Viscosity deviations and excess Gibbs free energy of activation of binary mixtures of propionaldehyde with ethanol at 298.15, 308.15 and 318.15 K.

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Abstract:

The densities and viscosities of binary mixtures over the entire range of all compositions of propionaldehyde with ethanol at 298.15, 308.15 and 318.15 K have been studied in this present work. Viscosity deviations ($\Delta\eta$), molar volumes Vm, excess molar volumes V^E and excess free energies of activation of viscous flow ΔG^{*E} have been determined from the experimental data. Viscosity deviations, excess molar volumes and excess free energies of activation of viscous flow were calculated and correlated Redlich-Kister polynomial equation.

Key words: Density, Viscosity, Viscosity deviation, Excess molar volume, Binary system, propionaldehyde.

Introduction

Studies on viscosity have been performed on binary systems of propionaldehyde with ethanol. However, there is a little of information on the effect of temperature on the viscosity of binary mixtures propionaldehyde with ethanol. Study of effect of temperature on the viscosity of a liquid is important and has been studied by some researchers. However, study of the effect of temperature on viscosity and density of binary liquid mixtures of propionaldehyde with ethanol is rarely reported. Therefore, the main objective of this study was to produce the data on the effect of temperature on the viscosity of binary liquid mixtures. Furthermore, the thermo-physical properties of binary liquid mixtures and their analysis in terms of interpretative models constitute a very interesting subject [1-2]. The characterization of mixtures through their thermodynamic and transport properties is important from the fundamental viewpoint of understand their mixing behavior [3-7]. Liquid mixtures consisting of aldehydes and alcohols are of great importance in the field of industries such as in Petrochemical, Pharmaceutical and Dye [8, 9]. A thorough knowledge of transport properties of non-aqueous solutions is essential in many chemical and industrial applications [10].

The studies of excess properties such as deviation in viscosity, excess molar volume, excess Gibbs free energy of activation of viscous flow molecular interactions of binary mixtures are useful in understanding the nature of intermolecular interactions between two liquids [11-12]. Binary liquid mixtures due to their unusual behavior have attracted considerable attention due to their importance from both theoretical and practical point of view because these mixtures are used in titration, calorimetry and reaction calorimetry, among other uses [14].

In this present paper, density (ρ) and viscosity (η) of binary mixtures of propionaldehyde and ethanol are reported at various temperatures 298.15, 308.15 and 318.15 K. Deviation in viscosity ($\Delta\eta$), molar volume (V_m), excess molar volume (V^E) and excess Gibbs free energy of activation of viscous flow (ΔG^{*E}) have been calculated from the density ((ρ), and viscosity (η), data. Calculated deviation in viscosity and excess functions were fitted to the Redlich-Kister polynomial equation and the results analyzed in terms of molecular interactions.

Experimental Methods

Propionaldehyde and ethanol used for this investigation were obtained from SD fine chemicals India. Propionaldehyde and ethanol used were of analytical grade (AR)

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having minimum purity of 99.9 %. The purities of propionaldehyde and ethanol were cross checked by determination of their densities at different temperatures. The densities of pure propionaldehyde & ethanol and their binary mixtures were measured by using a single-arm pycometer calibrated at the working temperatures with doubly distilled water. The sensitivity of the pycnometer corresponded to a precision in density of 1×10^{-3} gm cm^{-3}. The binary liquid mixtures of different known concentrations were prepared in stoppered measuring flasks. The weight of the sample was measured using electronic digital balance with an accuracy of ± 0.0001 gm. An Ubbelohde viscometer (of 20 ml capacity) was used in the viscosity measurement and efflux time was determined using a digital clock to within ± 0.01 Sec. The experimental temperature was controlled using kinematic viscosity bath with an accuracy of ± 0.10K.

Results and Discussion

The viscosity of different binary mixtures of propionaldehyde with ethanol at various temperatures and calculated data of deviation in viscosity ($\Delta\eta$), molar volume (V_m), excess molar volume (V^E) and excess Gibbs free energy of activation of viscous flow (ΔG^{*E}) are given in tables below.

Propionaldehyde with Ethanol at 298.15, 308.15 and 318.15 K.

Table: 1-a   At 298.15:

x_1	ρ (g cm^{-3})	η (mPa.s)	$\Delta\eta$ (mPa.s)	V_m cm^{3}mol^{-1}	V^E cm^{3}mol^{-1}	ΔG^{*E} J.mol^{-1}
0	0.7848	1.0812	0	43.1487	0	1698.212
0.0829	0.7869	1.0113	-0.0349	45.0021	0.0990	1848.335
0.1691	0.7889	0.9392	-0.052	47.0321	0.1538	2008.332
0.2582	0.7904	0.8691	-0.0629	49.2878	0.1880	2158.265
0.3518	0.7931	0.7967	-0.0667	51.7271	0.1976	2307.365
0.4488	0.7952	0.7255	-0.0649	54.4627	0.1912	2454.225
0.5498	0.7973	0.6543	-0.0611	57.5342	0.1720	2368.265
0.6552	0.7993	0.5822	-0.0512	60.9821	0.1423	2248.265
0.7651	0.8014	0.5107	-0.0415	64.8901	0.1044	2103.269
0.8799	0.8035	0.4328	-0.0331	69.3482	0.0628	2003.376
1	0.8056	0.3765	0	74.5014	0	1997.365

Table: 1-b At 308.15:

x_1	ρ (g cm^{-3})	η (mPa.s)	$\Delta\eta$ (mPa.s)	V_m cm^{3}mol^{-1}	V^E cm^{3}mol^{-1}	ΔG^{*E} J.mol^{-1}
0	0.7762	0.8953	0	43.7119	0	1766.466
0.0829	0.7777	0.8409	-0.0324	45.5653	0.1113	1916.589
0.1691	0.7792	0.7861	-0.0495	47.5953	0.1661	2076.586
0.2582	0.7807	0.7415	-0.0604	49.8511	0.2003	2226.519
0.3518	0.7821	0.6959	-0.0642	52.2903	0.2099	2375.619
0.4488	0.7836	0.6508	-0.0624	55.0259	0.2035	2522.479
0.5498	0.7851	0.6049	-0.0586	58.0974	0.1843	2436.519
0.6552	0.7866	0.5604	-0.0487	61.5453	0.1546	2316.519
0.7651	0.7881	0.5163	-0.039	65.4533	0.1167	2271.523
0.8799	0.7896	0.4699	-0.0306	69.9114	0.0751	2171.63
1	0.7911	0.3461	0	75.0646	0	2065.619

Table: 1-c At 318.15:

x_1	ρ (g cm^{-3})	η (mPa.s)	$\Delta\eta$ (mPa.s)	V_m cm^{3}mol^{-1}	V^E cm^{3}mol^{-1}	ΔG^{*E} J.mol^{-1}
0	0.7611	0.8179	0	44.5015	0	1864.831
0.0829	0.7630	0.7541	-0.0292	46.3549	0.1327	2014.954
0.1691	0.7650	0.6993	-0.0463	48.3849	0.1875	2174.951
0.2582	0.7669	0.6547	-0.0572	50.6406	0.2217	2324.825
0.3518	0.7688	0.6091	-0.061	53.0799	0.2313	2473.984
0.4488	0.7708	0.5641	-0.0592	55.8155	0.2249	2620.456
0.5498	0.7727	0.5181	-0.0554	58.8871	0.2057	2534.812
0.6552	0.7747	0.4736	-0.0455	62.3349	0.176	2414.236
0.7651	0.7766	0.4295	-0.0358	66.2429	0.1381	2369.854
0.8799	0.7785	0.3831	-0.0274	70.7010	0.0965	2261.995
1	0.7805	0.3041	0	75.8542	0	2163.984

To investigate the molecular interaction between Propionaldehyde and ethanol, viscosity deviation, excess molar volumes and excess Gibbs free energy of activation of viscous flow have been evaluated from experimental density and viscosity using equations 1 and 2 respectively.

$$V^E = \frac{x_1 M_1 + x_2 M_2}{\rho_m} - \left(\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2}\right)$$ ----------- (1)

$$\Delta\eta = \eta_m - (x_1\eta_1 + x_2\eta_2)$$ ------------- (2)

where x_1 and x_2 are the mole fractions calculated from mass fractions. M_1 and M_2 are molar masses, ρ_1 and ρ_2 are densities, η_1 and η_2 are the viscosities of pure components 1 and 2 respectively. ρ_m and η_m are the density and viscosity of the mixture.

The excess Gibbs free energy of activation of viscous flow was obtained from equation 3.

$$\Delta G^{*E} = RT[ln\eta_m V_m - (x_1 ln\eta_1 V_1 + x_2 ln\eta_2 V_2)]$$ -------------------- (3)

where R is the universal constant of gases, T is the absolute temperature, V_1 and V_2 are the molar volumes of component 1 and 2, x_1 and x_2 represents the mole fraction of component 1 and 2.

V_m is obtained from equation 4 below.

$$V_m = \frac{x_1 M_1 + x_2 M_2}{\rho_m}$$ ----------------- (4)

Where η_1, η_2 and η_m are the viscosity of component 1 and 2 and mixture respectively

Figure 1-a: The plots of deviation in viscosity against mole fraction at 298.15, 308.15 and 318.15 K for binary mixtures of **Propionaldehyde with ethanol**.
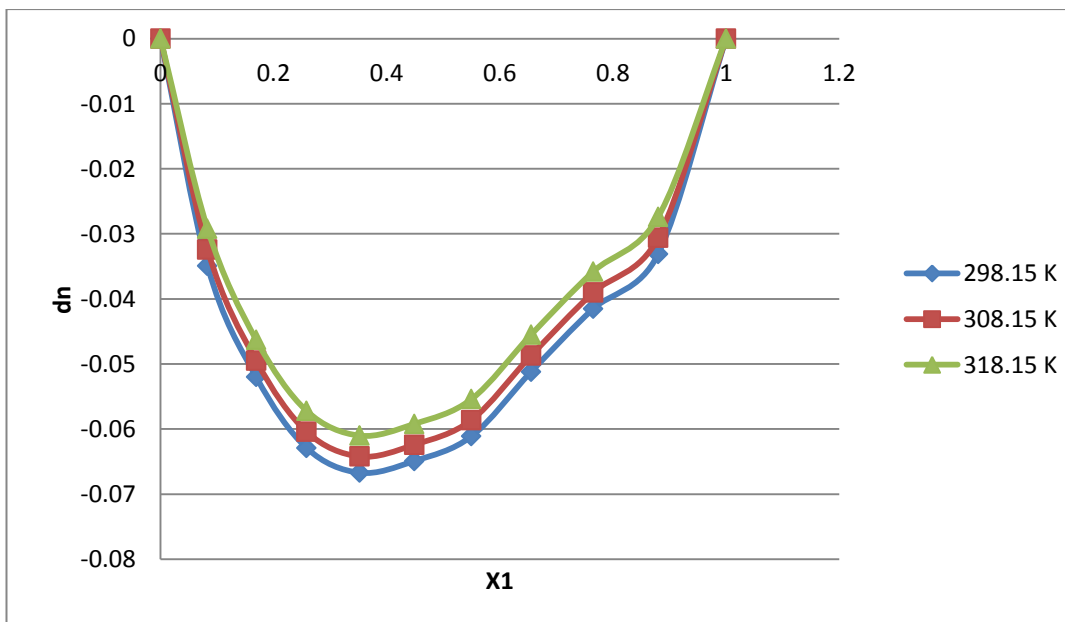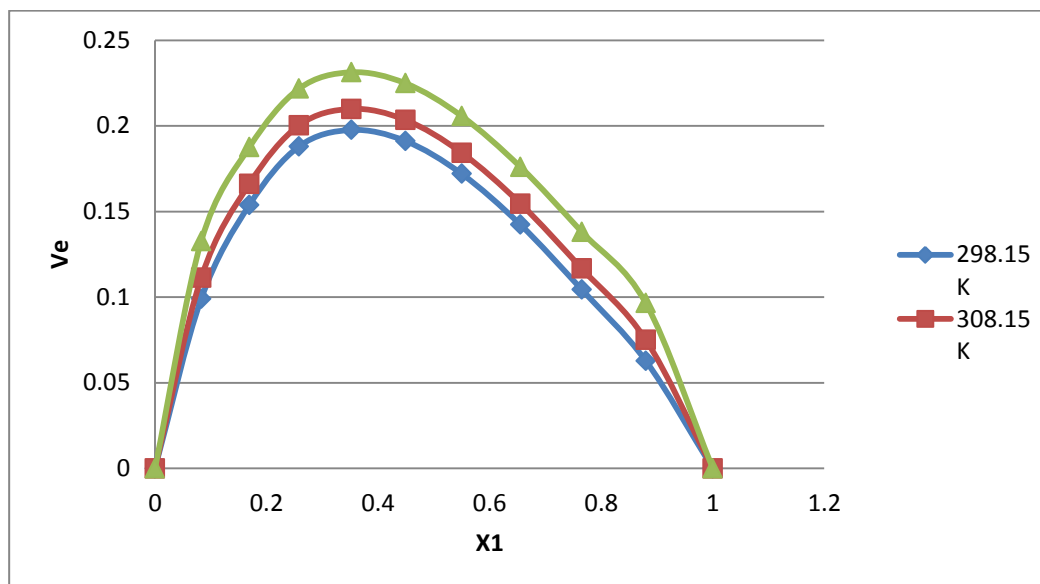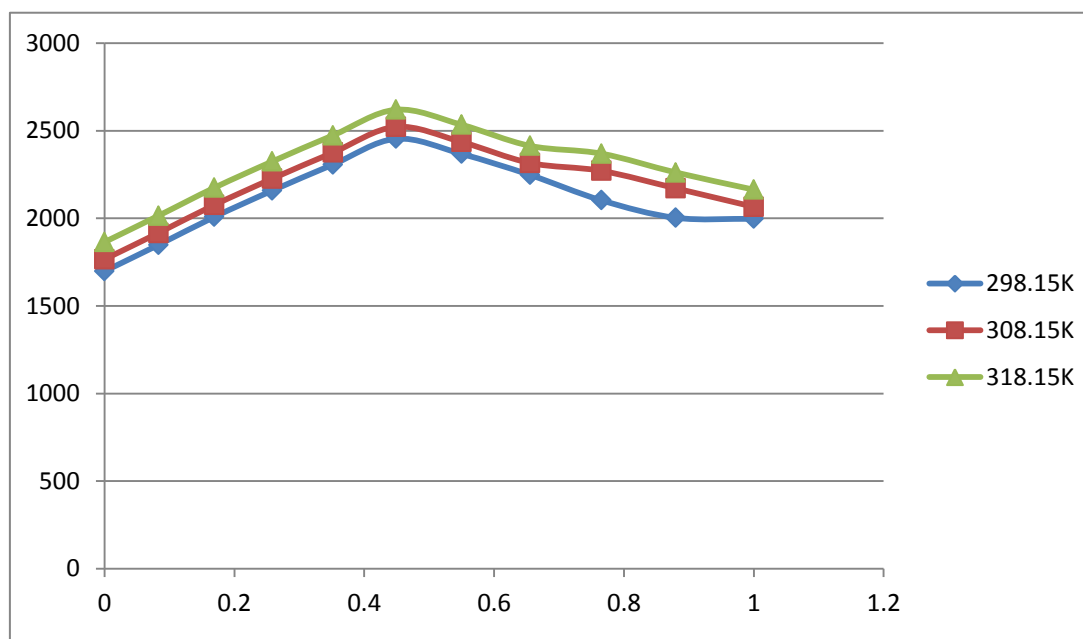

Figure: 1-b. The plots of excess molar volumes against mole fraction for binary mixtures of **Propionaldehyde with ethanol** at 298.15, 308.15 and 318.15 K.

Figures 1-c: The plots of **excess free energies of activation of viscous flow, ΔG*E** against mole fraction at 298.15, 308.15 and 318.15 K for binary mixtures of propinaldehyde with ethanol.

The experimental values of densities and viscosities of studied binary mixtures of propionaldehyde with ethanol at 298.15 K, 308.15 K and 318.15 K over the entire composition range expressed by mole fraction x_1 of propionaldehyde are listed in Tables 1-a to 1-c. The densities and viscosities of the studied binary mixtures are found decreased with increasing temperature and increased with increasing of mole fraction of propionaldehyde. Qualitative explanation for the behavior of binary mixtures with the change in mole fraction can be suggested from the experimental data obtained under study. Deviations in viscosity can be explained by means of relative strength of molecular interaction between like and unlike molecules. The sign and extent of dη depends on the combined effect of factors like molecular size and shape of the propionaldehyde and ethanol in addition to intermolecular forces. For the systems where dispersion, induction and dipolar forces are operating, the values of viscosity deviations are found to be negative, whereas the existence of specific interactions between the mixing components of the various binary systems tends to make viscosity deviations positive (6). Figure 1-a, shows the graphical variations of dη for binary mixtures of

propionaldehyde with ethanol at 298.15, 308.15 and 318.15 K. The values of dη are found negative for binary mixtures of propionaldehyde with ethanol at all experimental temperatures. As temperature increases dη values became more negative. A minima of plot x_1 Vs dη values for all binary mixtures occurs at equimolar concentrations at all experimental temperatures. Furthermore negative dη values for all the binary mixtures indicate that the dispersion forces are dominant and furthermore the existence of dispersion forces indicates that the component molecules have different molecular size and shapes (10).

Figure 1-b shows graphical variation of V^E for binary mixtures of propionaldehyde with ethanol at 298.15, 308.15 and 318.15 K. In the investigation V^E are found positive for all the binary mixtures of propionaldehyde with ethanol at all experimental temperatures. The maxima of plot x_1 against V^E is obtained at equimolar concentration for all binary mixtures. The V^E values are found increased with increase in the temperature for all binary mixtures. As the temperature increases V^E also increases because of inconvenient interstitial accommodation due to thermal agitations among propionaldehyde and ethanol. The positive values of V^E in the present investigation are resultant of specific interactions   formation of hydrogen bonds resulting in positive contribution (3, 4).

Figure 1-c show the variation of excess Gibb's free energy of activation of viscous flow ΔG^{*E}. The vales of excess Gibb's free energy of activation of viscous flow ΔG^{*E} for all binary mixture are found positive which attributes the dominance of specific interaction between propionaldehyde and ethanol and size effect of the mixing components (11). Positive values of ΔG^{*E} represents hydrogen bonding between the molecules are dominant (13). ΔG^{*E} values increased with increase in temperature in all cases however ΔG^{*E} values are found almost constant for methanol at all studied temperatures.

Conclusion:

The deviation in viscosity, excess molar volume and excess Gibbs free energy of activation of viscous flow for the systems Propionaldehyde + ethanol at 298.15, 308.15 and 318.15 K has been reported. The deviation in viscosity of the binary systems Propionaldehyde + ethanol are found to be negative and increases with temperature

while excess molar volumes are positive for all binary systems. There is intermolecular interaction among the components of the binary mixtures leading to possible hydrogen bond formation of the type Ŏ---H-O between unlike molecules confirming intermolecular hydrogen bond formation between propionaldehyde and the ethanol mixtures.

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