Batch Determination of Excess Molar Variables for Butanol and Acetonitrile Binary Mixtures

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Abstract

In this study, the experimental excess molar enthalpy, entropy and excess molar Gibb's free energy changes for the binary mixtures of butanol and acetonitrile have been measured at 345 K by means of a bomb calorimeter. The binary experimental excess molar enthalpy and Gibb's free energy values were correlated by means of the Liebermann-Fried solution theory model equation. The result showed that Liebermann-Fried solution theory model was able to closely represent the experimental excess molar enthalpy and excess molar Gibb's free energy data for the binary system with reasonable accuracy. The correlated and predicted results for all thermodynamic quantities measured have been drawn on a Table and plotted as well. The plots obtained revealed that the mixture has strong attractive forces and therefore deviate negatively from Raoult's line. This deviation will strongly help in the development and in-depth comprehension of thermal separation processes and molecular structures of fluid mixtures.

Keywords: Binary mixture; Butanol; Acetonitrile; Excess molar variables; The Liebermann-Fried theory equation

Introduction

The study of excess molar thermodynamic properties of liquid mixtures is very important for designing the thermal separation processes, developing solution theory models and to have a better understanding of molecular structure and interactions involved in the fluid mixtures. In particular, heat of mixing or excess molar enthalpy data of binary solvent mixtures has great industrial and theoretical significance [1].

Decrease in the value of petroleum resources and increase in the use of energy coupled with environmental deterioration have encouraged global utilization of efficient, economical and environment friendly petroleum refining process. During the period from 1915 to the late 1970's, tetraethyl lead was extensively used for its excellent anti-knocking properties which resulted in the improvement of the engine's efficiency and life span. But research conducted through 1960 to 1970 revealed that using tetraethyl lead in gasoline had harmful effect on man. Therefore, use of tetraethyl lead as a gasoline addictive was banned all over the world.

The addition of oxygenated compounds to gasoline as additives instead of lead reduces the emissions of hazardous compounds mainly carbon monoxide. Ethers and other organic compound containing oxygen have been suggested as gasoline additives [2].

In this context the use of oxygenated organic compound as gasoline blending agents, requires the knowledge of thermodynamic properties of mixtures involving hydrocarbons and its derivatives.

Experimental data of the thermodynamic properties of these mixtures are required for process design calculation as well as to provide essential knowledge (i.e., types of molecular structures and interactions) from the theoretical point of view.

Excess thermodynamic properties (excess molar enthalpy, entropy, Gibbs free energy, etc.) are of considerable practical importance to the development of chemical and petrochemical processes [3]. The effects resulting from the mixing of two or more pure streams at constant temperature and pressure is of direct relevance to the design of process equipment. In particular the heat effect is directly related to the design of heat exchangers. For example, the heat duty is directly proportional to excess molar enthalpy; which is one of the important thermodynamic properties of mixtures. Excess molar enthalpies can be either measured experimentally or estimated on the basis of solution theories.

When two liquids are mixed, the resulting change in physical properties may be considered as the sum of several contributions due to changes in energetic, free volume and molecular orientation order and due to steric hindrance. In case of liquid mixtures containing more than two components, the situation becomes more complicated.

Acetonitrile is an aprotic solvent used mainly in the purification of butadiene in refineries. It is widely used in the production of batteries. Acetonitrile is also found useful in industrial and biochemical processes because of its high dielectric constant [4].

However, butanol is a colorless, mobile protic solvent of medium volatility. It is used as feedstock for organic syntheses and most especially in the production of biofuel. Butanol can also be added to diesel fuel to reduce soot emissions [5].

There is little or obsolete information on the thermodynamic excess molar properties of this all-important binary mixtures containing butanol and acetonitrile.

The obscurity in relationship between the thermodynamic excess molar quantities and the molecular interactions or orientations of the mixture of these benign solvents have provoked this study to measure the experimental excess molar entropy and Gibbs free energy changes

of binary mixture consisting of butanol and acetonitrile. Experimental data was used to test the applicability of Liebermann-Fried model.

Materials and Methods

Analytical grade butanol and acetonitrile was bought for this research work. The chemicals were stored in Type 4A molecular sieve beds and were used without further purification. They were later degassed using low heat. The properties along with the source and purities of the chemicals used in this study are listed in Table 1.

Chemical	Source	Purity	Measured density in g/ml
Butanol	Sigma Aldrich	> 99%	0.81
Acetonitrile	Sigma Aldrich	> 99%	0.786

Table 1: Source, purity and densities of component liquids at 298.15 K.

The densities were measured using the formula,

$$Density = \frac{Mass}{Volume}(1)$$

Degassing of liquid

Dissolved gases in pure component liquid have erroneous effect on the thermodynamic property measurement (excess molar enthalpy, vapor-liquid equilibria and density). Most of the gases (air, nitrogen, oxygen, hydrogen and carbon dioxide etc.) that are dissolved in hydrocarbons decrease the density except carbon dioxide, which increases the density [6].

In flow micro calorimetric excess molar enthalpy measurement, dissolved gas increases the possibility of bubble formation in the mixing cell. This bubble formation leads to erroneous results of excess molar enthalpy [7]. To avoid these shortcomings, all the component liquids were degassed by means of low heating.

Experimental set up

The batch heating method was adopted for this research. The calorific value of the two solvents was determined using this method. It is a batch process and not continuous therefore no flow diagram for the process. Different masses of water (100 g, 150 g, and 200 g) was heated in batches. The quantity of solvent used to boil the water to boiling point in a given period of time was determined by weighing the burner before and after each experiment. The wick of the burner was changed after every experiment to avoid error. The formula used in calculating the calorific value was in accordance to the principle of conservation of mass and energy meaning that the energy released by the solvent was equal to the amount of energy absorbed by the water and the water boiler. The water boiler was made up of stainless-steel material. The energy released was equal to the mass of the solvent multiplied by the calorific value. Mathematically,

Energy=MCV (2)

The energy absorbed by the water,

Energy=$M_wC_{Pw}\Delta T$ (3)

The energy absorbed by the water boiler is expressed as,

Energy=$M_sC_{Ps}\Delta T$ (4)

Hence,

MCV=$M_wC_P\Delta T + M_sC_{Ps}\Delta T$ (5)

This implies that,

$$CV = \frac{M_wC_{Pw}\Delta T + M_sC_{ps}\Delta T}{M}(6)$$

Where CV is the calorific value of the solvent, M_w is the mass of water, C_{Pw} is the specific heat capacity of water, ΔT is the change of temperature, M_s is the mass of stainless steel, C_{Ps} is the specific heat capacity of stainless steel and M is the mole of solvent used.

The experimental set-up consists of a dial thermometer, water boiler, burner and the wind shield. The wind shield also helps to prevent heat loss to the environment. The water boiler is also covered to prevent heat loss. Any change in temperature in the mixing cell was detected by the dial thermometer.
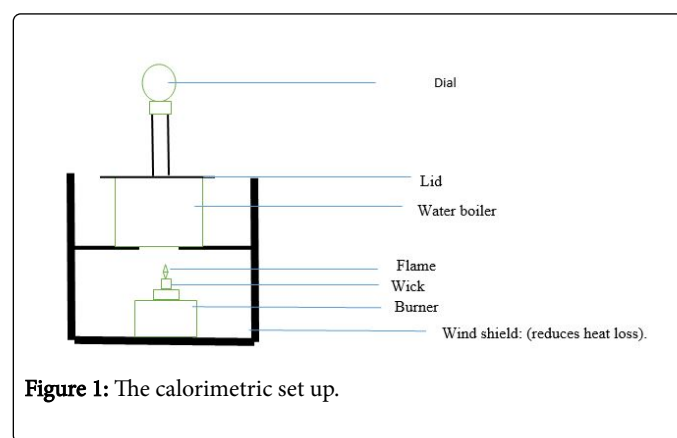

Figure 1: The calorimetric set up.

Results and Discussion

The excess molar entropy and Gibbs free energy of the mixture of two solvents are presented and discussed (Tables 2 and 3).

Mass of water used (g)	100	150	200
No. of mol of solvent used (mol)	0.03	0.04	0.05
Enthalpy of solvent (KJ/mol)	-1220.1	-1306.95	-1359.06
Entropy of solvent (J/K/mol)	-0.0076	-0.01	0.013
Gibbs free energy (kJ/mol)	-1217.46	-1303.47	-1355.08
lnK_{eq}	421.5	451.28	469.15

Table 2: Thermodynamics properties of butanol at 345 K.

Mass of water used (g)	100	150	200
No of mol of solvent used (mol)	0.07	0.09	0.11
Enthalpy of solvent (kJ/mol)	-522.9	-580.87	617.65
Entropy of solvent (J/K/mol)	-0.065	-0.082	-0.101
Gibbs free energy (kJ/mol)	-500.28	-552.33	-582.6
lnK_{eq}	173.2	191.22	201.7

Table 3: Thermodynamics properties of acetonitrile at 345 K.

Binary mixtures

The two solvents were mixed using different volume ratios. The butanol was used as higher volume of 50 cm^3 and acetonitrile's volume varied and vice versa. The enthalpy of mixing gave a zero-value indicating an ideal mixing situation.
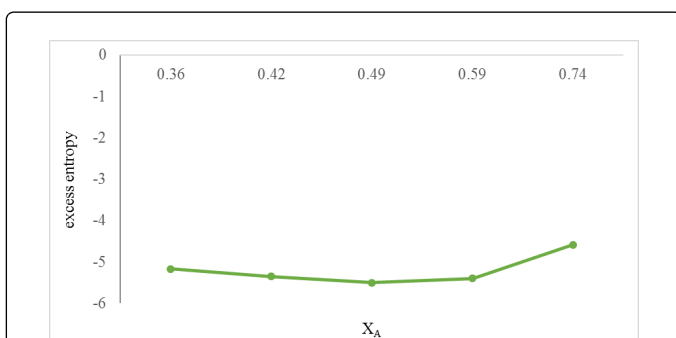
Excess molar properties

Figure 2: Excess molar entropy against X_A using butanol at a constant volume of 50 cm^3 and acetonitrile varied for 100 g of water at 345 K.
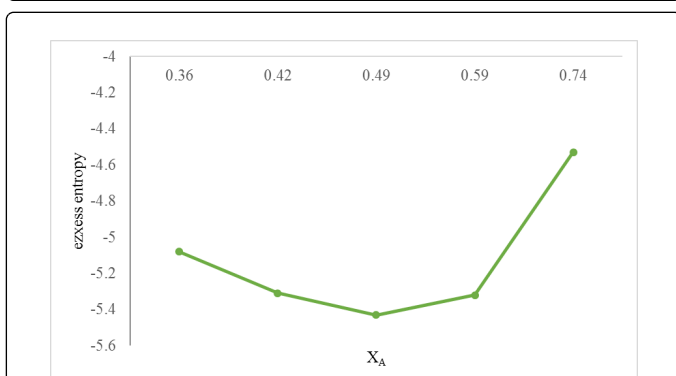

Figure 3: Excess molar entropy against X_A using butanol at a constant volume of 50 cm^3 and acetonitrile varied for 150 g of water at 345 K.
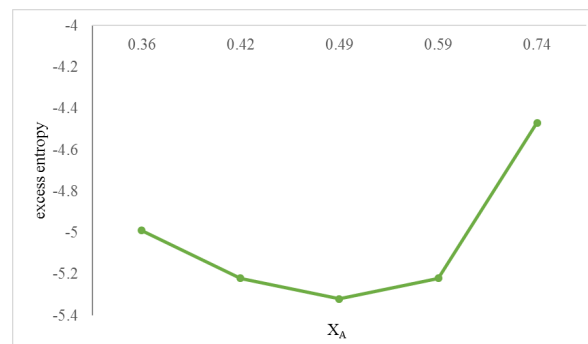

Figure 4: Excess molar entropy against X_A using butanol at a constant volume of 50 cm^3 and acetonitrile varied for 200 g of water at 345 K.
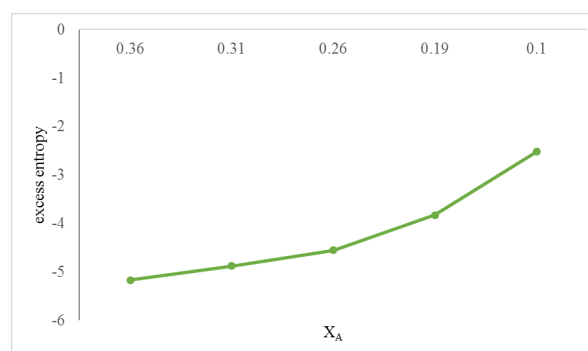

Figure 5: Excess molar entropy against X_A using acetonitrile at a constant volume of 50 cm^3 and butanol varied for 100 g of water at 345 K.
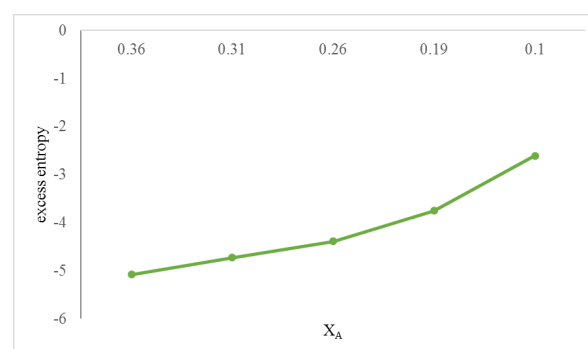

Figure 6: Excess molar entropy against X_A using acetonitrile at a constant volume of 50 cm^3 and butanol varied for 150 g of water at 345 K.
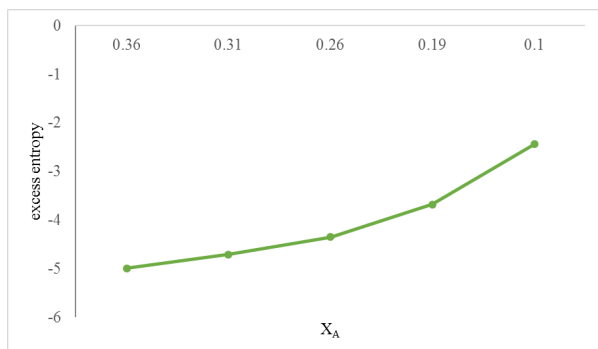
Figure 7: Excess molar entropy against X_A using acetonitrile at a constant volume of 50 cm^3 and butanol varied for 200 g of water at 345 K.
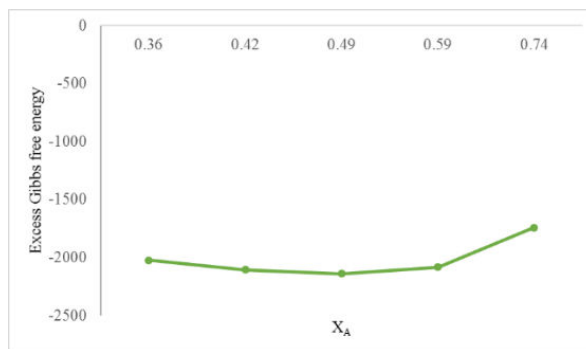

Figure 10: Excess molar Gibbs free energy against X_A using butanol at a constant volume of 50 cm^3 and acetonitrile varied for 200 g of water at 345 K.
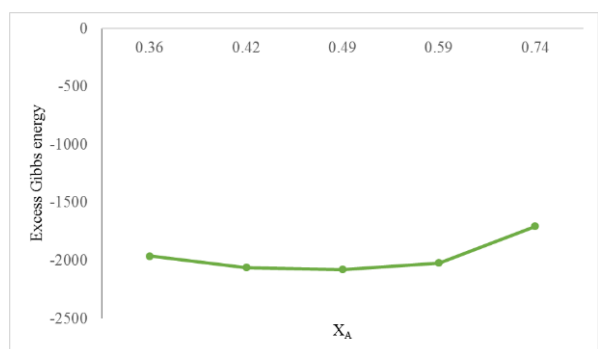
Excess Gibbs free energy

Figure 8: Excess molar Gibbs free energy against X_A using butanol at a constant volume of 50 cm^3 and acetonitrile varied for 100 g of water at 345 K.

Figure 11: Excess molar Gibbs free energy against X_A using acetonitrile at a constant volume of 50 cm^3 and butanol varied for 100 g of water at 345 K.

Figure 9: Excess molar Gibbs free energy against X_A using butanol at a constant volume of 50 cm^3 and acetonitrile varied for 150 g of water at 345 K.
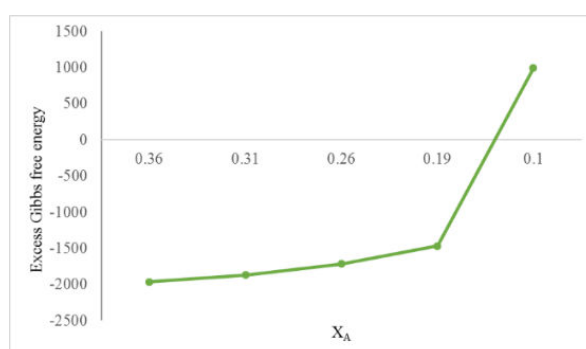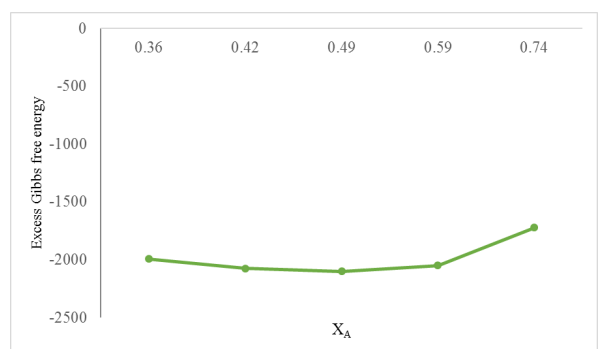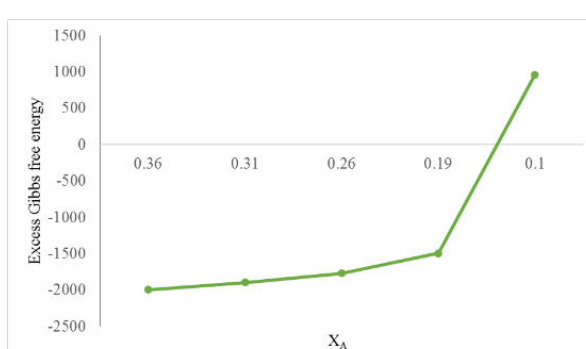

Figure 12: Excess molar Gibbs free energy against X_A using acetonitrile at constant volume of 50 cm^3 and butanol varied for 150 g of water at 345 K.
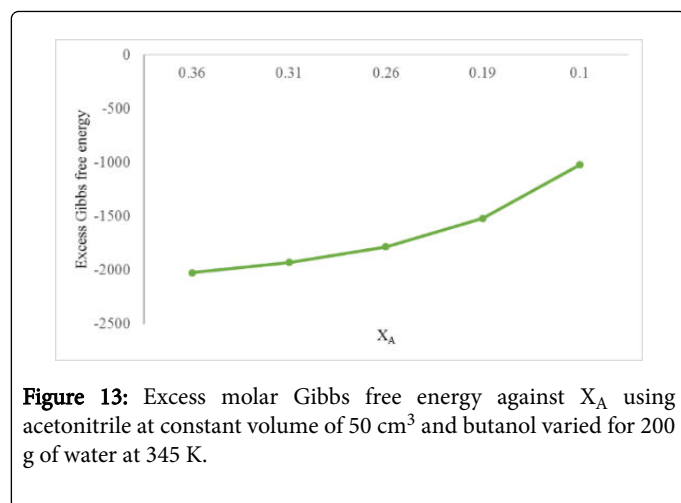
Figure 13: Excess molar Gibbs free energy against X_A using acetonitrile at constant volume of 50 cm^3 and butanol varied for 200 g of water at 345 K.

Experimental data correlation: Binary mixtures

The experimental excess molar enthalpies and Gibb's free energy of the binary system is correlated by means of the Liebermann-Fried model.

Liebermann-Fried model

Previously, Wang et al. [8] found that the Liebermann-Fried model can be used for representing both binary and multi-component mixtures. For representing multi-component mixtures, only the properties of the pure components and interaction parameters derived from an analysis of the excess enthalpies of their constituent binaries are required. Details of the thermodynamic relations in connection with the derivation of Liebermann-Fried model are described by Peng et al. [9].

To facilitate the understanding of the application of the Liebermann-Fried model, only the equations used in the excess molar enthalpy calculation process were presented here (Tables 4 and 5).

The expression for $H^{M,Xs}$ of a N-component mixture has the following form;

$$H^{M,Xs} = \frac{2RTx_A x_B [In(A_{12}A_{21})]^2}{(x_A + x_B A_{12})(x_B + x_A A_{21})[2 - In(A_{12}A_{21})]}$$
$$\left[\frac{x_B A_{12}}{x_A + x_B A_{12}} + \frac{x_A A_{21}}{x_B + x_A A_{21}} - \frac{2}{In(A_{12}A_{21})} \right]$$
$$- RT^2 \left[\frac{x_A x_B (V_{m1} - V_{m2})(\alpha_{p1} - \alpha_{p2})}{x_A V_{m1} + x_B V_{m2}} \right] (7)$$

For butanol			
Mass of water (g)	**A_{12}**	**A_{21}**	**σ (J/mol)**
100	0.8	0.57	0.05
150	1.23	0.8	0.08
200	0.57	0.8	0.09

Table 4: Liebermann-Fried model parameters A_{12} and A_{21}, and standard deviations, σ, for the representations of the excess molar

enthalpies $H^{M,Xs}$ of the constituent binary mixtures using butanol as higher proportion (50 cm^3) respectively for 100 g, 150 g and 200 g of water at 345 K.

For acetonitrile			
Mass of water (g)	**A_{12}**	**A_{21}**	**σ (J/mol)**
100	0.8	0.57	0.05
150	1.23	0.8	0.07
200	0.57	0.8	0.1

Table 5: Liebermann-Fried model parameters A_{12} and A_{21}, and standard deviations, σ, for the representations of the excess molar enthalpies $H^{M,Xs}$ of the constituent binary mixtures using acetonitrile as higher proportion (50 cm^3) respectively for 100 g, 150 g and 200 g of water at 345 K.

The excess molar Gibb's free energy value was also correlated using the Liebermann-Fried model. The values of the Liebermann-Fried model interaction parameters A_{12} and A_{21}, for the binary mixture are given in Tables 6 and 7.

For butanol			
Mass of water (g)	**A_{12}**	**A_{21}**	**σ (J/mol)**
100	0.8	0.57	1.1
150	1.23	0.8	1.09
200	0.57	0.8	1.12

Table 6: Liebermann-Fried model parameters A_{12} and A_{21}, and standard deviations, σ, for the representations of the excess molar Gibb's free energy $G^{M,Xs}$ of the constituent binary mixtures using butanol as higher proportion (50 cm^3) respectively for 100 g, 150 g and 200 g of water at 345 K.

For acetonitrile			
Mass of water (g)	**A_{12}**	**A_{21}**	**σ (J/mol)**
100	0.8	0.57	1.97
150	1.23	0.8	2
200	0.57	0.8	2.05

Table 7: Liebermann-Fried model parameters A_{12} and A_{21}, and standard deviations, σ, for the representations of the excess molar Gibb's free energy $G^{M,Xs}$ of the constituent binary mixtures using acetonitrile as higher proportion (50 cm^3) respectively for 100 g, 150 g and 200 g of water at 345 K.

Discussion

The result of thermodynamic property of butanol showed that the binary mixtures studied exhibit exothermic mixing behavior i.e. mixing of component was accompanied with release of heat. It can be compared to the result obtained by Manjunathan [10] for the binary mixture of DNBE and p-Xylene.

The result of the thermodynamic properties of acetonitrile and butanol presented in Tables 2 and 3 revealed that an increase in the mass of water brought about a corresponding increase in the number of moles of solvent used. The difference between the two was that the values for acetonitrile were far smaller than that of butanol. Therefore, butanol was a better solvent than acetonitrile because it had more energy to do work than acetonitrile. The enthalpy of the solvent became more negative.

The result equally revealed that the values of the entropy were very low which indicates that the reaction was partially chaotic. The excess molar Gibbs free energy as well became more negative as the mass of water increased (Figures 11-13).

The excess molar entropy at higher proportion of butanol as presented in Figures 2-4, showed a negative deviation from Raoult's line. It was observed that as the amount of water increased; the thermodynamic properties remained the same that is as the amount of work increased, an equal amount of energy was consumed.

Equally the excess molar entropy at higher proportion of acetonitrile as presented in Figures 5-7 showed an initial increase followed by a stepwise decrease. The values of the Gibbs free energy were negative indicating spontaneity. The equilibrium was constant in all, indicating that the process of mixing does not affect the equilibrium constant.

The relationship between the excess molar quantities (Gibbs free energy and entropy) and the mole fraction as presented in Figures 2-13 showed a slight negative deviation from ideality. This result was similar to the relationship between excess molar volume and mole fraction on DMSO+ benzene binary mixture [11-13].

The result further showed that from the relatively low heat of mixing values of the above systems, it was observed that only few hydrogen bond formations took place between the unlike molecules and the interactions of unlike molecules are only moderately strong [10].

The large exothermic excess molar enthalpy values of the binary systems indicate not much energy was needed to break the hydrogen bonds between the molecules [14].

It was also observed that the predicted value for molar excess enthalpy using the Liebermann-Fried model was lower than the experimental value. This can be compared to the result obtained by Tusel-Langer et al. [15] for Methyl tert-butyl ether and n-heptane.

Conclusion

The experimental determination of excess molar enthalpy, entropy and Gibbs free energy for binary mixtures of butanol and acetonitrile using different masses of water has been successfully performed. On the basis of the results obtained in this study, the following conclusions were drawn:

1. The heat of the binary system studied was exothermic in nature.

2. The range for the standard error of the excess molar enthalpies and excess molar Gibb's free energy for the binary mixture was less than 0.05.

3. The Liebermann-Fried model can be used to correlate the excess molar enthalpy and excess molar Gibb's free energy of binary mixtures successfully.

4. The data generated will be of importance in separation process design.

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