THE IJES

Quantum Analysis of Viscosity Coefficient of Multi-Components Liquid Mixtures

[1,] Dikko A. B., [2,] De D. K., [3,] Alkasim A., [4,] Ahmed A. D.

[1, 3,4,] *Department of Physics, School of Pure and Applied Sciences, Modibbo Adama University of Technology, Yola, Nigeria*
[2] *Staff of Kaduna State University, Kaduna, Nigeria.*

--**ABSTRACT**---
A liquid mixture viscosity as a function of composition is extremely complex. Theoretical considerations have offered little help in explaining these complexities. Attempts made so far to derive a generalized expression for viscosities of all mixtures resulted in equations with many undetermined constants, and no method allows a reliable prior prediction of these constants. These methods, therefore, are purely descriptive. In this paper, we made an attempt to analyse the viscosity of liquid mixtures employing Schrödinger equation. We came up with a

model $\psi_i(r)\psi_i(r)^* = \sum_n \psi_{ni}(r)\psi_{ni}(r)^* \exp\left(E_{ni}/K_B T\right)$ *that should account for the viscosity coefficient*

of a liquid mixture when the knowledge of the potential $U_n(r) + \Sigma U_{1-n}(r)$ would be available for the molecules of the liquid mixture.

I.   INTRODUCTION

Some pairs of liquids are miscible in all proportions and complete series of mixed crystals are formed by certain pairs of crystalline solids. Other pairs of liquids and solid substances are practically immiscible. A third group is formed by pairs which are miscible in limited proportions. Miscibility depends upon the temperature, and in general is favoured by the chemical similarity of the substances concerned. Water does not mix with hydrocarbons, is miscible with methyl and ethyl alcohols, partially miscible with butyl and amyl alcohols, but practically immiscible with higher members of the alcohol series. When two partially miscible liquid substances A and B are brought together, then, in general, two layers are formed which contain different proportions of A and B. The composition of these layers so-called conjugate pairs, (Wohlfarth, 2009) depends on the temperature. As a rule, the difference between the conjugates diminishes with rise of temperature and in some cases may ultimately disappear. The temperature at which this occurs is the critical solution temperature and above this the two substances are miscible in all proportions. Increased miscibility is sometimes produced by a fall of temperature and a few pairs of substances are known for which both upper and lower critical temperatures can be observed. Nicotine and water, for example, are completely miscible below 61° C and above 210° C; between these limits they are only partially miscible.

Since the properties of pure liquids are largely dependent on the attractive forces between the molecules, it is extremely unlikely that the relations connecting the properties of liquid mixtures with those of their components can be of the same simple nature as those which characterize the corresponding gaseous systems. In some cases the mixing of two liquids is accompanied by very pronounced changes in volume, by a rise or fall of temperature and by other effects. For other liquid pairs, such effects are so small as to be scarcely measurable. The relations between the properties of liquid mixtures and those of their components may be conveniently shown by plotting the measured property against the composition of the mixture. The property–composition curves obtained in this way sometimes deviate but little from the straight line which corresponds with the simple mixture rule, but for other mixtures large deviations are found, and frequently the curves show a maximum or a minimum, (Hulya, 2000). These deviations result to the excess values which are the differences between the experimental and the theoretical values.

II.   METHOD

For a temperature range from the freezing point to somewhere around the normal boiling temperature, it is often a good approximation to assume that the logarithm of the viscosity of liquids is linear in the reciprocal absolute temperature. In general, pure liquid viscosities at high reduced temperatures are usually correlated with some variation of the law of corresponding states, such as the model by Sastri (1992). At low temperatures, most methods are empirical and involve a group contribution approach. Current liquid mixture correlations are essentially mixing rules relating pure component viscosities to composition. Little theory has been shown to be applicable to estimating liquid viscosities within a reasonable accuracy.

Almost all methods to estimate or correlate liquid mixture viscosities assume that values of the pure component viscosities are available. Thus the methods are, in reality, interpolative. Nevertheless, there is no agreement on the best way to carry out the interpolation. Irving (1977) surveyed more than 50 equations for binary liquid viscosities and classified them by type. He pointed out that only very few do not have some adjustable constant that must be determined by experimental data and the few that do not require such a parameter are applicable only to systems of similar components with comparable viscosities. He recommended the one-constant Grunberg-Nissan equation as being widely applicable with reasonable accuracy except for aqueous solutions (Grunberg and Nissan, 1949

The predictive methods for viscosity of liquid mixtures include semi-theoretical and empirical models. Most semi-theoretical models (Shuai *et al,*1984*;* Barrufet and Setiadarma*,* 2003*;* Al-Besharah *et al,*1987*;* Liu *et al,*1999 and Li, 1992) for petroleum fractions, which have a theoretical framework but parameters determined from experimental data, are based on either the corresponding-states approach or the modified Chapman-Enskog theory. A wide variety of liquid-mixture viscosity prediction formulas (Irving, 1977) use the simple-mixing-rule equation based on calculations of the weighted average of the component viscosities. In order to also contribute by different approaches to get reasonable theoretical model for the analysis of viscosity coefficient of liquid mixtures, we decided to do our approach from the quantum point of view.

III.   RESULTS AND DISCUSSIONS

The viscosity coefficient, μ of a liquid, (De and Dikko, 2012) is given by

$$\mu = B \exp \left(E_a / k_B T \right) \tag{1}$$

For a multi component liquid mixtures

$$\mu = p_1 \mu_1 + p_2 \mu_2 + --- + p_n \mu_n = \sum P_n \mu_n \tag{2}$$

where μ_n is the viscosity coefficient of the liquid component *n*, whose mole fraction in the mixture is P_n, and P_n is related to $V_1, V_2 ----- V_n$ by the equation

$$P_n = \frac{\left(V_n \rho_n / M_n \right)}{\left(V_1 \rho_1 / M_1 + V_2 \rho_2 / M_2 + --- + V_n \rho_n / M_n \right)} \tag{3}$$

where ρ_n and M_n are the densities and molecular weights of the components respectively. The experimentally determined, μ_{ex} will differ from μ of equation (2) by

$$\mu_{ex} = \mu + \mu^E \tag{4}$$

μ^E is the excess viscosity which is a correction to equation (2) arising out of interaction that include clusters formation, caging, etc, (Nagasawa et al, 2003) among the molecules of different components of the liquid mixture. Assuming that the interaction between molecules are of a pair wise nature accomplished by central forces having a potential $U(r)$ and a radial distribution $G(r)$. These two important parameters determine the equation of state of the liquid. If the liquid is assumed to consist of spherically symmetric molecules the equation of state is given by the following equation:

$$\frac{PV}{K_B T} = 1 - \left(\frac{2\pi}{3 V K_B T} \right) \int_0^\infty \frac{dU(r)}{dr} G(r) r^2 dr \tag{5}$$

where *P* is the pressure, Temperature, K_B is the Boltzmann constant and *V* is the average volume per particle of liquid.

In a pure liquid, the distribution function $G_n(r)$ may be written as

$$G_n(r) = \sum_i P_{ni} \psi_n(r) \psi_n(r)^* \tag{6}$$

Ψ_n is the quantum mechanical wave function of a molecule of the liquid type n at position r and the Schrödinger equation for the molecule of nth component liquid may be expressed as

$$\left(\frac{-\hbar^2 \nabla^2}{8\pi^2 m} + U_n(r) \right) \psi_n(r) = E_n \psi_n(r) \tag{7}$$

P_n is expressed in average number of molecules of the nth type per unit volume of the liquid. In a multi-component liquid mixture,

$$G(r) = \sum_{1=n} G_n(r) \quad \text{and} \quad U(r) = \sum_{1-n} \sum U_n(r) + \sum U_{1-n}(r) \tag{8}$$

Where

$$\psi(r) = \sum_i (p_n)^{\frac{1}{n}} \psi_n \tag{9}$$

The overall Schrödinger equation for the mixture of liquids may be written as

$$\left[-\frac{\hbar^2 \nabla^2}{2m} + U(r) \right] \Psi(r) = E\Psi(r) \tag{10}$$

$U(r)$ is the potential at a point r arising out of interaction between molecules in the liquid mixture. The exponent $\frac{1}{n}$ of p_n in the expression for $\Psi(r)$ in equation (9) is based on the assumption that the probability of finding a molecule of the nth type liquid in a small volume ΔV of the liquid mixture about the position r should be proportional to $p_n V$ and not to any other power of $p_n V$. The average energy per particle can then be written as:

$$E = 3k_B \frac{T}{2} + \left(\frac{\pi}{V}\right) \int_0^\infty U(r)G(r)r^2 dr \tag{11}$$

$G_n(r)$ depends on P_n of equation (2). Ideally it is expected to have also an implicit dependence on temperature also, at least through the term P. E is the activation energy embedded in the second term of the above equation (11) for the average energy. Once E_a can be evaluated, the μ of the resulting liquid mixture and hence μ^E can be evaluated from equations (1) and (11). This correction of μ^E is obviously a function of P_n, true nature of which is not yet theoretically known but expected to be obtained from above equations.

The detailed explanation for this very interesting observation from the molecular physics point of view is left for future work including the theoretical computation of μ^E from above model. Once μ^E can be understood theoretically then equations (2) - (4) can form the basis of a new emerging technology of analyzing the concentration of the liquid components of any liquid mixture which does not contain dissolved solid materials.

From equation (11) the temperature variation of activation energy E_a can be accounted for in the first order by considering the thermal expansion of the volume and consequently the thermal variation of G(r) through the term P. It may be mentioned that the thermal expansion coefficients (Cutnell *et al*, 1995) for methyl alcohol, ethyl alcohol and water respectively: 1240, 1200 and 207 times 10^{-6}. From above theory it is expected that $-\delta E_a/\delta T$ for ethyl alcohol would be about six times than for alcohol-water mixtures. This latter theoretical conjecture yet remains to be validated by experiments. One thing that is clear from the above model is that it can clearly account for the decrease of μ of liquid with temperature. Another dependence on temperature may also come from the Boltzmann population of the different eigen energy levels E of equation (6) in which case $\Psi(r)\Psi_i(r)^*$ in equation (6) may be replaced as

$$\psi_i(r)\psi_i(r)^* = \sum_n \psi_{ni}(r)\psi_{ni}(r)^* \exp\left(E_{ni}/K_B T\right) \tag{12}$$

When the knowledge of $U_n(r) + \Sigma U_{1-n}(r)$ would be available for the molecules of the liquid mixture, the above model together with equation (1) should account for the viscosity coefficient of a liquid mixture.

IV. CONCLUSION

The model developed in this paper reveals that with further studies and the knowledge of the potential for the molecules of the liquid mixture, a better theoretical model can be developed for the analysis of multi-component liquid mixtures.

REFERENCES

[1] Al-Besharah, J.M., Salman, O.A., and Akashah, S.A., (1987) "Viscosity of Crude Oil Blends," *Industrial & Engineering Chemical Research*, **Vol. 26**, pp. 2445-2449.

[2] Barrufet, M.A., and Setiadarma A., (2003), "Reliable Heavy Oil-Solvent Viscosity Mixing Rules for Viscosities up to 450 K, Oil-Solvent Viscosity Ratios up to 4×105, and any Solvent Proportion," *Fluid Phase Equilibria*, **Vol. 213** pp. 65-79.

[3] Cutnell, J.D. and Jhonson K. (1995) W. PHYSICS 3RD Edition, *John* Wiley & Sons, Inc. pp.367

[4] D. K. De and A. B. Dikko, (2012), An Innovative Technique of Liquid Purity Analysis and its Application to Analysis of Water Concentration in Alcohol-water Mixtures and Studies on Change of Activation Energies of the Mixtures, *Applied Physics Research, Canadian Center of Science and Education.* **Vol.4 No.4** pp. 98 -114

[5] Hulya, Y. (2000), Excess Properties of Alcohol - Water Systems at 298.15 K. *Turk J Phys* **26** , pp 243 = 246

[6] Irving, J.B., (1977) "Viscosity of Binary Liquid Mixtures: The Effectiveness of Mixture Eq.s," *National Engineering Laboratory Report*, **No. 630**, East Kilbride, Glasgow, Scotland.

[7] Li, C.,(1992) "Rheological Behavior of Crude Oil Blends," *MS Thesis*, China University of Petroleum-Beijing.

[8] Liu, T., Sun, W., Gao, Y., and Xu, C. (1999), "Study on the Ordinary Temperature Transportation process of Multi-Blended Crude," *Oil & Gas Storage and Transportation*, **Vol. 18**, pp. 1-7.

[9] Nagasawa, Y, Y. Naka-gawa, A. Nagafuji, T. Okada and H. Miyasaka, (2003), *J. Mol. Structure*, J. P., pp.217-223.

[10] Shuai Wan, Zheng Wei, Xiaopeng Chen and Jie Gao, (2009) Pendant Drop Method for Interfacial Tension Measurement Based on Edge Detection Method. *IEEE*, **978**,1-4244-4131.

[11] Wohlfarth C. (2009), Viscosity of Pure Organic Liquids and Binary liquid Mixture. *Lechner Manfred Dieter (Ed)*, **V II**, 376pp.