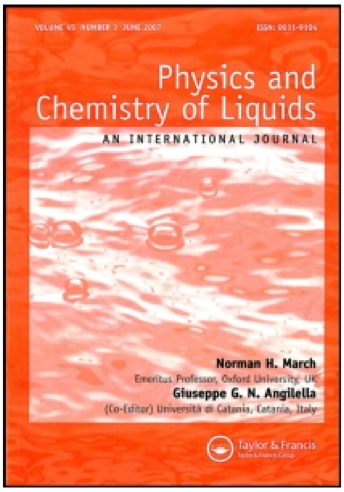

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Viscosity *Versus* Pressure, Temperature and Composition of the Ternary System Heptane Methylcyclohexane 1-Methylnaphtalene. Comparative Analysis of Some Models

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VISCOSITY *VERSUS* PRESSURE, TEMPERATURE AND COMPOSITION OF THE TERNARY SYSTEM HEPTANE + METHYLCYCLOHEXANE + 1-METHYLNAPHTALENE. COMPARATIVE ANALYSIS OF SOME MODELS

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This paper reports results concerning the dynamic viscosity η of three pure substances (heptane, methylcyclohexane, and 1-methylnaphtalene), their three associated binaries and the ternary as a function of pressure (up to 100 MPa), temperature (303.15, 323.15, and 343.15 K) and molar fraction. All our previously published experimental values (810 points) have been used in order to test several representative models of the dynamic viscosity, such as a self-referencing model, a model based on the corresponding state concept, a model based on the hard sphere theory, a model based on residual viscosity, mixing laws and the coupling of these mixing laws with the self-referencing model. An intrinsic inefficiency of the models involving one or more adjustable parameters have been shown. Good performances given by coupling the self referencing model with the Grunberg and Nissan mixing rule, properly modified, have been emphasised, as the absolute average deviation (1.97%) is of the magnitude of the experimental uncertainty. Similar results have been highlighted with the model derived from the hard sphere theory (Dymond–Assael equation).

Keywords: Viscosity; hydrocarbons; ternary; high pressure; models

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INTRODUCTION

For several years, our laboratory has been working on viscosity of hydrocarbons in order to characterise the behaviour of petroleum fluids. The main goal of this type of studies is to be able to simulate and predict the behaviour of crude oils as a function of pressure and temperature using as few characteristics of the fluid as possible. The first problem encountered in petroleum engineering is the very high number of compounds in a given fluid. To simplify the problem, the fluid is fractionated by distillation in petroleum cuts which complex compositions contain much less compounds. Generally, the method used to define the fractions is to choose boiling points ranges, but it is also possible to define number of carbon atoms intervals. In this case, the remaining fraction named C_{n+} contains information on compounds with a carbon atoms number greater or equal to n. The initial problem remains the same and it is possible to represent a fraction by a number of representative molecules. Following the remarks of Le Roy [1] on the composition of a pure synthetic fluid to represent a petroleum fluid we selected three subtances: heptane, methylcyclohexane and 1-methylnaphtalene. The dynamic viscosity η and density ρ as a function of temperature (303.15, 323.15 and 343.15 K) and pressure (up to 100 MPa) of the three pure substances and the three associated binary mixtures have already been published [2] as well as of the ternary mixture [3]. The measurements have been carried out with a falling body viscometer and the viscosity is measured within 2%. A total of 810 experimental values have been gathered (54 for the pure substances, 126 for each binary mixture and 378 for the ternary mixture) which represent 3 pure substances, 21 different binary mixtures (3 × 7) and 21 different ternary mixtures (Fig. 1). The whole set of these measurements allowed us to test various models of the dynamic viscosity η as a function of pressure which have very different origins.

ANALYSIS OF THE RESULTS FOR PURE SUBSTANCES

In order to assess and compare the performance of various models, we defined the following quantities:

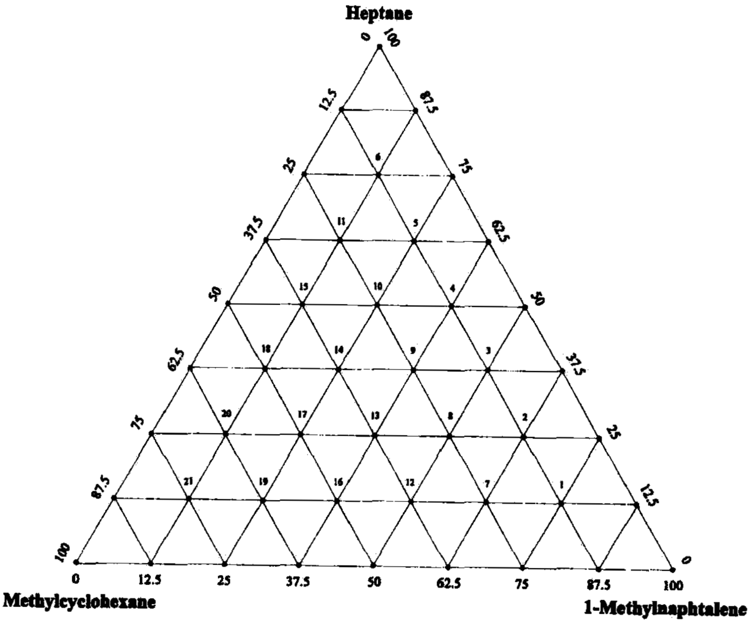

FIGURE 1 Representation of the three pure substances, the three binary mixtures and the ternary mixture (points 1 to 21) in the ternary diagram (molar fractions).

$$\mathrm{Dev}(i) = 100 \cdot (\eta_{\mathrm{exp}} - \eta_{\mathrm{cal}})/\eta_{\mathrm{exp}}$$

$$\mathrm{Dev\ abs}(i) = |\mathrm{Dev}(i)| \geq 0$$

$$\mathrm{AAD} = \frac{1}{\mathrm{Nb}} \sum_{i=1}^{\mathrm{Nb}} \mathrm{Dev\ abs}(i)$$

$$\mathrm{Bias} = \frac{1}{\mathrm{Nb}} \sum_{i=1}^{\mathrm{Nb}} \mathrm{Dev}(i)$$

$$\mathrm{DM} = \mathrm{MAX}(\mathrm{Dev\ abs}(i))$$

in which Nb is the number of experimental points, η_{exp} the measured viscosity and η_{cal} the value calculated using a given model. The quantity AAD (Average Absolute Deviation) indicates how close the calculated curves are to the experimental curves and the quantity Bias indicates how well the experimental points are distributed to either side of the calculated curves. Finally DM characterises the maximum error that can be generated using a given representation.

The Self-referencing Model

Presentation of the Model

This model has been originally developed by Kanti *et al.* [4] in order to model the viscous behaviour of petroleum cuts which complex structure is difficult to handle. For this kind of fluids, it is difficult to use equations based on physical properties such as molar mass, critical pressure and temperature or acentric factor, as for a mixture they have to be known for each of the components. The approach is derived from earlier work by Kashiwagi and Makita [5]. They represented the dynamic viscosity η at temperature T as a function of P simply on the basis of measurement at $P_0 = 0.1$ MPa and at temperature T considered. This assumes that this particular value contains within itself information specific to the fluid studied. They proposed the formulation:

$$\ln\left[\frac{\eta(P,T)}{\eta(0.1,T)}\right] = E\ln\left[\frac{D+P}{D+0.1}\right] \quad (P \text{ in MPa}) \qquad (1)$$

in which E and D are constants to be adjusted. This relationship proves highly satisfactory if it is used substance by substance and isotherm by isotherm. It requires measurement of viscosity at $P_0 = 0.1$ MPa for each temperature but the determination of E and D implies prior knowledge of $\eta(0.1,T)$ for several values of T. In order to remedy this disadvantage Kanti *et al.* [4] modified the previous representation and proposed to adopt the form:

$$\eta(0.1,T) = \eta(0.1,T_0)\exp\left[\alpha\left(\frac{1}{T}-\frac{1}{T_0}\right)\right]$$

according to the relationship of Van Velzen *et al.* [6] and to develop the coefficient α in the form $\alpha = gy_0^2 + hy_0 + i$ with $y_0 = \ln\eta(0.1, T_0)$, T_0 being an arbitrarily selected reference temperature. They also proposed to develop E and D in the form of the trinomials $E = ay^2 + by + c, D + 0.1 = dy^2 + ey + f$ with $y = \ln\eta(0.1,T)$. Incorporating these different expressions into Eq. 1 yields the following relationship involving 9 parameters ($a-i$):

$$\ln\left[\frac{\eta(P,T)}{\eta(0.1,T_0)}\right] = (ay^2+by+c)\ln\left[1+\frac{(P-0.1)}{dy^2+ey+f}\right] + (gy_0^2+hy_0+i)\left(\frac{1}{T}-\frac{1}{T_0}\right) \tag{2}$$

where $y = y_0 + (gy_0^2 + hy_0 + i)(1/T - 1/T_0)$ and $y_0 = \ln\eta(0.1, T_0)$. This formulation has the advantage that it only requires one experimental determination at atmospheric pressure and temperature T_0. It is for that reason that this method can be referred to as a self referencing model. It is not essential to choose ambient temperature as T_0. The method does not involve molar mass, nor any other physical properties or critical parameters. It can be applied without restriction indifferently to pure substances, to synthetic mixtures or to chemically very rich systems such as petroleum cuts for which Kanti *et al.* [4] originally developed it. The coefficients, $a, b, \ldots, i$ were determined by numerical analysis on an adjustment base consisting of linear alkanes ($C_7, C_{10}, C_{12}, C_{14}, C_{15}, C_{16}, C_{18}$) and alkylbenzenes (butyl, hexyl, octyl). These are indicated in Table I. Equation 2 is used with P in MPa, T_0 and T in K, $\eta(0.1, T_0)$ in mPa.s. On the basis of knowledge of the set of coefficients $a, b, \ldots, i$ the method can be used directly without further adjustment. For this reason it may be considered that it is general and predictive. On this subject it is appropriate to recall a recent paper [7] on heavy oils and bitumens, in which a similar idea is developed.

Application of the Model to Pure Substances

In Table II we present the results obtained for each of our three pure substances *versus* reference temperature T_0. For each substance we have 18 experimental values for viscosity from which we subtract one

TABLE I Coefficients values for the self-referencing model [4] (Eq. 2)

$a = 0.275832$	$b = 0.533739$	$c = 1.838385$
$d = 4.059832$	$e = 23.63475$	$f = 161.0261$
$g = 6.729026$	$h = 481.5716$	$i = 1278.456$

TABLE II Self-referencing model: results obtained for pure substances (influence of reference temperature T_0)

T_0 (*K*)	*AAD* (%)	*DM* (%)	*Bias* (%)
	Heptane		
303.15	7.83	18.27	−7.83
323.15	5.68	16.39	−4.03
343.15	6.31	13.47	3.00
	Methylcyclohexane		
303.15	5.97	8.76	5.10
323.15	8.33	13.46	7.85
343.15	13.38	20.19	13.38
	1-Methylnaphtalene		
303.15	12.48	22.04	−12.48
323.15	7.68	15.55	−6.25
343.15	6.30	17.17	2.33
	Total		
303.15	8.76	22.04	−2.15
323.15	7.23	16.39	1.60
343.15	8.66	20.19	6.24

reference point, for the calculation, so that we have 17 points for each substance and 51 in total. It is noticeable that the overall results are not significantly affected by the choice of the reference temperature T_0, although there might be some little variations if each substance is analysed independently. Nevertheless, the overall results are of the same order as those previously obtained for other substances [8]. They are very satisfactory in the sense that we have not done any adjustment of the parameters $a, b, \ldots, i$. This shows, as it has been suggested in the original article, that these parameters are not closely linked to the adjustment family and that they provide a good general representation of hydrocarbons.

The Corresponding-states Model with One Reference

Presentation of the Model

The basic idea is to characterise the behaviour of the fluid studied on the basis of the behaviour of another fluid, used as a reference, using a reduced pressure and a reduced temperature. The model has already been discussed by Pedersen *et al.* [9, 10], who, after modification of the basic model proposed by Ely and Hanley [11], suggested the following procedure:

$$\eta(P,T) = \eta_0(P',T')\left(\frac{T_c}{T_{c_0}}\right)^{-1/6}\left(\frac{P_c}{P_{c_0}}\right)^{2/3}\left(\frac{M}{M_0}\right)^{1/2}\left(\frac{\alpha}{\alpha_0}\right)$$

where

$$P' = P\cdot\frac{P_{c_0}}{P_c}\cdot\frac{\alpha_0}{\alpha}, \quad T' = T\cdot\frac{T_{c_0}}{T_c}\cdot\frac{\alpha_0}{\alpha}, \quad \alpha = 1 + 7.747\cdot 10^{-5}\rho_r^{4.265}M^{0.8579}$$

and

$$\rho_r = \frac{\rho_0\left(T\cdot\dfrac{T_{c_0}}{T_c}, P\cdot\dfrac{P_{c_0}}{P_c}\right)}{\rho_{c_0}}$$

In these relationships the subscript ⟪0⟫ appended to the reference substance, and the subscript ⟪c⟫ to the critical point, M designates the molar mass expressed in grams, ρ the density expressed in g/cm^3, and α is a corrective coefficient. The superscripts – 1/6, 2/3, 1/2 stem for the fact that the grouping $(RT)^{-1/6}P^{2/3}M^{1/2}$, in which R is the constant of ideal gases, has the dimension of a viscosity. The introduction of the parameter α implies the knowledge of the variations of the density of the reference as a function of P and T. Ducoulombier *et al.* [12] proposed the following development where the density of the reference is avoided:

$$\eta(P,T) = \eta_0(P',T')\left(\frac{T_c}{T_{c_0}}\right)^{A}\left(\frac{P_c}{P_{c_0}}\right)^{B}\left(\frac{M}{M_0}\right)^{C} \tag{3}$$

where $P' = P(P_{c_0}/P_c)$, $T' = T(T_{c_0}/T_c)$ and A, B and C are adjustable parameters. Using these different expressions requires only knowledge of the variations of the viscosity η_0 of the reference in temperature and pressure domains which do not coincide with the P and T domain explored for the system studied (because of the shift between P and P' and between T and T' for Eq. 3). It is therefore important to have a reference for which the (P', T') domain is as extensive as possible. Moreover, it will be felt intuitively that it is better to adopt a reference close to the system studied, because it is well-known that the principle of the corresponding states is not universal and only yields a general behaviour trend. Finally, we should point out that by adjustment on the alkanes, having selected n-C_{14} as a reference, Ducoulombier *et al.* [12] obtained the values $A = 1.385374$, $B = -0.756972$, $C = -0.532041$.

Application of the Model to Pure Substances

We used n-C_{14} ($M = 198.394$ g/mol, $T_c = 694$ K, $P_c = 1.6$ MPa) as reference because the variation of its viscosity is well known [12] in the range [295.15 – 373.15 K] and [0.1 – 100 MPa] and the parameters A, B and C given above. For a given substance and (P, T) set, we begin to calculate (P', T') to be associated with the reference and looking to see if the set obtained belongs to the known domain of the reference. Finally $\eta_0(P', T')$ is generated using an interpolation relationship on the known reference values. Then the value $\eta_{\mathrm{cal}}(P, T)$ of the substance is deducted using Eq. 3. Table III indicates the results obtained along with values of M, T_c, P_c (according to Yaws [13]) for the three pure substances. We may notice that according to the pressure – temperature range imposed by the reference, no viscosity has been estimated for heptane and that few values have been calculated for methylcyclohexane and 1-methylnaphtalene. The comparison of these calculated values with the experimental viscosities highlights a bad representation.

Model Derived from the Hard Sphere Theory

Presentation of the Model

Recently [14 – 19], a scheme has been developed for the simultaneous correlation of self-diffusion, viscosity, and thermal conductivity

TABLE III Corresponding-states model: results obtained for pure substances

	M (*g/mol*)	T_c (*K*)	P_c (*MPa*)	*Nb*	*AAD* (%)	*DM* (%)	*Bias* (%)
Heptane	100.205	540.3	2.74	0	–	–	–
Methylcyclohexane	98.189	572.2	3.47	5	47.65	55.14	47.64
1-Methylnaphtalene	142.201	672	3.60	5	20.62	28.46	20.62
Total	–	–	–	10	34.13	55.14	34.13

coefficient data of dense fluids over a wide range of temperatures and pressures. The basis of the method is that the transport coefficients of real dense fluids, expressed in terms of $V_r = V_0/V$ with V_0 the close-packed volume and V the molar volume, are assumed to be directly proportional to values given by the exact hard-sphere theory. The proportionality factor, described as a roughness factor R_x (for the property x), accounts for molecular roughness and departure from molecular sphericity. In order to obtain a consistent set of values for the molecular parameter V_0, it is important that at least two transport properties are correlated simultaneously. These should be the self-diffusion and viscosity coefficients, which provide the most critical test of any correlation scheme. Universal curves have been determined empirically for each reduced transport coefficient as a function of reduced density [15]. In this paper, we present only the procedure used to estimate the viscosity coefficient, in which the values for V_0 have been determined and presented elsewhere [15, 18].

It has been shown [20] that for rough spherical molecules the transport coefficients can be directly related to the smooth hard-sphere transport coefficients. A corresponding relationship between the experimental transport coefficients of rough nonspherical molecules and the smooth hard-sphere values (subscript shs) can therefore be assumed: $\eta_{\text{exp}} = R_\eta \eta_{\text{shs}}$ where R_η is the roughness factor for viscosity and is assumed to be independent of both temperature and density. Exact smooth hard-sphere transport viscosity are given by the product of the values from Enskog theory [21] and the computed corrections to Enskog theory: $\eta_{\text{shs}} = \eta_E(\eta/\eta_E)_{MD}$. Reduced coefficient of viscosity η^* is convenient to use [22] and is defined as follows:

$$\eta^*_{\text{exp}} = R_\eta \eta^*_{\text{shs}} = R_\eta \left[\frac{\eta_{\text{shs}}}{\eta_0}\right]\left[\frac{V}{V_0}\right]^{2/3}$$

where subscript ⟨⟨0⟩⟩ refers to the low-density hard-sphere coefficient in the first order approximation. Values from the reduced smooth hard-sphere viscosity can be calculated from experiment after substitution of the hard-sphere expressions which give:

$$\eta^*_{\text{shs}} = \frac{\eta^*_{\text{exp}}}{R_\eta} = 6.035 \cdot 10^8 \left[\frac{1}{MRT}\right]^{1/2} \frac{\eta_{\text{exp}} V^{2/3}}{R_\eta}$$

The determination of V_0 and the factor R_η at any temperature for the viscosity is accomplished by a well-established curve-fitting procedure. A plot of $\log \eta^*_{\text{exp}}$ *versus* $\log V$ from experiment is superimposed on universal plots of $\log \eta^*_{\text{shs}}$ *versus* $\log(V/V_0)$ from hard-sphere theory by vertical and horizontal adjustment from which the R_η factor and V_0 values are respectively obtained. The universal curves for the viscosity were developed from a consideration of both hard-sphere theory and experimental data for higher *n*-alkanes, and are expressed in terms of reduced volume V_r ($V_r = V_0/V$):

$$\log\left[\frac{\eta^*_{\text{exp}}}{R_\eta}\right] = \sum_{i=0}^{7} a_{\eta_i}(1/V_r)^i$$

where:

$$a_{\eta_0} = 1.0945 \qquad a_{\eta_4} = 797.6900$$
$$a_{\eta_1} = -9.26324 \qquad a_{\eta_5} = -1221.9770$$
$$a_{\eta_2} = 71.0385 \qquad a_{\eta_6} = 987.5574$$
$$a_{\eta_3} = -301.9012 \qquad a_{\eta_7} = -319.4636$$

This correlation scheme for the viscosity has been applied separately for *n*-alkanes [15] and for aromatics [18] for which the authors give the following correlations:

Alkanes from C_5H_{12} to $C_{16}H_{34}$:

$$R_\eta = 0.995 - 0.0008944 \cdot C + 0.005427 \cdot C^2$$
$$10^6 V_0 = 117.874 + 0.15(-1)^C + 0.25275T + 5.48 \cdot 10^{-4}T^2 - 4.2464 \cdot 10^{-7}T^3 + (C-6)(1.27 - 9 \cdot 10^{-4}T)(13.27 + 0.025 \cdot C)$$

Aromatics:

$$10^6 V_0 = -3324.7C^{-2} + 529.47C^{-1} + 12.163C + T(9.48786C^{-2} - 8.55176 \cdot 10^{-2}C + 6.03463 \cdot 10^{-3}C^2) + T^2(-1.5797 \cdot 10^{-3} + 3.9901 \cdot 10^{-4}C - 2.2309 \cdot 10^{-5}C^2)$$

where C is the number of carbon atoms.

Application of the Model to Pure Substances

Firstly, we applied the model using the coefficients adjusted on linear alkanes (for heptane and methylcyclohexane) and on aromatics (for 1-methylnaphtalene). For heptane we obtained AAD = 2.55%, DM = 5.05% and Bias = 2.16% which is a very good result emphasising the good evaluation of the coefficients by Assael *et al.* [15]. However, the estimation of the viscosity for methylcyclohexane using the same coefficients leads to AAD = 117%, DM = 185% and Bias = − 117%. These results can be explained by the fact that this substance is a cycloalkane and not a linear alkane. In the case of 1-methylnaphtalene, no result has been obtained: the correlation of dense fluid transport coefficients has been applied [18] to seven simple aromatic hydrocarbons: benzene, toluene, *o*-, *m*-, *p*-xylene, mesitylene and ethylbenzene, and give a correlation for the coefficients V_0 but none has been possible for R_η so that it has been impossible to estimate a value for R_η for 1-methylnaphtalene.

Secondly, we have fitted the coefficients a_{η_i}, V_0 and R_η on the 54 experimental values of viscosity for the pure substances. We then obtained better results (Tab. IV) for the pure substances as AAD are below the experimental uncertainty (for heptane, AAD = 0.5%). 1-methylnaphtalene is the substance which is less good represented with AAD = 2% even though.

TABLE IV Model derived from the hard sphere theory: results obtained from the adjustment of a_{η_i}, R_{η_i} and V_{0_i} on pure substances

$a_{\eta_0} = 1.192929$

$a_{\eta_1} = -8.104825$

$a_{\eta_2} = 70.617766$

$a_{\eta_3} = -343.986946$

$a_{\eta_4} = 910.564048$

$a_{\eta_5} = -1260.1597$

$a_{\eta_6} = 858.064815$

$a_{\eta_7} = -219.453339$

	Heptane	*Methylcyclo.*	*1-Methylnaph.*
R_η	1.1526970	1.0593564	0.8293858
V_0(303.15 K)	$9.517 \cdot 10^{-5}$	$8.902 \cdot 10^{-5}$	$10.898 \cdot 10^{-5}$
V_0(323.15 K)	$9.445 \cdot 10^{-5}$	$8.859 \cdot 10^{-5}$	$10.8 \cdot 10^{-5}$
V_0(343.15 K)	$9.382 \cdot 10^{-5}$	$8.844 \cdot 10^{-5}$	$10.71 \cdot 10^{-5}$
AAD (%)	0.50	1.37	2.00
DM (%)	1.53	5.87	7.75
Bias (%)	0.03	− 0.04	0.82

Model Based on Residual Viscosity

Presentation of the Model

Residual viscosity is defined as the difference between viscosity $\eta(T,P)$ and viscosity η^* of the ⟨⟨diluted gas⟩⟩ generally estimated at 0.1 MPa, and at the same temperature. The residual transport property concept comes from the works of Predvoditelev [23] on invariant quantities in the viscosity and heat transfer theory in liquids. Later, Abas-Zade [24] correlated data on thermal conductivity of liquids and gases and showed that thermal conductivity at a given density is temperature independent. The plot of residual thermal conductivity *versus* density with a log–log scale leads to a single curve for all data. It must be noticed that this type of plotting has already been used by Brebach and Thodos [25] for the viscosity. One of the correlations on viscosity widely used in the petroleum industry is the correlation of Jossi *et al.* [26] which is expressed as follows:

$$\left[\left(\eta-\eta^*\right)\xi+10^{-4}\right]^{1/4}=a_1+a_2\rho_r+a_3\rho_r^2+a_4\rho_r^3+a_5\rho_r^4$$

where ρ_r is the reduced density ($\rho_r=\rho/\rho_c$), ρ_c the critical density, and $\xi=T_c^{1/6}M^{-1/2}P_c^{-2/3}$ where T_c, P_c are the critical coordinates and M the molar mass. In order to evaluate η^*, the results of Stiel and Thodos [27] on pure substances are used:

$$\eta^*=34\cdot10^{-5}\frac{T_r^{0.94}}{\xi}\qquad \text{if } T_r\le1.5$$

$$\eta^*=17.78\cdot10^{-5}\frac{1}{\xi}[4.58T_r-1.67]^{5/8}\qquad \text{if } T_r>1.5$$

where $T_r=T/T_c$ is the reduced temperature. The values for a_i coefficients are:

$a_1=0.10230$ $a_2=0.023364$ $a_3=0.058533$
$a_4=-0.040758$ $a_5=0.0093324$

These values have been evaluated by Jossi *et al.* [26] by the mean of a numerical adjustment on eleven substances (liquids and gases): argon, nitrogen, oxygen, CO_2, SO_2, methane, ethane, propane, iso-butane, n-butane, n-pentane. The interval of the reduced densities is $0.02 \leq \rho_r \leq 3$. All these substances are non-polar except SO_2 which polarity is very weak. For polar substances a_i values must be changed. With these coefficients, viscosity is obtained in mPa.s if temperature is expressed in K, pressure in atm, density in g/cm^3 and molar mass in g/mol.

The procedure presented here shows an accumulation of various uncertainties and the performances depends on several factors:

First, the quality of the adjustment of coefficients a_i, which has orginally been done on a small data base. This data base is not, for example, representative of components involved in petroleum fluids. Recently Et-Tahir [28] gathered 2000 experimental points in a data base for which density and viscosity are known, in both liquid and gas states for the following compounds: methane, ethane, propane, butane, iso-butane, octane, toluene, benzene, o-xylene, 2,2-dimethylpropane. The only first 6 substances appear in the list of the substances used by Jossi for his adjustment. The interval for reduced density is $0.01 \leq \rho_r \leq 3.7$, whereas $\rho_r \leq 3$ in the original adjustment. With Jossi's coefficients, it has been obtained [28, 29] AAD = 10.6%, DM = 41% and Bias = 8.7%. With his own adjustment, Et-Tahir obtained AAD = 6%, DM = 29.6% and Bias = −0.5%. The new coefficients are:

$$a_1 = 0.1019246 \qquad a_2 = 0.024885 \qquad a_3 = 0.0507222$$
$$a_4 = -0.0326267 \qquad a_5 = 0.00758663$$

It has also been verified [28, 29] that the increase of the polynom degree of $\sum_{i=1}^{p} a_i \rho_r^{i-1}$ leads to no significant improvement for a degree greater than $4\,(p \geq 5)$.

Second, the precision on density. If no experimental data on density are available, Et-Tahir showed that among several equations of state the one of Lee and Kesler [30] generates the best values for density.

Finally, the precision of the characteristic values of the compounds of the data base such as the critical coordinates.

Application of the Model to Pure Substances

We first used the model with the original coefficients a_i given by Jossi and then with the new coefficients calculated by Et-Tahir. It can be seen (Tab. V) that the results are similar despite a slight deterioration of AAD but with an improvement for Bias which shows a better distribution of the points to either side of the calculated curves.

ANALYSIS OF THE RESULTS FOR MIXTURES

In this section we apply the same methods to the 756 experimental sets measured on mixtures (binaries and ternary). We also present models specific to mixtures.

The Self-referencing Model

It can be applied without changes taking into account binaries and ternaries since Eq. 2 involves no quantities dependent on the system's status as a pure substance or a mixture. The only information required for this model is the viscosity at 0.1 MPa and the reference temperature T_0 for the desired mixture composition. The model was successfully tested [4] in this way on petroleum cuts. On the basis of coefficients given in Table I and using Eq. 2, the results indicated in Table VI were obtained, for our binary and ternary mixtures (*versus* reference temperature T_0). As for the pure substances, there is little influence of the reference temperature and the overall results are excellent given the generality of the model.

We then used this self-referencing model a step further by readjusting the coefficients $a, b, \dots, i$ on all our experimental values (pure

TABLE V Model based on residual viscosity: results on pure substances

	AAD	*DM*	*Bias*	*Nb*
	Coefficients of Jossi *et al.*			
Heptane	9.40	16.82	−9.13	18
Methylcyclohexane	46.35	54.65	46.35	18
1-Methylnaphtalene	29.17	57.29	29.17	18
Total	28.31	57.29	22.13	54
	Coefficients of Et-Tahir			
Heptane	24.19	30.59	−24.19	18
Methylcyclohexane	37.57	49.26	37.57	18
1-Methylnaphtalene	26.80	57.19	26.22	18
Total	29.52	57.19	13.20	54

TABLE VI Self-referencing model: results obtained for mixtures (influence of reference temperature T_0)

T_0 (*K*)	*Nb*	*AAD* (%)	*DM* (%)	*Bias* (%)
		Heptane + Methylcyclohexane		
303.15	119	4.94	17.03	−4.03
323.15	119	4.75	15.40	−1.19
343.15	119	7.27	15.66	5.41
		Heptane + 1-Methylnaphtalene		
303.15	119	9.98	26.42	−9.98
323.15	119	8.52	25.59	−8.00
343.15	119	6.23	21.22	−2.47
		1-Methylnaphtalene + Methylcyclohexane		
303.15	119	7.80	24.20	−7.48
323.15	119	6.78	22.15	−5.30
343.15	119	6.28	19.59	−0.29
		Total binary mixtures		
303.15	357	7.57	26.42	−7.16
323.15	357	6.68	25.59	−4.83
343.15	357	6.59	21.22	0.88
		Ternary mixture Heptane + Methylcyclohexane + 1-Methylnaphtalene		
303.15	357	6.04	20.19	−5.89
323.15	357	5.55	20.74	−4.56
343.15	357	5.24	21.06	0.13
		Total mixtures		
303.15	714	6.81	26.42	−6.53
323.15	714	6.12	25.59	−4.70
343.15	714	5.92	21.22	0.51

substances, binary and ternary mixtures) for viscosity which represent 765 values (810 − 45 (reference points) = 765). Table VII gives the results thus obtained which are much better than the previous ones. There is still no influence of the reference temperature T_0 and the pure substances present the less good results whereas for mixtures (binaries and ternary) AAD are of the magnitude of the experimental uncertainty. This is certainly due to the statistical weight, which is 51 for pure substances and 714 (2 × 357) for mixtures. If a statistical weight of 7 is attributed to each value of viscosity of the pure substances (T_0 = 303.15 K), AAD is then equal to 4.42% for the pure substances (instead of 5.94%), 2.86% for the binaries (instead of 2.50%), 1.90% for the ternary (instead of 1.64%) and 2.52% in total (instead of

TABLE VII Self-referencing model: results obtained after re-adjusting the coefficients $a, b, \ldots, i$

	$T_0 = 303.15K$			$T_0 = 323.15K$			$T_0 = 343.15K$		
a	0.4931281			2.891825			2.8123762		
b	0.7281479			3.9599395			4.2387173		
c	1.4818608			2.358131			2.6727975		
d	48.265096			348.29264			350.58203		
e	83.969809			491.09148			551.4536		
f	149.74502			260.98578			314.30157		
g	190.30605			207.99495			194.58129		
h	515.2094			695.1635			742.60086		
i	1326.779			1519.0972			1661.4822		
	AAD	*DM*	*Bias*	*AAD*	*DM*	*Bias*	*AAD*	*DM*	*Bias*
Pure substances (51 pts)	5.94	16.42	5.25	6.48	17.88	6.02	7.00	19.16	6.58
Binaries (357 pts)	2.50	11.72	0.33	2.56	12.47	0.52	2.93	14.03	0.69
Ternary (357 pts)	1.64	7.57	0.24	1.65	7.76	−0.16	1.65	8.39	−0.46
Total (765 pts)	2.33	16.42	0.62	2.40	17.88	0.57	2.74	19.16	0.55

2.33%). DM is equal to 16.11% for the pure substances (instead of 16.42%), 10.72% for the binaries (instead of 11.72%), 7.05% for the ternary (instead of 7.57%) and 16.11% in total (instead of 16.42%). Bias is respectively equal to 3.62% (instead of 5.25%), −0.47% (instead of 0.33%), −0.19% (instead of 0.24%), and −0.06% in total (instead of 0.62%). An improvement can be observed but globally the performance of the representation is the same. So the interest of the method is once again confirmed.

The Corresponding-states Model with One Reference

This model can be used on mixtures after being adapted, as Eq. 3 involves critical coordinates T_c and P_c as well as molar mass. Many mixing rules can be found in the literature but we opted for those of Pedersen *et al.* [9] which have already been used [12]:

$$T_{c_{\text{mix}}} = \frac{\sum_i \sum_j x_i x_j \left[\left(\frac{T_{c_i}}{P_{c_i}} \right)^{1/3} + \left(\frac{T_{c_j}}{P_{c_j}} \right)^{1/3} \right]^3 [T_{c_i} T_{c_j}]^{1/2}}{\sum_i \sum_j x_i x_j \left[\left(\frac{T_{c_i}}{P_{c_i}} \right)^{1/3} + \left(\frac{T_{c_j}}{P_{c_j}} \right)^{1/3} \right]^3}$$

$$P_{c_{\text{mix}}} = \frac{8 T_{c_{\text{mix}}}}{\sum_i \sum_j x_i x_j \left[\left(\frac{T_{c_i}}{P_{c_i}} \right)^{1/3} + \left(\frac{T_{c_j}}{P_{c_j}} \right)^{1/3} \right]^3}$$

in which x_i and x_j are molar fractions. The molar masses are calculated with the linear relationship $M_{\text{mix}} = \sum_i x_i M_i$.

We first adopted n-C_{14} as reference with the associated A, B, and C coefficients proposed by Ducoulombier *et al.* [12]. Table VIII presents the results relative to the three binary mixtures and the ternary mixture. We can remark that the representation is not very satisfying. As it has been indicated [8, 28] the values for superscripts A, B, and C have been calculated for a given reference. We then used our experimental viscosities to re-adjust the A, B, and C coefficients, and the results are presented in Table IX. The values of the coefficients are then -21.692835 for A, 9.083572 for B and 15.828388 for C. An improvement can be observed but the performances are still much below those obtained, in the same conditions, with the self-referencing model. Moreover, this latter model has the advantage of describing the whole experimental temperature and pressure range whereas this current model induces a truncation due to the limitation on P' and T'.

TABLE VIII Corresponding state model: results obtained on mixtures with the initial values of A, B and C coefficients [12]

	Nb	*AAD*	*DM*	*Bias*
Heptane + Methylcyclohexane	10	39	48.36	39
Heptane + 1-Methylnaphtalene	75	6.13	16.27	2.30
Methylcyclohexane + 1-Methylnaphtalene	80	24.10	48.07	24.10
Total binaries	165	16.83	48.36	15.09
Ternary	220	15.93	40.90	15.58
Total	385	16.32	48.36	15.37

TABLE IX Corresponding state model: results obtained after re-adjusting the A, B, and C coefficients

	Nb	*AAD*	*DM*	*Bias*
Heptane	0	–	–	–
Methylcyclohexane	5	13.17	23.69	10.94
1-Methylynaphtalene	5	17.35	25.51	17.35
Heptane + Methylcyclohexane	10	10.72	19.68	9.17
Heptane + 1-Methylnaphtalene	75	6.25	21.84	− 1.09
Methylcyclohexane + 1-Methylnaphtalene	80	7.77	24.88	− 1.00
Ternary	220	6.49	27.18	− 1.25
Total	395	7.03	27.18	−0.52

Mixing Rules

General Background

The objective of these methods is to estimate the viscosity of a mixture from the knowledge of the viscosities of the pure substances, their molar fractions, with, in some cases, specific interaction parameters. Because of their structure these methods are not suitable for pure substances. A very large number of mixing rules have been proposed and there is no question in this paper of attempting an exhaustive review. One may find complementary information in the work of Kanti [31]. We considered only those which are most commonly used and which seem to be the most efficient. It is interesting to mention that two types of mixing rules can be emphasised: one type deals with ⟪ideal⟫ mixtures and the other one is associated with real mixtures. The first one implies no adjustable parameter because no interaction term is introduced whereas the second one do imply one or more adjustable parameters due to the corrective term involved.

Lichtenecker and Rother [32] have shown that if two substances (1) and (2) exhibit a certain property of intensity G_1 and G_2 and are mixed in the proportion θ and $1-\theta$, then the intensity G of the property of the mixture is such that:

$$G^k = \theta G_1^k + (1-\theta)G_2^k \quad (k \neq 0) \quad \text{or} \quad \operatorname{Ln} G = \theta \operatorname{Ln} G_1 + (1-\theta)\operatorname{Ln} G_2$$

In the mathematical development of the calculation, the variable θ is never specified and can either be molar fraction or weight fraction or the volume fraction. Similarly, the quantity G can either be the dynamic viscosity η or the kinetic viscosity η/ρ, or the electrical conductivity, or the dielectric constant, *etc.* The above approach leads, in particular, to the following classical formulations which have proved their effectiveness for various binary mixtures [31, 41] (for example: butylbenzene + tetradecane, heptane + nonylbenzene, decane + tetradecane):

$$\eta^{1/3} = x\eta_1^{1/3} + (1-x)\eta_2^{1/3} \tag{4a}$$

$$\eta^{1/3} = \phi\eta_1^{1/3} + (1-\phi)\eta_2^{1/3} \tag{4b}$$

$$\operatorname{Ln}\eta = x\operatorname{Ln}\eta_1 + (1-x)\operatorname{Ln}\eta_2 \tag{5}$$

where ϕ is the volume fraction of substance (1) and x its molar fraction. Eqs. 4a, 4b have been postulated previously by Kendall and Monroe [33] and Eq. 5 was introduced in an other way by Grunberg and Nissan [34]. The interest of the demonstration of Lichtenecker and Rother lies in the fact that it reveals a certain unity between these relationships which, at first sight, have nothing in common. As they involve no adjustable parameters they are said to be characteristic of an 《ideal》 behaviour though this is probably an inaccurate term. In fact, for a mixture of spherical compounds of similar size and properties, the relationship of Katti and Chaudhri [35] which has a more physical basis, has been justified theoretically, and may be thought more representative of an ideal behaviour. It is expressed in the form:

$$\mathrm{Ln}(\eta V) = x\mathrm{Ln}(\eta_1 V_1) + (1-x)\mathrm{Ln}(\eta_2 V_2) \tag{6}$$

in which V, V_1, V_2 are molar volumes. It is interesting to mention that this relationship can be calculated from Eyring's representation of the dynamic viscosity of a pure liquid [36]:

$$\eta = \frac{hN}{V}\exp\left[\frac{\Delta G}{RT}\right] \tag{7}$$

in which h is the Planck constant, N the Avogadro number, V the molar volume, R the constant of ideal gases, and ΔG the molar free enthalpy of activation of viscous flow. For a mixture ΔG is expressed as $\Delta G = \Delta G_{\text{ideal}} + \Delta G^E$, introducing the excess term ΔG^E which represents the deviation with respect to ideal state with $\Delta G_{\text{ideal}} = x\Delta G_1 + (1-x)\Delta G_2$. After substitution in Eq. 7 one obtains:

$$\mathrm{Ln}(\eta V) = x\mathrm{Ln}(\eta_1 V_1) + (1-x)\mathrm{Ln}(\eta_2 V_2) + \frac{\Delta G^E}{RT} \tag{8}$$

Consequently, Eq. 6 is the particular case of Eq. 8 associated with $\Delta G^E = 0$, and hence with the behaviour of an ideal mixture. In order to characterise real mixture Katti and Chaudhri [35] proposed the form $\Delta G^E = x(1-x)w$, for a binary mixture, for the additional term of Eq. 6 in which w is an adjustable parameter. In the same line of thinking, Grunberg and Nissan [34] have proposed to represent the viscosity of a non-ideal mixture with:

$$\text{Ln}\,\eta = x\text{Ln}\,\eta_1 + (1-x)\text{Ln}\,\eta_2 + x(1-x)d \tag{9}$$

It is assumed that interactive effects are reflected by the adjustable parameter d.

In the case of equations with adjustable parameters it is to be mentioned the relationship of Lobe [37] who proposed, for binary mixtures, the following expression:

$$\nu = \phi_1\nu_1 e^{\alpha_2^*\phi_2} + \phi_2\nu_2 e^{\alpha_1^*\phi_1} \tag{10}$$

where ν is the kinematic viscosity ($\nu = \eta/\rho$), $\alpha_1^* = \alpha_1/RT$ and $\alpha_2^* = \alpha_2/RT$. Lobe suggested that, if substance (1) is the compound with the lowest kinematic viscosity, and if kinematic viscosity of the binary mixture has a monotonous behaviour *versus* composition then:

$$\alpha_1^* = -1.7\ \text{Ln}(\nu_2/\nu_1) \quad \text{and} \quad \alpha_2^* = 0.27\ \text{Ln}(\nu_2/\nu_1) + (1.3\ \text{Ln}(\nu_2/\nu_1))^{1/2}$$

in which coefficients have been generated by numerical adjustment on experimental data.

In the case of a ternary mixture, the relationships here-above can be generalised as:

$$\eta^{1/3} = x_1\eta_1^{1/3} + x_2\eta_2^{1/3} + x_3\eta_3^{1/3} \tag{11}$$

$$\eta^{1/3} = \phi_1\eta_1^{1/3} + \phi_2\eta_2^{1/3} + \phi_3\eta_3^{1/3} \tag{12}$$

$$\text{Ln}\,\eta = x_1\,\text{Ln}\,\eta_1 + x_2\,\text{Ln}\,\eta_2 + x_3\,\text{Ln}\,\eta_3 \tag{13}$$

$$\text{Ln}(\eta V) = x_1\text{Ln}(\eta_1 V_1) + x_2\text{Ln}(\eta_2 V_2) + x_3\text{Ln}(\eta_3 V_3) \tag{14}$$

and

$$\text{Ln}\,\eta = x_1\,\text{Ln}\,\eta_1 + x_2\,\text{Ln}\,\eta_2 + x_3\,\text{Ln}\,\eta_3 + x_1x_2x_3d \tag{15}$$

$$\text{Ln}\,\eta = x_1\,\text{Ln}\,\eta_1 + x_2\,\text{Ln}\,\eta_2 + x_3\,\text{Ln}\,\eta_3 + d_{12}x_1x_2 + d_{13}x_1x_3 + d_{23}x_2x_3 \tag{16}$$

$$\mathrm{Ln}(\eta V) = x_1\,\mathrm{Ln}(\eta_1 V_1) + x_2\,\mathrm{Ln}(\eta_2 V_2) + x_3\,\mathrm{Ln}(\eta_3 V_3) + x_1 x_2 x_3 \frac{w}{RT} \tag{17}$$

$$\begin{aligned}\mathrm{Ln}(\eta V) = {} & x_1\mathrm{Ln}(\eta_1 V_1) + x_2\mathrm{Ln}(\eta_2 V_2) + x_3\mathrm{Ln}(\eta_3 V_3) \\ & + (x_1 x_2 w_{12} + x_1 x_3 w_{13} + x_2 x_3 w_{23})/RT\end{aligned} \tag{18}$$

$$\nu = \phi_1 \nu_1 e^{\alpha_2^* \phi_2 + \alpha_3^* \phi_3} + \phi_2 \nu_2 e^{\alpha_1^* \phi_1 + \alpha_3^* \phi_3} + \phi_3 \nu_3 e^{\alpha_1^* \phi_1 + \alpha_2^* \phi_2} \tag{19}$$

As it will be shown in the following analysis, the parameters d, w, d_{12}, $\alpha_1, \ldots$, depend on the nature of the system studied (molar mass for example), on the pressure and the temperature (except, perhaps, for w and α for which the T dependence of viscosity is imposed).

To finish this brief review we will mention the model proposed by Bloomfield and Dewan [38], connected with the theory of Flory [39, 40] which has recently been extended to high pressures [41, 42]. This model, valid for real mixtures, accounts for non-ideality without introducing adjustable parameters. But for a mixture, and for each (P, T) set it requires knowledge of the isothermal compressibility $\beta = 1/\rho\ (\partial\rho/\partial P)_T$ and the thermal expansion coefficient $\alpha = -1/\rho\ (\partial\rho/\partial T)_P$. The results obtained on the dissymetrical binary mixture heptane + nonylbenzene [41] are more than satisfactory (AAD = 5.7%, DM = 22.7%, Bias = 1.2%), whereas, for the binary mixture toluene + heptamethylnonane, Boned *et al.* [8] obtained less good results (AAD = 14.5%, DM = 34.1%, Bias = − 13.9%). The fact that α and β have to be known is a major obstacle to intense practical use.

Results Obtained with Ideal Mixing Rules

The models involved in this paragraph are those corresponding to Eqs. 11 to 14 applied to binary and ternary mixtures, with the condition $x_1 + x_2 + x_3 = 1$ where (1) is heptane, (2) is methylcyclohexane, and (3) is l-methylnaphtalene. The results are given in Table X. It can be seen that the best results are always given by the Grunberg and Nissan model (Eq. 13) for the entire set of data (binary and ternary mixtures)

TABLE X Results obtained with mixing rules without any adjustable parameter

		Bin 1+2	*Bin* 1+3	*Bin* 2+3	*Binaries*	*Ternary*	*Total*
	Nb	126	126	126	378	378	756
Equation 11	AAD	7.33	32.83	21.48	20.55	28.89	24.72
$\eta^{1/3}$ with x	DM	14.36	66.54	40.34	66.54	62.62	66.54
	Bias	-7.33	-32.83	-21.48	-20.55	-28.89	-24.72
Equation 12	AAD	5.72	31.27	24.31	20.43	28.99	24.71
$\eta^{1/3}$ with ϕ	DM	11.93	66.41	46.46	66.41	63.85	66.41
	Bias	-5.72	-31.27	-24.31	-20.43	-28.99	-24.71
Equation 13	AAD	6.10	19.46	15.88	13.81	18.59	16.20
Grunberg and	DM	12.33	39.11	29.45	39.11	39.91	39.11
Nissan ideal	Bias	-6.10	-19.46	-15.88	-13.81	-18.57	-16.19
Equation 14	AAD	5.87	20.02	15.77	13.89	18.99	16.44
Katti and	DM	12.09	40.08	29.69	40.08	39.52	40.08
Chaudhri ideal	Bias	-5.87	-20.02	-15.77	-13.89	-18.97	-16.43

as for the binary mixtures separately. This is a very interesting result as the model requires only knowledge of the composition and dynamic viscosity of each compound of the mixture, whereas for the model of Katti and Chaudhri (Eq. 14) the densities are also required.

Results Obtained with the Modified Grunberg and Nissan Model

In the previous paragraph we have discussed the performances of models without any adjustable parameter. The results are not satisfactory enough, and can be improved by introducing one or more parameters which might be representative somehow of the interaction within the system. In the case of Grunberg and Nissan model, we followed the approach presented below:

$$\mathrm{Ln}\,\eta = x_1 \mathrm{Ln}\,\eta_1 + x_2 \mathrm{Ln}\,\eta_2 + x_3 \mathrm{Ln}\,\eta_3 \tag{20}$$

$$\mathrm{Ln}\,\eta = x_1 \mathrm{Ln}\,\eta_1 + x_2 \mathrm{Ln}\,\eta_2 + x_3 \mathrm{Ln}\,\eta_3 + x_1 x_2 x_3 d \tag{21}$$

In this relationship, parameter d is involved only for the ternary system. For the binary mixtures, one of the molar fraction x_i is equal to zero and the corrective term is consequently equal to zero. Equation 21 has then been modified to:

$$\mathrm{Ln}\,\eta = x_1 \mathrm{Ln}\,\eta_1 + x_2 \mathrm{Ln}\,\eta_2 + x_3 \mathrm{Ln}\,\eta_3 + (x_1 x_2 + x_1 x_3 + x_2 x_3) d \tag{22}$$

where each binary mixture is involved in the same manner. The relationship can be made less symmetrical by introducing three parameters instead of one.

$$\mathrm{Ln}\,\eta = x_1 \mathrm{Ln}\,\eta_1 + x_2 \mathrm{Ln}\,\eta_2 + x_3 \mathrm{Ln}\,\eta_3 + d_{12}x_1x_2 + d_{13}x_1x_3 + d_{23}x_2x_3 \tag{23}$$

In this equation, coefficients d_{ij} are independent from pressure and temperature. The results obtained with Eq. 22 for each (P, T) set separately show that d_{ij} depends on P and T. We then proposed to use the following development:

$$\begin{aligned}\mathrm{Ln}\,\eta &= x_1 \mathrm{Ln}\,\eta_1 + x_2 \mathrm{Ln}\,\eta_2 + x_3 \mathrm{Ln}\,\eta_3 \\ &\quad + (x_1x_2 + x_1x_3 + x_2x_3)\frac{(a + bP)}{T}\frac{1}{1 + c\sum_{i=1}^{n} x_iM_i}\end{aligned} \tag{24}$$

where the corrective term depends on P and T, and on composition of the system. Finally, the best representation we found is:

$$\begin{aligned}\mathrm{Ln}\,\eta &= x_1 \mathrm{Ln}\,\eta_1 + x_2 \mathrm{Ln}\,\eta_2 + x_3 \mathrm{Ln}\,\eta_3 \\ &\quad + (ax_1x_2 + bx_1x_3 + cx_2x_3)\frac{(1 + dP)}{(1 + eT)}\frac{1}{1 + f\sum_{i=1}^{n} x_iM_i}\end{aligned} \tag{25}$$

The results obtained with (Eqs. 20–25) are displayed in Table XI which shows that the model with 6 parameters (Eq. 25) gives the best results for AAD (2.05%) as well as for DM (8.96%) and Bias (0.089%). It must be stressed that the absolute average deviation is equal to our experimental uncertainty, and that Eq. 24 (with three parameters) also gives very good results. If we compare the results obtained with Eqs. 24 and 25, the improvement induced by three more parameters (six instead of three) in Eq. 25 is not significant.

To give an illustration of this effect, Figures 2a and b represent the difference $\eta_{\mathrm{exp}} - \eta_{\mathrm{cal}}$ as a function of η_{cal} for Eqs. 20 (with no parameter) and 25 (with 6 parameters) respectively. For a perfect adjustment all the points would be on the horizontal axis. The figures show that the more parameters, the more accurate representation. Figures 3a and b represent the distribution of the number of points for the Bias. The narrower and centred on the smallest value the Gaussian curve the better the representation. Figures 4a–d represent the

TABLE XI Results obtained with the modified Grunberg and Nissan model (Nb = 756 pts)

Equation	*AAD*	*DM*	*Bias*	*Parameters*
20 0 parameter	16.20	39.11	− 16.19	–
21 1 parameter d	9.73	39.11	− 7.36	$d = -6.90061$
22 1 parameter d	5.36	19.94	− 0.14	$d = -0.632369$
23 3 parameters d_{12}, d_{13}, d_{23}	3.74	15.68	0.24	$d_{12} = -0.291556$ $d_{13} = -0.826204$ $d_{23} = -0.829229$
24 3 parameters a, b, c	2.66	8.99	− 0.14	$a = -34.9122$ $b = -0.356312$ $c = -0.00633747$
25 6 parameters $a, b, c,$ d, e, f	2.05	8.96	0.089	$a = -3196.099$ $b = -7761.503$ $c = -6332.30$ $d = 0.009670$ $e = 98.20869$ $f = -0.00493597$

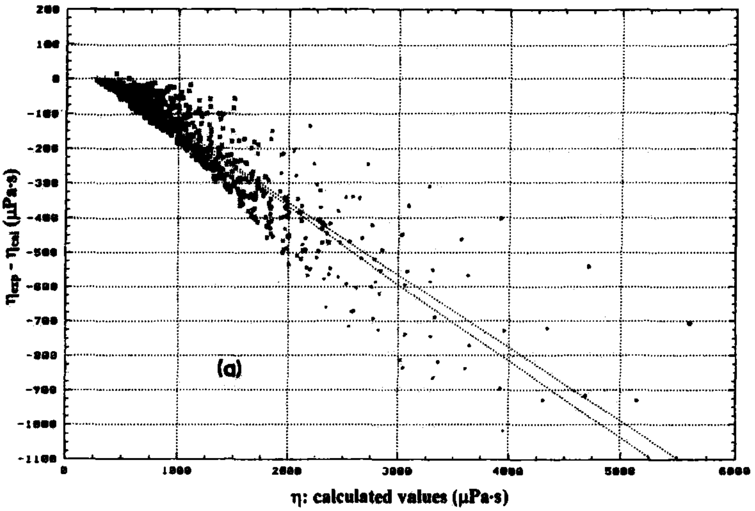

FIGURE 2 $\eta_{exp} - \eta_{cal} = f(\eta_{cal})$ for the Grunberg and Nissan model: (a) Ideal model – Eq. 20; (b) Modified with 6 parameters – Eq. 25.

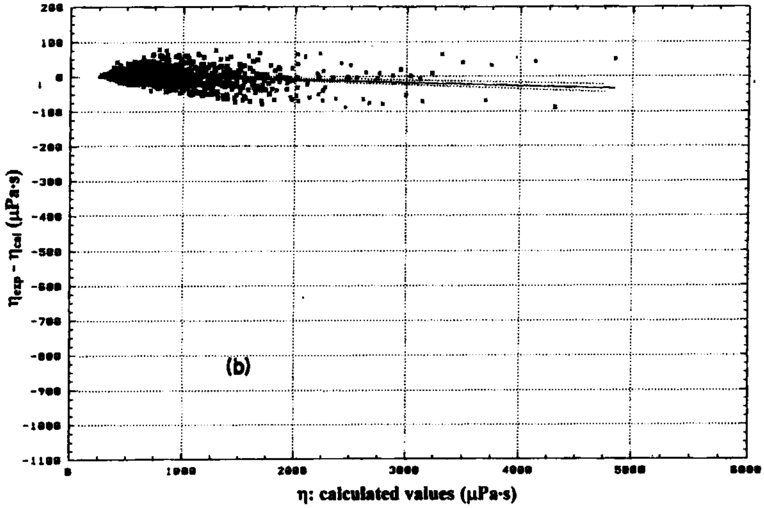

FIGURE 2 (Continued).

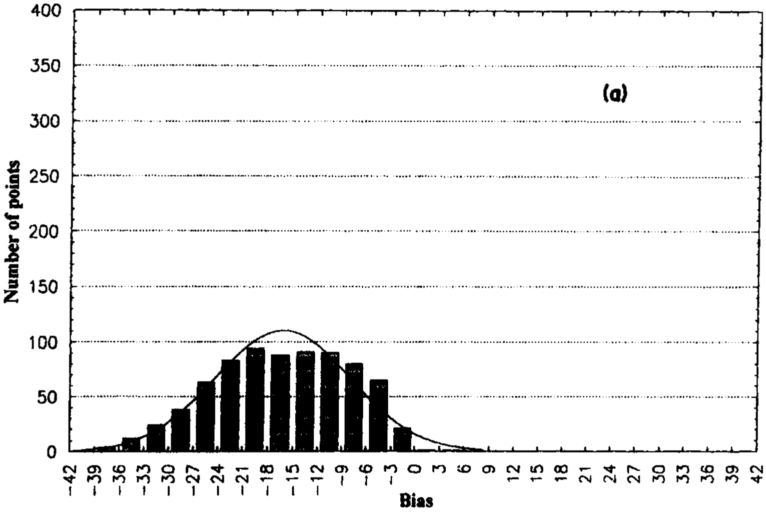

FIGURE 3 Number of points of the deviation (%) for the Grunberg and Nissan model: (a) Ideal model – Eq. 20; (b) Modified with 6 parameters – Eq. 25. (The maximum of the Gaussian curve corresponds to the Bias).

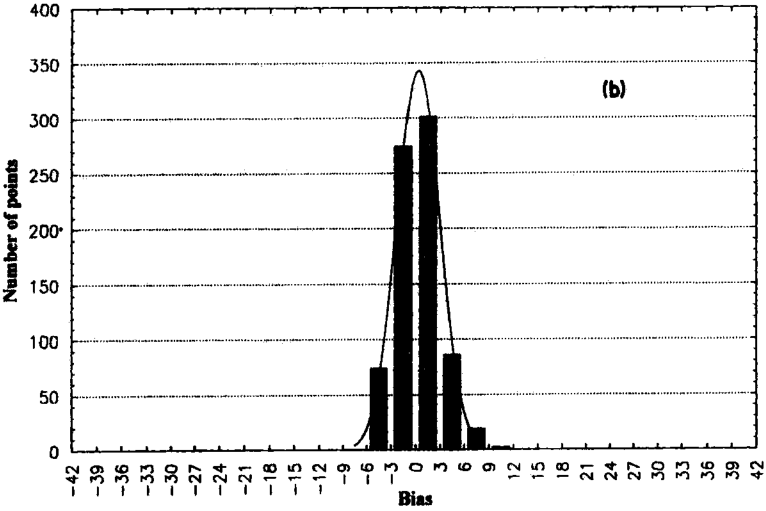

FIGURE 3 (Continued).

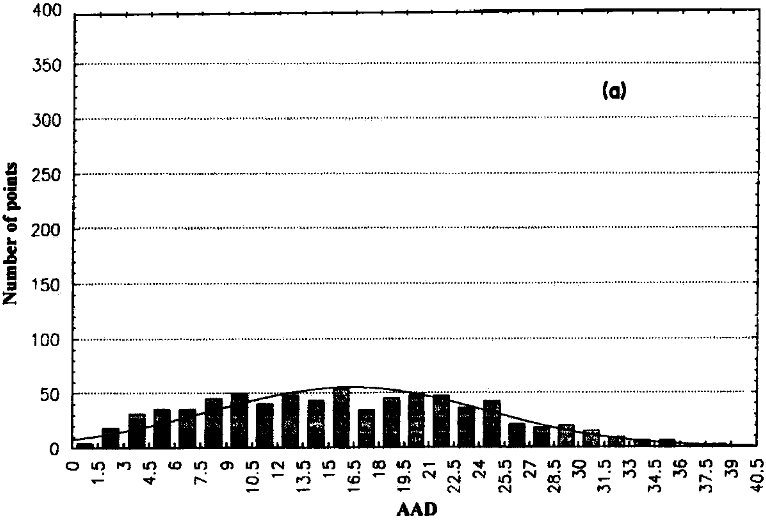

FIGURE 4 Number of points of the absolute deviation (%) for the Grunberg and Nissan model: (a) Ideal model – Eq. 20; (b) Modified with 1 parameter – Eq. 22; (c) Modified with 3 parameters – Eq. 24; (d) Modified with 6 parameters – Eq. 25. (The maximum of the Gaussian curve corresponds to the AAD).

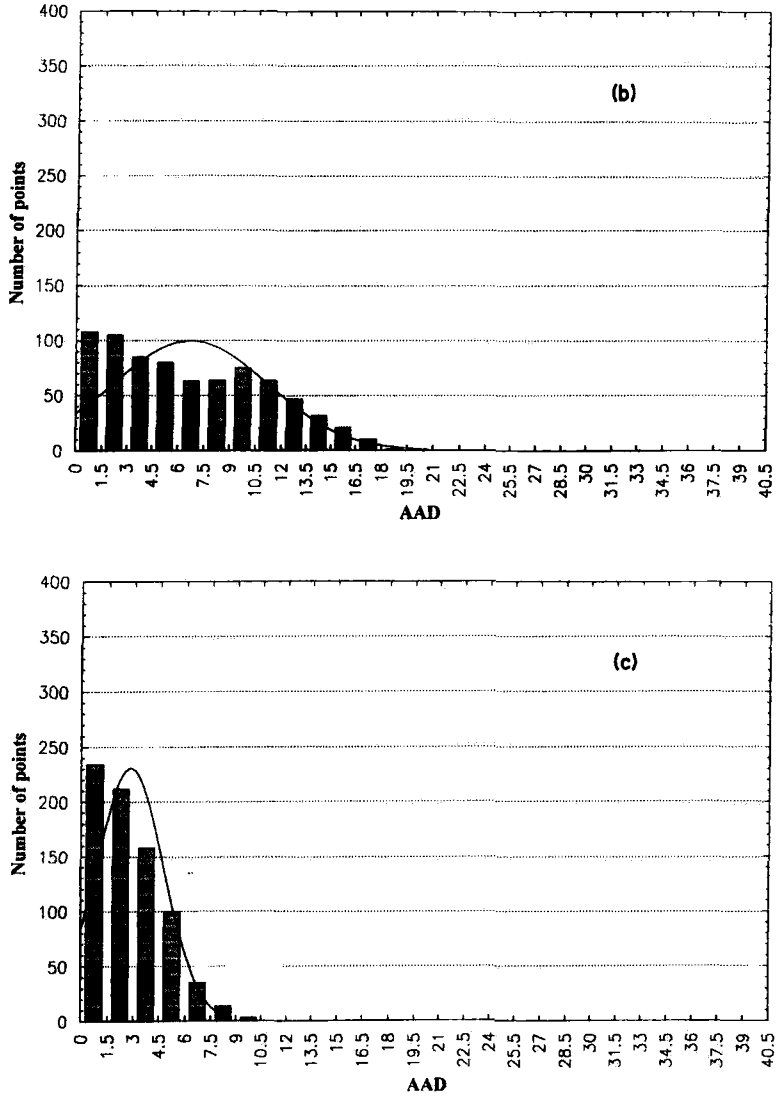

FIGURE 4 (Continued).

distribution of the number of points for the AAD for Eqs. 20, 22, 24 and 25 respectively. They show the improvement brought by the introduction of one parameter (Eq. 22), three parameters (Eq. 24) and six parameters (Eq. 25).

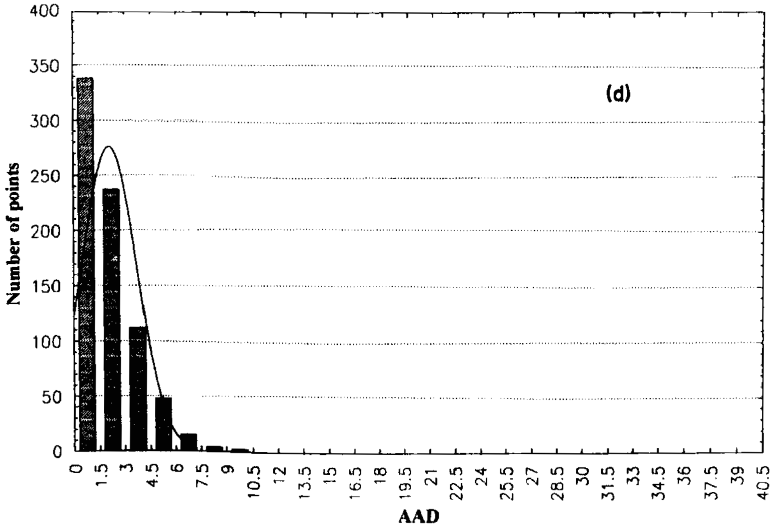

FIGURE 4 (Continued).

Results Obtained with the Modified Katti and Chaudhri Model

Considering the previous results and remarks, we used, for the Katti and Chaudhri's relationship, the following equations:

$$\mathrm{Ln}(\eta V) = x_1\mathrm{Ln}(\eta_1 V_1) + x_2\mathrm{Ln}(\eta_2 V_2) + x_3\mathrm{Ln}(\eta_3 V_3) \tag{26}$$

$$\begin{aligned}\mathrm{Ln}(\eta V) = {} & x_1\mathrm{Ln}(\eta_1 V_1) + x_2\mathrm{Ln}(\eta_2 V_2) + x_3\mathrm{Ln}(\eta_3 V_3) \\ & + (x_1x_2 + x_1x_3 + x_2x_3)\frac{W}{RT}\end{aligned} \tag{27}$$

$$\begin{aligned}\mathrm{Ln}(\eta V) = {} & x_1\mathrm{Ln}(\eta_1 V_1) + x_2\mathrm{Ln}(\eta_2 V_2) + x_3\mathrm{Ln}(\eta_3 V_3) \\ & + (x_1x_2 + x_1x_3 + x_2x_3)\frac{(a + bP)}{T}\frac{1}{1 + c\sum_{i=1}^{n} x_iM_i}\end{aligned} \tag{28}$$

$$\begin{aligned}\mathrm{Ln}(\eta V) = {} & x_1\mathrm{Ln}(\eta_1 V_1) + x_2\mathrm{Ln}(\eta_2 V_2) + x_3\mathrm{Ln}(\eta_3 V_3) \\ & + (ax_1x_2 + bx_1x_3 + cx_2x_3)\frac{(1 + dP)}{(1 + eT)}\frac{1}{1 + f\sum_{i=1}^{n} x_iM_i}\end{aligned} \tag{29}$$

where V_1, V_2, V_3 are the molar volumes (M_i/ρ_i) and R (Eq. 27) the constant of ideal gases. The results presented in Table XII for the modified Katti and Chaudhri model and in Table XI for the modified Grunberg and Nissan model are comparable. However, Katti and Chaudhri's relationship requires the knowledge of the molar volume (*i.e.* molar masses and densities).

Results Obtained with the Lobe Model

For the binary mixtures Eq. 10 has been used with the values for α_1^* and α_2^* coefficients given by Lobe. The results are presented in Table XIII.

For the ternary mixture following relationship (Eq. 19) has been used:

$$\nu = \phi_1 \nu_1 e^{\alpha_2^* \phi_2 + \alpha_3^* \phi_3} + \phi_2 \nu_2 e^{\alpha_1^* \phi_1 + \alpha_3^* \phi_3} + \phi_3 \nu_3 e^{\alpha_1^* \phi_1 + \alpha_2^* \phi_2}$$

TABLE XII Results obtained with the modified Katti and Chaudhri model (Nb = 756 pts)

Equation	*AAD*	*DM*	*Bias*	*Parameters*
26 0 parameter	16.44	40.08	– 16.43	–
27 1 parameter *w*	5.27	19.02	– 0.09	$w = -1722.61$ J/mol
28 3 parameters *a, b, c*	2.68	9.36	– 0.02	$a = -36.5414$ $b = -0.48241$ $c = -0.00635343$
29 6 parameters *a, b, c,* *d, e, f*	2.07	8.77	– 0.22	$a = -0.202062$ $b = -0.460418$ $c = -0.399362$ $d = 0.0096688$ $e = 0.00371141$ $f = -0.00532588$

TABLE XIII Results obtained with the original Lobe model

	Nb	*AAD*	*DM*	*Bias*
Bin 1	126	10.27	17.83	– 10.27
Bin 2	126	10.14	18.36	– 10.14
Bin 3	126	21.52	35.61	– 21.52
Total binaries	378	13.98	35.61	– 13.98

where ν_i is the kinematic viscosity ($\nu_1 = \eta_i/\rho_i$), ϕ_i the volume fraction and $\alpha_i^* = \alpha_i/RT$ (R: ideal gases constant). We have extended this model to our entire set of experimental data for mixtures (756 points in total). The adjustment of α_1, α_2 and α_3 coefficients gives:

$$\alpha_1 = -1353.7645\ \mathrm{J} \quad \alpha_2 = -635.7162\ \mathrm{J} \quad \alpha_3 = -4204.0778\ \mathrm{J}$$
$$\mathrm{AAD} = 9.79\% \quad \mathrm{DM} = 44.16\% \quad \mathrm{Bias} = -2.28\%$$

This model with three adjustable parameters gives much less good results if we compare them to those obtained with the mixing rules discussed in the previous paragraphs.

Association of the Self-referencing Model and Mixing Rules

This method has been developed by Et-Tahir [28] and Boned *et al.* [8]. Apart from the problem linked to the introduction of an adjustable parameter, which goes hand in hand with reduced predictive ability and improved reproducibility, the principal drawback of mixing rules, even ⟨⟨ideal⟩⟩ rules, lies in the fact that the viscosities of the pure subtances have to be known for each (P, T) set. We saw above that the self-referencing method yield to very acceptable results. The authors proposed to associate the self-referencing method applied to pure substances (to generate their viscosities *versus* P and T) with mixing rules (to generate the viscosity of each mixture as a function of the respective proportions of each constituent). Implementation of this procedure requires only knowledge of the viscosity of each of the components at 0.1 MPa and at the reference temperature T_0, to simulate the behaviour of the system *versus* P, T, and composition. In the case of our system, the knowledge of only 3 values of the viscosity η is required in order to generate 807 other values. It has been shown [28], for example, that the utilisation of the self-referencing method (with the coefficients calculated by Kanti) with the ⟨⟨ideal⟩⟩ Grunberg and Nissan mixing rule (with no adjustable parameter, Eq. 20) can simulate the behaviour of binary hexane + dodecane, up to 445 MPa, with a AAD equal to 7.8%. For binary octane + dodecane pressure is up to 505.5 MPa and AAD = 13.7%. If one limits the pressure up to

100 MPa and if one take only the substances with at least 6 carbon atoms (which are two conditions of Kanti's adjustment), Et-Tahir obtained AAD = 8.0%, DM = 44%, and Bias = – 0.5%, for 18 very different mixtures which represent 1399 values of viscosity.

In the same line of thinking, Werner [43] proposed, in order to represent the viscosity of a heavy crude oil, a symmetrical approach for the one presented above. Using a modified Grunberg and Nissan mixing rule, he generates first the viscosity of the system at 35 MPa and 373.15 K, and then he calculates, using the self-referencing method of Kanti with minor changes, the viscosities $\eta(P, T)$ of his system. After adjustment of the 12 coefficients of his model, he tested its applicability on real fluids on a wide viscosity range ($2 < \eta < 28000$ mPa.s) with pressure range [0.1 – 29 MPa] and temperature range [304.15 – 357.15 K]. For 76 experimental values, he obtained AAD = 23% and DM = 88%. If one takes into account the complexity of this type of crude oils with asphaltenes, his approach seems very encouraging.

In the following, we present the various associations of the self-referencing method with Grunberg and Nissan mixing rule that we carried out:

Self-referencing method	*+ Grunberg and Nissan mixing rule*
Kanti's coefficients	0 parameter (Eq. 20)
Kanti's coefficients	3 adjusted parameters (Eq. 24)
Kanti's coefficients	6 adjusted parameters (Eq. 25)
Adjusted coefficients	0 parameter (Eq. 20)
Adjusted coefficients	3 adjusted parameters (Eq. 24)
Adjusted coefficients	6 adjusted parameters (Eq. 25)

The performances of the here-above associations are presented in Tables XIV and XV *versus* reference temperature T_0. The results show that the coupling of the self-referencing method (Kanti's coefficients) with the ideal Grunberg and Nissan mixing rule (Tab. XIV) gives a reasonable representation if one needs only an idea of the behaviour of the system. No specific experiments are required apart from those at atmospheric pressure and at reference temperature (3 experimental values can generate 807 others, in our case). The results are improved progressively as the number of adjusted parameters increases. The best results are obtained by the adjustment of both self-referencing method

TABLE XIV Results obtained with the association of the self-referencing method (Kanti's coefficients) with mixing rules: influence of reference temperature T_0

	$T_0 = 303.15\,K$			$T_0 = 323.15\,K$			$T_0 = 343.15\,K$		
	AAD	*DM*	*Bias*	*AAD*	*DM*	*Bias*	*AAD*	*DM*	*Bias*
				Grunberg and Nissan ideal					
Pure substances (51 pts)	8.76	22.04	−5.07	7.23	16.39	−0.81	8.66	20.19	6.24
Binary mixtures (378 pts)	19.35	56.44	−19.28	15.15	48.98	−14.68	10.46	39.88	−7.07
Ternary mixture (378 pts)	25.85	71.86	−25.44	20.92	58.62	−20.91	13.19	45.92	−12.78
Total (807 pts)	21.72	71.86	−21.46	17.35	58.62	−16.72	11.63	45.92	−8.90
				Modified Grunberg and Nissan with 3 parameters					
Pure substances (51 pts)	8.76	22.04	−5.07	7.23	16.39	−0.81	8.66	20.19	6.24
Binary mixtures (378 pts)	4.90	16.36	−1.70	5.17	15.89	−0.46	6.17	17.97	2.01
Ternary mixture (378 pts)	2.30	12.15	0.43	2.62	10.15	0.37	3.68	12.99	0.59
Total (807 pts)	3.92	22.04	−0.92	4.11	16.39	−0.09	5.17	20.19	1.61
				Modified Grunberg and Nissan with 6 parameters					
Pure substances (51 pts)	8.76	22.04	−5.07	7.23	16.39	−0.81	8.66	20.19	6.24
Binary mixtures (378 pts)	3.00	14.03	−1.50	3.41	13.76	−0.57	4.77	14.14	1.84
Ternary mixture (378 pts)	1.91	13.68	0.73	2.26	8.87	0.33	3.49	11.30	0.35
Total (807 pts)	2.85	22.04	−0.39	3.11	16.39	−0.12	4.42	20.19	1.10

TABLE XV Results obtained with the association of the self-referencing method (adjusted coefficients) with mixing rules: influence of reference temperature T_0

	$T_0 = 303.15\,K$			$T_0 = 323.15\,K$			$T_0 = 343.15\,K$		
	AAD	*DM*	*Bias*	*AAD*	*DM*	*Bias*	*AAD*	*DM*	*Bias*
Grunberg and Nissan ideal									
Pure substances (51 pts)	13.51	45.02	13.15	13.03	47.95	12.86	14.31	47.05	14.13
Binary mixtures (378 pts)	5.07	33.42	1.07	5.34	36.50	0.72	4.79	35.38	2.16
Ternary mixture (378 pts)	5.53	30.08	−4.05	5.84	27.77	−4.40	4.68	22.52	−2.86
Total (807 pts)	5.82	45.02	−0.56	6.06	47.95	−0.91	5.34	47.05	0.57
Modified Grunberg and Nissan with 3 parameters									
Pure substances (51 pts)	2.76	15.06	0.52	2.71	13.94	1.68	3.16	15.46	1.71
Binary mixtures (378 pts)	3.04	14.34	−0.57	2.98	13.39	−0.23	3.35	17.66	−0.05
Ternary mixture (378 pts)	2.06	10.23	0.52	2.00	9.80	0.46	2.09	13.88	0.48
Total (807 pts)	2.56	15.06	0.01	2.50	13.94	0.21	2.75	17.66	0.31
Modified Grunberg and Nissan with 6 parameters									
Pure substances (51 pts)	3.30	11.09	1.74	2.93	9.59	1.95	3.57	9.61	2.61
Binary mixtures (378 pts)	1.74	8.97	0.16	1.61	10.55	−0.09	1.63	9.07	0.23
Ternary mixture (378 pts)	2.01	7.77	0.74	1.92	7.80	0.32	1.91	8.36	0.22
Total (807 pts)	1.97	11.09	0.45	1.84	10.55	0.11	1.88	9.61	0.23

and modified Grunberg and Nissan model with 6 parameters for which the AAD is lower than the experimental uncertainty whatever reference temperature is chosen.

The comparison of these results with those displayed in Table XI obtained with Eq. 25 show that we have a better AAD which is not a significant result as in both case the AAD is of the magnitude of the experimental uncertainty, but we have, in this case, a higher maximum deviation (DM = 11.09% instead of DM = 8.96% for Eq. 25).

The previous paragraph shows that it is possible to model precisely a complex system with 3 components (I), (II), and (III). For a real petroleum fluid these 3 components might be 3 well chosen fractions: (I) can represent the lowest viscosity component (heptane), (II) the medium viscosity component (methylcyclohexane), and (III) the highest viscosity component (1-methylnaphtalene). (I), (II), and (III) fractions can either be substances or mixtures of well chosen chemical species. If (I), (II), and (III) are mixtures, the system can be defined as a ⟪mixture of mixtures⟫. Le Roy [1] and Werner [43] showed that for real petroleum fluids, the ratio of the components in the cuts are constant and only the relative proportions of the cuts between each other vary. Usually, the molar fractions x_i of a petroleum fluid are difficult to estimate, this is the reason why, for petroleum cuts, this method involves the weight fractions p_i instead. With our well known ternary mixture, we used the coupling method presented above with the self-referencing model with adjusted parameters ($T_0 = 303.15\,\mathrm{K}$, $P_0 = 0.1\,\mathrm{MPa}$) and modified Grunberg and Nissan with 3 parameters, in which molar fractions x_i are replaced by weight fractions p_i. We obtained AAD = 4.4%, DM = 20.6%, and Bias = -0.3%. With the modified Grunberg and Nissan model with 6 parameters, AAD = 2.4%, DM = 15.4%, and Bias = -0.2%. The performances are lower than the one obtained with our method with molar fractions x_i (Tab. XV).

We then followed the approach of Werner [43] which consists of first calculating the viscosity of the mixture at (P_0, T_0) with a mixing rule and then estimating its viscosity at each (P, T) set using the self-referencing method. In these conditions, the variations of the viscosity *versus* P and T in the modified Grunberg and Nissan model disappear, which leads to a model with 2 or 4 adjustable parameters (instead of 3 and 6), plus 9 coefficients in the self-referencing method. First of all, we used the ideal mixing rule with x_i and the self-referencing method with Kanti's coefficients, and obtained AAD = 15.3%, DM = 31.6%, and Bias = – 15% which are better results than with our approach (21.7%, 71.9%, –21.5% respectively). Then, the calculation carried out with the modified mixing rule with 2 adjustable parameters and the self-referencing method with 9 adjustable parameters lead to AAD = 3.2%, DM = 19%, and Bias = –0.01%. The same calculation carried out with the mixing rule with 4 adjustable parameters leads to AAD = 2.7%, DM = 23.2%, and Bias = 0.4%. These results are less good than those obtained with our method and presented in Table XV, especially on the maximum deviation (2.0%, 11.1%, 0.5%).

The next step was to carry out the same calculations with the weight fractions instead of the molar fractions. We respectively obtained AAD = 22.0%, DM = 42.2%, and Bias = –21.8% (ideal mixing rule + self-referencing method with Kanti's coefficients), 5.0%, 18.6% and –0.5% (mixing rule with 2 parameters + self-referencing method with 9 parameters) and 2.5%, 18.7% and 0.2% (mixing rule with 4 parameters + self-referencing method with 9 parameters). This is still on the maximum deviation that the performances are less good.

Finally, we have chosen $P_0 = 40\,\text{MPa}$ and $T_0 = 323.15\,\text{K}$ (intermediate (P, T) set of our experimental field) and the calculations led to AAD = 2.9%, DM = 13%, and Bias = – 1.0% with the modified Grunberg and Nissan model with 4 parameters (with weight fractions p_i) and the self-referencing method with 9 adjustable parameters.

In order to conclude this paragraph, it is interesting to stress that the calculations carried out with either molar fractions or weight fractions yield very satisfying results whatever approach is followed.

Groups Contribution Method

Presentation of the Model

In this method the viscosity of a binary mixture is expressed as: $\mathrm{Ln}\,\eta = x\mathrm{Ln}\,\eta_1 + (1-x)\mathrm{Ln}\,\eta_2 + x(1-x)G_{12}$ which is the non-ideal Grunberg and Nissan model (Eq. 9) with $d = G_{12}$. The interaction parameter G_{12} depends on both components of the mixture, on temperature, and in some cases on molar fraction x. Isdale *et al.* [44]

proposed a groups contribution method in order to estimate G_{12} at 298 K. The procedure is as follows:

- First, component (1) must be chosen first following priority rules: the alcohol if there is, the acid, the component with the highest carbon atoms number, with the highest hydrogen atoms number, or with the highest —CH_3 groups number. If none of these rules can give the priority then G_{12} must be taken equal to zero, which means that the mixtures is considered as ⟨⟨ideal⟩⟩.
- Second, the quantities $\Sigma\Delta_1$ and $\Sigma\Delta_2$ have to be calculated using the increments given by Isdale *et al.* [44] and Reid *et al.* [45].
- Then, the parameter $W = 0.3161((N_1 - N_2)^2/(N_1 + N_2)) - 0.1188\,(N_1 - N_2)$ where N_1 and N_2 are the carbon atoms number of components (1) and (2) respectively. However, if either (1) or (2) has other atoms than carbon or hydrogen then W is taken equal to zero.
- Finally, G_{12} is evaluated as: $G_{12}(T = 298\,\text{K}) = \Sigma\Delta_1 - \Sigma\Delta_2 + W$

Moreover, in order to account for a temperature effect, a development of G_{12} is proposed: $G_{12}(T) = 1 - [1 - G_{12}(298\text{K})]((573 - T)/275)$ where T is expressed in Kelvin.

Results on Mixtures

It must be noticed that the method presented above does give only G_{ij} terms for binary mixtures and no G_{ijk} term for ternary mixtures. We then proceeded the following way: we have first calculated the three G_{ij} terms and then used the relationship:

$$\ln\eta = \sum_{i=1}^{3} x_i \ln\eta_i + x_1x_2G_{12} + x_1x_3G_{13} + x_2x_3G_{23}$$

The results displayed in Table XVI shows a good representation of the binary heptane + methylcyclohexane (Bin 1 + 2) and very bad representation of binary mixtures containing 1-methylnaphtalene and consequently of the ternary mixture. This can be explained by the fact that 1-methylnaphtalene contains a double phenyl ring which is certainly not, in terms of groups contribution, equivalent to two independent phenyl rings. In similar method used for the representation of specific heat the group naphtyl ($C_{10}H_7$) is considered as an entity. We have then estimated the Δ term associated to this group using data of the binary mixtures (Bin 1 + 3 and Bin 2 + 3) in which 1-methylnaphtalene is involved and found $\Delta = -0.4435$. The results are displayed in Table XVII. Note that the contribution of 1-methylnaphtalene to G_{ij} is $\Sigma\Delta_i = \Delta_{\text{naphtyl}} + \Delta_{\text{ortho-substitution}} + \Delta_{CH_3}$. We have also estimated the Δ term associated to this group using all the data and found $\Delta = -0.4646$. The results are displayed in Table XVIII. After estimating the contribution of the double phenyl ring, results are improved, but from a conceptual point of view a term G_{ijk} for the ternary mixtures must be added as the interactions between components (i) and (j) must be affected by component (k).

Moreover, despite the good results obtained in Tables XVII and XVIII, the contribution of the group naphtyl has probably not been correctly estimated, as the adjustment has been proceeded on a narrow data base. Finally, all the results presented (Tabs. XVI – XVIII) show less good performances in the case where the correction of G_{12} as a function of temperature is used. This means that the parameters given by the author [44] for this correction have not general values.

TABLE XVI Groups contribution method: results obtained with the contribution of two phenyl rings for 1-methylnaphtalene

	No correction (*G_{ij} at* 298 *K*)			
$G_{12} = -0.036$	$G_{31} = 1.318$		$G_{32} = 1.0958$	
	AAD	*DM*	*Bias*	*Nb*
Bin 1 + 2	5.40	11.45	−5.40	126
Bin 1 + 3	48.32	84.65	−48.32	126
Bin 2 + 3	42.84	69.91	−42.84	126
Total binaries	32.18	84.65	−32.18	378
Ternary	46.24	83.65	−46.24	378
Total	39.21	84.65	−39.21	756
	With correction in T (*$G_{ij}(T)$*)			
	AAD	*DM*	*Bias*	*Nb*
Bin 1 + 2	7.31	16.29	−7.31	126
Bin 1 + 3	47.98	84.53	−47.98	126
Bin 2 + 3	42.60	69.83	−42.60	126
Total binaries	32.63	84.53	−32.63	378
Ternary	47.19	83.71	−47.16	378
Total	39.91	84.53	−39.91	756

TABLE XVII Groups contribution method: results obtained with the adjustment of the naphtyl group contribution for 1-methylnaphtalene on the binary mixtures

	No correction (G_{ij} *at* 298 K)			
$G_{12} = -0.036$	$G_{31} = -0.8437$		$G_{32} = -0.8797$	
	AAD	*DM*	*Bias*	*Nb*
Bin 1+2	5.40	11.45	−5.40	126
Bin 1+3	4.37	14.93	−1.91	126
Bin 2+3	3.59	14.85	1.77	126
Total binaries	4.45	14.93	−1.85	378
Ternary	4.22	12.32	−0.48	378
Total	4.33	14.93	−1.16	756
	With correction in T ($G_{ij}(T)$)			
	AAD	*DM*	*Bias*	*Nb*
Bin 1+2	7.31	16.29	−7.31	126
Bin 1+3	5.60	15.67	−5.15	126
Bin 2+3	4.13	9.35	−1.44	126
Total binaries	5.68	16.29	−4.63	378
Ternary	5.63	14.43	−4.64	378
Total	5.65	16.29	−4.64	756

TABLE XVIII Groups contribution method: results obtained with the adjustment of the naphtyl group contribution for 1-methylnaphtalene on all the experimental values

	No correction (G_{ij} *at* 298 K)			
$G_{12} = -0.036$	$G_{31} = -0.8648$		$G_{32} = -0.9008$	
	AAD	*DM*	*Bias*	*Nb*
Bin 1+2	5.40	11.45	−5.40	126
Bin 1+3	4.32	14.47	−1.51	126
Bin 2+3	3.67	15.27	2.15	126
Total binaries	4.46	15.27	−1.58	378
Ternary	4.17	12.64	−0.09	378
Total	4.33	15.27	−0.84	756
	With correction in T ($G_{ij}(T)$)			
	AAD	*DM*	*Bias*	*Nb*
Bin 1+2	7.31	16.29	−7.31	126
Bin 1+3	5.34	15.22	−4.77	126
Bin 2+3	4.01	8.99	−1.08	126
Total binaries	5.55	16.29	−4.39	378
Ternary	5.42	14.20	−4.27	378
Total	5.48	16.29	−4.33	756

Model Derived from the Hard Sphere Theory

This model can be adapted in order to be used on mixtures by using the following relationships proposed by Assael *et al.* [16] and Mensah-

Brown and Wakeham [46]:

$$V_{0_m} = \sum_{i=1}^{n} x_i V_{0_i} \quad R_{\eta_m} = \sum_{i=1}^{n} x_i R_{\eta_i} \quad M_m = \sum_{i=1}^{n} x_i M_i$$

The parameters a_{η_i}, R_{η_i} and V_{0_i} have been fitted on the 54 experimental values of viscosity and have been reported in Table IV. These parameters have been used to generate the viscosity of the binary and ternary mixtures for which we obtained AAD = 8.49%, DM = 29.6%, Bias = − 8.46% (for the binaries) and obtained AAD = 13.58%, DM = 35.04%, Bias = − 13.58% (for the ternary).

The parameters a_{η_i}, R_{η_i} and V_{0_i} have then been fitted on the 810 experimental values of viscosity of pure substances as well as of mixtures. Table XIX gives the detailed results. For the overall results, AAD = 3.5%, and DM = 18.7% which are very satisfying results, and it can be noticed that 1-methylnaphtalene gives the less good results. The reason might be the complex chemical structure of this compound. It must also be noticed that the values for a_{η_i} parameters presented in Tables IV and XIX are very close to those given by Assael *et al.* [14].

We finally used a_{η_i} parameters given by the authors and fitted only R_{η_i}, V_{0_i} on the 810 experimental values of viscosity. The results are displayed in Table XX, and it can be noticed that those obtained for the mixtures are better than those obtained on the same mixtures with the a_{η_i}, R_{η_i} and V_{0_i} parameters adjusted on pure substances. This shows the universality of the a_{η_i} parameters and that the R_{η_i} and V_{0_i} parameters are characteristic of the system studied.

Model Based on Residual Viscosity

Before this model can be applied to mixtures it has to be adapted, as it involves critical coordinates T_c, P_c for the fluid studied as well as its equivalent molar weight. For mixtures, Herning and Zipperer [47] defined η^* and ξ with:

$$\eta^* = \frac{\sum_{i=1}^{n} x_i \eta_i^* M_i^{1/2}}{\sum_{i=1}^{n} x_i M_i^{1/2}} \qquad (30)$$

TABLE XIX Model derived from the hard sphere theory: results obtained from the adjustment of a_{η_i}, R_{η_i} and V_{0_i} on the 810 experimental values

$a_{\eta 0}$	$a_{\eta 1}$	$a_{\eta 2}$	$a_{\eta 3}$	$a_{\eta 4}$	$a_{\eta 5}$	$a_{\eta 6}$	$a_{\eta 7}$
1.19998917	– 7.93991139	61.6482962	– 332.83701	964.00471	– 1371.82892	903.146976	– 206.904386

	Heptane	*Methylcyclo.*	1-*Methylnaph.*	*Binaries*	*Ternary*	*Total*
R_η	1.17092351	1.12421949	0.76885643	–	–	–
V_0 (303.15 K)	$9.5499 \cdot 10^{-5}$	$8.9109 \cdot 10^{-5}$	$11.022 \cdot 10^{-5}$	–	–	–
V_0 (323.15 K)	$9.4278 \cdot 10^{-5}$	$8.8296 \cdot 10^{-5}$	$10.937 \cdot 10^{-5}$	–	–	–
V_0 (343.15 K)	$9.3354 \cdot 10^{-5}$	$8.7644 \cdot 10^{-5}$	$10.852 \cdot 10^{-5}$	–	–	–
AAD (%)	4.37	9.01	13.92	3.38	2.93	3.55
DM (%)	7.46	14.75	18.73	12.59	13.18	18.73
Bias (%)	4.18	9.63	13.92	2.23	– 1.86	0.77

TABLE XX Model derived from the hard sphere theory: results obtained from the adjustment of R_{η_i} and V_{0_i} on the 810 experimental values (a_{η_i}: original coefficients)

	Heptane	*Methylcyclo.*	1-*Methylnaph.*	*Binaries*	*Ternary*	*Total*
R_η	1.34756612	1.29609442	0.91217406	–	–	–
V_0 (303.15 K)	$9.1943 \cdot 10^{-5}$	$8.5719 \cdot 10^{-5}$	$10.631 \cdot 10^{-5}$	–	–	–
V_0 (323.15 K)	$9.0758 \cdot 10^{-5}$	$8.5099 \cdot 10^{-5}$	$10.511 \cdot 10^{-5}$	–	–	–
V_0 (343.15 K)	$8.9937 \cdot 10^{-5}$	$8.4385 \cdot 10^{-5}$	$10.429 \cdot 10^{-5}$	–	–	–
AAD (%)	4.50	9.12	18.91	3.55	3.20	3.87
DM (%)	9.02	14.64	33.32	15.66	14.59	33.32
Bias (%)	4.15	8.90	18.91	2.39	–2.26	0.77

and

$$\xi = \frac{\left(\sum_{i=1}^{n} x_i T_{c_i}\right)^{1/6}}{\left(\sum_{i=1}^{n} x_i M_i\right)^{1/2}\left(\sum_{i=1}^{n} x_i P_{c_i}\right)^{2/3}} = T_{c_m}^{1/6} M_m^{-1/2} P_{c_m}^{-2/3} \qquad (31)$$

which have been used by Jossi *et al.* [26].

In Eq. 31, pseudo-critical coordinates T_{c_m}, P_{c_m}, M_m are supposed to be of a linear form. A mixture can be considered as a pseudo-pure substance for which pseudo-critical coordinates can be defined, using so called ⟪external rules⟫. In their works on this model Et-Tahir [28] and Alliez *et al.* [29] studied up to ten mixing rules. In our case we only considered the following rules:

Herning and Zipperer [47] (HZ rule):

$$T_{c_m} = \sum_{i=1}^{n} x_i T_{c_i} \quad P_{c_m} = \sum_{i=1}^{n} x_i P_{c_i} \quad M_m = \sum_{i=1}^{n} x_i M_i \quad V_{c_m} = \sum_{i=1}^{n} x_i V_{c_i}$$

which allows the calculation of $\rho_{c_m} = M_m / V_{c_m}$

Spencer and Danner [48] (SPDA rule):

$$T_{c_m} = \frac{\sum_{i=1}^{n} x_i V_{c_i} T_{c_i}}{\sum_{i=1}^{n} x_i V_{c_i}} \quad P_{c_m} = \frac{T_{c_m}}{\sum_{i=1}^{n} x_i \frac{T_{c_i}}{P_{c_i}}} \quad M_m = \sum_{i=1}^{n} x_i M_i \quad V_{c_m} = \sum_{i=1}^{n} x_i V_{c_i}$$

Pedersen *et al.* [9] (PED rule):

$$T_{c_m} = \frac{\sum_i \sum_j x_i x_j \left[\left(\frac{T_{c_i}}{P_{c_i}}\right)^{1/3} + \left(\frac{T_{c_j}}{P_{c_j}}\right)^{1/3}\right]^3 \left[T_{c_i} T_{c_j}\right]^{1/2}}{\sum_i \sum_j x_i x_j \left[\left(\frac{T_{c_i}}{P_{c_i}}\right)^{1/3} + \left(\frac{T_{c_j}}{P_{c_j}}\right)^{1/3}\right]^3}$$

$$P_{c_m} = \frac{8 T_{c_m}}{\sum_i \sum_j x_i x_j \left[\left(\frac{T_{c_i}}{P_{c_i}}\right)^{1/3} + \left(\frac{T_{c_j}}{P_{c_j}}\right)^{1/3}\right]^3}$$

$M_m = \sum_{i=1}^{n} x_i M_i$, $V_{c_m} = \sum_{i=1}^{n} x_i V_{c_i}$ η^* is evaluated by the mean of the Eq. 30 for the three rules.

These three rules have been chosen due to historical anteriority and simplicity for HZ rule, and due to the fact that SPDA and PED rules are among the ten rules studied by Et-Tahir which have the best performances.

We used the model with both coefficients of Jossi and Et-Tahir for the three different external rules, and the results are displayed in Tables XXI and XXII. It can be seen that the results are not affected by the choice of the rule whereas a slight improvement is brought if the coefficients of Et-Tahir are used. As for pure substances, the global results are of the same order for AAD and DM but Bias is much lower with Et-Tahir's coefficients than with Jossi's ones. This shows again a better distribution of the experimental points to either sides of the calculated curves.

We then re-adjusted a_i coefficients, for each rule, on the 810 experimental values. The results displayed in Table XXIII, are improved for AAD and DM but not significantly, and with a deterioration of the Bias.

This method seems not to be the most effective even if it has been used sometimes in the petroleum industry. Let's notice, in conclusion,

TABLE XXI Model based on residual viscosity: results obtained with the coefficients of Jossi (influence of external rule)

Rule	*Mixture*	*AAD*	*DM*	*Bias*	*Nb*
	Binary 1 + 2	18.56	45.78	17.39	126
	Binary 1 + 3	13.59	36.99	− 8.31	126
ZH	Binary 2 + 3	28.63	48.67	28.63	126
	Total binaries	20.26	48.67	12.57	378
	Ternary	12.50	39.18	7.33	378
	Total	16.38	48.67	9.95	756
	Binary 1 + 2	18.88	45.93	17.81	126
	Binary 1 + 3	13.71	36.94	− 8.47	126
PED	Binary 2 + 3	28.33	48.53	28.33	126
	Total binaries	20.31	48.53	12.56	378
	Ternary	12.50	39.18	7.28	378
	Total	16.41	48.53	9.92	756
	Binary 1 + 2	18.95	45.97	17.89	126
	Binary 1 + 3	14.02	36.83	− 8.87	126
SPDA	Binary 2 + 3	28.10	48.40	28.10	126
	Total binaries	20.36	48.40	12.37	378
	Ternary	12.44	39.05	6.97	378
	Total	16.40	48.40	9.67	756

TABLE XXII Model based on residual viscosity: results obtained with the coefficients of Et-Tahir (influence of external rule)

Rule	*Mixture*	*AAD*	*DM*	*Bias*	*Nb*
	Binary 1+2	14.18	39.59	5.02	126
	Binary 1+3	22.04	38.36	−17.97	126
ZH	Binary 2+3	21.46	47.16	21.41	126
	Total binaries	19.23	47.16	2.82	378
	Ternary	12.61	35.32	−2.87	378
	Total	15.92	47.16	−0.03	756
	Binary 1+2	14.20	39.76	5.50	126
	Binary 1+3	22.19	38.57	−18.14	126
PED	Binary 2+3	21.14	47.05	21.07	126
	Total binaries	19.18	47.05	2.81	378
	Ternary	12.58	35.46	−2.92	378
	Total	15.88	47.05	−0.05	756
	Binary 1+2	14.22	39.80	5.59	126
	Binary 1+3	22.56	39.13	−18.58	126
SPDA	Binary 2+3	20.88	46.97	20.82	126
	Total binaries	19.22	46.97	2.61	378
	Ternary	12.70	36.05	−3.26	378
	Total	15.96	46.97	−0.33	756

that if the adjustment of a_i coefficients is only based on the pure substances experimental values the results are much more improved for themselves (HZ rule: AAD = 19.9%, DM = 58.6%, Bias = 13.5%), but no significant improvement can be observed for the overall results including binaries and ternary (HZ rule: AAD = 18.3%, DM = 58.6%, Bias = 8.5%).

CONCLUSION

This paper reports results concerning the dynamic viscosity η of three pure substances (heptane, methylcyclohexane, and 1-methylnaphtalene), their three associated binaries and the ternary as a function of pressure (up to 100 MPa), temperature (303.15, 323.15 and 343.15 K) and molar fraction. All our experimental values (810 points) have been used in order to test several models which have different origins. We have shown an intrinsic inefficiency of the models involving one or more adjustable parameters as they often closely depend on the adjustment data base.

However, let's mention the good performances given by coupling the self referencing model with the modified Grunberg and Nissan

TABLE XXIII Model based on residual viscosity: results obtained after re-adjusting of the coefficients a_i (influence of external rule)

Rule	*Mixture*	*AAD*	*DM*	*Bias*	*N*
	Heptane	18.52	35.49	– 18.52	18
	Methylcyclo.	38.13	53.39	38.13	18
	1-Methylnaphta.	20.17	46.64	20.03	18
	Pure substances	25.60	53.39	13.21	54
ZH	Binary 1 + 2	15.06	44.33	8.25	126
	Binary 1 + 3	17.46	34.93	– 15.50	126
	Binary 2 + 3	23.98	47.26	23.98	126
	Total binaries	18.83	47.26	5.58	378
	Ternary	11.68	37.38	1.98	378
	Total	15.95	53.39	4.41	810
	Heptane	18.18	31.52	– 18.18	18
	Methylcyclo.	38.72	53.22	38.72	18
	1-Methylnaphta.	20.87	47.74	20.72	18
	Pure substances	25.92	53.22	13.75	54
PED	Binary 1 + 2	15.03	44.29	9.21	126
	Binary 1 + 3	17.66	34.82	– 15.52	126
	Binary 2 + 3	23.74	46.93	23.74	126
	Total binaries	18.81	46.93	5.81	378
	Ternary	11.64	37.18	1.93	378
	Total	15.94	53.22	4.53	810
	Heptane	18.33	36.41	– 18.33	18
	Methylcyclo.	38.07	53.57	38.07	18
	1-Methylnaphta.	20.38	46.72	20.29	18
	Pure substances	25.59	53.57	13.34	54
SPDA	Binary 1 + 2	15.29	44.75	8.86	126
	Binary 1 + 3	17.64	35.27	– 15.67	126
	Binary 2 + 3	23.67	47.21	23.67	126
	Total binaries	18.86	47.21	5.62	378
	Ternary	11.68	37.52	1.93	378
	Total	15.96	53.57	4.41	810

mixing rule. This method requires only knowledge of the viscosity of each component at a chosen (P_0, T_0) set, and leads to an absolute average deviation of the magnitude of the experimental uncertainty. The model derived from the hard sphere theory which involves adjustable parameters and universal coefficients, gives also good results. If a high precision is not required, then some models without any further adjustable parameters (using parameters already fitted) can be satisfactorily used.

Apart from the representations presented here, many other possible models for the evaluation of the dynamic viscosity can be found, which present various difficulties in their implementation as well as theoretical justification. From a practical point of view, it is useless to develop very complex models as they often give not a reliable and general representation of the phenomenon. For example, the model presented by Wang and Mauritz [49], for pure substances (but not for mixtures), necessitates knowledge of specific volume for each (P, T) set, the minimal conformation energies, the form factor, the activation energies, *etc*. Another model, presented by Wang *et al.* [50], based on free volume, involved 4 adjustable parameters for each pure substance and 2 interaction parameters for each binary mixture. Let's also mention here the utilisation of equations of states to represent viscosity and thermal conductivity of pure substances [51], which involves 5 adjustable parameters for each substance. The interest of these methods is more of a conceptual order than of a practical one. Suzuki *et al.* [52] propose a relationship based on empirical multiparametric correlation which involves 5 descriptive parameters: molar fraction, dipolar momentum, critical temperature, molar magnetic susceptibilities and cohesion energy. They represent with a single equation the viscosity of 230 different pure substances (AAD = 17.6%) but only at atmospheric pressure and at 293.15 K. This is limitating especially as the case of mixtures is not approached.

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