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Volumetric Behaviour of Binary Mixture of Dual Purpose Kerosene (DPK) and Automotive Gas Oil (AGO) at 303K

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Abstract:
The study of volume changes in binary mixtures is attracting considerable interest from researchers due to the degree of molecular interaction between the mixed solvent molecules and their importance in many chemical industries and engineering disciplines. The experimental values of densities (ρ) and viscosities (η) of pure and binary mixtures of dual-purpose kerosene (DPK) and automotive gas oil (AGO) were obtained over the whole range of mixture composition at a temperature of 303 K. The experimental data obtained were employed to determine the excess molar volume (V_m^E), excess viscosity (VE), and excess Gibb's free energy of activation (ΔGE) based on the molecular interactions arising due to the structural effect of the mixture. The measured viscosity values were correlated with Grunberg and Nissan, Kendel and Monroe, and Frenkel's semi-empirical models to evaluate the best fit for the system. The results acquired were explained according to their structural differences, strength, and nature of intermolecular interactions in the binary mixture. The experimental result revealed that the binary mixture of DPK and AGO shows positive excess molar volume and negative excess viscosity. Weak, specific interactions were responsible for the dispersion force in the binary mixtures.

Keywords: Density, viscosity, excess parameters, semi empirical models, binary mixture.

I. INTRODUCTION

The thermodynamics of organic solvents and non-electrolyte liquid mixtures have attracted significant attention from scholars due to their wide importance in the areas of mass transfer, heat transfer, and chemical separation (Kemeakegha et al., 2021).

The molecular nature of a liquid mixture is different from that of individual liquids on account of the existence of strong intermolecular interactions between the component liquid molecules and their state of disorder (Alauddin et al., 2022). Investigation of the physical properties of liquid mixtures, such as electric conductivity, density, and viscosity, is extremely vital in the fields of chemistry, engineering, agriculture, petroleum exploration, and the design of machines and instruments (Maduelusi et al., 2017; Boisa and Odagwe, 2019).

The study of changes in the thermodynamic properties of liquid mixtures and their level of deviation from ideal behavior has given fundamental qualitative and quantitative information on the molecular structure and intermolecular interaction in solvent mixtures (Lakshmi et al., 2014). These intermolecular interactions between solvent mixtures are an indication of the extent of deviation from the ideal behavior of individual solvents, which shows their excess properties. The deviations observed from solvent mixtures are related to synergy between mixture components and are accredited to differences in the chemical compositions of the individual solvents and experimental conditions such as temperature differences and mixing mole ratios of mixture components (Venkatramana et al., 2014).

Dual-purpose kerosene (DPK), popularly called kerosene, and automotive gasoline oil (AGO), popularly called diesel, are petroleum products produced from the processing of crude oil at refineries (Ikeora and Okoye, 2015). About 40% of the fuel used in Nigerian road transportation is automotive gas oil. Petroleum product adulteration has increased over the years, particularly in developing countries like Nigeria, due to its high consumption rate with the intent of maximizing profit in their businesses with total disregard for the hazardous effects on end users (Onojake et al., 2012). Petroleum adulteration is the intentional mixing of petroleum products with other refined products that are in high demand with the aim of making more profit (Ikeora and Okoye, 2015). Adulteration of petroleum products leads to economic loss, deterioration of engines, loss of trust, and environmental and health issues in the form of increased emissions of harmful gases that affect the quality of air (Yang et al., 2016; Boadu, 2019). There is a need to examine the purpose of adulteration in order to establish whether petroleum product adulteration is a conscious attempt to increase the margin gain by petroleum retailers or oil marketing companies by studying the volumetric and viscometric properties of dual-purpose kerosene and automotive gasoline oil.

The volumetric and viscometric properties of solvent mixtures obtained from measurements of the densities and viscosities of their individual solvents and solvent mixtures are useful in determining the nature and type of intermolecular interactions present in the component molecules (Satish et al., 2016). The nature of molecular interactions in binary solvent mixtures can be elucidated using excess thermodynamic functions. The measured values of density and viscosity of solvent mixtures were used to estimate the excess thermodynamic functions of the solvent system, such as excess molar volume (V_m^E), excess viscosity (ηE), and excess free energy of activation (ΔG^(*E)). The major factors that establish the degree of deviations of mixed solvents from ideal behavior and, hence, the excess thermodynamic properties of the solvent mixtures are polarity and the size of molecules (Shimomura et al., 2010). There have been reports of charge transfers and structural variations between the solvent components leading to specific molecular interactions (Gowrisankar et al., 2012). To investigate the degree of deviation in the binary mixtures of dual-purpose kerosene (DPK) and automotive gas oil (AGO), we stated in this paper the excess molar volume (ΔG^(*E)), excess viscosity (ηE), Grunberg-Nissan interaction parameter (d12), and excess Gibb's free energy of activation over the whole range of composition at 303 K.

II. MATERIALS AND METHODS

Dual-purpose kerosene (DPK) and automotive gas oil (AGO) were purchased from a major filling station in Owerri, Imo State. The purity of the pure solvents was ascertained by measuring the densities at 303 K, and the values were comparable with those of the literature at the same temperature. The binary solvent mixtures were prepared by mole ratio. All solvents and solvent mixtures were weighed using atom electronic balance with a precision of 0.0001g. The binary mixtures were prepared over the ratio of 90:10, 80:20, 70:30, 60:40, 50:50, 40:60, 30:70, 20:80, and 10:90 for X1:DPK and X2: AGO, respectively.

Densities of pure solvents and their binary mixtures were measured using a 100 ml borosilicate glass pycnometer with a uniform capillary stopper. The viscosities of pure solvents and binary mixtures were measured using an NDJ-85N viscometer with a precision of 0.01 %. The viscometer and pycnometer were calibrated with distilled water at 303 K. The temperatures of the measurements were controlled using an electronic thermostatic water bath. Triplicate measurements of all experiments were conducted, and averaged readings were taken.

III. RESULTS AND DISCUSSION

To investigate the molecular interaction between dual-purpose kerosene (DPK) and automotive gasoline oil (AGO), excess molar volumes (V_m^E), deviation in viscosity (Δη), and excess Gibbs free energy of activation of viscous flow (ΔG*E) were calculated from experimental density and viscosity using the method described by Nleonu et al., 2020.

$$V_m^E = \frac{x_1M_1+x_2M_2}{\rho_m} + \left[\frac{x_1M_1}{\rho_1} + \frac{x_2M_2}{\rho_2}\right] \quad (1)$$

$$\eta^E = \eta_m - (x_1\eta_1 + x_2\eta_2) \quad (2)$$

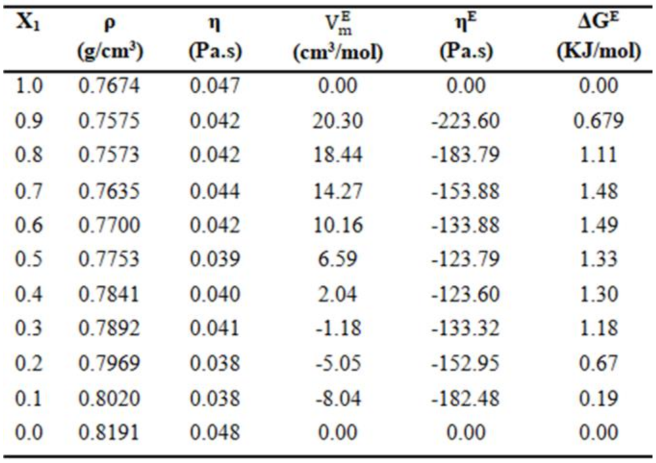
$$\Delta G^{*E} = RT[\ln\eta_m V_m - (x_1\ln\eta_1 V_1 + x_2\ln\eta_2 V_2)] \quad (3)$$

$$V_m = \frac{x_1M_1+x_2M_2}{\rho_m} \quad (4)$$

Where x_1 (DPK) and x_2 (AGO) are the mole fractions calculated from mass fractions. M_1 (170.33 g/mol) and M_2 (223.91 g/mol) are molar masses, ρ_1 and ρ_2 are densities, and η_1 and η_2 are the viscosities of pure components 1 and 2, respectively. ρ_m and η_m are the densities and viscosities of the mixture.

The experimental data on densities (Δ), viscosities (η), and the calculated values of excess molar volume (V_m^E), excess viscosity (η^E), and excess free energy of activation for viscous flow (ΔG^E), for the binary mixture of dual-purpose kerosene and automotive gas oil at 303 K are presented in Table 1. Excess thermodynamic functions reveal the degree of deviation of a liquid mixture from its pure behavior and show it to be completely sensitive to the molecular interactions between the component molecules of liquid mixtures. The strength of molecular interaction between component molecules of liquid mixtures depends on the sign and magnitude of these excess functions.

TABLE 1: EXPERIMENTAL DENSITIES (P), VISCOSITY DEVIATION (ΔH), EXCESS VISCOSITY (η^E), MOLAR VOLUME (V_M), EXCESS MOLAR VOLUME (V_M^E) AND EXCESS GIBB'S FREE ENERGY (ΔG^E) FOR THE BINARY MIXTURE OF HOUSEHOLD KEROSENE AND PREMIUM MOTOR SPIRIT AT 303 K.



X_1	ρ (g/cm³)	η (Pa.s)	V_m^E (cm³/mol)	η^E (Pa.s)	ΔG^E (KJ/mol)
1.0	0.7674	0.047	0.00	0.00	0.00
0.9	0.7575	0.042	20.30	-223.60	0.679
0.8	0.7573	0.042	18.44	-183.79	1.11
0.7	0.7635	0.044	14.27	-153.88	1.48
0.6	0.7700	0.042	10.16	-133.88	1.49
0.5	0.7753	0.039	6.59	-123.79	1.33
0.4	0.7841	0.040	2.04	-123.60	1.30
0.3	0.7892	0.041	-1.18	-133.32	1.18
0.2	0.7969	0.038	-5.05	-152.95	0.67
0.1	0.8020	0.038	-8.04	-182.48	0.19
0.0	0.8191	0.048	0.00	0.00	0.00

EXCESS MOLAR VOLUME

A change in excess molar volume (V_m^E) of the DPK and AGO systems as a function of the mole fraction of individual liquid components at 303 K is displayed in Figure 1. The examination of the result illustrated that the binary mixture of DPK and AGO was positive over the mole fraction of 0.9–0.4 DPK and negative over the 0.3–0.1 mole ratio composition. The excess molar volume values were observed to decrease with the decrease in the mole fraction of dual-purpose kerosene and show a maximum at a mole ratio of 0.9 (Figure 1). The positive deviation observed from the 0.9–0.4 mole fraction of DPK in this work suggested volume expansion, and the negative deviation implies volume reduction in the binary mixture. The excess molar volume of a liquid mixture can be explained by the chemical, geometrical, and physical contributions of individual molecules in the mixtures. Volume reduction resulting in negative (V_m^E) can be attributed to chemical or specific interactions, and these interactions result in the formation of hygrogram bonds and other complex-forming interactions. Volume expansion is caused by physical interactions involving primarily dispersion forces, leading to a positive contribution (Nleonu *et al*., 2020). Negative contributions can also arise from structural contributions coming from the geometrical fitting of one component into other components due to variation in the molar volume of component molecules and free volume between the component molecules.

The V_M^E result shows that dispersion forces arising from physical interactions are predominant in these mixtures, as depicted by the noticed positive values of V_m^E (Ezeibe et al., 2021). The positive and negative deviation recorded in this study from the pure behavior of DPK and AGO depends predominantly on the physical and structural interactions of the components. The high volume expansion observed at a high mole fraction of DPK is suspected to arise from weak intermolecular interaction or repulsive forces between the molecules, which were observed to reduce as the mole fraction of DPK decreased. The large difference in their molecular weight may be another possibility for their interactions. The negative values observed at low mole fractions of DPK may also occur due to structural contributions arising from interstitial accommodation of DPK partially into the structural network of AGO.

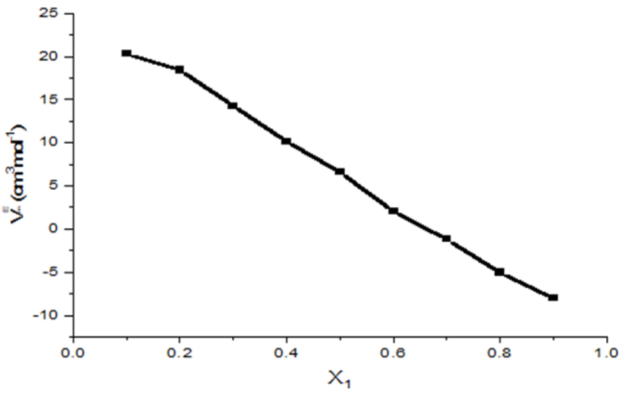


Figure 1: Plot of excess molar volume (V_m^E) against mole fractions of DPK.

EXCESS VISCOSITY

The plot of variation in excess viscosity (η^E) against mole fraction at 303 K for the DPK and AGO systems is presented in Figure 2. The values of deviation in excess viscosity of the mixture were found to be negative over the whole range of composition. The excess viscosities were seen to be more negative with the decrease in mole fraction of dual-purpose kerosene. The negative values of the η^E binary mixture of the DPK and AGO systems revealed that the viscosity of the mixture was lower than the corresponding pure solvents. Shaik *et al.* (2014) have reported weak interactions being accountable for negative excess viscosity in binary mixtures. The results obtained revealed that weak interactions occur between the mixture components, and some physical forces of attraction, like dispersion forces, are more prevalent in the mixtures (Alauddin *et al*., 2022).

In addition, the deviation in viscosity may also be attributed to the difference in molar volume of the individual solvents, which favoured the accommodation of smaller molecules by the larger ones. At 303 K, AGO with a molar weight of 223 g/mol tends to accommodate DPK with a molecular weight of 170.33 g/mol.

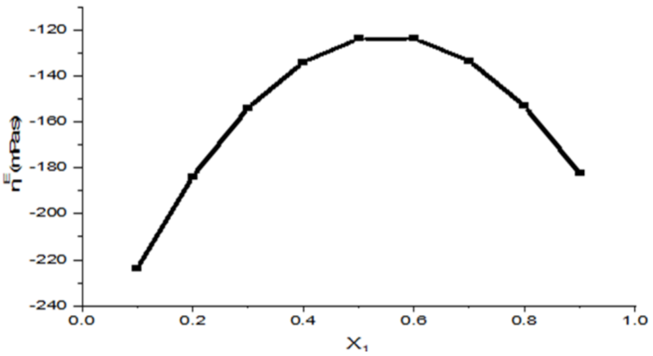


Figure 2: Plot of excess viscosity (ηE) against mole fractions of DPK (X1)

EXCESS GIBB'S FREE ENERGY

The plot of the deviation in excess Gibb's free energy of activation for viscous flow (ΔG^{*E}) against the mole fraction of DPK is displayed in Figure 3. It was observed that (ΔG^{*E}) was positive for the system for the whole range of compositions. The plot of (ΔG^{*E}) shows the maximum value at $x_1 = 0.6$ and the minimum at $x_1 = 0.1$, respectively. In the present work, the observed positive values of ΔG^{*E} indicate that specific interactions between the individual solvents were predominant (Houkhani *et al*., 2007). The large positive values of ΔG^{*E} were attributed to the dominant physical forces rather than chemical forces in the mixture components (Rathnam *et al*., 2012).

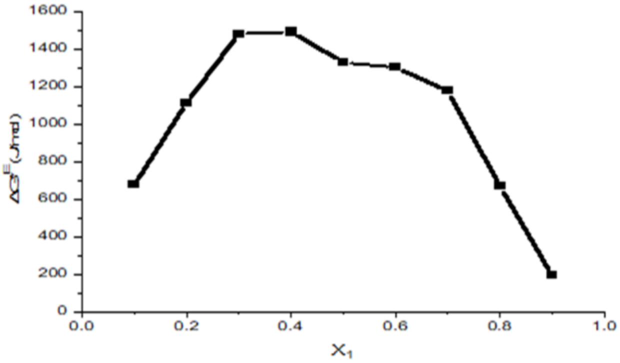


Figure 3: Plot of excess Gibb's free energy (ΔG^{*E}) against mole fractions of DPK (X_1)

SEMI-EMPIRICAL MODELS

The experimental viscosity data were further correlated with semi-empirical model equations to ascertain the nature of interaction between the binary mixtures using the Frenkel model (5), Hind model (6), Grunberg-Nissan model (7), and Kendral-Monroe model (9), respectively. The semi-empirical models in multi-component mixtures have been interpreted to provide the following information:

$$\ln\eta_m = x_1^2\ln\eta_1 + x_2^2\ln\eta_2 + 2x_1x_2\ln\eta_{12} \quad (5)$$

$$\ln\eta_m = 0.5\eta_1 + 0.5\eta_2 \quad (6)$$

$$\ln\eta_m = x_1\ln\eta_1 + x_2\ln\eta_2 + x_1x_2d_{12} \quad (7)$$

$$\eta_m = \left(x_1\eta_1^{1/3} + x_2\eta_2^{1/3}\right)^3 \quad (8)$$

$$E\eta_m = x_1x_2\left(x_1\eta_1^{1/3} + x_2\eta_2^{1/3}\right)^3 \quad (9)$$

Were x_1, x_2 are the mole fractions, η_1, η_2, η_m are the viscosity of pure solvents of DPK, AGO, and mixture.

Interpretation of observed viscosity deviations helps to recognize the models that best define the characteristics of the systems and envisage the interaction parameter that should be improved when the models have multiple contributors (Dikio, 2013). The empirical models of Grunberg-Nissan (d_{12}), Frenkel ($\ln\eta_{12}$), and Kendall-Monroe ($E\eta_m$) were used to evaluate the deviation in viscosities of binary mixtures of DPK and AGO. The values of the empirical relations studied are shown in Table 2. The Grunberg-Nissan interaction parameter (d_{12}) explains qualitative information about the molecular interaction between the individual molecules in a binary liquid mixture. The d_{12} calculated was negative for the whole mole fraction. The negative values of the Grunberg-Nissan parameter show that the binary system of DPK and AGO exhibited weak interaction between the individual molecules and domination of dispersion forces in the system (Kemeakegha *et al.*, 2021). The Frenkel model values were negative, while the Kendall-Monroe model values were positive across the entire composition range for the system studied. The values obtained revealed that all the empirical relations gave a justifiable fit, but the viscosity values generated using Grunberg-Nissan were the lowest, confirming their agreement with the experimental values.

TABLE 2: GRUNBERG-NISSAN, FRENKEL AND KENDALL-MONROE SEMI-EMPIRICAL MODELS FOR BINARY MIXTURES OF DPK AND AGO.

	Grunberg-Nissan	Frenkel	Kendall-Monroe
x_1	d_{12}	$\ln\eta_{12}$	$E\eta_m$
0.9	-1.46	-0.03	0.012
0.8	-0.81	-0.09	0.026
0.7	-0.38	-0.14	0.038
0.6	-0.52	-0.19	0.045
0.5	-0.79	-0.21	0.048
0.4	-0.71	-0.20	0.045
0.3	-0.68	0.15	0.038
0.2	-1.35	0.10	0.026
0.1	-2.39	0.03	0.012

IV. CONCLUSION

The present work investigated the volumetric and viscometric properties of the binary mixture of dual-purpose kerosene (DPK) and automotive gas oil (AGO) at 303 K. Based on the experimental data on density and viscosity, excess molar volume (V_m^E), excess viscosity (ηE), and excess Gibb's free energy of activation of viscous flow (〖ΔG〗 ^(*E)) were determined. The experimental values of viscosity were correlated with the semi-empirical relations of viscosity, such as the Grunberg-Nissan, Frenkel, and Kendall-Monroe models. The experimental result revealed that the binary system shows positive excess molar volume and negative excess viscosity. The observed positive values of (〖ΔG〗 ^(*E)) and negative values of d12 indicate physical interaction between the component molecules, and dispersion forces were predominant in the binary mixtures. We therefore conclude that weak, specific interactions were present in the studied binary liquids at 303 K.

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