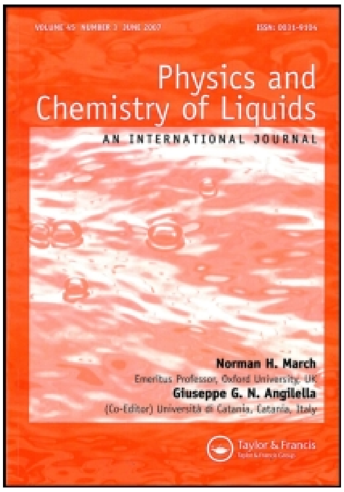

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A NEW FREE VOLUME MODEL FOR DYNAMIC VISCOSITY AND DENSITY OF DENSE FLUIDS *VERSUS* PRESSURE AND TEMPERATURE

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This article presents a model based on the free volume concept, which describes the variations of dynamic viscosity and density *versus* temperature and pressure for the dense fluids (density > 200 $kg \cdot m^{-3}$). This model involves 6 constants for each pure compound: 3 for viscosity and 4 for density (1 constant is common to both quantities). Moreover if the viscosity and the density are known at a pressure and temperature of reference, it is sufficient to use 4 constants per pure compound.

If the density is assumed to be known the model fits the viscosity data with an average absolute deviation of 3.8% for 3297 data corresponding to 41 very different pure compounds (alkanes, alkylbenzenes, cycloalkanes, alcohols, carbon dioxide, refrigerants). If the pressure is lower than 110 MPa the average absolute deviation is 2.8% for viscosity (2977 points). The model gives also good results for water (3.6%).

If the density is unknown, for pressures lower than 110 MPa the model represents viscosity with an average absolute deviation of 3.5% and for the density the average absolute deviation is 1.5%.

Keywords: Transport; Dense fluids under pressure

INTRODUCTION

The very well known model of dynamic viscosity proposed by Eyring and his collaborators [1] leads to the Arrhenius equation type

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$\eta = A\exp(B/T)$. This model describes the behavior of many low-weight molecular liquids. However it is not satisfactory for many other liquids as various articles have stressed (see for example [2] and [3]). This is mainly due to the fact that it involves only one mechanism of molecular relaxation. A modification of the model [4] consists in expressing viscosity in the following form $\eta = \eta_s(v_s/v) + \eta_g(v - v_s)/v$ where v_s is the specific volume of the solid, v that of the liquid. The authors [4] consider that the liquid consists of "quasi-solid" molecules having only degrees of freedom for vibration, and "quasi-gas" molecules with degrees of freedom for translation. The term η_g is a term of "quasi-gas" viscosity derived from kinetic theory.

Cohen and Turnbull [5] have developed a theory based on free volume. This theory assumes that the liquid consists of hard spheres. Molecular diffusion is possible when a vacant volume (larger than minimal volume v^* which allows the displacement of a molecule) is present in the liquid. Then a molecule can jump into the vacancy. The average free volume v_f is defined as being the volume of the cage which contains the molecule, less the hard volume v_0 of the molecule. The theory leads to $\ln(\eta/\sqrt{T}) = A' + (B'/v_f)$ where $v_f = v - v_0$ was expressed as being the difference between the specific molecular volume and the molecular volume of reference v_0 (hard volume). This theory is interesting because it justifies (at constant temperature) the empirical relation of Doolittle [6]

$$\eta = Ae^{B/f_v} \tag{1}$$

where $f_v = v_f/v_0$ is the free volume fraction. The basic idea is that resistance to the flow depends on the relative number of molecules compared to free volume, which is intuitively acceptable.

A substantial number of developments have been based on the above ideas. Let us state here that the idea of free volume was naturally used for polymers (see for example [7] and [8]). The interested reader can refer to Ferry's work [9] on the viscoelastic properties of polymers. Besides, certain theories combine the two approaches of Eyring and Cohen and Turnbull (for example [2]). They generally lead to an evaluation of the free volume of the liquids, larger than that suggested by the theory of Cohen and Turnbull. The free volume idea appears then in various forms (for example [10] and [11]).

Among recently published work Wang *et al.* [12] develop a model which provides an average absolute deviation of 4.1% for 1169 experimental data relating to 25 pure compounds (polar and nonpolar) and 3.3% for 1142 data relating to 10 binaries. They do not provide indications on the maximum absolute deviation DMax. They cover the field of pressure in some cases up to 500 MPa. For pure compounds, they have the worst representation for water (6.8%), ethanol (5.4%) and N-propanol (4.8%). They obtain 1.4% for the system N-octane + N-dodecane between 0.1 and 500 MPa and $T = 298, 323, 348$ K. Their theory uses 4 adjustable parameters for each pure compound and two additional parameters per binary, these last parameters having to be adjusted with each temperature. Moreover it is necessary to know the density. Also let us state that Doolittle's relation allows a good estimate of the pressure of vitreous transition of compounds such as glycerol and dibuthylphthalate, a transition which occurs when viscosity is higher than $10^{10}\,P$ [13]. The concept of free volume has been recently employed [14] to interpret the temperature variations of the viscosity of various alcohols (pentanol, heptanol, nonanol and their isomers) and of vinyl acetate. These variations are not in agreement with the Arrhenius law in the temperature range 298.15 K to 443.15 K. Finally we should mention the recent work of Lei Qun Fang *et al.* [15] based on Eyring's model, which needs two adjustable parameters (and also vapor pressure, saturated liquid volume and the heat of vaporization) but is limited to saturated liquids. These authors develop viscosity in the following form:

$$\eta = \frac{RT}{\gamma V} \exp\left[\frac{\alpha \Delta U_{\text{vap}} + PV}{RT}\right]$$

where ΔU_{vap} is the energy of vaporization at the temperature T, V the volume of the saturated liquid and P the vapor pressure. The adjustable parameters are α and γ. It is expressed as a function of ΔU_{vap} because they think that the bonds which must be broken during the movement of the viscous fluid are the same as those which are broken at vaporization. However, the introduction of the parameter α reduces the interest of this assumption because this parameter depends on each compound and does not have a universal value. For 106 compounds and 1473 experimental data they obtain an average absolute deviation of 1.51% and the maximum value DMax = 11.96%. Examination of their results indicates 4.6% for methane (DMax = 8.73%), 3.6% for benzene (DMax = 9.7%), 2.7% for 2-propanol (DMax = 8.5%), 3.4% for water (DMax = 8.0%) and 6.4% for *N*-butyric acid (DMax = 12.0%). Mixtures were not considered in this work.

The basic ideas of the previous models are very general and the problem of the representation of the pressure-temperature variations of viscosity is largely open and not closed. In what follows we propose to present an approach in order to model the viscosity of Newtonian fluids (condensed *a priori*) with small molecules. This approach is based on the free volume concept and on the diffusion models of the linear molecules. Let us recall here that, just as the mass (concentration of a tracer for example) or heat, the momentum of a fluid can be transported by diffusion. Contrary to concentration and heat, momentum is vectorial. However the diffusion equation of momentum shows that kinematic viscosity $\nu = \eta/\rho$ is like a coefficient of diffusion for momentum, similar to the coefficients D for concentration or κ for heat. Our model tries to connect viscosity to molecular structure. We will see moreover that the free volume calculated for viscosity leads also to the determination of density, according to pressure and temperature.

PRESENTATION OF THE MODEL

Relation Between Viscosity and the Microstructure

When a fluid is sheared with a rate $\dot{\gamma}(t)$ (t: time) the viscosity is defined by the ratio $\eta = (\sigma(t)/\dot{\gamma}(t))$ where $\sigma(t)$ is the shear stress. For a Newtonian fluid η = Cte. The shear stress is a function of the linear viscoelastic properties of a material as expressed by the Boltzmann constitutive equation $\sigma(t) = \int_{-\infty}^{t} G(t-t')\dot{\gamma}(t')dt'$ where $G(t)$ is the relaxation function of the fluid. For a constant shear rate one obtains $\eta = \int_0^{+\infty} G(t)dt$. It is thus sufficient to know the relaxation function $G(t)$ to determine the dynamic viscosity η. Among the many models of $G(t)$, the dumbell model and generalized dumbell models make it possible to connect viscosity to the microstructure. In the dumbell model the molecule is described by spheres connected by a spring. The molecule moves in a fluid with identical molecules of molar mass M. On each sphere are exerted the viscous friction forces associated to Stockes's law and the spring force. The assessment of the forces leads to the relaxation function $G(t) = (\rho RT/M)\exp(-t/\tau_H)$ where τ_H is the average time necessary for the molecule to change its conformation. It is the characteristic relaxation time and it is given by $\tau_H = (\xi b^2/12kT)$ where b^2 is the average quadratic length of the spring, *i.e.*, of the molecule, and ξ the friction coefficient of a sphere. Then $\eta = \int_0^{+\infty} G(t)dt = (\rho N_a \xi b^2/12M)$ where N_a is the Avogadro number. In the model of the generalized dumbell (or Rouse model for polymers), a molecule is considered as a succession of N dumbells (length b) joined to each other and able to take different orientations. Calculation leads to $G(t) = (\rho RT/M)\sum_{p=1}^{\infty}\exp(-tp^2/\tau_R)$ with $\tau_R = (\xi b^2 N^2/6\pi^2 kT)$. The integration of $G(t)$ provides $\eta = (\rho N_a \xi b^2 N^2/36M)$. In both cases one can write viscosity in the form:

$$\eta = \frac{\rho N_a \xi L^2}{M} \tag{2}$$

where L appears as an average quadratic length. For a linear molecule, calculation shows that $L^2 = b^2/12$ and for a Gaussian molecule $L^2 = \langle r^2\rangle N/36$ where $\langle r^2\rangle$ is the mean quadratic end to end distance of the molecule. For a spherical molecule $L^2 = 3\langle r^2\rangle/5 = 3\langle d^2\rangle/20$ where d is the diameter. The friction coefficient ξ is related to the mobility of the molecule and to the diffusion process. The interested reader will find a more detailed presentation of these results, especially used for polymers, in a reference work [16].

Free Volume

This concept was introduced previously. The free volume fraction defined by $f_v = v_f/v_0$ is characteristic of the empty space between molecules. To determine it, Allal *et al.* [17] use the results obtained by Nechitailo [18], which show that free volume v_f can be written in the form $v_f = (4kT/k_s)^{3/2}$ where k_s is the stiffness of the background.

To calculate this stiffness it necessary to make two assumptions:

- The molecule is in a state such that the molecular potential energy of interaction with its neighbors is E/N_a (N_a: Avogadro number).
- The mean displacement of the molecule is b_d such that $v_0 = b_d^3$.

Under these conditions the stiffness k_s is defined by $(1/2)\ k_s b_d^2 = (E/N_a)$. This gives $v_f = b_d^3(2RT/E)^{3/2}$ *i.e.*, $v_f = v_0(2RT/E)^{3/2}$. Thus the free volume fraction is defined in [17] by:

$$f_v = \frac{v_f}{v_0} = \left(\frac{2RT}{E}\right)^{3/2} \tag{3}$$

If the variations in temperature are small one can develop Eq. (3) in first order in T and write $f_v(T) = f_v(T_0) + \alpha_f(T - T_0)$ and one obtains $\alpha_f = (3/2T_0)(2RT_0/E)^{3/2}$ the thermal coefficient of expansion of the free volume fraction.

In addition f_v is also *a priori* a function of the pressure P. The energy E is the potential energy of molecular interaction. Taking for E the average of interaction energies of an individual molecule one has from a thermodynamic point of view an internal energy. We assume $E = E_0 + PN_a v = E_0 + PV$ where $N_a v = V$ is the volume M/ρ of the fluid and v the volume occupied by a molecule (hard volume plus free volume: $v = v_0 + v_f$). A similar assumption was presented in the model [15], where PV is connected to the energy necessary to form the vacant vacuums available for the diffusion of the molecules and where E_0 is connected to the barrier energy which the molecule must cross to diffuse. Moreover as the connections which must be broken are the same ones as those broken in the process of vaporization these authors [15] think that E_0 is related to the internal energy of vaporization (they propose a relation of proportionality). Also let us state that in the theory of Macedo *et al.* [2], the energy term which appears in viscosity is in the form $E_0 + Pv_f N_a = E_0 + PV - PN_a v_0$ similar to the one which we propose. Mention here that in Flory's [16] statistical thermodynamic model of fluids $E = -\beta/V = -\beta\rho/M$. In the following numerical calculations this possibility will also been considered. Taking into account our assumption, Eq. (2) changes into:

$$f_v = \left(\frac{2RT}{E_0 + PM/\rho}\right)^{3/2} \tag{4}$$

The Coefficient of Friction and Viscosity

Equation (2) shows that viscosity is connected to the molecular friction coefficient. In addition Eq. (1) indicates that it is also related to the free volume fraction f_v. The combination of both leads us to write $\xi = \xi_0 \exp(B/f_v)$ and thus:

$$\eta = N_a \rho \frac{L^2}{M} \xi_0 \exp(B/f_v) \tag{5}$$

It is possible to determine the quantity ξ_0. The term ξ_0 is the value of the friction coefficient when $f_v \gg B$ *i.e.*, when f_v becomes very large. It will be noticed that independently of the pressure, this is the case for high temperatures (the system is in a not dense state). For a molecule we already indicated that the potential energy is E/N_a. We assume that this energy is dissipated by a friction force F defined by the relation $F = \xi_0 \bar{v}$ where $\bar{v}$ is the molecular velocity. This dissipation corresponds to a length b_f which is of the order of $v^{1/3} = (V/N_a)^{1/3} = (M/\rho N_a)^{1/3}$. Notice here that $v^{1/3}$ is the length of the side of the cubic cage which surrounds the molecule. This length is equivalent to the diameter d of the associated molecular sphere. Allal *et al.* [17] obtain $(E/N_a) = \xi_0 \bar{v} b_f$. By also assuming that all the thermal energy of activation is transformed into kinetic energy $(3kT/2) = (1/2)(M/Na)\bar{v}^2$ *i.e.*, $\bar{v}^2 = (3RT/M)$. By combining these relations $\xi_0 = (E/N_a b_f)(M/3RT)^{1/2}$. The Eq. (5) gives:

$$\eta = \frac{\rho L^2 (E_0 + (PM/\rho))}{b_f \sqrt{3RTM}} \exp\left[B\left(\frac{E_0 + (PM/\rho)}{2RT}\right)^{3/2}\right] \tag{6}$$

Writing $\ell_m = (L^2/b_f)$, homogeneous with a length, one sees that the equation involves 3 parameters which are ℓ_m, E_0, and B which are characteristic of the molecule. Moreover it is necessary to know the density ρ.

Density

Density is defined by the ratio of the mass to total volume occupied $v = v_f + v_0$. Therefore $\rho = M/(N_a v)$. The molar mass M is perfectly definite for a given molecule. The volume v occupied by a molecule is the sum of two contributions.

The first contribution is the hard volume v_0 of the molecule. It corresponds to the electronic cloud systems of the atoms of the molecule which define an impenetrable volume called "Van der Waals's volume" noted v_w independent of the pressure and temperature. To obtain the hard volume v_0 it is necessary to correct the volume v_w by adding the volume induced by the vibrations and elongations of the atomic bonds and one uses $v_0 = Cv_w$ where the multiplying factor C depends on the temperature and the pressure. The simplest assumption is $C = (1 + z_T T)(1 - z_P P)$ where z_T and z_p are to be adjusted, like v_w. This assumption (first approximation) is valid only if density varies little with pressure and temperature *i.e.*, far from the critical point.

The second contribution corresponds to the free volume v_f such that $f_v = v_f/v_0$ and then $v_f = v_0 f_v$. Thus $v = v_f + v_0 = v_0(1+f_v) = C(P,T)v_w(1 + (2RT/E)^{3/2})$ and

$$\rho = \frac{M}{N_a v_w (1 + z_T T)(1 - z_P P)(1 + (2RT/E)^{3/2})} \tag{7}$$

where $E = E_0 + PV = E_0 + PM/\rho$ (or $E = -\beta\rho/M$). The density appears also in the right term of the equation. Thus Eq. (7) can be used to determine ρ using the 4 parameters v_w, z_T, z_P and E_0. As η also depends on ρ (Eq. (6)) it follows from there that the theory developed above makes it possible to determine simultaneously η and ρ using the 6 parameters ℓ_m, E_0, B, v_w, z_T and z_P.

Finally, it will be noted that if η_{ref} and ρ_{ref} are the dynamic viscosity and the density at the reference pressure P_{ref} and the reference temperature T_{ref} then we obtain:

$$\eta = \eta_{\mathrm{ref}} \frac{\rho}{\rho_{\mathrm{ref}}} \left(\frac{E_0 + (PM/\rho)}{E_0 + (P_{\mathrm{ref}} M/\rho_{\mathrm{ref}})} \right) \sqrt{\frac{T_{\mathrm{ref}}}{T}} \times \exp\left[B \left(\left(\frac{E_0 + (PM/\rho)}{2RT} \right)^{3/2} - \left(\frac{E_0 + (P_{\mathrm{ref}} M/\rho_{\mathrm{ref}})}{2RT_{\mathrm{ref}}} \right)^{3/2} \right) \right] \tag{8}$$

and

$$\rho = \rho_{\mathrm{ref}} \frac{(1 + z_T T_{\mathrm{ref}})}{(1 + z_T T)} \frac{(1 - z_P P_{\mathrm{ref}})}{(1 - z_P P)} \frac{[1 + (2RT_{\mathrm{ref}}/(E_0 + (MP_{\mathrm{ref}}/\rho_{\mathrm{ref}})))^{3/2}]}{[1 + (2RT/(E_0 + (MP/\rho)))^{3/2}]} \tag{9}$$

It is interesting to notice that in these relations the parameter ℓ_m no longer appears. Thus, if one knows the *P-T* variations of ρ, and the value η_{ref} at P_{ref} and T_{ref}, then η depends only on two parameters E_0 and B (Eq. (8)). Likewise if one knows ρ_{ref} at P_{ref} and T_{ref}, then ρ depends only on the three parameters E_0, z_T and z_P (Eq. (9)). By combining the two relations one needs the four parameters E_0, B, z_T and z_P to represent simultaneously ρ and η.

DATABASE AND CHARACTERIZATION OF THE RESULTS

We constituted a database with 41 pure compounds from very different chemical families: alkanes (linear and ramified, light and heavy), alkylbenzenes, cycloalkanes, alcohols, carbon dioxide, fluoroalkanes (refrigerants). In Table I we present for each pure compound its name, the molar mass, the enthalpy of vaporization at 25°C [19, 20] and an estimate of the Van der Waals volume, noted v_p, calculated using a group contribution method (see for example [21]). We indicate also the bibliographical references which provide the η and ρ data. The case of water has been considered separately (Ref. [48] for viscosity and [49] for density).

In order to evaluate the performances of these models, it is necessary to introduce quantities characteristic of the results obtained. One notes η_{exp} the experimental value of viscosity and η_{cal} the value calculated using the model. For each point we define the following quantities:

$$\begin{aligned} \text{Deviation} &= 100(1 - \eta_{\mathrm{cal}}/\eta_{\mathrm{exp}})\ (\%) \\ \text{Absolute deviation} &= |\text{Deviation}|\ (\%) \end{aligned}$$

These quantities are expressed as a percentage (we define identical quantities for the density). Then for all the points considered we define

TABLE I Database used for the analysis

Compound	*Reference*	*Molar mass (Kg/mole)*	*Enthalpy of vaporization at 25°C (J/mole)*	*Volume $N_a v_p$ (cm^3/mole)*
Methane	45	0.016043	*	17.1087
Ethane	26	0.03007	5048	27.3394
Propane	32	0.044097	14604	37.5700
Butane	37	0.058124	20910	47.8007
Pentane	26 + 37	0.07215	26433	58.0313
Hexane	26 + 24 + 35	0.086177	31537	68.2620
Heptane	25	0.100205	36366	78.4926
Octane	26 + 27 + 35	0.11423	41051	88.7233
Nonane	26	0.1283	46430	98.9539
Decane	36 + 39	0.142284	49914	109.1846
Dodecane	27	0.170337	58003	129.6459
Tetradecane	34	0.198391	65727	150.1072
Hexadecane	40	0.226	72646	170.5684
Isobutane	30	0.058124	19085	47.7885
2,2,Dimethylpropane	31	0.07215	21835	58.0086
2,2,4,4,6,8,8,Hepta-methylnonane	29	0.226	Unknown	170.4880
2,6,10,14,Tetra-methylpentadécane	29	0.269	Unknown	211.2013
Benzene	22 + 28	0.078113	33628	48.3589
Toluene	29	0.09214	37793	59.5089
orto-Xylene	29	0.106167	43580	70.6588
meta-Xylene	29	0.106167	42964	70.6588
para-Xylene	29	0.106167	42502	70.6588
Buthylbenzene	34	0.134221	48806	90.2008
Nonylbenzene	34	0.204335	68090	141.3541
Phenyldodecane	29	0.246	79852	172.0460
cis-Decaline	3	0.138252	48434	95.4041
trans-Decaline	3	0.138252	47262	95.4041
1-Methylnaphtalène	25	0.142201	58314	Unknown
Cyclohexane	40	0.084161	32896	61.3839
Methylcyclohexane	25 + 29	0.0981888	35211	71.6024
2-Propanol	38	0.0601	44713	49.2885
Diacetone alcohol	38	0.11616	Unknown	81.4401
Methanol	24	0.032042	38093	28.8397
Ethanol	24	0.046069	43107	39.0703
n-Propanol	24	0.0601	47884	49.3010
n-Butanol	24	0.074122	50795	59.5316
Trichlorofluoro-methane (R11)	23	0.13737	24712	46.0501
Dichlorodifluoro-methane (R12)	23	0.12091	16570	37.2590
1,1,Difluoroethane (R152a)	23	0.06605	17947	44.9290
Carbon Tetrachloride	47	0.153823	32654	51.4263
Carbon dioxide	26 + 46	0.04402	5546	20.9346
Water	48 + 49	0.018015	43990	13.9564

the three following characteristic quantities:

$$\text{Average absolute deviation} = \text{DAM} = \frac{1}{Nb}\sum_{i=1}^{Nb} \text{Absolute deviation } (i)$$

$$\text{Maximum deviation} = \text{DMax} = \text{MAX}(\text{Absolute deviation } (i))$$

$$\text{Average deviation} = \text{Bias} = \frac{1}{Nb}\sum_{i=1}^{Nb} \text{Deviation } (i)$$

The average absolute deviation characterizes the fact that the experimental points are more or less close to the calculated curve. The average deviation characterizes the more or less good distribution of the experimental points on both sides of the calculated curve. Finally DMax characterizes the maximum deviation produced by the model.

RESULTS OF NUMERICAL ANALYSIS

The Density ρ is Assumed Known

Initially we used the (Eqs. (6) and (8)) where the density ρ appears explicitly. To calculate the viscosity we need to determine the parameters ℓ_m, E_0, B (Eq. (6)) or the two parameters E_0 and B (Eq. (8)). Let us specify here that during the fit process we minimized DAM. A first analysis showed that for the least dense fluids, *i.e.*, the light alkanes, the results are not very satisfactory. For example in the case of methane if one considers the 703 points of the database [45] with $90.38\,\text{K} < T < 600\,\text{K}$ and $0.1\,\text{MPa} < P < 200\,\text{MPa}$, one obtains DAM = 38.84%, DMax = 99.8%, Bias = 30.6%. The deviations are very high at low pressures. Calculation indicates that the density ρ must be higher than a value of the order of about $200\,\text{kg}\cdot\text{m}^{-3}$. For methane we obtained in this last case (274 points) DAM = 10.65%, DMax = 34.3% and Bias = 1.79%. If ρ is higher than $300\,\text{kg}\cdot\text{m}^{-3}$ (155 points) then DAM = 6.29%, DMax = 22.06% and Bias = 0.05%. Therefore we carried out calculations imposing for all the data that $\rho > 200\,\text{kg}\cdot\text{m}^{-3}$. Table II indicates for each pure compound the pressure and temperature intervals which correspond to this condition as well as the number of associated data points. There are in all 3297 values (plus 35 values for water). Table III shows the

TABLE II Pressure and temperature intervals for the points which satisfy the condition $\rho > 200\,\mathrm{kg \cdot m^{-3}}$ (3332 data points)

Compound	*Nb points*	P_{min} (*MPa*)	P_{max} (*MPa*)	T_{min} (*K*)	T_{max} (*K*)
Methane	274	0.1	200	90.38	600
Ethane	156	2.5	50	273.15	423.15
Propane	26	6.89	34.47	173.15	273.15
Butane	135	0.69	68.95	310.93	510.93
Pentane	413	0.1	55.16	273.15	510.93
Hexane	292	0.1	500	273.15	448
Heptane	18	0.1	100	303.15	343.15
Octane	324	0.1	505.5	273.15	448
Nonane	240	0.1	50	273.15	423.15
Decane	80	0.1	231.8	292.62	423.75
Dodecane	32	0.1	501.6	298.27	373.21
Tetradecane	18	0.1	100	313.15	353.15
Hexadecane	16	0.1	150.5	298.15	348.15
Isobutane	66	0.69	55.16	310.93	510.93
2,2,Dimethylpropane	94	0.69	55.16	310.93	444.26
2,2,4,4,6,8,8,Heptamethylnonane	30	0.1	100	298.15	363.15
2,6,10,14,Tetramethylpentadécane	29	0.1	100	298.15	363.15
Benzene	56	0.1	402.2	298.38	373.17
Toluene	30	0.1	100	298.15	363.15
orto-Xylene	30	0.1	100	298.15	363.15
meta-Xylene	24	0.1	100	298.15	363.15
para-Xylene	15	0.1	100	313.15	353.15
Buthylbenzene	18	0.1	100	313.15	353.15
Nonylbenzene	18	0.1	100	313.15	353.15
Phenyldodecane	30	0.1	100	298.15	363.15
cis-Decaline	45	0.1	360	288.71	372.04
trans-Decaline	51	0.1	360	288.71	388.15
1-Methylnaphtalène	18	0.1	100	303.15	343.15
Cyclohexane	26	0.1	100	298.15	348.15
Methylcyclohexane	48	0.1	100	298.15	363.15
2-Propanol	18	0.1	100	303.15	343.15
Diacetone alcohol	18	0.1	100	303.15	343.15
Methanol	18	0.1	25.43	298.15	323.15
Ethanol	20	0.1	27.56	298.15	323.15
n-Propanol	20	0.1	27.86	298.15	323.15
n-Butanol	20	0.1	28.27	298.15	323.15
Trichlorofluoromethane (R11)	32	1.4	18.9	273.15	333.15
Dichlorodifluoromethane (R12)	32	1.15	15.1	273.15	333.15
1,1,Difluoroethane (R152a)	32	1.45	17.7	273.15	333.15
Carbon Tetrachloride	27	0.1	147.5	283.2	328.3
Carbon dioxide	408	0.56	453.2	220.01	373.15
Water	35	0.1	100	273.15	373.15

TABLE III Results obtained for the points which satisfy the condition $\rho > 200\,\mathrm{kg \cdot m^{-3}}$. Density is assumed to be known

Compound	ℓ_m (*Å*)	E_0 (*J/mole*)	*B*	*Nb points*	*DAM*	*DMax*	*Bias*
Methane	0.8052000	9592.2000	0.0629000	274	10.65	34.33	1.79
Ethane	1.4695864	8623.4740	0.1364979	156	3.15	22.36	−1.11
Propane	0.8424370	24577.727	0.0589878	26	1.08	4.30	−0.29
Butane	0.8821640	23615.299	0.0944296	135	1.15	5.26	−0.32
Pentane	0.8440835	32747.847	0.0627691	413	2.52	11.62	−0.26
Hexane	0.6743440	51944.497	0.0350355	292	3.81	78.67	−0.52
Heptane	0.7103977	56508.036	0.0352772	18	1.36	4.50	−0.05
Octane	0.5273559	80751.743	0.0250355	324	4.96	33.63	0.17
Nonane	0.6363625	64586.668	0.0412388	240	1.28	8.54	−0.40
Decane	0.4488705	97966.530	0.0247645	80	2.21	8.21	−0.09
Dodecane	0.2508876	153745.330	0.0171587	32	7.21	18.61	−0.77
Tetradecane	0.3724672	141885.634	0.0195815	18	1.84	7.21	−0.83
Hexadecane	0.2284553	180877.436	0.0167531	16	1.87	5.18	−0.49
Isobutane	0.8826764	21918.434	0.1147150	66	1.44	7.85	−0.39
2,2,Dimethylpropane	0.5712338	27256.798	0.1446728	94	3.27	40.93	−1.38
2,2,4,4,6,8,8,Heptamethylnonane	0.3241911	116725.864	0.0334846	30	1.56	6.94	−0.30
2,6,10,14,Tetramethylpentadécane	0.1092172	224009.962	0.0164295	29	3.80	12.25	0.95
Benzene	0.3573470	56034.640	0.0563613	56	2.05	14.60	−0.47
Toluene	0.5355698	58487.985	0.0416452	30	0.87	2.53	0.02
orto-Xylene	0.5698882	63727.727	0.0412907	30	1.64	3.76	−0.02
meta-Xylene	0.4761951	68104.604	0.0348891	24	0.80	3.71	−0.16
para-Xylene	0.3948495	72743.968	0.0350849	15	1.21	3.69	−0.29
Buthylbenzene	0.5550050	82428.794	0.0306726	18	2.73	10.49	−0.26
Nonylbenzene	0.3415081	146830.612	0.0202677	18	2.03	8.12	−1.00
Phenyldodecane	0.1686537	197497.410	0.0170963	30	1.68	4.08	0.14
cis-Decaline	0.2843184	93729.528	0.0461780	45	5.06	14.62	0.11
trans-Decaline	0.4006113	93767.067	0.0372779	51	3.95	13.22	−0.69
1-Methylnaphtalène	0.2000257	103613.291	0.0400777	18	1.73	5.85	0.13
Cyclohexane	0.4038518	48440.258	0.0883506	26	0.77	1.87	−0.06

TABLE III (Continued)

Compound	ℓ_m (*Å*)	E_0 (*J/mole*)	*B*	*Nb points*	*DAM*	*DMax*	*Bias*
Methylcyclohexane	1.0285425	46628.555	0.0562811	48	2.24	12.30	−0.89
2-Propanol	0.0432416	85947.356	0.0689605	18	1.52	4.96	−0.26
Diacetone alcohol	0.0950815	104141.555	0.0467462	18	1.10	3.90	−0.28
Methanol	0.2747431	43552.611	0.0841593	18	0.16	0.48	−0.09
Ethanol	0.1799174	58987.184	0.0774167	20	0.38	1.64	−0.23
n-Propanol	0.0904710	77580.067	0.0694284	20	0.30	1.15	−0.05
n-Butanol	0.0779140	91014.080	0.0590825	20	0.28	1.23	−0.07
Trichlorofluoromethane (R11)	0.7038072	32472.854	0.0792887	32	0.29	1.30	−0.10
Dichlorodifluoromethane (R12)	0.6463938	21807.550	0.1223570	32	0.69	3.13	−0.27
1,1,Difluoroethane (R152a)	0.5594791	21855.713	0.1283800	32	0.51	2.41	−0.19
Carbon Tetrachloride	0.4864731	52472.322	0.0593815	27	1.57	4.80	−0.63
Carbon dioxide	0.2588575	23909.320	0.0981847	408	6.84	30.97	−0.75
Total				3297	3.83	78.67	−0.22
Water	0.0078162	402699.782	0.0047323	35	3.63	17.35	1.03

results obtained. It is noted that if the fit is very satisfactory for certain compounds up to 400 MPa (benzene, decaline, octane, carbon dioxide), it is sometimes unsatisfactory at very high pressures (hexane). This is undoubtedly related to the fact that the development of energy was written in the form of $E_0 + PV$ and that the term PV is not the best term to represent variations of E with pressure. The proximity of the critical point is sometime an explanation. However if one restricts the pressure to the experimental conditions of many references, *i.e.*, $P < 110$ MPa (there are then 2977 points and 35 additional points for water), the representation of η is then very satisfactory, comparable with that of other recent models [12, 15]. The results are provided in Table IV. It is for the 2,2-dimethylpropane that the maximum deviation is highest (40.93%) with an average absolute deviation for this compound of 3.27%. It will be noted that methane has the highest absolute average deviation DAM (9.35%) which is partly related to the fact that the representation of the methane molecule by a dumbell model is too far away from reality. Except for methane and carbon dioxide the absolute average deviation of each other compounds is smaller than 4%. Mention here that for water we found DAM = 3.63%, DMax = 17.35% and Bias = 1.03%.

In addition, the variations of E_0 *versus* the enthalpy of vaporization E_v at 25°C (Fig. 1) correspond to a regular curve of the form $E_0 = aE_v^2 + bE_v + c$. Note that the E_v-RT quantity corresponds to what is called the cohesion energy, which is consistent with the remark made above on the nature of the bonds broken during the molecular diffusion process. The only exception of the database is water for which E_0 is too high. This is certainly due to the very polar character of water. So we carried out the numerical analysis (with the same statistical weight for each compound) by supposing $E_0 = aE_v^2 + bE_v + c$ adjusting for each compound (except water) the parameters ℓ_m and B. For certain compounds the value of E_v at 25°C (Tab. I) is not known and there are in this case 2699 values in the database. We obtained DAM = 2.65%, DMax = 41.57%, Bias = −0.38% and it is still for the 2,2-dimethylpropane that the maximum deviation is largest (DAM = 3.28% and DMax = 41.57%). The interested reader will be supplied with detailed results for each compound upon request. We found $a = 3.37839 \cdot 10^{-5}$, $b = -0.27818303$,

TABLE IV Results obtained for the points which satisfy the condition $\rho > 200\,\text{kg}\cdot\text{m}^{-3}$ and $P < 110\,\text{MPa}$. The density is assumed to be known

Compound	ℓ_m (*Å*)	E_0 (*J/mole*)	*B*	*Nb points*	*DAM*	*DMax*	*Bias*
Methane	0.9127040	7075.9990	0.1255726	201	9.35	37.29	0.87
Ethane	1.4695864	8623.4740	0.1364979	156	3.15	22.36	−1.11
Propane	0.8424370	24577.727	0.0589878	26	1.08	4.30	−0.29
Butane	0.8821640	23615.299	0.0944296	135	1.15	5.26	−0.32
Pentane	0.8440835	32747.847	0.0627691	413	2.52	11.62	−0.26
Hexane	0.7907931	41979.528	0.0492035	285	2.36	27.08	0.09
Heptane	0.7103977	56508.036	0.0352772	18	1.36	4.50	−0.05
Octane	0.6979222	56398.407	0.0437986	295	2.05	26.51	−0.82
Nonane	0.6363625	64586.668	0.0412388	240	1.28	8.54	−0.40
Decane	0.4959059	86965.542	0.0295993	67	1.38	6.14	−0.36
Dodecane	0.3692642	116003.825	0.0239963	14	1.55	3.63	0.45
Tetradecane	0.3724672	141885.634	0.0195815	18	1.84	7.21	−0.83
Hexadecane	0.2049311	177467.853	0.0178136	12	1.49	3.64	0.08
Isobutane	0.8826764	21918.434	0.1147150	66	1.44	7.85	−0.39
2,2,Dimethylpropane	0.5712338	27256.798	0.1446728	94	3.27	40.93	−1.38
2,2,4,4,6,8,8,Heptamethylnonane	0.3241911	116725.864	0.0334846	30	1.56	6.94	−0.30
2,6,10,14,Tetramethylpentadécane	0.1092172	224009.962	0.0164295	29	3.80	12.25	0.95
Benzene	0.3857266	50519.887	0.0659246	44	0.43	2.54	0.01
Toluene	0.5355698	58487.985	0.0416452	30	0.87	2.53	0.02
orto-Xylene	0.5698882	63727.727	0.0412907	30	1.64	3.76	−0.02
meta-Xylene	0.4761951	68104.604	0.0348891	24	0.80	3.71	−0.16
para-Xylene	0.3948495	72743.968	0.0350849	15	1.21	3.69	−0.29
Buthylbenzene	0.5550050	82428.794	0.0306726	18	2.73	10.49	−0.26
Nonylbenzene	0.3415081	146830.612	0.0202677	18	2.03	8.12	−1.00
Phenyldodecane	0.1686537	197497.410	0.0170963	30	1.68	4.08	0.14
cis-Decaline	0.3789990	78301.047	0.0572970	15	2.43	8.61	−0.23
trans-Decaline	0.5188219	74921.684	0.0493200	18	1.45	2.70	0.30
1-Methylnaphtalène	0.2000257	103613.291	0.0400777	18	1.73	5.85	0.13
Cyclohexane	0.4038518	48440.258	0.0883506	26	0.77	1.87	−0.06

Methylcyclohexane	1.0285425	46628.555	0.0562811	48	2.24	12.30	−0.89
2-Propanol	0.0432416	85947.356	0.0689605	18	1.52	4.96	−0.26
Diacetone alcohol	0.0950815	104141.555	0.0467462	18	1.10	3.90	−0.28
Methanol	0.2747431	43552.611	0.0841593	18	0.16	0.48	−0.09
Ethanol	0.1799174	58987.184	0.0774167	20	0.38	1.64	−0.23
n-Propanol	0.0904710	77580.067	0.0694284	20	0.30	1.15	−0.05
n-Butanol	0.0779140	91014.080	0.0590825	20	0.28	1.23	−0.07
Trichlorofluoromethane (R11)	0.7038072	32472.854	0.0792887	32	0.29	1.30	−0.10
Dichlorodifluoromethane (R12)	0.6463938	21807.550	0.1223570	32	0.69	3.13	−0.27
1,1,Difluoroethane (R152a)	0.5594791	21855.713	0.1283800	32	0.51	2.41	−0.19
Carbon Tetrachloride	0.4965893	50618.410	0.0629066	21	1.07	3.77	−0.66
Carbon dioxide	0.3511195	15879.693	0.1866042	313	5.46	24.80	−1.64
Total				2977	2.78	40.93	−0.43
Water	0.0078162	402699.78	0.0047323	35	3.63	17.35	1.03

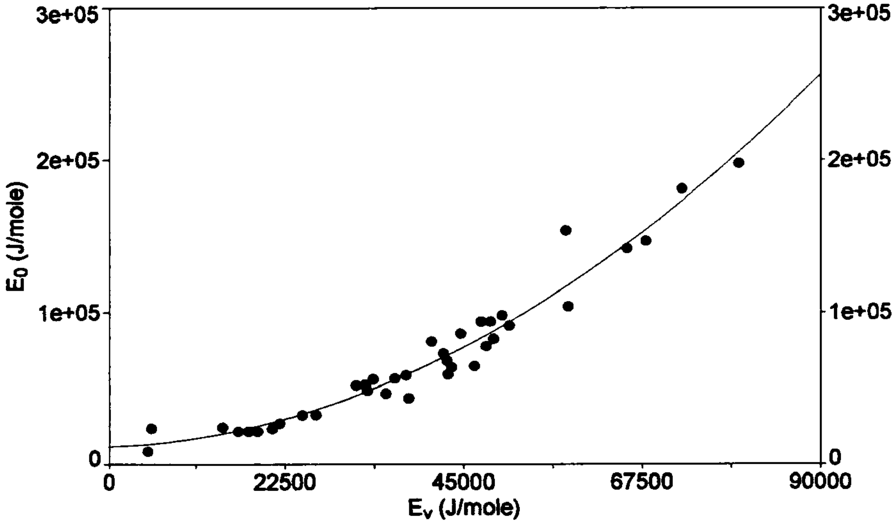

FIGURE 1 Variations of E_0 *versus* E_v.

$c = 16889.36$ (E_0 and E_v, in $\mathrm{J \cdot mol^{-1}}$). There is of course a small variation on ℓ_m and B. For example in the case of heptane one obtains $\ell_m = 0.89761212$ Å instead of 0.7103977 Å and $B = 0.03573292$ instead of 0.0352772.

Using $E = -\beta\rho/M$ gives AAD = 9.55%, DMax = 82.8% (carbon dioxide) and Bias = 2.98% and using $E = -\beta\rho/M + PV$ gives AAD = 2.79%, DMax = 76.91% and Bias = 0.83%. For water we obtained AAD = 7.46%, DMax = 32.60% and Bias = 2.86%. Compared to the values indicated in Table IV there is no improvement.

Next, we tested the model using Eq. (8), which uses the reference viscosity η_{ref} (P_{ref}, T_{ref}). There are then 2936 points after exclusion of the 41 reference points. Initially we adjusted E_0 for every compound (DAM = 3.34%, DMax = 50.72%, Bias = –0.24%). For water we obtained DAM = 3.95%, DMax = 11.69%, Bias = –0.40%. Then we assumed that $E_0 = aE_v^2 + bE_v + c$ (except water). In this last case, where there is no more than one characteristic constant per compound (B) and three identical constants for all the compounds ($a = 2.14502 \cdot 10^{-5}, b = 0.5428218, c = 6342.8676$), one notes the very good fit (DAM = 3.47%, DMax = 42.78%, Bias = –0.10%) for the 2662 values ($\rho > 200\,\mathrm{kg \cdot m^{-3}}$ and $P < 110\,\mathrm{MPa}$). The results concerning each compound will be supplied upon request.

Finally, in Eq. (6) we have assumed that $L^2 = 3\langle d^2 \rangle/20$ (see Ref. [50]) with $d = v^{1/3} = (V/N_a)^{1/3} = (M/\rho N_a)^{1/3}$ (hypothesis of spherical molecule, as already indicated above), and that $b_f = A \cdot d$ (A is the friction dissipation length expressed in number of molecular spherical diameter). In that case $\ell_m = (L^2/b_f) = (3v^{1/3}/20A)$ is now a function of the pressure and of the temperature because v depends on ρ. It is necessary to adjust A, B and E_0. The results are presented in Table V and should be compared with those of Table IV. Although still satisfactory, the total result is less good than that of Table IV because if the assumption of spherical molecules is fulfilled for many compounds for other compounds this assumption is not fulfilled and is consequently a rude approximation.

The Density ρ is not Known

In this case the equations to be used are the Eqs. (6) and (7). We determine simultaneously η and ρ with six parameters, the parameter

TABLE V Results obtained for the points which satisfy the condition $\rho > 200\,\mathrm{kg \cdot m^{-3}}$ and $P < 110\,\mathrm{MPa}$. The density is assumed to be known. Hypothesis: $L^2 = 3\langle d^2 \rangle/20$ and $b_f = A \cdot d$

Compound	E_0 *(J/mole)*	*B*	*A*	*Nb points*	*DAM*	*DMax*	*Bias*
Methane	7943.0782	0.1415637	0.9258432	201	9.87	56.66	−2.39
Ethane	8703.4667	0.2611983	0.7360779	156	5.13	30.87	−1.66
Propane	23980.096	0.0654548	0.9330665	26	1.33	4.28	−0.11
Butane	23147.833	0.1131127	1.0806484	135	1.37	6.76	−0.50
Pentane	31767.602	0.0740849	1.1458476	413	2.93	16.56	−0.64
Hexane	41108.160	0.0550760	1.2430026	285	2.67	27.21	−0.24
Heptane	56159.890	0.0367613	1.3635858	18	1.46	6.47	−0.42
Octane	55872.593	0.0468131	1.5115753	295	2.24	23.60	−1.01
Nonane	63613.934	0.0440701	1.6928213	240	1.52	10.19	−0.67
Decane	86515.404	0.0310111	2.2498301	67	1.51	7.86	−0.46
Dodecane	115003.52	0.0247494	3.0626756	14	1.73	3.99	0.35
Tetradecane	138694.13	0.0203917	3.0594531	18	1.95	7.94	−0.92
Hexadecane	175164.71	0.0186813	6.3419659	12	1.53	4.18	0.23
Isobutane	21757.634	0.1330354	1.1042280	66	1.74	9.54	−0.43
2,2,Dimethylpropane	26414.330	0.1689704	1.8415998	94	4.53	61.71	−2.17
2,2,4,4,6,8,8,Heptamethylnonane	116431.13	0.0340203	3.7894233	30	1.48	6.58	−0.29
2,6,10,14,Tetramethylpentadécane	222015.92	0.0168310	11.939501	29	3.77	11.75	0.94
Benzene	49838.307	0.0694596	2.1795616	44	0.51	2.29	−0.05
Toluene	57419.776	0.0445270	1.6559096	30	0.98	3.38	−0.16
orto-Xylene	63130.855	0.0428666	1.5996908	30	1.74	4.81	−0.12
meta-Xylene	67951.248	0.0366038	2.0098916	24	0.79	4.17	0.04
para-Xylene	69911.656	0.0378908	2.2568081	15	1.13	3.82	−0.07
Buthylbenzene	81470.933	0.0321389	1.8141820	18	2.75	10.38	−0.35
Nonylbenzene	145442.40	0.0209249	3.3926920	18	2.08	8.36	−0.96
Phenyldodecane	196751.28	0.0173801	7.2543154	30	1.63	3.98	0.13
cis-Decaline	79211.377	0.0576634	2.7673475	15	2.42	8.01	0.17
trans-Decaline	74373.046	0.0505435	1.9203107	18	1.58	2.70	0.09
1-Methylnaphtalène	98609.468	0.0431383	4.4796657	18	1.78	6.09	0.42

Cyclohexane	48104.013	0.0915508	2.2327950	26	0.81	2.47	−0.13
Methylcyclohexane	46413.513	0.0595055	0.9395336	48	2.41	13.04	−1.20
2-Propanol	83672.325	0.0726285	18.006520	18	1.64	5.88	−0.42
Diacetone alcohol	103234.48	0.0482436	10.043320	18	1.09	3.84	−0.18
Methanol	40704.503	0.0965821	2.2542532	18	0.19	0.60	−0.10
Ethanol	57408.082	0.0825070	4.0177973	20	0.41	1.57	−0.23
n-Propanol	77011.915	0.0709378	8.6015204	20	0.28	1.04	−0.04
n-Butanol	91188.040	0.0597055	10.943911	20	0.29	1.00	−0.11
Trichlorofluoromethane (R11)	33004.445	0.0829063	1.2771840	32	0.36	1.60	−0.09
Dichlorodifluoromethane (R12)	21795.703	0.1373376	1.4212549	32	0.93	4.84	−0.51
1,1,Difluoroethane (R152a)	20581.123	0.1598730	1.4815952	32	0.72	3.49	−0.38
Carbon Tetrachloride	49831.159	0.0662594	1.7177258	21	1.15	4.10	−0.72
Carbon dioxide	15823.682	0.2359828	2.5392617	313	8.34	71.16	−3.52
Total				2977	3.42	71.16	−1.04
Water	335111.57	0.0062988	51.372810	35	3.52	16.88	1.23

E_0 being common to both quantities. The numerical analysis was done by minimizing $S = \mathrm{DAM}_\eta + \mathrm{DAM}_\rho$. However, with carbon dioxide we noticed that the density deviation increases at the lowest densities near the critical conditions ($P_c = 7.39\,\mathrm{MPa}, T_c = 304.2\,\mathrm{K}, \rho_c = 464\ \mathrm{kg \cdot m^{-3}}$). It is important to point here that if the density is known there is no problem for viscosity even near the critical conditions (see Tab. IV). So in this part of the paper we have taken into account for carbon dioxide only the highest values of density $\rho > 880\,\mathrm{kg \cdot m^{-3}}$ (152 values from Ref. [46]). At $T = 303.05\,\mathrm{K}$, very near of T_c, this implies $P > 20\,\mathrm{MPa} \approx 3P_c$ (see Ref. [46]). Table VI presents the values obtained for the six parameters and Table VII presents the values of DAM, DMax and Bias for η, and ρ. With regard to η, there is always an excellent representation (DAM = 3.51%). It will be observed that it is still the 2,2-dimethylpropane which corresponds to the maximum value of DMax. With regard to ρ the overall average deviation is 1.51%. The maximum deviation 45.3% is for 2,2-dimethylpropane at the lowest value of density: $306\,\mathrm{kg \cdot m^{-3}}$ ($\rho_c = 238\,\mathrm{kg \cdot m^{-3}}$). The results are comparable with those obtained using an equation of state. A comparative analysis of the performances presented by various equations of state was carried out by [41]. One of the most powerful equations is that of Lee and Kesler [42]. With this equation, Ye obtained 2.4% for benzene between 0.1 MPa and 170 MPa, and from 203.15 to 323.15 K, whereas we obtain 0.27%. In the same way for dodecane we obtain 0.54% whereas Ye obtained 0.7%. For cyclohexane we have 0.27% and Ye indicates 0.2%. For 1009 experimental points and 12 pure compounds he obtains an average deviation of 1.2%. However there are much more precise representations of the density (for example [43]). If one considers this last model for 606 points it has DAM = 0.17% and DMax = 1.09%. For example for benzene (up to 400 MPa) it has DAM = 0.27% and DMax = 0.83%. For hexadecane the model obtained 0.08% and 0.19% at pressures up to 425 MPa (whereas we have 0.27% and 1.1% up to 100 MPa). We should mention briefly that this model, developed for the density of alkanes and alkylbenzenes only, is a model with 12 universal parameters (they are the same for all the compounds of these two chemical families) where the compounds are broken up into internal chain segments, end-chain segments

TABLE VI Results obtained for the points which satisfy the condition $\rho > 200\,\mathrm{kg\cdot m^{-3}}$ and $P < 110\,\mathrm{MPa}$. The density is assumed to be unknown. Values of the 6 characteristic parameters adjusted simultaneously on the density ρ and dynamic viscosity η

Compound	ℓ_m (*Å*)	E_0 (*J/mole*)	*B*	$N_a v_w$ (*cm*^{3}*/mole*)	$z_T \cdot 10^6$ (K^{-1})	$z_P \cdot 10^{10}$ (Pa^{-1})
Methane	1.02940001	5829.71121	0.167577829	22.9087	4146.82912	35.3549769
Ethane	1.37039239	8236.06462	0.182836464	19.6173	6778.81224	49.8082043
Propane	0.84130000	24626.6026	0.05879226	49.4222	1917.30929	13.8206814
Butane	0.88832836	23437.4399	0.095257261	58.0980	2039.17435	21.4607119
Pentane	0.87566457	32125.5269	0.063206242	67.6086	2141.18465	21.0686019
Hexane	0.80281902	42182.2087	0.048055664	83.7427	1729.71725	14.8877392
Heptane	0.72001664	56018.2585	0.035577672	99.7780	1452.94790	8.40949420
Octane	0.71323162	55933.5265	0.043933125	108.535	1572.13454	11.6828002
Nonane	0.63640381	64446.0573	0.04141677	123.427	1437.11537	12.8720739
Decane	0.50889482	85295.5359	0.030351039	140.660	1254.86225	10.0903256
Dodecane	0.36737624	114925.066	0.024476782	166.100	1225.93347	8.62899158
Tetradecane	0.39755134	139444.946	0.019725749	190.145	1217.17324	7.25687409
Hexadecane	0.2119295	174251.283	0.01821443	211.219	1278.7281	7.4878063
Isobutane	0.88337801	21829.9967	0.11559419	53.6190	2602.08374	24.8732075
2,2,Dimethylpropane	0.59106106	26602.7681	0.149184595	53.6742	3817.39716	40.5842542
2,2,4,4,6,8,8,Heptamethylnonane	0.31922299	116759.019	0.033610763	236.322	735.103520	6.55962614
2,6,10,14,Tetramethylpentadecane	0.10921495	224011.981	0.01642921	274.438	857.882796	6.42614738
Benzene	0.38754145	50236.9165	0.06648279	62.6489	1288.00449	7.11872578
Toluene	0.53869328	57915.6365	0.042317005	79.3000	1067.54398	6.77382087
orto-Xylene	0.56973629	64057.3668	0.040928254	94.0586	898.453901	6.50437768
meta-Xylene	0.47204837	68329.2252	0.034769954	91.2883	1106.38488	6.97741601
para-Xylene	0.39258960	71667.3715	0.036110264	98.7641	805.480161	6.79586833
Buthylbenzene	0.55500471	82315.5546	0.030732900	113.406	1200.65909	6.45379976
Nonylbenzene	0.34150812	146789.132	0.020274530	183.284	999.560978	6.12226173
Phenyldodecane	0.16984624	196020.805	0.017270253	230.356	839.572348	5.72197420
cis-Decaline	0.38939585	77127.5983	0.058266784	118.517	963.249437	6.09568294
trans-Decaline	0.51985098	74944.6537	0.049268376	119.193	1064.81468	7.26565435

TABLE VI (Continued)

Compound	ℓ_m (*Å*)	E_0 (*J/mole*)	*B*	$N_a v_w$ (*cm^3/mole*)	$z_T \cdot 10^6$ (K^{-1})	$z_P \cdot 10^{10}$ (Pa^{-1})
1-Methylnaphtalène	0.20775263	100767.824	0.041514090	113.236	757.895622	4.49166352
Cyclohexane	0.40385165	48439.222	0.088348370	72.2843	1529.74224	8.62554129
Methylcyclohexane	1.05077090	46463.7618	0.055957552	94.3841	1060.68666	7.61622486
2-Propanol	0.03805254	86318.6327	0.070377510	61.8480	773.522851	7.29364552
Diacetone alcohol	0.09340571	103123.105	0.047689490	94.8872	998.546068	5.75263496
Methanol	0.2749014	43525.5294	0.084238750	27.8776	1364.20954	11.2496282
Ethanol	0.17985911	58990.0403	0.077418200	40.2888	1415.81857	9.76523195
n-Propanol	0.08973519	79428.0881	0.066792350	54.7130	1184.94544	8.87918156
n-Butanol	0.07610517	93464.2694	0.05677598	68.2878	1112.51848	8.68004735
Trichlorofluoromethane (R11)	0.70662143	32546.7328	0.078694791	55.3718	1980.19234	14.9556477
Dichlorodifluoromethane (R12)	0.63246120	22409.6654	0.117188686	34.3203	4834.11629	31.2130942
1,1,Difluoroethane (R152a)	0.57459609	21529.1772	0.130063133	25.7873	5291.41584	29.1697213
Carbon Tetrachloride	0.49658929	50618.4102	0.0629061	68.7960	1230.80119	7.11018406
Carbon dioxide	0.52330814	12274.2727	0.23224285	20.2015	2792.7933	9.50021455
Water	0.00798260	397514.720	0.00481400	15.5400	537.90749	3.8958684

TABLE VII Results obtained for the points which satisfy the condition $\rho > 200\,\mathrm{kg \cdot m^{-3}}$ and $P < 110\,\mathrm{MPa}$. The density is assumed to be unknown. Values of the average absolute deviations, deviations maximum and bias obtained after simultaneous adjustment on ρ and η from the 6 characteristic parameters of each compound

		η			ρ		
Compound	*Nb points*	*DAM*	*DMax*	*Bias*	*DAM*	*DMax*	*Bias*
Methane	201	12.87	57.82	−0.68	6.30	38.99	−2.91
Ethane	156	6.59	45.39	−2.46	5.40	49.12	−2.89
Propane	26	1.32	4.92	−0.44	0.31	1.69	−0.17
Butane	135	1.63	8.17	−0.44	0.68	3.13	−0.28
Pentane	413	3.28	25.85	−0.83	1.19	13.06	−0.54
Hexane	285	2.79	27.21	−0.43	0.95	18.23	−0.47
Heptane	18	1.64	6.22	−0.30	0.46	1.68	−0.15
Octane	295	2.21	21.30	−1.01	0.66	12.20	−0.12
Nonane	240	1.60	9.69	−0.55	0.45	2.46	−0.18
Decane	67	1.62	9.28	−0.67	0.62	3.74	−0.16
Dodecane	14	1.69	3.78	−0.03	0.54	2.43	−0.38
Tetradecane	18	1.97	8.31	−1.05	0.38	1.54	−0.20
Hexadecane	12	1.62	3.94	−0.10	0.27	1.08	0.04
Isobutane	66	2.12	10.01	−0.67	1.02	4.53	−0.42
2,2,Dimethyl-propane	94	5.71	100.1	−3.44	3.89	45.26	−1.36
2,2,4,4,6,8,8,Hepta-methylnonane	30	1.52	7.01	−0.46	0.34	1.51	−0.18
2,6,10,14,Tetra-methylpentadécane	29	3.70	11.04	0.86	0.30	1.38	−0.12
Benzene	44	0.61	2.59	−0.15	0.27	2.85	−0.14
Toluene	30	1.06	3.48	−0.18	0.37	1.36	−0.16
orto-Xylene	30	1.80	5.15	−0.22	0.36	1.45	−0.16
meta-Xylene	24	0.86	4.41	0.14	0.33	1.14	−0.14
para-Xylene	15	1.05	4.34	0.08	0.26	1.08	−0.10
Buthylbenzene	18	2.85	10.46	−0.16	0.33	1.17	−0.05
Nonylbenzene	18	2.14	8.48	−0.94	0.25	0.77	−0.02
Phenyldodecane	30	1.65	4.08	0.25	0.31	1.34	−0.13
cis-Decaline	15	2.48	8.87	−0.06	0.31	1.07	−0.09
trans-Decaline	18	1.53	2.96	0.23	0.45	1.91	−0.22
1-Methylnaph-talène	18	1.79	6.18	0.36	0.20	0.89	−0.14
Cyclohexane	26	0.86	2.33	−0.01	0.27	0.68	0.02
Methylcyclohexane	48	2.46	14.48	−1.00	0.44	1.48	−0.14
2-Propanol	18	1.89	5.82	−0.72	0.48	2.23	−0.08
Diacetone alcohol	18	1.11	4.50	−0.27	0.22	0.87	−0.07
Methanol	18	0.22	0.73	−0.13	0.06	0.25	−0.04
Ethanol	20	0.42	1.77	−0.25	0.05	0.15	−0.02
n-Propanol	20	0.28	1.08	−0.06	0.11	1.34	−0.10
n-Butanol	20	0.31	1.11	−0.14	0.05	0.17	−0.03
Trichiorofluoro-methane (R11)	32	0.41	1.75	−0.19	0.14	0.62	−0.05
Dichlorodifluoro-methane (R12)	32	1.13	5.88	−0.57	0.48	2.51	−0.25

TABLE VII (Continued)

		η			ρ		
Compound	*Nb points*	*DAM*	*DMax*	*Bias*	*DAM*	*DMax*	*Bias*
1,1,Difluoroethane (Rl52a)	32	0.97	5.26	−0.51	0.53	2.61	−0.21
Carbon Tetra-chloride	21	1.22	3.94	−0.68	0.26	0.79	−0.03
Carbon dioxide	152	6.97	17.71	4.67	1.88	12.97	−1.01
Total	2816	3.51	100.1	−0.49	1.51	49.12	−0.68
Water	35	3.43	16.64	0.87	0.25	0.96	−0.08

and benzene rings segments, and where the interactions take place between these various elements. We can thus conclude that the method that we propose, although comparable for its results with the classical equations of state, is less efficient from the performance point of view than specific methods relating to the density (but limited to particular chemical families). The interest of our work is however that its highlights the relation between η and ρ. Mention here that for water we obtained good results in this way ($\mathrm{DAM}_\rho = 0.25\%$ and $\mathrm{DAM}_\eta = 3.43\%$).

For the ρ determination, Eq. (7) needs the van der Waals volume v_w. It is possible, by a group contribution method (detailed for example in [21] and [44]) to estimate this quantity. We noted v_p the value thus estimated (Tab. I). It is only for l-methylnaphtalene that the estimate was not possible. Figure 2 represents the numerical values of v_w (Tab. VI) according to the v_p values (Tab. I). The representative curve is linear, *i.e.*, $v_w = \alpha v_p$ where α appears as a universal parameter, identical for all the compounds considered ($\alpha = 1.270159$). The difference between v_w and v_p is of the same order as the differences which can be observed on polymers (where the factor is sometimes about 1.6).

One can also use jointly Eqs. (8) and (9) utilizing ρ_{ref} and η_{ref}. There are then four characteristic parameters per pure compound: ℓ_m, B, z_T and z_P. The values obtained on viscosity are generally comparable to the values of Table IV. For water we obtained $\mathrm{DAM}_\rho = 0.26\%$ and $\mathrm{DAM}_\eta = 3.86\%$. For 2,2-dimethylpropane $\mathrm{DAM}_\rho = 4.16\%$ and $\mathrm{DAM}_\eta = 6.03\%$. For benzene $\mathrm{DAM}_\rho = 0.28\%$ and $\mathrm{DAM}_\eta = 0.61\%$.

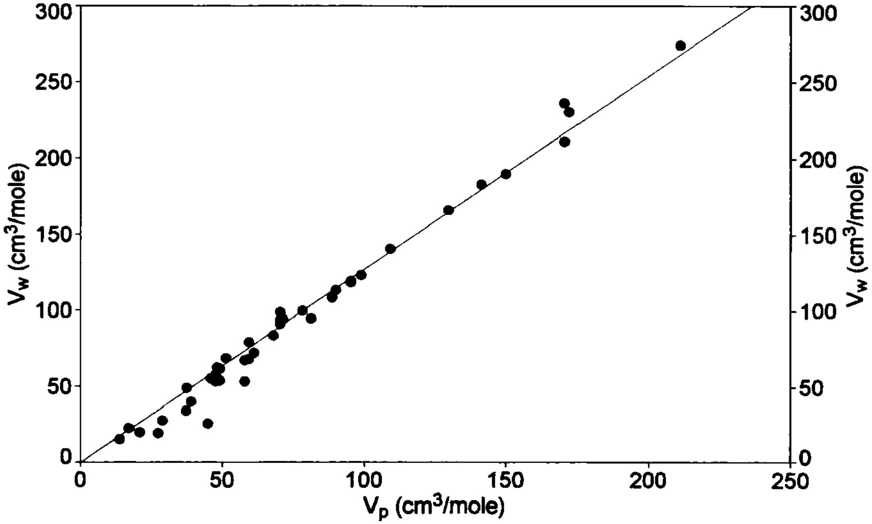

FIGURE 2 Variations of the Van der Waals volume v_w numerically determined *versus* v_p volume calculated by a group contribution method.

CONCLUSION

A new correlation scheme for the dynamic viscosity of the pure compounds, based on the free volume concept is proposed. It represents the viscosity-temperature-pressure relation in a very satisfactory way in a broad interval of pressures and temperatures and it applies to very varied compounds. Moreover the model provides a satisfactory representation of the density (far from the critical conditions). It is now necessary to study the possibility of extending the model to the mixtures and to other properties (auto-diffusion coefficient). In a future work those aspects will be considered.

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