EXCESS MOLAR VOLUMES, SURFACE TENSIONS, VISCOCITY DEVIATION AND FTIR SPECTROSCOPY OF 1-BUTANOL-ETHYL ACETATE BINARY SYSTEM MIXTURE

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Abstract: *The physical properties (viscosity, surface tension and density) were computed in laboratory using different laboratory equipment for binary and pure system at (P=1 atm and T=25℃). At mole fraction 0.5, the excess volume was found to be positive value while the deviation in viscosity and surface tension was found as negative values at the same mole fraction. Experimental excess properties were compared using Redlich-Kister equation and showed acceptable standard deviation. The inter molecular interaction of the 1-Butanol and Ethyl acetate found to be negligible and the vulnerability of the hydrogen bonds according to the FTIR spectra to a mixture of 1-Butanol and Ethyl acetate is consistent with the positive values of excess volume. Overlying the values of surface tension and the deviation in viscosity was found as negative values for all mole fractions studied.*

Keywords: 1-butanol, Density, Ethyl acetate, Viscosity, FTIR analysis, Excess molar volume, Surface tension and Molecular interaction.

INTRODUCTION

Many of industrial processes require a large amount of information related to the physical and chemical properties of different types of fluids. Physical and chemical properties, for example, excess properties and intermolecular interactions are very important factors that affect the molecular structure and lead to the non-ideal deviation in the transport phenomena (fluid flow, the mass and heat transfer) [1-5]. Several studies have been carried out to study the excess thermodynamic properties of different types of non-aqueous liquids mixture [6-21]. The importance of thermodynamic excess properties is not only useful for the design and study of transport phenomena, but also for obtaining the appropriate data, which is the basis for the development of new predictive equations and linking them with special relationships. On the other hand, the practical data for the density of the binary liquid mixture was used to calculate the excess volume property related to the intermolecular interactions [22-24]. Anwar discussed changes in the values of excess thermodynamic properties with the change in composition and the temperature and their impact on hydrogen bonds and their effect on the mixing process [25]. Shekaari et al. used the excess properties in studying the polymer's effectiveness and demonstrated increased effectiveness by increasing the molar mass of polymer [26]. From above survey we conclude that 1-Butanol and Ethyl acetate are important solvents and have been used in many industrial processes and there is a need for thermodynamic process data which is the basis for theoretical and design purposes. The current study provides practical and

numerical data for the excess molar volume, the surface tension deviation and the viscosity deviation. The Redlich-Kister equation was used for correlation of the practical data. FTIR analysis was obtained and checked for 1-Butanol – Ethyl acetate binary liquid mixture as well as to clarify the excess and the deviation property.

1. EXPERIMENTAL

1.1. MATERIALS AND METHOD

1-Butanol and Ethyl acetate were obtained from the Fisher scientific (United Kingdom). The binary mixtures were prepared for the experiment using an electronic balance by CPA-225D, Germany, and manufactured by Sartorius. The measured weight accuracy was $\pm$ 0.01 mg. The density is measured using the densometer (Anton bar, DSA5000M, Austria). The calibration of the densometer was performed using degassed distilled water. Ethanol had been used to clean the tube of the vibrator for the densometer. The surface tension properties of the pure and binary of 1-Butanol and Ethyl acetate are determined using a surface tension measuring device (LY-1068 tensometer, China) . The accuracy of this device is within range $\pm$ 0.0001. The capillary viscometer was used to determine the viscosity of the pure and the binary mixture of 1-Butanol and Ethyl acetate. The viscosity was calibrated using distilled water and Ethanol. The accuracy of this device has been determined where it within a value of $\pm$ 0.028 m^2.s-1. The FTIR spectra of the 1-Butanol and Ethyl acetate liquid system are recorded using Bruker, Tensor II, Germany. The reading clarity of this device was within the 1 cm^{-1} for the spectrum range between 4000-400 cm^{-1}.

2. THE RESULTS AND DISCUSSION

2.1. THE DENSITY AND EXCESS MOLAR VOLUME

The densities of pure and mixture for 1-Butanol and Ethyl acetate have been measured in practically and have been tabulated in **table (1)** and **table (2)** . The measured density was obtained at 25°C and at normal pressure. The excess molar volume was calculated according to the following equation and the values were set in **table (2)**.

$$V^E = V_m - \sum_{j=1}^{2} x_i V_i \cdots (1)$$

Where (V_m) were calculated from the practical values of the mixture density according to equation (2).

$$V_m = \frac{[\sum_{i=1}^{2} x_i (M_{wi})]}{\rho} \cdots (2)$$

Where:

V_m: mixture molar volume.

V_i: 1-Butanol or Ethyl acetate volume.

Mw: molecular weight of the 1-Butanol or Ethyl acetate.

ρ: density of the mixture volume.

x_i: mole fraction of the 1-Butanol.

Figure (1) shows the change in molar volume with the molar fraction of 1-Butanol. The nonlinear increase was observed in excess molar volume with increased molar fraction. The non-ideal behavior of the excess molar volume can be due to the interactions and the intermolecular in the binary system of the liquid mix of 1-Butanol and Ethyl acetate, which have been explained by other researches [27]. The positive value of the excess molar volume was obtained for all fractions and the highest value of the molar volume was obtained at the value of the molar fraction 0.3**.**

Table 1: Experimental data of surface tension (σ), density (ρ) and viscosity (μ) for pure 1-Butanol and Ethyl acetate at 25 ^{o}C.

No.	Substance	M.wt	ρ	σ	μ
1	1-Butanol	74.123 g/mol	0.810 g/cm^3	24.93 Dyn/cm	2.544 Cp
2	Ethyl acetate	88.106 g/mol	0.9 g/cm^3	24 Dyn/cm	0.423 Cp

Table 2: Deviation of the surface tension (δ$_σ$), surface tension (σ), density of the mixture (ρ$_m$), excess of molar volume (V^E), viscosity (μ$_{mix}$) and deviation of the viscosity (δμ) for the 1-Butanol and Ethyl acetate mixture at standard conditions.

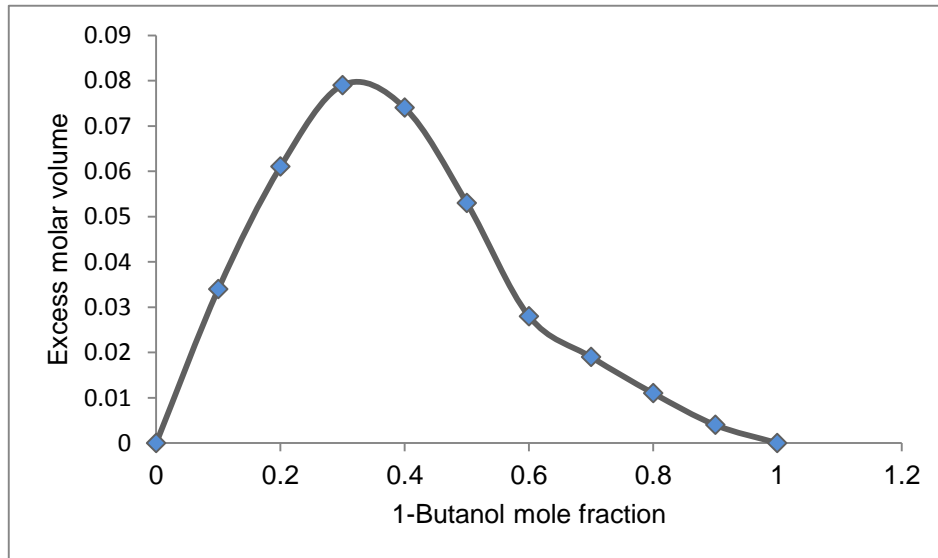| X_1	X_2	ρ_m	V^E	σ	δ_σ	μ_{mix}	μ
0.1	0.9	0.819	0.034	23.803	-0.29	0.601	-0.034
0.2	0.8	0.882	0.061	23.646	-0.54	0.772	-0.075
0.3	0.7	0.873	0.079	23.599	-0.68	0.970	-0.089
0.4	0.6	0.864	0.074	23.722	-0.65	1.194	-0.077
0.5	0.5	0.856	0.053	23.935	-0.53	1.419	-0.064
0.6	0.4	0.847	0.028	24.188	-0.37	1.643	-0.052
0.7	0.3	0.838	0.019	24.361	-0.29	1.871	-0.036
0.8	0.2	0.828	0.011	24.594	-0.15	2.099	-0.02
0.9	0.1	0.819	0.004	24.777	-.006	2.323	-0.008
1	0	0.81	0	24.93	0	2.544	0

Figure 1: Excess molar volume as a function of 1-Butanol mole fraction for the 1-Butanol-Ethyl acetate binary mixture.

From our results related to the excess molar volume, we can put a mathematical equation showing the change in the values of the excess molar volume with the change of the molar fraction values of this binary mixture:

$$V^E = 0.0932\ X^4 + 0.8283\ X^3 - 1.2984\ X^2 + 0.5699\ X - 0.0038$$

The equation that was concluded above agreement with the results of study carried out Jiménez et al. [27].

2.2. SURFACE TENSION DEVIATION

The values of the deviation in surface tension were calculated from the surface tension practical data and according to the following equation [27]:

$$\Delta\sigma = \sigma_m - (x_1\sigma_1 + x_2\sigma_2) \quad ...(3)$$

The change in surface tension deviation values with the molar fraction of 1-Butanol is illustrated in **figure (2)** and is summarized in **table (2)** . The negative behavior in the surface tension deviation values of all the specified molar fraction values is clearly shown.
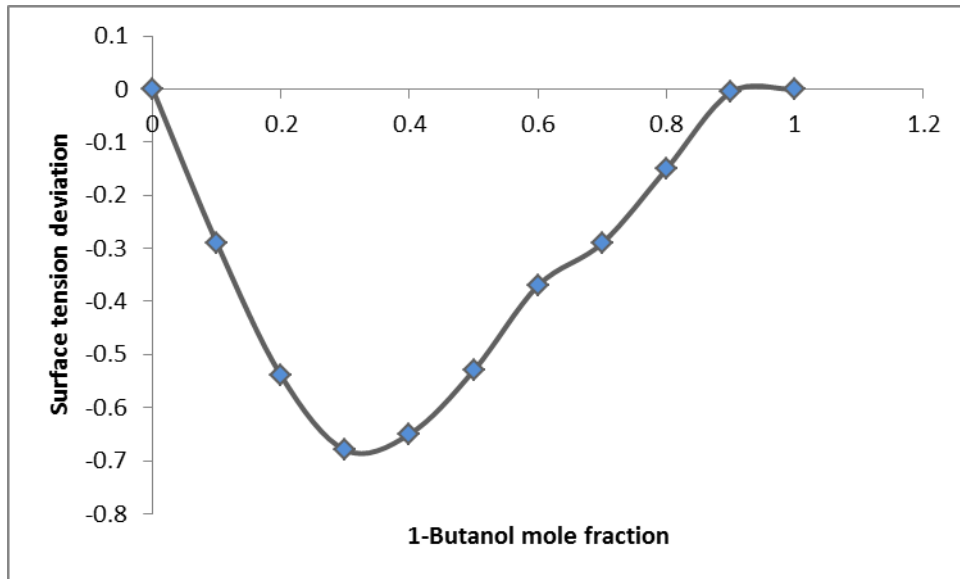
Figure 2: Surface tension deviation as a function of 1-Butanol mole fraction for the 1-Butanol-Ethyl acetate binary mixture.

From our results related to the surface tension deviation, we can put a mathematical equation showing the change in the values of the surface tension deviation with the change of the molar fraction values of this binary mixture:

$$\delta_\sigma = -1.0897\ X^4 - 2.3221\ X^3 + 7.6295\ X^2 - 4.2358\ X + 0.00184$$

The equation that was concluded above agreement with the results of study carried out Jiménez et al. [27]

2.3. VISCOSITY DEVIATION

The viscosity deviation was computed from the practical data of the viscosity of the pure and the binary mix liquid at the different mole fractions using the following equation [27]:

$$\Delta\eta = \eta_m - (x_1\eta_1 + x_2\eta_2) \cdots (4)$$

The calculated values for the deviation in viscosity were set in **table (2)** and were illustrated in **figure(3)**. All these values for the deviation of the viscosity are negative values. The lowest value of the deviation in viscosity was at 0.3 molar fraction of 1-Butanol.
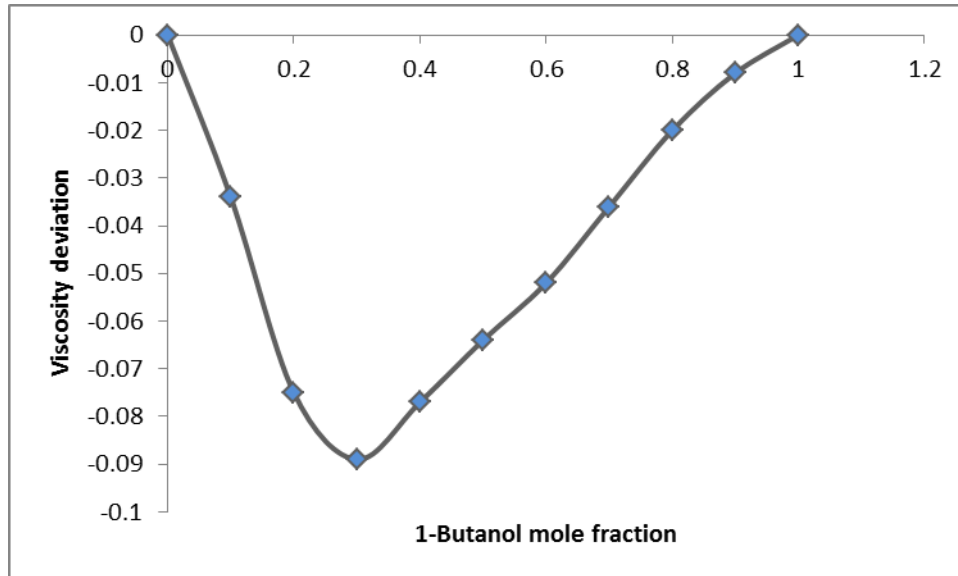
Figure 3: Viscosity deviation as a function of 1-Butanol mole fraction for the 1-Butanol-Ethyl acetate binary mixture.

From our results related to the viscosity deviation, we can put a mathematical equation showing the change in the values of the viscosity deviation with the change of the molar fraction values of this binary mixture:

$$\mu = 0.1369 \, X^4 - 0.844 \, X^3 + 1.3054 \, X^2 - 0.603 \, X + 0.0038$$

The equation that was concluded above agreement with the results of study carried out Ȁlvarez et al. [28]

2.4. REDLICH-KISTER CORRELATION

The values of excess molar volume, surface tension deviation and viscosity deviation were corrected relative to the Redlich-Kister equation as the following [29]:

$$V^{RE} = X_1 X_2 \sum_{i=0}^{2} A_i (X_1 - X_2)^i \cdots (5)$$

Where:

X_1, X_2: are the mole fraction of 1-Butanol and Ethyl acetate respectively.

A_i: are the coefficients of the Redlich-Kister equation and tabulated in the **table (3).**

The standard deviation (SD) of the binary system was computed using equation (6) and the results were tabulated in **table (3)** [27].

$$SD = \left(\frac{\sum_{i=1}^{M} \left(F_{exp}^{E} - F_{cal}^{E} \right)^2}{M - N} \right)^{1/2} \cdots (6)$$

M, N: Are the experimental samples and the constraints number respectively.

The experimental results showed a reasonable deviation from theoretical values as shown in **table(3)** .

Table 3: The coefficients of Redlich–Kister equation in the case of correlation the excess molar volume (V^E), surface tension deviation (δ_σ) and viscosity deviation for the samples of 1-Butanol-Ethylacetate mixture at (T=25°C and P=1 atm).

Function	Temperature, ^{o}C	a_0	a_1	a_2	a_3	a_4	SD
V^E	25 ^{o}C	-0.0038	0.5699	-1.2984	0.8283	-0.0932	0.0004
δ_σ	25 ^{o}C	0.00184	-4.2358	7.6295	-2.3221	-1.0897	0.00003
δ_μ	25 ^{o}C	0.0038	-0.603	1.3054	-0.844	0.1369	0.0006

2.5. FTIR AND INTERMOLECULAR INTERACTION

FTIR spectroscopy analysis is an effective and very important analysis of the properties of polar chemicals and can be used to regulate functional group and molecular interaction [30]. In the **figure (4)** below, the FTIR analysis of the 1-Butanol-Ethyl acetate mixture was developed. The FTIR spectra for a mixture of 1-Butanol – Ethyl acetate at different mole fractions showed a very important behavior for hydrogen bonds and demonstrated the non-ideal behavior and deviation in the thermodynamic properties as explained in the previous sections. As seen in the FTIR, the amplitude of the hydrogen top indicates the effect of the intermolecular interaction and the sharpness due to obvious the intermolecular interaction as well. For the pure 1-Butanol, the spectra shows a broad O-H stretch at 3350 cm^{-1} while the most important peak in the pure Ethyl acetate showed a strong C=O peak at 1750 cm^{-1}. While, for the 1-Butanol – Ethyl acetate mixture, the increase in molar fraction caused a weak displacement in the place of the C=O peak to a maximum wave number. The effect of hydrogen bonding is weak for the current mixture and has led to weakness intermolecular interaction between 1-Butanol and Ethyl acetate. The result of the FTIR spectrum is consistent with the result of the excess volume and the conclusions were clarified by other researchers [31]. The physical effect mainly involves non - qualitative physical correlations, breaking down the hydrogen bonds in the molecules themselves, weaker dipole – dipole interaction, and interstitial accommodation due to different the molar volumes and the free volumes between undesirable molecules, producing in positive

excess molar volume values. The chemical and the structural-geometrical effects was created due to the specific interactions such as forming of hydrogen bonds, charge – transfer (donor– acceptor) complexes, strong dipole–dipole interactions, differences in the size, shape of the component molecules, and making a negative volume excess values [32 - 35]. The concentration based thermophysical properties denotes that the deviation from the ideal behavior of the mixtures and to be provided an indication of the interactions between unlike components in the mixtures.
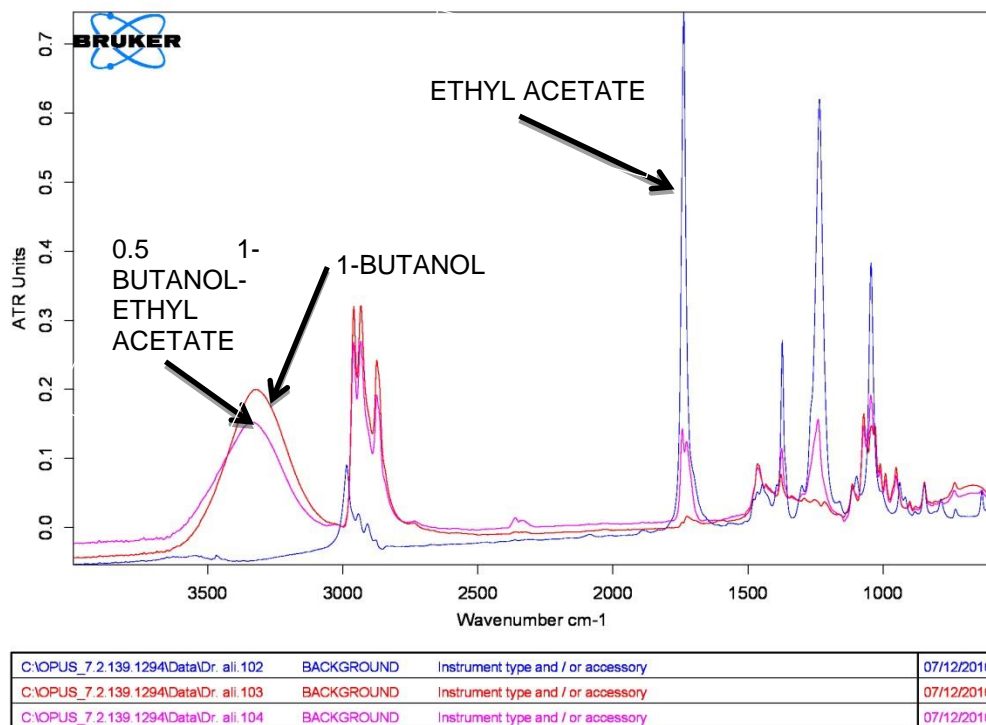
Figure 4: FTIR Spectra of 1-Butanol, ethyl acetate and binary mixture of 0.5-0.5 1-Butanol-Ethylacetate at Temperature=25°C and Pressure=1 atm.

CONCLUSIONS

1-The practical result of excess volume, surface tension deviation and viscosity deviation showed a non-ideal behavior with changing in molar fraction.

2. The correction of excess properties using the Redlich-Kister equation showed an acceptable deviation from the practical results.

3. The result of the FTIR showed compatibility with the result of excess volume and demonstrated internal hydrogen bonds between 1-Butanol and Ethyl acetate was weak for the mixture and can be concluded that there is a weakness in the place of the upper C=O peak of the highest wave number.

4. Determination of excess thermodynamic properties and refractive index of other mixing systems not previously addressed.

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