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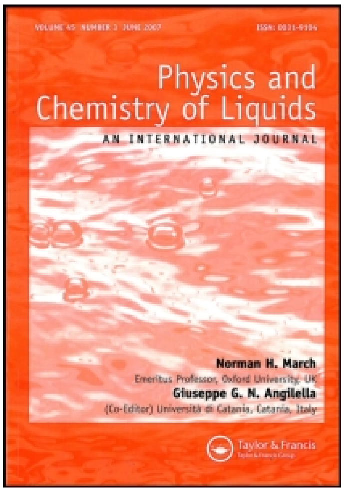

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A New free Volume Model for Dynamic Viscosity of Dense Fluids *Versus* Pressure and Temperature. Extension to a Predictive Model for not Very Associative Mixtures

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A NEW FREE VOLUME MODEL FOR DYNAMIC VISCOSITY OF DENSE FLUIDS *VERSUS* PRESSURE AND TEMPERATURE. EXTENSION TO A PREDICTIVE MODEL FOR NOT VERY ASSOCIATIVE MIXTURES

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This article presents the extension of a viscosity model to mixtures. This model, based on the free volume concept, has been previously validated for pure dense components. This model involves three physical constants for each pure compound. If the viscosity is known at a reference pressure and temperature it is sufficient to use two constants per pure compound.

The model has been adapted in order to obtain a predictive expression able to represent with accuracy the pressure–temperature variations of the dynamic viscosity of a mixture knowing only the characteristic parameters of each pure compound and the composition. The database used contains 3440 data points relative to 15 binaries, 4 ternaries and 1 system with more than three constituents. The model's results are also compared with those calculated from the very well-known Grunberg and Nissan's mixing law, and Katti and Chaudhri's mixing law.

Keywords: Free volume; Viscosity; High pressure; Mixture

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1. INTRODUCTION

The very well known model of dynamic viscosity η proposed by Eyring and his collaborators [1] leads to the Arrhenius equation type $\eta = A\exp(B/T)$ and 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]). Cohen and Turnbull [4] have developed a theory based on free volume. This theory assumes that the liquid consists of hard spheres. The theory leads to $\mathrm{Ln}(\eta/\sqrt{T}) = A' + B'/v_f$ where $v_f = v - v_0$ (average free volume) is the difference between the specific molecular volume v and the molecular volume of reference v_0 (hard volume). This theory is interesting because it justifies at constant temperature the empirical relation of Doolitle [5]: $\eta = A\exp(B/f_v)$ where $f_v = v_f/v_0$ is the free volume fraction and B is the characteristic of the free volume overlap. A substantial number of developments have been based on the above ideas. The problem of the representation of the pressure–temperature variations of viscosity is largely open and not closed. Recently [6] we have proposed an approach in order to model the viscosity of newtonian fluids (condensed *a priori*) with small molecules (not polymers for example). This approach connects viscosity to molecular structure *via* a modelisation of the free volume fraction. The viscosity is the product of the fluid modulus $\rho RT/M$ by the mean relaxation time of the molecule defined by $N_a L^2/(RT)$ and one can write [6] viscosity in the form:

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

where ρ is the density, N_a is the Avogadro number, M is the molar mass, ζ the friction coefficient of a molecule, and L an average characteristic molecular quadratic length. For a gaussian molecule, calculation shows that $L^2 = 3\langle r^2\rangle/5$ (r: radius). The friction coefficient ζ is related to the mobility of the molecule and to the diffusion process (diffusion of the momentum for viscosity). Moreover we have shown [6, 7] that the free volume fraction is at the temperature T defined by:

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

assuming that the molecule is in a state such that the molecular potential energy of interaction with its neighbors is E/N_a. We assume [6] that $E=E_0+PM/\rho$ (P: pressure) where the term $PM/\rho=PV$ 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. R is the gas constant. This expression of E is an approximation valid for dense fluids ($\rho \geq 200\,\mathrm{kg} \cdot \mathrm{m}^3$ [6]). The combination of both equations leads to write ζ in the form $\zeta=\zeta_0 \exp(B/f_v)$ and thus:

$$\eta=\frac{\rho N_a L^2 \zeta_0 \exp(B/f_v)}{M}$$

But it has been demonstrated [6, 7] that:

$$\zeta_0=\frac{E}{N_a b_f}\left(\frac{M}{3RT}\right)^{1/2}$$

where b_f is the dissipation length of the energy E. Finally we obtain:

$$\eta=\frac{\rho\ell(E_0+(PM/\rho))}{\sqrt{3RTM}}\exp\left(B\left(\frac{E_0+(PM/\rho)}{2RT}\right)^{3/2}\right) \tag{1}$$

where $\ell=L^2/b_f$ is homogeneous with a length. This equation involves 3 physical parameters ℓ, E_0 and B which are characteristic of the molecule. It will be noted that if η_{ref} and ρ_{ref} are the dynamic viscosity and density at the reference pressure P_{ref} and the reference temperature T_{ref} then we obtain:

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

and in this relation the length parameter ℓ disappears.

The model was tested [6] using a database of 41 compounds of very different chemical families: alkanes (linear and ramified, light and heavy), alkylbenzenes, cycloalkanes, alcohols, fluoroalkanes (refrigerants), carbon dioxide and water. The numerical analysis showed that the model provides good results if the sample density is higher than approximately $200\,\mathrm{kg \cdot m^{-3}}$. For the pressures range $P < 110\,\mathrm{MPa}$ there are 3012 points in the database and the average absolute deviation is 2.8%. By using a reference point there are two parameters to adjust by pure substances and the average absolute deviation is 3.3%.

Taking into account the good estimation of the dynamic viscosity of the pure substances using this model it is now advisable to consider its extension to mixtures. The object of this article is on the one hand to present the procedure to obtain a predictive model for nonassociative mixtures (knowing only the parameters characteristic of the pure substances) and on the other hand to discuss the numerical results obtained on various mixtures.

2. EXTENSION OF THE MODEL TO MIXTURES

The generalization of Eq. (1) to mixtures requires definition of the associated quantities M_m, B_m, E_{0m}, ℓ_m and ρ_m. With regard to the molar mass M_m to be associated with the mixture it seems reasonable to propose $M_m = \Sigma x_i M_i$ where x_i is the molar fraction of the component (i). For the density ρ, in the nearly non-associative case, a good approximation is to consider that the systems are almost ideal and thus $\rho_m = M_m / V_m$ with $V_m = \Sigma x_i V_i$ and $V_i = M_i / \rho_i$. This relation neglects a possible effect related to the excess volume effect which is generally small (even for rather associative systems). This assumption seems reasonable.

There is then the E_{0m} term. For a binary mixture (1)+(2) assuming that the system consists of "cells" one obtains the well-known relation $E_{0m} = x_1^2 E_{01} + 2x_1 x_2 E_{12} + x_2^2 E_{02}$ and one uses Berthelot's relation $E_{12} = (E_{01} E_{02})^{1/2}$. For a system with more than 2 components one uses $E_{0m} = \Sigma_i \Sigma_j x_i x_j E_{ij}$ with $E_{ij} = (E_{0i} E_{0j})^{1/2}$.

The B_m term intervenes in the expression of viscosity while being associated with the free fraction of volume f_v in the term $\exp(B/f_v)$ and the ℓ_m term seems to be a multiplying coefficient in Eq. (1). After several attempts to establish the mixture rules to associate with these 2 quantities we propose: $B_m = \Sigma x_i B_i$ et $1/\ell_m = \Sigma x_i / \ell_i$.

We have thus 5 rules to determine the quantities M_m, B_m, E_{0m}, ℓ_m and ρ_m to be associated with the mixtures. These quantities are only calculated from those related to the pure substances and from the composition. In this sense, our model is entirely predictive. Moreover if one assumes known P_{ref} and T_{ref} and the variations $\eta(P_{\text{ref}}, T_{\text{ref}}, x_i)$ of the mixture to be known (for example at atmospheric pressure and ambient temperature, which is generally easy to know) only M_m, B_m, E_{0m} and ρ_m remain to be determined.

3. DATABASE AND CHARACTERIZATION OF THE RESULTS

We used a database built up on the basis of various studies carried out at the laboratory for pressures ranging between 0.1 and 100 MPa and for temperatures ranging between 293.15 and 373.15 K. The systems studied are varied. First the mixtures [8] Decane + Tetradecane, Butylbenzene + Tetradecane, Heptane + Nonylbenzene and Decane + Tetradecane + Butylbenzene which are far from associative. Then the binaries [9] Toluene + Pristane, Toluene + 1-Methylnaphtalene and Toluene + 2,2,4,4,6,8,8-Heptamethylnonane. These binaries are considered as "contrasted" *i.e.*, for a given P, T set the dynamic viscosities of the pure substances are very different. For example at $P = 0.1$ MPa and $T = 298.15$ K one has $\eta = 0.551$ mPa.s for toluene and 6.781 mPa.s for pristane. They are however rather nonassociative insofar as with given P and T conditions the variations of dynamic viscosity η with the composition are monotonous. Then we considered the three binaries [10] Methylcyclohexane + 1-Methylnaphtalene, Heptane + 1-Methylnaphtalene and Heptane + Methylcyclohexane as well as the associated ternary [11] Heptane + Methylcyclohexane + 1-Methylnaphtalene. They are rather nonassociative systems. Let us notice that this ternary is roughly representative of the C_{5+} fraction of a light oil. To have a broader database containing chemically very different compounds we also took into account the binary [12] Tridecane + 1-Methylnaphtalene and the binaries [13] Tridecane + 2,2,4,4,6,8,8-Heptamethylnonane and 1-Methylnaphtalene + 2,2,4,4,6,8,8-Heptamethylnonane. To evaluate the performances of the model with mixtures with more than 2 components, in addition to the 2 ternaries already indicated, we considered [13] the ternary Tridecane + Heptylbenzene + Heptylcyclohexane (1 composition) and the system with 5 components

Tridecane + 1-Methylnaphtalene + 2,2,4,4,6,8,8,Heptamethylnonane + Heptylbenzene + Heptylcyclohexane. Let us indicate that these 5 pure substances have a boiling point at $P = 0.1$ MPa close to 510 K and that this mixture is representative of a distillation cut of heavy oil. Finally to see the limits of the method we also considered very associative systems: the ternary [14] Water + 2-Propanol + Diacetone alcohol and the binaries [15] Water + 2-Propanol, Water + Diacetone alcohol (and in addition 2-Propanol + Diacetone alcohol which is not associative). The systems containing water are very associative and at given P and T conditions the dynamic viscosity η goes through a marked maximum when the composition changes. Thus, the whole of this database includes 16 pure substances (539 values) which constitute 20 mixtures (3440 values).

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

$$\text{Deviation} = 100(1 - \eta_{\text{cal}}/\eta_{\text{exp}})(\%)$$

$$\text{Absolute deviation} = |\text{Deviation}|(\%)$$

These quantities are expressed as percentages. For all the points considered we define the three following characteristic quantities:

$$\text{Average Absolute Deviation} = \text{AAD} = \frac{1}{N_b}\sum_{i=1}^{i=N_b} \text{Absolute deviation}(i)$$

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

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

(N_b is the total of experimental points).

The average absolute deviation (AAD) characterizes the fact that the experimental points are more or less close to the calculated curve. The average deviation (Bias) characterizes the quality of the distribution of the experimental points on either side of the calculated curves. If AAD = Bias then all the experimental points are above the calculated curves. If AAD = −Bias then all the experimental points are below the calculated curves. Finally DMax characterizes the maximum deviation produced by the model.

4. RESULTS OF THE NUMERICAL ANALYSIS

4.1. Case of the Pure Substances

As it is essential to know the 3 parameters characteristic of each pure substance it is advisable to discuss briefly here the results obtained with pure compounds. If a reference point is assumed to be known, it is enough to determine E_0 and B with Eq. (2). Table I provides the results obtained by taking $P_{ref} = 0.1$ MPa and the smallest value of the temperature for T_{ref} (293.15, 298.15 or 303.15 K according to cases). The very good overall restitution will be noticed since the greatest value of the maximum deviation is 14.9% for Pristane which is a highly ramified alkane. It will be also noted that for the same compound, if one considers 2 different bibliographical references there is a small difference in the results, related to experimental uncertainty on the determinations of dynamic viscosity η and density ρ. Without a

TABLE I Results obtained for various pure substances using a reference point (Eq. (2))

Components	*Reference*	*NB*	T_{ref}*(K)*	*AAD* (%)	*DMax* (%)	*Bias* (%)
1-Methylnaphtalene	[10, 11]	17	303.15	1.9	6.6	−0.6
1-Methylnaphtalene	[12, 13]	41	293.15	2.5	11.4	0.4
1-Methylnaphtalene	[9]	29	298.15	2.9	6.3	−1.1
2,2,4,4,6,8,8-Heptamethylnonane	[12, 13]	41	293.15	2.5	12.2	0.7
2,2,4,4,6,8,8-Heptamethylnonane	[9]	29	298.15	1.6	7.0	−0.4
2-Propanol	[14, 15]	17	303.15	1.6	5.4	−0.6
Butylbenzene	[8]	17	313.15	3.0	13.1	1.6
Decane	[8]	17	313.15	3.0	6.4	0.9
Diacetone Alcohol	[14, 15]	17	303.15	1.2	3.9	−0.3
Heptane	[10, 11]	17	303.15	1.4	4.5	0.0
Heptylbenzene	[12, 13]	41	293.15	1.7	6.5	−0.3
Heptylcyclohexane	[12, 13]	41	293.15	1.6	5.1	−0.5
Methylcyclohexane	[10, 11]	17	303.15	2.9	7.4	−1.0
Methylcyclohexane	[9]	29	298.15	2.1	12.0	−0.7
Nonylbenzene	[8]	17	313.15	2.6	5.8	−0.1
Pristane	[9]	28	298.15	4.5	14.9	−1.6
Tetradecane	[8]	17	313.15	2.3	5.6	0.5
Toluene	[9]	29	298.15	1.1	3.2	−0.7
Tridecane	[12, 13]	41	293.15	2.2	8.6	−0.1
Water	[14, 15]	17	303.15	1.6	5.5	−1.1

point of reference, E_0, B and ℓ are determined using Eq. (1). Table II provides the results obtained which are better than in the previous case (maximum deviation of 12.5% instead of 14.9%). Figure 1 shows the

TABLE II Results obtained for various pure substances without using a reference point (Eq. (1))

Components	*Reference*	*NB*	*AAD* (%)	*DMax* (%)	*Bias* (%)
1-Methylnaphtalene	[10, 11]	18	1.7	5.9	0.1
1-Methylnaphtalene	[12, 13]	42	2.4	11.2	0.4
1-Methylnaphtalene	[9]	30	2.9	7.9	0.0
2,2,4,4,6,8,8-Heptamethylnonane	[12, 13]	42	1.8	11.2	0.2
2,2,4,4,6,8,8-Heptamethylnonane	[9]	30	1.6	6.9	−0.3
2-Propanol	[14, 15]	18	1.5	5.0	−0.3
Butylbenzene	[8]	18	2.7	10.5	−0.3
Decane	[8]	18	1.4	6.1	−0.4
Diacetone Alcohol	[14, 15]	18	1.1	3.9	−0.3
Heptane	[10, 11]	18	1.4	4.5	−0.1
Heptylbenzene	[12, 13]	42	1.7	6.7	−0.5
Heptylcyclohexane	[12, 13]	42	1.5	5.1	−0.5
Methylcyclohexane	[10, 11]	18	2.5	10.5	−0.6
Methylcyclohexane	[9]	30	2.0	12.5	−1.3
Nonylbenzene	[8]	18	2.0	8.1	−1.0
Pristane	[9]	29	3.8	12.3	1.0
Tetradecane	[8]	18	1.8	7.2	−0.8
Toluene	[9]	30	0.9	2.5	0.0
Tridecane	[12, 13]	42	2.3	9.1	−0.1
Water	[14, 15]	18	1.3	4.4	−0.4

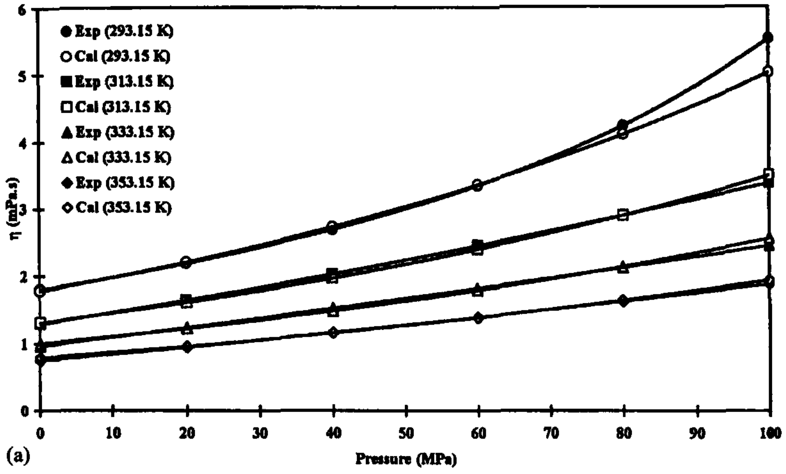

FIGURE 1 Comparison between the experimental and calculated values of dynamic viscosity η. (a) Tridecane (b) Heptylcyclohexane.

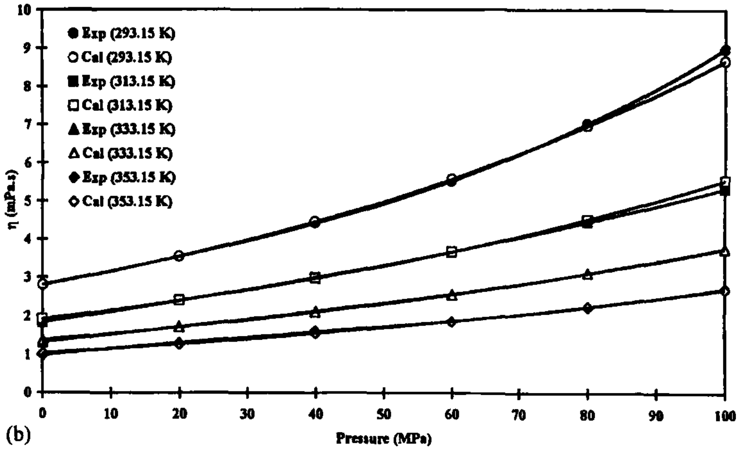

FIGURE 1 (Continued).

comparison between experimental values and calculated values for Tridecane and Heptylcyclohexane.

4.2. Case of the Mixtures

If a reference point is known the values of E_0 and B for the pure substances indicated in Table I are used and of course the same P_{ref} and T_{ref} conditions. The results are provided in Table III. For the not very associative systems there is a very good fit. On the other hand for the very associative systems of the Water + Alcohol type the resulting calculations are not satisfactory. Thus the suggested mixing rules do not account for the very strong interactions, here due to the omnipresence of the hydrogen bond.

The results obtained when no reference point is used are indicated in Table IV. The Water + Alcohol systems are not indicated, the deviations being in this case very large. For the not very associative systems the good representation shows that this model presents a predictive character in a dense state.

4.3. Comparison with Usual Mixing Laws

For comparison with Table IV we indicated in Table V the values obtained by using the predictive forms of the very well-known

TABLE III Results obtained for various mixtures using a reference point (Eq. (2) and mixing rules for the characteristic parameters)

Mixtures	*NB*	T_{ref} (*K*)	*AAD* (%)	*DMax* (%)	*Bias* (%)
Decane + Tetradecane	119	313.15	3.1	8.3	0.3
Butylbenzene + Tetradecane	119	313.15	3.3	7.0	2.4
Heptane + Nonylbenzene	119	313.15	3.5	10.7	0.3
Decane + Tetradecane + Butylbenzene	85	313.15	4.1	7.7	3.8
Toluene + Pristane	86	298.15	5.5	19.7	2.6
Toluene + 1-Methylnaphtalene	87	298.15	4.3	17.4	2.9
Toluene + 2,2,4,4,6,8,8-Heptamethylnonane	87	298.15	2.9	12.6	−2.0
Heptane + Methylcyclohexane	119	303.15	2.8	8.2	2.4
Heptane + 1-Methylnaphtalene	119	303.15	3.4	13.0	2.5
Methylcyclohexane + 1-Methylnaphtalene	119	303.15	5.1	14.4	4.5
Heptane + 1-Methylnaphtalene + Methylcyclohexane	357	303.15	4.3	14.6	2.7
Tridecane + 1-Methylnaphtalene	287	293.15	3.0	8.7	0.9
Tridecane + 2,2,4,4,6,8,8-Heptamethylnonane	287	293.15	3.4	16.3	−2.8
1-Methylnaphtalene + 2,2,4,4,6,8,8-Heptamethylnonane	287	293.15	2.6	8.0	1.3
Tridecane + Heptylbenzene + Heptylcyclohexane	41	293.15	3.0	5.9	2.9
Tridecane + Heptylbenzene + Heptylcyclohexane + 1-Methylnaphtalene + 2,2,4,4,6,8,8-Heptamethylnonane	41	293.15	3.8	9.0	1.8
Water + 2-Propanol	153	303.15	28.1	64.8	28.1
Water + Diacetone Alcohol	153	303.15	20.4	45.6	20.4
Diacetone Alcohol + 2-Propanol	153	303.15	2.2	8.1	1.0
Water + 2-Propanol + Diacetone Alcohol	612	303.15	22.6	59.7	22.5

TABLE IV Results obtained for various mixtures without using a reference point (Eq. (1) and mixing rules for the characteristic parameters)

Mixtures	*NB*	*AAD* (%)	*DMax* (%)	*Bias* (%)
Decane + Tetradecane	126	4.0	10.0	−1.0
Butylbenzene + Tetradecane	126	3.9	10.9	−3.5
Heptane + Nonylbenzene	126	8.0	16.1	6.9
Decane + Tetradecane + Butylbenzene	90	5.0	11.2	−5.1
Toluene + Pristane	89	15.7	25.7	14.0
Toluene + 1-Methylnaphtalene	90	15.3	25.5	15.3
Toluene + 2,2,4,4,6,8,8-Heptamethylnonane	90	10.7	18.8	10.7
Heptane + Methylcyclohexane	126	9.0	17.5	−9.0
Heptane + 1-Methylnaphtalene	126	10.2	18.1	9.7
Methylcyclohexane + 1-Methylnaphtalene	126	7.7	16.3	6.1
Heptane + 1-Methylnaphtalene + Methylcyclohexane	378	8.0	18.5	7.6
Tridecane + 1-Methylnaphtalene	294	16.2	33.1	−16.2
Tridecane + 2,2,4,4,6,8,8-Heptamethylnonane	294	2.8	13.8	−1.6
1-Methylnaphtalene + 2,2,4,4,6,8,8-Heptamethylnonane	294	10.9	21.0	−10.9
Tridecane + Heptylbenzene + Heptylcyclohexane	42	3.0	6.1	2.8
Tridecane + Heptylbenzene + Heptylcyclohexane + 1-Methylnaphtalene + 2,2,4,4,6,8,8-Heptamethylnonane	42	11.3	19.3	−11.3

TABLE V Results obtained for various mixtures using Grunberg Nissan's and Katti Chaudhri's mixing laws

	NB	*AAD* (%)	*DMax* (%)	*Bias* (%)
Mixtures (*Grunberd and Nissan*)				
Decane + Tetradecane	126	2.1	5.7	2.1
Butylbenzene + Tetradecane	126	3.1	7.3	3.1
Heptane + Nonylbenzene	126	9.8	18.5	9.8
Decane + Tetradecane + Butylbenzene	90	1.8	5.1	−0.7
Toluene + Pristane	89	6.2	16.1	4.7
Toluene + 1-Methylnaphtalene	90	15.0	41.8	−14.8
Toluene + 2,2,4,4,6,8,8-Heptamethylnonane	90	7.3	22.0	−2.2
Heptane + Methylcyclohexane	126	6.1	12.3	−6.1
Heptane + 1-Methylnaphtalene	126	19.5	39.1	−19.5
Methylcyclohexane + 1-Methylnaphtalene	126	15.9	29.5	−15.9
Heptane + 1-Methylnaphtalene + Methylcyclohexane	378	18.6	38.9	−18.6
Tridecane + 1-Methylnaphtalene	294	12.2	21.6	−12.2
Tridecane + 2,2,4,4,6,8,8-Heptamethylnonane	294	6.1	24.1	−6.0
1-Methylnaphtalene + 2,2,4,4,6,8,8-Heptamethylnonane	294	10.1	22.5	−10.1
Tridecane + Heptylbenzene + Heptylcyclohexane	42	1.3	5.6	0.3
Tridecane + Heptylbenzene + Heptylcyclohexane + 1-Methylnaphtalene + 2,2,4,4,6,8,8-Heptamethylnonane	42	11.0	20.0	−11.0
Mixtures (*Katti and Chaudhri*)				
Decane + Tetradecane	126	2.8	6.7	2.8
Butylbenzene + Tetradecane	126	5.5	10.1	5.5
Heptane + Nonylbenzene	126	11.8	20.3	11.8
Decane + Tetradecane + Butylbenzene	90	2.2	6.6	1.4
Toluene + Pristane	89	16.7	28.2	16.7
Toluene + 1-Methylnaphtalene	90	13.9	40.0	−13.6
Toluene + 2,2,4,4,6,8,8-Heptamethylnonane	90	10.3	26.9	7.1
Heptane + Methylcyclohexane	126	5.9	12.1	−5.9
Heptane + 1-Methylnaphtalene	126	20.0	40.1	−20.0

Methylcyclohexane + 1-Methylnaphtalene	126	15.8	29.7	−15.8
Heptane + 1-Methylnaphtalene + Methylcyclohexane	378	19.0	39.5	−19.0
Tridecane + 1-Methylnaphtalene	294	9.0	17.6	−9.0
Tridecane + 2,2,4,4,6,8,8-Heptamethylnonane	294	5.7	23.2	−5.6
1-Methylnaphtalene + 2,2,4,4,6,8,8-Heptamethylnonane	294	4.7	14.7	−9.0
Tridecane + Heptylbenzene + Heptylcyclohexane	42	1.4	5.4	0.5
Tridecane + Heptylbenzene + Heptylcyclohexane + 1-Methylnaphtalene + 2,2,4,4,6,8,8-Heptamethylnonane	42	8.9	17.8	−8.9

Grunberg and Nissan's (G.N.) [16] and Katti and Chaudhri's [17] (K.C.) mixing laws:

$$\mathrm{Ln}(\eta_m) = \Sigma x_i \mathrm{Ln}(\eta_i)(\mathrm{G.N})$$

$$\mathrm{Ln}(\eta_m V_m) = \Sigma x_i \mathrm{Ln}(\eta_i V_i)\ (\mathrm{K.C.})\ \text{with}\ V_i = M_i/\rho_i$$

where in the case of relation KC the density ρ of the mixture is estimated by supposing that the system is ideal. As the various tables show, the results obtained with the extension to the mixtures of our model are often better than those provided by the traditional mixing laws (which in addition require knowledge of the variations $\eta(P, T)$ of the pure substances). It is true that the improvement is not always very significant but the principal interest of our model lies especially in the fact that its base has a deeper physical significance, based on the molecular microstructure.

As an illustration Figure 2 represents the experimental curve obtained at 100 MPa and 293.15 K for the binary 1-Methylnaphtalene +

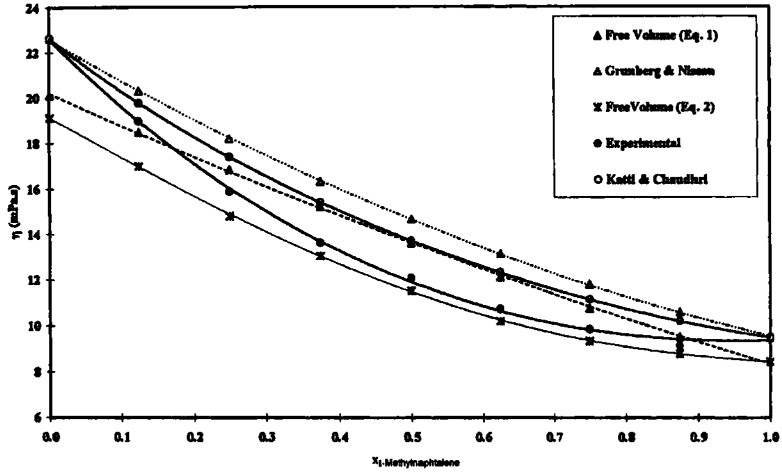

FIGURE 2 Binary 1-Methylnaphtalene + Heptamethylnonane at $P = 100\,\mathrm{MPa}$ and $T = 293.15\,\mathrm{K}$. Variations of dynamic viscosity according to the composition. Comparison between the experimental values and the values calculated by various models.

Heptamethylnonane as well as the curves calculated from the K.C. and G.N. laws and of our model (with and without reference point). In this case we are in the most unfavourable situation for the selected P, T set is that for which dynamic viscosities of the pure substances are the most poorly represented (11.2% of error at this point for 1-Methylnaphtalene and 11.2% of error at this point for Heptamethylnonane). It will be observed that the result is better for the mixtures than for the pure substances. Figure 3 relates to binary Tridecane + Heptamethylnonane according to pressure with $x_{\text{Tridecane}} = 0.5$ and $T = 293.15\,\text{K}$. Figure 4 relates to binary Heptane + 1-Methylnaphtalene (different determination [10] of 1-Methylnaphtalene compared to that from Figure 2 [13]) at $P = 100\,\text{MPa}$ and $T = 303.15\,\text{K}$ where the pure substances are this time represented very well by our model (1.7% for 1-Methylnaphtalene and 1.4% for Heptane under these P, T conditions). Figure 5 relates to the same binary at $P = 60\,\text{MPa}$ and $x_{\text{Heptane}} = 0.5$ according to the temperature. Finally Figure 6 corresponds to the variations of the dynamic viscosity of the mixture with 5 components according to the pressure at

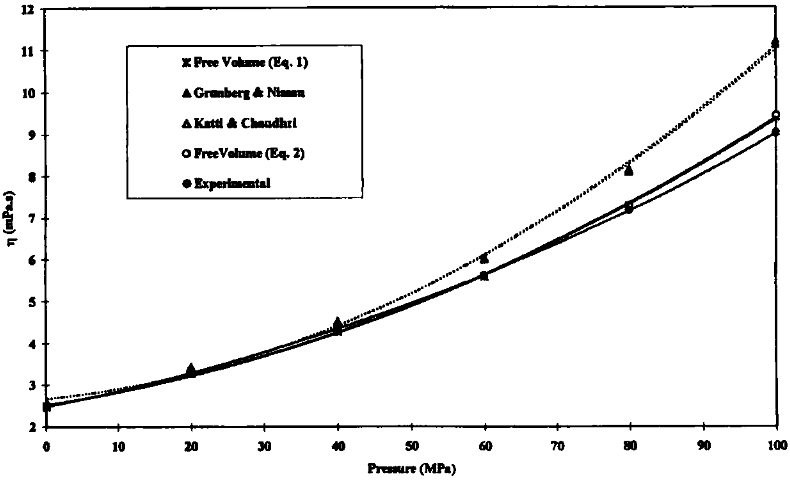

FIGURE 3 Binary Tridecane + Heptamethylnonane. Variations of dynamic viscosity according to the pressure at $x_{\text{Tridecane}} = 0.5$ and $T = 293.15\,\text{K}$. Comparison between the experimental values and the values calculated by various models.

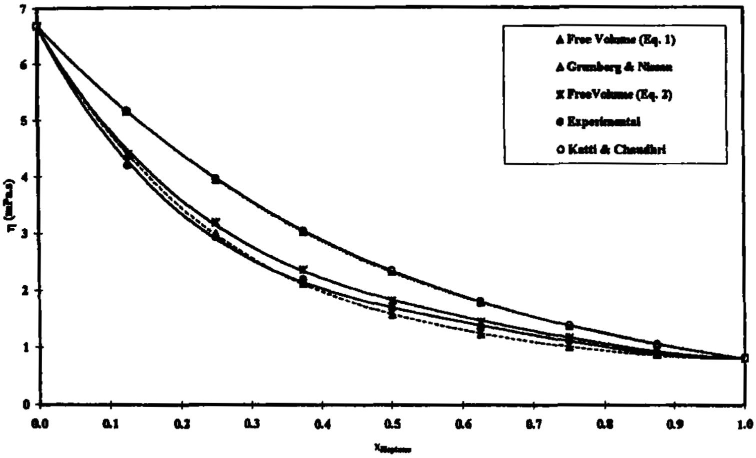

FIGURE 4 Binary Heptane + 1-Methylnaphtalene. Variations of dynamic viscosity according to the composition at $P = 100$ MPa and $T = 303.15$ K. Comparison between the experimental values and the values calculated by various models.

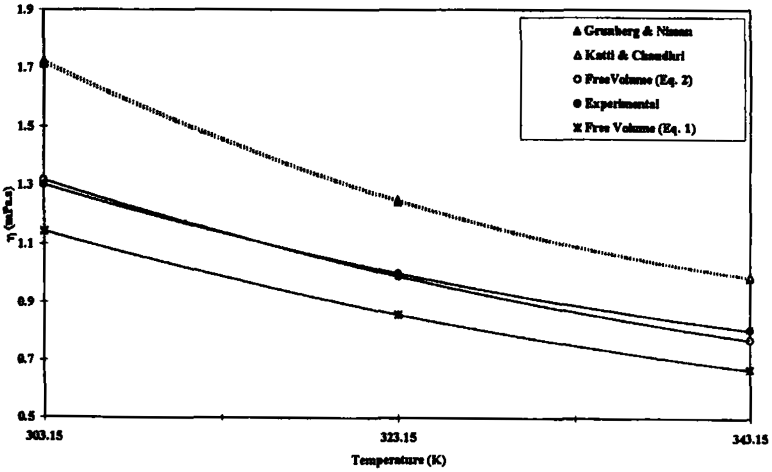

FIGURE 5 Binary Heptane + 1-Methylnaphtalene. Variations of dynamic viscosity according to the temperature at $x_{Heptane} = 0.5$ and $P = 60$ MPa. Comparison between the experimental values and the values calculated by various models.

$T = 293.15$ K. All these figures are characteristic of the analysis which we made of the experimental data of our database using the various models suggested previously.

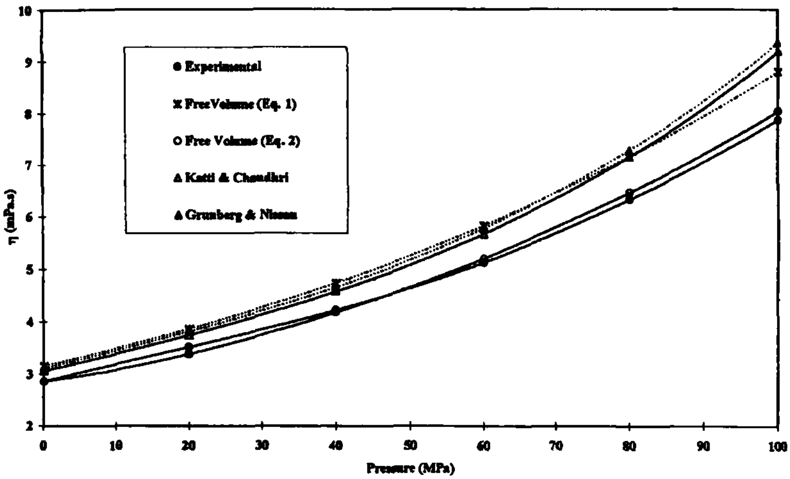

FIGURE 6 Mixture with 5 components. Variations of dynamic viscosity according to the pressure at $T = 293.15\,\mathrm{K}$. Comparison between the experimental values and the values calculated by various models.

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