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Empirical and Semi-theoretical Methods for Predicting the Viscosity of Binary *n*-Alkane Mixtures[1]

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In this study, empirical and semi-theoretical methods for predicting the viscosity of binary mixtures of *n*-alkanes are presented at atmospheric pressure and in the temperature range from 288 to 333 K. In the empirical viscosity calculation method, a modified version of the Andrade equation and a simple mixture rule are used. The proposed semi-theoretical method employs both the Enskog's hard-sphere theory for dense fluids and the principle of corresponding states. The viscosities of binary mixtures of *n*-heptane with *n*-hexane and *n*-nonane covering different compositions were calculated using these methods which require only critical properties and the normal boiling point as input data. The predictions were compared with accurate experimental data in the literature. Highly satisfactory results were obtained. The percent average absolute deviations amount to 1.2 and 0.9% utilizing the empirical and semi-theoretical viscosity methods, respectively, for 27 data points.

KEY WORDS: binary *n*-alkane mixtures; empirical viscosity calculation method; hydrocarbons; semi-theoretical viscosity prediction method; viscosity.

1. INTRODUCTION

Viscosity data of pure organic liquids and their mixtures are indispensable for process design in petrochemical and chemical industries. Unfortunately, reliable data on this important physical property are not abundant due to several experimental difficulties in its measurement [1–6]. However,

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several empirical, semi-theoretical, and theoretical models for predicting the viscosity of pure components and mixtures are available in the literature as described in several excellent reviews [7–9].

All of the viscosity methods of hydrocarbon mixtures use mixing rules. The mixture rules were used extensively by the well known McAllister, Tham and Gubbins, Mo and Gubbins, Grunberg Nissan, and Di-Pippo methods [7, 8–10]. Empirical viscosity methods use mixing rules and/or parameters correlated with mixture ratio–viscosity, pressure–viscosity, or temperature–viscosity equations [7, 11–16]. Semi-theoretical models have a sound theoretical background, but the parameters are obtained from experimental data. Semi-theoretical models use one of the following theories: the principle of corresponding states, statistical mechanics model, reaction rate theory, square well theory, Lennard-Jones, hard-sphere theory, or their modifications [8, 9]. Ely and Hanley [17] suggested the extended corresponding states approach. Other similar methods of viscosity predictions are available in the literature [18–20]. Assael et al. [4, 5] applied Dymond's approach to the Enskog hard-sphere theory. Another of their studies were based on the hard-sphere theory of Dymond–Assael [10, 21–22].

Our prediction methods for viscosity are based on empirical and semi-theoretical methods. The proposed empirical method employs a modified version of the Andrade equation [11–16, 23, 24, 26] to predict viscosities of binary *n*-alkane mixtures. The semi-theoretical method has a sound theoretical background. This method requires minimum and easily obtainable data as input. The proposed semi-theoretical method, based on both the Enskog's hard-sphere theory for dense fluids and the principle of corresponding states, was successfully applied for predicting the viscosity and thermal conductivity of pure organic liquids. In our previous studies, we considered viscosities of pure organic liquids (C_5–C_{20}) and light petroleum fractions (C_5–C_{15}). The average absolute deviations were 2% for 75 pure hydrocarbon and 42 petroleum fractions. Details are presented elsewhere [24–27]. The viscosity measurements of binary *n*-alkane mixtures were performed with the vibrating-wire instrument by Assael et al. [4, 5]. The uncertainty of the viscosity data was estimated to be ±0.5%. In this work, predicted viscosities of binary *n*-alkane mixtures would be compared with the accurate experimental measurements mentioned above.

2. EMPIRICAL AND SEMI-THEORETICAL METHODS

In this study, empirical and semi-theoretical methods are presented for predicting the viscosity of binary mixtures of *n*-heptane with *n*-hexane and *n*-nonane at four different compositions and temperatures.

2.1. Empirical Viscosity Method

In this work, the viscosity of mixture was calculated via the following equation:

$$\eta_{\mathrm{mix}} = \sum x_i \eta_i \tag{1}$$

The critical properties (T_{c},P_{c}), the molar mass (M), and the normal boiling point (T_{b}) were calculated according to simple combination rules.

$$T_{\mathrm{c}} = \sum x_i T_{\mathrm{c}i} \tag{2}$$

$$P_{\mathrm{c}} = \sum x_i P_{\mathrm{c}i} \tag{3}$$

$$M = \sum x_i M_i \tag{4}$$

$$T_{\mathrm{b}} = \sum x_i T_{\mathrm{b}i} \tag{5}$$

x_i is the mass fraction for component *i*. Here, the empirical viscosity method, developed for binary *n*-alkane mixtures and based on the Andrade [11] equation utilizing T_{r} and η^* instead of T and η, respectively, is used.

$$\log \eta * = -A + B / T_{\mathrm{r}} \tag{6}$$

η^* is the reduced dynamic viscosity, converted to the dynamic viscosity via the following equation:

$$\eta = \eta * T_{\mathrm{c}}^{-1/6} M^{1/2} P_{\mathrm{c}}^{-2/3} \tag{7}$$

where T_{r} is the reduced temperature, T/T_{c}. The parameters A and B were calculated for 75 organic liquids separately using as many experimental viscosity-temperature data points as available. Details are presented elsewhere [26].

2.2. Semi-Theoretical Viscosity Method

The semi-theoretical method based on Enskog's hard-sphere theory for dense fluids and the principle of corresponding states was proposed and successfully applied for predicting the viscosity of pure organic liquids and petroleum fractions. Details of the methodology are presented elsewhere [24–27].

This work is based on the following model for the dynamic viscosity of liquids: at a given reduced temperature and pressure, the reduced dynamic viscosity η^* can be calculated by adding a correction term to the reduced dynamic viscosity of a simple monatomic liquid at the same reduced conditions. At low and moderate pressures, the effect of pressure on the liquid dynamic viscosity can be neglected. According to the proposed method [24–27], the reduced dynamic viscosity of liquid mixtures (η^*) at a given reduced temperature (T_r) and 0.1 MPa, can be calculated by adding a correction term ($\eta^*{}_f$) to the reduced dynamic viscosity term of pure organic liquids ($\eta^*{}_m$). $\eta^*$is determined as follows:

$$\eta * (T_r, \theta) = \eta_m * (T_r) + \eta *_f (T_r, \theta) \tag{8}$$

where $\eta^*{}_m$ is the reduced dynamic viscosity of a monatomic liquid and $\eta^*{}_f$ is a correction term which employs the θ parameter. θ was selected as the best choice for all organic liquid groups where θ is the reduced temperature at the normal boiling point. θ is calculated for mixtures as follows:

$$\theta = \sum x_i T_{bi} / \sum x_i T_{ci} \tag{9}$$

In our work, $\eta^*{}_m$was determined for n-alkanes;

$$\eta_m * = 10^{-9}[6.799 - 8.760T_r + 2.816T_r^2] \tag{10}$$

Although it is developed for n-alkanes, Eq. (10) proved to be satisfactory for other kinds of organic liquids and their mixtures as well. The $\eta^*{}_f$ (T_r, θ) function was determined for alkanes according to the following equations:

$$\eta *_f (T_r, \theta) = \eta_f^{/}(T_r)\eta_f^{//}(\theta) \tag{11}$$

$$\eta *_f (T_r, \theta) = 0.0271T_r^{-5.285}[-130.5 + 720.5\theta - 1329\theta^2 + 825.1\theta^3] \tag{12}$$

The reduced dynamic viscosity (η^*) of pure organic liquids is calculated using Eqs. (8)–(12). The reduced dynamic viscosity is converted to the dynamic viscosity via Eq. (7). Finally, the dynamic viscosity of binary *n*-alkane mixtures is determined according to Eq. (1). In this work, predicted viscosities of binary *n*-alkane mixtures were compared with accurate experimental data measured by Assael et al. [4]. The percent average absolute deviations were obtained by the following equation:

$$\mathrm{AAD}\ (\%) = \frac{100}{27}\sum_{i=1}^{27}\left(\frac{\left|\eta_{i,\mathrm{calc}} - \eta_{i,\mathrm{exp}}\right|}{\eta_{i,\mathrm{exp}}}\right) \tag{13}$$

3. RESULTS

Table I summarizes the calculated average absolute deviations with empirical and semi-theoretical methods. The average absolute deviations were 1.25 and 0.87%, respectively, for 27 data points. Figure 1 shows comparisons of the calculated viscosity values of mixtures using the empirical method with experimental viscosity values. Figure 2 shows comparisons for *n*-alkane mixtures for the calculated viscosities using the semi-theoretical method with experimental viscosities.

The empirical viscosity results from this study are as accurate as the other empirical methods covered in Table II. Table III summarizes the average deviations of selected organic liquid mixture viscosities according to several semi-theoretical methods. When compared with others published recently, the proposed empirical and semi-theoretical viscosity correlations yield highly satisfactory results for mixtures.

4. CONCLUSION

In conclusion, for predicting viscosities of binary *n*-alkane liquid mixtures over a wide temperature range at atmospheric pressure, the correlations developed in this study have some advantages over other such correlations. Utilization of both the principle of corresponding states and Enskog's hard-sphere theory for dense fluids has led to practical and accurate viscosity predictions for mixtures.

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Table I. Empirical and Semi-Theoretical Viscosity Calculation Results

n-Alkane mixtures	Temperature range (K)	Data points	Empirical AAD[a] (MAD[b]) %	Semi-theoretical AAD (MAD) %
n-Heptane + *n*-Hexane	288.28–323.23	14	0.510 (0.933)	0.618 (0.965)
n-Heptane + *n*-Nonane	293.75–333.25	13	2.046 (4.478)	1.138 (2.183)
Total	288.28–333.25	27	1.249 (4.478)	0.869 (2.183)

[a] AAD $(\%) = \frac{100}{27}\sum_{i=1}^{27}\left(\frac{|\eta_{i,\mathrm{calc}} - \eta_{i,\mathrm{exp}}|}{\eta_{i,\mathrm{exp}}}\right)$, average absolute deviation.

[b] MAD, maximum absolute deviation.

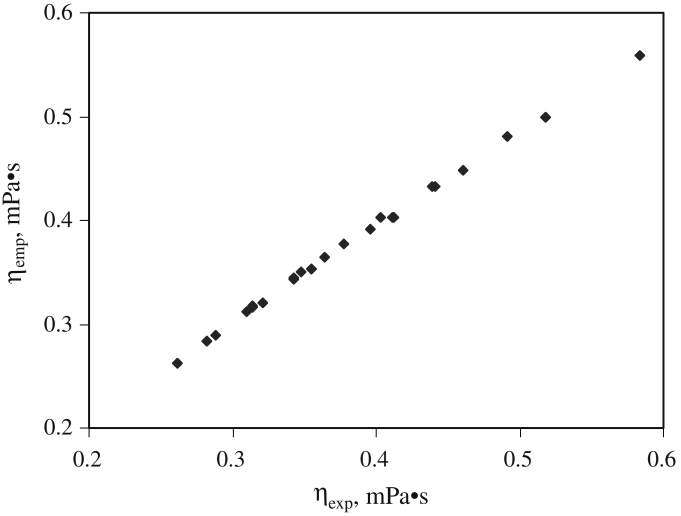

Fig. 1. Comparison of the calculated empirical viscosity results and experimental viscosities of mixtures.

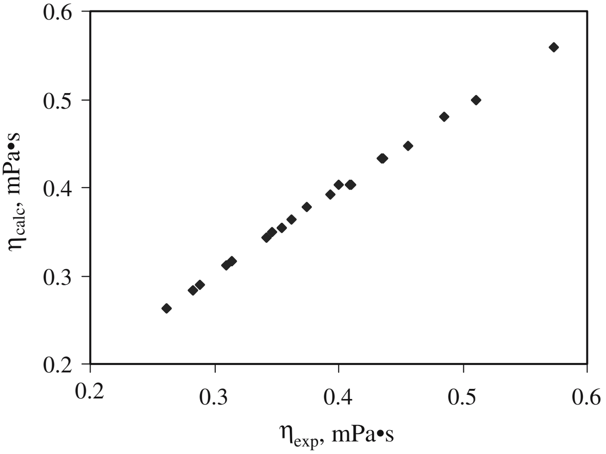

Fig. 2. Comparison of the calculated semi-theoretical viscosity results and experimental viscosities of mixtures.

Table II. Empirical Methods for Viscosity Predictions of Pure Organic Liquid Mixtures

Methods	Mixtures	Correlations	Data points	Average accuracy (%)
Lee (1966) [12]	*n*-Metane-*n*-Decane	Simple Mixture Rule	217	<4
Katti (1966) [13]	Benzene–Cyclohexane, Carbontetrachloride–Cyclohexane, Carbontetrachloride–Benzene	Grunberg–Nissan	26	5.7–17.6
Mussche-Verhoeye (1975) [14]	10 binary and 1 ternary	Mc-Allister Heric	169	1–3 4–5
Aasen (1990) [2]	7 mixtures	Arrhenius – Doolittle	35	1.9–3.8
Serrano (1990) [1]	3 binary and 1ternary	Mc-Allister	221	0.3–0.4
Alan and Teja (1991) [15]	11 binary mixtures	Simple Mixture Rule, ECN	353	5.8
Our Method (2002)	*n*-Heptane + *n*-Hexane, *n*-Heptane + *n*-Nonane	Simple Mixture Rule, Andrade	27	1.2

Table III. Semi-Theoretical Methods for Viscosity Predictions of Pure Organic Liquid Mixtures

Methods	Mixtures	Correlation[a]	Data points	Average accuracy (%)
Ely-Hanley (1981) [17]	26 binary	ECSP	455	7
Teja-Rice (1981) [18]	29 binary	ECSP	1010	3.8
Wei-Rowley (1984) [19]	24 binary	NRTL	191	1.6–5.2
Ducoulombier (1986) [20]	4 binary and 1 ternary	ECSP	63	10.6
Assael (1992) [4]	3 binary	EHST	114	<3.5
Assael (1992) [5]	32 binary, 2 ternary, 3 quaternary	EHST	1284	>5
Assael (2000) [6]	*n*-Hexane + Toluene	Dymond–Assael	21	7
	n-Hexane + Cyclohexane		14	5
Assael (2001) [21]	n-Hexane + n-Heptane	Dymond–Assael	35	9.5
Our Method (2002)	*n*-Heptane + *n*-Hexane, *n*-Heptane + *n*-Nonane	ECSP and EHST	27	0.9

[a] ECSP: extended corresponding states principle; EHST: Enskog's hard-sphere theory; NRTL: nonrandom two-liquid.

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