Excess molar volume and isentropic compressibility for the binary mixture (Ethyl acetate + 1-Alkanols) at 303.15K.

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Abstract: Densities (ρ) and sound velocity (u) for the binary mixtures of ethyl acetate with 1-methanol, 1-ethanol, 1- propanol, 1- butanol, 1-hexanol and 1-octanol were measured over the entire composition range at 303.15 K. From the experimental data, excess molar volume (V^E), isentropic compressibility (K_s) and deviation in isentropic compressibility (ΔK_s) have been calculated. The excess molar volume (V^E) and excess isentropic compressibility (K_s^E) were found to be negative at the 303.15K. The thermodynamic properties have been discussed in terms of nature of molecular interactions between the components of the mixture.

Keywords: Density, Ultrasonic sound velocity, Excess volume, isentropic compressibility, molecular interactions, 1-Alkanols.

Nomenclature

ρ Densities of liquid

u, Ultrasonic velocity

u^E, excess ultrasonic velocity

V^E, Excess values of molar volume

K_s, isentropic compressibility

ΔK_s, deviation in isentropic compressibility

X_1, Mole fraction of ethyl acetate

Y^E, Thermodynamic excess function

1. Introduction

The present paper is part of our ongoing research on the thermodynamic properties of binary liquid mixtures containing ethyl acetate with 1-alkanols. Therefore their binary liquid mixture properties are needed as a useful database in a variety of industrial application. In recent years, these have been a considerable development in the experimental investigation of the thermodynamic properties of liquid mixtures, which are used in many industrial applications. The knowledge of the thermodynamic properties of non-electrolyte solutions is essential in the chemical industry involving chemical separations, heat transfer and fluid flow. Studies of thermodynamic properties are of considerable interest not only due to industrial importance but also on the grounds that they lead to a better understanding of the molecular interactions between the liquid mixture constituents and the extension of solution theories because they depend on solute - solute, solvent-solvent and solute - solvent interaction and the structural effect arising from interstitial accommodation. Excess thermodynamic properties are crucial for the chemical process design [1-2] as well as for progress in the thermodynamic theories and modeling of the liquid state. Excess compressibility and excess molar volumes give important information about intermolecular forces determining the properties of the mixtures. Studies on the ethyl acetate + 1-alkanols mixtures due to their simple structure components are of particular interest. Moreover, 1-alkanol molecules are self-associating; it is of interest to see how they behave in the presence of ethyl acetate molecule i.e. the extent to which hydrogen bonding and self-association of 1-alkanol molecule change in mixture.

In continuation to our work on thermodynamic studies of binary liquid mixtures [3-5]. In the present study, we report the experimental density (ρ) and speed of sound velocity (u) over the whole composition range at temp. at 303.15 K. From these data experimental densities and ultrasonic sound velocity, excess molar volume (V^E_m), isentropic compressibility (K_s) and excess isentropic compressibility (K^E_s) have been calculated for each of binary liquid mixtures at the 303.15 K.

The excess thermodynamic function introduced by Scatchard in the year 1931, provided a way to represent directly the deviation of solution from ideal behavior [6]. The difference between the thermodynamic function of mixing for a real system and the value corresponding to a perfect solution at the some temperature, pressure and composition is called the excess thermodynamic parameters denoted the super script E. Thus, any excess parameter Y^E is given by

$$Y^E = Y^M_{real} - Y^M_{ideal}$$

2. Materials and Method

2.1 Apparatus and Procedures

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) 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 [7] value of the density of pure water at 303.15 K. 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 303.15K 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. 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 303.15K. 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 were 1125, 1084, 1141, 1182, 1196,1298 and 1327 m.s-1 respectively, which compare well with the corresponding literature values. The viscosity was measured by means of a suspended Ubbelohde type viscometer [8] calibrate was done at 303.15K with double distilled water and purified methanol. An electronic digital stop watch with readability of ±0.01 was used for the flow time measurements. 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 303.15K

component	Density (ρ) g-m^{-3}		Ultrasonic Velocities (u) m.s^{-1}	
	Observed	Literature	Observed	Observed
Ethyl acetate	0.8820	0.8885 [10]	1125	1115.0 [6]
1-Methanol	0.7840	0.7817 [10]	1084	1084.0 [15]
1-Ethanol	0.7720	0.7808 [10]	1141	1144.3[11]
1-Propanol	0.8070	0.8003 [14]	1182	1182.6[11]
1-Butanol	0.8040	0.8020 [11]	1196	1196.6[11]
1-Hexanol	0.8128	0.8118[11]	1298	1282.0[12]
1-Octanol	0.8242	0.8187 [11]	1327	1330.8 [13]

2.2 Chemicals

The chemicals (AR grade) employed were supplied by Merck. Chem. Ltd. India, Their purities (in mass percent) were ethyl acetate 99%, 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 the chemicals were purified by a method given in the literature [9]. The purity of the liquids was also checked by measuring their densities, viscosities and sound velocities at 303.15K and were in agreement with the literature values [10-15] are depicted in Table -I.

3 Result and Discussion

The experimental density (ρ), ultrasonic sound velocity (u), excess molar volume (V^E_m), isentropic compressibility (K_s) and excess isentropic compressibility (K^E_s) for all the binary system of ethyl acetate with 1-alkanol at the 303.15 K. were given in Table 2. The excess volume data were calculated from the densities of pure liquids and their mixtures using the following equations:

$$V^E = \frac{\sum_{i=1}^{n} X_i M_i}{\rho_m} - \sum_{i=1}^{n} \frac{X_i M_i}{\rho_i}$$

Where X, M and ρ are mole fraction, molar volume and density respectively. The subscript i and m represent pure components and mixture, respectively. The isentropic compressibility (K_s) [16-17] were calculated by using Newton-Laplace equation given below

$$K_s = 1/u^2.\rho$$

Where ρ is the density and u is the sound velocity of the binary mixtures. Further, deviation in isentropic compressibility (ΔKs) was calculated using the following relation

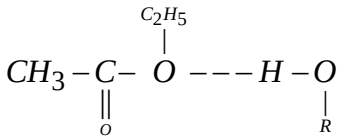
$$\Delta K_1 = K_s - X_1 K_{s.1} - X_2 K_{s.2}$$

Where $K_{s.1}$ and $K_{s.2}$ are the isentropic compressibility of the pure component 1 and 2 respectively.

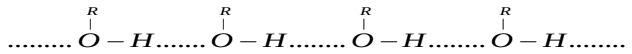
The plots of excess molar volume V^E with mole fraction X_1 for the binary mixtures of ethyl acetate with 1-methanol, 1- ethanol, 1- propanol, 1- butanol, 1- hexanol and 1- octanol at 303.15 K were depicted in Figure 1 The V^E values of are negative sign at the temperature for these

systems over the whole composition range, Generally, V^E 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 [18-20] on the other hand; the negative V^E 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 V^E 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 V^E 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.

In the present investigation the negative excess molar volume (V^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 or to structural contributions arising from the geometrical fitting of one component (1-alkanol) into the other (ethyl acetate) due to difference in the free volume between components.



In order to substantiate the presence of interaction between the molecules, it is essential to study the excess parameter such as molar volume. The deviation of physical property of the liquid mixtures from the ideal behavior is a measure of the interaction between the molecules which is attributed to either adhesive or cohesive forces. In the present study, 1-alkanols in a polar and has self - association character in other polar organic solvents.



The negative values of excess molar volume (V^E) indicate the presence of strong molecular interaction. We may conclude that 1-alkanols, which is a self – associating polar organic liquid has a tendency to form complexes with ethyl acetate and the increase in its dilution causes disruption of aromatic C – H bond stretching as the self – association of 1-alkanols is disrupted.

The deviation in isentropic compressibility (ΔK_s) is plotted in Figure 2 for the binary systems of ethyl acetate with 1- alkanols at 303.15 K. The ΔK_s values are negative over the entire composition range at the 303.15 K which are under the investigation and this may be attributed due to the relative strength of effect which influence the free space between component molecules as described in the literature [21] The algebraic values of ΔK_s 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.

Table 2. Experimental Results for the binary Liquid Mixtures of Ethyl Acetate (1) + 1-alkanols (2) at 303.15 K

Mole fraction of ethyl acetate (X_1)	Density (ρ) $g.m^{-3}$	Sound velocity (u) $m.s^{-1}$	Excess molar volume (V^E) $m^3.mol^{-1}$	Isentropic compressibility ($K_{Smix.} \times 10^{-9}$) Pa^{-1}	Deviation of isentropic compressibility ($\Delta K_{Smix} \times 10^{-9}$) Pa^{-1}
Ethyl Acetate + 1- Methanol					
0.0000	0.7840	1084	0.0000	1085.4	0.00
0.1039	0.7968	1099	-0.5220	1003.9	-61.8
0.2248	0.8192	1103	-0.3607	1003.3	-39.4
0.3129	0.8395	1105	-0.2738	965.4	-60.6
0.4370	0.8483	1110	-0.0096	956.7	-45.8
0.5474	0.8675	1114	-0.8712	928.8	-52.8
0.6409	0.8709	1117	-0.6500	920.2	-43.6
0.7128	0.8790	1118	-0.0285	910.1	-40.1
0.8164	0.8792	1122	-0.5525	903.4	-27.1
0.9104	0.8805	1123	-0.2460	900.5	-12.2
1.0000	0.8820	1125	0.0000	895.8	0.00

Ethyl Acetate + 1- Ethanol					
0.0000	0.7720	1141	0.0000	994.9	0.00
0.1049	0.8025	1137	-0.9925	963.8	-20.6
0.2090	0.8157	1135	-0.8333	951.6	-22.6
0.3105	0.8278	1134	-0.7488	939.3	-24.8
0.4166	0.8392	1133	-0.6766	928.1	-25.4
0.5094	0.8496	1132	-0.7367	918.4	-25.9
0.6076	0.8604	1131	-0.8895	908.5	-26.2
0.7150	0.8639	1130	-0.3142	906.5	-17.5
0.8069	0.8776	1128	-0.9900	895.4	-19.4
0.9030	0.8827	1126	-0.7994	893.5	-11.9
1.0000	0.8820	1125	0.0000	895.8	0.00
Ethyl Acetate + 1-Propanol					
0.0000	0.8070	1182	0.0000	886.8	0.00
0.1074	0.8133	1173	-0.3926	893.5	+5.75
0.2086	0.8262	1169	-0.0367	885.6	-3.10
0.3145	0.8321	1161	-0.3441	891.5	-1.85
0.4099	0.8428	1159	-0.0424	883.3	-7.22
0.4758	0.8509	1154	-0.2743	882.4	-8.65
0.5430	0.8609	1150	-0.8030	878.2	-13.4
0.6127	0.8647	1142	-0.6987	886.7	-5.62
0.7564	0.8685	1138	-0.1101	889.0	-4.57
0.9126	0.8788	1134	-0.1990	884.8	-10.16
1.0000	0.8820	1125	0.0000	895.8	0.00
Ethyl Acetate + 1- Butanol					
0.0000	0.8040	1196	-0.0000	869.5	0.00
0.1063	0.8056	1194	-0.8345	870.6	-1.69
0.2151	0.8168	1184	-0.5817	873.3	-1.84
0.3213	0.8269	1180	-0.3843	868.5	-9.46
0.4327	0.8322	1176	-0.8105	868.8	-12.0
0.5192	0.8420	1170	-0.4592	867.5	-15.6
0.6266	0.8424	1167	-0.3690	871.6	-14.3
0.7124	0.8581	1154	-0.3085	875.0	-13.1
0.8127	0.8666	1142	-0.1866	884.7	-6.17
0.9044	0.8742	1134	-0.0946	889.4	-3.81
1.0000	0.8820	1125	-0.0000	895.8	0.00
Ethyl Acetate + 1- Hexanol					
0.0000	0.8128	1298	0.0000	730.2	0.00
0.0996	0.8214	1292	-0.4563	729.2	-17.4
0.2225	0.8338	1287	-0.1760	724.0	-43.0
0.3149	0.8355	1275	-0.5914	736.2	-46.1
0.4151	0.8406	1257	-0.3884	752.9	-46.0
0.5186	0.8466	1247	-0.2545	759.5	-56.5
0.6083	0.8544	1240	-0.4384	761.1	-69.8
0.7096	0.8617	1222	-0.4080	777.0	-70.6
0.8066	0.8672	1210	-0.1591	787.5	-76.2
0.9041	0.8780	1192	-0.4926	801.5	-78.4
1.0000	0.8820	1125	0.0000	895.8	0.00
Ethyl Acetate + 1- Octanol					
0.0000	0.8242	1327	-0.0000	688.9	0.00
0.1056	0.8259	1312	-0.4286	703.3	-7.43
0.2095	0.8300	1294	-0.4369	719.4	-12.8
0.3174	0.8318	1275	-0.9254	739.4	-15.1
0.4286	0.8387	1239	-0.6490	776.6	-0.97
0.5083	0.8400	1225	-0.0790	793.2	-0.81
0.6196	0.8444	1214	-0.3244	803.5	-13.5
0.7090	0.8586	1192	-0.8566	819.6	-15.9
0.8064	0.8651	1164	-0.1286	853.1	-2.65
0.9044	0.8716	1148	-0.2536	870.5	-5.53
1.0000	0.8820	1125	-0.0000	895.8	0.00

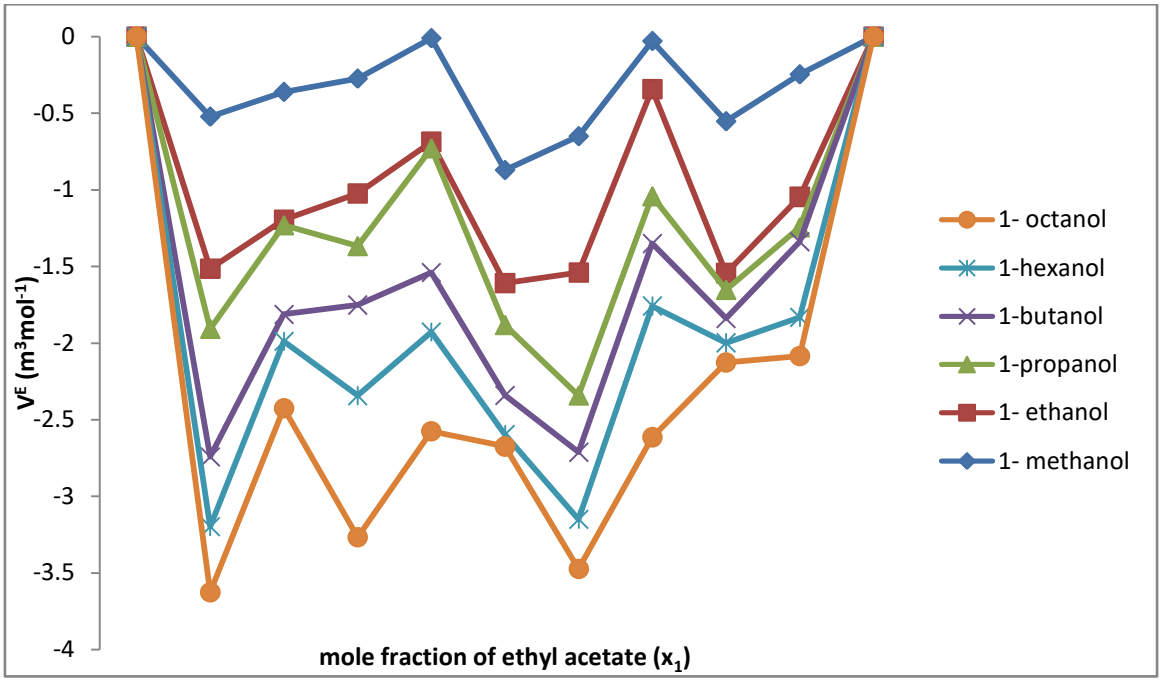


Figure 1. Plots of excess molar volume (V^E) versus mole fraction of ethyl acetate (x_1) at 303.15K for binary mixtures of ethyl acetate with 1-methanol, 1-ethanol, 1-propanol, 1-butanol, 1- hexanol and 1-octanol.

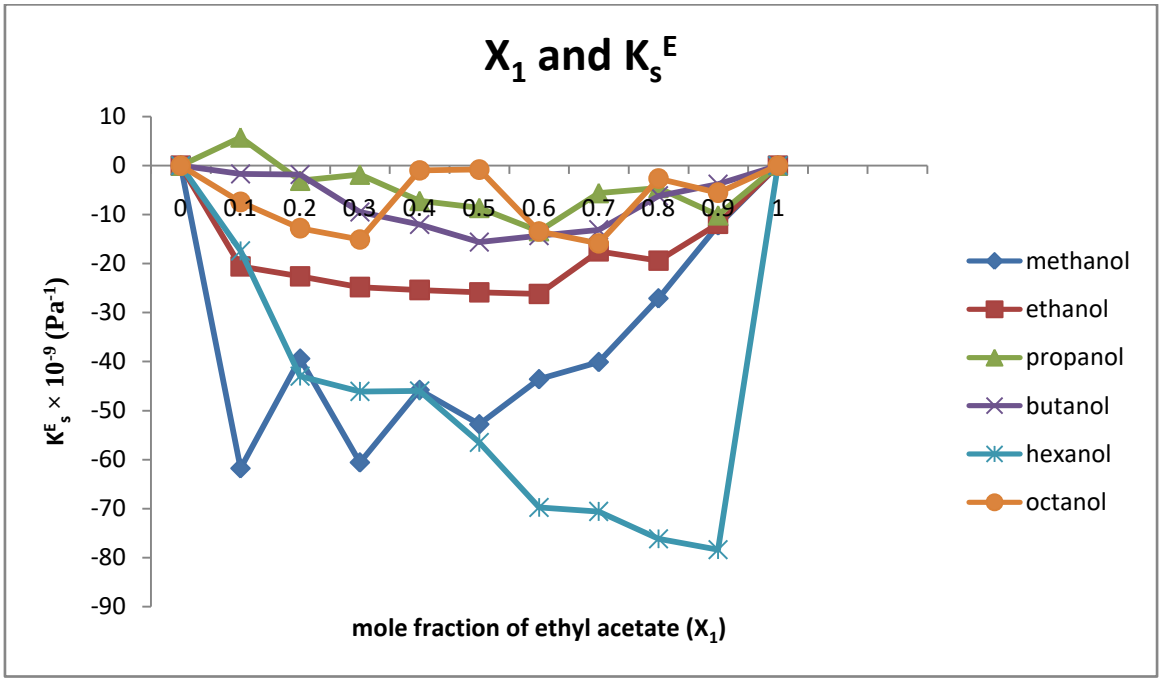


Figure 2. Plots of excess isentropic compressibility (K_S^E) versus mole fraction of ethyl acetate at 303.15K for binary mixtures of ethyl acetate with 1-methanol, 1-ethanol, 1-propanol, 1-butanol, 1-hexanol and 1-octanol.

4 Conclusion

In the present investigation the excess volumes and excess isentropic compressibility were calculated for the binary mixtures containing ethyl acetate with 1-methanol, 1- ethanol, 1- propanol, 1- butanol, 1-hexanol and 1- octanol at 303.15 K. The values of V^E and ΔKs shows negative sign at this temperature for all the binary mixtures over the whole composition ranges. As the chain length of 1- alkanol molecule increases from 1- methanol to 1- octanol. The results of these studies may be used for examining the suitability of these mixtures for practical applications such as in point varnished printing ink, leather industry and pharmaceutical industry. This study can be taken as a

reference and the thermodynamic properties of many other binary mixtures can be studied.

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Declarations Conflict of interest

The authors have no competing interests to declare that are relevant to the content of this article.

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