Gibbs energy additivity approaches in estimation of density of fatty

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Abstract. Density is important physical property of a liquid. In this work, correlation of density of fatty acids (FA) is correlated to the Martin's rule of free energy additivity for estimated density from either (1) its number of carbon atoms (of fatty acid, z) and number of double bonds (n_d) or (2) its saponification number (SN) and iodine value (IV). Data collected from literatures were used to validate, and support the proposed models. The proposed equations are easy to use and the estimated density values of FA at different temperatures form agree well with the literature values. The average absolute deviation of density of FA at 297.05 and 394.25 K is 0.17%.

1. Introduction

Fatty acids are long chains of lipid-carboxylic acid found in animal and vegetable fats and oils. Fatty acids are used as lubricants, in cooking and food engineering, and in the production of soaps, detergents, biodiesel and cosmetics. Density or specific gravity data are important in numerous chemical engineering unit operations in the fatty acid industry [1]. Although experimental determination of fatty acid density is not difficult, a simple and accurate model is greatly desirable. A good mathematical model is not only provided a rapid estimation of density. The method for estimating the density is reliable, it is more convenient to develop the simulation model of biodiesel profoundly. Halvoson *et al.* [2] pointed out that two criteria were important for estimating the density of fatty acids. First, all of the commonly encountered saturated and unsaturated fatty acids must be included in the density estimation scheme. Second, the estimation scheme must account for the temperature dependency of density.

Rackett equation [3] is a classical model for estimation of liquid density base on critical properties and an empirical parameter, Z_{RA}, for each acid as the basis for computing density as a function of temperature. The modified Rackett equation is as follows:

$$\rho = \frac{M}{\frac{RT_c}{P_c} Z_{RA}^{[1+(1-T/T_c)]^{2/7}}} \quad (1)$$

where ρ is density; M is molar mass; R is universal gas constant; Tc, and Pc, are the critical temperature and pressure, respectively; T is absolute temperature; is the Rackett parameter, a correlating parameter unique to each compound, Z_{RA} for fatty acid were reported in Halvorsen *et al.* [2].

However, the Rackett model is very complex. It requires the knowledge of critical temperature, critical pressure and compressibility factor, which in turn requires the acentric factor of the molecule.

Phankosol *et al.* [4] approached the relationship between density and Gibbs free energy of volumetric expansion for estimating fatty acid methyl ester and biodiesel was shown in equation (2),

$$\rho = \mathrm{A}e^{\sum \frac{\Delta G}{RT}} \tag{2}$$

where ρ is density; ΔG is Gibbs free energy; R is universal gas constant; T is absolute temperature; A is constant.

In this study, Gibbs energy additivity was proposed as an alternative approach model for estimation of density of fatty acids at different temperatures are easily estimated from its carbon numbers and numbers of double bonds.

2. Theory

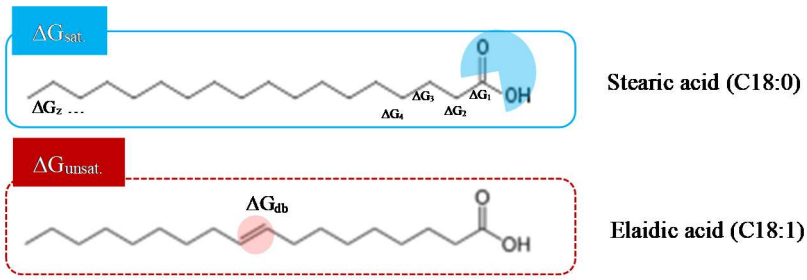

Figure 1. Gibbs free energy additivity and fatty acid (FA) molecular structure.

For a compound saturated FA having the molecular structure of CH_3-$(CH_2)_{z-1}$-X, Martin [5] divided the molecule into different groups; X, CH_2, CH_3. The free energy of transfer from solution to gas of the molecule (in gas chromatography) was derived from the sum of the Gibbs free energies of all the contribution groups.

$$\Delta G_{sat} = \Delta G_f + \Delta G_1 + \Delta G_2 + \ldots + \Delta G_z \tag{3}$$

ΔG_1 … ΔG_z are the free energies of the methylene and methyl groups, which are not very different. Thus, they are average to δG and equation (3) is shortened to equation (4),

$$\Delta G_{sat} = \Delta G_f + z\delta G \tag{4}$$

For unsaturated FA, ΔG arises from interaction of a double bond is assigned as G_{db} and the total change in ΔG for the unsaturated FA (ΔG_{unsat}) is

$$\Delta G_{unsat} - \Delta G_{sat} = n_d \Delta G_{db} \tag{5}$$

where n_d is number of double bonds in the FA. Combining equation (4) and equation (5):

$$\Delta G = \Delta G_f + z\delta G + n_d \Delta G_{db} \quad (6)$$

where ΔG_f is the free energy of the functional group, f; ΔG is the change in free energy/carbon atom; ΔG_{db} is the change in free energy/double bond; z is the number of carbon atoms; n_d is number of double bond (s) in the molecule.

Substitution equation (6) into equation (2) and expansion the free energy to enthalpy and entropy forms,

$$\ln\rho = a + bz + \frac{c}{T} + \frac{dz}{T} + en_d + \frac{fn_d}{T} \quad (7)$$

where $a = \ln A - \frac{\Delta S_f}{R}, b = -\frac{\delta S_f}{R}, c = \frac{\Delta H_f}{R}, d = \frac{\delta H}{R}, e = \frac{\Delta H_{db}}{R}, f = -\frac{\Delta S_{db}}{R}$.

Equation (7) was successfully applied for estimation of density of biodiesel by Phankosol *et al.* [4].

3. Materials and Methods

3.1. Density data

The density values of fatty acids were obtained from the report of Halvorsen *et al.* [2] was measured by using hydrometer procedures in the same hath.

3.2. Numeric constants of equation (7)

All the six numeric constants of equation (7) were solved by multiple linear regression according to Phankosol *et al.* [4,6,7] as shown equation for estimating fatty acid density ($g.cm^{-3}$) in equation (8),

$$\ln\rho = -0.4346 - 0.00161z + \frac{105.58}{T} - \frac{0.212z}{T} + 0.0558n_d - \frac{13.54n_d}{T} \quad (8)$$

3.3. Statistical analysis

The deviations (D), average absolute deviations (AAD), Bias, standard error ($\sigma_{\bar{x}}$) and coefficient of determination (R^2) were calculated by equations (9) to (13), respectively;

$$D(\%) = \frac{P_{exp} - P_{cal}}{P_{exp}} 100\% \quad (9)$$

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

$$Bias(\%) = \frac{100}{N} \sum_{i=1}^{N} \left[\frac{P_{exp} - P_{cal}}{P_{exp}} \right] \quad (11)$$

$$\sigma_{\bar{x}} = \frac{\sigma}{n} \quad (12)$$

$$R^2 = \left[\frac{n\sum_{i=1}^{n} P_{exp} P_{cal} - \left(\sum_{i=1}^{n} P_{exp}\right)\left(\sum_{i=1}^{n} P_{cal}\right)}{\sqrt{\left[\sum_{i=1}^{n} P_{exp}^2 - \left(\sum_{i=1}^{n} P_{exp}\right)^2\right]\left[\sum_{i=1}^{n} P_{cal}^2 - \left(\sum_{i=1}^{n} P_{cal}\right)^2\right]}} \right]^2 \quad (13)$$

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

4. Results and Discussion

Percent differences between the calculated by equation (8) and literature density values are listed in the parentheses, at 297.05 and 394.25 K are shown relative deviations (D (%)) in figure 2. The estimated density values for fatty acid agrees well with the literature values. The Bias and AAD (%) were -0.003% and 0.17%, respectively. The correlation between the reported density and estimated values using equation (8) is linear with the slope, intercept, R^2 and standard error of 0.9941, -0.0053, 0.9926, and 0.0022, respectively.

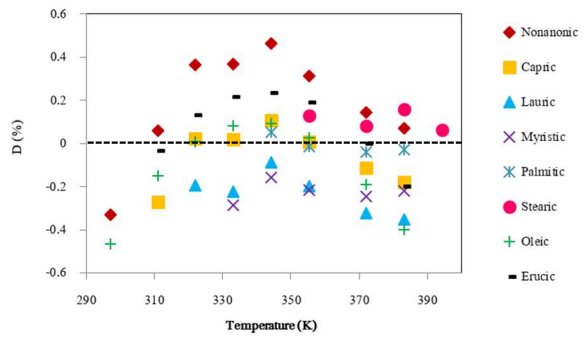

Figure 2. Relative deviations (D(%)) between densities of fatty acid by equation (8) and the experimental values reported by Halvorsen *et al.* [1].

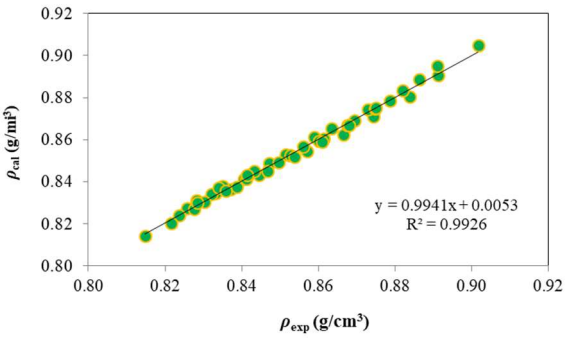

Figure 3. Correlation of the estimated densities (ρ_{cal}) to the experiment values (ρ_{exp}) [2] fatty acid at 297.05 and 394.25 K.

The z and n_d can be converted to IV and SN according to equations (14) to (16) [4].

$$n_d = \frac{(IV)(M)}{25,400} \quad (14)$$

$$z = \frac{M + 2n_d - 46}{14} \quad (15)$$

$$M = \frac{56,000}{SN} \quad (16)$$

Equation (12) is obtained by combining equations (8), (14) to (16) and it can be used for estimation of density of biodiesel at different temperatures from the SN and IV value.

$$\ln\rho = -0.42932 - \frac{6.44032}{SN} + \frac{106.2756}{T} - \frac{848.042}{(SN)T} + \frac{0.122851(IV)}{SN} - \frac{30.0016(IV)}{(SN)T} \quad (17)$$

The densities of fatty acids estimated by equation (17) (at different temperatures) were very close to those calculated using the z and n_d.

5. Conclusions

This work provides an Gibbs energy additivity approaches for estimation liquid density to its fatty acid structure at different temperatures (297.05 and 394.25 K). Hence, density of a fatty acid can be predicted either from the z and n_d (equation (8)) of fatty acids or from the SN and IV (equation (17)) with approximately the same accuracy.

Acknowledgments

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