

NEW APPROACH TO ESTIMATING THE CRITICAL PRESSURES OF N-ALKANES < C₂₁ BY GROUP CONTRIBUTION

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ABSTRACT

A Group Contribution Equation (GCE) was developed in this study that correlates, with good accuracy, the critical pressures (P_c) of n-alkanes. The equation was tested without the compressibility factor (ΔZ_b), and error in estimated P_c was generally below 20%. The input of ΔZ_b reduces the error to below 10%. The deviations lie around 5% for majority of the n-alkanes.

Keywords: Critical pressures, Vaporization enthalpies, Trouton's rule, Clausius-Clapeyron equation, n-alkanes

INTRODUCTION

Designs in industrial processes and calculations in mixtures with multiple components require reliable data of properties of pure substances. Experimental determination of critical constants for many compounds poses a challenge to scientists, when these substances easily decompose under extreme temperature and pressure conditions. Such a challenge is readily overcome by prediction models (Owczarek and Blazej, 2006; Otoibrise, 2020). Basic aspects of the structures of chemical components like atoms and bonds are similar in diverse molecules (Constantinou and Gani, 1994; Marrero and Gani, 2001). A Group Contribution Equation (GCE) uses the aforementioned principle to correlate properties of compounds with their structure (Constantinou and Gani, 1994; Tahami *et al.*, 2019; Otoibrise and Orotomah, 2022). Organic compounds comprise mainly of carbon, hydrogen and may be oxygen, nitrogen, halogens and sulphur. A combination of the former with single, double or triple bond,

gives rise to thousands of organic substances. The number of carbon atoms in alcohols and n-alkanes have been correlated with their boiling temperatures and critical properties using GCE (Kreglenski and Zwolinski, 1961; Tsonopoulus, 1987; Gray *et.al.*, 1989; Teja *et.al.*, 1990; Magoulas and Tassios, 1990). Notwithstanding the accuracy of these prediction models, the extent of their application was queried by other researchers (Tsonopoulos and Tan, 1993). GCEs correlating number of carbon atoms with T_c and P_c for n-alkanes were also reported by Lemmon and Goodwin (2000). The predicted properties were consistent with experimental measurements for carbon atoms less than twenty. The authors assumed that their GCEs could be used to extrapolate higher carbon numbers, the correctness of this assumption is subject to available experimental data. This work is aimed at predicting P_{cs} of n-alkanes within C₁-C₂₀ range using a new GCE and the conventional temperature-dependence correlations.

Computational Method

Clausius-Clapeyron Equation (CCE) is the root of several vapour pressure equations that are widely applied in industrial processes. The vapour pressure of a liquid at any temperature

The CCE describes this relationship as:

$$\ln P = \frac{-\Delta H_{\text{vap}}}{RT} + \frac{\Delta S_{\text{vap}}}{R} \quad (1)$$

$\frac{-\Delta H_{\text{vap}}}{R}$ and $\frac{\Delta S_{\text{vap}}}{R}$ is a constant. A graph of $\frac{1}{T}$ (x-axis) vs $\ln P$ (y-axis) yields a straight line with the slope correlated to ΔH_{vap} and the y-intercept correlated to ΔS_{vap} . R is the ideal gas constant which is equal to $8.314 \text{ JK}^{-1}\text{mol}^{-1}$. Equation (2) is the differential form of the CCE.

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

The compressibility factor (Z) is suitable for expressing deviations from the ideal gas law.

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

For sublimation or vaporization, change in compressibility factor is unity. Hence;

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

The assumption in equation (4) modifies equation (2) as;

$$\frac{\partial P}{\partial T} = \frac{\Delta H P}{\Delta Z R T^2} \quad (5)$$

Equation (5) can be rearranged to give equation (6).

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

Equation (6) can be expressed logarithmically as;

$$\partial \ln P = \frac{\Delta H}{\Delta Z R} \left(\frac{\partial T}{T^2} \right) \quad (7)$$

Assuming there are no temperature and pressure changes in H ; equation (7) becomes:

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

A modified CCE is obtained when equation (8) is integrated. This is expressed in equations

(9 & 10).

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

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

$$\text{Trouton's rule is expressed as } \Delta H_b = T_b \Delta S_b \quad (11)$$

Consequently, Equation (10) can be modified and simplified to give equations (12 & 13).

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

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

$P_b = 1$ atmosphere pressure and $\Delta Z_b \equiv 1$. Consequently equation (13) becomes

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

Introducing the Ambrose parameter, (X), equation (14) can be modified using the binomial theorem (Ambrose, 1978).

$$1/(1+X) = \frac{T_c - T_b}{T_c} \quad (15)$$

Substituting $1/(1+X)$ for $\frac{T_c - T_b}{T_c}$ in equation (14) gives

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

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

Equation (17) is proposed GCE for prediction of P_c for n-alkanes.

RESULTS AND DISCUSSION

Experimental thermodynamic and critical properties for predicting P_c in this study are shown on table 1. $\Delta H_{vap(T_b)}$ and T_b were sourced from Majer and Svoboda (1985) and Ruzicka and Majer

(1994) respectively. T_{cs} were obtained from the work of Ambrose and Tsonopoulos, (1995). P_{cs} were got from Owczarek and Blazej, (2006).

Table 2 is the result of P_{cs} predicted by equation (17). The deviations (D %) of the predicted P_c from experimental P_c are also shown on Table 2. The deviations were calculated with equation (18).

$$D = \frac{P_{c(calc.)} - P_{c(exp.)}}{P_{c(exp.)}} \times 100 \quad (18)$$

Without ΔZ_b , the error in estimated P_c never went beyond 20%. If ΔZ_b is estimated from an equation of state, the error is between 5 - 10%. A greater percentage of the values are below 5% error or deviation.

From equation (17), a plot of $(1+X)\ln(P_c/(atm))$ versus N_c will yield a linear graph with slope equivalent to the contributions of CH_2 and CH_3 groups in the proposed GCE for P_c prediction in n-alkanes.

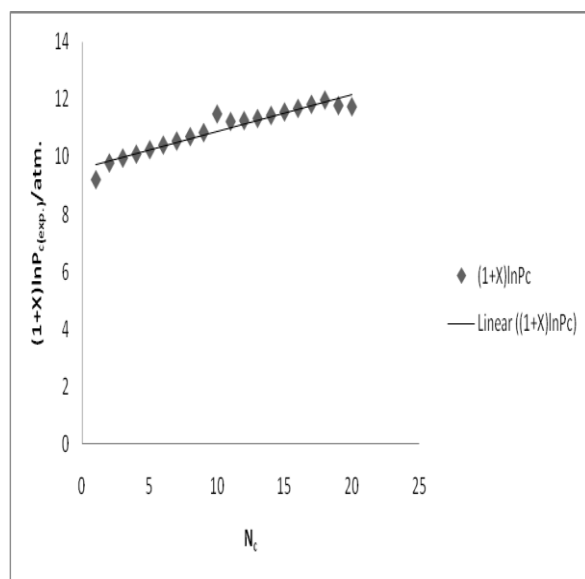
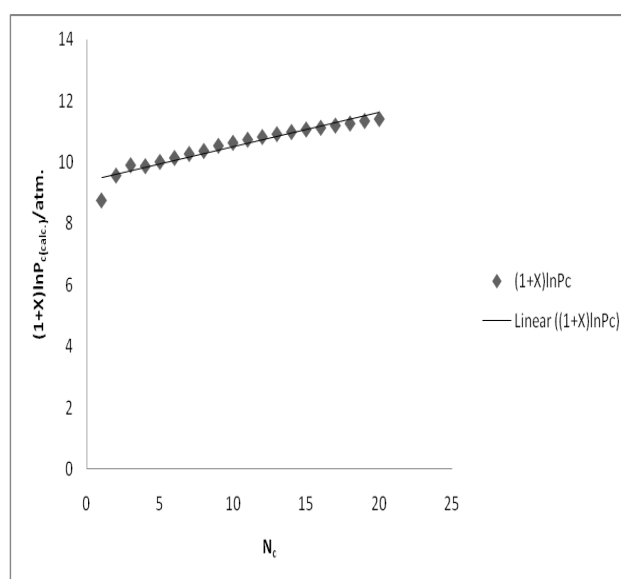
Table1: Experimental thermodynamic and critical properties of C₁-C₂₀ n-Alkanes

n-Alkane	N_c	$\Delta H_{vap}(T_b)/(KJmol^{-1})$	$T_b/(K)$	T_c/K	$P_{c(exp)}/atm$
Methane	1	8.19	111.52	190.56	45.40
Ethane	2	14.69	184.4	305.32	49.14
Propane	3	19.04	230.9	369.83	42.04
Butane	4	22.4	272.5	425.12	37.43
Pentane	5	25.76	309.06	469.70	33.26
Hexane	6	28.85	341.73	507.49	29.51
Heptane	7	31.77	371.5	540.13	26.94
Octane	8	34.41	398.67	568.88	24.57
Nonane	9	37.18	423.82	594.55	22.50
Decane	10	39.58	447.15	607.70	20.82
Undecane	11	41.91	468.9	638.80	19.82
Dodecane	12	44.09	489.32	658.10	17.96
Tridecane	13	46.2	508.47	675.90	16.58
Tetradecane	14	48.16	526.58	692.40	15.49
Pentadecane	15	50.08	543.6	707.70	14.61
Hexadecane	16	51.84	559.86	722.10	13.82
Heptadecane	17	53.58	575	735.50	13.22
Octadecane	18	55.23	589.3	748.20	12.73
Nonadecane	19	56.93	602.9	760.10	11.45
Eicosane	20	58.49	616	771.40	10.66

Source: Majer and Svoboda (1985); Ruzicka and Majer (1994); Ambrose and Tsonopoulos, (1995); Owczarek and Blazej, (2006).

Table 2: Predicted P_{cs} and their Deviations from Experimental P_{cs} .

n-Alkane	Formula	N_c	$P_{c(calc)} / atm$	$P_{c(exp)} / atm$	Deviation (%)
Methane	CH ₄	1	38.05	45.40	-16.19
Ethane	C ₂ H ₆	2	44.47	49.14	-9.50
Propane	C ₃ H ₈	3	41.50	42.04	-1.28
Butane	C ₄ H ₁₀	4	34.80	37.43	-7.03
Pentane	C ₅ H ₁₂	5	30.84	33.26	-7.28
Hexane	C ₆ H ₁₄	6	27.57	29.51	-6.57
Heptane	C ₇ H ₁₆	7	24.81	26.94	-7.91
Octane	C ₈ H ₁₈	8	22.34	24.57	-9.08
Nonane	C ₉ H 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

Fig.1a: A Plot of $(1+X) \ln P_{c(exp.)}$ versus N_c Fig.1b: A Plot of $(1+X) \ln P_{c(calc.)}$ versus N_c

Figures 1a and 1b show that the GCE in this study estimated P_{cs} with a very good agreement with experimental P_{cs} . The GCE can extrapolate P_c for higher molecular weight n-alkanes. The equation had a tendency to under predict P_c of the lower n-alkanes. The intercept on the vertical axis and slope of figure

1b are (9.610 ± 0.105) and (0.097 ± 0.012) respectively. The slope is the contribution of each CH_2 and CH_3 group for P_c prediction in equation (17). Figure 2 is a comparative plot of experimental and predicted P_{cs} .

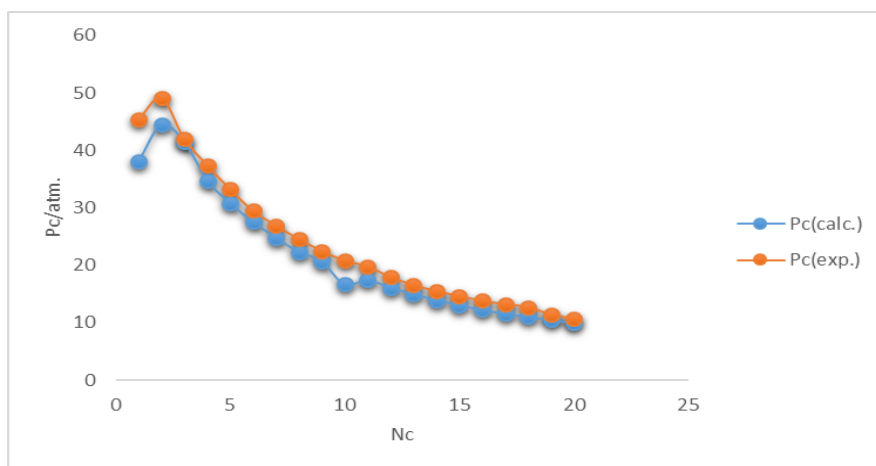


Fig. 2: Plot of experimental and predicted P_c versus N_c .

CONCLUSION

The P_{cs} of C_1 - C_{20} n-alkanes were predicted with a new GCE. The method was based on temperature-dependence Group Contribution correlations. The impute parameters were (T_c) , (T_b) , and vaporization enthalpies at the boiling points of the n-alkanes. The results were compared with experimental P_{cs} . The results were generally in good agreement with accessible experimental P_{cs} .

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