WORLD JOURNAL OF PHARMACEUTICAL RESEARCH
SJIF Impact Factor 8.084
Volume 9, Issue 7, 207-214. Research Article ISSN 2277– 7105

VOLUMETRIC BEHAVIOUR OF BINARY MIXTURES OF ETHANOL AND METHANOL AT 303 AND 308K

Nleonu E. C.*[1], Ezeibe, A. U.[1], Onwusonye J.C.[2], Okeke P. I.[3] and Ibeh G. C.[4]

[1]Department of Chemistry, Federal Polytechnic Nekede, Owerri-Imo State.
[2]Department of Microbiology/Biochemistry, Federal Polytechnic Nekede, Owerri-Imo State.
[3]Department of Basic Sciences, Alvan Ikoku Federal College of Education, Owerri – Imo State.
[4]Department of Mathematics and Statistics, Federal Polytechnic Nekede, Owerri-Imo State.

Article Received on 15 May 2020,
Revised on 05 June 2020,
Accepted on 25 June 2020
DOI: 10.20959/wjpr20207-17966

***Corresponding Author**
Nleonu E. C.
Department of Chemistry,
Federal Polytechnic Nekede,
Owerri-Imo State.

ABSTRACT

This research work was undertaken to examine the molecular interaction between binary mixture of ethanol and methanol by determing the densities (ρ), viscosity deviation ($\Delta\eta$), excess viscosity (η^E), molar volume (V_m), Excess Molar Volume (V^E) and excess Gibb's free energy (ΔG^E) at 303 and 308K over the entire composition mole fractions. The excess properties were found to be either negative or positive depending on the mole fractions of the mixtures. The positive value of Excess Molar Volume (V^E) shows volume expansion on mixing indicating weaker interactions than the interactions of the pure solvents. This work is of significance to the law enforcement agencies in monitoring alcohol producers against adulteration of ethanol products.

KEYWORDS: Binary mixture, Density, Viscosity, Molar volume, Thermodynamic parameter.

INTRODUCTION

Thermodynamics is a fundamental subject of great importance in physical chemistry and chemical engineering (Patil *et al*., 2011). Thermodynamic property is one which serves to describe a system. Studies on thermodynamic and transport properties are important in understanding the nature of molecular interactions in binary liquid mixtures. These properties are extremely useful for designing many types of transport and process equipment in chemical industries (Dakua *et al*., 2006).

Among the various thermodynamic properties, the excess molar volume V^E, has been of much interest for the practical purpose of determining composition from the density measurement (Shalmashi and Amani, 2014). Density, viscosity and excess molar volume are significant for the design of new processes and the study of molecular interactions in binary liquid system (Shalmashi and Amani, 2014). There has been a recent upsurge of interest to obtain information on intermolecular interactions in binary systems. Alcohols are important in pharmaceutical synthesis, wine industries, petrochemicals and serves as a solvent for many solutions.

Any drinkable liquid that contains from 5 -95% ethanol is an alcoholic beverage. The remaining fractions are often called congeners. Congeners are biologically active chemicals (chemicals which exert an effect on the body or brain) and are often contained in alcoholic beverages (Osobamiro, 2013). Congeners are produced in the process of fermentation, ageing or when organic chemicals in the beverage break down. They may also be added during production process to improve the taste, smell and appearance of the beverage (Silva and Malcata, 1999). The presence of methanol as a congener is undesirable in alcoholic beverages as is toxic due to its metabolic products- formaldehyde and formic acid (Cortes *et al*., 2005).

Methanol poisoning has been reported in the media as a result of illegal manufacturing and distribution of contaminated alcoholic beverages which may be due to deliberate adulteration or poor production process. These incidents unfortunately have serious consequences leading to injury and loss of life. In the present work, we report experimental data for densities (ρ), viscosity deviation ($\Delta\eta$), excess viscosity (η^E), molar volume (V_m), Excess Molar Volume (V^E) and excess Gibb's free energy (ΔG^E) at 303 and 308K. This study is expected to give some information about the volume changes in these binary solutions that indicate possible interactions between the binary mixture, such as molecular associations and dipole-dipole interactions. This work is of significance to the law enforcement agencies in monitoring alcohol producers against adulteration of ethanol products.

METHODOLOGY

The chemicals used in the present work are HPLC grade of ethanol and methanol of minimum assay of 99.8% and was used as such without further purification.

The densities of the pure components and binary mixtures were measured using an approximate 100cm^3 Gay-Lussac pycnometer. The temperature of the solution in the pycnometer was kept constant in using thermostated water bath ±0.5K. Once the solution reached the desired temperature, they were weighed within ±0.001g with an analytical balance. The solution of each composition was prepared fresh. A set of 9 compositions from (10 to 90)%v/v, and pure solvents was prepared and their densities were measured at the average of at least three measurements.

Viscosity measurements were carried out using NDJ-8SN viscometer with precision ± 0.01 and range of 0.01- 2000Pa.s.

Experimental values of density are used to calculate V^E of the mixtures (Li et al., 2008).

$$V^E = \frac{x_1 M_1 + x_2 M_2}{\rho} - \left[\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2}\right] \text{------------}1$$

Where M_1 and M_2 are the molecular weights of ethanol and methanol; ρ_1 and ρ_2 are the densities, and; x_1 and x_2 are the mole fractions of the respective components. The symbol ρ stands for the mixture density.[7]

RESULTS AND DISCUSSION

Experimental data on densities (ρ), viscosity deviation ($\Delta\eta$), excess viscosity (η^E), molar volume (V_m), Excess Molar Volume (V^E) and excess Gibb's free energy (ΔG^E) for the Ethanol with Methanol Solution at 303 and 308K over the whole composition mole fractions are presented in Table 1 and 2.

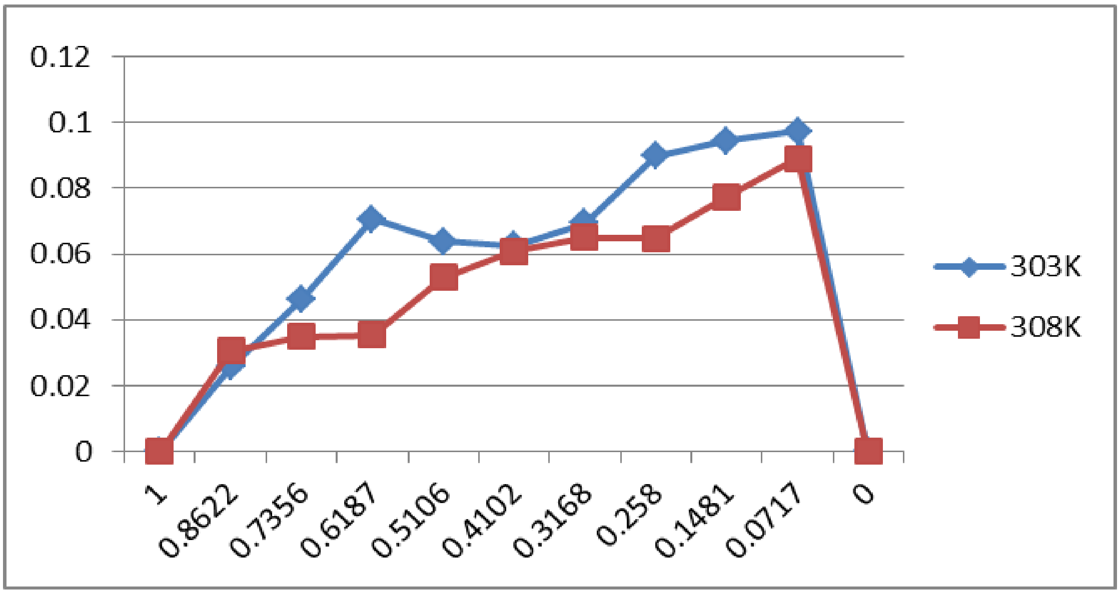

Figure 1: Excess molar volume against mole fraction for ethanol-methanol mixture at 303 and 308K.

The plot of excess molar volume (V^E) over all concentration range of ethanol-methanol mixture is presented in Figure 1 and was all positive. The positive values of V^E suggest dominance of dispersion forces between them (Dakua *et al*., 2006). Excess molar volume is the result of contributions from several opposing effects. These may be divided into three types, namely physical contributions contribute a positive term to V^E. The chemical or specific intermolecular interactions result in a volume decrease and contribute negative values to V^E. The structural contributions are mostly negative and arise from several effects, especially from interstitial accommodation and changes in the free volume. The positive values of excess molar volume (V^E) obtained for the mixtures studied at 303 and 308K may be attributed to physical contributions of the individual components, which are nonspecific interactions between the real species present in the mixture (Vural *et al*., 2011). The positive value of V^E over the entire composition range suggests strong hydrogen bonding intermolecular interaction for the system.

Table 1: Experimental densities (ρ), viscosity deviation ($\Delta\eta$), excess viscosity (η^E), molar volume (V_m), Excess Molar Volume (V^E) and excess Gibb's free energy (ΔG^E) for the Ethanol with Methanol Solution at 303K.

x_1	Density (g/cm^3)	$\Delta\eta$ (Pa.s)	η^E (Pa.s)	V_m(cm^3/mol)	V^E (cm^3/mol)	ΔG^E (J/mol)
1.0	0.7636	0.00	0.00	0.00	0.00	-2571.44
0.8622	0.7517	0.009	0.0256	58.7158	0.9233	1515.98
0.7356	0.7522	0.014	0.0460	56.3155	0.8567	2179.29
0.6187	0.7500	0.014	0.0706	54.2939	0.9900	2374.63
0.5106	0.7521	0.006	0.0639	52.1255	0.8145	2083.98
0.4102	0.7504	-0.008	0.0625	50.3666	0.9063	1227.57
0.3168	0.7494	-0.013	0.0694	48.6852	0.9466	1033.03
0.2580	0.7499	0.0006	0.0897	47.5527	0.8979	1563.65
0.1481	0.7498	-0.008	0.0943	45.5027	0.8738	768.15
0.0717	0.7527	-0.014	0.0974	43.9031	0.6827	25.23
0.0	0.7647	0.00	0.00	0.00	0.00	-2322.26

Table 2: Experimental Densities (ρ), viscosity deviation ($\Delta\eta$), excess viscosity (η^E), molar volume (V_m), Excess Molar Volume (V^E) and excess Gibb's free energy (ΔG^E) for the Ethanol with Methanol Solution at 308K.

x_1	Density (g/cm^3)	$\Delta\eta$ (Pa.s)	η^E (Pa.s)	V_m(cm^3/mol)	V^E (cm^3/mol)	ΔG^E (J/mol)
1.0	0.7511	0.00	0.00	0.00	0.00	-2869.65
0.8622	0.7474	0.017	0.0305	59.0537	0.2916	1821.69
0.7356	0.7456	0.009	0.0349	56.8140	0.4175	1980.45
0.6187	0.7468	0.001	0.0354	54.5265	0.3143	1690.66
0.5106	0.7480	0.006	0.0530	52.4112	0.2191	2122.19

0.4102	0.7485	0.004	0.0608	50.4945	-0.1782	1994.89
0.3168	0.7456	0.006	0.0650	48.9333	0.3622	1622.96
0.2580	0.7487	-0.007	0.0647	47.6290	0.1565	1135.76
0.1481	0.7505	-0.003	0.0775	45.4602	0.0411	861.29
0.0717	0.7467	-0.001	0.0890	44.2559	0.2645	680.96
0.0	0.7512	0	0.00	0	0	-1834.79

The measured values of viscosities of liquid mixtures and those of pure components were used to calculate the viscosity deviation (Δη) and excess viscosity (η^E) in the liquid mixtures using the relation in equation 2 and 3 respectively (Satish *et al*., 2016; Dikko *et al*., 2015).

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

$\eta^E = \eta_m - (x_1\eta_1 - x_2\eta_2)$-----------3

Where η_m, η_1 and η_2 are the viscosities of liquid mixtures, ethanol and methanol respectively and x_1 and x_2 are the mole fractions of ethanol and methanol respectively.

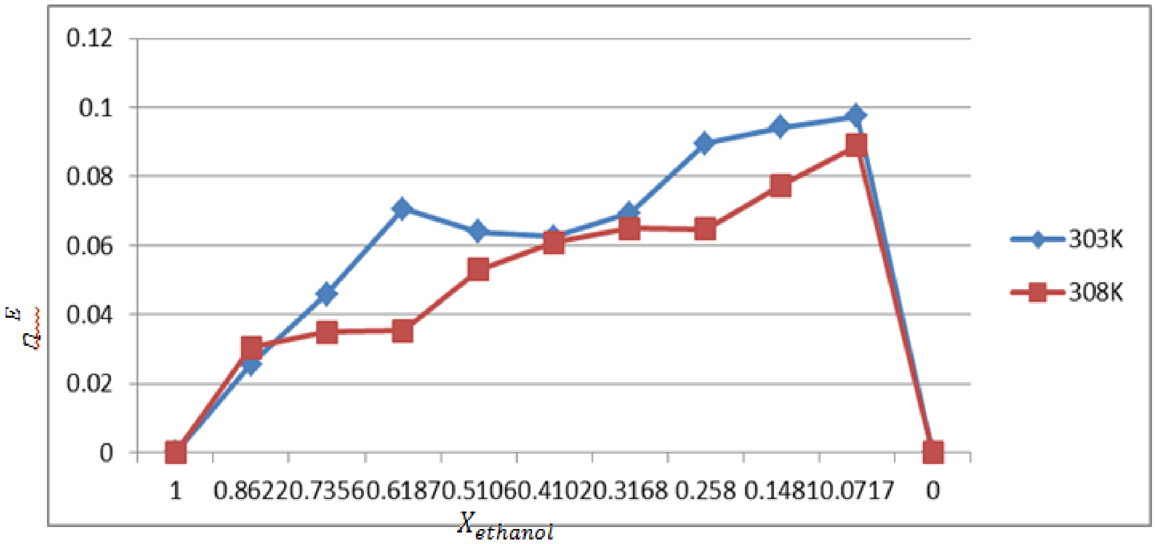

Figure 2: Excess viscosity Against Mole Fraction for Ethanol-Methanol Mixture at 303 and 308K.

The values of excess viscosity and deviation in viscosity at 303 and 308K for binary mixtures of ethanol and methanol are presented in Table 1 and 2. A perusal of the tables shows that the values of Δη gave positive and negative values. In general, the negative values of Δη imply the presence of dispersion forces in the mixtures; while positive values may be attributed to the presence of specific interactions (Dakua *et al*., 2006). The positive values of the deviation in viscosity Δη, suggest strong intermolecular interaction while the negative values of the deviation observed indicates the existence of weak intermolecular interactions upon mixing ethanol and methanol. This reveals that the strength of the specific forces is not the factor influencing the viscosity deviation in the liquid mixture but combination of an interactive and non-interactive forces are responsible in the positive and negative interactions of the mixture (Satish *et al*., 2016). The plot of excess viscosity of the mixtures is indicated in Figure 2, shows positives values in the entire mole concentration at the two studied temperatures. The viscosity behaviors of these mixtures are mainly due to changes in the liquid associated structures of alcohol (Dikko *et al*., 2015). The positive values of excess viscosity, shows that the interactions are high in ethanol-methanol mixtures. The magnitude of the excess viscosity increases as the volume of methanol increases. Various molecule, mix and dissolve in each other if they have the same type of polarity. In solvents such as alcohol, which can take part in hydrogen bond formation, self-association of alcohol may be increased in favour of hydrogen – bonded forms between the solute and solvent (Dikko *et al*., 2015).

The excess Gibb's free energies of activation $\Delta G^{\#E}$ for viscous flow have been calculated using equation 4 (Satish *et al*., 2016).

$\Delta G^{\#E} = RT[ln\eta_m V_m - (x_1 ln\eta_1 V_1 + x_2 ln\eta_2 V_2)$ ----------4

Where V_m, V_1 and V_2 are the molar volume of the mixture, ethanol and methanol respectively while the other items retain their usual significance.

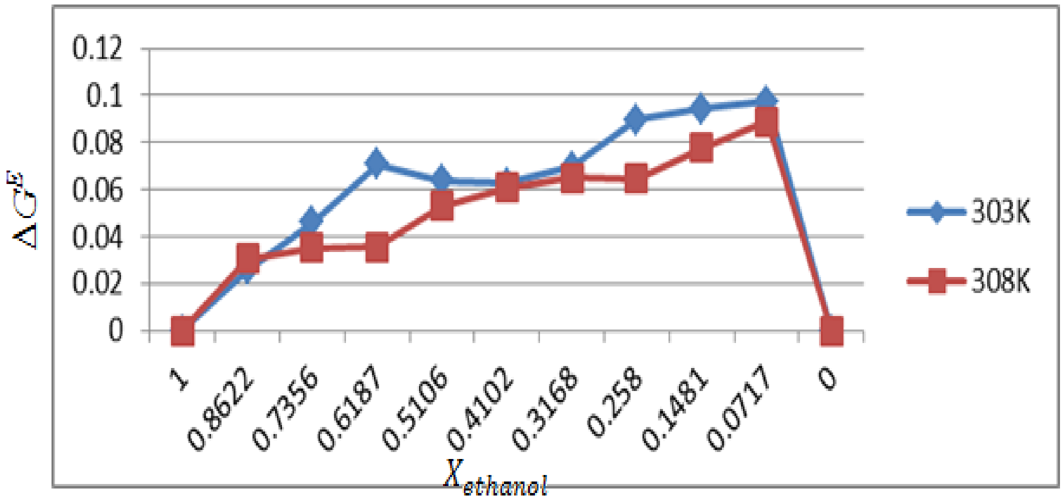

Figure 3: Excess Gibb's free energy of activation Againt Mole Fraction for Ethanol-Methanol Mixture at 303 and 308K.

The plots of excess Gibb's free energy of activation of viscous flow against mole fraction at 303 and 308K for binary mixtures of ethanol and methanol are presented in figure 3. Excess Gibb's free energy of activation of viscous flow was found to be positive for all mixtures. The positive values of excess Gibb's free energy of activation of viscous flow show the presence of specific and strong interactions in the studied systems (Satish *et al*., 2016).

CONCLUSION AND RECOMMENDATIONS

The Experimental data in this study shows densities (ρ), viscosity deviation ($\Delta\eta$), excess viscosity (η^E), molar volume (V_m), Excess Molar Volume (V^E) and excess Gibb's free energy (ΔG^E) for the binary mixture of Ethanol and Methanol Solution at 303 and 308K over the whole composition mole fractions. The results suggest strong intermolecular interactions among the components of the binary mixtures resulting to increase in volume of the mixtures. Federal regulatory agencies in charge of food and drugs should be encouraged to carry out routine monitoring of alcoholic producers to prevent adulteration of ethanol products.

ACKNOWLEDGEMENT

The authors are thankful to Head of Chemistry Department and management of Federal Polytechnic Nekede, Owerri-Imo for providing research facilities for the research work.

Conflict of Interest

The authors have not declared any conflict of interest.

REFERENCES

1. Cortes, S., Gil L. and Fernandez, E. Volatile Composition of traditional and industrial Orujo Spirits. Food Control, 2005; 16: 383-388.
2. Dakua, K.V., Sinha, B. and Roy, N.M. Studies on Excess Molar Volumes and Viscosity Deviations of Binary Mixturs of Butylamine and N, N-dimethylformamide with some Alkyl Acetates at 298.15K. Indian Journal of Chemistry, 2006; 45: 1381-1389.
3. Dikko, A.B., Eyube, E.S. and Eke, E. Studies on Density, Viscosity, Partial Molar Volume, Excess Molar Volume and Excess Viscosity of panadol in methanol + water System at 309.15K. IOSR Journal of Applied Chemistry, 2015; 7(3): 63-66.
4. Li, Q.S., Tian, M.Y. and Wang, S. Densities and Excess Molar Volume for Binary Mixtures of 1, 4-Butanediol + 1, 2-Propanediol, + 1,3-Propanediol, and + Ethane-1,2-diol from 293.15 to 328.15K. J. Chem. Eng. Data., 2008; 53: 271-274.

5. Osobamiro, T. Analysis of Some Contaminants Commonly Found in Alcoholic Beverages. American Eurasian Journal of Scientific Research, 2013; 8(1): 53-56.
6. Patil, P.P., Patil, S.R., Borse, A.U. and Hundiwale, D.G. Density, Excess Molar Volume and Apparent Molar Volume of Binary Liquid Mixtures. Rasayan J. Chem., 2011; 4(3): 599-604.
7. Satish, B.M., Machale, G.R., Gayakwad, S.V. and Naikwade, D.S. Density, Viscosity and Excess Gibbs Free Energy of Activation of Binary Systems of Formaldehyde with Methanol, Ethanol, n-Propanol and N-Butanol at Temperatures 298.15, 308.15 and 318.15K. International Journal of Engineering Trends and Technology, 2016; 41(5): 249-255.
8. Shalmashi, A. and Amani, F. Densities and Excess Molar Volumes for Binary Solution of Wtater + Ethanol, + Methanol and + Propanol from (283.15 to 313.15K). Latin American Applied Research, 2014; 44: 163-166.
9. Silva, M.L. and Malcata, F.X. Effects of Time of Grape Pomace Fermentation and Distillation Cuts on the Chemical Composition of Grape Marcs. Zeitschrift für Lebensmittel-Untersuchung und Forschung A, 1999; 208: 134-143.
10. Vural, S.U., Muradoglu, V. and Vural, S. Excess Molar Volumes and Refractive Index of Binary Mixtures of Glycerol + Methanol and Glycerol + Water at 298.15 and 303.15K. Bull. Chem. Soc. Ethiop., 2011; 25(1): 111-118.