Correlations of dynamics viscosity and kinematic viscosity of fatty acid from Gibbs energy additivity

S Puttala[1], S Phankosol[1*], T Techapirom[1], T Chum-in[2] and K Krisnangkura[3]

[1] Faculty of Science and Technology, Bansomdejchaopraya Rajabhat University, Bangkok, 10600, Thailand
[2] Faculty of Science, Chandrakasem Rajabhat University, Bangkok, 10900, Thailand.
[3] School of Bioresources and Technology, King Mongkut's University of Technology Thonburi (Bangkhuntien), Bangkok, 10150, Thailand
*Corresponding's author: s.phankosol@gmail.com

Abstract. Dynamic viscosity and kinematic viscosity are important physical properties of a liquid. In this work, correlation of dynamic viscosity and kinematic viscosity of fatty acids (FA) are correlated to the Martin's rule of free energy additivity for estimated kinematic viscosity and dynamic viscosity from their own equations. The proposed equations for estimating viscosity and density of FA are correlated to number of carbon atoms, number of double bond(s) and temperature. Data collected from literatures were used to validate and support the proposed models. The proposed equations are easy to use and the estimated dynamic viscosity and kinematic viscosity values of FA at different temperatures agree well with the literature values. The average absolute deviation of dynamic viscosity and kinematic viscosity of FA at 288.15 and 394.25K are 4.14 and 4.37, respectively. The estimated outside temperature between 288.15 and 394.25K may be possibly estimated by this model but accuracy may be lower.

1. Introduction

Fatty acid is important component of lipids. Fatty acids are comprised of hydrocarbon chains terminating with carboxylic acid groups. Viscosity of fatty acids and their mixtures are important in the design of process equipment for the oil and fatty acid industry. For example, viscosity is an essential parameter in estimating the efficiency of distillation columns for separation of fatty acids [1]. There are actually two quantities that are called viscosity. A basic difference between the dynamic and kinematic viscosity measurements is density. Taking density (ρ) out of the equation provides a way to convert between a kinematic (μ) and a dynamic (η) viscosity measurement. The formula for the conversion is:

$$\eta = \mu \times \rho \tag{1}$$

Experimental determination of kinematic and a dynamic viscosity of fatty acid from different sources and processes is time consuming, but they are necessary for mathematical models. The Andrade equation (equation (2)) [2] was a good equation that correlates dynamic viscosity (η) to the Gibbs free energy of viscous flow (ΔG) and absolute temperature (T),

$$\eta = A_0 e^{-\frac{\Delta G}{RT}}$$

(2)

or

$$\ln\eta = A_1 + \frac{B_1}{T}$$

(3)

where A_0 and A_1 are constant and $\ln A_0$, respectively.
          B_1 is $\Delta G/R$.
          R is universal gas constant.

However, equation (3) just correlated the dynamic viscosity to temperature without structural information. In this study, attention was paid on the Martin's rule of free energy additivity. The free energy of viscous flow for fatty acid in equation (2) was expanded to the enthalpy and entropy forms.

2. Theory
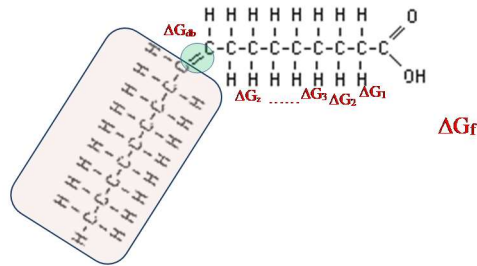
Figure 1. Correlation of free energy additivity
and fatty acid molecular structure.

Phankosol *et al.* [3] modified Martin's rule [4] for unsaturated hydrocarbon molecule was derived from the sum of the Gibbs free energies of all contributed groups, the Gibbs free energy contribution from the structural groups are additive.

$$\Delta G = \Delta G_f + \sum_{i=1}^{z} \Delta G_i + \sum_{j=1}^{nd} \Delta G_{db,i}$$

(4)

or

$$\Delta G = \Delta G_f + z\delta G + n_d \Delta G_{db}$$

(5)

where ΔG_f is the Gibbs free energy of the functional group, f; δG is the change in Gibbs free energy/carbon atom; z is the number of carbon atoms; n_d is number of double bond(s) in the molecule; i is carbon atom; j is double bond.

As aforementioned, molecular motion or flowing of liquid depends on the interactive force among molecules, it is speculated that, for n-alkanes or any other functional

homologous series, the molecular interactive force will increase as the chain length is increased and number of double bond(s) is decrease [5].

Substitution equation (5) into equation (2) and expansion the free energy to enthalpy and entropy forms,

$$\ln \eta = a + bz + \frac{c}{T} + \frac{dz}{T} + en_d + \frac{fn_d}{T} \tag{6}$$

where $\quad a = \ln A_0 + \dfrac{\Delta S_f}{R}$, $b = +\dfrac{\delta S_f}{R}$, $c = -\dfrac{\Delta H_f}{R}$, $d = -\dfrac{\delta H}{R}$, $e = -\dfrac{\Delta H_{db}}{R}$, $f = \dfrac{\Delta S_{db}}{R}$

3. Materials and Methods

3.1. Experimental data

The dynamic viscosity and density values of fatty acids were obtained from the report of Noureddini *et al.* [6,7]. The kinematic viscosity of fatty acids can be determined from the relationship in equation (1).

3.2. Numeric constants of equation (6)

All the four numeric constants of equation (6) were solved by multiple linear regression according to Phankosol *et al.* [3,8,9] as shown equation for estimating fatty acid dynamic viscosity (cP) in equation (7),

$$\ln \eta = -4.9365 - 0.00502z + \frac{1585}{T} + \frac{67.35z}{T} - 0.439n_d + \frac{44.208n_d}{T} \tag{7}$$

3.3. Statistical analysis

The absolute deviations (AD), average absolute deviations (AAD), Bias, standard error ($\sigma_{\bar{x}}$) and coefficient of determination (R^2) were calculated by equations (8) and (12), respectively.

$$AD(\%) = \frac{P_{exp} - P_{cal}}{P_{exp}} 100\% \tag{8}$$

$$AAD(\%) = \frac{100}{N} \sum_{i=1}^{N} \left[\left| \frac{P_{exp} - P_{cal}}{P_{exp}} \right| \right] \tag{9}$$

$$Bias(\%) = \frac{100}{N} \sum_{i=1}^{N} \left[\frac{P_{exp} - P_{cal}}{P_{exp}} \right] \tag{10}$$

$$\sigma_{\bar{x}} = \frac{\sigma}{N} \tag{11}$$

$$R^2 = \left[\frac{N \sum_{i=1}^{N} P_{exp} P_{cal} - \left(\sum_{i=1}^{N} P_{exp} \right) \left(\sum_{i=1}^{N} P_{cal} \right)}{\left(\left[\sum_{i=1}^{N} P_{exp}^2 - \left(\sum_{i=1}^{N} P_{exp} \right)^2 \right] \left[\sum_{i=1}^{N} P_{cal}^2 - \left(\sum_{i=1}^{N} P_{cal} \right)^2 \right] \right)^{\frac{1}{2}}} \right]^2 \tag{12}$$

where P_{exp} stands for experimental value reported, P_{cal} is the calculated value and N is the number of data points.

4. Results and Discussion

The dynamic viscosity of fatty acid might consider as the training data. The dynamic viscosity of fatty acid were used as validated set. All the dynamic viscosity estimated with equation (7) were in good agreement with those experiment data [6,7]. The Bias and AAD (%) were -0.58% and 4.14%, respectively. The correlation between the reported dynamic viscosity and estimated values using equation (7) is linear with the slope, intercept, R^2 and standard error of -0.054, 1.017, 0.992 and 0.052, respectively.
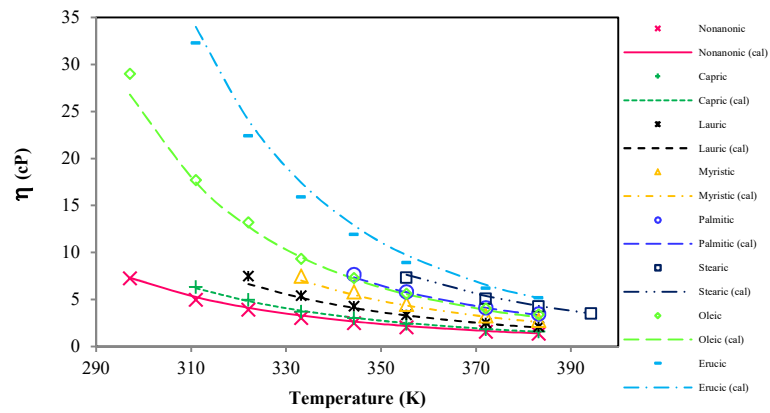
Figure 2. Experimental [6,7] and calculated dynamic viscosities of fatty acids by equation (7)

A similar Gibbs energy additivity approach for estimation of density (g.cm^{-3}) was proposed by our groups [1,10], as shown in equation (13).

$$\ln\rho = -0.4346 - 0.00161z + \frac{105.58}{T} - \frac{0.212z}{T} + 0.0558n_d - \frac{13.54n_d}{T} \tag{13}$$

Equation (1) is the natural logarithmic form of equation (14),

$$\ln\mu = \ln\eta - \ln\rho \tag{14}$$

Thus, $\ln\mu$ equation (14) can be directly obtained by substitution equation (7) and equation (13) into equation (14),

$$\ln\mu = -4.5019 - 0.0486z + \frac{1480.09}{T} + \frac{67.562z}{T} - 0.4948n_d + \frac{57.748n_d}{T} \tag{15}$$

where μ is kinematic viscosity in mm^2.s^{-1}.

The estimated is kinematic viscosity values for fatty acid agrees well with the literature values in temperature 288.15 and 394.25 K. The Bias and AAD (%) were -0.003% and 0.17%, respectively. Equation 15 can be simplified to determine kinematic viscosities of

individual fatty acid at different temperatures. The numeric constants of the simplified equations are very close to those of Andrade [2].

5. Conclusions

By using the Gibbs energy additivity method, η and μ can be directly correlated to the Gibbs energy associated with viscosity of fatty acid. Their relationship has never been described in literature. The derived equation can be accurately applied for estimation of η and μ of a fatty acid from the number of carbon atoms and number of double bond(s).

Acknowledgments

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