JETIR.ORG ISSN: 2349-5162 | ESTD Year : 2014 | Monthly Issue
JOURNAL OF EMERGING TECHNOLOGIES AND INNOVATIVE RESEARCH (JETIR)
An International Scholarly Open Access, Peer-reviewed, Refereed Journal

Study of Intermolecular Interactions in Binary Liquid Mixtures of Cyclic Ether with 1-Alkanols through Ultrasonic Speed Measurements.

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Abstract: The analysis of thermodynamic properties 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 data for density (ρ), ultrasonic velocities (u) and refractive indices (n) of pure 1,4-dioxane, 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. The molecular refraction (R_m), excess molecular refraction (R_m^E) and excess molar volume (V^E) were calculated from the experimental data. The results are discussed in term of molecular interactions between the components of the binary mixtures. Excess molar volumes have also been estimated from measurements of refractive indices.

Keywords: Refractive indices, density, ultrasonic velocity, molar volume, mass refraction, 1- alkanol, molecular interaction.

1 Introduction:

The present work is a continuation of our research work (Nizamul, 2014) on the thermodynamic properties of binary liquid mixtures. Alkanols are considered as amphiphilic materials of biological and industrial importance (Charles, 2000 and Ali, 2005) is a high energy reaction solvent having a wide range of application (Parker, 1969 and Zellerbach, 1998). Alkanols are self-associated through hydrogen bonding. Therefore, interesting result may be obtained regarding molecular interaction between these component molecules in the binary mixtures. In this paper we report measured density (ρ), ultrasonic velocity (u) and refractive indices (n) of the binary mixtures of 1,4-dioxane with 1- propanol, 1- butanol, 1- hexanol and 1-octanol along with those of the pure liquids at 303.15 K, covering the entire composition range expressed by the mole fraction(X_1) of 1,4-dioxane. From the experimental values of ρ, u and n the molar refraction (R_m), excess molar refraction (R_m^E), and excess molar volume (V^E) have been calculated. The studies of refractive indices are being increasingly used as tools (Aminabhavi, 1999, Amalendu, 1998, Al- Dujalu, 2000, Prakash

2008 and Anil, 2008) for investigation of the physical properties of pure components and the nature of intermolecular interaction between the liquid mixture constituents. Refractive indices measurements of binary liquid mixtures are essential for determination of composition of binary mixtures usually for non-ideal mixtures where experimental measurements are performed directly over the entire range of composition. The review of literation (Aralaguppi, 1999) on acoustical studies of solution reveals that refractive indices measurements are also used to estimate the different elastic properties of the molecule from which the type of molecular interactions can be very well understood. (Pandey, 1999) 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 mixtures. A relatively new method (Anthony, 2002) 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:

The chemicals (AR grade) employed were supplied by Merck. Chem. Ltd. India, Their purities (in mass percent) were 1, 4-dioxane 99%, 1-propanol 99.2%, 1-butanol 99.5%, 1- hexanol 99.3% and 1-octanol 99%. All the chemicals were purified by a method given in the literature (Vogl, 1989). 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 (Mahendra, 2005, Aralaguppi, 1999, Aralaguppi, 2005, Al-Kandary, 2009, Tojo, 2001 Gyan, 2008, Elangovan, 2013 and Anil, 2014)are depicted in Table -I.

The densities of pure liquids and their binary mixtures were measured (303.15 K) 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 (Stokes, 1965) 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 multifrequency ultrasonic interferometer (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 I. Physical properties of pure components at 303.15 K

Component	Density, ρ (g-m^{-3})		Refractive index,n		Ultrasonic velocity, u(m-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:

Table- II shows the experimental values of densities (ρ), refractive indices (n) and ultrasonic velocity (u) of pure 1,4-dioxane, 1-propanol, 1-butanol, 1-hexanol and 1-octanol over the whole composition range at 303.15 K 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 II. Experimental value of densities (ρ), ultrasonic velocity (u), refractive indices (n) , molar refraction (R_m) , excess molar refraction(R^E_m) 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)	ρ (kg.m^{-3})	u (m-s^{-1})	Refractive indices (n)	Molar refraction (R_m) m^3 mol^{-1}	Excess molar refraction (R^E_m) m^3 mol^{-1}	V^E (m^{3}mole^{-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, 1981) .

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.

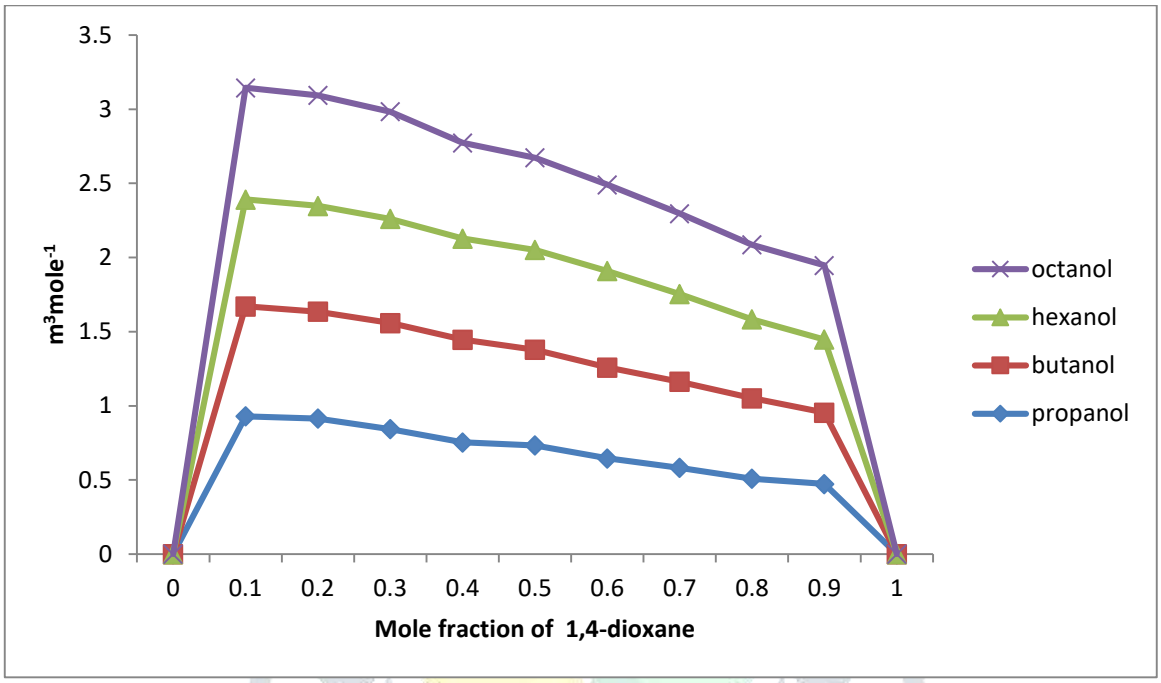

Fig.1. Plots of excess molar volume (V^E) versus mole fraction of 1,4-dioxane (X_1) at 303.15 K for binary mixtures of 1,4-dioxane with 1- propanol, 1- butanol, 1-hexanol and 1-octanol.

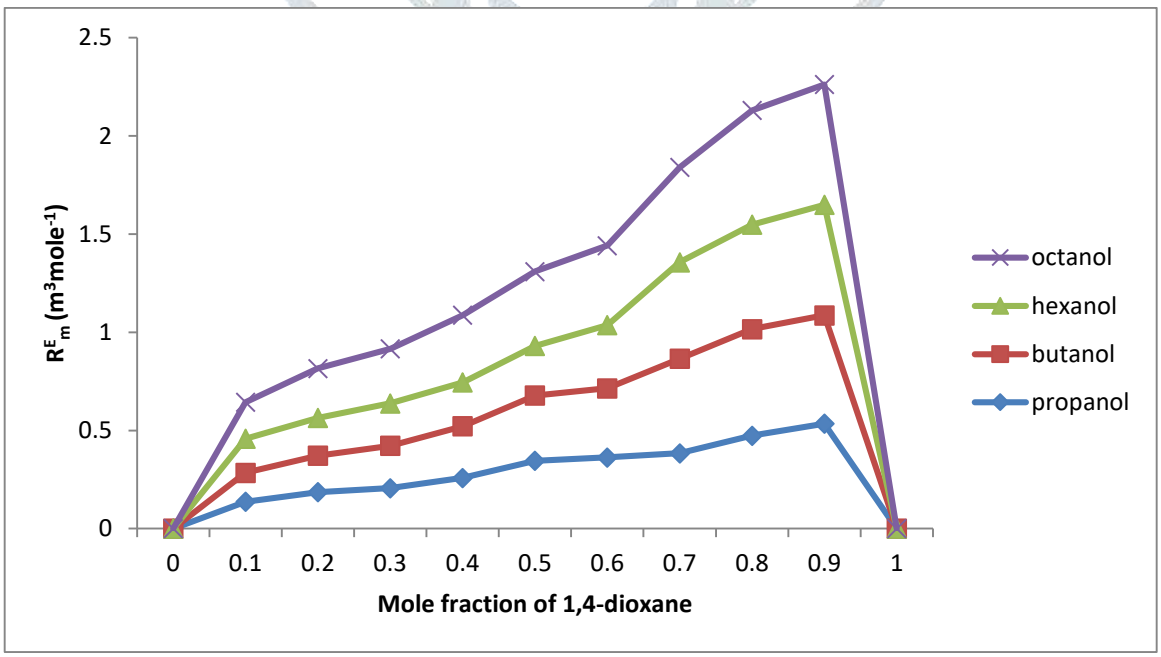

Fig.2. Plots of excess molar refraction (R_m^E) versus mole fraction of 1,4-dioxane (X_1) at 303.15 K for binary mixtures of 1,4-dioxane with 1- propanol, 1- butanol, 1-hexanol and 1-octanol.

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.

As the size of the alkyl group increase from 1-propanol to 1- octanol the steric hindrance also increases, resulting in decreased interaction between 1,4-dioxane and alkanol molecule, and , hence the strength of interaction should follow the sequence 1- propanol > 1- butanol > 1- hexanol > 1- octanol. Thus, the extent of positive deviation supports our view. Similar behaviors in V^E with composition has also been reported for ethanol + 1- hexanol (Oswal, 2004), N,N- dimethylacetamide + 1- hexanol and DMSO + N,N-dimethylformide (Ali, 2000)binary 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.

Acknowledgement:

The authors are very much thankful to the Head of the Department of Chemistry Bundelkhand University, Jhansi for proving the facilities for Research work.

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