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Estimation of pure component properties. Part 4: Estimation of the saturated liquid viscosity of non-electrolyte organic compounds via group contributions and group interactions

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ABSTRACT

A new group contribution method for the prediction of pure component saturated liquid viscosity has been developed. The method is an extension of the pure component property estimation techniques that we have developed for normal boiling points, critical property data, and vapour pressures. Predictions can be made from simply having knowledge of the molecular structure of the compound. In addition, the structural group definitions for the method are identical to those proposed for estimation of saturated vapour pressures. Structural groups were defined in a standardized form and fragmentation of the molecular structures was performed by an automatic procedure to eliminate any arbitrary assumptions. The new method is based on liquid viscosity data for more than 1600 components. Results of the new method are compared to several other estimation methods published in literature and are found to be significantly better. A relative mean deviation in viscosity of 15.3% was observed for 813 components (12,139 data points). By comparison, the Van Velzen method, the best literature method in our benchmarking exercise produced a relative mean deviation of 92.8% for 670 components (11,115 data points). Estimation results at the normal boiling temperature were also tested against an empirical rule for more than 4000 components. The range of the method is usually from the triple or melting point to a reduced temperature of 0.75–0.8. Larger than average deviations were observed in the case of molecules with higher rotational symmetry, but no specific correction of this effect was included in this method.

1. Introduction

Due to the importance of reliable information on liquid viscosity data for many practical applications, numerous researchers have worked on the subject. The literature concerning liquid viscosity is therefore quite extensive. Many attempts have been made to correlate and estimate the viscosity of saturated or compressed liquids as a function of temperature, pressure, and chemical constitution. Theoretical approaches have, however, not been sufficiently successful, and at present there is no theory available that allows the estimation of liquid viscosity within the required accuracy.[1]

In addition, the various theoretical approaches do not sufficiently link liquid viscosity to a set of molecular properties in a similar way, as for example, gas viscosity is linked to molecular cross-section, which itself can be expressed as function of collision energy (temperature). These theoretical approaches are therefore out of the scope of this work and will not be discussed any further. A brief review of correlation methods, as well as empirical estimation approaches will be presented below. The improved approach for the estimation of liquid viscosity presented in this paper is based on our previous work on normal boiling temperatures [1,2], critical property data [3] and vapour pressures [4,5]. As in the previous work, the Dortmund Data Bank (DDB [6]) was employed as the main source for experimental data.

Even though the exact mechanisms governing liquid viscosity and vapour pressure are dissimilar, there are several similarities between these properties for a component:

- The energy required to remove a component from the liquid phase into the vapour phase or to break an existing structure of the liquid (in order to move liquid layers in opposite directions or with

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[1] In the well-known "Properties of Gases and Liquids", Poling, Prausnitz, and O'Connell point out that "little theory has been shown to be applicable to estimating liquid viscosities".

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different velocity) is to a great part dependent on intermolecular attraction.
- As observed by many researchers and reviewed and extended by Smith et al. [7], the viscosity at the normal boiling temperature usually falls into a rather narrow range suggesting a link between these two properties.
- The energy required for evaporation or displacement of liquid layers is supplied by the available thermal energy RT. Thus, both vapour pressure and viscosity approximately obey an equation of the form $f(T) = \exp(A - (B/T))$.

As temperature increases, the vapour pressure increases, while viscosity decreases. Thus volatility (vapour pressure) would better compare to fluidity (the reciprocal of viscosity).

Major dissimilarities affecting the development of estimation methods between liquid viscosity and vapour pressure lie in the availability and type of experimental information for both properties:

- For the temperature range employed in this work, there is less than a third of the amount of experimental data available for liquid viscosity as compared to vapour pressure. It was therefore an advantage to develop a vapour pressure model before starting on liquid viscosity. Consequently, knowledge obtained from the development of the vapour pressure estimation method [4] proved to be important here. It was assumed that the same molecular properties determine, in different ways, vapour pressure and viscosity. Therefore, the exact same differentiation of structural groups that was required for vapour pressure estimation was also required for viscosity estimation.
- A large amount of vapour pressure data is available at a reference pressure of 1 atm (the normal boiling temperature) providing a convenient reference point. Viscosity data are often available at 25 °C. After several unsuccessful developments within this work it had to be concluded that a varying viscosity value at a fixed temperature is not a useful reference.

Vapour pressure data are needed for a variety of chemical engineering and thermodynamic calculations. These data are the main factor determining the distribution of a component between the liquid and vapour phase and therefore the key property for the design of distillation columns. Liquid viscosity data on the other hand are needed for the design of fluid transport and mixing processes (pipes, pumps, stirred reactors, etc.) and have a direct and large effect on heat transfer coefficients (heat exchangers, conduction processes, etc.) and diffusion coefficients (macro-kinetic in chemical reactors). The accuracy required of the calculated viscosity, however, is far less than that required of vapour pressure. Both the amount and quality of liquid viscosity data in literature is lower than for the case of vapour pressures. Current available estimation methods for liquid viscosity are generally of poor quality.

2. General behavior and available methods

If a shearing stress τ is applied to a unit area of a confined fluid, the fluid will move with a velocity gradient $\partial u/\partial y$ such that its maximum velocity is at the point where the stress is applied. Now, if the local shear stress per unit area at any point is divided by the velocity gradient, the ratio obtained is defined as the viscosity of the fluid. Fluids, for which the shearing stress depends linearly on the velocity gradient, are called Newtonian fluids. These fluids obey the equation:

$$\tau = \eta \frac{\partial u}{\partial y} \qquad (1)$$

Only Newtonian fluids will be considered in this work.

The viscosity of gases at low densities and sufficiently high temperatures can often be described by a simple equation taking into account the mean free path and transported momentum difference (Boltzmann equation). The liquid viscosity on the other hand is governed by a different mechanism, and thus, is out of the scope of the Boltzmann equation. Besides being significantly larger, liquid viscosity shows temperature dependence opposite to that of gases. In addition, it shows significant density dependence which is not present in gases. Models for the interpretation of liquid viscosity range from simplified models such as Eyring's activated state theory and its successive modifications to approaches like Enskog's hard sphere theory, and finally include rigorous mechanical approaches in the form of the distribution function or time-correlation function methods. These types of methods mostly produce unsatisfactory results and will not be discussed further in this work.

For the correlation of liquid viscosity, similar equations can be used as in the case of vapour pressure. As viscosity diverges near the critical point, correlations employing the critical point as reference must use a hypothetical critical viscosity value.

The most simple correlation equation was first proposed by de Guzman [8], but is more commonly known as the Andrade equation:

$$\ln \frac{\eta}{\eta_{\text{ref}}} = A + \frac{B}{T} \qquad (2)$$

Vogel [9] proposed another variation by the introduction of a third constant similar to the Antoine equation for vapour pressures:

$$\ln \frac{\eta}{\eta_{\text{ref}}} = A + \frac{B}{T + C} \qquad (3)$$

Porter [10] was the first to draw attention to the relationship between liquid viscosities and vapour pressures, when he showed that the logarithm of viscosity for mercury and water depends more linearly on the logarithm of vapour pressure than on the inverse temperature. This provides a good argument for the assumption that liquid viscosity and vapour pressure are influenced in a similar way. Drucker [11] proposed an analytic formulation of this relation:

$$\ln \eta = A + B \ln P \qquad (4)$$

However, Drucker reported that large deviations from Eq. (4) were observed for strongly associating liquids. During this work we found that the constants in the Drucker equation did not follow group contribution as well as the Vogel parameters (with the parameter C set to a certain value).

As in the case of vapour pressure, several more flexible equations are available for data correlation, but their parameters are usually more difficult to estimate due to stronger intercorrelation.

A number of group contribution methods for the estimation of saturated liquid viscosity are available in literature. The methods considered for comparison in this work are given in Table 1. A detailed description of these methods together with equations and group parameter tables is given by Nannoolal [17]. Further methods like those of Bhethanabotla [18] and Przezdziecki and Sridhar [19] and methods with a limited range of applicability have not been evaluated.

Table 1
Group contribution methods for the estimation of saturated liquid viscosity considered in this work.

Year	Reference
1972	Van Velzen et al. [12]
1974	Orrick and Erbar [13]
1985	Skubla [14]
1987	Joback and Reid [15]
1992	Sastri and Rao [16]