DEVELOPMENT AND APPLICATION OF SIMHA EQUATION OF STATE TO CALCULATION OF THE DENSITY OF CERTAIN ALKANES AND THEIR MIXTURES

HONGGANG ZHOU, BERNARD LAGOURETTE*, JACQUES ALLIEZ
and PIERRE XANS

Laboratoire de Physique des Matériaux Industriels, Centre Universitaire de Recherche Scientifique, Université de Pau et des Pays de l'Adour, Avenue de l'Université, 64000 PAU (France)

FRANÇOIS MONTEL

*Société Nationale ELF-AQUITAINE, C.S.T.C.S., Avenue Larribau,
64018 PAU CEDEX (France)*

ABSTRACT

Zhou, H., Lagourette, B., Alliez, J., Xans, P. and Montel, F., 1989. Development and application of Simha equation of state to calculation of the density of certain alkanes and their mixtures. *Fluid Phase Equilibria*, 47: 153–169.

In this paper we propose a method for evaluating the interaction parameters between segments of linear n-alkane molecules in order to calculate the densities of alkanes (from n-C_5 to n-C_{24}) and their mixtures, in the melt state, in a wide range of temperature and pressure, from the equation of state of Simha and Somcynsky. With this aim in view, a unique set of 7 parameters characterizing the chemical family is defined. A comparison between the experimental data taken from the literature and the calculated values gives a reasonable agreement on more than 800 experimental points.

INTRODUCTION

Thermodynamic equations of state are very useful for describing fluid behavior; in particular they are used in the oil industry to predict the $P-V-T$ properties of hydrocarbons and deposit fluids in reservoir conditions.

Simple equations such as the van der Waals equation or equations derived from it such as the widely used Redlich–Kwong (1949) or Peng–Robinson (1976) equations, provide a description of the general properties of the liquid

---

* Author to whom correspondence should be addressed.

state that is more qualitative than quantitative. In particular, these equations of state are inadequate for the calculation of densities which is one of our research interests. On this subject, it might be useful to recall the existence of empirical methods for determining the density of liquids, either at atmospheric pressure, for example the method proposed by Rackett (1970) or as a function of pressure, as in the Thomson–Brobst–Hankinson (TBH) method (1982). The latter technique provides acceptable results compared to experimental data in the pressure interval 1–689 bars (maximum deviation approximately 1.7% for n-alkanes), but it requires not only knowledge of the critical properties and the acentric factor of the body under study, but also necessitates the use of 16 empirical coefficients. At pressures above 689 bars (the upper limit fixed by TBH) the deviation with respect to experimental data increases and may exceed 4% for this chemical family.

Without denying the practical interest of the above techniques, it should be pointed out that using them for extensive pressure ranges (for example up to 5000 bars) would require further adjustments. Moreover the lack of physical significance of the various coefficients involved rules out the possibility of obtaining information on the other thermodynamic properties of the substances, unlike state equations.

Bearing in mind the complexity of the molecular structure of hydrocarbon constituents, we therefore turned our attention to "solid-type" approaches to the dense liquid state, based on the theory of cells and that of "cell-holes". The cellular theory of liquids, originally introduced for molecules with spherical symmetry, has been adapted by Prigogine et al. (1953, 1957) to macromolecular liquids: polymers and polymer solutions. In this way they were able to determine the partition function and equations of state representative of these bodies. Referring to hypotheses close to those of previous authors but using the theory of cell-holes, Simha and Somcynsky (1969) calculated an equation of state for chain molecule liquids. In subsequent publications, Jain and Simha (1979a, b, 1980, 1981) have formulated equations of state for a number of substances, introducing the necessary modifications, particularly those for short chain liquid hydrocarbons and their mixtures.

Since our concern is to investigate dynamic viscosity (Ducoulombier et al., 1985, 1986), and how it can be represented in terms of temperature and pressure, by studying petroleum products or constituents of petroleum products, knowledge of the densities of a considerable number of bodies is essential. We found the prediction possibilities offered by the Simha and Somcynsky techniques attractive, and as a result we made a number of modifications to be able to measure the densities (as a function of temperature and pressure) of single-constituent alkanes and alkanes mixtures.

SIMHA AND SOMCYNSKY METHOD

Review of the method

The theory is based on a quasi-network model with vacant or occupied sites. Occupied sites can be filled by a complete molecule or a segment of a molecule. The configurational distribution function contains three essential components (Simha and Somcynsky, 1969): network energy; random mixture of molecules and unoccupied sites; distribution function of s segments of a molecule at their sites representing the free volume of the molecule. All these factors depend on the fraction of occupied sites.

The equation of state obtained in this way, represented in its reduced form, can be written

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}} = \left[1 - 2^{-1/6}y(y\tilde{V})^{-1/3}\right]^{-1} + \frac{2y}{\tilde{T}}(y\tilde{V})^{-2}\left[1.011(y\tilde{V})^{-2} - 1.2045\right] \quad (1)$$

It is completed by the free energy minimization condition to yield the equation

$$\frac{s}{3c}\left[\frac{(s-1)}{s} + y^{-1}\ln(1-y)\right] = \frac{y}{6\tilde{T}}(y\tilde{V})^{-2}\left[2.409 - 3.033(y\tilde{V})^{-2}\right]$$
$$+ \left[2^{-1/6}y(y\tilde{V})^{-1/3} - \tfrac{1}{3}\right]\left[1 - 2^{-1/6}y(y\tilde{V})^{-1/3}\right]^{-1} \quad (2)$$

These relationships were determined after calculation of the total interaction energy E_0 of the lattice, giving

$$E_0 = (1/2)yNq_z\epsilon^*\left[1.011\left(\frac{v^*}{\omega}\right)^4 - 2.409\left(\frac{v^*}{\omega}\right)^2\right] \quad (3)$$

or $E_0 = (\tfrac{1}{2})yNq_z\Phi$ with

$$\Phi = \epsilon^*\left[1.011\left(\frac{v^*}{\omega}\right)^4 - 2.409\left(\frac{v^*}{\omega}\right)^2\right] \quad (4)$$

In the above equations, y designates the fraction of cell centers occupied. The number of segments s of each molecule and the number $3c$ of independent external degrees of freedom of the molecular chain are related according to Jain and Simha (1981) by the equation $3c = s + 3$. $\tilde{P}$, $\tilde{V}$, $\tilde{T}$ represent the pseudo-reduced magnitudes defined by

$$\tilde{P} = \frac{P}{P^*} \qquad \tilde{V} = \frac{V}{V^*} \qquad \tilde{T} = \frac{T}{T^*}$$

with

$$P^* = q_z\frac{\epsilon^*}{sv^*} \qquad V^* = Nsv^* \qquad T^* = q_z\frac{\epsilon^*}{ck} \quad (5)$$

where k is the Boltzmann constant.

$q_z = s(z - 2) + 2$ designates the number of sites in intermolecular contact with one molecule. In the case of a cubic lattice with centered faces, the number z of first neighbors of a site is 12. In addition, ϵ^* (minimum attraction energy) and v^* (repulsion volume) are characteristic parameters of the interaction potential of the segments of the substance under study.

In eqns. (1) and (2) above, for a given P, T set, the two unknown values are y and $\tilde{V}$; ϵ^*, v^* and s are adjustable parameters specific to each substance.

The Simha–Somcynsky equation of state considerably improves the theoretical representation of variations of the density of liquid n-alkanes with P, T, compared with other existing methods. For each alkane tested, over a wide range of pressure and temperature (up to 8000 bars for P, and between 30 and 150°C for T), it gives density values deviating from the experimental values by an average of only 0.2%. This remarkable result was achieved by introducing into eqns. (1) and (2) the coefficients ϵ^*, v^*, and s appropriate for the alkanes studied (nC_6, C_9, C_{11}, C_{12}, C_{16}, C_{17}) (Jain and Simha, 1981).

Therefore, the parameters ϵ^*, v^* and s must be determined for each substance. Practically, this requires precise experimental density data for different P and T conditions for each substance studied. However in the above reference the authors suggest empirical relationships for the n-paraffins (with $6 \leq n \leq 17$) between chain length (in fact the number n of carbon atoms in the molecule) and the scaling parameters s, V^*, T^*, thus facilitating predictions for the other members of the series.

Simha's theoretical model has been applied by Jain and Simha (1980) to the case of mixtures involving several constituents. Its use requires that the binary interaction parameters must be rigorously determined from the experimental results (for different P, T sets) relative to the r constituents and the $r(r-1)/2$ binary systems.

For a system with two constituents, Jain and Simha suggest a process of determination by regression of the scaling parameters V^*, T^*, based on experimental values of the density of the mixture at different temperatures and for a very low pressure isobar ($\tilde{P} \to 0$). While this approach does reduce the number of measurements that have to be made before the equation of state can be used, it does not however dispense completely with experimentation on the mixture.

Suggested modification

As a result of reflections on the geometrical configuration of a linear alkane molecule, we were able to introduce into eqns. (1) and (2) a unique set of seven coefficients. This set is representative both of the different

members of the series of liquid alkanes (with $n \geq 5$) and of their mixtures (independently of the number of constituents and of the composition). By adopting this set of coefficients, the volumetric behavior as a function of P, T of alkane mixtures can be theoretically described without having to introduce other data.

Observing that the volume occupied by an alkane molecule with n carbon atoms is not equivalent to n times that of methylene, we considered the possible existence of an overlap of the zones of influence of two neighboring centers of mass. Designating the volume of a cell as ω, the common zone will be $f\omega$, where f is the characteristic overlap factor.

In this representation, the volume occupied by an alkane molecule with n carbon atoms is

$$v_n = n\omega - (n - 1)f\omega = n(1 - f)\omega + f\omega$$

Since each linear molecule is divided into s segments, each of which is contained in a cell, we also have $v_n = s\omega$ and hence $s = n(1 - f) + f$.

It should also be noted that this relation remains coherent for a methane ($n = 1$), in which case each molecule represents one segment ($s = 1$).

In the representation we are proposing, only the parameter f needs to be adjusted. The best fit between experimental and computed values for the density of alkanes is obtained with $f \approx 2/3$ which then gives

$$s = (n + 2)/3. \tag{6}$$

It should be observed in this context that a linear relationship between s and n has also been proposed by Jain and Simha (1981) ($s = 0.394 + 0.352 n$) in which the two coefficients, after adjustment, are empirical.

In order to establish the relations between the characteristic energy parameters (ϵ^* and v^* in Simha's equation) and the molecular structure of the alkanes, we will assume that this kind of molecule is made up of two chain "ends" and the remaining ($s - 2$) segments that we propose to call "internal" segments.

The interaction energies between the alkane molecules can thus be considered as the result of three types of interaction between segments: end of chain–end of chain; end of chain–internal segment; internal segment–internal segment.

It is therefore possible to define all the interactions explicitly in terms of six general parameters, whatever the alkane under study: ϵ_{bb}^* (minimum end–end interaction energy), ϵ_{cc}^* (minimum internal–internal interaction energy), ϵ_{bc}^* (minimum end–internal interaction energy), v_{bb}^* (end–end characteristic volume), v_{cc}^* (internal–internal characteristic volume) and v_{bc}^* (end–internal characteristic volume).

It is now necessary to relate the resulting energy parameters ϵ^* and v^* involved in eqns. (1) and (2) to these six parameters. To do so, we introduce the following four quantities into the developments: $P_b = 2/s$, probability of

finding a "chain-end" segment in an occupied cell; $P_c = 1 - P_b$, probability of finding an "internal" segment in an occupied cell; $q_{bz} = 2(z - 1)$, number of neighboring prime sites that do not belong to the same molecule in the two chain "ends"; $q_{cz} = (s - 2)(z - 2)$, number of neighboring prime sites that do not belong to the same molecule, out of the $(s - 2)$ "internal" segments of the molecule considered. (A "chain-end" segment has only $z - 1$ neighbors belonging to other molecules from the total number of neighbors z, and this number decreases to $z - 2$ for an "internal" segment.)

The total energy of a network, obtained by adding together the three types of interaction, is then expressed as follows

$$E_0 = \tfrac{1}{2} y N \left[q_{bz} (P_b \phi_{bb} + P_c \phi_{bc}) + q_{cz} (P_b \phi_{bc} + P_c \phi_{cc}) \right] \tag{7}$$

designating

$$\Phi_{kl} = \epsilon_{kl}^* \left[1.011 \left(\frac{v_{kl}^*}{\omega} \right)^4 - 2.409 \left(\frac{v_{kl}^*}{\omega} \right)^2 \right]$$

by analogy with eqn. (4).

This expression of E_0 should be compared with the formula of interaction energy given by Simha:

$$E_0 = \tfrac{1}{2} y N q_z \epsilon^* \left[1.011 \left(\frac{v^*}{\omega} \right)^4 - 2.409 \left(\frac{v^*}{\omega} \right)^2 \right]$$

By identifying the coefficients of the terms in $1/\omega^4$ and $1/\omega^2$ in each of the above expressions for E_0, one can rigorously deduce the equations which correlate the characteristic parameters ϵ^*, v^* of the Simha–Somcynsky equation with the characteristic parameters of the different types of segmental interaction, as well as with the molecular structure parameter s.

$$q_z \epsilon^* v^{*2} = p_b q_{bz} \epsilon_{bb}^* v_{bb}^{*2} + p_c q_{cz} \epsilon_{cc}^* v_{cc}^{*2} + (p_b q_{cz} + p_c q_{bz}) \epsilon_{bc}^* v_{bc}^{*2} \tag{8a}$$

$$q_z \epsilon^* v^{*4} = p_b q_{bz} \epsilon_{bb}^* v_{bb}^{*4} + p_c q_{cz} \epsilon_{cc}^* v_{cc}^{*4} + (p_b q_{cz} + p_c q_{bz}) \epsilon_{bc}^* v_{bc}^{*4} \tag{8b}$$

By solving this pair of equations the values of ϵ^* and v^* can be determined. These values are then inserted into eqns. (1) and (2) to represent the single-constituent alkanes.

We subsequently used the same method to study alkane mixtures. To do so, we made use of the fact that the mean number of segments $\langle s \rangle$ per molecule is defined by

$$\langle s \rangle = \sum_i N_i s_i / \sum_i N_i$$

($\sum_i N_i = N$ = total number of network molecules).

The probabilities of a cell being occupied by "end" or "internal" segments then become

$$P_b = 2 \sum_i N_i / \sum_i N_i s_i = 2/\langle s \rangle$$

$$P_c = 1 - P_b = (\langle s \rangle - 2)/\langle s \rangle$$

and the total energy is expressed as

$$E_0 = \sum_i \frac{N_i}{2} y \left[q_{ibz} (P_b \Phi_{bb} + P_c \Phi_{bc}) + q_{icz} (P_b \Phi_{bc} + P_c \Phi_{cc}) \right] \tag{9}$$

where $q_{ibz} = 2(z - 1) = q_{bz}$ and $q_{icz} = (s_i - 2)(z - 2)$. Then

$$\sum_i N_i q_{icz} = \sum_i N_i s_i (z - 2) - \sum_i 2 N_i (z - 2)$$

$$= \langle s \rangle (z - 2) \sum_i N_i - 2(z - 2) \sum_i N_i$$

$$= N \langle q_{cz} \rangle$$

The result is that the total interaction energy E_0 in the case of a mixture of alkanes (eqn. (9)) is similar to eqn. (7) for single-constituent alkanes. This means that the 6 parameters determined for the single-constituent alkanes can be applied directly to mixtures without having to make additional measurements. One only needs to know the values of ϵ_{bb}^*, ϵ_{cc}^*, ϵ_{bc}^*, v_{bb}^*, v_{cc}^*, v_{bc}^*.

COMPARISON WITH EXPERIMENTAL DATA

Method used

From data available from the literature providing values of the density with T, P of alkanes, namely nC_6, nC_8, nC_{10}, nC_{12} and nC_{16} (Dymond et al., 1980, 1981) we optimize our 6 parameters characterizing the family of alkanes. The best fit is obtained with

$$\epsilon_{bb}^* = 26637 \text{ bar cm}^3 \text{ mol}^{-1}$$

$$\epsilon_{cc}^* = 30915 \text{ bar cm}^3 \text{ mol}^{-1}$$

$$\epsilon_{bc}^* = 32804 \text{ bar cm}^3 \text{ mol}^{-1}$$

and

$$v_{bb}^* = 38.535 \text{ cm}^3 \text{ mol}^{-1}$$

$$v_{cc}^* = 49.483 \text{ cm}^3 \text{ mol}^{-1}$$

$$v_{bc}^* = 41.803 \text{ cm}^3 \text{ mol}^{-1}$$

(adopting a value of $2/3$ for f).

TABLE 1

Mean and maximum deviations between experimental and calculated specific volumes for the five reference alkanes (measurements made by Dymond et al.)

Product	Number of points	Temperature (K)	P_{max} (bar)	D_{mean} (%)	D_{max} (%)
n-C_6	37	298.3–373.4	4196	0.22	0.69
n-C_8	41	298.2–373.1	5055	0.22	0.67
n-C_{10}	19	298.3–373.1	4202	0.16	0.34
n-C_{12}	32	298.3–373.2	5016	0.16	1.02
n-C_{16}	28	298.1–373.2	4251	0.08	0.19

These values suggest the following few comments. First of all, it will be observed that the volumes v_{kl}^*, associated with the various types of segmental interaction, have comparable orders of magnitude. The same is true of the characteristic energies ϵ_{kl}^*. More detailed examination shows that in fact the characteristic volume v_{cc}^* of the repulsion between two internal segments (from two different molecules) is greater than that corresponding to interaction between two chain-end segments, v_{bb}^*. This can be understood physically if one takes into account the fact that the number of carbon atoms included in an internal segment is greater than the number of atoms of a chain-end segment, a result which follows from both eqn. (6) and the relationship $n = (s - 2)n_c + 2n_b$, which expresses the number of carbon atoms of the alkane molecule as a function of the number of carbon atoms in internal segments (n_c) and chain-end segments (n_b) respectively.

Secondly, the concept of overlap factor, f, introduced in this study assumes that for a chain-molecule liquid, a segment (or in other words an occupied cell) is made up of several carbon atoms. The numerical value $f = 2/3$ results simply from the optimization of the regressed data (eqn. (6)). With the values of the parameters indicated above, highly satisfactory results are obtained for these single-constituent alkanes, as shown in Table 1. In this table and in the following tables, the deviations are calculated from the relations

$$D = 100(V_{exp} - V_{cal})/V_{exp}$$

and

$$D_{mean} = (100/N_T) \sum_{j=1}^{N_T} \left| (V_{exp\,j} - V_{cal\,j})/V_{exp\,j} \right|$$

V_{exp} and V_{cal} designate the experimental and calculated values respectively on the physical quantity involved.

TABLE 2

Overall results of comparison between experimental and calculated values for various binary mixtures (measurements made by Dymond et al.)

Mixture	Number of points	Temperature (K)	P_{max} (bar)	D_{mean} (%)	D_{max} (%)
0.8 n-C_6					
0.2 n-C_{16}	41	298.2–373.1	5019	0.23	0.58
0.6 n-C_6					
0.4 n-C_{16}	44	298.1–373.2	5028	0.14	0.55
0.4 n-C_6					
0.6 n-C_{16}	38	298.1–373.2	4184	0.14	0.35
0.2 n-C_6					
0.8 n-C_{16}	36	298.1–373.2	4461	0.11	0.30
0.5 n-C_8					
0.5 n-C_{12}	38	298.2–373.2	5055	0.20	0.63
0.501 n-C_6					
0.499 n-C_{12}	24	298.1–373.2	4551	0.29	0.67
0.5 n-C_{10}					
0.5 n-C_{16}	16	348.1–373.3	4228	0.14	0.26

Applications

We used this model, with the same numerical values of the 7 parameters (ϵ_{bb}^*, ϵ_{bc}^*, ϵ_{cc}^*, v_{bb}^*, v_{bc}^*, v_{cc}^*, f) to calculate the density of binary mixtures of alkanes, for which the experimental values have already been reported in the literature by Dymond et al. (1980, 1981, 1982). Agreement of the computed and experimental values is very satisfactory, with a mean deviation of 0.18% (for 237 reference points), whilst the maximum deviation is less than 0.7% (Table 2).

As an example, Table 3 shows the agreement between the experimental densities and those calculated by our method for the binary mixture nC_6–nC_{16} (with nC_6 molar fraction = 0.4). As we have already pointed out, the pair of equations (1) and (2) can be used to calculate two quantities for given values of P and T in one operation: the specific volume, and y, the fraction of occupied cell centers.

It should be stressed that the results relating to nC_6–nC_{16} mixtures, which are obtained without adjustments involving low pressure measurements, yield better results than those indicated in the article of Jain and Simha (1980). The average deviation for all the points of this binary mixture (159 points) is, using our method, 0.16%; the normal deviation remains less than 0.58%, although the pressure range investigated extends beyond 5 kbars.

Since the above experimental findings all come from the same authors, it might be thought that the parameters obtained are characteristic of these

TABLE 3

Example of comparison for each P, T set of the experimental and calculated values of specific volume for the mixture 40% n-C_6 +60% n-C_{16} (Dymond et al., 1980)

Experimental data			Calculated values		
P (bar)	T (K)	V (cm^3 g^{-1})	V (cm^3 g^{-1})	y	Deviation (%)
1	298.1	1.3416	1.3396	0.8773	− 0.15
43	298.1	1.3353	1.3345	0.8796	− 0.06
90	298.1	1.3287	1.3290	0.8820	0.02
157	298.1	1.3201	1.3216	0.8853	0.11
216	298.1	1.3134	1.3154	0.8880	0.15
316	298.1	1.3029	1.3055	0.8924	0.20
369	298.1	1.2979	1.3006	0.8945	0.21
418	298.1	1.2935	1.2962	0.8965	0.21
462	298.1	1.2898	1.2924	0.8981	0.20
572	298.1	1.2814	1.2833	0.9021	0.15
1	323.1	1.3759	1.3732	0.8567	− 0.20
258	323.1	1.3385	1.3399	0.8714	0.14
521	323.1	1.3110	1.3126	0.8833	0.13
776	323.1	1.2898	1.2906	0.8929	0.06
1110	323.1	1.2671	1.2665	0.9032	− 0.05
1269	323.1	1.2574	1.2564	0.9075	− 0.08
1532	323.1	1.2424	1.2413	0.9138	− 0.09
1784	323.1	1.2288	1.2284	0.9192	− 0.03
1	348.3	1.4124	1.4094	0.8356	− 0.21
49	348.3	1.4035	1.4012	0.8391	− 0.16
87	348.3	1.3966	1.3951	0.8418	− 0.11
498	348.3	1.3398	1.3415	0.8651	0.13
1020	348.3	1.2923	1.2941	0.8856	0.14
1371	348.3	1.2687	1.2695	0.8962	0.06
1673	348.3	1.2516	1.2514	0.9038	− 0.01
2026	348.3	1.2340	1.2331	0.9114	− 0.07
2499	348.3	1.2134	1.2119	0.9200	− 0.12
2971	348.3	1.1952	1.1939	0.9271	− 0.11
1	373.2	1.4514	1.4478	0.8144	− 0.25
43	373.2	1.4422	1.4393	0.8179	− 0.20
96	373.2	1.4314	1.4292	0.8222	− 0.16
499	373.2	1.3676	1.3689	0.8480	0.10
914	373.2	1.3236	1.3252	0.8669	0.12
1409	373.2	1.2858	1.2861	0.8837	0.02
2022	373.2	1.2513	1.2493	0.8992	− 0.15
2989	373.2	1.2105	1.2062	0.9168	− 0.35
4000	373.2	1.1763	1.1727	0.9296	− 0.31
4184	373.2	1.1707	1.1674	0.9316	− 0.28

measurements and perhaps not of the family of alkanes, thus depriving our method of much of its interest. This is why we confronted the values estimated on the basis of our approach with the densities of other single-

TABLE 4

Mean and maximum deviations between experimental and calculated specific volumes for various substances and mixtures

Product	Number of points	Temperature (K)	P_{max} (bar)	D_{mean} (%)	D_{max} (%)
n-C_5	13	295.1	24000	0.32	0.62
n-C_7	112	198.3–310.6	2634	0.21	0.66
n-C_9	140	303.2–423.2	8000	0.43	1.16
n-C_{24}	36	333.5–371.5	124	0.45	0.61
n-C_6					
n-C_8					
n-C_{10}	14	298.1	1000	0.19	0.53
n-C_{12}					
n-C_{14}					
n-C_6 + n-C_{10} various compositions	15	298.1	1000	0.20	0.43
n-C_8 + n-C_{12} various compositions	15	298.1	1000	0.15	0.37
n-C_{10} + n-C_{14} various compositions	15	298.1	1000	0.11	0.26
0.5 n-C_{10} + 0.5 n-C_{14}	104	298.1–358.1	4301	0.20	0.54
0.5 n-C_{12} + 0.5 n-C_{16}	84	298.1–358.1	3313	0.11	0.36
0.6 n-C_{10} + 0.2 n-C_{14} + 0.2 n-C_{16}	91	298.1–358.1	3591	0.11	0.35
0.182 n-C_6 + 0.146 n-C_8 + 0.104 n-C_{12} + 0.568 n-C_{16}	54	294.6–392.4	401	0.71	1.27

TABLE 5

Example of comparison for the ternary mixture 0.6 n-C_{10} + 0.2 n-C_{14} + 0.2 n-C_{16} (experimental values from Snyder et al., 1974)

Experimental data			Calculated			Experimental data			Calculated		
P (bars)	T (K)	V (cm³ g⁻¹)	V (cm³ g⁻¹)	y	Deviation (%)	P (bars)	T (K)	V (cm³ g⁻¹)	V (cm³ g⁻¹)	y	Deviation (%)
1	298.1	1.3423	1.3396	0.8773	−0.20	417	338.1	1.3396	1.3392	0.8683	−0.03
17	298.1	1.3398	1.3377	0.8782	−0.16	504	338.1	1.3293	1.3300	0.8723	0.06
36	298.1	1.3380	1.3354	0.8792	−0.20	624	338.1	1.3179	1.3182	0.8774	0.03
70	298.1	1.3330	1.3313	0.8810	−0.12	727	338.1	1.3082	1.3089	0.8815	0.05
102	298.1	1.3301	1.3277	0.8826	−0.18	939	338.1	1.2913	1.2914	0.8891	0.01
139	298.1	1.3256	1.3236	0.8844	−0.15	1035	338.1	1.2845	1.2842	0.8922	−0.02
209	298.1	1.3179	1.3161	0.8877	−0.13	1146	338.1	1.2770	1.2764	0.8955	−0.05
280	298.1	1.3103	1.3090	0.8909	−0.10	1239	338.1	1.2705	1.2701	0.8982	−0.03
357	298.1	1.3034	1.3017	0.8941	−0.13	1391	338.1	1.2612	1.2605	0.9023	−0.06
416	298.1	1.2968	1.2964	0.8964	−0.04	1517	338.1	1.2539	1.2530	0.9054	−0.07
479	298.1	1.2927	1.2909	0.8988	−0.13	1667	338.1	1.2453	1.2447	0.9089	−0.05
558	298.1	1.2849	1.2844	0.9016	−0.03	1787	338.1	1.2398	1.2383	0.9116	−0.12
625	298.1	1.2802	1.2792	0.9039	−0.09	1945	338.1	1.2320	1.2304	0.9148	−0.12
697	298.1	1.2744	1.2737	0.9062	−0.05	2067	338.1	1.2264	1.2247	0.9172	−0.14
762	298.1	1.2702	1.2690	0.9083	−0.09	2296	338.1	1.2167	1.2145	0.9213	−0.18
831	298.1	1.2644	1.2642	0.9103	−0.01	2483	338.1	1.2098	1.2068	0.9243	−0.25
966	298.1	1.2558	1.2553	0.9141	−0.04	2698	338.1	1.2009	1.1984	0.9276	−0.21
1039	298.1	1.2523	1.2507	0.9160	−0.13	2920	338.1	1.1937	1.1904	0.9307	−0.28
1090	298.1	1.2486	1.2476	0.9173	−0.08	3021	338.1	1.1898	1.1869	0.9321	−0.24
1170	298.1	1.2438	1.2429	0.9193	−0.07	3168	338.1	1.1854	1.1819	0.9339	−0.29

1	318.1	1.3689	1.3663	0.8609	−0.19	1	358.1	1.4267	1.4243	0.8272	−0.17
19	318.1	1.3663	1.3638	0.8620	−0.18	17	358.1	1.4235	1.4213	0.8285	−0.15
99	318.1	1.3543	1.3531	0.8667	−0.09	41	358.1	1.4188	1.4170	0.8304	−0.13
140	318.1	1.3497	1.3479	0.8690	−0.13	69	358.1	1.4134	1.4121	0.8325	−0.10
213	318.1	1.3407	1.3392	0.8728	−0.11	204	358.1	1.3904	1.3905	0.8418	−0.00
313	318.1	1.3284	1.3280	0.8777	−0.03	323	358.1	1.3729	1.3738	0.8490	0.07
525	318.1	1.3070	1.3072	0.8869	0.01	416	358.1	1.3607	1.3620	0.8541	0.09
626	318.1	1.2987	1.2983	0.8907	−0.03	524	358.1	1.3479	1.3494	0.8596	0.11
783	318.1	1.2895	1.2895	0.8946	−0.00	633	358.1	1.3365	1.3377	0.8646	0.09
828	318.1	1.2825	1.2821	0.8977	−0.03	730	358.1	1.3264	1.3280	0.8688	0.12
944	318.1	1.2739	1.2737	0.9014	−0.02	835	358.1	1.3172	1.3183	0.8730	0.09
1035	318.1	1.2681	1.2674	0.9040	−0.05	1035	358.1	1.3009	1.3014	0.8803	0.04
1146	318.1	1.2602	1.2602	0.9071	−0.01	1144	358.1	1.2925	1.2931	0.8839	0.04
1242	318.1	1.2552	1.2542	0.9096	−0.08	1249	358.1	1.2855	1.2854	0.8872	−0.01
1519	318.1	1.2392	1.2385	0.9162	−0.05	1387	358.1	1.2762	1.2760	0.8912	−0.01
1658	318.1	1.2318	1.2313	0.9192	−0.05	1523	358.1	1.2677	1.2673	0.8949	−0.03
1803	318.1	1.2259	1.2242	0.9221	−0.15	1666	358.1	1.2594	1.2588	0.8985	−0.05
1925	318.1	1.2200	1.2185	0.9244	−0.12	1795	358.1	1.2525	1.2515	0.9016	−0.08
2069	318.1	1.2145	1.2121	0.9270	−0.20	2018	358.1	1.2413	1.2398	0.9064	−0.12
1	338.1	1.3972	1.3945	0.8442	−0.20	2207	358.1	1.2323	1.2306	0.9102	−0.14
18	338.1	1.3935	1.3918	0.8454	−0.13	2618	358.1	1.2158	1.2127	0.9175	−0.26
32	338.1	1.3912	1.3895	0.8463	−0.12	2831	358.1	1.2076	1.2043	0.9208	−0.28
69	338.1	1.3848	1.3838	0.8488	−0.07	2979	358.1	1.2006	1.1987	0.9230	−0.16
204	338.1	1.3646	1.3648	0.8571	0.01	3229	358.1	1.1937	1.1899	0.9264	−0.32
313	338.1	1.3514	1.3511	0.8631	−0.02	3431	358.1	1.1872	1.1832	0.9290	−0.34
						3591	358.1	1.1823	1.1781	0.9309	−0.35

constituent alkanes and mixtures. For all of these substances, the suggested method eliminates the need for a considerable number of measurements prior to adjustment. Consequently, we compared the results obtained with our parameters with the values of density of n-C_5 (Houck, 1974), n-C_7 (Muringer et al., 1985), n-C_9 (Grindley and Lind, 1978), n-C_{24} (Peters et al., 1987), n-C_6, C_8, C_{10}, C_{12}, C_{14} (Takagi and Teranishi, 1985), binary mixtures (Takagi and Teranishi, 1985; Snyder et al., 1974), one ternary mixture (with a molar composition of 0.6 C_{10} + 0.2 C_{14} + 0.2 C_{16}) (Snyder et al., 1974) and one quaternary mixture (Gouel, 1979).

It will be observed that this new confrontation is still satisfactory, since the mean deviation is about 0.27% (with 693 reference points), with the maximum deviation not more than 1.27% (Table 4).

These results seem to us particularly convincing since the pressure and temperature ranges investigated were extended with respect to earlier work and particularly because of the number of substances tested and the diversity of their compositions (including a quaternary mixture).

Similarly to Table 3 which showed data for a binary mixture, Table 5 presents all the experimental and calculated values of density for the ternary mixture nC_{10} + nC_{14} + nC_{16}, along with the fraction of occupied cell centers y.

CONCLUSIONS

The method described enables the densities of alkanes and their mixtures to be deduced from modified Simha and Somcynsky equations. Similar results could have been obtained directly by the Simha method provided that a sufficient number of experimental determinations had first been carried out. We have partly eliminated this obligation, which is a particularly heavy handicap for multi-component systems, by limiting to 7 the number of characteristic parameters of the family studied that have to be determined by numerical adjustment from experimental reference data.

Applied to 10 single-constituent systems (5 of which were selected as test substances), 7 binary mixtures of various compositions, one ternary mixture and one quaternary mixture, over a wide range of temperature (198.3–423.2 K) and pressure (1–24 000 bars), our proposal yields results of a similar level of performance to those given by the Simha method. The tests we carried out and which we have reported in this paper support the hypothesis that with the values of the parameters indicated above (ϵ_{bb}^*, ϵ_{bc}^*, ϵ_{cc}^*, v_{bb}^*, v_{bc}^*, v_{cc}^*, f) one can reasonably predict the values of the densities of alkanes and their mixtures in the liquid state (within the pressure and temperature ranges concerned), to a maximum deviation of about 1%. We are currently working on adapting this procedure to a chemical family other than alkanes and to

mixtures of substances from different families, and particularly to branched and not just linear molecules.

LIST OF SYMBOLS

$3c$	number of independent external degrees of freedom of a molecular chain
E_0	total interaction energy of a network
f	characteristic overlap factor
k	Boltzmann constant
n	number of carbon atoms for a given alkane molecule
N	number of molecules
N_T	number of experimental points
P	pressure
P^*	scaling pressure
$\tilde{P}$	pseudo reduced pressure
P_b	probability of finding a chain end segment in an occupied cell
P_c	probability of finding an internal segment in an occupied cell
q_z	number of nearest neighbor sites per chain
q_{bz}	number of neighboring prime sites for the two ends of a chain
q_{cz}	number of neighboring prime sites for the $s - 2$ internal segments of a chain
r	number of constituents in a mixture
s	number of segments per molecule
T	temperature
T^*	scaling temperature
$\tilde{T}$	pseudo reduced temperature
v^*	characteristic volume per segment
v_n	volume of an alkane molecule with n carbon atoms
v_{kl}^*	characteristic repulsion volume of intersegmental interaction
V	volume
V^*	scaling volume
$\tilde{V}$	pseudo reduced volume
y	fraction of cell centers occupied
z	coordination number
$\langle \ \rangle$	mean value
ϵ^*	characteristic energy per segment
ϵ_{kl}^*	minimum attractive energy parameter of intersegmental interaction
ω	cell volume

Subscripts

i	component i
j	experimental point j
k, l	segment type k, segment type l ($k = b$, c; $l = b$, c)

REFERENCES

Ducoulombier, D., Lazare, F., Saint Guirons, H. and Xans, P., 1985. Viscosimètre à corps chutant permettant de procéder à des mesures de viscosité de liquides sous hautes pressions. Rev. Phys. Appl., 20: 735–740.

Ducoulombier, D., Zhou, H., Boned, C., Peyrelasse, J., Saint Guirons, H. and Xans, P., 1986. The pressure (1–1000 bars) and temperature (20–100°C) dependence of the viscosity of hydrocarbons. J. Phys. Chem., 90: 1692–1700.

Dymond, J.H., Young, K.J. and Isdale, J.D., 1980. Transport properties of nonelectrolyte liquid mixtures – II. Viscosity coefficients for the n-hexane + n-hexadecane system at temperatures from 25 to 100°C at pressures up to the freezing pressure or 500 MPa. Int. J. Thermophys., 1: 345–373.

Dymond, J.H., Robertson, J. and Isdale, J.D., 1981. Transport properties of nonelectrolyte liquid mixtures — III. Viscosity coefficients for n-octane, n-dodecane, and equimolar mixtures of n-octane + n-dodecane and n-hexane + n-dodecane from 25 to 100°C at pressures up to the freezing pressure or 500 MPa. Int. J. Thermophys., 2: 133–154.

Dymond, J.H., Robertson, J. and Isdale, J.D., 1982. (P, ρ, T) of some pure n-alkanes and binary mixtures of n-alkanes in the range 298 to 373 K and 0.1 to 500 MPa. J. Chem. Thermodyn., 14: 51–59.

Gouel, P., 1979. Etude des corrélations entre la composition des mélanges d'hydrocarbures et leurs propriétés physiques. Thèse Doctorat ès Sciences-Institut National Polytechnique de Toulouse (France).

Grindley, T. and Lind, J.E. Jr., 1978. The residual energy and entropy of hydrocarbon liquids and their relation to the liquid structure. J. Chem. Phys., 68: 5046–5052.

Houck, J.C., 1974. High pressure measurements of density, velocity of sound, and bulk moduli of pentane and 2-methylbutane and their mixtures. J. Res. Nat. Bur. Stand., 78A: 617–622.

Jain, R.K. and Simha, R., 1979a. Statistical thermodynamics of short chain molecular liquids: n-nonane. J. Chem. Phys., 70(06): 2792–2796.

Jain, R.K. and Simha, R., 1979b. Statistical thermodynamics of short chain molecular liquids. II. n-heptadecane. J. Chem. Phys., 70(11): 5329–5330.

Jain, R.K. and Simha, R. 1980. On the statistical thermodynamics of multicomponent fluids: equation of state. Macromolecules, 13: 1501–1508.

Jain, R.K. and Simha, R., 1981. Theoretical equation of state for n-paraffin liquids. Ber. Bunsenges Phys. Chem., 85: 626–628.

Muringer, M.J.P., Trappeniers, N.J. and Biswas, S.N., 1985. The effect of pressure on the sound velocity and density of toluene and n-heptane up to 2600 bar. Phys. Chem. Liq., 14: 273–296.

Peng, D.Y. and Robinson, D.B., 1976. A new two-constant equation of state. Ind. Eng. Chem. Fundam., 15: 59–64.

Peters, C.J., Van Der Kool, H.J. and De Swaan Arons, J., 1987. Measurements and calculations of phase equilibria for (ethane + tetracosane) and (p, V_m^*, T) of liquid tetracosane. J. Chem. Thermodyn., 19: 395–405.

Prigogine, I., Trappeniers, N. and Mathot, V., 1953. Statistical thermodynamics of r-Mers and r-Mer solutions. Disc. Faraday Soc., 13: 93–107.

Prigogine, I., Bellemans, A. and Mathot, V., 1957. The molecular theory of solutions. North-Holland, Amsterdam.

Rackett, H.G., 1970. Equation of state for saturated liquids. J. Chem. Eng. Data, 15: 514–517.

Redlich, O. and Kwong, J.N.S., 1949. On the thermodynamics of solutions. V. An equation of state. Fugacities of gaseous solutions. Chem. Rev., 44: 233–244.

Simha, R. and Somcynsky, Th., 1969. On the statistical thermodynamics of spherical and chain molecule fluids. Macromolecules, 2: 342–350.

Snyder, P.S., Benson, M.S., Huang, H.S. and Winnick, J., 1974. PVT properties of liquid n-alkane mixtures. J. Chem. Eng. Data, 19: 157–161.

Takagi, T. and Teranishi, H., 1985. Ultrasonic speeds and thermodynamics for binary solutions of n-alkanes under high pressures. Fluid Phase Equilibria, 20: 315–320.

Thomson, G.H., Brobst, K.R. and Hankinson, R.W., 1982. An improved correlation for densities of compressed liquids and liquid mixtures. AIChE J., 28: 671–676.