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Thermophysical properties of Ethyl acetate with 1-Alkanol binary mixtures at 303.15 K.

Seema Agarwal and Dhirendra Kumar Sharma*

Department of Chemistry, Bundelkhand University, Jhansi,Uttarpradesh, India

***Corresponding author:** Dhirendra Kumar Sharma, Department of Chemistry, Bundelkhand University, Uttarpradesh, India.
E-mail: dhirendra.dr@rediffmail.com*

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 ethyl acetate, 1-methanol, 1-ethanol, 1-propanol, 1-butanol, 1-hexanol, 1- octanol and their binary mixtures with ethyl acetate as a common component over the whole composition range at 303.15 K. The molecular refraction (Rm), excess molecular refraction (R_m^E) and excess molar volume (VE) were calculated from the experimental data. Negative values of these excess molar volume and excess molar refraction appear for all analyzed systems. The structure and specific characteristics of different molecules in considered mixtures and determined non ideal behavior allow the insight in to possible type of interactions in the mixture, interstitial accommodation and structural effect. 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.

INTRODUCTION

In continuation of our studies on thermodynamic, acoustic and transport properties of some binary mixtures of ethyl acetate with 1-alkanols the present paper reports the excess molar volume (V_m^E) and excess molar refraction (R_(m)^E) for binary solvent mixtures containing ethyl acetate, 1- methanol, 1-ethanol, 1-propanol, 1-butanol, 1-hexanol, 1- octanol over the entire mole fraction range at 303.15 K. Density, refraction index and speed of sound represent thermo physical properties of a fluid that characterize each pure substance in the liquid state, as well as their mixtures. Knowledge of these properties is very important for design and operation of separation processes and equipment in the chemical industry, calculation of heart exchangers, fluid transport, as well as for the development of new thermodynamic models. Theoretical significance of the investigation of thermodynamic as well as transport properties of liquid mixtures is reflected in extension of the database with new experimental values [1]. Various substance and their mixtures are used in the industry and for many of them literacy values of thermodynamic properties and related quantities do not exist. On the other hand, density and the excess molar volume, primarily, but also other deviation properties, are the best indicators of molecular interactions, structural changes and packing effects in mixtures. Ethyl acetate is highly miscible with all organic compounds, such as glycols, ketones, alcohols, and esters [2]. It is most commonly used in mixtures with alcohols, and a combination with 20% ethanol found application as an excellent solvent for cellulose acetate. Alkanols are considered as amphiphilic materials of biological and industrial importance is a high energy reaction solvent having a wide range of application. Alkanols are self-associated through hydrogen bonding [3].

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 ethyl acetate with 1-methanol, 1-ethanol, 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 (X1) of ethyl acetate. From the experimental values of ρ, u and n the molar refraction (Rm), excess molar refraction (R_m^E), and excess molar volume (VE) have been calculated. Refractive index is one of the most important properties of liquid. The measurement of the refractive index of liquids is in important work in engineering and science [4]. Transmission and refraction detections near critical angles related to total internal reflection are common methods in refractive index measurement. When a ray of light passes from one medium to another, it suffers refraction, that is change in direction. If it passes from a less dense to a denser medium, it is refracted towards the normal so that the angle of refraction (r) is less that the angle of incidence (I) the refractive index (n) of the medium is the ratio of velocity of light in vacuum to the velocity of light in the medium. Refractive index is an important additive property of the structural arrangement of atom in molecule refractive index can be measured easily with high degree of accuracy.

MATERIALS AND METHODS

The studies of refractive indices are being increasingly used as tools 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 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 [5].

Pandey 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 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.

Experimental

The chemicals (AR grade) employed were supplied by Merck. Chem. Ltd. India, Their purities (in mass percent) were ethyl acetate 99.4%, 1-methanol 99.27%, 1-ethanol 99.2%, 1-propanol 99.2%, 1-butanol 99.5%, 1- hexanol 99.3% and 1-octanol 99%. All chemicals was stored over sodium hydroxide pellets for several days and fractionally distilled twice. All the chemicals were purified by a method given in the literature. Ethyl acetate was dried over K2CO3 filtered and distilled were discarded. All the chemicals were stored to minimize adsorption of moisture. 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 are depicted in **(Table 1).**

Table 1: Physical properties of pure components at 303.15 K.

Compon	**Density, ρ ($g-m^{-3}$)**		**Refractive index, n**		**ltrasonic velocity, u (m-s-1)**	
	O	**L**	**O**	**L**	**O**	**L**
Ethyl	0	0	1.	1	1	1
1-	0	0	1.	1	1	1
1-	0	0	1.	1	1	1
1-	0	0	1.	1	1	1
1-	0	0	1.	1	1	1
1-	0	0	1.	1	1	1
1-	0	0	1.	1	1	1

Density

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 cm3. 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, India) 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 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 ethyl acetate, 1-methanol, 1-ethanol, 1- propanol, 1-butanol, 1-hexanol and 1-octanol at 303.15 K were 0.8820, 0.7840, 0.7720, 0.8070, 0.8040, 0.8128 and 0.8242 g-m-3which compare well with corresponding literature values of respectively.

Sound velocity

The ultrasonic velocities were measured using a multifrequency ultrasonic interferometer (Model F-80D, Mittal Enterprises, New Delhi, India) working at 3 MHz. The meter was calibrated with water and benzene at 303.15 K. The measured values of ultrasonic velocities of pure ethyl acetate, 1-methanol, 1-ethanol, 1- propanol, 1-butanol, 1-hexanol and 1-octanol at 303.15K were1125, 1084, 1141, 1182, 1196, 1298 and 1327 m.s- 1 respectively, which compare well with the corresponding literature values.

Refractive index

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 ethyl acetate, 1- methanol, 1-ethanol, 1-propanol, 1-butanol, 1-hexanol and 1-octanol at 303.15 K were 1.374, 1.351, 1.362, 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, Varanasi, (U.P.) India) accurate to 0.01 mg.

RESULT AND DISCUSSION

Shows the experimental values of densities (ρ), refractive indices (n) and ultrasonic velocity (u) of pure ethyl acetate, 1-methanol, 1-ethanol, 1-propanol, 1-butanol, 1-hexanol and 1-octanol over the whole composition range at 303.15 K, the derived parameter Rm (using Lorentz-Lorenz

equation) were calculated from the following relation

$$Rm = (n2mix.^{-} 1) / (n2mix. + 2) Vmix.$$

Where Vmix. =(X1M1+X2M2)/ρ) is the molar volume of the mixture X1 and X2 are the mole fractions of component 1 (ethyl acetate) and component 2 (alkanols); and M1 and M2 are their molar masses. Results of excess and deviation properties provide insights into the positive or negative deviation from the ideal mixture, indicating which interactions are prevalent in the systems under study. When mixing pure components deviations from the ideal mixture can be smaller or larger depending on the formation of different types of intermolecular bonds and interactions and the packing ability. Dipole-dipole and H-bond interactions between hetero molecules in the mixture lead to negative excess molar volumes, as well as structural effects such as favorable interstitial accommodation and efficient packing. On the other hand, disruption of dipole-dipole interactions and intermolecular hydrogen bonds between molecules of the same substance when put in a mixture.

Alcohols are organic compounds with a highly polar hydroxyl group, which enables interconnection of molecules with strong hydrogen bonds and construction of associated liquids. In mixtures with another organic component, alcohol molecules tend to dissociate from the aggregates and form hydrogen bonds with molecules of another kind. The degree of dissociation from the aggregate depends on the affinity towards the proton of a functional group of another molecule, a proton acceptor.

Table 2: Experimental value of densities (ρ), ultrasonic velocity (u), refractive indices (n) , molar refraction (Rm) , excess molar refraction(R_m^E) and excess molar volume(VE) of mole fraction X1 of ethyl acetate for the binary mixtures at 303.15 K.

Mole fraction Ethyl acetate (x1) Ethyl acetate + 1-Methanol	Density (ρ) (kg.m-3)	Sound velocity(u) (m-s-1)	Refractive indices (n)	Molar refraction (Rm) m3 mol-1	Excess molar Refractive (RE) m3 mol-1	Excess molar volume (VE) (m3mole-1)
Ethyl acetate + 1-Methanol						
0	784	1084	1.351	8.81621	0	0
0.1039	796.8	1099	1.355	10.3575	-0.08649	-0.52201
0.2248	819.2	1103	1.358	11.9678	-0.10468	-0.66072
0.3129	839.5	1105	1.359	13.0028	-0.19321	-0.77383
0.437	848.3	1110	1.361	14.7471	-0.286	-0.80962
0.5474	867.5	1114	1.362	16.038	-0.34032	-0.87129
0.6409	870.9	1117	1.365	17.4401	-0.34722	-0.95002
0.7128	879	1118	1.367	18.3941	-0.40011	-0.62853
0.8164	879.2	1122	1.37	20.0192	-0.22475	-0.55257
0.9104	880.5	1123	1.372	21.4475	-0.11293	-0.546
1	882	1125	1.374	22.8137	0	0
Ethyl acetate + 1-Ethanol						
0	772	1141	1.362	13.236	0	0
0.1049	802.5	1137	1.363	13.9869	-0.24449	-0.99258
0.209	815.7	1135	1.364	14.9896	-0.25814	-1.83336
0.3105	827.8	1134	1.364	15.919	-0.29148	-1.9488
0.4166	839.2	1133	1.365	16.9285	-0.29776	-2.67661
0.5094	849.6	1132	1.366	17.7873	-0.32786	-2.73675
0.6076	860.4	1131	1.367	18.6876	-0.3678	-2.88955
0.715	863.9	1130	1.368	19.8355	-0.24897	-1.31421
0.8069	877.6	1128	1.369	20.5656	-0.19937	-0.99
0.903	882.7	1126	1.371	21.5843	-0.18045	-0.79942
1	882	1125	1.374	22.8137	0	0
Ethyl acetate + 1-Propanol						
0	807	1182	1.387	17.5291	0	0
0.1074	813.3	1173	1.386	18.2224	-0.12567	-0.39267
0.2086	826.2	1169	1.385	18.7007	-0.16896	-0.43678
0.3145	832.1	1161	1.383	19.3145	-0.18312	-0.64416
0.4099	842.8	1159	1.381	19.7179	-0.22265	-0.84248

0.4758	850.9	1154	1.379	19.9402	-0.22355	-0.97433
0.54307	860.9	1150	1.378	20.1672	-0.23184	-1.80306
0.6127	864.7	1142	1.377	20.5498	-0.21732	-0.69878
0.7564	868.5	1138	1.376	21.4751	-0.15131	-0.41016
0.9126	878.8	1134	1.375	22.3135	-0.13831	-0.19909
1	882	1125	1.374	22.8137	0	0
Ethyl acetate + 1-Butanol						
0	804	1196	1.398	22.2503	0	0
0.1063	805.6	1194	1.396	22.5485	-0.23857	-0.83451
0.2151	816.8	1184	1.394	22.5878	-0.2466	-0.98179
0.3213	826.9	1180	1.39	22.5364	-0.25524	-1.38436
0.4327	832.2	1176	1.387	22.6801	-0.28624	-1.8105
0.5192	842	1170	1.383	22.5451	-0.30247	-2.45928
0.6266	842.4	1167	1.381	22.8436	-0.24053	-1.369
0.7124	858.1	1154	1.379	22.6445	-0.20583	-1.30851
0.8127	866.6	1142	1.377	22.6877	-0.12022	-0.88668
0.9044	874.2	1134	1.375	22.7211	-0.10855	-0.79466
1	882	1125	1.374	22.8137	0	0
Ethyl acetate + 1-Hexanol						
0	812.8	1298	1.412	31.2751	0	0
0.0996	821.4	1292	1.392	29.1433	-1.28833	-0.45637
0.2225	833.8	1287	1.39	28.1553	-1.33664	-1.17608
0.3149	835.5	1275	1.387	27.5395	-1.97072	-1.59146
0.4151	840.6	1257	1.382	26.6683	-1.99365	-1.8884
0.5186	846.6	1247	1.38	25.9568	-1.42977	-2.25452
0.6083	854.4	1240	1.379	25.3184	-0.80869	-1.43844
0.7096	861.7	1222	1.378	24.6634	-0.60649	-1.408
0.8066	867.2	1210	1.376	24.0303	-0.41933	-0.75911
0.9041	878	1192	1.375	23.3212	-0.30344	-0.49263
1	882	1125	1.374	22.8137	0	0
Ethyl acetate + 1-Octanol						
0	824.2	1327	1.429	40.7338	0	0
0.1056	825.9	1312	1.426	39.0179	-0.17754	-0.42861
0.2095	830	1294	1.424	37.3191	-0.34121	-0.43692
0.3174	831.8	1275	1.422	35.6967	-0.65183	-0.92541
0.4286	838.7	1239	1.42	33.8439	-0.79156	-1.04906
0.5083	840	1225	1.416	32.5073	-0.88283	-1.07905
0.6196	844.4	1214	1.392	29.3651	-0.66444	-1.32444
0.709	858.6	1192	1.386	34.2732	-0.34644	-0.85666
0.8064	865.1	1164	1.384	26.0149	-0.26642	-0.72863
0.9044	871.6	1148	1.379	24.4268	-0.09897	-0.25366
1	882	1125	1.374	22.8137	0	0

Ethyl acetate is also a polar compound, which acts as H-bond acceptor, and therefore there is a possibility of intermolecular interactions in mixtures with alcohols. Depending on the strength of these two types of interactions, disruption of bonds between molecules of alcohol and formation of new ones between molecules in the mixture, negative deviation from ideal behaviour can be noticed. Another possibility to interact are dipol-dipol interactions. Since the dipole moment of ethyl acetate is higher than the ones for investigated alcohols, it can be concluded that these interactions are stronger between molecules of acetate than those with alcohol molecules. The molar refraction (R_m) for the pure liquid ethyl acetate, 1-methanol, 1-ethanol, 1- propanol, 1- butanol, 1- hexanol and 1- octanol have been calculated using Lorentz- Lorenz equation. The calculated values for all the liquid are listed in Table II. The molar refraction for six binary liquid mixtures ethyl acetate + 1-methanol, ethyl acetate + 1-ethanol, ethyl acetate + 1-propanol, ethyl acetate + 1-butanol, ethyl acetate + 1-hexanol and ethyl acetate + 1-octanol have been calculated using equation 1 and

calculated values are recorded in Table II. The excess molar refraction (R_m^E) have been calculated through molar fraction of the mixture and ideal molar refraction

$$R_m^E = R_m - (X_1 R_{m.1} + X_1 R_{m.2})$$

The value of excess molar refraction (R_m^E) for these system are also enlisted in Table II. The variation of excess molar refraction (R_m^E) with mole fraction (X_1) of ethyl acetate at 303.15 K for the binary mixture of ethyl acetate with 1-alkanol are displayed in Figure 1.

A perusal of Table II show that the value of molar refraction increase with increase in mole fraction of the ethyl acetate (X_1). The table also show that the value of excess molar refraction (R_m^E) are negative for all the binary liquid system ethyl acetate + 1-methanol, ethyl acetate + 1-ethanol, ethyl acetate + 1-propanol, ethyl acetate + 1-butanol, ethyl acetate + 1-hexanol and ethyl acetate + 1-octanol at 303.15 K. In the present investigation the negative excess molar refraction (R_m^E) for binary mixtures of ethyl acetate with 1-alkanols may be attributed to hydrogen bond formation through dipole-dipole interaction between 1-alkanol and ethyl acetate molecule to structural contribution arising from the geometrical fitting of component (1-alkanols) in to the other (ethyl acetate) due to difference in the free volume between components.

The molar refraction (Rm) increases with the chain length in the homologes series from 1-methanol to 1-octanol while it decreases with an increase in ethyl acetate concentration (Table- II). The average value of Rm for the -CH2 group estimated from the data for 1-methanol, 1-ethanol, 1-propanol, 1-butanol, 1-hexanol and 1-octanol comes out to be constant. This is in good agreement with the value of Rm of C and H, moreover, the value of Rm obtained for the – CH2 group of the present alkanols is in close agreement with the value 4.6440×10-6 m3 mol-1 for the alkanols series reported by Sjoblom et.al 29. The functions, VE are highly sensitive to intermolecular interactions between the component molecules of the mixture. The values of the functions VE were computed using the following relation

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

Where Mi is molar masses of the ith component respectively. The plots of excess molar volume VE with mole fraction $X1$ for the binary mixtures of ethyl acetate with 1- methanol, 1- ethanol, 1- propanol, 1- butanol, 1- hexanol and 1- octanol at 303.15 K were depicted in Fig. 2

The VE values of are negative sign at the temperature for these systems over the whole composition range, Generally, VE values may be explained in term of physical, chemical and structural factors. It is a consequence of the rapture of the hydrogen bonding in the self-associated alkanol molecules on the other hand; the negative VE data are attributed in terms of charge- transfer complex, dipole-dipole interactions and formation of intermolecular hydrogen bonding between component molecules. Further, the sign and magnitude of VE also very with the structural characteristics of the component molecules arising from the geometrical fitting of one component in to the structure of the other component because of the difference in the size, shape, orientation of the components and the free volume. In present investigation chemical interactions are prevailing in the mixture of ethyl acetate with 1-alkanol due to the existence of strong intermolecular hydrogen bond (H-----OH) between the H- atom of the ester group of ethyl acetate and oxygen atom of the O-H group of 1- alkanol. The algebraic value of VE for the mixtures of ethyl acetate with 1-alkanols fall in the order 1- methanol < 1- ethanol < 1-propanol < 1- butanol < 1- hexanol < 1- octanol. The above order indicates the strength of interactions between component molecules decreases due to decrease in polarizability of alkanol molecules.

Figure 1: Plots of excess molar refraction (R_m^E) versus mole fraction of ethyl acetate (X1) at 303.15 K for binary mixtures of ethyl acetate with 1- methanol, 1-ethanol,1- propanol, 1- butanol, 1-hexanol and 1-octanol.

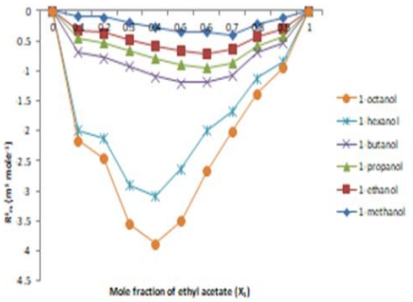
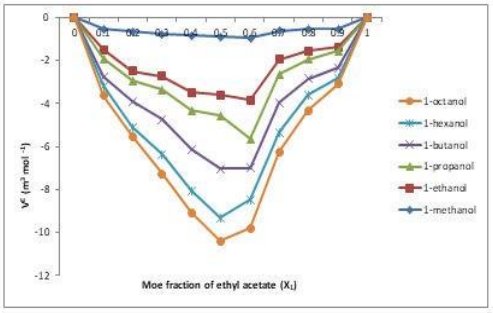


Figure 2: Plots of excess molar volume (VE) versus mole fraction of ethyl acetate (X1) at 303.15 K for binary mixtures of ethyl acetate with 1-methanol, 1-ethanol, 1- propanol, 1- butanol, 1-hexanol and 1-octanol



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 ethyl acetate with 1-methanol, 1-ethanol, 1- propanol, 1-butanol, 1-hexanol and 1-octanol out of these measured data, the excess molar volume (VE), molar refraction (Rm) and excess molar reflection (R_m^E) have been calculated. The negative deviations are observed in the case of excess molar volume VE and excess molar refraction[R]_m^E, are observed for all binary mixtures of ethyl acetate with 1-methanol, 1-ethanol, 1-propanol, 1-butanol, 1-hexanol, 1-octanol.The results are analyzed in the sight of molecular interactions between

The components. It may be concluded that the interaction resulting in the interstitial accommodation of ethyl acetate in to 1-alkanols are the predominant factor over dipole-dipole interaction.

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