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Viscometric investigation of binary, ternary and quaternary liquid mixtures: Comparative evaluation of correlative and predictive models

Ranjan Dey *, Aditya Harshavardhan, Shashwat Verma

Department of Chemistry, BITS Pilani K K Birla Goa Campus, Zuarinagar 403726 Goa, India

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ABSTRACT

Transport properties provide a deep and meaningful insight of the various interactions taking place in binary and higher component liquid mixture. Literature reveals scarcity of data on ternary and higher order multicomponent liquid mixtures. Absolute viscosities of four binary, one ternary and one quaternary systems containing benzene, cyclohexane, n-hexane and n-decane at 298.15 K have been evaluated. These systems have significant usage and applications in multifarious industries, viz., chemical, pharmaceutical, and petrochemical. Sixteen approaches have been employed involving empirical, semi-empirical, correlative and predictive models including McAllister 3 and 4 body, Grunberg–Nissan, Wijk, Hind, Katti-Chaudhri and Tamura–Kurata. The absolute average percentage deviations (AAPDs) have been used to compare their predictive capabilities. The modified McAllister relation, which employs the ECN approach developed for 308 K, shows its versatility by proving its validity even at 298.15 K.

1. Introduction

Over the years, studies of transport properties have been undertaken by several workers due to their applicability in terms of design calculations. Amongst all the transport properties under investigation, viscosity studies have been the most actively pursued researched parameter owing to its multi dimensional industrial application especially in the field of petrochemicals and reservoir engineering. Furthermore the study of viscosity assumes enormous significance in the light of process & product design where momentum transport plays a key role. Viscosity data provides a valuable insight [1–4] into the structure and interactions in mixed solvents and is needed to evaluate mass transport and heat transfer operations by proving its utility in various design aspects especially for pipeline and fluid flow calculations. Keeping in view the demands of the industry, viscosity measurements [5–8] of binary and higher order liquid mixtures find immense significance in heat exchangers, mixers, agitators etc.

An exhaustive literature survey points towards a critical shortage of viscosity data pertaining to ternary and higher order multicomponent liquid mixtures. This lack of data stems from the difficulty arising in the estimation of viscosity with the addition of a new component beyond the binary. Hence, such a study comprising of the evaluation of aforementioned parameter for ternary and higher order multicomponent liquid mixtures assumes primary importance. Literature survey [2,4,7,8] also reveals the absence of a universal viscosity model for prediction of higher order liquid mixtures from properties of pure components. The aim of the present investigation is an attempt in that direction.

In the last decades, a number of empirical, semi-empirical, correlative and predictive equations have been proposed by several workers and can be found in literature. These include some well known approaches [7,9] like the ones proposed by Kendall–Munroe, Frenkel, Hind–Ubbelhode, Bingham, Additive relations, etc. Flory theory [7] and the Bertrand–Acree–Burchfield (BAB) approach have also been employed to compute viscosity of multicomponent liquid mixtures. A number of correlative models for predicting viscosity have been proposed viz., Redlich–Kister [10,11], Grunberg–Nissan [12,13], Katti–Chaudhri [14,15], McAllister [16], Eyring absolute rate theory model [17], corresponding-state theory, significant structure theory, group contribution method and model based on kinetic theory [18]. A very comprehensive review of the entire empirical, semi empirical and other methods employed for the estimation of viscosity of binary liquid mixtures has been carried out by Lee and Lee [18]. Comparatively lesser work has been done on the experimental and theoretical aspects of viscosity of multicomponent liquid systems [19]. A study of literature reveals that very few studies are available related to viscosity of multicomponent liquid mixtures beyond ternary [20–22].

For the present investigation, sixteen viscosity models, comprising of empirical, semi-empirical, correlative and predictive approaches have been put to test. The various predictive viscosity models employed are Bingham [7], Frenkel [8,17], Kendall–Munroe [17], Hind–Ubbelhode [23], Eyring [17], Gambill [24,25], Refutas [26] and Sutherland–Wassiljewa [17,27] relation. Seven correlative methods have also been

* Corresponding author.
E-mail address: ranjandey@goa.bits-pilani.ac.in (R. Dey).

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employed viz., Hind [13,28–30], Grunberg–Nissan, Wijk [13,31], Katti–Chaudhri, Tamura–Kurata [15,32], McAllister 3 body [16] and 4 body [13,33] models. Furthermore, a modified McAllister relation pioneered by Nhaesi–Asfour [34] has also been utilized which employs a method for calculating values of the binary interaction parameters of the McAllister 3 body model by using the pure component properties. In the process, the correlative nature of the McAllister equation gets converted to a predictive approach. This approach makes use of the Effective Carbon Number (ECN) [35] of non n-alkane compounds.

These viscosity models have been put to test to check their validity and applicability over binary, ternary and quaternary liquid mixtures. The evaluated results have been compared with the experimental data leading to a comparative study as regards their merits/demerits. The experimental viscosity values and the parameters of the pure components for the present investigation have been taken from literature [36].

In the present investigation, viscosities have been computed at 298.15 K over the entire mole fraction range by the aforementioned approaches for:

Four binary systems:
- cyclohexane (1) + benzene (2)
- n-hexane (1) + cyclohexane (2)
- n-hexane (1) + benzene (2)
- n-decane (1) + cyclohexane (2)

One ternary system:
- n-hexane (1) + cyclohexane (2) + benzene (3)

One quaternary system:
- n-decane (1) + n-hexane (2) + cyclohexane (3) + benzene (4)

2. Theory

Various models using different approaches [37] have been employed for the evaluation of viscosity at 298.15 K.

The relation proposed by Bingham [7] who took into consideration the ideal mixing of solutions, for binary mixtures is given by:

$$\eta = x_1\eta_1 + x_2\eta_2 \tag{1}$$

where x_1 and x_2 represent the mole fractions of two components and $\eta_1$and η_2 represents their viscosities in the pure state.

Kendall and Munroe [17] proposed the viscosity relation by taking the logarithmic additives. The viscosity expression for the binary system assumes the form

$$\ln\eta = x_1 \ln\eta_1 + x_2 \ln\eta_2. \tag{2}$$

But these equations have been proposed by taking into account the ideal mixing of solutions, which is not always true.

Frenkel [8,17] took into consideration the interaction between molecules and developed the following logarithmic relation for non-ideal binary mixtures,

$$\ln\eta = x_1^2 \ln\eta_1 + x_2^2 \ln\eta_2 + x_1x_2 \ln\eta_{12}. \tag{3}$$

where η_{12} is a constant.

For binary liquid mixtures, the relation suggested by Hind & Ubbelhode [23] takes the form

$$\eta = x_1^2\eta_1 + x_2^2\eta_2 + 2x_1x_2\eta_{12}. \tag{4}$$

The relation proposed by Eyring [17] for the binary liquid mixtures is given by

$$\ln\ \eta V = x_1(\ln\ \eta_1V_1) + x_2(\ln\ \eta_2V_2) \tag{5}$$

where all the symbols have their usual meaning.

Gambill's relation [24,25] for kinematic viscosity of the mixture is given by:

$$\nu^{1/3} = x_a\nu_a^{\frac{1}{3}} + x_b\nu_b^{\frac{1}{3}}. \tag{6}$$

Refutas [26] used the Viscosity Blend Number (VBN) concept to compute viscosity by proposing:

$$\mathrm{VBN_i} = 14.534\{\ \ln[\ln(\nu_i + 0.8)]\} + 10.975 \tag{7}$$

$$\mathrm{VBN_m} = \Sigma_{i=1}^{n} x_i\mathrm{VBN_i} \tag{8}$$

$$\nu_m = \exp\left(\exp\left(\frac{\mathrm{VBN_m} - 10.975}{14.534}\right)\right). \tag{9}$$

Sutherland–Wassiljewa [17,27] developed a relation to compute viscosity which is given as:

$$\eta = \Sigma_i \frac{x_i\eta_i}{\Sigma_j A_{ji}x_j} \tag{10}$$

A_{ij} and A_{ji} are the adjustable parameters called Wassiljewa coefficients and are given by

$$A_{ij} = \frac{1}{4}\left[1 + \left(\frac{\eta_i}{\eta_j}\right)^{1/2}\left(\frac{M_j}{M_i}\right)^{3/8}\right]. \tag{11}$$

McAllister [16] propounded the three body interaction approach and proposed the correlative model by developing the cubic equation on the basis of Eyring's absolute rate theory for calculating kinematic viscosities of liquid mixtures [28,29]. The equation takes the form:

$$\begin{aligned}\ln(\nu) = &\sum_i^n x_i^3 \ln(\nu_i M_i) - \ln\left(\sum_i^n x_i M_i\right) \\ &+ 3\sum_i^n \sum_{\substack{j \\ j\neq i}}^n x_i^2 x_j \ln(A_{ij}M_{ij}) \\ &+ 6\sum_i^n \sum_{\substack{j \\ j\neq i}}^n \sum_{\substack{k \\ k>j}}^n x_i x_j x_k \ln(A_{ijk}M_{ijk})\end{aligned} \tag{12}$$

where A_{ij} and A_{ji} are the interaction parameters and

$$M_{ij} = \frac{2M_i + M_j}{3}$$

$$M_{ijk} = \frac{M_i + M_j + M_k}{3}.$$

McAllister further introduced the four body interaction model [13,33] wherein he visualized a three dimensional treatment [16]. This model presents a more practical and realistic picture than the 3 body