Research article

Volumetric and viscometric determination of binary liquid mixtures of 2-ethoxyethanol and amyl acetate at temperatures of (298.15 and 303.15) k

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ABSTRACT

Densities and viscosities have been determined at temperatures of (298.15 and 303.15) K for binary liquid mixtures of 2-ethoxyethanol with amyl acetate over the entire range of solvent composition. From the experimentally determined values, excess molar volume, V^E, excess viscosity, η^E and excess Gibbs free energy of activation of viscous flow, G^{*E} have been calculated. These calculated excess thermodynamic functions were fitted to Redlich-Kister polynomial equation to obtain the fitting coefficients and standard deviations. The values of excess molar volume, V^E were negative and that of the excess viscosities, η^E were found to be positive, while excess Gibbs free energy of activation of viscous flow, ΔG^{*E} were negative over the whole range of solvent composition for the binary systems at the studied temperatures. The behavior of these excess functions with composition of the mixtures have been discussed in respect of molecular interactions between the components of liquid systems. The mixture viscosities were correlated using empirical relations like Grunberg-Nissan, Frenkel, Hind, Wijk and Kendall-Monroe model equations. Comparison of these interaction parameters have been engaged to explain the intermolecular interactions between the alkoxy alcohol and the ester.

INTRODUCTION

Data generated from experimental determination of density and viscosity for binary liquid mixtures are very useful for practical and theoretical purposes. Determination of these excess functions of binary mixtures obtained experimentally have given so much relevance in Chemical and Engineering industries [1].The knowledge of these excess thermodynamic parameters of binary liquid mixtures is needed in the design of many chemical and engineering systems, such as chemical separations, heat and mass transfer systems, and fluid flow [2]. Binary mixtures of solvent systems have been reported by several authors to have resulted to specific interactions such as hydrogen bonding, dipole-dipole interactions and charge transfer reactions, whereby given rise to strong and weak interactions between like and unlike molecules in the mixtures leading to deviations from ideality. These changes in binary liquid mixtures are usually accompanied with differences in the chemistry and molecular buildup of the mixing solvents in the system as well as changes in temperature and the mixing ratios of the participating solvents [3-6].

Esters like ketones are carbonyl compounds which are highly polar and thus have the ability to associate with other polar groups [7]. However, esters have two electron-withdrawing groups (alkoxy and carbonyl) and so are known to be more polar than ketones. The carbonyl group of esters acts as a proton acceptor (in hydrogen bonding) and confers enough polarity within the functional group for steady coexistence of the dipoles required for binary solution interactions.

They are biodegradable and thus used as important constituents of numerous products such as cosmetics, printing, marine engine oils, drugs, hydraulic fluids, compressor, automotive oils [8]. Amylacetate is useful in coatings, extraction of solvents for pharmaceuticals, cleaning fluids and leather polishes. The potential use of esters in industries has necessitated numerous researches on esters with other organic solvents [9].

In binary liquid combinations, alkoxyethanols such as 2-methoxyethanol (2-ME), 2-ethoxyethanol (2-EE), and 2-butoxyethanol (2-BE) are often utilized as solvents. Co-emulsifiers, dyes, and lacquers all contain 2-ethoxyethanol [10]. 2-ethoxyethanol is a popular solvent used in laboratories and the chemical industry, and it create both intermolecular and intramolecular hydrogen bonds. This

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ability arouse the interest of many researchers to probe into the various properties of systems involving this solvent [11]. These compounds with a carbonyl group (C=O) are strongly hydrogen–bond acceptors. Several other researchers have studied the excess properties of binary solvent mixtures of esters and other organic solvents [12]. In this work, the experimentally determined data of the densities and viscosities of 2-ethoxyethanol with the amylacetate system have been measured. Excess molar volume (V^E), excess viscosity (η^E), and excess Gibbs free energy of activation of viscous flow (ΔG^{*E}) were computed. The Redlich-Kister polynomial equation connects these thermodynamic characteristics [13].

The coefficients of the polynomial equation were computed by the nonlinear least square fit method. The values of these excess functions obtained were employed to calculate the standard deviation of the system. The work is aimed to relate the derived thermodynamic properties obtained from density and viscosity data to the interactions between the components of the solvent systems on a molecular level which many industrial applications requiring transport phenomena of single solvents and solvent mixtures, such as mass and heat transfer, would benefit greatly from this knowledge. The generated results were analyzed in terms of intermolecular interactions through hydrogen bonding between the hydrogen atom of the (-OH) group of the 2-ethoxyethanol and the oxygen atom of the carbonyl group (C=O) of the ester in the solvent mixtures [14-15].

MATERIALS AND METHODS
Materials
The reagents, amylacetate and 2-ethoxyethanol were procured from Merck, Germany and used without further purification. The purity of these solvents is (99%) for amylacetate and (99.95%) for 2-ethoxyethanol. The densities and viscosities of the pure solvents are tabulated in Table 1. The purity of the pure solvents was verified by comparing their determined densities (ρ), with those reported in the open literature. The experimentally obtained values are in closed agreement with those of the open literature.

Density measurement
Binary mixtures of the pure solvents were prepared by weight in an airtight stopper bottle. The exact volumes of the cosolvents were calculated from their densities at 298.15K and mixed. The compositions of the mixtures ranged from 0.0001 to 0.9993 mole fraction of the 2-ethoxyethanol. All weighings were done using a Sartorius Analytical Balance with a precision of $\pm10^{-4}$. The densities of the pure solvents and their binaries were determined with a 10mL capacity single stem capillary pyknometer at the working temperatures of (298.15 and 303.15$\pm$0.01) K. The pyknometer was calibrated with doubly distilled water at atmospheric pressure and at the working temperatures. The accuracy of the density

measurements was estimated to be $\pm1 \times 10^{-4}$ gcm^{-3}.

Viscosity measurement:
An Ostwald U-tube viscometer A type (Germany) with sufficiently long efflux time was used for viscosity measurements. An electronic digital stopwatch with a readability of $\pm$0.01s was used for the flow time measurements. At least three replicate readings of each data point obtained which were reproducible to $\pm$0.05s and the results were averaged. All measurements were carried out in a thermostatic water bath (TE-8A, Techne, Germany) controlled to $\pm$0.01 K.

Table 1: Comparison of experimental pure densities, ρ (g/cm3) and viscosities, η (mPs) values with literature values at 298.15 K

Solvent	Temperature	Experimental Density	Literature density	Experimental viscosity	Literature Viscosity
2-ethoxyethanol	298.15K	1.1151	1.1150[a]	1.6332	1.6300[c]
Amylacetate	298.15K	0.8756	0.8760[b]	0.8156	0.8620[d]

RESULTS
The results of densities (ρ) and viscosities (η) of binary mixtures and their excess thermodynamic characteristics: excess molar volumes (V^E), excess viscosities (η^E), and excess Gibbs free energy of activation of viscous flow (ΔG^{*E}) of binary mixture at (298.15 and 303.15) K have been presented in Table 2. These excess thermodynamic parameters were computed from the density and viscosity data using equations 1 to 4.

$$x_1 M_1\left(1/\rho - 1/\rho_1\right) + x_2 M_2\left(1/\rho - 1/\rho_2\right) \qquad (1)$$

$$\eta^E = \eta - (x_1\eta_1 - x_2\eta_2) \qquad (2)$$

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

$$V_m = \frac{x_1 M_1 + x_2 M_2}{\rho} \qquad (4)$$

where ρ, η and V are density, viscosity and molar volume of the mixture, M_1 and M_2 are molar masses, η_1 and η_2 are viscosities, V_1 and V_2 are molar volumes of 2-ethoxyethanol and amylacetate respectively. R is the universal gas constant and T is absolute temperature in Kelvin. X is the mole fraction of 2-ethoxyethanol.

The computed excess molar volumes (V^E), excess viscosities, (η^E) and excess Gibbs free energies of activation for viscous flow (ΔG^{*E}) of the solvent systems over the solvents composition range are shown in Table 2 and are represented in Figures. 1, 2 and 3 respectively.

The results of densities (ρ) and viscosities (η) of binary mixtures and their excess thermodynamic properties such as excess molar volumes (V^E), excess viscosities (η^E) and excess Gibbs free energy of activation of viscous flow (ΔG^{*E}) at (298.15 and 303.15) K as a function of composition of the binary mixtures have been presented in Table 2. These excess thermodynamic parameters were calculated from the density and viscosity data using equations 1 to 4.

$$V^E = x_1 M_1\left(1/\rho - 1/\rho_1\right) + x_2 M_2\left(1/\rho - 1/\rho_2\right) \qquad (1)$$

$$\eta^E = \eta - (x_1\eta_1 - x_2\eta_2) \qquad (2)$$

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

$$V_m = \frac{x_1 M_1 + x_2 M_2}{\rho} \qquad (4)$$

Where ρ, η and V are density, viscosity and molar volume of the mixture, M_1 and M_2 are molar masses, η_1 and η_2 are viscosities, V1 and V_2 are molar volumes of 2-ethoxyethanol and amylacetate respectively. R is the universal gas constant and T is absolute temperature in Kelvin. X is the mole fraction of 2-ethoxyethanol.

The calculated excess molar volumes (V^E), excess viscosities, (η^E) and excess Gibbs free energies of activation for viscous flow (ΔG^{*E}) of the solvent systems over the solvents composition range are shown in Table 2 and are represented in Figures. 1, 2 and 3 respectively. The V^E, η^E and ΔG^{*E} for the binary systems obtained were fitted by four parameter Redlich – Kister [26]. Polynomial equation 5 and 6 by the least-squares method and the values are tabulated in Table 3 with the standard deviations (σY^E) of binary solvents systems defined by equation 7.

$$Y^E = x_1 x_2 [A_0 + A_1(x_1-x_2) + A_2(x_1-x_2)^2 + A_3(x_1-x_2)^3] \qquad (5)$$

$$Y^E = x(1-x) \sum_{i=0}^{n} A_i (2x-1)^i \qquad (6)$$

Y^E represents V^E, η^E or ΔG^{*E}; n is number of coefficients and A_i, the fitting coefficients.

$$\sigma Y^E = \sqrt{\frac{\sum(Y^E expt. - Y^E calc.)^2}{m-n}} \qquad (7)$$

In Eq. 7, m is the number of experimental data points and n, the number of coefficients, which was considered to be 4 in this calculations.

Some empirical relations like Grunberg-Nissan, Frenkel, Hind, Wijk and Kendall – Monroe model equations having one adjustable parameter been employed to evaluate the viscosity (η) of the binary liquid mixtures. Grunberg-Nissan [31] provided the following empirical equation,

$$ln\eta = x_1 ln\eta_1 + x_2 ln\eta_2 + x_1 x_2 d' \qquad (8)$$

Where d' is an adjustable parameter proportional to the interchange energy, which is independent of the mixture composition and represents a measure of the intermolecular interactions between unlike molecules? Frenkel derived the following equation [32]:

$$ln\eta = x_1^2 ln\eta_1 + x_2^2 ln\eta_2 + 2x_1 x_2 ln\eta_{12} \qquad (9)$$

Hind [33] proposed the following relationship as:

$$\eta = x_1^2 \eta_1 + x_2^2 \eta_2 + 2x_1 x_2 \eta_{12} \qquad (10)$$

Where η_{12} is Frenkel and Hind interaction parameter, and is independent of the composition, which was obtained from the relation:

$$\eta_{12} = 0.5\eta_1 + 0.5\eta_2 \qquad (11)$$

Wijk [34] provided the following equation,

$$lg\eta = x_1^2 lg\eta_1 + x_2^2 lg\eta_2 + 2x_1 x_2 lg\eta_{12} \qquad (12)$$

Kendall and Monroe model was used to analyze the viscosity of binary mixtures based on zero adjustable parameter as [35]:

$$\eta_m = \left(x_1 \eta_1^{1/3} + x_2 \eta_2^{1/3}\right)^3 \qquad (13)$$

$$E\eta_m = x_1 x_2 \left(x_1 \eta_1^{1/3} + x_2 \eta_2^{1/3}\right)^3 \qquad (14)$$

Where $E\eta_m$ is the modified Kendall-Monroe equation [36].

The fitting parameters of Eqs. (8, 9, 10, 12 and 14) were obtained from the experimental data by non-linear least squares methods. The correlativity of these models was tested by calculating the Average Standard Deviation (APD) between the experimental and the calculated viscosity as shown in equation 15.

$$APD = \frac{100}{N} \sum_{i=1}^{N} \left[\frac{\eta_{exptal} - \eta_{calcd}}{\eta_{exptal}}\right] \qquad (15)$$

η_{expt} and η_{calcd} are the viscosities of experimental and calculated data, N, the number of experimental data points in each set and i the number of numerical coefficients in the equations.

The results obtained for the correlation parameters are tabulated in Table 5.

These values show that Frenkel, Hind, Wijk and Kendall-Monroe correlations are positive over the entire range of solvents composition, while Grunberg-Nissan correlation values are both negative and positive for the solvent system at the investigated temperatures. Venkatenswarlu *et al* reported that positive values of Grunberg-Nissan, Hind and Tamura-Kurata adjustable parameters indicate specific interactions and the negative values suggests weak interactions between the unlike molecules of the mixture.

Therefore, the positive viscosity values for Frenkel, Hind, Wijk, Kendall–Monroe parameters are indicative of specific interactions. The observed negative and positive values of Grunberg – Nissan interaction parameter affirm that both specific and dispersive forces of interactions are taking place, which is in accordance with the excess viscosities, η^E and excess Gibbs free energy of activation for viscous flow, (ΔG^{*E}) for the binary solvent systems. Out of the five different empirical equations used to correlate the experimental viscosity data, the values obtained from the Grunberg-Nissan parameter were lowest. Hence, Grunberg-Nissan correlation equation is more convenient and fits better than others.

The APD values that was obtained from equation (eq. 14) are reported in Table 6. The values obtained from Wijk and Hind are very small compared to Frenkel, Grunberg-Nissan and Kendall-Monroe. The values of Wijk and Hind are negative while that of Frenkel, Grunberg-Nissan and Kendall -Monroe are positive. This also assert the fact that both specific and dispersive forces of interactions are taking place in the studied solvent systems.

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Table 2: Densities and viscosities of the binary mixtures of 2-ethoxyethanol with amyl acetate at (298.15 and 303.15) K

x_1	298.15 K		303.15 K	
	P	H	P	H
0.0001	0.8673	0.6815	0.8640	0.6652
0.0508	0.8677	0.6826	0.8647	0.8275
0.1020	0.8681	0.8341	0.8647	1.1204
0.1533	0.8692	1.2674	0.8654	2.1453
0.2010	0.8734	3.4195	0.8686	3.1601
0.2522	0.8894	5.0433	0.8860	4.2642
0.3034	0.8909	8.2418	0.8869	5.3122
0.3511	0.9051	7.8063	0.9010	6.2479
0.4024	0.9250	7.4815	0.9211	7.2685
0.4501	0.9333	7.9371	0.9324	7.6693
0.5013	0.9417	9.0231	0.9380	8.0289
0.5523	0.9654	9.4916	0.9609	8.0535
0.6003	0.9938	10.0434	0.9882	8.0115
0.6513	1.0100	10.6559	1.0121	8.1397
0.7025	1.0299	11.9627	1.0252	8.1785
0.7502	1.0397	12.5809	1.0349	8.1652
0.8015	1.0800	12.4585	1.0835	8.3480
0.8527	1.0887	12.8054	1.0828	9.7820
0.9004	1.1072	13.2160	1.0994	11.3502
0.9516	1.1069	13.8328	1.0999	11.5586
0.9993	1.1115	16.3324	1.1063	11.8275

DISCUSSION

Excess Molar Volumes (V^E)

The variations of excess molar volumes, V^E of the binary liquid mixtures of 2–ethoxyethanol and amyl acetate at the studied temperatures are shown in Figure. 1. The plot shows that excess molar volumes, V^E are negative for the system at the temperatures investigated, with a minima at $x_1 = 0.5$ for the binary mixtures. Values of excess molar volumes were found to increase with an increase in temperature, which is shown in Table 3. The excess molar volumes may be influenced possibly by two effects; which is mainly by the association through intermolecular hydrogen bonding between the –OH group in 2–ethoxyethanol and the hydrogen atoms in the ester. The second effect arising from the difference in molecular volume between the two components in the binary system, which is due to geometrical effect. The increase of this difference leads to the excess molar volume, V^E becoming more negative.

Negative excess molar volume, V^E is the sum of multiple opposing effects, including chemical, physical, and structural influences. Charge-transfer complexes, dipole–dipole and dipole–induced dipole interactions, and H-bonding between component molecules are examples of chemical or specialized interactions that cause volume contractions, resulting in negative excess molar volume.

The physical interactions or nonspecific interactions are weak and hence contributes a positive V^E, while the structural contributions are mostly negative and arises from several effects such as interstitial accommodation and due to variations in molar volume and free volume between components, geometrical fitting of one component into another is possible. The full range of solvent composition at the examined temperatures of the investigated excess molar volumes, V^E of the binary mixes were all negative. Table 3 and Figure 1 illustrate the results. The excess molar volumes of binary mixtures are plotted, and there are minima in the mole fraction range of 0.50 for alkoxyethanol. The negative excess molar volume, V^E is attributed mainly to the association between the amyl acetate and 2-alkoxyethanol through dipole-dipole interactions, geometrical effects and interactions between the component molecules. The strength of the connections formed by interactions between dissimilar molecules was greater than that of the connections formed by interactions between like molecules. Similar trend has been observed for alkoxyethanols and amines binary mixtures at 298.15K by Kemeakegha [5]. Shelar also observed negative excess molar volumes for binary mixtures of o-chlorophenol and esters [16], indicating that component molecules of the mixtures were closer together in the liquid mixture than in the pure state, implying strong attractive interactions between the component molecules, such as hydrogen bonds, dipole-dipole interactions, and other specific interactions between unlike molecules.

Figure 1. Plots of excess molar volume of 2-ethoxyethanol (1) + amylacetate (2) at (298.15 and 303.15) K
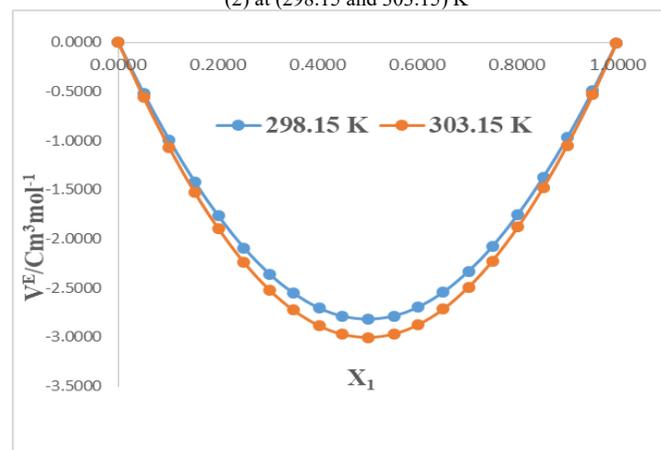
Excess Viscosities (η^E)

According to Fort and Moore, deviation in viscosity tends to be more positive as the strength of the interaction increases. The strength of intermolecular interactions can be estimated qualitatively using viscosity variation [17]. According to Pikkarainan, the variance in viscosities may be explained by taking into account the following elements. (i) Differences in size and shape of component molecules, as well as the lack of dipolar linkage in pure components, which may lead to a reduction in viscosity, and (ii) specific interactions between unlike components such as hydrogen bond formation and charge-transfer complexes may cause increase in viscosity in mixtures compared to the pure components. The former effect according to the author produces negative deviation in viscosity and the latter effect produces positive deviation in viscosity.

Table 2 shows that the values of η^E are positive for 2–ethoxyethanol + amylacetate systems over the entire solvent composition ranges at the investigated temperatures. The positive excess viscosities, η^E are generally observed for systems where specific interactions of hydrogen bond formation, strong dipole-dipole forces etc. between components molecules as reported by Sharma et al [18]. The positive excess viscosity, η^E values increase with an increase in temperature, which is an indications of specific interactions dominating the system. The following authors have attributed positive η^E values as arising from specific interactions [19-20]. While the negative η^E values indicate dispersion forces. In this present investigation, the positive, η^E values of the binary mixtures can be attributed to dipole–dipole interactions resulting in the formation of electron-transfer complexes between unlike molecules and hydrogen bond formation. The plots of η^E versus x_1 have been presented in Figure. 2 and the values are shown in Tables 3. A close look at this Figure shows that the plots are parabolic and are characterized by the presence of well-defined minima that occur at mole fraction of 0.5 indicating the presence of complex formation between the mixing components. The sign and magnitude of the deviation in viscosity depends on the combined effect of factors such as molecular size, shape and intermolecular forces. In general for systems where dispersion forces are operative, η^E values are found to be negative [21-22].

whereas charge transfer, hydrogen bonding interactions and other chemical forces leading to the formation of complex species between unlike component molecules result in positive excess viscosity, η^E. The sign depend upon the dominant factor. A perusal of Table 3 shows that the values of η^E for the binary systems are positive over the whole range of solvents composition at the investigated temperatures. The observed positive values of η^E at the investigated temperatures are indicative of specific forces operating in the mixtures. Studies where dispersion and dipolar interactions are operative, η^E values are negative, whereas dipole-dipole interactions between like molecules and other forces resulted in positive values. Specific interaction which causes positive deviations in viscosities have been reported by Sankar in their study [23], binary mixtures of amine and cyclic ketones, and Binary mixtures of N-Methyl Aniline with Methyl Isobutylketone + 3-Pentanone, and + Cycloalkanones by Gowrisankar [24].

The positive contribution of η^E of the binary mixtures observed were as a result of specific forces contributing to stronger intermolecular interactions between the solvent molecules.

Excess Gibbs free energy of Activation for Viscous Flow (ΔG^{*E})

The excess Gibbs free energy of activation for viscous flow, ΔG^{*E}, was observed as a result of particular forces contributing to increased intermolecular contacts between the solvent molecules. The

molecular interactions of liquid mixtures are dealt with by ΔG^{*E} [25]. The deviation of excess Gibbs free energy of activation of viscous flow, ΔG^{*E} in the binary mixtures of amylacetate and 2-ethoxyethanol is shown in Figure. 3.

Figure 2: Plots excess viscosities of 2-ethoxyethanol (1) + amylacetate (2) at (298.15 and 303.15) K
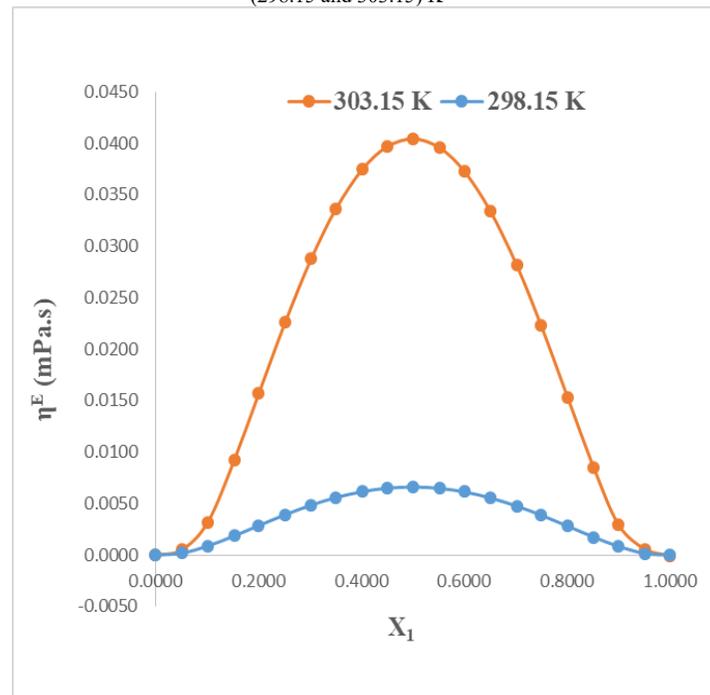
Figure 3: Plots of excess Gibbs free energy of 2-ethoxyethanol (1) + amylacetate (2) at (298.15 and 303.15) K
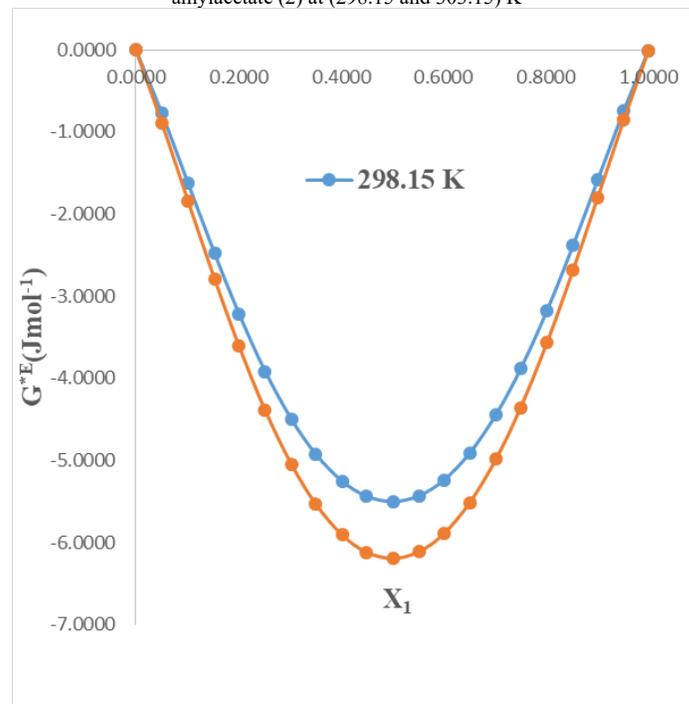
The values are negative for the binary systems over the entire composition range at all temperatures. As the temperature increases from 298.15K to 303.15K, ΔG^{*E} values becomes more negative which affirmed that weak specific interactions are taking place.

Table 3: Excess molar volume (V^E), excess viscosity (η^E) and excess Gibbs' free energy of activation of viscous flow (G^{*E}) of binary mixtures o ethoxyethanol and Amylacetate at (298.15 and 303.15) K

298.15 K				303.15 K			
x_1	V^E	η^E	G^{*E}	x_1	V^E	η^E	G^{*E}
0.0001	0.0000	0.0000	0.0000	0.0001	0.0000	0.0000	0.0000
0.0508	-0.5153	0.0002	-0.7725	0.0508	-0.5584	0.0005	-0.8914
0.1020	-0.9898	0.0009	-1.6237	0.1020	-1.0689	0.0032	-1.8429
0.1533	-1.4166	0.0019	-2.4737	0.1533	-1.5250	0.0092	-2.7852
0.2010	-1.7667	0.0029	-3.2122	0.2010	-1.8973	0.0157	-3.6055
0.2522	-2.0899	0.0039	-3.9135	0.2522	-2.2393	0.0226	-4.3892
0.3034	-2.3560	0.0049	-4.4972	0.3034	-2.5198	0.0288	-5.0470
0.3511	-2.5508	0.0056	-4.9242	0.3511	-2.7244	0.0336	-5.5321
0.4024	-2.7013	0.0062	-5.2525	0.4024	-2.8822	0.0375	-5.9077
0.4501	-2.7855	0.0065	-5.4350	0.4501	-2.9703	0.0397	-6.1175
0.5013	-2.8154	0.0066	-5.4994	0.5013	-3.0015	0.0404	-6.1919
0.5523	-2.7826	0.0065	-5.4286	0.5523	-2.9672	0.0396	-6.1102
0.6003	-2.6949	0.0061	-5.2386	0.6003	-2.8755	0.0373	-5.8917
0.6513	-2.5422	0.0056	-4.9055	0.6513	-2.7154	0.0334	-5.5107
0.7025	-2.3283	0.0048	-4.4364	0.7025	-2.4907	0.0282	-4.9782
0.7502	-2.0760	0.0039	-3.8831	0.7502	-2.2246	0.0223	-4.3551
0.8015	-1.7495	0.0028	-3.1753	0.8015	-1.8791	0.0153	-3.5644
0.8527	-1.3693	0.0017	-2.3764	0.8527	-1.4746	0.0084	-2.6774
0.9004	-0.9686	0.0008	-1.5833	0.9004	-1.0462	0.0030	-1.7981
0.9516	-0.4919	0.0002	-0.7337	0.9516	-0.5332	0.0006	-0.8476
0.9993	-0.0074	0.0000	-0.0098	0.9993	-0.0080	0.0000	-0.0116

Negative values of ΔG^{*E} is an indication of the presence of weak physical forces in the binary system. On the contrary, positive values of ΔG^{*E} suggest strong specific interactions (like hydrogen bonding and dipole- dipole interactions) between unlike molecules [26]. The negative values of ΔG^{*E} in the studied binaries of 2-ethoxyethanol and amylacetate show that the interactions of the binary systems are weak. Accordingly El-Banna and Mohamed [27], shi Xiaoqin [28], posited that positive values of ΔG^{*E} indicate strong specific interaction whereas their negative values show weaker interaction. In this work, we deduced that the negative values of ΔG^{*E} for the binary systems is an indication of the presence of weak interactions between the components of the mixture.

Guganathan and Kumar reported the same trend in their work thermophysical studies of binary liquid mixture of methyl acetate and alkoxyethanols [29]. Rathnam, observed the same trend in their investigations in the binary mixtures of diethylmalonate with acetophone, cyclopentanone, 3–pentanone, and inferred that positive ΔG^{*E} values decreases with increase in temperature of the mixtures. Other workers observed the same trends in their studies and stated that ΔG^{*E} values increase with an increase in temperature which confirm the presence of specific and strong interactions in the systems [30].

However, the behaviour of the binary mixtures of 2–ethoxyethanol + amylacetate shows that specific interactions (dipole – dipole) are taking place with decreasing intensity.

Correlation of viscosity by some semi empirical models

Interpreting the intermolecular interactions in the liquid mixture, some empirical and semi empirical

equations have been employed for the correlation of the viscosity of liquid mixtures. The equations of Grunberg–Nissan, Frenkel, Hind, Wijk and Kendall-Monroe were used to evaluate the viscosities of binary mixtures of 2-alkoxyethanol and amylacetate. Experimental and calculated values of viscosity (η) for the mixtures at the investigated temperatures are shown in Table 5. The table shows parameters calculated from Eqs. (8, 9, 10, 12 and 14) and their corresponding standard deviations (σ) for the binaries of 2-alkoxyethanol and amylacetate at temperatures of (298.15 and 303.15) K.

The values show that all the empirical relations gave a reasonable fit, but the viscosity values calculated using Hind et al. are comparatively in agreement with the experimental values. The values of interaction parameter (d') calculated were different from those of the other theories, which are positive for the systems 2-alkoxyethanol + amylacetate at the two temperatures. Fort and Moore reported that if the d' parameter is positive [31] , then the system exhibits strong Interaction; and if is negative it shows weak interaction.

The d' value according to Nigam and Mahl is regarded as an approximate measure of the strength of the interaction between the components [32].

Accordingly, the authors stated that:

i). if $\Delta\eta > 0$, $d' > 0$,

The magnitude of both are large then strong specific interaction would be possible;

ii). If $\Delta\eta < 0$, $d' > 0$,

Weak specific interaction would be present;

iii). If $\Delta\eta < 0$, $d' < 0$,

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The magnitude of both are large then the dispersion force would be dominant.

In this study the $\Delta\eta$ values of binary mixtures of 2-alkoxyethanol and amylacetate are positive while the values of d' at lower mole fractions of 2-ethoxyethanol were negative and at higher mole fractions the values becomes positive. We therefore, assert that weak specific interactions are present in the binary mixtures.

Table 4: Coefficients of Redlich-Kister equation and standard deviation values for the binary mixtures of 2-ethoxyethanol and Amylacetate at (298.15 and 303.15) K

298.15K					
Functions	A_0	A_1	A_2	A_3	σ
V^E(cm^3 mol^{-1})	-35.1284	0.0004	0.0006	0.0008	8.9734
η^E(mPa.s)	-0.0106	0.0224	-0.0048	0.0005	0.0017
G^{*E}(J mol^{-1})	-46.2965	-30.5820	5.8340	1.6700	16.8258
303.15K					
V^E(cm^3 mol^{-1})	-38.2166	-1.3197	-0.0795	0.0142	9.6048
η^E(mPa.s)	-0.2200	0.8099	-0.1725	-0.0003	0.1456
G^{*E}(J mol^{-1})	-55.1385	-27.0534	1.7944	2.3420	18.9312

Table 5: Viscosity data correlation parameters Hind, Wijk, Grunberg-Nissan, Frenkel and Kendall-Monroe values of the binary mixtures of 2-ethoxyethanol and amylacetate at (298.15 and 303.15) K.

	Hind	Wijk	Grunberg-Nissan	Frenkel	Kendall-Monroe	Hind	Wijk	Grunberg-Nissan	Frenkel	Kendall-Monroe
X_1	η_{12}	$lg\eta$	d'	$ln\eta_{12}$	$E\eta_m$	η_{12}	$lg\eta$	d'	$ln\eta_{12}$	$E\eta_m$
	2-ethoxyethanol (1) + amylacetate (2) @ 298.15K					2-ethoxyethanol (1) + amylacetate (2) @ 303.15K				
0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0508	0.8275	0.2073	-9.8425	0.2073	0.0530	0.6306	0.1811	-9.8425	0.1811	0.0396
0.1020	1.5720	0.3938	-14.9160	0.3938	0.1264	1.1979	0.3440	-14.9160	0.3440	0.0946
0.1533	2.2276	0.5580	-16.5168	0.5580	0.2212	1.6975	0.4875	-16.5168	0.4875	0.1661
0.2010	2.7562	0.6904	-15.8918	0.6904	0.3290	2.1003	0.6031	-15.8918	0.6031	0.2474
0.2522	3.2367	0.8108	-13.8306	0.8108	0.4651	2.4664	0.7083	-13.8306	0.7083	0.3504
0.3034	3.6272	0.9086	-11.0385	0.9086	0.6208	2.7640	0.7937	-11.0385	0.7937	0.4684
0.3511	3.9100	0.9795	-8.2605	0.9795	0.7808	2.9795	0.8556	-8.2605	0.8556	0.5899
0.4024	4.1270	1.0338	-5.4488	1.0338	0.9647	3.1449	0.9031	-5.4488	0.9031	0.7297
0.4501	4.2478	1.0641	-3.2126	1.0641	1.1413	3.2369	0.9295	-3.2126	0.9295	0.8643
0.5013	4.2905	1.0748	-1.3438	1.0748	1.3296	3.2695	0.9389	-1.3438	0.9389	1.0079
0.5523	4.2436	1.0630	-0.0644	1.0630	1.5062	3.2337	0.9286	-0.0644	0.9286	1.1428
0.6003	4.1178	1.0315	0.6435	1.0315	1.6518	3.1379	0.9011	0.6435	0.9011	1.2542
0.6513	3.8976	0.9764	0.9570	0.9764	1.7711	2.9701	0.8529	0.9570	0.8529	1.3459
0.7025	3.5868	0.8985	0.9423	0.8985	1.8381	2.7332	0.7849	0.9423	0.7849	1.3978
0.7502	3.2162	0.8057	0.7552	0.8057	1.8358	2.4508	0.7038	0.7552	0.7038	1.3969
0.8015	2.7304	0.6840	0.4935	0.6840	1.7429	2.0807	0.5975	0.4935	0.5975	1.3270
0.8527	2.1556	0.5400	0.2710	0.5400	1.5322	1.6426	0.4717	0.2710	0.4717	1.1673
0.9004	1.5391	0.3855	0.1463	0.3855	1.2052	1.1728	0.3368	0.1463	0.3368	0.9187
0.9516	0.7904	0.1980	0.0848	0.1980	0.6845	0.6023	0.1730	0.0848	0.1730	0.5220
0.9993	0.0120	0.0030	0.0022	0.0030	0.0114	0.0091	0.0026	0.0022	0.0026	0.0087

Table 6: Fitting parameters with Average Percentage Deviation (APD) values of the binary mixtures of 2-ethoxyethanol and Amyl acetate at (298.15 and 303.15) K

2-EtOH+Amyl Binary mixtures	Hind		Grunberg-Nissan		Wijk		Frenkel		Kendall-Monroe	
	η_{12}	APD	d'	APD	$Lg\eta$	APD	$ln\eta_{12}$	APD	$E\eta_m$	APD
298.15K	57.1119	-0.1257	-1.5548	3.3900	14.3066	-11.2190	14.3066	3.6832	19.8111	4.0332
303.15 K	43.5211	0.0796	-4.6401	4.5708	12.4978	-52.1407	12.4978	3.6539	15.0395	4.0576

CONCLUSION

The investigation of the study revealed that, the density and viscosity of the binary mixtures of 2-alkoxyethanol and amylacetate have been experimentally measured at temperatures of (298.15 and 303.15) K. From the experimental values of density and viscosity, excess molar volume, excess viscosity and excess Gibbs free energy of activation of viscous flow are determined. The experimental values of viscosity were correlated with the semi empirical relations of viscosity like Grunberg-Nissan, Frenkel, Hind, Wijk and Kendall-Monroe. Among the relations, Hind relation gave comparatively better agreement with the experimental values than others. From the observed negative values of V^E, positive values of $\Delta\eta$ and negative values of ΔG^{*E} and negative and low positive values of (d?) interaction parameter, we therefore conclude that weak specific interactions are present among the studied binary liquids at the investigated temperatures.

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