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GROUP CONTRIBUTION METHOD FOR ESTIMATING THE CRITICAL PRESSURES OF C_1-C_{20} n-ALKANES

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ABSTRACT

To develop a new and useful method for evaluating and predicting the critical pressures (P_c) of n-fatty acids and esters, logarithmic equations were developed that correlate, with good agreement, the n-fatty acid and ester critical pressures with the corresponding n-alkane critical pressure. The test with n-alkanes showed that even without the compressibility factor (ΔZ_b), the error in estimated P_c was never more than about 20%. However, when ΔZ_b is estimated from an equation of state, the error is never more than 10%; indeed the majority of the values lie around 5%.

Key Words: critical pressures, n-alkanes, enthalpies of vapourisation, Trouton's rule, Clausius-Clapeyron equation.

INTRODUCTION

The accurate evaluation of the critical properties of pure-substances is essential for any calculations in multi-component mixtures as well as for many designs in industrial processes. Critical constants have been experimentally determined for a limited number of compounds, as the decomposition processes and the necessity of obtaining accurate measurements in extreme conditions of high temperature and pressure constitute the main obstacle in the measurement process. In this case, prediction methods are the only means by which those properties may be determined (Owczarek and Blazej, 2006).

Kreglenski and Zwolinski (1961), Tsonopoulus (1987), Gray et.al., (1989), Teja et.al., (1990), and Magoulas and Tassios (1990), have proposed correlating critical properties and normal boiling point to the number of carbon atoms in the molecule for homologous series, such as n-alkanes and alkanols. Although these correlations have been found to be accurate, their range of application has been questioned by Kreglenski and Zwolinski (1961) and Tsonopoulos and Tan (1993).

Dargahi and Jafari (2015), used two versions of statistical associating fluid theory (SAFT) equation of state, namely modified SAFT-BACK and original SAFT, to calculate the critical temperatures and pressures of ten n-alkanes (C_1-C_{10}). The absolute average percentage deviation of their results from experimental values indicated that the modified SAFT-BACK was good in its prediction of the critical properties of the n-alkanes. However, the original SAFT equation exhibited significant limitations in predicting the critical properties of the n-alkanes.

Lemmon and Goodwin (2000), reported equations for the estimation of critical temperatures and pressures of the n-alkanes as functions of the carbon number. Based on the consistency of the critical parameter for n-alkanes < C_{20} with experimental data and the probable ability of two simple functions obtained from the work of Teja et al. (1990), to extrapolate to higher carbon numbers, they assumed that acceptable prediction of the critical temperature and pressure may be obtained for the higher alkanes from the correlations they presented. However, they were of the opinion that new measurements of the critical temperature and pressure are needed to verify their assumption.

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 (Constantinou and Gani, 1993, 1994). The smallest common constituents are the atoms and the bonds. All organic components for example, are built of carbon, hydrogen, oxygen, nitrogen, halogens and may be sulphur. Together with a single, a double and a triple bond, there are only ten atom types and three bond types to build thousands of components. The next slightly more complex building blocks of compounds are functional groups which are themselves built of few atoms and bonds.

The objective of this work is the prediction of the crirtical pressures of n-alkanes ranging from C_1-C_{20} by means of a new predictive method based on Group Contribution and the traditional temperature-dependence correlations.

Theoretical Approach

Many of the vapour pressure equations that are used in industry today have their roots in the Clausius-Clapeyron equation. The vapour pressure of a liquid at any temperature is mathematically correlated with the enthalpy (ΔH_{vap}) and entropy (ΔS_{vap}) of vapourisation. The Clausius-Clapeyron equation describes this relationship as:

$$\ln P = \frac{-\Delta \mathrm{Hvap}}{RT} + \frac{\Delta \mathrm{Svap}}{R} \qquad (1)$$

$\frac{-\Delta \mathrm{Hvap}}{R}$ and $\frac{\Delta \mathrm{Svap}}{R}$ is a constant. Hence a graph of $\frac{1}{T}$ (x-axis) vs lnP (y-axis) will yield a straight line with the slope correlated to ΔH_{vap} and the y-intercept correlated to $\Delta S_{vap.}$ R in this case is equal to 8.314 $JK^{-1}mol^{-1}$ (Wikipedia, 2011). Equation (2) is the differential form of the Clausius – Clapeyron equation.

$$\frac{\partial P}{\partial \mathrm{T}} = \frac{\Delta HP}{RT^2} \qquad (2)$$

Developing the New Method

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

$$Z = \frac{PV}{RT} \qquad (3)$$

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

$$\Delta Z = Z_g - Z_l = Z_g - Z_s = 1 \qquad (4)$$

We can then write equation (2) as;

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$$\frac{\partial P}{\partial \mathrm{T}} = \frac{\Delta HP}{\Delta ZRT^2} \qquad (5)$$

Rearranging equation (5) gives

$$\frac{\partial P}{P} = \frac{\Delta H}{\Delta ZR}\left(\frac{\partial T}{T^2}\right) \qquad (6)$$

Equation (6) can be expressed logarithmically as;

$$\partial \ln P = \frac{\Delta H}{\Delta ZR}\left(\frac{\partial T}{T^2}\right) \qquad (7)$$

If we assume that *H* that does not vary with temperature and pressure; equation (7) may be simplified to give

$$\partial \ln P = \frac{\Delta H_b}{\Delta Z_b R}\partial\left(\frac{1}{T}\right) \qquad (8)$$

Integrating equation (8) 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.

$$\int_{P_b}^{P_c} \partial \ln P = \frac{\Delta H_b}{\Delta Z_b R}\int_{T_b}^{T_c} \partial\left(\frac{1}{T}\right) \qquad (9)$$

$$\therefore \ln P_c - \ln P_b = \frac{\Delta H_b}{\Delta Z_b R}\left(\frac{1}{T_b} - \frac{1}{T_c}\right) \qquad (10)$$

From Trouton's rule $\Delta H_b = T_b \Delta S_b$ at the boiling point (11)

Substituting for ΔH_b in equation (10) we have

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

Equation (12) can be simplified to give

$$\ln\left(\frac{P_c}{P_b}\right) = \frac{\Delta S_b}{\Delta Z_b R}\left(\frac{T_c - T_b}{T_c}\right) \qquad (13)$$

If pressure is expressed in units of atmospheres, then P_b =1atm. Consequently equation (13) can be re-written as

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

As a first approximation, we take ΔZ_b =1. Hence equation (14) becomes

$$\ln\left(P_c/(atm)\right) = \frac{\Delta S_b}{R}\left(\frac{T_c - T_b}{T_c}\right) \qquad (15)$$

We can use the binomial theorem to write equation (15) by introducing the Ambrose (1978) parameter, (*X*).

$$X = \frac{T_b}{T_c - T_b} \qquad (16)$$

$$1/(1+X) = \frac{T_c - T_b}{T_c} \qquad (17)$$

Substituting $1/(1+X)$ for $\frac{T_c - T_b}{T_c}$ in equation (15) gives

$$\ln\left(P_c/(atm)\right) = \frac{\Delta S_b}{R}\left(\frac{1}{1+X}\right) \qquad (18)$$

$$\therefore (1+X)\ln\left(P_c/(atm)\right) = \frac{\Delta S_b}{R} \qquad (19)$$

Equation (19) is the basis is of the new Group Contribution method proposed by this study for prediction of P_c for n-alkanes.

RESULTS AND DISCUSSION

Tables 1 and 2 contain the thermodynamic and critical properties required for the prediction of the critical pressures of the C_1-C_{20} n-alkanes by the basic equation. N_c represents the number of carbon atoms in each n-alkane. The critical temperatures on Table 2 were prescribed by Ambrose and Tsonopoulos, (1995). The recommended experimental critical pressures of the C_1-C_{20} n-alkanes are as stipulated by Owczarek and Blazej, (2006).

Table 3 shows the P_c values predicted by equation (19). The deviations (D %) of the predicted P_c values ($P_{c_{(calc.)}}$) from experimental P_c values ($P_{c_{(\exp.)}}$) are also presented on Table 3.

Table1: C_1-C_{20} n-Alkanes and their Experimental ΔH at the Boiling Point.

n-Alkane	Formular	N_c	$\Delta H_{vap(T_b)}$ /(KJmol^{-1})	T_b /(K)
Methane	CH_4	1	8.19	111.52
Ethane	C_2H_6	2	14.69	184.4
Propane	C_3H_8	3	19.04	230.9
Butane	C_4H_{10}	4	22.4	272.5
Pentane	C_5H_{12}	5	25.76	309.06
Hexane	C_6H_{14}	6	28.85	341.73
Heptane	C_7H_{16}	7	31.77	371.5
Octane	C_8H_{18}	8	34.41	398.67
Nonane	C_9H_{20}	9	37.18	423.82
Decane	$C_{10}H_{22}$	10	39.58	447.15
Undecane	$C_{11}H_{24}$	11	41.91	468.9
Dodecane	$C_{12}H_{26}$	12	44.09	489.32
Tridecane	$C_{13}H_{28}$	13	46.2	508.47
Tetradecane	$C_{14}H_{30}$	14	48.16	526.58
Pentadecane	$C_{15}H_{32}$	15	50.08	543.6
Hexadecane	$C_{16}H_{34}$	16	51.84	559.86
Heptadecane	$C_{17}H_{36}$	17	53.58	575
Octadecane	$C_{18}H_{38}$	18	55.23	589.3
Nonadecane	$C_{19}H_{40}$	19	56.93	602.9
Eicosane	$C_{20}H_{42}$	20	58.49	616

Source: Majer and Svoboda (1985) and Ruzicka and Majer (1994).

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Table 2: Critical Temperatures (T_c) and experimental critical pressures (P_c) of C_1-C_{20} n-Alkanes

n-Alkane	Formula	N_c	T_c / K	$P_{c_{(\exp)}} / MPa$	$P_{c(\exp)} / atm$
Methane	CH_4	1	190.56	4.60	45.40
Ethane	C_2H_6	2	305.32	4.88	49.14
Propane	C_3H_8	3	369.83	4.26	42.04
Butane	C_4H_{10}	4	425.12	3.79	37.43
Pentane	C_5H_{12}	5	469.70	3.37	33.26
Hexane	C_6H_{14}	6	507.49	2.99	29.51
Heptane	C_7H_{16}	7	540.13	2.73	26.94
Octane	C_8H_{18}	8	568.88	2.49	24.57
Nonane	C_9H_{20}	9	594.55	2.28	22.50
Decane	$C_{10}H_{22}$	10	607.70	2.11	20.82
Undecane	$C_{11}H_{24}$	11	638.80	2.01	19.82
Dodecane	$C_{12}H_{26}$	12	658.10	1.82	17.96
Tridecane	$C_{13}H_{28}$	13	675.90	1.68	16.58
Tetradecane	$C_{14}H_{30}$	14	692.40	1.57	15.49
Pentadecane	$C_{15}H_{32}$	15	707.70	1.48	14.61
Hexadecane	$C_{16}H_{34}$	16	722.10	1.40	13.82
Heptadecane	$C_{17}H_{36}$	17	735.50	1.34	13.22
Octadecane	$C_{18}H_{38}$	18	748.20	1.29	12.73
Nonadecane	$C_{19}H_{40}$	19	760.10	1.16	11.45
Eicosane	$C_{20}H_{42}$	20	771.40	1.08	10.66

Source: Ambrose and Tsonopoulos, (1995) and Owczarek and Blazej, (2006).

Table 3: Predicted P_c Values and their Deviations from Experimental P_c Values.

n-Alkane	Formula	N_c	$P_{c(calc)} / atm$	$P_{c(\exp)} / atm$	Deviation E (%)
Methane	CH_4	1	38.05	45.40	-16.19
Ethane	C_2H_6	2	44.47	49.14	-9.50
Propane	C_3H_8	3	41.50	42.04	-1.28
Butane	C_4H_{10}	4	34.80	37.43	-7.03
Pentane	C_5H_{12}	5	30.84	33.26	-7.28
Hexane	C_6H_{14}	6	27.57	29.51	-6.57
Heptane	C_7H_{16}	7	24.81	26.94	-7.91
Octane	C_8H_{18}	8	22.34	24.57	-9.08
Nonane	C_9H_{20}	9	20.70	22.50	-8.00
Decane	$C_{10}H_{22}$	10	16.66	20.82	-19.98
Undecane	$C_{11}H_{24}$	11	17.45	19.82	-11.96
Dodecane	$C_{12}H_{26}$	12	16.11	17.96	-10.30
Tridecane	$C_{13}H_{28}$	13	14.99	16.58	-9.59
Tetradecane	$C_{14}H_{30}$	14	13.94	15.49	-10.01
Pentadecane	$C_{15}H_{32}$	15	13.06	14.61	-10.61
Hexadecane	$C_{16}H_{34}$	16	12.21	13.82	-11.65
Heptadecane	$C_{17}H_{36}$	17	11.54	13.22	-12.71
Octadecane	$C_{18}H_{38}$	18	10.96	12.73	-13.90
Nonadecane	$C_{19}H_{40}$	19	10.47	11.45	-8.56
Eicosane	$C_{20}H_{42}$	20	9.98	10.66	-6.38

The deviations on Table 3 were calculated according to the relation:

$$D = \frac{P_{c_{(calc.)}} - P_{c_{(\exp.)}}}{P_{c_{(\exp.)}}} \times 100 \qquad (20)$$

The test with n-alkanes showed that even without ΔZ_b, the error in estimated P_c was never more than about 20%. However, when ΔZ_b is estimated from an equation of state, the error is never more than 10%; indeed the majority of the values lie around 5%.

If we consider the binomial expression in equation (19), a plot of $(1+X)\ln\left(P_c/(atm)\right)$ versus N_c will produce a linear graph whose slope is equivalent to the contributions of the CH_2 and CH_3 groups in the prediction of P_c for the n-alkanes.

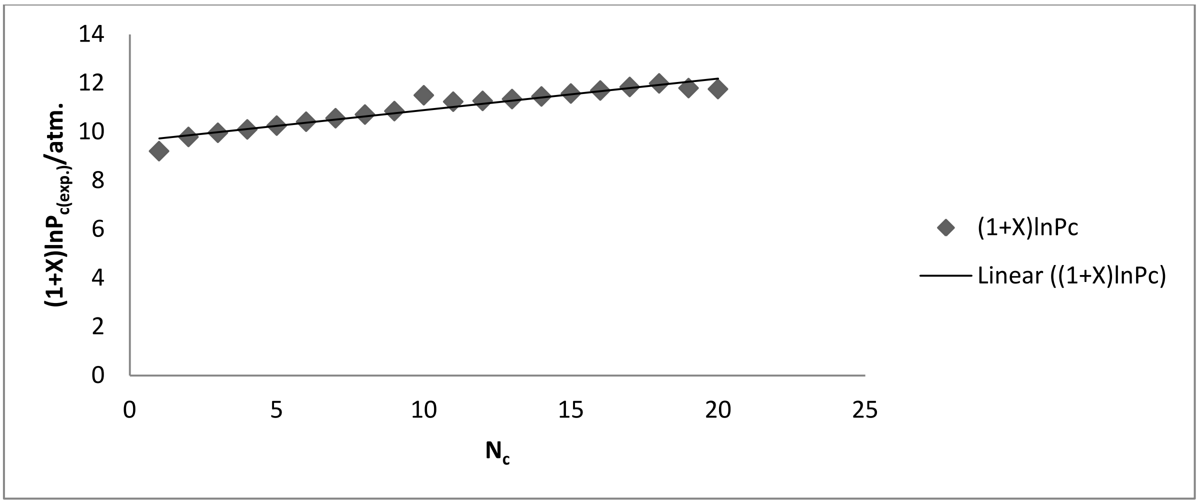

Fig.1: A Plot of (1+*X*) ln$P_{c(exp.)}$ Versus N_c for C_1-C_{20} n-Alkanes.

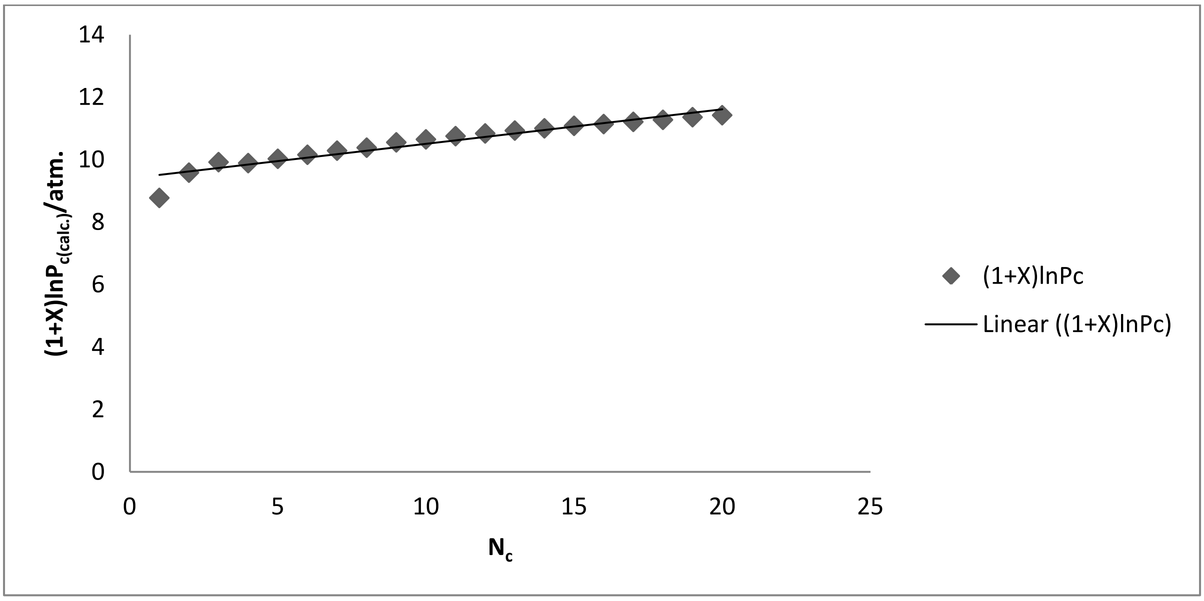

Fig.2: A Plot of (1+*X*) ln$P_{c(calc.)}$ Versus N_c for C_1-C_{20} n-Alkanes.

A cursory look at figures 1 and 2 reveals that the predictive method developed in this study yielded P_c values that had a very good agreement with experimental P_c values. The basic equation developed in this work can be used to extrapolate P_c for higher molecular weight n-alkanes, where experimental data is difficult to obtain or nonexistent. This group contribution method however, had a tendency to under predict critical pressures of the lower molecular weight n-alkanes.

A plot of (1+X) ln$P_{c(calc.)}$ Versus N_c for each n-alkane on Table 1results in straight line. Using the deviations of predicted P_c values from experimental P_c values as degrees of uncertainties in our predictive method, the plot in figure 2 resulted in the following equation:

$$(1+X)\ln\left(P_c/(atm)\right)=\left(9.610\pm0.105\right)+\left(0.097\pm0.012\right) \quad (21)$$

Where; (9.610±0.105) and (0.097±0.012) represent the intercept on the vertical axis and slope of the linear graph respectively. The latter is the contribution of each CH_2 and CH_3 group in the prediction of P_c for each C_1-C_{20} n-alkane.

The critical pressures of the C_1-C_{20} n-alkanes 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-alkanes. The results were compared with experimental critical pressures of the n-alkanes. The results were generally in good agreement with experimental P_c values cited in the literature.

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