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Critical constants and acentric factors for long-chain alkanes suitable for corresponding states applications. A critical review

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Abstract

Several methods for the estimation of the critical temperature T_c, the critical pressure P_c, and the acentric factor ω for long-chain n-alkanes are reviewed and evaluated for the prediction of vapor pressures using Corresponding States (CS) methods, like the Lee–Kesler equation and the cubic equations of state. Most reliable and recent literature methods proposed for the estimation of the acentric factor of heavy alkanes yield similar values and the emphasis is, thus, given to the determination of the best sets of T_c and P_c. Various extrapolation schemes proposed for this purpose and several general group-contribution methods were investigated in this work. The correlations proposed by K. Magoulas and D. Tassios, Thermophysical properties of n-alkanes from C_1 to C_{20} and their prediction for higher ones, *Fluid Phase Equilibria, 56* (1990) 119–140; A.S. Teja, R.J. Lee, D.J. Rosenthal, M. Anselme, Correlation of the critical properties of alkanes and alkanols, *Fluid Phase Equilibria, 56* (1990) 153–169; W. Hu, J. Lovland and P. Vonka, Generalized vapor pressure equations for n-alkanes, 1-alkenes, and 1-alkanols, Presented at the 11th Int. Congress of Chemical Engineering, Chemical Equipment Design and Automation CHISA '93, 29 August-3 September, 1993; and the recent group-contribution method by L. Constantinou and R. Gani, New Group Contribution Method for Estimating Properties of Pure Compounds, *AIChE J., 40* (10) (1994) 1697–1710; provide the most promising results.

Keywords: Long-chain alkanes; Acentric factors; n-alkanes; Vapor pressures

1. Introduction

Vapor pressures, critical properties and acentric factors for heavy n-alkanes (above n-eicosane) are very important in the petrochemical industry and also in the characterization of heavy oil/gas components. Critical properties have been experimentally determined for n-alkanes up to nC_{18} and prediction schemes are often utilized for the heavier thermally unstable alkanes.

The critical properties and the acentric factor are used in various corresponding states (CS) methods, like the Lee–Kesler (LK) equation for the vapor pressure, the cubic Equations of State (EoS), and others. Cubic EoS, in particular, require very accurate values of the critical properties and the acentric factor (especially T_c and ω; see [1]) for reliable pure component vapor pressures which, together with the mixing and combining rules, are of significant importance for reliable phase equilibrium calculations.

For the important and extensively studied homologous series of n-alkanes, various Group-Contribution (GC) and extrapolation methods have been proposed for the estimation of T_c and P_c. These methods are useful in that they can extrapolate successfully to the heavier members (above nC_{20}) for which experimental critical data are not available. Most of these methods provide accurate or at least reasonably good correlation of the existing experimental critical data (C_1–nC_{18} or nC_{20}) but the values of the predicted, by the various methods, critical properties above n-eicosane often differ significantly (see Table 1).

It is difficult to evaluate directly the predictive capability of these estimation methods, since experimental critical data for heavy n-alkanes (above nC_{20}) are not available. Only recently, Nikitin et al., [5] presented experimental critical properties until nC_{24} (with rather large error bars), and Siepmann et al., [6] used Molecular Simulation (MS) for the determination of the critical temperature and density for some heavy n-alkanes up to nC_{48} (also with rather large error bars). Provided that reasonable ω-values for the heavy alkanes are known, indirect approaches for the evaluation of the various methods may be used and useful conclusions can be drawn. In this work several three-parameter corresponding-states methods are used for the calculation of vapor pressure and other related properties.

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Table 1

a: Critical temperatures (K) for some long-chain *n*-alkanes as predicted by several group-contribution methods and other correlations

N_c	Magoulas	Joback [a]	Ambrose [a]	C-Gani	Elhassan	Teja	Tson/Tan	Hu
22	786.24	791.27	791.71	777.61	796.61	791.45	787.31	789.63
24	802.62	815.03	810.43	794.12	817.32	809.96	803.98	807.65
28	829.86	864.52	843.02	823.20	854.53	842.11	832.11	838.89
40	882.83	1066.2	914.34	889.88	944.08	912.18	889.61	907.24
60	924.13	2201.7	984.79	964.93	1051.3	982.13	941.77	977.39
100	950.33	−865	1049.3	1058.7	1196.9	1051.7	989.31	1053.6

[a] T_b from Tsonopoulos [2] correlation.

b: Critical pressures (in bar) for some long-chain *n*-alkanes as predicted by several group-contribution methods and other correlations

N_c	Magoulas	Joback	Ambrose	C-Gani	Elhassan	Teja	Tson/Tan	Hu
22	10.01	9.02	10.99	9.48	10.37	11.08	11.43	10.59
24	8.97	8.06	10.17	8.58	9.52	10.49	10.63	9.75
28	7.28	6.55	8.86	7.19	8.16	9.69	9.4	8.41
40	4.14	3.91	6.38	4.78	5.65	8.73	7.26	5.92
60	1.84	2.05	4.36	3.14	3.66	8.45	5.66	3.94
100	0.4796	0.8544	2.66	2.095	2.10	8.42	4.43	2.34

c: Normal boiling point values for long-chain alkanes predicted by various methods

N_c	Tsonopoulos	Teja	Joback	C-Gani [a]	C-Gani [b]
22	641.71	641.16	702.96	610.01	614.53
24	664.51	663.56	748.72	627.42	632.37
28	704.96	703.05	840.24	658.23	663.96
40	796.59	790.76	1114.8	729.44	737.00
60	891.19	877.51	1572.4	810.29	819.98
80	947.74	926.39	2030.0	867.62	878.84
100	983.91	955.86	2487.6	912.07	924.47

[a] Hydrocarbons version ([3]).

[b] Full version ([4]).

The purpose of this work is to review and evaluate some of the most important existing methods for the estimation of T_c, P_c and ω for heavy hydrocarbons and to recommend the best sets (of critical data and acentric factor) which are suitable for CS applications, like generalized cubic EoS, but further to determine the general reliability of the various methods for extrapolation to the heavier members of a homologous series. (The investigated methods and why they have been selected are presented in the next section.) Towards this target a number of calculations have been performed:

1. Vapor pressure predictions for several heavy hydrocarbons will be performed with the LK equation, the CS equations recently proposed by Brandani [7], and two cubic EoS, the modification of SRK ([8]) proposed by Graboski and Daubert [9] and the translated modified Peng–Robinson EoS [10,11].
2. Vapor pressure calculations at the normal boiling point will be performed with the LK equation and the tmPR EoS. The normal boiling points for the heavy n-alkanes will be estimated using the reliable correlation suggested by Tsonopoulos [2] which is expected to be accurate until, at least, up to nC_{36}. The boiling point by Tsonopoulos will be compared with the values predicted by the methods of Joback and Reid [12], Teja et al. [13] and Constantinou and Gani [4].
3. The acentric factors of heavy n-alkanes will be calculated from the LK equation using the critical properties as estimated by the various methods and the normal boiling points obtained from Tsonopoulos correlation. The calculated ω-values will be compared with recent methods for the estimation of acentric factor. It will be investigated whether the ω-values as calculated from the LK equation follow physically correct trends with the molecular weight.

First we present the investigated methods for T_c, P_c and ω and then we discuss the CS equations used. We proceed with the results, the discussion, our recommendations and the conclusions.

2. Methods for the estimation of the critical temperature and the critical pressure

Most methods proposed for the estimation of T_c and P_c, either general or only for n-alkanes, can be divided in two categories:

1. The methods with no finite limiting value/or limiting behavior for T_c (and P_c), like the GC-methods of Lyder-

Table 2
Information regarding the limiting behavior/values for the critical temperature, the critical pressure and the normal boiling point (of *n*-alkanes) obtained from various extrapolation correlations and group-contribution methods

Extrapolation/GC method	T_c (K)	P_c (bar)	T_b (K)
Tsonopoulos [2]	959.98	0.0	1071.28
Gray et al. [27]	959.98	0.0	–
Magoulas and Tassios [11]	959.98	0.0	–
Teja et al. [13]	1143.8	8.4203	1013.4
Hu et al. [26]	1354.65	0.0	–
Lydersen [14]	$T_c/T_b \rightarrow 0$	0.0	–
Elhassan et al. [20]	nlim	0.0	–
Morgan and Kobayashi [28]	981.38	0.0	–
Soave [24]	lim	–	–
Ambrose [18]	$T_c \rightarrow T_b$	0.0	–
Fedors [22]	lim	–	–
Constantinou and Gani [4]	lim	1.371	lim ($T_b < T_c$)
Joback and Reid [12]	$T_c/T_b \rightarrow 0$	0.0	nlim
Kreglewski [21]	960.0	0.0	1078
Bolotin and Shelomentsev [30]	955.4	–	1087
Robinson et al. [25]	897.9	2.22	–
Tsonopoulos and Tan [23]	1072.72	2.68 or 0.0519	–

lim = limiting behavior (without specific limiting value).
nlim = non-limiting behavior (in the sense that when $N_c \rightarrow \infty$ then $T_c/T_b \rightarrow \infty$).

sen [14], Joback (1984) [15], Somayajulu [16], Klincewicz and Reid [17] and Ambrose [18], Ambrose [19], and the method recently proposed by Elhassan et al. [20].

2. The methods with a finite limiting value or limiting behavior for the critical temperature and a zero or a non-zero limiting value for the critical pressure ([4,21,22,13,23–26,29]).

Some of the most characteristic methods for T_c, P_c and T_b and information on their limiting behavior are presented in Table 2.

To demonstrate the significant difference in the T_c and P_c values estimated from some of the above mentioned methods for long-chain alkanes (number of carbon atoms $N_c > 20$), calculated critical properties are presented in Table 1.

The Lydersen, Joback and Ambrose GC-methods require knowledge of the normal boiling point for the estimation of the critical temperature. The recent GC-method by Constantinou and Gani [4] is more general in the sense that the critical temperature (and pressure) are estimated only from the structure of the compound. The, often not experimentally available for heavy hydrocarbons, normal boiling point (T_b) is not needed. The critical temperatures estimated from the Lydersen/Ambrose/Joback methods shown in Table 1 are based on the T_b calculated from the Tsonopoulos [2] correlation. In this case, the so-calculated T_c for nC_{80} and nC_{100} with Lydersen and Jobacek are negative. T_b values for heavy n-alkanes estimated from various methods ([2,13,15,3,4]) are given in Table 1. All group-contribution methods for the estimation of the critical temperature requiring a value for T_b yield their best results when the latter is calculated from the reliable Tsonopoulos correlation, as will be shown later.

In this work the following methods for the estimation of the critical properties will be compared (unless otherwise mentioned T_c is in K and P_c is in bar):

2.1. *The correlations of Magoulas and Tassios [11]:*

$$\ln(959.98 - T_c) = 6.81536 - 0.211145 N_c^{2/3} \quad (1)$$

$$\ln P_c = 4.3398 - 0.3155\, N_c^{0.6032} \quad (2)$$

Eqs. (1) and (2) are applicable only to n-alkanes. The equation for the critical temperature is exactly the one suggested by Tsonopoulos [2], while that of the critical pressure is a modification of similar equations proposed by Tsonopoulos [2] and Gray et al. [27].

2.2. *The correlations of Teja et al. [13]:*

$$\ln(1143.8 - T_c) = 7.15908 - 0.303158\, N_c^{0.469609} \quad (3)$$

$$\ln(P_c - 0.84203) = 1.75059 - 0.196383\, N_c^{0.890006} \quad (P_c : \text{MPa}) \quad (4)$$

Eqs. (3) and (4) are based on the hole theory of fluids and can only be used for n-alkanes. Notice that it is implied that the limiting value of the critical pressure (at infinite carbon number) is 8.4203 bar.

2.3. *The correlations of Hu et al. [26]*

$$T_c = \frac{0.38106 + N_c}{0.0038432 + 0.0017607\, N_c^{0.5} + 0.00073827\, N_c} \quad (5)$$

$$P_c = \frac{10}{0.19694 - 0.059777\, N_c^{0.5} + 0.46718\, N_c} \quad (6)$$

These are among the most recent correlations of critical properties for n-alkanes. As pointed out by the authors and can be seen through the inspection of Table 1, the values for the critical temperature resemble those of Teja et al. correlation, while those of the critical pressure are relatively close to the values estimated by another recently proposed correlation method, that of Tsonopoulos and Tan [23] (see later).

2.4. *The correlations of Tsonopoulos and Tan [23]*

These have been derived for n-alkanes and are based on Flory's theory:

$$T_c = \frac{\tilde{T}_c}{C_0 + C_1 S^{-1} + C_2 S^{-2}} \tag{7}$$

$$P_c = \frac{\tilde{P}_c(b_0 + b_1 S^{-1} + b_2^{-2})}{(\alpha_0 + \alpha_1 S^{-1} + \alpha_2^{-2})^2} \tag{8}$$

The c_i, b_i and a_i values are estimated from experimental data. The parameter s is related to the molecular weight of the n-alkane ($MW = 14.027s - 12.011$). Both the critical temperature and critical pressure assume finite limiting values (see Table 2).

2.5. *The correlations of Morgan and Kobayashi [28]*

$$T_c = 981.38 - 10^{(2.95993 - 0.0860146\, N_c^{0.6667})} \tag{9}$$

$$P_c = 10^{(0.84888 - 0.0112727\, N_c^{0.6667})} \tag{10}$$

Eqs. (9) and (10) are correlations applicable exclusively to n-alkanes. They have been developed based on recent experimental critical data for n-alkanes from Teja et al. [13] up to nC_{18} (for the critical temperature) and nC_{15} (for the critical pressure). Morgan and Kobayashi [28] have also developed a correlation for the acentric factor of n-alkanes, which is discussed in the next section.

2.6. *The GC-method of Lydersen [14]*

This is a general group-contribution method applicable to a variety of organic compounds. Only primary (first-order) groups are involved in the calculations. In the case of n-alkanes, the resulting equations are:

$$\frac{T_c}{T_b} = (0.567 + 0.02N_c - (0.02N_c)^2)^{-1} \tag{11}$$

$$P_c = \frac{MW}{(0.34 + 0.0227N_c)^2} \times 1.01325 \tag{12}$$

The estimation of the critical temperature requires knowledge of the normal boiling point, which has to be estimated from an independent method (e.g. [15,4]).

2.7. *The GC-method of Ambrose [18]*

It is a general method used for the estimation of the critical properties for different families of organic compounds. The method is considered particularly accurate (see [31]) but, in addition to first-order groups, many corrections caused by structural, terminal and other effects are made which make the application of the method for complex compounds rather cumbersome.

However, for n-alkanes the corresponding equations are rather simple:

$$\frac{T_b}{T_c} = \frac{1.242 + 0.138\, N_c}{2.242 + 0.138\, N_c} \tag{13}$$

$$P_c = MW(0.339 + 0.226N_c)^{-2} \tag{14}$$

As in the method of Lydersen, the estimation of T_c requires an accurate value for T_b. In the case of n-alkanes, a suitable correlation can be used (e.g. [2]). The critical pressure equations for n-alkanes of the Lydesren and Ambrose methods are very similar, but the equations for the critical temperature differ significantly both in form and in the actual values. The critical temperature and critical pressure equations of Ambrose are not fully consistent with each other, as also pointed out by Morgan and Kobayashi [28]. The equation for the critical temperature implies that $T_c \rightarrow T_b$ at infinite chain length. This suggests that, in principle, $P_c^{\lim} = 1$ atm (the vapor pressure at T_b). However, the Ambrose equation for the critical pressure yields a zero limiting value at infinite molecular weight, as can be seen from Eq. (14).

2.8. *The GC-method of Joback and Reid [12]*

This is a general GC-method, in fact it is an extension and improvement of the classical method of Lydersen. Here T_b is also required for the estimation of the critical temperature. In the case of n-alkanes, the corresponding equations are:

$$\frac{T_c}{T_b} = (0.584 + 0.965(2 \times 0.0141 + (N_c - 2) \times 0.0189) - (2 \times 0.0141 + (N_c - 2))) \tag{15}$$

$$P_c = (0.113 + 0.0032(3N_c + 2) - 2 \times (-0.0012))^{-2} \tag{16}$$

2.9. *The recent GC-method of Constantinou and Gani [3,4]*

The GC-method by Constantinou and Gani is the most recent method of this kind and deserves special attention. The method uses second-order in addition to first-order groups to capture the fine differences in molecular structure and differences between isomers. Evidently, for n-alkanes no second order contributions are involved. Constantinou and Gani presented in 1993 a version of their method only for hydrocarbons and later (1994) they extended their method to include a variety of organic compounds. The general C-Gani method has, thus, the same range of applicability as the methods of Lydersen, Ambrose and Joback, but is overall more accurate than the latter. An additional very important point regarding the C-Gani method is that the normal boiling point is not required for the estimation of the critical temperature. This represents a significant advantage over the previous GC-methods. In this work, both the hydrocarbon version and the general C-Gani methods are tested.

The T_c and P_c equations for n-alkanes according to the hydrocarbon-version of the C-Gani method are:

$$T_c = 186.481 \ln[2\times 1.3788 + (N_c - 2)\ \times 3.1136] \tag{17}$$

$$P_c = \frac{1}{(0.1068 + 2\times 0.018377 + (N_c - 2)\ \times 0.00903)^2} \tag{18}$$

The critical temperature exhibits a limiting behavior (without reaching a specific limiting value), similar to that of the methods of Fedors [22] and Soave [24]. The critical pressure has a zero limiting value, in agreement with many literature methods. In their general method, Constantinou and Gani retained the same limiting behavior for the critical temperature, but assumed that the critical pressure has a finite limiting value (= 1.3706 bar). The equations for n-alkanes are:

$$T_c = 181.128 \ln[2\times 1.6781 + (N_c - 2)\times 0.00903)^2 \tag{19}$$

$$P_c = 1.3706 + \frac{1}{(0.100220 + 2\times 0.019904 + (N_c - 2)\times 0.010558)^2} \tag{20}$$

2.10. *The correlations of Elhassan et al. [20]*

These recent correlations are based on the observation (made also by other researchers, see Kontogeorgis et al., [32]) that the quantities T_c^2/P_c and T_c/P_c are almost proportional to the molecular weight for each homologous series. Elhassan et al. developed the following equations for n-alkanes:

$$\ln\left(\frac{T_c^{2.5}}{P_c}\right) = 4.38614 + 1.73728 \ln(\mathrm{MW} + 1.78062) \tag{21}$$

$$\ln\left(\frac{T_c}{P_c}\right) = -3.70171 + 1.38315 \ln(\mathrm{MW} + 25.3538) \tag{22}$$

2.11. *The method of Robinson et al. [25]*

They developed a unified method for T_c, P_c and ω for n-alkanes based on the Asymptotic Behavior Correlation (ABC) principle. The critical values from the method of Robinson et al. have been used by several researchers, e.g. Gasem and Robinson [33] in their comparison of the performance of SPHCT and SRK EoS.

2.12. *The old method of Nakanishi et al. [34]*

$$\frac{1}{T_c} = 0.000702 + \frac{0.004192}{N_c^{2/3}} \tag{23}$$

$$P_c = \frac{80.37\times 1.01325}{N_c^{2/3}[1 + 0.1675 N_c^{2/3}]} \tag{24}$$

It is one of the oldest correlation attempts for n-alkanes. It has some merit because of its derivation from the cell model by Kurata and Isida [35].

The above twelve methods represent a good selection of either or both widely used and accepted procedures or theoretically-based approaches, including the most recent ideas. We decided not to evaluate old methods (e.g. Forman–Thodos, Nokay), the GC-methods of Klincewicz and Reid and Daubert and Bartakovits (which apparently have some problems for n-alkanes), and methods proposed only for one of the two critical properties (e.g. Fedors method for T_c and Nath method for P_c).

3. Methods for the estimation of the acentric factor for long-chain n-alkanes

In addition to T_c and P_c, CS equations require a value for the acentric factor ω. The vapor pressure calculations from cubic EoS are rather sensitive to ω, in addition to T_c. Several correlations for n-alkanes and general GC-methods for the estimation of ω have, especially recently, appeared in the literature. They are briefly summarized in this section.

3.1. *The Magoulas and Tassios method*

Magoulas and Tassios [11] proposed a method for the estimation of the acentric factor based on its definition. Critical properties are taken from the correlations given by the same authors. The vapor pressure at reduced temperature equal to 0.7 is obtained from the Antoine equation, with constants calculated by regression of 7 points (T_p, P^s) at $T_r = 0.7$ where T_p is the boiling point temperature at P^s. The so-estimated ω can be correlated with the number of carbon atoms N_c of the n-alkane:

$$\omega = 0.194778 + 3.15382 10^{-2} N_c + 1.73473 10^{-4} N_c^2 - 1.13389 10^{-6} N_c^3 + 8.96972 10^{-9} N_c^4 \tag{25}$$

Eq. (25) is only applicable to normal alkanes.

3.2. *The Kontogeorgis et al. method*

A method for the estimation of the acentric factor of high MW compounds (MW > 150) which uses only the van der Waals volume as input information has been developed recently by Kontogeorgis et al. [32]. Experimental ω-values for n-alkanes/1-alkenes up to n-eicosane were used to develop the following linear relationship between the logarithm of the acentric factor and the van der Waals volume:

$$\ln \omega = -4.91118 + 0.895296 \ln V_w \tag{26}$$

Table 3
Acentric factors for long-chain *n*-alkanes, as predicted by various group-contribution and extrapolation methods

N_c	Magoulas	Morgan	Hoshino	Robinson	Han-Peng	Kontogeorgis et al.	Const. et al.
22	0.9626	0.9093	0.986	0.9654	0.9631	0.96568	0.96487
24	1.0389	0.9673	1.0578	1.0363	1.0320	1.0416	1.0417
28	1.195	1.0792	1.1918	1.1772	1.1634	1.19158	1.1901
40	1.6842	1.4325	1.517	1.6035	1.5168	1.6295	1.5979
60	2.583	2.4175	1.803	–	2.0114	2.33114	2.1782
100	3.6149	8.4031	1.415	–	2.7958	3.6683	3.0966

where V_w is the van der Waals volume (in $cm^3\ gmol^{-1}$), as calculated by the method of Bondi [36]. For n-alkanes V_w is related to N_c:

$$V_w = 6.8781 + 10.2306N_c \tag{27}$$

Upon substitution of Eq. (27) in Eq. (26) we get:

$$\ln \omega = -4.91118 + 0.895296 \ln(6.8781 + 10.2306N_c) \tag{28}$$

Eq. (28) is, like Eq. (25), only applicable to (high MW) n-alkanes. Eq. (26) can be, in principle, applied to any high-molecular weight compound.

3.3. *The Hoshino et al. method*

Hoshino et al. [37] proposed a GC-method for the estimation of the acentric factor for hydrocarbons. The Hoshino et al. method is purely predictive, since it requires the knowledge of only the chemical structure of the compound. The method accounts for terminal effects and side-chain connections (for branched hydrocarbons) and the authors report a mean deviation of 2.2% for 59 hydrocarbons. For n-alkanes, ω is a quadratic function of N_c:

$$\omega = 0.092 + [0.0527 - 0.0004(N_c - 2)](N_c - 2) \tag{29}$$

According to Eq. (29), ω is an increasing function of N_c, until approximately nC_{68} where it reaches a maximum ($\omega^{max} = 1.83$), it then decreases with the carbon atom number and at a very high molecular weight ($N_c > 136$) negative ω-values are obtained. This represents a physically unrealistic behavior, since ω is generally not expected to go through a maximum but to increase monotonically with increasing molecular weight ([38,39]).

3.4. *The Robinson et al. method*

Robinson et al. [25] used a procedure based on the so-called ABC correlation to derive an asymptotic relationship between the acentric factor and N_c. Their equation leads to a limiting value of the acentric factor at very high molecular weights, which, unlike the Hoshino et al. method, can be considered as a physically realistic behavior.

3.5. *The Morgan–Kobayashi (1991) method*

In addition to the above mentioned correlations for T_c and P_c, Morgan and Kobayashi developed a correlation for the estimation of the acentric factor of n-alkanes:

$$\omega = -0.0358 + 0.06348N_c - 1.254910^{-3}N_c^2 + 1.46410^{-5}N_c^3 \tag{30}$$

3.6. *The GC-method of Han and Peng*

Han and Peng [40] recently presented a general GC-method for ω. The authors report a mean deviation of 4.2% for 219 compounds. The Han and Peng method overcomes the problem of the Hoshino et al. approach for n-alkanes. The acentric factor has a limiting behavior, which for n-alkanes is expressed as:

$$\omega = 0.004423[\ln(3.3063 + 3.4381N_c))]^{3.651} \tag{31}$$

3.7. *The GC-method of Constantinou et al.*

Constantinou et al. [41] extended their second-order GC method to the estimation of the acentric factor and the liquid molar volume for a variety of organic compounds. Their method avoids using the Platt number (total number of pairs of carbon atoms which are three bonds apart) employed in the method of Han and Peng and performs slightly better than the latter with an average error of 3%. In the case of n-alkanes the equation is:

$$\exp\left(\left(\frac{\omega}{0.4085}\right)^{0.505}\right) - 1.1507 = 0.29602 \times 2 + (N_c - 2) \times 0.14691 \tag{32}$$

Typical acentric factor values for heavy n-alkanes as estimated by the various methods are presented in Table 3. The acentric factor can also be estimated through a CS vapor pressure equation, as will be discussed later.

4. Corresponding states methods for vapor pressure calculations

The methods for the estimation of the critical properties and the acentric factor mentioned in the previous sections will be tested for vapor pressure calculations with CS equations. The CS methods which will be considered are hereafter briefly described.

4.1. Cubic EoS

Two cubic EoS, the modification of the Soave–Redlich–Kwong ([8]) EoS by Graboski and Daubert (1978; SRK-GD) [9] and the translated modified Peng–Robinson EoS developed by Magoulas and Tassios [11] will be considered. Like all other three parameter cubic EoS, these equations represent applications of the three parameter CS principle. The exact equations together with the temperature dependency of the attractive term (fitted to vapor pressure data for low molecular weight compounds) can be found in the original publications. Vapor pressure and saturated liquid volume predictions for heavy n-alkanes will be presented. Further, the predictive capability of these EoS will be tested by calculating the vapor pressure at the normal boiling point for the heavy n-alkanes. T_b for these alkanes will be estimated using the Tsonopoulos correlation [2].

4.2. The Brandani equations

Brandani [7] proposed recently two CS equations of the form:

$$\ln P_r^s = f^{(0)}(T_r) + \omega f^{(1)}(T_r) \quad \text{(B1)} \qquad (33)$$

$$\ln P_r^s = f^{(0)}(T_r) + \omega f^{(1)}(T_r) + \omega^2 f^{(2)}(T_r) \quad \text{(B2)} \qquad (34)$$

where P_r^s ($=P^s/P_c$) is the reduced vapor pressure and the $f(T_r)$ functions are given by a Wagner-type equation:

$$\ln f^{(i)}(T_r) = \frac{1}{T_r}[\alpha_1 + \alpha_2\tau^{1.5} + \alpha_3\tau^{2.5} + \alpha_4\tau^5 + \alpha_5\tau^{10}] \qquad (35)$$

$$\tau = 1 - T_r \qquad (36)$$

The parameters α_1–α_5 for the $f^{(i)}(T_r)$ functions (of Eqs. (33) and (34)) were fitted to experimental vapor pressure data for 25 nonpolar substances and are given by Brandani [7]. He reports very good vapor pressure predictions for 55 nonpolar compounds of relatively low molecular weight, with a mean deviation of 0.75% using Eq. (33) and 0.68% using Eq. (34). Both Eqs. (B1) and (B2) will be used in this work for vapor pressure calculations for heavy n-alkanes.

4.3. The Lee–Kesler (LK) vapor pressure equation

4.3.1. Description of the method

The vapor pressure equation proposed by Lee and Kesler [42] is a Pitzer-type CS expression which relates the reduced vapor pressure with the reduced temperature and the acentric factor:

$$\begin{aligned}\ln P_r^s = {} & 5.92714 - 6.09648/T_r - 1.28862 \ln T_r \\ & + 0.169347\, T_r^6 + \omega(15.2518 - 15.6875/T_r \qquad (37) \\ & - 13.4721 \ln T_r + 0.43577\, T_{re}^6)\end{aligned}$$

The LK equation accurately predicts the vapor pressure of many nonpolar fluids, especially in the temperature range between T_b and T_c. Since Eq. (37) is a first order expansion with respect to ω, it might not be applicable to heavy n-alkanes (above nC_{18}) having high acentric factor values. As it will be shown in the next two sections, the LK equation may be successfully applied to non-polar high MW compounds.

4.3.2. Acentric factors from vapor pressure equations

When a vapor pressure equation is applied to the normal boiling point an expression for the acentric factor can be derived. In the case of the LK equation the corresponding expression for ω is ([31]):

$$\omega = \frac{\alpha}{\beta} \qquad (38)$$

$$\begin{aligned}\alpha = {} & -\ln P_c - 5.92714 + 6.09648\Theta^{-1} \\ & + 1.28862 \ln \Theta - 0.169347\Theta^6 \qquad (39)\end{aligned}$$

$$\begin{aligned}\beta = {} & 15.2518 - 15.6875\Theta^{-1} \\ & - 13.4721 \ln \Theta + 0.43577\Theta^6 \qquad (40)\end{aligned}$$

$$\Theta = \frac{T_b}{T_c} \qquad (41)$$

The only input information in Eqs. (38)–(41) is the T_c, the P_c and an accurate value for T_b.

Other reduced vapor pressure correlations may be used to derive equations for the acentric factor. When the simple Clausius–Clapeyron equation:

$$\log P^s = A + \frac{B}{T} \qquad (42)$$

is applied to the normal boiling point, the following relation originally proposed by Edmister et al. [43] is derived:

$$\omega = \frac{3}{7}\frac{\Theta}{1-\Theta}\log P_c - 1 \qquad (43)$$

An equation for the acentric factor similar to the LK one (Eqs. (38)–(41)) may be derived from the first Brandani Eqs. (B1), (33). When, however, the second Brandani Eqs. (B2), (34) is applied to T_b, a quadratic equation with respect to ω is derived and the estimation of ω is somewhat more complicated. Similar ω-equations have been derived from other CS vapor pressure equations (e.g. Chen et al. [44]).

Reid et al. [31] state that the LK equation provides accurate ω-values for many hydrocarbons. It has been shown ([32]) that the LK equation provides reasonably good predictions for ω even for high MW and some polar compounds. This indicates that the LK equation may be potentially used for high MW, mostly nonpolar compounds, especially at reduced temperatures close to 0.7.

4.3.3. Vapor pressure predictions for the nC_{18}–nC_{20} n-alkanes

To investigate whether CS methods can be applied with success to high MW alkanes, we have performed vapor pressure calculations with several CS equations for the three high

Table 4
Average percentage absolute deviation between experimental and predicted vapor pressures for nC_{18}, nC_{19} and nC_{20} using different CS equations. The experimental critical data and acentric factors proposed by Ambrose (and reported by Magoulas and Tassios [11]) are used. (Experimental vapor pressure data are from Ambrose (nC_{18}, nC_{19}, nC_{20}), and Chirico et al., [45] for nC_{20})

Compound	LK	B1	B2	SRK	tmPR
nC_{18}	1.1	1.9	3.7	3.8	1.9
nC_{19}	1.4	2.2	3.7	3.1	2.1
nC_{20} (Amb)	2.0	2.7	4.6	3.4	2.4
nC_{20} (Chir)	1.6	3.3	1.5	2.9	1.4

Amb. = experimental vapor pressure data from Ambrose.
Chir. = experimental vapor pressure data from Chirico et al. [45].
All experimental vapor pressure data for nC_{18}, nC_{19}, and nC_{20} (Amb) correspond to temperatures above 350 K.

molecular weight alkanes (nC_{18}, nC_{19}, nC_{20}) for which reliable T_c, P_c, and ω data are available and they are shown in Table 4. The critical properties and the acentric factors used are the ones suggested by Ambrose and reported by Magoulas and Tassios [11]. In Table 4, the average percentage absolute deviations between the experimental and the predicted vapor pressures are shown with the LK equation (Eq. (37)), the two equations proposed by Brandani ((B1) and (B2), Eqs. (33) and (34)), and the two cubic EoS mentioned previously (the SRK-GD and the t-m PR). The predictions with all CS equations are very good for all three hydrocarbons. It is rather surprising that somewhat worse results are obtained with Eq. B2. In the case of n-eicosane, two different sources of experimental data were used ([18,19,45]) but no significant difference in the predictions of the various equations for the different data sets is observed. Thus, it can be concluded that the LK equation may be used with some confidence for high molecular weight alkanes provided that accurate T_c, P_c and ω values are available.

5. Results and discussion

5.1. Screening of the various methods for the estimation of T_c and P_c

As a result of the large number of methods available for the estimation of the critical properties and acentric factor of n-alkanes, we decided to make a preliminary investigation in order to select the best methods, which deserve further study. In order to do so, we have performed sample vapor pressure predictions with a typical cubic EoS (t-m PR) for nC_{22} and nC_{28} for which recent and reliable experimental vapor pressure data are available ([45,46]). Further, in order to establish the effect of the acentric factor on the vapor pressure predictions we have performed calculations using the various methods for estimating ω (described in Section 3) as well as using the 'corresponding' ω for each 'T_c/P_c method'.

By 'corresponding' ω we define the acentric factor calculated from the Pitzer definition of ω:

$$\omega = -\log \frac{P^s}{P_c}\Big|_{T/T_c=0.7} - 1 \tag{44}$$

using the experimental vapor pressures and the T_c, P_c as estimated by the various methods. It is evident that the ω estimated from Eq. (44) should be the one which yields the best vapor pressures for each 'T_c/P_c method'. Table 5 presents experimental values for T_c, P_c and ω for four heavy n-alkanes, where the acentric factor for nC_{22} is estimated from Eq. (44) using the experimental critical properties and the recent vapor pressure measurements from [46].

The results are summarized in Tables 8 and 9. The various methods present significantly different behavior especially for the heavy n-alkane and the following observations can be made:

(i) Several methods (Joback, Elhassan, Nakanishi and Morgan) yield a 'corresponding' ω value for nC_{22} lower than the 'near-experimental' ω-value for nC_{20} (suggested by Ambrose), which is evidently a physically unrealistic behavior.

(ii) The T_c/P_c methods which yield 'corresponding' ω for nC_{22} closer to the 'experimental' value shown in Table 5 are: Magoulas–Tassios, Ambrose, Teja, Hu, Robinson. The corresponding ω for nC_{22} estimated from the Tsonopoulos–Tan and Constantinou–Gani methods are above unity.

(iii) The Joback and Lydersen methods yield the very 'problematic result' for the corresponding acentric factors: $\omega_{28} < \omega_{22}$. All the other methods yield the physically correct behavior $\omega_{28} > \omega_{22}$.

(iv) The best vapor pressure predictions are obtained, irrespectively of the ω-value (within a reasonable ω-values range), from the following T_c/P_c methods: Magoulas–Tassios, Ambrose, Constantinou–Gani, Teja, Hu and Robinson.

The Tsonopoulos–Tan method (which results in rather large corresponding ω-values) yields percentage deviations for nC_{28} above 11% even with the corresponding ω. The same

Table 5
Experimental critical properties and acentric factors for some high molecular weight *n*-alkanes

N_c	T_c (K)	P_c (bar)	ω
18	746	13.0	0.812
19	758	12.3	0.844
20	769	11.6	0.891
22	785.6	10.01	0.96202

Table 6
Average percentage absolute deviation between experimental and calculated vapor pressures for nC_{22} using the t-m PR EoS and various methods for the estimation of the critical properties and acentric factors. (Experimental data from Morgan and Kobayashi [46])

Method for Tc,Pc	ω^{corresp}	% dev ω^{corresp}	% dev $\omega^{\text{Mag-Tas}}$	% dev $\omega^{\text{Con et al.}}$	% dev ω^{Hoshino}
Magoulas-Tassios	0.9645	2.1	1.5	2.2	8.6
Joback	0.8738	6.6	21.4	22.	27.2
Lydersen	0.9827	4.6	2.0	1.3	5.6
Ambrose	0.9557	3.1	5.3	5.9	12.3
C-Gani[1]	1.01374	2.2	14.9	14.2	6.9
C-Gani[2]	1.0207	5.7	12.9	12.1	4.9
Elhassan	0.8871	3.4	20.5	21.3	26.6
Teja	0.96157	3.5	3.7	4.6	11.
Tsonopoulos	1.0124	6.7	9.9	8.9	2.5
Hu	0.9583	2.6	3.9	4.7	11.
Robinson	0.9504	1.1	4.2	4.9	11.1
Morgan	0.90459	3.9	14.9	15.5	21.1
Nakanishi	0.86245	2.1	29.2	29.8	35

Table 7
Acentric factors for nC_{28} calculated from the definition (Eqs. (67) and (44)) using the various methods for the estimation of critical properties. The calculations are based on two sources of experimental vapor pressure data (Chirico et al., [45]; Morgan and Kobayashi, [46])

Method for Tc,Pc	ω using Morgan data	ω using Chirico data
Magoulas-Tassios	1.1827	1.1939
Joback	0.81926	0.8275
Lydersen	0.93409	0.944
Ambrose	1.1427	1.1532
C-Gani[a]	1.2065	1.2178
C-Gani[b]	1.2430	1.2544
Elhassan	1.0022	1.0117
Teja	1.1901	1.20085
Tsonopoulos	1.2719	1.283
Hu	1.1587	1.1695
Robinson	1.1649	1.1762
Morgan	1.0847	1.09565
Nakanishi	1.0252	1.0333

holds for the methods of Elhassan, Joback, Lydersen, while the old method of Nakanishi was rejected for the reasons mentioned previously.

Finally, one interesting result with the Teja method is that, in contradiction with all other T_c/P_c methods, the best vapor pressures results are not obtained with the 'corresponding' ω.

Based on all the aforementioned observations, the following methods seem promising and will be further investigated (also with other CS methods than the t-m PR EoS):

- Magoulas–Tassios
- Ambrose
- Constantinou and Gani
- Hu and co-workers
- Robinson
- Teja and co-workers (with the reservation mentioned above)

However, some basic calculations will be performed with all T_c/P_c methods investigated in this work.

Table 8
Average percentage absolute deviation between experimental and calculated vapor pressures for nC_{28} using the t-m PR EoS and various methods for the estimation of the critical properties and acentric factors. (Experimental data from Morgan and Kobayashi [46])

Method for Tc,Pc	% dev ω^{corresp}	% dev $\omega^{\text{Mag-Tas}}$	% dev ω^{Robinson}	% dev ω^{Han}
Magoulas-Tassios	1.5	5.4	0.4	4.9
Joback	41.8	66.4	64.1	62.2
Lydersen	16.9	57.	54.	51.5
Ambrose	2.8	18.9	13.7	9.5
C-Gani[a]	2.1	1.6	7.6	12.5
C-Gani[b]	4.3	11.5	18.	23.3
Elhassan	10.9	45.1	41.5	38.5
Teja	7.5	9.1	3.8	2.
Tsonopoulos	10.6	15.1	22.1	27.8
Hu	2.8	14.3	8.7	4.3
Robinson	1.7	8.3	2.8	1.9
Morgan	7.6	26.	21.5	17.8
Nakanishi	3.1	46.	42	39.2

[a] Hydrocarbon version [3].
[b] Full version [4].

Table 9
Average percentage absolute deviation between experimental and calculated vapor pressures for nC_{28} using the t-m PR EoS and various methods for the estimation of the critical properties and acentric factors. (Experimental data from Chirico et al., [45])

Method for Tc,Pc	% dev ω^{corresp}	% dev $\omega^{\text{Mag-Tas}}$	% dev ω^{Robinson}	% dev ω^{Han}
Magoulas-Tassios	3.1	3.4	3.4	9.
Joback	64.7	67.6	65.1	62.9
Lydersen	24.5	58.3	55.1	52.7
Ambrose	4.4	19.1	13.1	8.3
C-Gani [a]	3.9	4.6	11.8	17.8
C-Gani [b]	7.4	15.3	23.1	29.7
Elhassan	15.8	46.3	42.2	38.8
Teja	11.2	9.1	3.4	2.9
Tsonopoulos	15.9	17.1	25.4	32.2
Hu	4.5	13.6	7.4	2.5
Robinson	2.1	5.9	2.1	6.
Morgan	10.4	25.1	19.8	15.3
Nakanishi	4.6	48.	43.9	40.6

[a] Hydrocarbon version [3].
[b] Full version [4].

5.2. Vapor pressures for heavy n-alkanes with the best methods

Experimental and reliable vapor pressure data are available for nC_{22}/nC_{24} ([46]), and nC_{28} ([45]; [46]). Typical results with all CS methods investigated are given for nC_{28} in Tables 10 and 11 (using two different values for the acentric factor) in the form of mean average absolute deviations between the experimental and the predicted vapor pressures. The difference between the acentric factor values predicted by the various methods is not significant and, thus, emphasis is given to the determination of the best sets of T_c and P_c for vapor pressure calculations. We have also performed calculations (not presented here) for nC_{32}, nC_{40} and nC_{60} (for which no accurate experimental data area available and the predictions of the various methods are compared with the estimated vapor pressures from the Antoine equation using the constants given by Kudchadker and Zwolinski [47]). The following conclusions summarize our observations:

Table 10
Average percentage absolute deviation between experimental and calculated vapor pressures for nC_{28} using various methods for the estimation of the critical properties and different CS equations. (Experimental data from Chirico et al., [45]). The acentric factor of nC_{28} (= 1.195) is estimated from Magoulas-Tassios method [11]

Method	LK	B1	B2	SRK	tmPR
Magoulas	2.7	8.0	1.7	2.8	3.4
Teja et al.	3.1	2.3	4.5	8.5	9.1
Ambrose [a]	13.6	8.8	14.8	18.0	19.1
C-Gani [b]	10.9	16.6	9.9	6.3	4.6
C-Gani [c]	22.1	28.3	21.1	17.2	15.3
C-Gani [d]	24.2	30.6	23.3	19.3	17.4
Hu	7.9	3.2	9.1	12.4	13.6
Robinson	3.6	6.6	2.4	4.4	5.9

[a] T_b from Tsonopoulos correlation.
[b] Hydrocarbons version [3].
[c] Full version ([4]).
[d] Full version ([4]) with the acentric factor from Ref. [41].

1. Several methods yield errors typically below 20% and can be, thus, considered adequate for preliminary design: the correlation of Magoulas/Tassios, Teja et al., Hu et al., Robinson et al., and the recent GC-method by Constantinou and Gani. The correlations of Magoulas/Tassios and Teja yield the best results, with typical errors less than 10%, especially when combined with the cubic EoS. The method of Robinson is equally good but less general. The overall performance of the Constantinou/Gani method is rather good and, for the heavier alkanes (above nC_{28}), comparable with the best correlations. The Constantinou–Gani method yields an error of 20% for nC_{22}, but the predictions improve for the heavier alkanes: 5%–15% for nC_{28} (depending on the version used), and around 10% for nC_{32} and nC_{36} (surprising as it may be, this behavior is justified by a direct comparison with the recently available critical data for heavy alkanes, as will be shown later). For the lighter alkanes (up to nC_{28}), the hydro-

Table 11
Average percentage absolute deviation between experimental and calculated vapor pressures for nC_{28} using various methods for the estimation of the critical properties and different CS equations. (Experimental data from Chirico et al., [45]). The acentric factor of nC_{28} (= 1.1772) is estimated from Robinson et al. ([25]) method

Method	LK	B1	B2	SRK	tmPR
Magoulas-DT	9.6	15.4	8.7	4.9	3.4
Teja et al.	3.9	9.5	2.7	4.8	3.4
Ambrose [a]	7.5	2.8	8.6	12.1	13.1
C-Gani [b]	18.3	24.4	17.4	13.5	11.8
C-Gani [c]	30.2	36.9	29.3	25.1	23.1
Hu	2.6	4.1	2.6	6.2	7.4
Robinson	6.6	12.1	5.7	2.1	2.1

[a] T_b from Tsonopoulos correlation.
[b] Hydrocarbons version ([3]).
[c] Full version ([4]).

Table 12
Vapor pressures at the normal boiling point for heavy *n*-alkanes using the tmPR EoS and various methods for the estimation of the critical properties. The acentric factors of *n*-alkanes are estimated from Magoulas and Tassios (1990). The normal boiling point values for heavy *n*-alkanes are estimated from Tsonopoulos (1987) correlation. (By definition the vapor pressure at T_b is 1 atm = 1.01325 bar)

Compound	Magoulas	Lydersen	Joback	Elhassan	Teja	Tsonop.	Robinson
nC_{22}	1.017	1.074	0.843	0.888	1.034	1.142	0.979
nC_{24}	1.018	0.966	0.747	0.849	1.056	1.181	0.973
nC_{28}	1.016	0.679	0.516	0.759	1.108	1.265	0.961
nC_{40}	1.025	0.032	0.035	0.498	1.320	1.606	0.964
nC_{60}	1.025	*	*	0.182	1.619	2.293	–

* No convergence is achieved.

Compound	Ambrose	C-Gani [a]	C-Gani [b]	C-Gani [c]	Morgan	Hu	Nakanishi
nC_{22}	1.0203	1.0969	1.109	1.107	0.8959	1.0172	0.8732
nC_{24}	1.0167	1.0873	1.1195	1.1168	0.8767	1.0197	0.8623
nC_{28}	0.9976	1.0449	1.1184	1.1223	0.8338	1.0132	0.8295
nC_{40}	0.9306	0.8616	1.0536	1.0958	0.7277	0.9747	0.7149
nC_{60}	0.7941	0.5225	0.830	0.9351	0.5779	0.8261	0.4851

[a] Hydrocarbons version ([3]).
[b] Full version ([4]).
[c] Full version ([4]) with the acentric factor from Constantinou et al. ([41]).

carbon version of Constantinou/Gani method performs better than the general version. However, for nC_{32} and especially for nC_{36}, both versions perform equally well. There is even a tendency of the general method to perform better. These results make the Constantinou/Gani method a very reliable general method for estimating critical properties of heavy n-alkanes suitable for cubic EoS.

2. For the heavier alkanes (above nC_{32}), the Magoulas/Tassios correlation is the best with an error below 5% for nC_{32} and nC_{40} and even around 10% for nC_{60}. The Robinson method is also very good. The Teja and Hu methods are somewhat less accurate than the Magoulas approach: 10%–20% error for nC_{32} and nC_{40} and 40%(Teja)–60%(Hu) for nC_{60}. The predictions of the Constantinou and Gani method are very impressive, with the new general method performing best for nC_{36} and nC_{40}: the predictions are typically below 15%.

5.3. Vapor pressure predictions at T_b

Predictions of the vapor pressure for heavy n-alkanes (up to nC_{60}) at their normal boiling point (as estimated by the reliable Tsonopoulos correlation) with the t-m PR EoS are given in Table 12. The accuracy of the methods can be easily assessed by observing how close to 1.01325 bar (= 1 atm) are the vapor pressure predictions. In full agreement with the complete vapor pressure calculations presented above, we observe that:

- The Lydersen and Joback methods fail almost immediately. The Elhassan, Nakanishi and Tsonopoulos-Tan methods also clearly fail after nC_{28}, and even for lighter alkanes (above nC_{20}) the predictions are only fair (error around 25%).
- The other methods yield reasonably good predictions at T_b. Somewhat worse is the method of Morgan (18% error for nC_{28}). This is in agreement with the performance of the methods in the whole temperature range.
- Of the correlations investigated, the best overall performance is clearly obtained with the method of Magoulas/Tassios: the error is always less than 2% even for nC_{60}, a really impressive result. Hu's correlation is the second best (error 4% for nC_{40} and 18% for nC_{60}), while Teja's method is less accurate in T_b-calculations (30% deviation for nC_{40} and 60% for nC_{60}). Of course all these conclusions may be subject to change if more accurate T_b data or correlations for this purpose for heavy alkanes become available in the literature.
- The GC-methods of Ambrose and Constantinou/Gani perform very well, considering the general nature of these methods. The Ambrose method yields better estimates of the vapor pressure at T_b for the lighter alkanes, but the Constantinou–Gani method performs better for the heavier ones. Further, the general Constantinou–Gani method (also with ω from Constantinou et al.) performs amazingly well (and better than the hydrocarbon version) for the heaviest alkanes (nC_{40}, nC_{60}), comparable with the best correlations. This implies that the Constantinou–Gani methods can be safely used for extrapolations to heavy compounds.

5.4. Acentric factors for heavy alkanes from the Lee–Kesler equation

Fig. 1 presents a plot of the acentric factor of n-alkanes as calculated by the LK equation using various methods for the estimation of the critical properties. T_b is estimated from the correlation of Tsonopoulos [2]. Based on what has been demonstrated previously in this work, we can assume that both the LK equation and the Tsonopoulos correlation for the normal boiling point are reasonably good until, at least nC_{40}

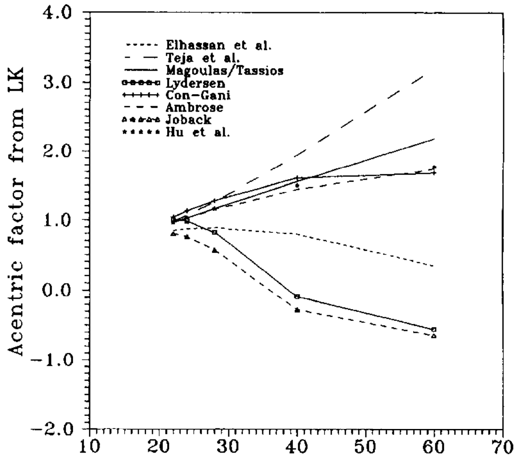

Fig. 1. Acentric factors for heavy n-alkanes (up to nC_{60}) calculated from the Lee-Kesler equation, using various methods for the estimation of the critical properties.

(and possibly nC_{60}, which is the upper limit of the plot shown in Fig. 1). The idea behind the plot shown in Fig. 1 is to investigate whether the various methods for estimating the critical properties yield 'physically reasonable trends and values' for the acentric factor, as the latter is calculated by a corresponding-states equation (here LK). By saying 'physically reasonable trends', we imply that ω should increase monotonically with the number of carbon atoms (or the molecular weight) of the n-alkane. The latter trend is correctly followed by most methods proposed for the estimation of the acentric factor ([11,40,41]).

As can be seen in Fig. 1, the GC-methods of Lydersen and Joback and the method of Elhassan follow a decreasing trend of ω with chain length and are thus not suitable methods for heavy n-alkanes, in agreement with the conclusions made from the vapor pressure comparison. All other methods follow the correct molecular weight trend of ω, but the methods of Constantinou–Gani (general), Magoulas–Tassios and Hu yield more reasonable ω-values compared to the other methods and should thus be recommended for use in CS applications. This conclusion is also in agreement with the previous investigation. As a note added to proof, we mention the calculated (through the LK equation) ω values for nC_{40} (using various T_c/P_c methods): Magoulas/Tassios: 1.56, Ambrose: 1.45, Teja: 1.95, Tsonopoulos/Tan: 2.37, Morgan: 0.96, Hu: 1.50, Nakanishi: 1.19, Constantinou–Gani: 1.61. We also report, for comparison purposes, the ω-values for nC_{40}, as estimated by some direct methods: Magoulas and Tassios [11]: 1.68; Han and Peng [40]: 1.52; Constantinou et al. [41]: 1.59.

5.5. Direct comparison with experimental data

Tables 13 and 14 present a direct comparison of critical temperatures and pressures as estimated by the methods compared in this work and as found from recent experimental measurements ([5]) and Molecular simulation data ([6]). The n-alkanes for which experimental/MS critical data are available are nC_{21}–nC_{24} and nC_{48} and, thus, an evaluation of the capabilities of the various methods up to very heavy

Table 13
Experimental and calculated critical temperature (K) for some long-chain *n*-alkenes

N_c	Exper. value	Magoulas	Teja	Ambrose	Hu	C-Gani [c]	C-Gani [d]
21	777.6 [a]	777.2	781.45	781.63	779.89	769.38	768.75
22	785.6 [a]	786.2	791.4	791.71	789.63	778.53	777.608
23	789.7 [a]	794.7	800.94	801.29	798.88	787.25	786.049
24	799.8 [a,e]	802.6	809.9	810.43	807.66	795.58	794.12
48	923.7197 [b]	903.9	945.08	947.78	939.83	929.326	923.715

[a] Experimental data of Nikitin et al., [5].
[b] Molecular simulation data of Siepmann et al., [6].
[c] Hydrocarbons version ([3]).
[d] Full version ([4]).
[e] The MS value for the critical temperature of nC_{24} is 796.94 K.

Table 14
Experimental and calculated critical pressures (in bar) for some long-chain *n*-alkanes

N_c	Exper. value	Magoulas	Teja	Ambrose	Hu	C-Gani [b]	C-Gani [c]
21	10.3 [a]	10.59	11.45	11.45	11.06	10.07	9.989
22	9.82 [a]	10.01	11.08	10.99	10.58	9.517	9.478
23	9.15 [a]	9.48	10.77	10.57	10.15	9.008	9.012
24	8.66 [a]	8.97	10.49	10.17	9.75	8.538	8.585
48	–	2.946	8.54	5.386	4.937	3.201	3.925

[a] Experimental data of Nikitin et al., [5].
[b] Hydrocarbons version ([3]).
[c] Full version ([4]).

compounds is possible. The purpose of the direct comparison is to establish which of these methods are more suitable for extrapolations to heavy n-alkanes and also yield accurate critical properties which may be used in a variety of applications, and not just vapor pressures.

It seems that two of the methods are the best: the correlation of Magoulas/Tassios and the GC-method of Constantinou and Gani. The method of Hu is the next most accurate approach, while those of Ambrose and Teja show significant differences from the experimental data, both for the critical pressure and the critical temperature. More specifically,

(i) The correlation of Magoulas/Tassios yields excellent critical temperatures and pressures up to nC_{24}, but seems to have small problems upon extrapolation to very heavy n-alkanes: the estimated critical temperature of nC_{48} deviates from the MS data by 20 K.

(ii) Both versions of the Constantinou–Gani method yield T_c for the two lighter n-alkanes which deviates around 10 K from the experimental values. Although P_c is very accurately estimated, this slight problem in the estimation of the critical temperature is the reason for the somewhat larger vapor pressure errors with the method for nC_{22} (given above). The agreement in T_c improves significantly after nC_{23}, and the method yields excellent (the best of all methods) agreement with the MS value of T_c for nC_{48}. This is clear proof of the superiority of the Constantinou–Gani method (over the others) for large extrapolations.

(iii) The errors of the Ambrose and Teja methods in the estimation of the critical pressure is rather large, and although not very important for vapor pressure calculations, this might be a drawback in other applications where a more accurate value for the critical pressure is needed. Also in this case, the Constantinou–Gani method is the best alternative (Magoulas method becomes progressively less accurate for the heavier members and is, of course, restricted to n-alkanes).

(iv) The methods of Hu, though less accurate than Magoulas/Tassios up to nC_{24}, extrapolates equally well to the heavy nC_{48}. The methods of Teja and Ambrose are only slightly worse than that of Magoulas and Hu for nC_{48}. Thus, the only method which clearly shows the best extrapolation behavior is that of Constantinou and Gani and is highly recommended.

6. Conclusions

Several methods for the estimation of the critical properties and acentric factor of n-alkanes are reviewed and tested for their suitability, especially when used in corresponding states methods, like cubic EoS, for vapor pressure calculations. We have investigated both correlations developed specifically for n-alkanes and general group-contribution methods, which can be used for a variety of organic compounds. Our primary interest was to establish the best methods for extrapolation to heavy alkanes for which experimental critical data are not available. We have realized that most methods for the estimation of the acentric factor of n-alkanes yield similar values. The correlations of Magoulas and Tassios [11], Kontogeorgis et al. [32] and the general GC-method by Constantinou et al. [41] can be safely used for this purpose. We focused, thus, on the determination of the best methods for the estimation of the critical temperature and pressure and, towards this purpose, a number of calculations/tests have been performed: vapor pressure predictions for heavy n-alkanes (up to nC_{60}), vapor pressures at T_b, saturated liquid volumes, ω-calculations through the LK equation and even direct comparison with recent experimental and molecular simulation critical data for some heavy n-alkanes. The purpose of making all these different tests was to investigate the overall performance of the different estimation methods for the important family of n-alkanes, with emphasis on the CS applications. We are particularly interested in those estimated critical properties which, when combined with generalized cubic EoS, will yield reasonably good vapor pressures. This is of crucial importance for successful phase equilibrium calculations for mixtures with hydrocarbons: the better the pure component vapor pressures are predicted, the less the interaction parameters will correct for the pure-component behavior and, thus, the easier they will be predicted. All the various types of calculations led to the same conclusions which are briefly summarized here:

(i) The classical GC-methods of Lydersen and Joback are completely unsuitable for heavy alkanes, no matter which value is used for the estimation of the normal boiling point (required for the estimation of T_c with these methods). The old correction of Nakanishi is also non-suitable, despite its theoretical derivation. The same conclusion holds for several recent correlations, especially those by Elhassan et al. [20] and Tsonopoulos and Tan [22]. Despite the plausible assumptions used for their derivation or, in the case of Tsonopoulos method, their theoretical background, they cannot be safely used for extrapolation to heavy alkanes.

(ii) Several methods yield reasonably good or excellent results. Although there is some dependency on the CS equation used, the general conclusions hold, regardless of which CS equation is employed. The five best methods were: three correlations, specifically for n-alkanes, those of Magoulas and Tassios [11], Teja et al. [13], Hu et al. [26] and two GC-methods, the classical method of Ambrose and the recent GC-method of Constantinou and Gani [4]. The correlation of Magoulas–Tassios and the GC-method by Constantinou–Gani yield by far the best results and are the methods to be used in future applications involving heavy alkanes. The Magoulas and Tassios method can be safely used and may be preferred up to nC_{40}. However, if heavier alkanes are involved or if a method with a general applicability is required, the group-contribution method of Constantinou/Gani is a better choice. The latter GC method is the only GC approach not requiring the normal boiling point for the estimation of T_c and furthermore it is, without doubt, the best method for extrapolation to heavy alkanes. Since (i) much of the improvement achieved with the Constantinou/Gani method is due to its special characteristics, like the limiting behavior of the critical properties and (ii) the properties of other heavy compounds approach those of heavy alkanes, we can safely state that the GC-approach of Constantinou and Gani generally represent a very successful method for estimating the critical properties of heavy compounds and is probably the best method available nowadays for extrapolations.

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