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Volumetric properties of binary mixture containing biodiesel and alcohol at various temperatures (T=298.15-318.15 K).

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Abstract

Density (ρ) and speed of sound (u) of the binary mixture containing sunflower biodiesel (S) and alcohol (1-Pentanol) were measured at different temperatures ranging from 298.15 K - 318.15 K. An Anton Paar vibrating U-tube densimeter (DSA5000M) was used to measure the density (ρ) and speed of sound of the binary mixture over the entire mole fraction. Further the excess molar volume (V_m^E **)** and isentropic compressibility (K_S^E) were calculated by using calculated data of density (ρ) and speed of sound (u) and the measured data were also correlated by using Redlich- Kiser equation. The speed of sound (u) values were also predicted theoretically by using following relations like Nomoto, Van deal, impedance etc. The effect of temperature also have been studied.

Key words. Excess molar volume, sunflower biodiesel, alcohol, Redlich –Kister

Introduction

Global warming effect, fossil fuel fading assets, and higher petroleum prices are the main issues driving worldwide interest on the development of alternative renewable, biodegradable and sustainable biofuels. The researchers from various field and countries are working on it desperately. Biofuels such as biodiesel are considered to be a potential candidate to replace Petro-diesel fuels. [1, 2]. Biodiesel is renewable oxygenated and biodegradable fuel whose properties are very similar to diesel [3]. Biodiesel has the desired properties which lowering the net gas emissions from the transportation sector. The most common method to obtain biodiesel is transesterification [4, 5]. Biodiesel is long chain fatty acid methyl ester [6]. A lot of raw material is available for preparation of biodiesels. Most common raw materials are sunflower, palm oil, rapeseed oil, soyabean oil [7-9]. Still the direct use of biodiesel and alcohols in diesel engine does not gives satisfactory effects on engine operation due to some limitations which promotes the blending and formation of binary mixtures [6]. The polar and non-polar structural behavior of biodiesel molecule encourage the blending of biodiesel and alcohols. The binary mixture of Biodiesel and alcohols helps to improve emission, performance and combustion. As pentanol and its isomers have better blend stability and miscibility and high energy density which helps to avoid the problems occur during blending with low carbon alcohols. Researchers have been working hard in recent years to develop new techniques. Researchers are continuously shows interest in the thermo-physical properties of biodiesels and alcohols mixtures for understanding the molecular systems and interactions in compounds, because thermodynamic properties plays an important role for scientific study and commercial process design. In our present work the volumetric properties of S (1) + 1P (2) binary mixture were measured at different temperature range. The ρ and speed of sound (u) was correctly measured with the help of DSA5000M then the value was perfectly correlated with the help of Redlich-kister polynomial equation. The data was best fitted and found to be in good agreement.

Experimental section

Material and method

Sunflower biodiesel was supplied by Sun Chem Pvt Ltd and 1- Pentanol of analytical grade was supplied by TCI with reported purity greater than 99%. The fatty acid methyl ester composition of biodiesel was analyzed by GC-MS profile. Proper care of purity was taken. For the purpose of this study, the binary mixture were created by mass using an analytical. Density of S (1) + alcohol (2) binary mixture were measured by using DSA 5000M, over the entire mole fraction range with uncertainty $\pm$ 0.01 K and the equipment was calibrated by using doubly distilled water and dry air [10, 11]. All of the mixtures were kept sealed, and the measurements were done right after they were made.

Results and Discussion

Excess Molar Volume

The density (ρ) and speed of sound (u) of S (1) + alcohol (2) binary mixture were measured at different temperature range from 298.15 -318.15. V_m^E and (K_S^E) of S (1) + alcohol (2) binary mixture has been calculated by using measured ρ and u values in Eq. (1) and shown in Table 1 and Fig 1.

$$V^E = \sum_{i=i}^{j} x_i\, M_i\, (\rho_{ij})^{-1} - \sum_{i=i}^{j} x_i\, M_i\, (\rho_i)^{-1} \qquad (1)$$

Where ρ is the density of mixture and ρ_i are the density of its pure components. x_i are the mole fractions and M_i is the molar mass of components (ith) in the mixture. The excess molar volume have been fitted to Redlich -kister equation

$$X_m^E\ (X = V) = x_i\, x_j \left[\sum_{n=0}^{3} X^{(n)}\, (x_i - x_j)^n\right] \qquad (2)$$

Where x_1 and x_2 are mole fractions of '1' and '2' components respectively. The standard deviation ($\sigma(X_m^E)$) and adjustable parameters $\left(X^{(n)}\right)$ were calculated by using (3) and shown in Table 4.

$$\sigma\left(X_m^E\right) = \left\{ \frac{\sum\left(X_m^E(\exp.) - X_m^E(Cal.)\right)^2}{(m-n)} \right\}^{1/2} \qquad (3)$$

Table 1. Excess molar volume ($V_m^E / cm^3\ mol^{-1}$) of binary liquid mixture at different temperatures and 0.1 MPa pressure.

x_1	$V_m^E(298.15K)$	$V_m^E(303.15K)$	$V_m^E(308.15K)$	$V_m^E(313.15K)$	$V_m^E(318.15K)$
S (1) + 1P (2)					
0.0998	0.0709	0.0778	0.0860	0.0951	0.1049
0.1512	0.1021	0.1109	0.1224	0.1332	0.1461
0.2114	0.1331	0.1450	0.1587	0.1746	0.1908
0.3296	0.1748	0.1899	0.2069	0.2258	0.2463
0.4378	0.1922	0.2082	0.2266	0.2474	0.2695

0.5346	0.1942	0.2106	0.2292	0.2500	0.2720
0.6422	0.1750	0.1885	0.2074	0.2204	0.2391
0.7399	0.1580	0.1691	0.1776	0.1919	0.2083
0.8396	0.1237	0.1309	0.1462	0.1576	0.1619
0.9139	0.0761	0.0821	0.0893	0.0981	0.0996

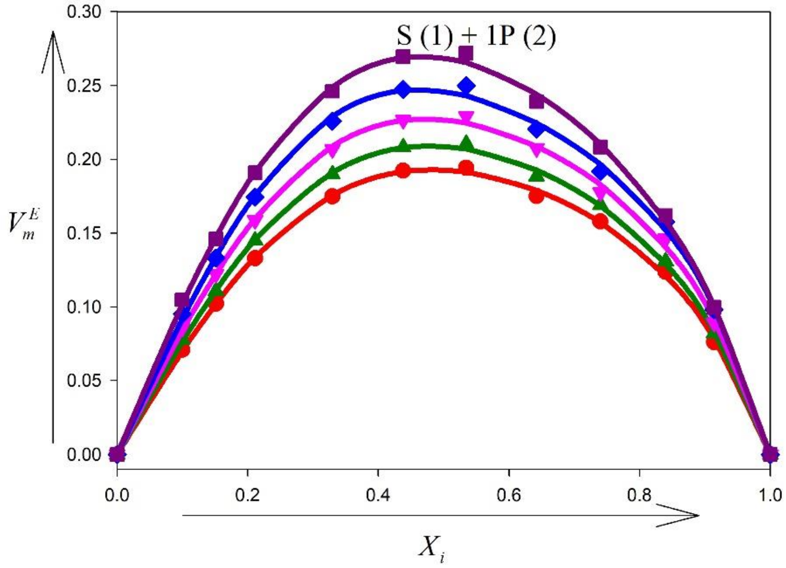

Fig 1. Excess molar volume, V_m^E, for Sunflower biodiesel (S) (x_i) + 1-Pentanol (1P) $(1-x_i)$ as a function of mole fraction at different temperatures ((●)298.15K, (▲)303.15K, (▼)308.15K, (♦)313.15K, (■)318.15K.); Solid lines (Redlich-Kister equation.); Symbols (Exptl.).

Excess isentropic compressibility

The excess isentropic compressibility $\left(k_s^E\right)$ for binary liquid mixtures were measured by equation (4) and shown in Table 2 and Fig. 2.

$$k_s^E = k_s - k_s^{id} \tag{4}$$

$$k_s = \left(u^2 \rho\right)^{-1} \tag{5}$$

$$k_s^{id} = \sum_{i=i}^{k} \phi_i \left[k_{s,i} + \frac{T v_i \alpha_i^2}{C_{P,i}} \right] - T\left(\sum_{i=i}^{k} x_i v_i\right) \frac{\left(\sum_{i=i}^{k} \phi_i a_i\right)^2}{\left(\sum_{i=i}^{k} x_i C_{P,i}\right)} \tag{6}$$

Where $C_{P,i}$, ϕ_i, α_i, v_i and $k_{s,i}$ heat capacity, volume fraction, thermal expansion coefficient, molar volume and isentropic compressibility for the pure components respectively.

The k_s^E values have been fitted to R.K. equation (2). The standard deviation σ and adjustable parameters $X^{(n)}$ were derived by use of Eq. (3) and date is given in Table 4.

The u values were also predicted theoretically by using following relations given below

Nomoto's relation [9]

$$u = \left(\frac{R_m}{V_{mix}}\right)^3 = \left[\frac{x_1R_1 + x_2R_2}{x_1V_1 + x_2V_2}\right]^3 \tag{7}$$

$$R_m = \left[\frac{\left(M_i u_i^{1/3}\right)}{\rho_i^*}\right] \tag{8}$$

Van Deal ideal mixing relation [10]

$$\frac{1}{x_1M_1 + x_2M_2} \cdot \frac{1}{u_{id.mix}^2} = \frac{x_1}{M_1u_1^2} + \frac{x_2}{M_2u_2^2} \tag{9}$$

Impedance dependence relation [11]

$$u = \frac{\sum\left(x_iZ_i\right)}{\sum\left(x_i\rho_i^*\right)} \tag{10}$$

$$Z_i = \mu_i\rho_i^*$$

Table 2. Excess isentropic compressibities (K_S^E) of binary liquid mixture at different temperature and 0.1 MPa pressure.

x_1	$K_S^E(298.15K)$	$K_S^E(303.15K)$	$K_S^E(308.15K)$	$K_S^E(313.15K)$	$K_S^E(318.15K)$
S (1) + 1P (2)					
0.0998	-2.67E-08	-2.78E-08	-2.88E-08	-2.97E-08	-3.07E-08
0.1512	-3.44E-08	-3.56E-08	-3.68E-08	-3.81E-08	-3.94E-08
0.2114	-3.99E-08	-4.14E-08	-4.28E-08	-4.42E-08	-4.57E-08
0.3296	-4.39E-08	-4.55E-08	-4.71E-08	-4.87E-08	-5.04E-08
0.4378	-4.24E-08	-4.40E-08	-4.55E-08	-4.71E-08	-4.87E-08
0.5346	-3.84E-08	-3.98E-08	-4.12E-08	-4.26E-08	-4.41E-08
0.6422	-3.11E-08	-3.21E-08	-3.33E-08	-3.44E-08	-3.57E-08
0.7399	-2.38E-08	-2.46E-08	-2.54E-08	-2.63E-08	-2.72E-08
0.8396	-1.57E-08	-1.63E-08	-1.69E-08	-1.75E-08	-1.81E-08
0.9139	-9.15E-09	-9.12E-09	-9.33E-09	-9.56E-09	-9.88E-09

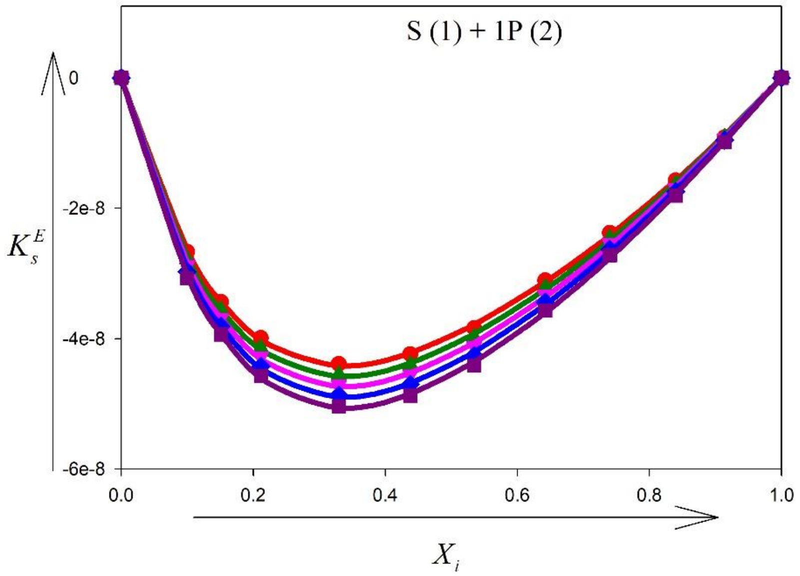

Fig 2. Excess isentropic compressibility, K_s^E, for Sunflower biodiesel (S) (x_i) + 1-Pentanol (1P) $(1-x_i)$ as a function of mole fraction at different temperatures ((●)298.15K, (▲)303.15K, (▼)308.15K, (♦)313.15K, (■)318.15K.); Solid lines (Redlich-Kister equation.); Symbols (Exptl.).

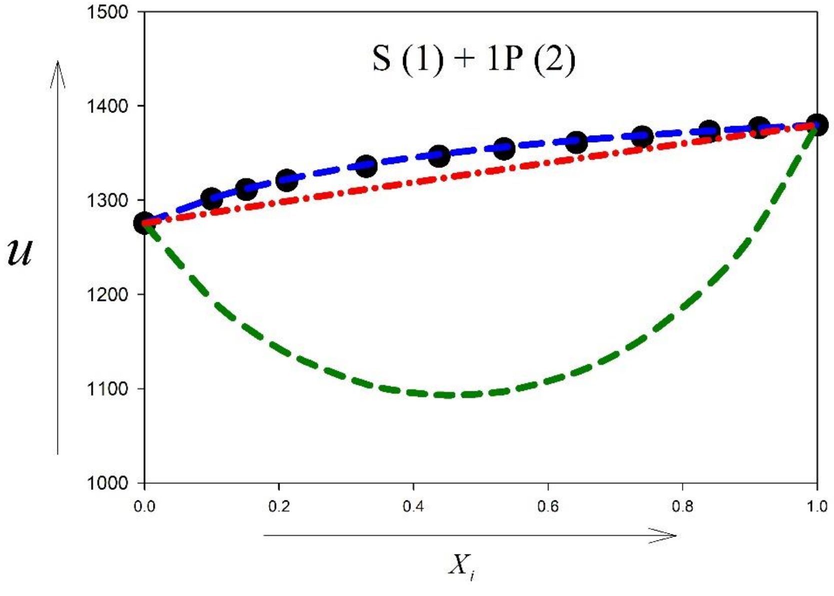

Fig 3. Expt. and predicted values of ultrasonic speed, u, for Sunflower biodiesel (S) (x_i) + 1-Pentanol (1P) $(1-x_i)$as a function of mole fraction at 298.15 K ((●)Experimental, (-----)Nometo, (-----)Van Deal and (-·-·-·-)Impedance)

Table 3. Standard deviation ($\sigma(u)$) of calculated values of u by using various correlations for binary liquid mixtures at different temperatures.

System	T/K	Nomoto	Van Dael	Impedance
S (1) + 1P (2)	298.15 K	0.11	13.42	1.23
	303.15 K	0.10	13.43	1.24
	308.15 K	0.10	13.44	1.24
	313.15 K	0.10	13.45	1.24
	318.15 K	0.11	13.45	1.24

Table 4. Values of adjustable parameters $\left(X^{(n)}\right)$ of Redlich–Kister equation and standard deviation $\sigma\left(X^{E}\right)$.

S (1) + 1P (2)	T/K	$X^{(1)}$	$X^{(2)}$	$X^{(3)}$	$X^{(4)}$	$\sigma\left(X^{E}\right)$
$V_m^E / cm^3\ mol^{-1}$	298.15	0.7715	-0.0421	0.1653	0.2548	0.0022
	303.15	0.8353	-0.0595	0.1696	0.2736	0.0022
	308.15	0.9076	-0.0791	0.1989	0.3155	0.0034
	313.15	0.9845	-0.1224	0.2246	0.3981	0.0042
	318.15	1.0753	-0.1233	0.1866	0.3108	0.0036
$K_S^E / T\ Pa^{-1}$	298.15	-1.58E-07	9.54E-08	-6.88E-08	2.70E-08	3.62E-10
	303.15	-1.64E-07	9.87E-08	-7.01E-08	3.08E-08	3.78E-10
	308.15	-1.70E-07	1.02E-07	-7.20E-08	3.34E-08	3.86E-10
	313.15	-1.76E-07	1.05E-07	-7.38E-08	3.57E-08	3.94E-10
	318.15	-1.82E-07	1.08E-07	-7.56E-08	3.70E-08	4.07E-10

The V_m^E values for S (1) with 1P (2) is found positive over whole composition range of mole fraction shown in Fig. 1. Variation in V_m^E with change in composition can be explained in terms of molecular structural, physical and chemical factors. The difference in shape, size of components and free volume arises due to structural characteristics. However, decrease in dipolar association or dissociation of the components or hydrogen bond formation between unlike molecules can affect the physical and chemical factors. As biodiesel is a polar and non-associating liquid while 1P involves hydrogen bonding due to presence of hydroxyl groups. So sunflower biodiesel is non-associating while 1P is associated liquid in pure state [12-15]. Consequently, addition of biodiesel leads to disruption of H- bonding in 1P. It causes increase in V_m^E and the same is reflected in experimental results. Even this disruption continues with increasing temperature and consequently V_m^E values for the binary mixtures increase. The temperature increases from 298.15 K to 318.15 K, the interstitial accommodation of the unlike molecule increases which might be due to lattice expansion at elevated temperatures. This causes more positive V_m^E values from 298.15 to 318.15 K as shown in Fig.1.

K_s^E values provide information related to close packing of molecules and compressibility of liquid mixture. These information are based on various contributions including intermolecular interaction, close packing of molecules and depolymerization of associated molecular species. The first two factors lead to increase in density and hence make the mixture less compressible while the third factor lead to decrease in density and make the mixture more compressible. From the fig 2, it is clear that K_s^E values are negative over the whole fraction range. It is because of dominance of first two factors over third factor.

In addition, we applied various correlations like Van Dael, Impedance dependence and Nomoto to analyzed the u data and interpret in terms of standard deviation in (Table 3 & Fig. 3).

Conclusions

This study reported the density(ρ)and speed of sound (u) data for the S (1) + 1P(2) binary mixture over the entire mole fraction range for temperature range 298.15- 318.15 K. Based on ρ and u data, V_m^E and K_s^E were evaluated and correlated with Redlich-Kister equation. V_m^E values are found positive for all compositions. Further, speed of sound (u) values were also correlated by various correlations like Nomoto, Van deal, impedance etc. The analysis of the excess thermo-physical property clearly indicates the existence of weak interactions between the S and 1P molecules. It has been found that the interactions between S (1) + 1P (2) molecules decreases from 298.15 K to 318.15 K.

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