

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 (ΔZ_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.

$$\frac{\partial P}{\partial T} = \frac{\Delta H P}{R T^2} \quad (1)$$

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;

$$\Delta Z = Z_g - Z_l = Z_g - Z_s = 1 \quad (3)$$

We can then write equation (3) as;

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

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;

$$\partial \ln P = \frac{\Delta H_b}{\Delta Z_b R} \partial \left(\frac{1}{T} \right) \quad (7)$$

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 ΔH_b and ΔZ_b respectively.

$$\int_{P_b}^P \partial \ln P = \frac{\Delta H_b}{\Delta Z_b R} \int_{T_b}^{T_c} \partial \left(\frac{1}{T} \right) \quad (8)$$

$$\ln P_c - \ln P_b = \frac{\Delta H_b}{\Delta Z_b R} \left(\frac{1}{T_b} - \frac{1}{T_c} \right) \quad (9)$$

From Trouton's rule

$$\Delta H_b = T_b \Delta S_b \quad (10)$$

at the boiling point

Substituting for ΔH_b in equation (9) we have:

$$\ln \left(\frac{P_c}{P_b} \right) = \frac{T_b \Delta S_b}{\Delta Z_b R} \left(\frac{T_c - T_b}{T_b T_c} \right) \quad (11)$$

Hence,

$$\ln \left(\frac{P_c}{P_b} \right) = \frac{\Delta S_b}{\Delta Z_b R} \left(\frac{T_c - T_b}{T_c} \right) \quad (12)$$

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

$$\ln (P_c / (\text{atm})) = \frac{\Delta S_b}{R \Delta Z_b} \left(\frac{T_c - T_b}{T_c} \right) \quad (13)$$

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

$$\ln (P_c / (\text{atm})) = \frac{\Delta S_b}{R} \left(\frac{T_c - T_b}{T_c} \right) \quad (14)$$

The Ambrose [19] parameter X is given as;

$$X = \frac{T_b}{T_c - T_b} \quad (15)$$

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

$$\ln (P_c / (\text{atm})) = \frac{\Delta S_b}{R} \left(\frac{1}{1+X} \right) \quad (16)$$

Hence,

$$(1+X) \ln (P_c / (\text{atm})) = \frac{\Delta S_b}{R} \quad (17)$$

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

$$(1+X) \ln (P_c / (\text{atm})) = \left(\frac{A_1 + A_2}{2.5} \right) + W_1 N_c + W_2 \quad (18)$$

(For saturated n-fatty acids) and

$$(1+X) \ln (P_c / (\text{atm})) = \left(\frac{A_1 + A_2}{2.7} \right) + W_1 N_c + W_2 - DW_3 \quad (19)$$

(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 $-\text{COO}-$ and $-\text{CH}$ 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.

$$(1+X)\ln P_c = \frac{\left(\frac{A_1 + A_2 + A_3}{1.3}\right) + W_1(N_c - 4) + 3V_1 + V_2}{W_1(N_c - 4)} \quad (20)$$

$$(1+X)\ln P_c = \frac{\left(\frac{A_1 + A_2 + A_3}{1.3}\right) + W_1(N_c - 4) + 3V_1 + V_2 - DW_3}{W_1(N_c - 4)} \quad (21)$$

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	$-\text{CH}_2-$	0.096
W_1	$-\text{CH}_3$	0.096
W_2	$-\text{COOH}$	0.316
W_3	$-\text{CH}=\text{CH}-$	0.206
V_1	$-\text{COO}-$	0.203
V_2	$-\text{CH}$	0.014

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 2. Thermodynamic Properties of n-Fatty Acids.

Name	N_c	$\Delta H_{\text{(vap)}}/T_b/\text{K}$ Jmol^{-1}	T_b/K	$\Delta S_{\text{(vap)}}/\text{K}$ Jmol^{-1}	$\Delta S_{\text{(vap)}}/\text{R}$
Caproic Acid	6	64.66 ^a	478.70 ^a	0.1351	16.2496
Caprylic Acid	8	70.02 ^a	512.30 ^a	0.1367	16.4395
Capric Acid	10	N/A	541.92 ^b	-	-
Lauric Acid	12	N/A	571.40 ^b	-	-
Myristic Acid	14	N/A	599.00 ^b	-	-
Palmitic Acid	16	N/A	622.30 ^b	-	-
Stearic Acid	18	N/A	648.10 ^b	-	-
Oleic Acid	18	67.40 ^c	633.00 ^c	0.1065	12.8070
Linoleic Acid	18	N/A	624.10 ^d	-	-
Linolenic Acid	18	N/A	622.70 ^d	-	-

Source: ^aGokel, (2004); ^bCunico et.al, (2013); ^cMajer and Svoboda, (1985) and ^dRuzicka and Majer, (1994); ^eEstimated from the Method of Constantinou and Gani. N/A= Not available.

The critical pressures predicted by equations (18) and (19) and their deviations from experimental values are presented in Table 3. The deviations in Table 3 were calculated according to the relation:

$$D = \frac{P_{c(\text{calc.})} - P_{c(\text{exp.})}}{P_{c(\text{exp.})}} \times 100 \quad (22)$$

Table 3. Experimental Critical Temperatures (T_c) and Pressures (P_c) of Fatty Acids.

Name	N	T_c (exp.)/K	P_c (exp.)/atm.
Caproic Acid	6	663.00 ^a	33.33 ^a
Caprylic Acid	8	694.26 ^a	27.43 ^a
Capric Acid	10	726.00 ^a	22.21 ^a
Lauric Acid	12	743.43 ^a	18.43 ^a
Myristic Acid	14	765.19 ^a	16.23 ^a
Palmitic Acid	16	785.22 ^a	14.49 ^a
Stearic Acid	18	805.09 ^a	13.10 ^a
Oleic Acid	18	795.17 ^{b *}	N/A
Linoleic Acid	18	793.68 ^{b *}	N/A
Linolenic Acid	18	792.18 ^{b *}	N/A

Source: ^aCunico et.al, (2013) and ^bSales-Cruz et.al, (2010). *Estimated by the Method of Constantinou and Gani.

The deviations of predicted critical pressures from experimental values were between (0-7)%, except for Caproic acid and Caprylic acid; where the method under predicted the critical pressures with deviations of -6.64% and -11.31% 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.

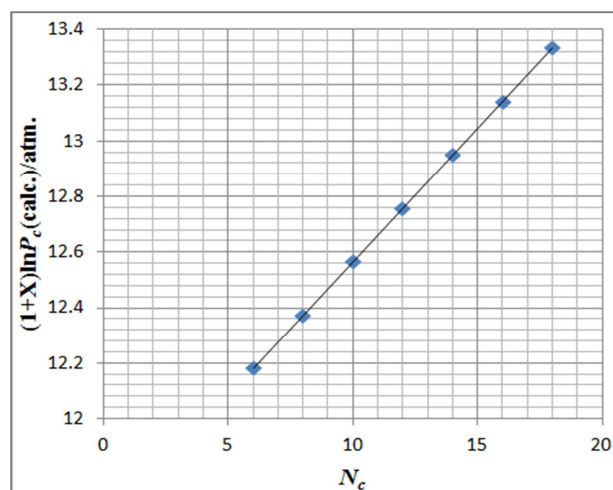
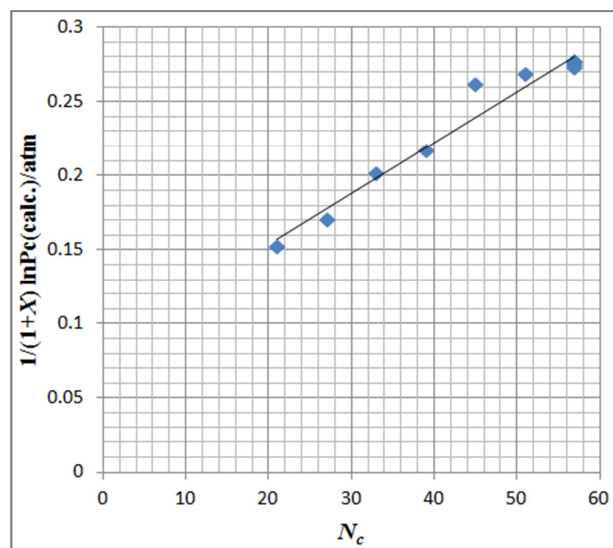
Name	N	P_c (calc.)/atm.	Deviations (%)
Caproic Acid	6	29.56	-11.31
Caprylic Acid	8	25.61	-6.64
Capric Acid	10	23.69	6.66
Lauric Acid	12	18.94	2.77
Myristic Acid	14	16.55	1.97
Palmitic Acid	16	14.73	1.66
Stearic Acid	18	13.21	0.84
Oleic Acid	18	12.26	-
Linoleic Acid	18	13.22	-
Linolenic Acid	18	12.69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

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	$P_c/\text{atm.}$
Tricaproin	$C_{21}H_{38}O_6$	21	10.51
Tricaprylin	$C_{27}H_{50}O_6$	27	7.31
Tricaprin	$C_{33}H_{62}O_6$	33	6.70
Trilaurin	$C_{39}H_{74}O_6$	39	5.67
Trimyristin	$C_{45}H_{86}O_6$	45	6.20
Tripalmitin	$C_{51}H_{98}O_6$	51	5.31
Tristearin	$C_{57}H_{110}O_6$	57	4.76
Triolein	$C_{57}H_{104}O_6$	57	4.56
Trilinolein	$C_{57}H_{98}O_6$	57	4.38
Trilinolenin	$C_{57}H_{92}O_6$	57	4.20

**Fig. 1.** A Plot of $(1+X)\ln P_c(\text{calc.})$ 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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