflects the decreasing strength of interaction between unlike molecule in the mixture.

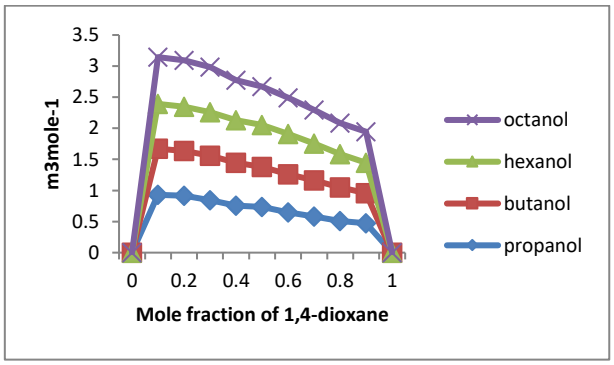

Fig. 1: Plots of Excess Molar Volume (V^E) Versus Mole Fraction of 1,4-Dioxane (X_1) at 303.15 K For Binary Mixtures of 1,4-Dioxane with 1- Propanol, 1- Butanol, 1-Hexanol and 1-Octanol.

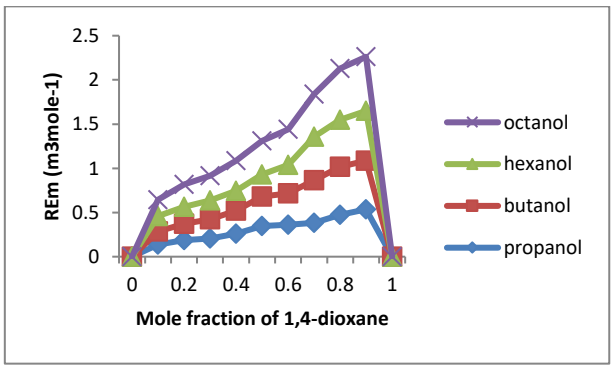

Fig. 2: Plots of Excess Molar Refraction (R_m^E) Versus Mole Fraction of 1,4-Dioxane (X_1) at 303.15 K for Binary Mixtures of 1,4-Dioxane with 1- Propanol, 1- Butanol, 1-Hexanol and 1-Octanol.

The observed positive trends in V^E values 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 H - bonding and dipole – dipole interaction between unlike molecule. The V^E values increase in the sequence 1- propanol < 1- butanol < 1- hexanol< 1- octanol which also reflects the decreasing strength of interaction between unlike molecule in the mixture.

4. Conclusion

In this paper, an attempt is made to measure densities (ρ), ultrasonic velocity (u) and refractive indices (n) at 303.15 K over the entire range of mixture composition of 1, 4-dioxane with 1- propanol, 1-butanol, 1-hexanol and 1-octanol out of these measured data, the excess molar volume (V^E), molar refraction (R_m) and excess molar reflection (R_m^E) have been calculated.

The positive deviations are observed in the case of excess molar volume V^E and excess molar refraction R_m^E, are observed for all binary mixtures of 1,4-dioxane with 1-propanol, 1-butanol, 1-hexanol, 1-octanol. These are specific interactions present in the mixtures studied.

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