New Group Contribution Method for Predicting the Critical Pressures of Fatty Acids and Triglycerides

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Abstract: A new and useful method for evaluating and predicting the critical pressures ($P_c$) of n-fatty acids and triglycerides was developed in this study. Logarithmic equations which required critical temperature ($T_c$) and normal boiling temperature ($T_b$) were proposed for the fatty acids and their corresponding triglycerides. The method predicted with good accuracy the critical pressures ($P_c$) of the n-fatty acids, even without the input of the compressibility factor ($\Delta Z_b$). The deviations of predicted critical pressures from experimental values were between (0-7)%, except for Caproic and Caprylic acids; where the method under predicted the critical pressures with deviations of -6.64% and -11.31% respectively. Experimental $P_c$ values for the triglycerides were not available in the open literature for comparison.

Keywords: Critical Pressures, n-Fatty Acids, Triglycerides, Enthalpies of Vapourisation, Trouton’s Rule, Clausius-Clapeyron Equation

1. Introduction

The implementation of many equation of state methods, require critical properties of organic compounds [1]. It is not always possible to find experimental values in the literature and since measurement is expensive and time consuming or sometimes even difficult or impossible, estimation/group contribution methods, which need only the structural information of the molecule are generally of great value [2 - 4].

A Group Contribution method uses the principle that some simple aspects of the structures of chemical components are always the same in many different molecules. The smallest common constituents are the atoms and the bonds. By using group or atom properties, the physical properties of pure compounds and mixtures can be predicted. [5 - 8]. Kreglenski and Zwolinski [9], Tsonopoulos [10], Gray et al. [11], Teja et al. [12], and Magoulas and Tassios [13], proposed Group Contribution methods that correlated critical properties and normal boiling point to the number of carbon atoms in the molecule for homologous series, such as normal alkanes and alkanols. These correlations have been found to be accurate [5]. However, their range of application was questioned by Kreglenski and Zwolinski [9] and Tsonopoulos and Tan [14].

There are a large number of group contribution methods for the estimation of physical Properties [2], in particular the critical pressure, available in literature. In summary, current methods cannot provide a simple and accurate estimation of the critical pressure across all compounds. Most methods have high average absolute deviations from experimental values available in literature. Hence, the objective of this study was to develop a reliable group contribution estimation method for the prediction of the critical pressures of fatty acids and esters (triglycerides). A data base of this sort is of utmost significance in the analysis and design of plants for separation and purification of vegetable oils.

2. Experimental Data

We did not carry out any experimental measurements ourselves, this work is purely theoretical and computational. However, experimental thermodynamic and critical properties of the fatty acids were obtained from the works of Gokel [15]; Cunico et al. [3]; Majer and Svoboda [16]; Ruzicka and Majer [17]; Sales-Cruz et al [18].
3. Development of the New Method

Many of the vapour pressure equations that are used in industry today have their roots in the Clausius-Clapeyron equation. Equation (1) is the differential form of the Clausius–Clapeyron equation.

\[
\frac{\partial P}{\partial T} = \frac{\Delta H P}{RT^2} \quad (1)
\]

Deviations from the ideal gas law are expressed in terms of the compressibility factor \(Z\).

\[
Z = \frac{PV}{RT} \quad (2)
\]

In the case of vapourisation or sublimation, we can assume that the change in compressibility factor is unity. Hence;

\[
\Delta Z = Z_f - Z_i = Z_f - Z_e = 1 \quad (3)
\]

We can then write equation (3) as;

\[
\frac{\partial P}{P} = \frac{\Delta H}{\Delta Z R T^2} \quad (4)
\]

Rearranging equation (4) gives;

\[
\frac{\partial P}{P} = \frac{\Delta H}{\Delta Z R} \left( \frac{\partial T}{T^2} \right) \quad (5)
\]

Equation (5) can be expressed logarithmically as;

\[
\partial \ln P = \frac{\Delta H}{\Delta Z R} \left( \frac{\partial T}{T^2} \right) \quad (6)
\]

If we assume that \(H\) does not vary with temperature and pressure; equation (6) may be simplified to give;

\[
\partial \ln P = \frac{\Delta H_e}{\Delta Z_e R} \left( \frac{\partial T}{T} \right) \quad (7)
\]

Integrating equation (7) will give rise to a two-component, modified Clausius-Clapeyron equation. The enthalpy of vapourisation and the compressibility factor for the fluid is at the boiling point \(\Delta H_e\) and \(\Delta Z_e\) respectively.

\[
\int_{T_i}^{T_f} \partial \ln P = \frac{\Delta H_e}{\Delta Z_e R} \ln \left( \frac{T_f}{T_i} \right) \quad (8)
\]

\[
\ln P_f - \ln P_i = \frac{\Delta H_e}{\Delta Z_e R} \left( \frac{1}{T_f} - \frac{1}{T_i} \right) \quad (9)
\]

From Trouton’s rule

\[
\Delta H_b = T_b \Delta S_b \quad (10)
\]

at the boiling point

Substituting for \(\Delta H_b\) in equation (9) we have;

\[
\ln \left( \frac{P_f}{P_i} \right) = \frac{T_b \Delta S_b}{\Delta Z_e R} \left( \frac{T_f - T_i}{T_f T_i} \right) \quad (11)
\]

Hence,

\[
\ln \left( \frac{P_f}{P_i} \right) = \frac{\Delta S_b}{R \Delta Z_e} \left( \frac{T_f}{T_i} - 1 \right) \quad (12)
\]

If pressure is expressed in units of atmospheres, then \(P_b\) = 1 atm. Consequently equation (12) can then be written as;

\[
\ln \left( \frac{P_f}{1 \text{ atm}} \right) = \frac{\Delta S_b}{R \Delta Z_e} \left( \frac{T_f}{T_i} - 1 \right) \quad (13)
\]

As a first approximation, we take \(P_b = 1\). Hence equation (13) becomes;

\[
\ln \left( \frac{P_f}{1 \text{ atm}} \right) = \frac{\Delta S_b}{R} \left( \frac{T_f}{T_i} - 1 \right) \quad (14)
\]

The Ambrose [19] parameter \(X\) is given as;

\[
X = \frac{T_b}{T_f - T_b} \quad (15)
\]

Substituting \(X\) into equation (14) will give rise to a basic equation for predicting \(P_c\)

\[
\ln \left( \frac{P_f}{1 \text{ atm}} \right) = \frac{\Delta S_b}{R} \left( \frac{1}{1 + X} \right) \quad (16)
\]

Hence,

\[
(1 + X) \ln \left( \frac{P_f}{1 \text{ atm}} \right) = \frac{\Delta S_b}{R} \quad (17)
\]

Equation (17) is the basic Group Contribution approach for predicting \(P_c\) for n-alkanes [20]. A plot of \((1+X)\ln P_f\) versus number of carbon atoms for n-alkanes gave a straight line graph, whose slope accounted for the contributions of the –CH\(_3\) and –CH\(_2\) groups. In order to obtain the contribution of the –COOH group in n-fatty acids and –CH=CH– group in unsaturated n-fatty acids, a modification of equation (17) was necessary. The modification gave rise to two new equations viz.

\[
(1 + X) \ln \left( \frac{P_f}{1 \text{ atm}} \right) = \left( \frac{A_1 + A_2}{2.5} \right) + W_1 N_e + W_2 \quad (18)
\]

(For saturated n-fatty acids) and

\[
(1 + X) \ln \left( \frac{P_f}{1 \text{ atm}} \right) = \left( \frac{A_1 + A_2}{2.7} \right) + W_1 N_e + W_2 - DW_2 \quad (19)
\]

(For unsaturated n-fatty acids)

A further modification of equations (18) and (19) gave rise to two new equations, accounting for the contributions of the –COO– and –CH\(_3\) groups in each triglyceride. Equations (20) and (21) were proposed for the prediction of \(P_c\) for triglycerides of saturated and unsaturated fatty acids respectively.
\[(1+X) \ln P_c = \left(\frac{A_1 + A_2 + A_3}{1.3}\right) + W(v(N_c - 4) + 3V_1 + V_2)\]
\[\frac{1}{W(N_c - 4)}\]  
(20)

\[(1+X) \ln P_c = \left(\frac{A_1 + A_2 + A_3}{1.3}\right) + W(v(N_c - 4) + 3V_1 + V_2 - DW)\]
\[\frac{1}{W(N_c - 4)}\]  
(21)

\(A_1, A_2\) and \(A_3\) in equations \((18 - 21)\) are constants with values of 9.62, 18.60 and 1.50 respectively. \(D\) = number of \(-\text{CH} = \text{CH}-\) groups in each molecule of the unsaturated fatty acid. \(N_c\) = number of carbon atoms. Table 1 contains the values of other parameters in equations \((18 - 21)\).

### Table 1. Contributions of Groups to the Prediction of \(P_c\)

| Symbol | Group          | Contribution |
|--------|----------------|--------------|
| \(W_1\) | \(-\text{CH}_3\) | 0.096        |
| \(W_2\) | \(-\text{COOH}\) | 0.096        |
| \(W_3\) | \(-\text{CH} = \text{CH}_2\) | 0.316        |
| \(V_1\) | \(-\text{COOH}\) | 0.206        |
| \(V_2\) | \(-\text{CH}_3\) | 0.203        |

### Table 2. Thermodynamic Properties of n-Fatty Acids.

| Name       | \(N_c\) | \(\Delta H_{\text{vap}} / \text{KJ/mol}\) | \(T_s / \text{K}\) | \(\Delta S_{\text{vap}} / \text{KJ/mol}^\circ\) | \(\Delta S_{\text{vap}} / \text{R}\) |
|------------|---------|------------------------------------------|-------------------|-----------------------------------------------|-----------------------------------|
| Caproic Acid | 6       | 64.66\(^\circ\)                        | 478.70\(^\circ\) | 0.1351                                        | 16.2496                           |
| Caprylic Acid | 8       | 70.02\(^\circ\)                       | 512.30\(^\circ\) | 0.1367                                        | 16.4395                           |
| Capric Acid | 10 N/A  | 541.92\(^\circ\)                      | -                  | -                                              | -                                 |
| Lauric Acid | 12 N/A  | 571.40\(^\circ\)                      | -                  | -                                              | -                                 |
| Myristic Acid | 14 N/A  | 599.00\(^\circ\)                      | -                  | -                                              | -                                 |
| Palmitic Acid | 16 N/A  | 622.30\(^\circ\)                      | -                  | -                                              | -                                 |
| Stearic Acid | 18 N/A  | 648.10\(^\circ\)                      | -                  | -                                              | -                                 |
| Oleic Acid | 18 67.40\(^\circ\) | 633.00\(^\circ\) | 0.1065                                       | 12.8070                           |
| Linoleic Acid | 18 N/A  | 624.10\(^\circ\)                      | -                  | -                                              | -                                 |
| Linolenic Acid | 18 N/A  | 622.70\(^\circ\)                      | -                  | -                                              | -                                 |

Source: *Gokel, (2004);*Cunico et.al, (2013); *Majer and Svozoba, (1985) and *Ruzicka and Majer, (1994); *Estimated from the Method of Constantinou and Gani. N/A= Not available.

4. Results and Discussion

The experimental thermodynamic properties of the n-fatty acids in this study are presented in Table 2. Experimental properties for some of the fatty acids were not available in the literature. Experimental critical properties of the fatty acids that were available in the literature are shown in Table 3.

### Table 3. Experimental Critical Temperatures (\(T_s\)) and Pressures (\(P_c\)) of Fatty Acids.

| Name       | \(N\) | \(T_s / \text{K}\) | \(P_c / \text{atm}\) | Deviations (%) |
|------------|-------|-------------------|----------------------|---------------|
| Caproic Acid | 6     | 663.00\(^\circ\)  | 33.33\(^\circ\)      |               |
| Caprylic Acid | 8     | 694.26\(^\circ\)  | 27.43\(^\circ\)      |               |
| Capric Acid | 10    | 726.00\(^\circ\)  | 22.21\(^\circ\)      |               |
| Lauric Acid | 12    | 743.43\(^\circ\)  | 18.43\(^\circ\)      |               |
| Myristic Acid | 14    | 765.19\(^\circ\)  | 16.23\(^\circ\)      |               |
| Palmitic Acid | 16    | 785.22\(^\circ\)  | 14.49\(^\circ\)      |               |
| Stearic Acid | 18    | 805.09\(^\circ\)  | 13.10\(^\circ\)      |               |
| Oleic Acid | 18    | 795.17\(^\circ\)  | N/A                  |               |
| Linoleic Acid | 18    | 793.68\(^\circ\)  | N/A                  |               |
| Linolenic Acid | 18    | 792.18\(^\circ\)  | N/A                  |               |

The deviations of predicted critical pressures from experimental values were between (0-7)\(^\circ\), except for Capric acid and Cappyric acid, where the method under predicted the critical pressures with deviations of -6.64% and -11.31\(^\circ\) respectively from experimental \(P_c\) values. It is pertinent to note that the predictive capability of our equation improved with increase in chain length of the fatty acids.

### Table 4. Predicted \(P_c\) of n-Fatty Acids and Their Deviations from Experimental Values.

| Name       | \(N\) | \(P_c / \text{atm}\) | Deviations (%) |
|------------|-------|----------------------|---------------|
| Caproic Acid | 6     | 29.56                | -11.31         |
| Caprylic Acid | 8     | 25.61                | -6.64          |
| Capric Acid | 10    | 23.69                | 6.66           |
| Lauric Acid | 12    | 18.94                | 2.77           |
| Myristic Acid | 14    | 16.55                | 1.97           |
| Palmitic Acid | 16    | 14.73                | 1.66           |
| Stearic Acid | 18    | 13.21                | 0.84           |
| Oleic Acid | 18    | 12.26                | -              |
| Linoleic Acid | 18    | 13.22                | -              |
| Linolenic Acid | 18    | 12.69                | -              |

Table 5 shows the \(P_c\) values for the triglycerides estimated with equations \((20)\) and \((21)\). As expected, \(P_c\) decreased with increase in the number of carbon atoms. However, the \(P_c\) predicted for trimyristin exhibited a slight deviation from this trend. This is attributable to the experimental boiling point found for trimyristin in the open literature. Experimental \(P_c\) values were not found in the open literature for the triglycerides to serve as a basis for comparison.

The available data for the fatty acids and triglycerides have been used to investigate the capability of the method for \(P_c\), developed in this study, to extrapolate higher carbon numbers of fatty acids and triglycerides. This assertion is illustrated in figures 1 and 2. In view of figures 1 and 2, one can expect the method developed in this study to provide reliable \(P_c\) values for a wide range of fatty acids and triglycerides. However, the unavailability of experimental data of \(P_c\) for triglycerides does not permit us to make a definite statement on the uncertainties to predicted \(P_c\) for the esters.
Table 5. Predicted $P_c$ of Triglycerides.

| Common Name | Formula | $N_c$ | $P_c$/atm. |
|-------------|---------|-------|-------------|
| Tricaprin    | C$_{21}$H$_{38}$O$_6$ | 21    | 10.51       |
| Tricaprylin  | C$_{27}$H$_{50}$O$_6$ | 27    | 7.31        |
| Tricaprin    | C$_{33}$H$_{62}$O$_6$ | 33    | 6.70        |
| Trimyristin  | C$_{39}$H$_{74}$O$_6$ | 39    | 6.70        |
| Trilaurin    | C$_{45}$H$_{86}$O$_6$ | 45    | 5.67        |
| Trimyristin  | C$_{51}$H$_{98}$O$_6$ | 51    | 5.31        |
| Trilaurin    | C$_{57}$H$_{110}$O$_6$ | 57    | 4.76        |
| Triolein     | C$_{57}$H$_{104}$O$_6$ | 57    | 4.56        |
| Triolein     | C$_{57}$H$_{98}$O$_6$ | 57    | 4.38        |
| Triolein     | C$_{57}$H$_{92}$O$_6$ | 57    | 4.20        |

Fig. 1. A Plot of $(1+X)\ln P_c$ (calc.) Versus $N_c$ for n-Fatty Acids.

Fig. 2. A Plot of $1/(1+X) \ln P_c$ Versus $N_c$ for the Triglycerides.

5. Conclusion

The critical pressures of the n-fatty acids and triglycerides were predicted through a new Group Contribution method. The method was based on Group Contribution and the traditional temperature-dependence correlations. The impute parameters were critical temperature ($T_c$), normal boiling temperature ($T_b$), enthalpies of vapourisation at the boiling temperatures of the n-fatty acids and triglycerides. The results were compared with experimental critical pressures of the n-fatty acids; unfortunately, no experimental data were found for the triglycerides in the open literature. The results were generally in good agreement with experimental $P_c$ values cited in the literature. The paucity of experimental data notwithstanding, we consider that the results for fatty acids and triglycerides are enough to validate the method.

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