Gibbs energy additivity approaches in estimation surface tension of fatty acids

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Abstract. Surface tension is important to ensure the efficiency of industrial operation units involving chemical reactions and extractive processes that use these compounds as solvents. In this work, the surface tension of fatty acids (FA) is correlated to Martin’s rule of free energy additivity for estimating surface tension. The proposed equations for estimating the surface tension of FAs are correlated to the number of carbon atoms (z), the number of double bond (s) (n) and temperature (T) to

\[ \gamma = 69.065 - 1.3614z + 0.13895T + 0.005209zT + 6.24n - 0.01612nT . \]

The proposed equations are easy to use and the estimated values of surface tension of FA at different temperatures agree well with the literature values.

1. Introduction

Fatty acids can differ in the length of their carbon chains (short-, medium-, or long-chain) and their level of saturation (unsaturated, polyunsaturated or saturated). Surface tension is an important physical property of fluids, especially in certain applications in the chemical processing industry [1]. Measurements of the surface tension at various temperatures require time consuming experiments. Accordingly, mathematical models are much more convenient. The van der Waals-type correlation [2] and linear equation reported by Reid et al. [3] are shown as in equation (1) and equation (2), respectively:

\[ \gamma = \gamma_0 \left( 1 - \frac{T}{T_c} \right)^n \]  \hspace{1cm} (1)

\[ \gamma = a_0 + b_0 T^{(c_C)} \]  \hspace{1cm} (2)

where \( \gamma \) is the surface tension (dynes·cm\(^{-1}\)), \( T \) is the temperature, \( T_c \) is the critical temperature, and \( \gamma_0, n, a_0 \) and \( b_0 \) are parameters used to fit the equation to the experimental data.

Phankosol et al. [4] proposed a relationship between surface tension and the Gibbs free energy of interfacial interaction of a liquid (\( \Delta G \)) for estimating fatty acid methyl esters and biodiesel, as shown as in equation (3):

\[ \Delta G = \gamma_0 \left( 1 - \frac{T}{T_c} \right)^n \]  \hspace{1cm} (3)
\[ \gamma = \left( \frac{\Delta G}{\Delta A} \right)_{T,P,n} \]  

(3)

where \( A \) is the surface area.

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

2. Theory

![Figure 1. Correlation of free energy additivity and saturated fatty acid molecular structure.](image)

The molecule of saturated fatty acid (FA), for example myristic acid (Lipid numbers: C14:0) show in figure 1, can be divided into 3 different groups of atoms: one COOH, one CH\(_3\) and 12 CH\(_2\) groups.

\[ \Delta G_{sat} = \Delta G_{COOH} + 12\Delta G_{CH_2} + \Delta G_{CH_3} \]  

(4)

Equation (4) can be arbitrarily reduced to 2 types of \( \Delta G \):

\[ \Delta G_{sat} = (\Delta G_{COOH} + \Delta G_{CH_3}) + 12\Delta G_{CH_2} + (\Delta G_{CH_3} + \Delta G_{CH_1}) \]  

(5.1)

\[ \Delta G_{sat} = (\Delta G_{COOH}) + 13\Delta G_{CH_2} + (\Delta G_{CH_1} + \Delta G_{CH}) \]  

(5.2)

\[ \Delta G_{sat} = (\Delta G_{COOH}) + 13\Delta G_{CH_2} + \Delta G_{CH_3} \]  

(5.3)

\[ \Delta G_{sat} = (\Delta G_{COOH}) + 14\Delta G_{CH_2} \]  

(5.4)

Set, \( \Delta G_f = \Delta G_{COOH} \)

Thus, the general form of equation (5.4) for all saturated fatty acid methyl esters (FA) is:

\[ \Delta G_{sat} = \Delta G_f + z\Delta G_{CH_2} \]  

(6)

where \( z \) is the number of carbon atoms on the fatty acid chain.

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

\[ \Delta G_{unsat} - \Delta G_{sat} = n_d \Delta G_{db} \]  

(7)

where \( n_d \) is number of double bonds in the FAME.

Combining equation (6) and equation (7):
\[ \Delta G = \Delta G_f + z\Delta G + n_d\Delta G_{db} \quad (8) \]

where \( \Delta G_f \) is the free energy of the functional group, \( f \); \( \Delta G \) is the change in free energy/carbon atom; \( \Delta G_{db} \) 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.

Substituting equation (8) into equation (3) and expanding the free energy to enthalpy and entropy forms:

\[ \gamma = a + bz + cT + dzT + en_d + fn_dT \quad (9) \]

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

3. Materials and Methods

3.1 Surface tension data

The surface tension values of fatty acids were obtained from the report of Chumpitaz et al. [1], in which they were measured by using a K12 tensiometer (Krüss GmbH).

3.2 Numeric constants of equation (9)

All six numeric constants of equation (9) were solved by multiple linear regression according to Phankosol et al. [4-6]. The equation for estimating fatty acid density (dynes·cm\(^{-1}\)) is shown in equation (10):

\[ \gamma = 69.065 -1.3614z -0.13895T + 0.005209T + 6.24n_d -0.01612n_dT \quad (10) \]

3.3 Statistical analysis

The deviations (D), absolute deviations (AD), average absolute deviations (AAD), Bias, standard error (\( \sigma_{\tau} \)) and coefficient of determination (\( R^2 \)) were calculated by equations (11) to (16), respectively:

\[ D(\%) = \frac{p_{exp} - p_{cal}}{p_{exp}} \times 100\% \quad (11) \]

\[ AD(\%) = \frac{|p_{exp} - p_{cal}|}{p_{exp}} \times 100\% \quad (12) \]

\[ AAD(\%) = \frac{100}{N} \sum_{i=1}^{N} \left[ \frac{p_{exp} - p_{cal}}{p_{exp}} \right] \quad (13) \]

\[ Bias(\%) = \frac{100}{N} \sum_{i=1}^{N} \left[ \frac{p_{exp} - p_{cal}}{p_{exp}} \right] \quad (14) \]

\[ \sigma_{\tau} = \frac{\sigma}{N} \quad (15) \]
\[ R^2 = \left[ \frac{N \sum_{i=1}^{N} P_{\text{exp}} - \left( \sum_{i=1}^{N} P_{\text{exp}} \right) \left( \sum_{i=1}^{N} P_{\text{cal}} \right)}{\left( \sum_{i=1}^{N} P_{\text{exp}}^2 - \left( \sum_{i=1}^{N} P_{\text{exp}} \right)^2 \right)} \right]^2 \]  

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

4. Results and Discussion

The surface tension of four types of saturated and unsaturated fatty acids at 293.15–363.15K estimated by equation (10) are calculated and shown in Table 1. The estimated surface tension values for fatty acids agrees well with the literature values. The Bias (%) and AAD (%) were 0.31% and 0.63%, respectively. The correlation between the reported surface tension and estimated values using equation (10) is linear with a slope, intercept, \( R^2 \) and standard error of 1.013, −0.441, 0.989, and 0.025, respectively.

Table 1. Deviations of surface tension (dynes cm\(^{-1}\)) of fatty acids estimated by equation (10) from literature values at different temperatures.

| T (K) | Capric acid | Lauric acid | Myristic acid | Palmitic acid |
|------|-------------|-------------|--------------|--------------|
|      | \( \gamma_{\text{cal}} \) | D(%) | \( \gamma_{\text{cal}} \) | D(%) | \( \gamma_{\text{cal}} \) | D(%) | \( \gamma_{\text{cal}} \) | D(%) |
| 293.15 | 30.32 | - | 30.7 | - | 31.0 | - | 32.8 | -0.11 |
| 303.15 | 29.55 | - | 30.0 | - | 30.4 | - | 32.2 | -0.29 |
| 313.15 | 28.79 | - | 29.3 | - | 29.9 | - | 31.6 | 0.94 |
| 323.15 | 28.03 | - | 28.7 | - | 29.3 | - | 31.0 | 0.17 |
| 333.15 | 27.26 | 0.51 | 28.0 | - | 28.8 | - | 30.4 | -0.55 |
| 343.15 | 26.50 | 0.05 | 27.3 | 1.83 | 28.2 | 0.00 | 29.8 | -0.55 |
| 348.15 | 26.11 | -0.56 | 27.0 | 1.43 | 27.9 | -0.26 | 29.5 | - |
| 353.15 | 25.73 | -0.36 | 26.7 | 1.70 | 27.6 | -0.27 | 29.1 | 0.48 |
| 358.15 | 25.35 | - | 26.4 | 1.76 | 27.4 | -0.03 | 28.8 | - |
| 363.15 | 24.97 | -0.48 | 26.0 | 1.89 | 27.1 | -0.18 | 28.5 | 0.08 |

Bias (%) | 0.31%

AAD (%) | 0.63%

The missing D(%) is due to no experimental data.

Although equation (10) is a good and simple model for estimating fatty acids at different temperature, determined of the \( z \) and \( n_d \) requires the knowledge of fatty acid composition. The analysis must be done with gas chromatography (GC) or high-performance liquid chromatography (HPLC). The saponification number (SN) and iodine value (IV) have long been used for the characterization of fats and oils and they require no special instrumentation. \( z \) and \( n_d \) can be converted to SN and IV according to equations (17), (18) and (19) [6].

\[
\frac{IV \times M}{25400} = n_d \quad (17)
\]

\[
z = \frac{M + 2n_d - 46}{14} \quad (18)
\]
\[ M = \frac{56000}{SN} \quad (19) \]

Equation (20) is derived from equation (10) with equations (17), (18) and (19) and can be used to estimate surface tension of fatty acids at different temperatures from the SN and IV values:

\[
\gamma = 73.532 - \frac{5445.87}{SN} - 0.156T - \frac{20.8T}{SN} + \frac{13.3627(IV)}{SN} - \frac{0.034(IV)T}{(SN)} \quad (20)
\]

The surface tension of fatty acids estimated by equation (20) (at different temperatures) were very close to those calculated using \( z \) and \( n_d \) (equation (10)). The plotted surface tension estimated by equations 10 and 20 was shown as in figure 2 and \( R^2 = 0.999 \). Equation (20) can be simplified to determine the surface tension of individual fatty acids at different temperatures. The numeric constants of the simplified equations are very close to those of Reid et al. [3] (equation (2)).

\[ \text{Figure 2. Correlation of surface tension estimated by equations 10 and 20.} \]

5. Conclusions
This work provides a simple empirical correlation of the surface tension of fatty acids. The surface tensions of fatty acids were easily estimated from both 1) the carbon numbers and number of double bond(s) and 2) the saponification and iodine values. Hence, the surface tension at different temperatures (293.15–363.15K) could be estimated. The estimated surface tension values were comparable to or better than those reported in the literature.

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