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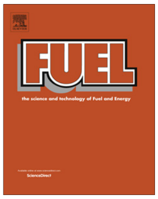

Full Length Article

Predicting the viscosity of n-alkane liquid mixtures based on molecular description

Thanh-Binh Nguyen [a,b], Nicolas Riesco [a,b], Velisa Vesovic [a,*]

[a] *Department of Earth Science and Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, United Kingdom*
[b] *Qatar Carbonates and Carbon Storage Research Centre (QCCSRC), Imperial College London, London SW7 2AZ, United Kingdom*

HIGHLIGHTS

- A new model has been developed to predict the viscosity of liquid mixtures.
- The mixture is represented by a single pseudo-component.
- The characterization is by an appropriate molecular weight.
- The model was validated using data on n-alkane mixtures.
- It is a first step in dealing with industrial fluids of ill-defined composition.

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ABSTRACT

A new model has been developed to predict the viscosity of liquid, n-alkane mixtures. It represents a mixture by a single pseudo-component characterized by an appropriate molecular weight and calculates the viscosity by means of the modified, extended hard-sphere model (EHS) that makes use of an universal function relating reduced viscosity to reduced volume. For mixtures that contain n-alkanes with a similar number of carbon atoms, the molecular weight of the pseudo-component is simply given by the molecular weight of the mixture. For more asymmetric mixtures, the choice of the molecular weight is a function of the difference in the number of carbon atoms, between the longest and the shortest chain. The proposed model is a precursor of a new family of models that do not require the knowledge of detailed composition of the mixture, but still take advantage of the underlying molecular description. The developed model, named 1-component Extended Hard-Sphere (1-cEHS), predicted, in general, the viscosity of binary and multicomponent n-alkane mixtures with uncertainty of 5%, even when the mixtures contain very long n-alkanes. For highly asymmetric binary mixtures of alkanes the predictions deteriorated, but improved for highly asymmetric multicomponent mixtures indicating that the presence of the intermediate alkane species leads to a better prediction.

We have also tested two other viscosity models, the extended hard sphere (EHS) and Vesovic-Wakeham (VW), that also rely on kinetic theory to provide the molecular description, but require a full compositional specification of the mixture. They can also predict the viscosity within 5%, but the presence of the long chain n-alkanes in a mixture as well as the high asymmetry, leads to deterioration of the prediction.

1. Introduction

In numerous industrial applications that involve the flow of fluids, knowledge of the viscosity is an essential pre-requisite for good design and optimal operations [1,2]. The plethora of conditions and fluids of interest, primarily mixtures, precludes relying on experimental means alone. The experimental data has to be supplemented by models that can predict the viscosity of fluids as a function of temperature, pressure and composition. The development of generic, predictive models is best achieved if such models have some basis in the underlying physical theory. This ensures reliability and accuracy with well-defined estimates of uncertainty that are essential for any engineering applications. For dilute gases, where only the binary molecular interactions are present, it is possible not only to establish a rigorous molecular description of

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[*] Corresponding author.
E-mail address: v.vesovic@imperial.ac.uk (V. Vesovic).

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the viscosity, but also to make use of it to compute the viscosity directly from precise, ab initio intermolecular potentials. At low pressure, in the limit of zero density, we are now in position to calculate the viscosity of gases consisting of simple molecules, both pure and mixtures, with an uncertainty commensurate with the best experimental measurements over a wide temperature range [3–9].

The situation for liquids is markedly different as the underlying theory of viscosity is incomplete. Consequently a number of different approximate approaches have been taken to model viscosity resulting in numerous models available in literature. They range from the purely empirical and correlative, where the experimental data used govern both the form and predictive power of the model, to semi-theoretical, where approximations made allow for sufficient simplification. Although kinetic theory would be a natural choice for the development of the theoretical basis, a lack of a proper generalization of the Boltzmann equation for liquids has hampered progress and led to other formulations based on approaches that do not necessarily take molecular description as the starting point. Successful viscosity models have been proposed based on the corresponding states theory [10–17], free-volume concept [18–21], the friction theory [22–26], the relationship with residual entropy [27–30], density scaling [31–33], the effective carbon number approach [34,35] and the expanded fluid based approach [36–38] among others.

In this work we limit our investigation to modelling viscosity of liquids based on a molecular approach using the kinetic theory as our starting point. For liquids and dense fluids in general the only tractable solutions developed to date are based on the assumption that the molecules interact as hard spheres and that their collisions are uncorrelated. The resulting Enskog equation [39] for the viscosity of a dense hard-sphere fluid has formed the basis for several semi-theoretical approaches, two of which in particular have found practical application: the Assael and Dymond (AD) approach [40,41] and the Vesovic-Wakeham (VW) model [42–45]. The former was initially developed for pure species and subsequently extended to mixtures, while the latter is the model for predicting the mixture viscosity based on the knowledge of the viscosity of pure species making up the mixture. In line with most methods for predicting the thermophysical properties, both models make use of mixing rules to evaluate a limited number of mixture parameters. Although the VW mixing rules are theoretically based, unlike the AD ones and most others used in viscosity models, one still requires a detailed composition of the mixture. For compositionally well-defined mixtures this is not an issue, as this is a readily available information. However, for most fluids of industrial interest (oil, heavier refinery fractions, coal liquids, pharmaceuticals) that may contain a large number of components, isomeric species or ill-defined large species, this is not the case. In this instance a different formulation is required which forfeits the full compositional formulation and usually relies on describing the mixture in terms of pseudo-components.

Here, we present a novel molecular model that represents the viscosity of the multicomponent mixture by a viscosity of a single pseudo-component which is characterized by an appropriate molecular weight. The model is based on the extended hard-sphere (EHS) approach [46,47], and hence retains the best available description in terms of the underlying molecular theory. It is important to point out that in this work we use the term pseudo-component in its most generic form implying not a real component, used to simplify the compositional description of the mixture. The concept of the single pseudo-component used here is thus different from pseudo-components as used in oil and gas processing (sub-surface and surface) or product design and development where the pseudo-component applications are not solely based on molecular weight and are often used for estimation of a wider range of properties. A number of empirical methods [34,35] have also used a single pseudo-component concept, defined by an effective carbon number rather than molecular weight, to predict the viscosity of oil and coal liquids with some success, but require at least a single viscosity measurement to obtain the effective carbon number.

We have tested the proposed model by validating it against a data set consisting of viscosity of liquid, *n*-alkane mixtures and have compared its performance to the performance of the EHS and VW models, the other two viscosity models that have basis in kinetic theory. The choice of *n*-alkane mixtures as a first test of the validity and accuracy of the proposed model was made for a number of reasons. Normal alkanes are one of the important classes of constituents of oil and are ubiquitous in petroleum and chemical processes. There exist numerous experimental viscosity data for *n*-alkane mixtures of low uncertainty, covering wide range of mixture composition and to a certain extent temperature and pressure. Presence of long-chain *n*-alkane species in the mixture will increase viscosity significantly, thus providing a stern test of the models. Normal alkanes structurally resemble long chains made up of ($-CH_2$) units and thus are ideal to test the usefulness of models consisting of chain-like molecules that are predominantly used in Molecular Dynamics simulations. Finally, *n*-alkanes are usually used as a precursor to developing models to predict the viscosity of fluids encountered in the petrochemical and chemical industries, where more complex molecular structures of hydrocarbon or non-hydrocarbon species may prevail.

In Section 2 we summarize the EHS model focusing on its most relevant features and use it as the basis for presenting the new model for mixtures. We complete the section by briefly summarizing the VW model. In Section 3 we compare the three models in their ability to predict the viscosity of liquid mixtures, containing *n*-alkane species. The comparison covers, binary mixtures, multicomponent mixtures, mixtures containing long-chain *n*-alkanes, and mixtures containing light *n*-alkanes.

2. Methodology

2.1. The extended Hard-Sphere model with traditional mixing rules

The recently proposed extended hard-sphere model [46,47] is the latest modification of the original hard-sphere model of Assael, Dymond and their collaborators [40,41]. The original method was developed to predict the viscosity of pure fluids by postulating that the reduced viscosity, η^*, is an universal function of the reduced molar volume, $V^* = V_m/V_0$. In applications to real fluids the molar core volume, V_0, is a weakly temperature-dependent adjustable parameter. Recently, a slight modification of the extended hard-sphere model [47] was proposed in order to ensure that the model can adequately describe the viscosity of pure, long chain *n*-alkanes up to tetratetracontane (n-$C_{44}H_{90}$) within ±5 % at atmospheric pressure and temperatures below 400 K. As this model forms the basis of the developments presented in this work, we will briefly summarize its main features.

The essence of the model is the universal correlation of the form,

$$\log_{10}(1+\Delta\eta^*) = \sum_{i=1}^{7} a_i/(V^*)^i, \tag{1}$$

where the coefficients a_i are given in the original work. The reduced excess viscosity, $\Delta\eta^*$, is defined by Ciotta et al. [46],

$$\Delta\eta^* \equiv \frac{16}{5}(2N_A)^{1/3}\left(\frac{\pi}{MRT}\right)^{1/2} V_m^{2/3}\left(\frac{\eta-\eta^{(0)}}{R_\eta}\right), \tag{2}$$