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Viscosity modeling of water + alkanediols mixtures

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ABSTRACT

In this study, both theoretical and empirical viscosity models were evaluated for binary associating liquid mixtures of water + 1,2-ethanediol, 1,3-propanediol, 1,4-butanediol, and 1,5-pentanediol. The interaction between molecules in the mixtures was analyzed using the calculation of excess energy of flow obtained from Eyring's absolute rate theory. Free volume (FV) viscosity model was coupled with Peng-Robinson (PR) and perturbed-chain statistical associating fluid theory (PC-SAFT) equation of states (EoS); friction theory (FT) was coupled with PR EoS; no significant difference was observed in the modeling results using different EoS. A new mixing rule was found to improve the modeling results of FT coupled with the PR EoS for the binary mixtures studied. The empirical models correlated viscosity of aqueous diol systems well with average absolute percent deviation (AAD%) < 1.

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1. Introduction

Transport properties of fluids such as viscosity are essential in process simulation and optimization for all industrial applications. Due to their importance, viscosity modeling is a well-studied area, where a wide range of models have been proposed. A theoretical description of the complex molecular interaction and structural arrangement in the liquid phase is difficult; the challenge is even greater for associating fluids. Despite the challenge, there are three main groups of viscosity models available, which are classified into theoretical, semi-theoretical, and empirical models. Theoretical models are based on statistical mechanics where intermolecular potential functions are correlated to viscosity. Theoretical models generally predict viscosity using molecular dynamics simulations. Semi-theoretical models have theoretical basis but include tuning parameters that are fitted to experimental viscosity data. Empirical models are correlations based on experimental observation, where viscosity is correlated to the composition, temperature, and pressure of the fluid. Semi-theoretical models, which generally reflect the correct trend of viscosity change due to temperature and pressure variation, often have a unified framework for predicting viscosity of both gasses and liquids. Two semi-theoretical models, namely, friction theory (FT) and free volume (FV) viscosity models, are capable of modeling viscosity of both nonpolar and polar mixtures [1–3]. In FT, the viscosity is modeled basing on the friction principles of classical mechanics and the Van der Waals theory of fluids [4]. In FV, the viscosity is modeled based on the free volume concept and molecular diffusion models [5]. A suitable EoS is required for both FT and FV models. Quinones-Cisneros et al. [4] first proposed the FT in conjunction with Soave-Redlich-Kwong (SRK) EoS and Peng-Robinson-Stryjek-Vera (PRSV) EoS. Using the SRK-FT or PRSV-FT modeling approach, the viscosity of pure normal alkanes can be modeled with AAD% from 1.20 to 3.76 and from 1.30 to 4.15, and the viscosity of normal alkane binary mixtures can be modeled with AAD% from 0.51 to 7.25 and from 1.03 to 7.40. In earlier work, Quinones-Cisneros et al. [6] coupled the FT with PC-SAFT and found improved viscosity prediction of pure alkane components with AAD% < 1.57. Tan et al. [1] coupled the FT with PR, SAFT and PC-SAFT EoS to model n-alkane mixture viscosities and found that FT coupled with SAFT yielded the best results with AAD% < 4.4. Almasi [7] studied FV and FT coupled with PRSV for modeling viscosity of ester + 2-alkanols mixtures; modeling results from FV had AAD% < 3 and modeling results from FT had AAD% < 1. In a similar study, FV was coupled with PC-SAFT to predict aniline + 1-alkanol binary mixture viscosity [2]. FV combined with PC-SAFT predicted mixture viscosity well with AAD% < 2.38, and the deviation decreased with increasing alcohol carbon chain length. In other research, Llovell et al. [8] used the FV theory coupled with soft-SAFT, and predicted the viscosity of n-alkane + n-alkane, hydrofluorocarbon + hydrofluorocarbon, and n-alkane + hydrofluorocarbon mixtures with AAD% < 5.32. Zeberg-Mikkelsen et al. [3] predicted viscosity of ethanol + non-polar (n-heptane or toluene) systems using the FT and FV coupled with PR EoS at temperature and pressure ranges of 293.15–353.15 K and 0.1–100 MPa, and the AAD% of predictions for PR-FT and PR-FV were 7.75 and 7.04 respectively. Finally, Burgess et al. evaluated FT and FV coupled with SRK, PR and PC-SAFT EoS to predict viscosity of hydrocarbon mixtures at ambient pressure up to 276 MPa and ambient temperature up to 533 K, and found that FV coupled with PC-SAFT gave the best results [9]. PC-SAFT FV predicted

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viscosity reliably for n-alkanes at pressures up to ~138 MPa but underpredicted n-alkane viscosity by up to 20% at pressures near 276 MPa. These studies suggest that FT and FV coupled with PR and PC-SAFT EoS are good semi-theoretical approaches to model viscosity of associating mixtures.

In this work, the performance of various viscosity models is investigated for water + 1,2-ethanediol (1,2-ED), 1,3-propanediol (1,3-PD), 1,4-butanediol (1,4-BD), and 1,5-pentanediol (1,5-PD) binary liquid mixtures. These aqueous alcoholic systems were studied not only because of their importance in industrial and biological applications but also because of their highly associating nature [10,11]. The experimental data was derived from previous research [11] and literature [12–15]. The dynamic viscosities were measured with an Anton Paar Lovis 2000 M rolling-ball automated viscometer. The standard uncertainty of the viscosity measurement is <0.5%. The densities were measured with an Anton Paar vibrating U-tube densitometer (DMA 500). The standard uncertainty of the density measurement is 0.001 $g\cdot cm^{-3}$. First, the mixture viscosity was modeled with the absolute rate theory developed by Eyring and coworkers to deduce the nature of the intermolecular interactions in associating mixtures [16]. Then, the mixture viscosity was modeled with two semi-theoretical models, namely friction theory coupled with PR EoS, and free volume theory coupled with both PR and PC-SAFT EoS. Last, the mixture viscosity was modeled with 5 temperature dependent and 11 composition dependent empirical models.

2. Viscosity modeling theories

2.1. Activation energy of flow

Eyring [16] suggested a correlation between thermodynamic properties and transport properties with the machinery developed in the theory of absolute reaction rate. Eyring proposed that an amount of energy E is required to detach a single molecule and make a hole during the process of fluid flow. This hole can take up various positions in the liquid that have the same energy. By analogy to the process of chemical reaction, the formation of holes is considered the rate determining step, and the energy required to make holes is considered the activation energy for fluid to flow. It is assumed that an individual molecule in a plane (or layer) occasionally acquires the activation energy necessary to slip over the potential barrier (arise from the confinement due to its neighbors) to the next equilibrium position in the same plane. The activation energy of flow ΔE_a, can be solved from measured viscosity η,

$$\eta = \frac{Nh}{V}\exp\left(\frac{\Delta E_a}{kT}\right) \tag{1}$$

in which h, N, V, k, and T are the Planck constant, Avogadro's number, molar volume, Boltzmann constant, and temperature, respectively. From the activation energy of flow, the related excess energy of flow parameter ΔE^{*E} according to Eq. (2) is:

$$\Delta E^{*E} = RT\left[\ln\left(\eta_{mix}V_{mix}\right) - \sum_i x_i \ln\left(\eta_i V_i\right)\right] \tag{2}$$

where the subscripts *mix* and *i* represent the mixture and pure component i, respectively.

2.2. Friction theory

Quiñones-Cisneros et al. proposed the friction theory [4,17] that expresses the fluid viscosity as a summation of contributions from the dilute gas viscosity term η_0 and a friction term η_f:

$$\eta = \eta_0 + \eta_f \tag{3}$$

where η_0 is defined as the viscosity at the zero density limit, η_f represents the viscous dissipation in flowing fluid that is analogous to the energy loss due to friction when two bodies move relative to each other.

The dilute gas viscosity η_0 can be obtained from the modified Chapman–Enskog theory proposed by Chung et al. [18], which is valid for both polar and non-polar components. The dilute gas viscosity η_0 is given by:

$$\eta_0 = 40.785\frac{\sqrt{M_W T}}{\nu_c^{2/3}\Omega^*}F_c \tag{4}$$

$$F_c = 1 - 0.275\omega + 0.059035\mu_r^4 + \chi \tag{5}$$

where T, ν_c, M_W and Ω^* are the absolute temperature, the critical volume, the molecular weight, and the reduced collision integral, respectively. In Eq. (5), ω is the acentric factor, μ_r is a dimensionless dipole moment in Debye, and χ is a correction factor for the hydrogen bonding interactions in associating components. To estimate the reduced collision integral Ω^*, the following empirical relation is applied:

$$\begin{aligned}\Omega^* = {} & \frac{1.16145}{T^{*0.14874}} + \frac{0.52487}{\exp(0.77320T^*)} + \frac{2.16178}{\exp(2.43787T^*)} - 6.435 \\ & \times 10^{-4}T^{*0.14874}\sin\left(18.0323\,T^{*-0.76830} - 7.27371\right)\end{aligned} \tag{6}$$

$$T^* = \frac{1.2593\,T}{T_c} \tag{7}$$

As previously mentioned, FT can be coupled with any EoS. For cubic type EoS, the friction term comes from contributions associated with the attractive pressure p_a and repulsive pressure p_r:

$$\eta_f = \kappa_r p_r + \kappa_a p_a + \kappa_{rr} p_r^2 \tag{8}$$

where κ_r, κ_a, and κ_{rr} are friction coefficients. For dense fluids at high pressure, the short-range repulsive forces will prevail over the long-range attractive forces. Hence, a second-order truncation of repulsive terms and a first-order truncation of attraction terms were implemented for the quadratic FT model. The repulsive pressure p_r and the attractive pressure p_a can be derived for any EoS such as PR EoS [19] and PC-SAFT EoS [20]. The friction parameters for a pure component can be well described with temperature dependent seven-constant parametric equations:

$$\kappa_r = \left[a_1\exp(\Gamma - 1) + a_2\left(\exp(2(\Gamma - 1)) - 1\right) + a_3\left(\exp(3(\Gamma - 1)) - 1\right)\right]/P_c \tag{9}$$

$$\kappa_a = \left[b_1\exp(\Gamma - 1) + b_2\left(\exp(2(\Gamma - 1)) - 1\right) + b_3\left(\exp(3(\Gamma - 1)) - 1\right)\right]/P_c \tag{10}$$

$$\kappa_{rr} = \left(c_4\left(\exp(4\Gamma) - 1\right)\right) \tag{11}$$

$$\Gamma = \frac{T_c}{T} \tag{12}$$

In Eqs. (9)–(12), $a_1, a_2, a_3, b_1, b_2, b_3$ and c_4 are the FT constants whose values are optimized to match the viscosity of pure systems at different temperatures.

For mixtures with n number of components, the viscosity at the dilute gas limit is given by,

$$\eta_0 = \exp\left[\sum_{i=1}^{n} x_i \ln\left(\eta_{0,i}\right)\right] \tag{13}$$

and the mixture friction contribution term is calculated by:

$$\eta_f = \kappa_{r,mix}p_{r,mix} + \kappa_{a,mix}p_{a,mix} + \kappa_{rr,mix}p_{r,mix}^2 \tag{14}$$

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