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Estimation of Thermophysical Properties of Heavy Hydrocarbons through a Group Contribution Based Equation of State

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This paper presents an improved version of a purely predictive thermodynamic model proposed previously by Coniglio et al. (*Fluid Phase Equilib.* **1993**, 87, 53–88). The main feature of this model is to be based on a Peng–Robinson type equation of state with parameters determined through homogeneous group contribution methods. The new model estimates vapor pressures, saturated liquid densities, heats of vaporization, saturated liquid heat capacities, and speed of sound in saturated liquids of a large number of hydrocarbons within the experimental accuracy, from the triple point to 2 bar. The required inputs for each compound are the molecular structure and the experimental normal boiling point or at least one vapor pressure measurement. The applicability of the new model was verified through prediction of vapor pressures of non-hydrocarbon organic compounds (acids, esters, alcohols, ...). The obtained results confirm the reliability of the new model when extrapolating to non-hydrocarbon organic compounds.

Introduction

Estimation of thermophysical properties of high boiling hydrocarbons plays an important role both in chemical industry for problems related to environment and in petroleum/petrochemical industry for problems related to the heavy cut modeling of crude oils at different steps of production (oilfield, tank storage, and, next, distillation).

Indeed, simulation, design, and analysis of chemical or petrochemical processes require accurate and consistent information on thermophysical properties of pure components and mixtures. Unfortunately, the required properties (phase behavior, thermal properties, ...) are generally neither available for all components nor available at all operating conditions of interest and then need to be estimated by thermodynamic models.

Various models have been proposed in the literature for estimating vapor pressures and heats of vaporization of pure components. These methods may be divided in two classes: first, those based on the Clausius–Clapeyron equation; second, those based on equation of state (EOS). The first class of methods, such as the Wagner (1973),² Lee and Kesler (1975),³ or Ambrose (1986)⁴ method, involves parameters which are specific to each compound and yields poor results for vapor pressures below 0.01 bar. As a result, these methods are not convenient for heavy hydrocarbons whose vapor pressures are much lower than this value in the temperature range of common interest (between 300 and 500 K). The second class of methods based on EOS is particularly interesting as it enables the calculation of vapor–liquid equilibria in a symmetric way (same equations applicable to both phases) and allows the derivation of all

thermodynamic properties calculated with reference to the ideal gas state. Furthermore, these EOS based methods are the only ones suitable for modeling processes operating under high-pressure conditions (such as supercritical processes or oilfields) or involving mixtures with permanent gases (i.e., methane, ethane, etc., such as in crude oils).

For chemical engineering applications, cubic EOS have been the most widely used for their performance and their simplicity. Their parameters (the temperature-dependent energy parameter a , the covolume b , and the volume correction c) are typically determined from the critical properties (T_C , P_C) and the acentric factor ω of the pure components. For heavy hydrocarbons, experimental values of these properties are, however, often not available because of reasons of thermal decomposition. They are then estimated by correlations which are often used outside their applicable range, as crude oils or process mixtures always contain compounds heavier than those considered in the parameter fitting procedure of the correlations.

Finally, chemical or petrochemical processes and crude oils involve currently complex mixtures that contain a lot of components (for example, more than 200 components for a crude oil) with various molecular structures or that are not properly defined in terms of composition and identity of components. Also, these mixtures contain typically heavy components whose few experimental properties are available in the literature. For such problems, the group contribution (GC) concept based exclusively on the molecular structure of the components is a helpful tool to estimate the missing pure component properties. Furthermore, consistent methods based on the GC concept with parameters estimated on cautiously selected experimental data offer safer extrapolation characteristics than correlations.

According to the previous considerations, Carrier et al. (1988, 1990)^{5,6} developed a cubic EOS particularly

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convenient for heavy hydrocarbons with parameters a , b and c estimated by GC methods. Furthermore, the authors expressed the temperature dependence of parameter a by introducing as reference temperature the normal boiling point T_b instead of the conventional critical temperature T_c . The model has however three main weaknesses: (i) The GC parameters of the covolume b were determined from a limited number of experimental critical properties that was possible to find in the literature. The estimated values of the covolume b may therefore be questionable for hydrocarbons heavier than n -dodecane. (ii) The group contributions of parameters a and b were determined on experimental data which were questioned and reviewed. (iii) The model was tested on only three classes of physical properties (vapor pressures, saturated liquid densities, and heats of vaporization).

Therefore, Coniglio et al. (1993)¹ proposed a new model based on a cubic EOS with parameters a , b , and c estimated through homogeneous GC methods by considering exclusively experimental properties that can easily be found for heavy compounds. With this objective, the authors expressed the temperature dependence of parameter a with the normal boiling point T_b as reference temperature as was made by Carrier et al. (1988, 1990).⁵⁻⁶ The model performs accurate estimations of vapor pressures, saturated liquid densities, heats of vaporization and saturated liquid heat capacities for a large variety of hydrocarbons.

An improved version of Coniglio et al.'s (1993)¹ model has been developed and is presented in this paper. The main improvements concern (i) the extension of the exclusively experimental databases selected to develop the model (more data including recently published vapor pressures, more classes of compounds, and more classes of properties), (ii) the formulation of new analytical expressions for the temperature-dependent parameter a and for the shape parameter m that plays the same role as the conventional acentric factor ω , and (iii) a simple procedure proposed to estimate easily the normal boiling point T_b which is required in the parameter a calculation. This procedure is suggested when no experimental data for T_b are available.

After the description of the proposed model, will be presented successively (i) the experimental databases selected to regress the model parameters and to test the model thermodynamic consistency, next (ii) the performances and limitations of the model when correlating and predicting various physical properties of heavy hydrocarbons, and finally (iii) the extension of the model to other classes of compounds.

Description of the Thermodynamic Model

The proposed model is based on the combination "cubic EOS-consistent volume correction" introduced by P  neloux et al. (1982)⁷ and Rauzy (1982).⁸

Equation of State. The cubic EOS used as departure function is of the Peng-Robinson (PR) type (1976)⁹ where the parameters a , b , and c have been modified to fit the estimation of high boiling hydrocarbon properties:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v^2 + 2bv - b^2} \quad \text{with } v_{\text{corrected}} = v - c(T) \quad (1)$$

Estimation of the Covolume b . The estimation of the

covolume b is related to the van der Waals volume V_w which is calculated by Bondi's GC method (Bondi, 1968).¹⁰ Assuming that for a molecule both properties are proportional and by taking methane as reference, we obtain

$$b = b_{\text{CH}_4} \left(\sum_{j=1}^7 V_{w,j} N_j + \sum_{k=1}^3 \delta V_{w,k} I_k \right) / V_{w,\text{CH}_4} \quad (2)$$

with $b_{\text{CH}_4} = 26.80 \text{ cm}^3 \text{ mol}^{-1}$ and $V_{w,\text{CH}_4} = 17.12 \text{ cm}^3 \text{ mol}^{-1}$, where $V_{w,j}$ is the contribution of the j th group to the van der Waals volume and N_j the number of groups of type j . $\delta V_{w,k}$ is the structural increment related to the k th intramolecular effect and I_k the number of corresponding occurrences. The value of the methane covolume b_{CH_4} is obtained from its critical properties ($T_c/K = 190.551$ and $P_c/\text{bar} = 45.992$, Friend et al., 1989).¹¹

Estimation of the Temperature Dependent Parameter a . The expression for function $a(T)$ must meet some basic requirements: (i) to be positive and finite for all temperatures; (ii) to approach a finite value (close to zero) as the temperature approaches infinity; (iii) second derivatives must exist so that heat capacities at constant volume C_v or pressure C_p can be calculated.

The polynomial form of the function $a(T)$ previously proposed by Coniglio et al. (1993)¹ exhibits a physically incorrect behavior according to the aforementioned considerations. Therefore, the exponential form proposed by Melhem et al. (1989)¹² has been adopted and modified to fit heavy hydrocarbon properties:

$$a(T) = a(T_b) \exp \left\{ f_1(m) \left[1 - \left(\frac{T}{T_b} \right)^x \right] - f_2(m) \left[1 - \left(\frac{T}{T_b} \right)^y \right] \right\} \quad (3)$$

where $a(T_b)$ is the value of the function $a(T)$ at the normal boiling temperature (Appendix I). Functions $f_1(m)$ and $f_2(m)$ are expressed in terms of two constants, C_1 and C_2 , which are characteristic of the function $a(T)$ and in terms of the shape parameter m which is characteristic of each compound and has a similar role as the acentric factor (Rogalski et al., 1991).¹³ The values of powers x and y were optimized to fit all the thermophysical properties considered in this work.

$$f_1(m) = \left[\frac{C_2}{(xC_2 - y)} \right] m - \left[\frac{C_1 y}{(xC_2 - y)} \right] \quad (4a)$$

$$f_2(m) = \left[\frac{1}{(xC_2 - y)} \right] m - \left[\frac{C_1 x}{(xC_2 - y)_2} \right] \quad (4b)$$

where $x = 0.4$, $y = 1/x$, $C_1 = 0.787820$, and $C_2 = -16.2469$.

Estimation of the Shape Parameter m . The quadratic expression proposed previously by Coniglio et al. (1993)¹ for estimating the shape parameter m exhibits an extremum around n -C₄₄ and then decreases until negative values are seen from n -C₉₅. For studies related to heavy cut crude oils with waxes or asphaltenes, however, one may have to estimate the properties of large molecules such as n -C₇₀. Obviously, no properties for such high molecular weight compounds will ever be measured and in that case the accuracy of any model will never be evaluated. Nevertheless, the model should

Table 1. Group Contributions and Structural Increments for the Estimation of the Shape Parameter m

groups	M	groups	M
alkanes		aromatics	
CH ₃	0.04963	ACH	0.03208
CH ₂	0.05024	AC substituted	0.04232
CH	0.02920	AC condensed rings	0.00714
C quaternary	0.00000		
structural increments		δm	
Normal Alkanes ^a			
$I_1 = N_c^{-0.5}$ for $N_c \geq 7$		0.07491	
Branched Alkanes ^{b,c}			
$I_2 = N_{c,p} + N_{\text{subst}} - 6$ for $N_c \leq 8$		0.01126	
$I_2 = 2$ for $N_c > 8$			
Ring Systems			
per cyclopentyl ring: I_3		−0.03804	
per cyclohexyl ring: I_4		−0.07293	
per isopropyl or <i>tert</i> -butyl group attached to an aromatic or naphthenic ring: I_5		0.01433	
Polynuclear Aromatics ^d			
$I_6 = 1$ for naphthalene and derived compounds		0.01561	
$I_6 = (-1)^{\alpha} 0.15 (N_{c,2} + 2N_{c,3})$ for other compounds (phenanthrene, pyrene, ...)			

^a N_c : total number of carbon atoms in the molecule. ^b Branched alkanes with neither quaternary carbon atoms nor substituted neighboring carbon atoms. ^c $N_{c,p}$: number of carbon atoms in the main chain. N_{subst} : number of substitutions. ^d α : number of aromatic rings in the molecule. $N_{c,2}$ and $N_{c,3}$: number of aromatic condensed ring carbon atoms in common with two or three rings, respectively.

be consistent in its limiting behavior with nonaberrant property estimations. Therefore, the polynomial form proposed by Coniglio et al. (1993)¹ was modified and the shape parameter m has been expressed in this work through a logarithmic form of a term S calculated on the basis of the GC concept:

$$m = C_3 + S - C_5 \ln(1 + C_4 S^2) \quad (5)$$

with

$$S = \sum_{j=1}^7 M_j N_j + \sum_{k=1}^6 \delta m_k I_k \quad (6)$$

and

$$C_3 = 0.30048, C_4 = 0.08425, C_5 = 0.88/\sqrt{C_4}$$

M_j is the contribution of the j th group to the shape parameter m and N_j the number of groups of the j th type. δm_k is the structural increment related to the k th intramolecular effect and I_k the number of corresponding occurrences. The group contributions and structural increments are given in Table 1. The group identification is exactly the same as the one used for the covolume b estimation. New structural increments, however, had to be defined here in order to account for different intramolecular effects that characterize the shape of a molecule: effect of chain length (for normal alkanes), of branching (gauche correction and blocked rotation for branched alkanes), of ring correction (different for cyclopentyl or cyclohexyl naphthenes), of intramolecular steric crowding (for isopropyl and *tert*-butyl group attached to an aromatic or naphthenic ring), and of plane geometry characteristic of polynuclear aromatics

Table 2. List of Compounds Requiring the Corrective Term Δm for the Estimation of the Shape Parameter m

compound	Δm
cyclopentane	-0.03911
cyclohexane	-0.04600
isopropylcyclopentane	-0.04326
benzene	0.03196
toluene	0.00972

coupled with the π orbital overlapping that helps to distinguish among catacondensed (triphenylene) or pericondensed (pyrene) compounds.

Five hydrocarbons of low molecular weight had to be treated individually (cyclopentane, cyclohexane, isopropylcyclopentane, benzene, toluene). Three of them are first in the homologous series (benzene, cyclopentane, cyclohexane) and exhibit then a particular behavior compared to derived branched compounds (for example, *n*-alkylbenzenes, *n*-alkylcyclopentanes, and *n*-alkylcyclohexanes, respectively). Their shape parameter m is estimated by eq 7 where the values of corrections Δm are given in Table 2.

$$m = C_3 + S - C_5 \ln(1 + C_4 S^2) + \Delta m \text{ with } S =$$

$$\sum_{j=1}^7 M_j N_j \quad (7)$$

Estimation of the Temperature-Dependent Volume Correction c . The same equations as those proposed by Coniglio et al. (1993)¹ are used in the new model. As they involve the shape parameter m , whose estimation method has been changed in this work (different equation and group contribution values, see previous section "Estimation of the shape parameter m "), new parameters had to be evaluated. The expressions are recalled in

$$c(T) = c(T_b)[1 + \alpha_0(1 - Y) + \beta_0(1 - Y)^2] + (-1 + \sqrt{2})b \text{ with } Y = \exp\left(1 - \frac{T}{T_b}\right) \quad (8)$$

$$\alpha_0 = \alpha_1 T_b^2 + \alpha_2 \text{ and } \beta_0 = \beta_1 T_b + \beta_2 \quad (9)$$

with $\alpha_1/10^{-6} = 1.89213$, $\alpha_2 = -0.25116$, $\beta_1/10^{-3} = 2.20483$, and $\beta_2 = -1.22706$.

The value of the volume correction at the normal boiling point $c(T_b)$ is

$$c(T_b) = \alpha_b T_b + \beta_b m^2 - S \quad (10)$$

where $\alpha_b = 0.27468$ and $\beta_b = -50.94930$. The term S is calculated by a procedure analogous to the one used for the estimation of the covolume b and the shape parameter m

$$S = \sum_{j=1}^7 C_j N_j + \sum_{k=1}^3 \delta C_k I_k \quad (11)$$

where C_j is the contribution of the j th group to $c(T_b)$ and N_j the number of groups of the j th type. δC_k is the structural increment related to the k th intramolecular effect and I_k the number of corresponding occurrences. The group and structural increment identification is

Table 3. Group Contributions and Structural Increments for the Estimation of the Volume Correction at the Normal Boiling Point $c(T_b)$

groups	C (cm ³ mol ⁻¹)	groups	C (cm ³ mol ⁻¹)
alkanes		aromatics	
CH ₃	35.9209	ACH	19.3874
CH ₂	13.2044	AC substituted	-4.2938
CH	-11.4445	AC condensed rings	7.4171
C quaternary	-36.3578		
structural increments		δC (cm ³ mol ⁻¹)	
per cyclopentyl and per cyclohexyl ring singly bonded or in condensed cyclic naphthene in trans conformation: I_1^a		44.2322	
per cyclopentyl and per cyclohexyl ring in condensed cyclic naphthene in cis conformation: I_2^b		46.1907	
per methylene ring condensed to aromatic ring (system): I_3^c		46.1120	

^a *trans*-Decaline. ^b *cis*-Decaline. ^c Tetraline, indane.

exactly the same as the one used for the estimation of the covolume b . Their values are given in Table 3.

As was encountered previously for the estimation of the shape parameter m , cyclopentane and cyclohexane had to be treated individually due to the particularities of their structures. For these two compounds, the $c(T_b)$ expression (eq 10) has to be corrected by adding a term Δc equal to 2.45810 for cyclopentane and 3.96556 for cyclohexane.

Estimation of the Normal Boiling Temperature. The proposed model needs as input the normal boiling temperature T_b which is used as reference temperature both for the estimation of the temperature-dependent parameter a and for the estimation of the temperature-dependent volume correction c . For very heavy hydrocarbons (much heavier than those considered in the model parameter regression), this datum is, however, not always properly known experimentally for reasons of thermal decomposition. In these circumstances, it is necessary to estimate it. Estimation methods for T_b that can be found in the literature, such as the Joback (1984),¹⁴ Constantinou and Gani (1994),¹⁵ or Avaullée et al. (1997)¹⁶ method, perform very well. A higher degree of accuracy in T_b estimations, however, is required to obtain satisfactory results when calculating vapor pressures with the proposed EOS-based model. Therefore, we choose in this work to estimate T_b via the proposed model with the knowledge of at least one vapor pressure measurement (T_o , P_o). At the temperature T_o , eq 3 becomes

$$a(T_o) = a(T_b) \exp \left\{ f_1(m) \left[1 - \left(\frac{T_o}{T_b} \right)^x \right] - f_2(m) \left[1 - \left(\frac{T_o}{T_b} \right)^y \right] \right\} \quad (12)$$

where the only unknown is T_b that was estimated by successive iterations in order to fit the vapor pressure P_o . When several measurements (T_o , P_o) were available, T_b was obtained by minimizing the percent average relative deviation in the vapor pressures (eq 13). Obviously, the reliability of this procedure should depend not only on the performance of the predictive model used but also on the accuracy of the available experimental vapor pressures and their location on the saturation pressure curve.

The proposed GC methods for estimating the parameters b , m , and $c(T_b)$ are illustrated in Appendix II.

Description of the Selected Experimental Databases

These databases should be divided in two classes: (i) The first is the databases used to estimate the GC parameters involved in the model. These are vapor pressures for the shape parameter m and liquid densities for the volume correction at the normal boiling temperature $c(T_b)$. This class of databases will be designated as class A. (ii) The second is the databases used to check the thermodynamic consistency of the model (heats of vaporization, saturated liquid heat capacities, and speed of sound in saturated liquids). This class of databases will be designated as class B.

Furthermore, the databases of class A (vapor pressures and saturated liquid densities) should also be divided in two subclasses: (ia) The first is the measurements selected to regress the GC parameters of the model. They concern low to high molecular weight hydrocarbons. This subclass of databases will be designated as class A1. (ib) The second is the measurements selected to evaluate the predictive abilities of the model with the GC parameters determined previously. They concern very high molecular weight hydrocarbons. This subclass of databases will be designated as class A2. Among the databases of class A, only those of class A1 will be described in detail below, due to the important role they play in the model development. Moreover, the class A2 databases have roughly the same features (with the exception of the number of compounds and the number of measurements involved that will be given in the tables of results).

Databases Selected for the Model Parameter Regression (Class A1). The successful character of a GC method depends not only on its own definition (analytical expressions and group identification) but also on the number and the quality of the measurements selected to fit the group parameters, since the latter have to be regressed on the whole of the experimental data. Furthermore, these data should cover a wide temperature range and a large number of classes of compounds. As far as we are concerned in this work, these compounds should be commonly found in crude oils (paraffines, naphthenes, alkylbenzenes, and polynuclear aromatics), and also, most of them should be high boiling hydrocarbons in order to increase the predictive abilities of the model (that will be evaluated in a second step with the databases of class A2). Obviously, the latter two requirements are also necessary for the databases used to check the thermodynamic consistency of the model (class B). For high boiling hydrocarbons, few property measurements are however available in the literature, although an important effort was made during the last 10 years.

(a) Vapor Pressure Database. The selected database comprises 128 hydrocarbons whose experimental normal boiling temperatures range from 300 to 600 K and experimental vapor pressures range from 10^{-6} to 7 bar. The whole of the database comprises 3385 data. As the vapor pressure measurements are of very different orders of magnitude and experimental accuracy, they were divided into three classes.

(i) The first is the very low vapor pressures (VLP) ranging from 10^{-6} to 0.01 bar. Most of them are from a French laboratory (Allemand et al., 1986;¹⁷ Sasse,

1988;¹⁸ Sasse et al., 1988;¹⁹ Kasehgari et al., 1993;²⁰ Viton, 1995;²¹ Mokbel et al., 1995;²² 1998)²³ or an American laboratory (Chirico et al., 1989),²⁴ both of them specialized in this kind of measurements. The experimental uncertainties typically given by the authors are ± 0.02 K for the temperature and $\pm 1\%$ for the pressure.

(ii) The second is the low vapor pressures (LP) ranging from 0.01 to 0.06 bar. The data are from various sources, and the experimental uncertainties on the temperature and pressure depend highly on the authors.

(iii) The third is the medium vapor pressures (MP) ranging from 0.06 to 2 bar (7 bar for some heavy alkylbenzenes and polynuclear aromatics). These are ebulliometric data of a great accuracy and most of them were made around 1945 by the NBS/American Petroleum Institute. The experimental uncertainties given by the authors are ± 0.003 K for the temperature and ± 0.06 mmHg for the pressure.

The relative proportions of each class of measurements in the whole of the database are 11, 7, and 82% respectively.

Furthermore, to build a vapor pressure database that could be consistent and reliable, the measurements were previously screened with the graphical method proposed by Wilsak and Thodos (1984)²⁵ and modified by Coniglio (1993)²⁶ for application to very low vapor pressures. During this step of screening, two features were noticed: (i) For VLP, two sets of measurements made by two different authors and showing an inner scattering very small can nevertheless exhibit a discrepancy of 2 to 12% between them, depending on the authors and the location of these measurements in the VLP range. In similar cases, all data were retained as it was impossible to decide which author made the most consistent measurements. (ii) Globally, there is a disparity of quality between the vapor pressure measurements (VLP, LP, and MP).

(b) Saturated Liquid Density Database. The experimental database of saturated liquid densities was built exclusively from the TRC Tables²⁷ and the Dreisbach compilation (1955,²⁸ 1959²⁹). The final database comprises 121 hydrocarbons whose normal boiling temperature ranges from 300 to 600 K and density data range from the triple point to a boiling temperature corresponding to 2 bar.

Databases Selected To Check the Thermodynamic Consistency of the Model (Class B). Like the previous databases, all experimental data considered here range from the triple point to 2 bar and cover a large variety of hydrocarbons found in crude oils (paraffines, naphthenes, alkylbenzenes and polynuclear aromatics). The latter were selected among very high boiling compounds in order to consolidate the evaluation of the predictive abilities of the model.

In the literature, thermal property measurements of pure compounds are much less numerous than vapor pressure measurements. Therefore, among the 128 hydrocarbons taken as reference to build the proposed model, experimental data could be collected only for few hydrocarbons: 69 compounds for the heats of vaporization $\Delta_{\text{vap}}H$ and the saturated liquid heat capacities C_{PL} . The $\Delta_{\text{vap}}H$ database is mainly from the Majer and Svoboda (1985)³⁰ compilation, which was completed with several other experimental data published more recently. The C_{PL} database is mainly from the TRC Tables²⁷ and the Stephan et al. (1987)³¹ compilation;

however, for naphthenes, no data were available in these compilations, and thus some measurements from various sources were considered.

The speed of sound measurements in saturated liquids W_L , particularly for heavy hydrocarbons, are scarce. Therefore, the final W_L database also comprises measurements made at atmospheric pressure, assuming small variations of the property at low pressures.

The experimental uncertainties typically given by the authors are 0.2–0.5% for the heats of vaporization, 0.1–0.2% for the saturated liquid heat capacities, and 0.2–0.01% for the speed of sound in saturated liquids.

Evaluation of the Performances and Limitations of the Proposed Model

The results obtained for the vapor pressures and the saturated liquid densities were distinguished in two classes according to the databases of class A1 and class A2; they are related to (i) the “correlation results” related to hydrocarbons which belong to the experimental databases selected for the model parameter regression (databases of class A1) and (ii) the “prediction results” related to hydrocarbons chosen out of these databases (databases of class A2). Only the second class of results will be described in detail below since the objective of a purely predictive model is to estimate as reliably as possible properties for which no verification can be made due to the lack of experimental data.

The results related to property X will be expressed in terms of percent average relative deviations ($\delta_r(X)\%$, eq 13) or average absolute deviations ($\Delta(X)$, eq 14) defined as

$$\delta_r(X) \% = \frac{100}{N_p} \sum_{i=1}^{N_p} \left| \frac{X_i^{\text{exp}} - X_i^{\text{cal}}}{X_i^{\text{exp}}} \right| \quad (13)$$

$$\Delta(X) = \frac{1}{N_p} \sum_{i=1}^{N_p} |X_i^{\text{exp}} - X_i^{\text{cal}}| \quad (14)$$

where N_p is the number of experimental determinations relating to the property X , whereas superscripts exp and cal refer respectively to the experimental and calculated values.

Vapor Pressure Predictions (Class A2 Database). Concerning first the vapor pressure correlations, the results were as follows: (i) $\delta_r(P_S) = 0.6\%$ for the overall data, which is very acceptable when considering the discrepancy in the quality of the data. Also, the deviations were the same regardless of the class of hydrocarbons involved. (ii) $\delta_r(P_S) = 2\%$ for the VLP, which is very satisfying and remains close to the experimental uncertainty related to this type of measurements. Concerning now the vapor pressure predictions, the results are summarized in Table 4 where distinction is made between heavy hydrocarbons whose experimental normal boiling point T_b is known (a) and those whose measured values T_b could not be found in the literature (b).

(a) Moderately Heavy Hydrocarbons Whose Experimental T_b Is Known. The experimental data of vapor pressures considered here are of much lower quality than those considered for the model parameter regression and are mainly VLP and LP data. Nevertheless, the obtained deviations confirm the predictive abilities of the proposed model which yields vapor pressure predictions of about the same accuracy as the

Table 4. Vapor Pressure Predictions with the Proposed Model. Results for Hydrocarbons Whose Experimental Normal Boiling Point T_b (a) Is Known (Number of Compounds, 23; T_b/K , 434 to 667; P_s/bar , 4×10^{-6} to 0.1) or (b) Is Not Available and Then Is Estimated via the Proposed Model (Number of Compounds, 55; estimated T_b/K , 430 to 750; P_s/bar , 3×10^{-6} to 0.8)

(i) Information by Class of Hydrocarbons				
class of hydrocarbons	(a) experimental T_b known		(b) T_b estimated via the proposed model	
	N_p	$\delta_r(P_s)$ (%)	N_p	$\delta_r(P_s)$ (%)
normal alkanes	218	1.33	190	1.79
branched alkanes			82	2.96
cyclopentanes	4	0.39	15	0.44
cyclohexanes	194	1.40	119	1.05
alkylbenzenes	158	3.58	519	2.10
polynuclear aromatics	124	1.80	196	2.05
overall	698	1.94	1121	1.97

(ii) Information by Pressure Range				
pressure range	(a) experimental T_b known		(b) T_b estimated via the proposed model	
	N_p	$\delta_r(P_s)$ (%)	N_p	$\delta_r(P_s)$ (%)
VLP	256	3.25	775	2.17
LP	134	2.15	122	1.44
MP	308	0.75	124	1.66

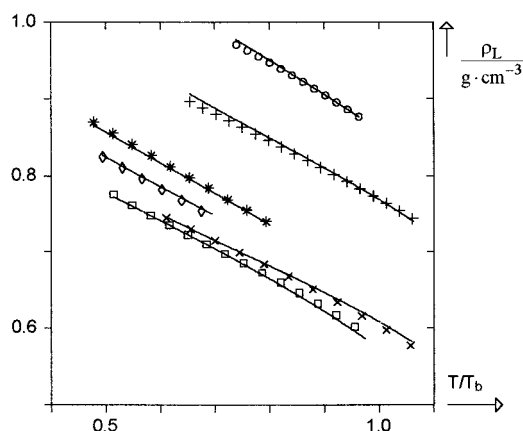


Figure 1. Saturated liquid density correlations. Analysis in terms of temperature for some classes of hydrocarbons: (x) *n*-decane; (\square) *n*-octadecane; (\diamond) *n*-decylcyclopentane; (*) *n*-decylbenzene; (+) *o*-xylene; (\circ) naphthalene.

VLP and LP correlations (deviation obtained here: $\delta_r(P_s) = 1.9\%$ for the data as a whole).

(b) Very heavy hydrocarbons whose T_b is estimated via the proposed model. It was observed that vapor pressures calculated by the proposed model (particularly the VLP) were very sensitive to errors made on T_b (a deviation $\Delta(T_b)/K = 1$ led to a deviation $\delta_r(P_s) = 5\%$ when considering VLP). Therefore, T_b needs to be known with a great accuracy.

To evaluate the degree of accuracy of the proposed procedure for estimating T_b , the hydrocarbons selected in the vapor pressure database used for the model parameter regression (database of class A1) were first considered. Assuming that their T_b was unknown, we estimated it by considering either the VLP or the LP measurements. The most accurate estimations were obviously obtained when considering vapor pressures located as close as possible to the normal boiling point. Nevertheless, the errors on T_b were never greater than 0.3 K, and the vapor pressures were calculated within the experimental accuracy of this type of measurements: 1% for the VLP and 0.2% for the LP. These results confirm the reliability of the proposed procedure for estimating T_b which was then applied to hydrocarbons related to the vapor pressure database of class A2.

From the obtained deviations presented in Table 4, it can be concluded that the proposed model yields very good vapor pressure predictions of the same accuracy as the one obtained for hydrocarbons with known T_b (deviation $\delta_r(P_s) = 2\%$ for the compounds as a whole). This feature is all the more satisfying since most of the vapor pressures considered here are VLP (70%) with even larger experimental uncertainty and discrepancy than could be observed for all the vapor pressure data considered previously (in the model parameter regression and in the vapor pressure predictions of hydrocarbons with experimentally known T_b). Furthermore, in some cases, the T_b estimates are very close or sometimes equal to those given by the TRC Tables.²⁷

Finally, a comparison of the method proposed by Kontogeorgis et al. (1997)³² which is based on the same idea as the one presented in this section has been made: (first step) estimate the key properties required for the calculation of the cubic EOS parameters with the knowledge of the structure of the compound and at least one vapor pressure measurement; (second step) estimate the vapor pressures of the compound over an extended temperature range. As Kontogeorgis et al. (1997)³² used the three-parameter corresponding state principle, the key properties in their method are, the critical temperature T_c , the critical pressure P_c and the acentric factor ω (whereas in our method the key properties are T_b and the shape parameter m since the EOS parameter b is directly calculated by Bondi's GC method, Bondi, 1968).¹⁰ Comparison of the vapor pressures predicted by the two methods was made for few hydrocarbons and showed that the method proposed in this paper performs somewhat better (for *n*-octacosane and *n*-decylcyclohexane, this work, $\delta_r(P_s) = 0.9\%$ and 2.2% , respectively, while for Kontogeorgis et al. (1997),³² $\delta_r(P_s) = 2.8\%$ and 9.2% , respectively). Kontogeorgis et al.'s (1997)³² method is however valid for larger classes of compounds, and therefore, further comparisons should

Table 5. Saturated Liquid Density Predictions

compound	T_b/K^a	reference for T_b	temperature/K		N_p	$\delta_r(\rho_L)$ (%)	reference for ρ_L
			min	max			
2-ethylnaphthalene	531.08	TRC (1969) ²⁷	273.15	413.15	15	1.31	TRC (1967) ²⁷
<i>n</i> -octylbenzene	537.55	TRC (1956) ²⁷	273.15	453.15	19	0.44	TRC (1953) ²⁷
<i>n</i> -decylcyclohexane	570.74	Camín (1955) ³³	273.15	383.15	12	0.31	TRC (1953) ²⁷
<i>n</i> -heptadecane	575.17	TRC (1970) ²⁷	298.15	603.15	32	0.86	TRC (1973) ²⁷
<i>n</i> -dodecylbenzene	600.75	TRC (1956) ²⁷	283.15	453.15	18	0.38	TRC (1953) ²⁷
<i>n</i> -nonadecane	603.75	TRC (1957) ²⁷	313.15	383.15	8	0.26	TRC (1973) ²⁷
overall					104	0.66	

^a The values of the normal boiling temperature T_b estimated via the proposed model are very close to those given in the cited references. Therefore, we choose to use the latter values of T_b in order to consider this trial as pure prediction.

Table 6. Estimation of Heats of Vaporization, Saturated Liquid Heat Capacities, and Speed of Sound in Saturated Liquids^a

class of hydrocarbons	thermal properties and speed of sound					
	N_p	$\delta_r(\Delta_{\text{vap}}H)$ (%)	N_p	$\delta_r(C_{PL})$ (%)	N_p	$\delta_r(W_L)$ (%)
normal alkanes	120	0.82	212	0.60	133	9.75
branched alkanes	77	0.41	444	2.59	164	8.84
cyclopentanes	14	0.29	122	2.98		
cyclohexanes	139	0.50	416	1.92	6	8.03
alkylbenzenes	151	0.50	177	1.45	40	10.35
polynuclear aromatics	102	1.14	83	1.79		
overall	603	0.66	1454	1.96	343	9.35

^a $\Delta_{\text{vap}}H$: number of compounds, 69; T_b/K , 310–615; T/K , 260–650. C_{PL} : number of compounds, 69; T_b/K , 310–610; T/K , 120–460. W_L : number of compounds, 28; T_b/K , 300–560; T/K , 200–470.

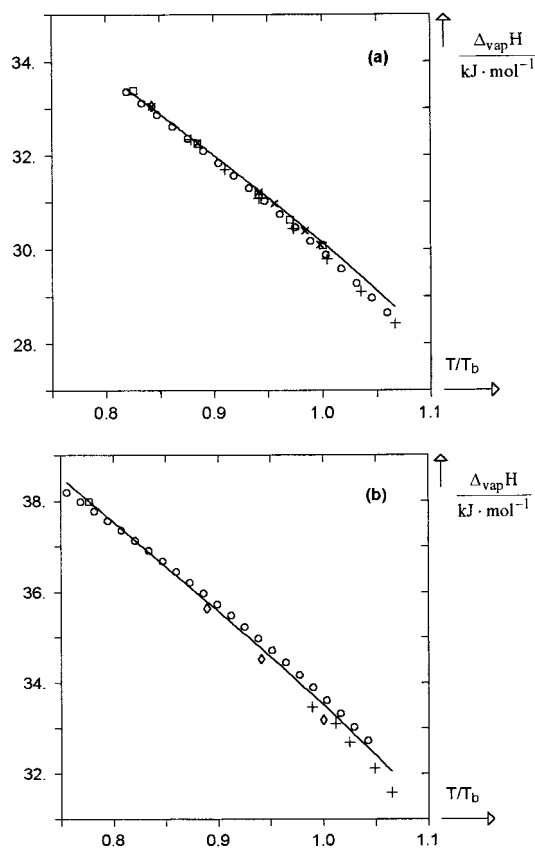


Figure 2. Heats of vaporization. Comparison between experimental (patterns) and calculated values with the proposed model (—). (a) Cyclohexane, $T_{\text{fus}}/K = 279.65$, $T_b/K = 353.86$, $\delta_r(\Delta_{\text{vap}}H)\%$ = 0.40 for 40 data: (+) Kozicki et al. (1961);³⁰ (□) Svoboda et al. (1973);³⁰ (x) Majer et al. (1979);³⁰ (◇) Shimizu et al. (1981);³⁰ (○) Stephan et al. (1987).³¹ (b) Toluene, $T_{\text{fus}}/K = 178.15$, $T_b/K = 383.77$, $\delta_r(\Delta_{\text{vap}}H)\%$ = 0.47 for 32 data: (□) Osborne et al. (1947);³⁰ (◇) Scott et al. (1962);³⁰ (+) Natarajan et al. (1985);³⁰ (○) Stephan et al. (1987).³¹

be made before drawing general conclusions. It can be said, however, that the main advantage of this work is to render possible the development of a GC method for T_b suitable with the cubic EOS used and to obtain thereby, a purely predictive model requiring absolutely none experimental information.

Saturated Liquid Density Predictions (Class A2 Database). Concerning first the density correlations, the calculated values obtained from the proposed volume correction are in very good agreement with experimental data (deviation for the data as a whole: $\delta_r(\rho_L)$

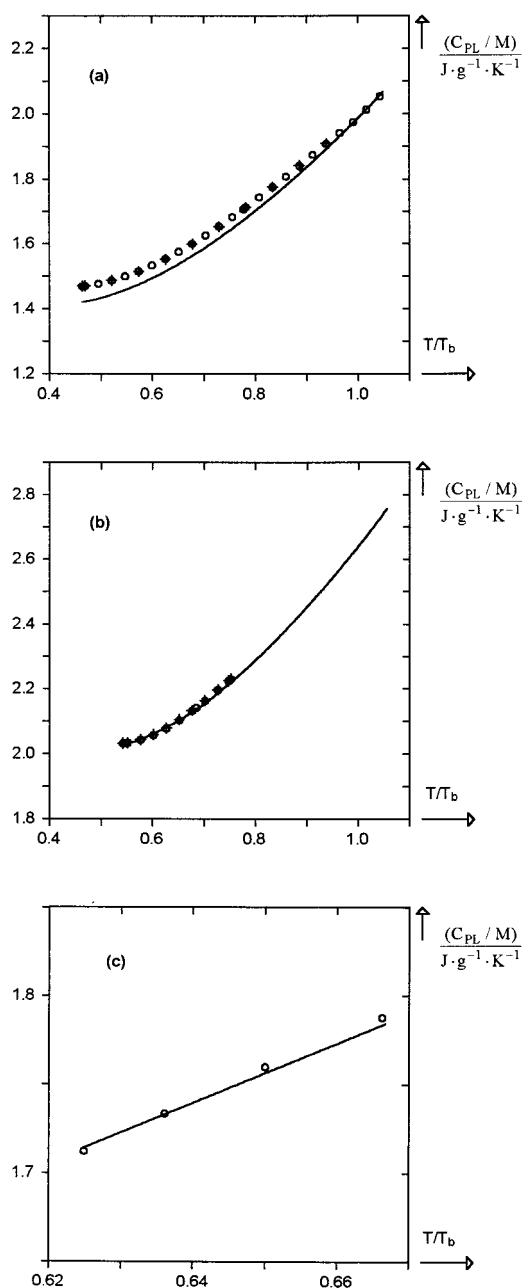


Figure 3. Saturated liquid heat capacities. Comparison between experimental (patterns) and calculated values with the proposed model (—). (a) Toluene, $T_{\text{fus}}/K = 178.15$, $T_b/K = 383.77$, $\delta_r(C_{PL})\%$ = 2.00 for 36 data: (x) Scott et al. (1962);³⁴ (○) TRC (1986).²⁷ (b) *n*-Octane, $T_{\text{fus}}/K = 216.35$, $T_b/K = 398.81$, $\delta_r(C_{PL})\%$ = 0.26 for 23 data: (○) Messerly et al. (1967);³⁵ (x) TRC (1976).²⁷ (c) Phenanthrene, $T_{\text{fus}}/K = 374.15$, $T_b/K = 613.37$, $\delta_r(C_{PL})\%$ = 0.14 for 4 data: (○) Finke et al. (1977).³⁶

= 0.5%). This feature is also illustrated in Figure 1 for some classes of hydrocarbons. Concerning now the density predictions, the obtained results are reported in Table 5 for several hydrocarbons. They are of about the same accuracy as the correlation results (deviation obtained here for the data as a whole: $\delta_r(\rho_L) = 0.7\%$) and confirm the reliability of the proposed model.

Thermal Properties and Speed of Sound in Saturated Liquids (Class B Databases). All the obtained results are summarized in Table 6.

(a) Heats of Vaporization. As can be observed, the proposed model yields very good estimates with an error of 0.7% for the overall data, which is of the same order

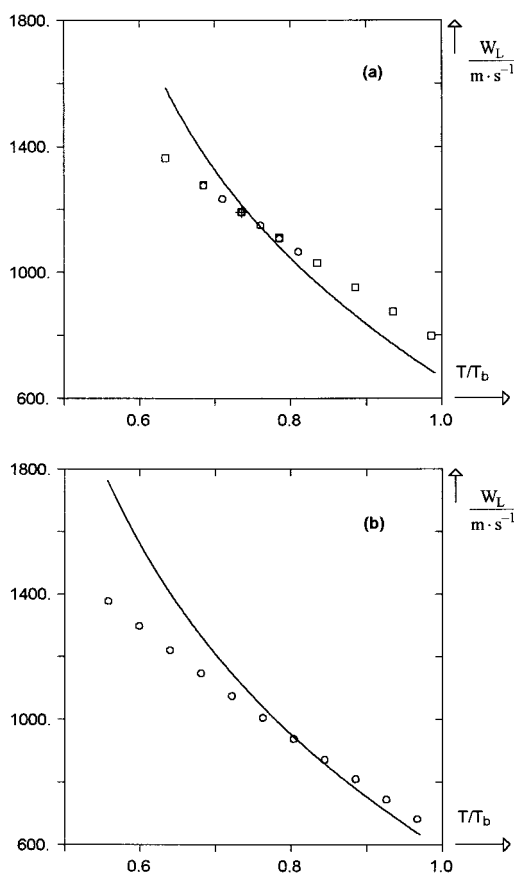


Figure 4. Speed of sound in saturated liquids. Comparison between experimental (patterns) and calculated values with the proposed model (—). (a) *n*-Octane: (○) Freyer et al. (1929);³⁷ (×) Geelen et al. (1955);³⁸ (□) Boelhouwer (1967).³⁹ (b) *n*-Heptadecane: (○) Boelhouwer (1967).³⁹

of magnitude as the experimental uncertainty for this type of measurements. Figure 2 shows that this behavior is exhibited over the entire experimental temperature range, which is unfortunately quite limited in these examples (for cyclohexane from 292 to 378 K, but for toluene from 298 to 409 K).

(b) Saturated Liquid Heat Capacities. Larger deviations are obtained for this property: the error is slightly less than 2% for the experimental data as a whole. From a previous work made by Coniglio (1993),²⁶ it can be said that the proposed model yields more accurate estimations than Carrier et al. (1988)⁵ or even Coniglio et al. (1993)¹ (errors obtained by considering the same experimental database as in this work: 5.3% and 2.3%, respectively). Furthermore, it should be noted that an EOS does not allow the direct calculation of the saturated liquid heat capacities C_{PL} but actually the difference ($C_{PL} - C_P^{id}$), where C_P^{id} is the ideal gas heat capacity. The latter property was estimated in this work through a semiempirical correlation (Coniglio et al. 1993)¹ leading to a deviation of 0.05% when compared with data from the TRC Tables.²⁷ Figure 3 illustrates the variation of the calculated and experimental C_{PL} in terms of temperature and confirms the satisfactory performance of the proposed method. Indeed, the proposed model estimates the shape of the experimental curves perfectly even when the vapor pressures used for the estimation of the EOS parameters were measured at higher temperatures.

Table 7. Group Contributions and Structural Increments for the Estimation of the Shape Parameter m^a

groups	M	groups	M
alkenes		oxygen derivatives	
=CH ₂	0.03296	COO	0.20363
=CH—	0.05010	COOH	0.58631
=C<	0.05799	OH	0.23489
structural increments		δm	
per single bond between conjugated		0.00158	
double bonds (C=C—C=C)			
per ring with 4 carbon atoms		0.01266	
per double bond adjacent to an		−0.25540	
alcohol group (>C=C—OH)			

^a Information required for the extension of the proposed model to other classes of compounds than hydrocarbons.

Table 8. Extension of the Proposed Model to Other Classes of Compounds: Vapor Pressure Predictions for Very High Boiling Compounds Whose Experimental Normal Boiling Point Is Unknown and Was Then Estimated via the Proposed Model

(i) Information by Class of Compounds			
class of compounds	N_p	number of compounds	$\delta_r(P_s)$ (%)
fatty acid methyl esters	221	10	2.23
fatty acid ethyl esters	39	7	2.85
fatty acid propyl esters	62	7	2.81
free fatty acids	158	4	3.75
overall	480	28	2.86
(ii) Information by Pressure Range			
pressure range	N_p	$\delta_r(P_s)$ (%)	
VLP	191	3.21	
LP	115	2.94	
MP	174	2.41	

(c) Speed of Sound in Saturated Liquids. The obtained deviations are quite large ($\delta_r(W_L) = 9\%$ for the data as a whole). Also, the variation of the property in terms of temperature depicted in Figure 4 shows that the calculated speeds of sound are neither systematically overestimated nor underestimated compared to experimental data (it could be said that the property is approximately overestimated below $0.75 T_b$ and underestimated above $0.75 T_b$). A similar behavior was denoted by Ye et al. (1992)⁴⁰ for various EOS, as well cubic ones (such as Soave–Redlich–Kwong, 1972;⁴¹ Peng–Robinson, 1976;⁹ Rauzy, 1982)⁸ as complex ones (chain of rotators by Chien et al. 1983;⁴² Simonet–Behar–Rauzy, 1985).⁴³

Extension of the Proposed Model to Other Classes of Compounds

In this work, the extension of the model to non-hydrocarbons was achieved by considering the vapor pressures of alkenes, esters, carboxylic acids, and alcohols, while free fatty acids and fatty acid esters were used for validation purposes. The two latter classes of compounds were chosen because of their various applications in food or biochemical industries, and also cosmetics. Their physical properties are not well-known experimentally, and even some of them cannot be measured because of thermal decomposition. Particularly, the vapor pressure measurements are available only from 0.3 bar. Therefore, a purely predictive thermodynamic model as reliable as possible plays an important role in the property estimation of these classes of compounds.

The extension of the model to non-hydrocarbon compounds will be considered as successful if two constraints are satisfied: (i) the vapor pressures should be estimated with a degree of accuracy similar to the one obtained previously for hydrocarbons; (ii) no change should be made to the model with the exception of adding the information missing for non-hydrocarbon compounds. This argument implies that (i) the analytical expressions, the values of the universal constants C_1 and C_2 (eqs 4) characteristic of the function $a(T)$, and the estimation methods of the EOS parameters b and m with the group contributions characteristic of hydrocarbons are kept constant in the model, and (ii) the group contributions related to the shape parameter m need to be estimated on the vapor pressure measurements of the new compounds since those related to parameter b are still determined from the van der Waals volumes estimated by Bondi's method (1968).¹⁰

The updated group contributions and structural increments to the shape parameter m are given in Table 7. The group identification is exactly the same as the one used for the covolume b ; however, the structural increments are different.

Vapor Pressure Database Selected for the Model Parameter Regression. The database was built by considering compounds with the desired functional groups (double bonds, carboxylic acid, ester, alcohol) and for which both experimental vapor pressures and normal boiling temperature T_b were available in the literature. According to the latter constraints, the final database comprises of 617 vapor pressure measurements of 33 compounds (methyl, ethyl, butyl, and ethenyl esters; carboxylic acids; alcohols; normal, branched, and cyclic alkenes) with the weakness of involving mainly acetates as candidates for the esters and compounds of low T_b (from 293.21 to 558.02 K).

Vapor Pressure Predictions. Concerning first the vapor pressure correlations, a deviation $\delta_r(P_S) = 1.6\%$ was obtained for the total data set. With the exception of the carboxylic acids, all classes of compounds were well fitted ($\delta_r(P_S) = 0.8\%$ by considering all compounds except the carboxylic acids). These results are quite satisfactory considering that most of the model parameters were evaluated on hydrocarbon data. Concerning now the vapor pressure predictions, the compounds considered here (free fatty acids and fatty acid methyl, ethyl, or propyl esters) have a very high normal boiling temperature T_b for which no experimental data were found in the literature. Therefore, this verification had to be carried out (unfortunately) by estimating T_b via the proposed model. The obtained results, reported in Table 8, show that the deviations are still acceptable ($\delta_r(P_S) = 2.9\%$ for the total data set).

Furthermore, the estimates of the normal boiling temperatures T_b obtained with the proposed model are very close to those obtained with the purely predictive method presented by Coniglio et al. (1995).⁴⁴ The disagreement between the T_b values estimated by the two techniques is 0.58% (i.e., $\Delta(T_b) \approx 3$ K) for the 28 compounds investigated here. This result is quite remarkable considering the very different theoretical features of these techniques (one based on the vapor pressure expression in terms of temperature by Abrams–Massaldi–Prausnitz (1974)⁴⁵ and the other one based on a PR type EOS (1976)⁹ with parameters estimated through the GC concept) and also confirms the reliability of the model developed in this work.

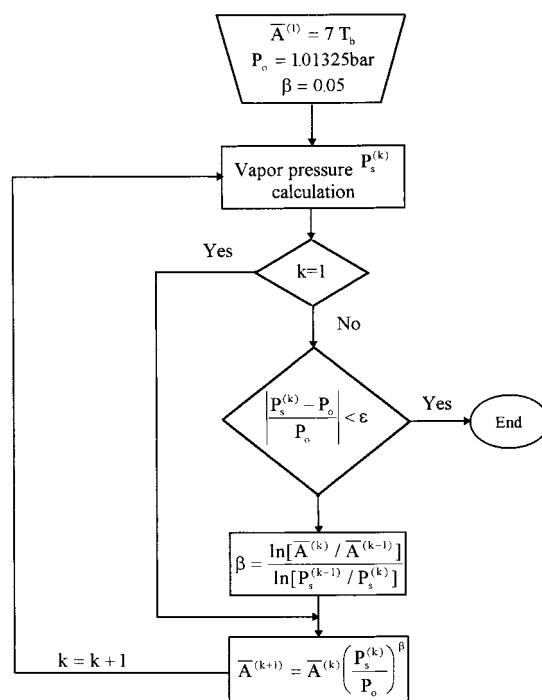


Figure 5. Flowchart depicting the calculation of the function $a(T)$ at the normal boiling temperature $a(T_b)$ ($A = a(T)/RT$).

From the above results, it can be concluded that the proposed model can be extended with confidence to other classes of compounds than hydrocarbons.

Conclusion

The model presented in this paper was developed by considering a large variety of hydrocarbons currently encountered in crude oils (alkanes, naphthenes, alkyl-benzenes, and polynuclear aromatics) whose normal boiling point ranges from 280 to 620 K. Based on a PR type EOS (1976)⁹ with parameters calculated through the GC concept, the required inputs of the model are, for each compound, the molecular structure, and the experimental T_b or at least one vapor pressure measurement.

Various classes of physical properties, such as vapor pressures, saturated liquid densities, heats of vaporization, saturated liquid heat capacities, and speed of sound in saturated liquids, are estimated (correlated and predicted) within experimental uncertainty for a wide range of pressures (from the triple point to 2 bar).

The vapor pressures are calculated with similar accuracy when T_b is determined via the proposed model. The procedure presented in this paper for the estimation of T_b is very simple and should be used when no experimental information on this property is available in the literature. Furthermore, the obtained estimations of T_b agree very well with the experimental data. This indicates that the procedure may also be used as a property estimation method for the compounds for which the proposed model is valid and at least one vapor pressure measurement is available.

By considering only vapor pressures, the model was extended successfully to other classes of organic compounds such as alkenes, carboxylic acids, esters, alcohols, free fatty acids, and fatty acid esters.

From the above results, it can be said that the modifications of the Coniglio et al. (1993)¹ model, originally developed for heavy hydrocarbons, lead to

Table 9. Sample of Calculation of the Function $a(T)$ at the Normal Boiling Temperature $a(T_b)$ for n -Eicosane (See Figure 5)

k	$\bar{A}^{(k)}$	$P_S^{(k)}$	$ (P_S^{(k)} - P_0)/P_0 $	β
1	4380.13	0.230204		0.05
2	4067.31	0.383248	6.21764×10^{-1}	0.145371
3	3531.23	0.910908	1.01003×10^{-1}	0.163249
4	3470.38	1.00449	8.64651×10^{-3}	0.177746
5	3465.03	1.01316	8.52730×10^{-5}	0.179509
6	3464.97	1.01325	6.90381×10^{-8}	-

improvements (i) in predictive character when applied to very high boiling compounds and (ii) in confidence when extrapolated in terms of temperature/pressure, classes of physical properties and classes of compounds.

Supporting Information Available: Appendix III related to the estimation of the normal boiling point T_b ; results are given for each hydrocarbon with comparison of the deviations in the vapor pressures obtained (a) by estimating T_b via the proposed model and (b) by considering estimates of T_b given in the literature. Appendix IV containing property estimation results (vapor pressures, saturated liquid densities, heats of vaporization, saturated liquid heat capacities, and speed of sound in saturated liquids) detailed for each investigated hydrocarbon, with the corresponding information: normal boiling point value whenever available, number of experimental data used with their temperature/pressure range, and finally their literature source(s). This material is available free of charge via the Internet at <http://pubs.acs.org>.

Abbreviations

EOS = equation of state
GC = group contribution
LP = low vapor pressure (from 0.01 to 0.06 bar)
MP = medium vapor pressure (from 0.06 to 7 bar)
PR = Peng–Robinson
VLP = very low vapor pressure (from 10^{-6} to 0.01 bar)

Nomenclature

a = temperature-dependent energy parameter of the cubic equation of state
 $a(T)$ = function taken as model for the temperature-dependent parameter a
 $a(T_b)$ = value of the function $a(T)$ at the normal boiling temperature
 $a(T_0)$ = value of the function $a(T)$ at the temperature T_0 corresponding to the vapor pressure P_0
 \bar{A} = intermediate variable equal to $a(T)/RT$
 b = covolume of the cubic equation of state
 b_{CH_4} = methane covolume calculated from the critical properties
 c = volume correction of the cubic equation of state
 $c(T)$ = temperature-dependent volume correction of the cubic equation of state
 $c(T_b)$ = value of the temperature-dependent volume correction $c(T)$ at the normal boiling temperature
 C_1, C_2 = constants characteristic of the function $a(T)$
 C_3, C_4, C_5 = constants involved in the estimation method related to the shape parameter m
 C_j = contribution of the j th group to $c(T_b)$
 C_p = molar heat capacity at constant pressure
 C_v = molar heat capacity at constant volume
 I_k = number of occurrences of the structural increment related to the k th intramolecular effect required for the estimation of a specific pure component property through the group contribution concept
 m = shape parameter
 M = molar mass (molecular weight)

M_j = contribution of the j th group to the shape parameter m
 $N_{c,2}$ = number of aromatic condensed ring carbon atoms in common with two rings
 $N_{c,3}$ = number of aromatic condensed ring carbon atoms in common with three rings
 N_j = number of groups of the j th type required for the estimation of a specific pure component property through the group contribution concept
 N_P = number of property measurements for a specific database as a whole
 P = pressure
 P_C = critical pressure
 P_S = vapor pressure
 T = temperature
 T_b = normal boiling temperature (normal boiling point)
 T_C = critical temperature
 v = molar volume
 V_W = van der Waals volume of a molecule
 V_{w,CH_4} = van der Waals volume of methane
 $V_{w,j}$ = contribution of the j th group to the van der Waals volume estimated by Bondi's method (1968)¹⁰
 W = speed of sound in a fluid
 x, y = powers of function $a(T)$

Superscripts

exp = experimental
cal = calculated
id = molar property related to the ideal gas

Subscripts

C = critical property
corrected = property calculated by a cubic equation of state corrected with a volume correction
fus = fusion
 L = related to the saturated liquid
 r = relative
 S = saturation
vap = molar property of vaporization

Greek Symbols

α = number of aromatic rings in a molecule
 α_1, α_2 = parameters involved in the calculation of α_b
 α_b, β_b = parameters expressed in terms of the normal boiling temperature in the estimation of $c(T_b)$
 β_1, β_2 = parameters involved in the calculation of β_b
 Δc = corrective term to the estimation of $c(T_b)$ required for two compounds: cyclopentane, cyclohexane
 δC_k = structural increment related to the k th intramolecular effect for the estimation of $c(T_b)$
 $\Delta_{vap}H$ = heat of vaporization
 Δm = corrective term to the estimation of the shape parameter m required for five compounds: cyclopentane, cyclohexane, isopropylcyclopentane, benzene, toluene
 $\Delta(\bar{X})$ = average absolute deviation in the property X
 δm_k = structural increment related to the k th intramolecular effect for the estimation of the shape parameter m
 $\delta_r(X)\%$ = percent average relative deviation in the property X
 $\delta V_{w,k}$ = structural increment related to the k th intramolecular effect for the estimation of the van der Waals volume by Bondi's method (1968)¹⁰
 ρ = density
 ω = acentric factor

Appendix I. Calculation of the Value of the Function $a(T)$ at the Normal Boiling Temperature

The calculation of the function $a(T)$ at all temperatures requires first the knowledge of $a(T)$ at the normal

Table 10. Illustration of the Group Contribution Methods for Estimating the Parameters b , m , and $c(T_b)$ of the Proposed Model

Decomposition in Groups Common to the Three Parameters b , m , and $c(T_b)$							
compound	groups						
	alkanes				aromatics		
	CH ₃	CH ₂	CH	C _{IV} ^a	ACH	AC _{IV} ^b	AC cond. rings ^c
<i>n</i> -butylcyclohexane	1	8	1	0	0	0	0
fluorene	0	1	0	0	8	4	0
pyrene	0	0	0	0	10	0	6

Decomposition in Structural Increments for the Estimation of the Shape Parameter m								
compound	structural increments							
	I_1	I_2	I_3	I_4	I_5	I_6		
						α	$N_{c,2}$	$N_{c,3}$
<i>n</i> -butylcyclohexane	0	0	0	1	0	0	0	0
fluorene	0	0	1	0	0	0	0	0
pyrene	0	0	0	0	0	4	4	2

Decomposition in Structural Increments Common to the Estimation of the Covolume b and the Volume Correction at the Normal Boiling Point $c(T_b)$								
compound	structural increments							
	I_1	I_2	I_3	I_4	I_5	I_6	I_7	I_8
<i>n</i> -butylcyclohexane	1	0	0	0	0	0	0	0
fluorene	0	0	1	0	0	0	0	0
pyrene	0	0	0	0	0	4	4	2

Calculation of the Covolume b			
$b \text{ (cm}^3 \text{ mol}^{-1}) = 26.80S/17.12$			
<i>n</i> -butylcyclohexane	$S = [1 (13.67) + 8 (10.23) + 1 (6.78)] + [1 (-1.14)]$	\Rightarrow	$b = 158.34 \text{ cm}^3 \text{ mol}^{-1}$
fluorene	$S = [1 (10.23) + 8 (8.06) + 4 (5.54)] + [1 (-1.66)]$	\Rightarrow	$b = 149.04 \text{ cm}^3 \text{ mol}^{-1}$
pyrene	$S = [10 (8.06) + 6 (4.74)]$	\Rightarrow	$b = 170.69 \text{ cm}^3 \text{ mol}^{-1}$

Calculation of the Shape Parameter m			
$m = 0.30048 + S - 3.03178 \ln(1 + 0.08425 S^2)$			
<i>n</i> -butylcyclohexane	$S = [1 (0.04963) + 8 (0.05024) + 1 (0.02920)] + [1 (-0.07293)]$	\Rightarrow	$m = 0.66611$
fluorene	$S = [1 (0.05024) + 8 (0.03208) + 4 (0.04232)] + [1 (-0.03804)]$	\Rightarrow	$m = 0.68996$
pyrene	$S = [10 (0.03208) + 6 (0.00714)] + [(-1)4 0.15 (4 + 2.2) (0.01561)]$	\Rightarrow	$m = 0.64573$

Calculation of the Volume Correction $c(T_b)$			
$c(T_b)/(\text{cm}^3 \text{ mol}^{-1}) = 0.27468 T_b - 50.94930 m^2 - S$			
<i>n</i> -butylcyclohexane, $T_b/K = 454.10$	$S = [1 (35.9209) + 8 (13.2044) + 1 (-11.4445)] + [1 (44.2322)]$	\Rightarrow	$c(T_b) = -72.22 \text{ cm}^3 \text{ mol}^{-1}$
fluorene, $T_b/K = 570.74$	$S = [1 (13.2044) + 8 (19.3874) + 4 (-4.2938)] + [1 (44.2322)]$	\Rightarrow	$c(T_b) = -62.84 \text{ cm}^3 \text{ mol}^{-1}$
pyrene, $T_b/K = 667.15$	$S = [10 (19.3874) + 6 (7.4171)]$	\Rightarrow	$c(T_b) = -76.37 \text{ cm}^3 \text{ mol}^{-1}$

^a C quaternary. ^b AC substituted. ^c AC condensed rings.

boiling temperature $a(T_b)$. Figure 5 gives the flowchart for calculation of $a(T_b)$.

When the considered temperature T is the normal boiling temperature, the corresponding pressure P_0 is equal to 1.01325 bar. For convenience, the vapor pressure is computed by considering the variable $\bar{A} = a(T)/RT$ instead of the function $a(T)$. The increment on variable \bar{A} is obtained by

$$\bar{A}^{(k+1)} = \bar{A}^{(k)} \left(\frac{P_s^{(k)}}{P_0} \right)^\beta \quad \text{with } \beta = \frac{\ln \left(\frac{\bar{A}^{(k)}}{\bar{A}^{(k-1)}} \right)}{\ln \left(\frac{P_s^{(k-1)}}{P_s^{(k)}} \right)} \quad (\text{A1})$$

where $P_s^{(k)}$ is the vapor pressure calculated at the k th iteration. The chosen initial guess values for $\bar{A}^{(1)}$ and β (Figure 5) help to have a rapid convergence. The out loop test ($\epsilon = 10^{-5}$) is based on minimizing the relative

deviation in the vapor pressure $\delta_r(P_s)$ (eq A2). The final value $\bar{A}^{(k+1)}$ is next multiplied by RT_b to obtain $a(T_b)$.

$$\delta_r(P_s) = \frac{|P_s^{(k)} - P_0|}{P_0} \quad (\text{A2})$$

A sample of the calculation is given for *n*-eicosane ($T_b = 617.20$ K) in Table 9.

Appendix II

Illustration of the group contribution methods for estimating the parameters b , m , and $c(T_b)$ of the proposed model is given in Table 10 (the methods are illustrated through three examples).

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