

# Performance of the Self-Referencing Model on the Determination of Viscosity versus Pressure and Temperature of Various Hydrocarbons and Their Mixtures

Mohamed Jaouad Malzi, Aziz Ettahir, Christian Boned, Kamal Kettani, Abdelmajid Bybi

Abstract: The predictive model of the viscosimetric behavior studied in this article is the self-referencing model developed in our laboratory by KANTI et al. The dominant idea of this method is to characterize the dynamic viscosity  $\eta(P,T)$  of a fluid just knowing its viscosity at  $P_0$ =0.1MPa and at a reference temperature  $T_0$  (generally ambient temperature). For this purpose, we used the database developed by us (more than 15000 experimental couples P, T of 56 references) from which we extracted 4304 viscosity values  $\eta(P,T)$  corresponding to 1866 experimental values of pure substances and 2213 of mixtures with 216 values of petroleum cuts Our study shows that the absolute average deviation respectively for pressures ≤ 1000 bars and ≤ 5055 bars (7.3% and 10.5%) obtained for pure substances (≥6 carbons) and (6.8 and 7.5%) for mixtures is satisfactory. when coupled with (GRUMBERG-NISSAN and KENDALL-MONROE equations) without adjustable parameters it was able to account satisfactory for the variation of the viscosity  $\eta(P,T,x)$  of the mixtures on the simple knowledge of the viscosity of the components of the mixture considered, at reference temperature  $T_0$  and at 0.1MPa. For all the mixtures studies an absolute average deviation respectively for pressures ≤1000 bar and ≤5055 bars of 8.6% and 9.8 without binary  $C_1+C_{10}$  and 12.5% and 13% with binary  $C_1+C_{10}$ was observed. It should also be noted that the self-referencing method seems to be particularly interesting for the restitution of the viscosities of systems containing heavy hydrocarbons in the liquid state and finds its limits for substances on gaseous state or light hydrocarbons (<6 carbons). The method depends also on the quality of the adjustment of the coefficients. If we consider that the coefficients were initially adjusted to moderately heavy substances, it might be interesting to resume the calibration procedure by including lighter substances.

Keywords: Viscosity, High Pressure, Temperature, Mixtures Of Hydrocarbons, Mixing Rule

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#### I. INTRODUCTION

In the petroleum industries there is an increasing pressing need for an effective tool for estimating various properties as a function of temperature, pressure and proportions of the substances which make up the mixture. This article focuses on the dynamic viscosity and on its representation at high pressures. Real fluids in oil reservoirs are complex fluids with a large number of components whose properties can be very different.

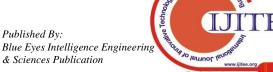
If many models exist to describe the variation of the viscosity  $\eta$ , for hydrocarbons and their mixtures, as a function of the temperature at atmospheric pressure, those describing the variations with the pressure are more rare and if they exist their application remains often complex and limited either at restricted pressure and temperature ranges, or at particular hydrocarbon families. Among the models of frequent use in the petroleum industry that we have studied, we can cite the model of the principle of states corresponding to a reference and two references [1] [2] [3] [4] [5] [6] [7] [8] and the correlation of the residual viscosity [9] [10] [11] and less responds to the self-reference model previously carried out in our laboratory by KANTI et al [31][12]. It is the latter which is the subject of the work of this article.

The aim of this work is to critically analyze the self-reference model developed in our laboratory over a wider range of data in  $\eta$  (P, T) couple and pressure. For this purpose, the data used were extracted from our database (created by ourselves) containing more than 15000 couples P,T of hydrocarbons and their mixtures from 56 references. The article focuses on a new development of this model that simplifies its use, so it is now possible to estimate the viscosity at high pressure and high temperature for the mixtures, knowing only the viscosities of the two pure components at 0.1 MPa and a reference temperature (often equal to 25  $^{\circ}$  C).

#### II. METHOD

# A. The self-referencing method:

In a previous study carried out at the laboratory [13][14]a method was presented whereby  $\eta(P,T)$  of fluid in the liquid state could be calculate from its viscosity at P<sub>0</sub>=0.1 MPa and a reference temperature T<sub>0</sub> (generally ambient temperature).



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As the coefficients used in the method are fixed independently of the nature of the system studied, this gives a character of generality to the model. The approach is derived from earlier work by KASHIWAGI and MAKITA [15]. They represented η at T as a function of P simply on the basis of measurement at P<sub>0</sub>=0.1 MPa and at the temperature T considered. This assumes that this particular value contains within itself information specific to the fluid studied. They proposed the flow formulation:

$$\ln[\eta(P,T)/\eta(0.1,T)] = E \ln[(D-P)/(D-0.1)] (P \text{ in } MPa)$$
 (1)

in which E and D are constants to be adjusted. This relationship requires measurement of η at P0=0.1 MPa and but the determination of E and D implies prior knowledge of  $\eta(0.1,T)$  for several values of T. In this sense it is not predictive except in so far as it allows interpolation between two values of P. In order to remedy this disadvantage one proposed to adopt the form:

$$\eta(0.1,T) = \eta(0.1,T_0) \exp[\alpha(1/T-1/T_0)]$$
 (2)

 $\alpha = gy0^2 + hy0 + i$  with  $\ln (\eta(0.1,T_0))$  To being an arbitrarily select reference temperature. One also proposed to develop E and D in the form of trinomials  $E = ay^2 + by + c$  and  $D = dy^2 + ey + f$  with  $y = \ln(\eta(0.1,T))$ . Incorporating these different expressions into equation 3 yields the following relationship involving 9 adjustable parameters (a to i):

$$\ln[\eta(P,T)/\eta(0.1,T_0)] = (ay^2 - by - c) \ln[1 - (P-0.1)/(dy^2 - ey - f)] - (gy \hat{v} - hy \hat{v} - i)(1/T-1/T_0)$$
 (3) Where  $y = y_0 - (gy \hat{v} - hy \hat{v} - i)(1/T-1/T_0)$  and  $y_0 = \ln(\eta(0.1,T_0))$  with  $P$  in MPa,  $T$ ,  $T_0$  in  $K$  and  $\eta$  in  $cP$ .

This formulation has the advantage that it only requires one experimental determination at 0.1 MPa and temperature T0. 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 T0. 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 one originally developed it. The coefficients a to i were determined [14] by numerical analysis on an adjustment base consisting of linear alkanes and alkylbenzenes. These are indicated in table I. On the basis of knowledge of the set of coefficients a...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 the paper of PUTTAGUNTA V.R. and al [16] on heavy oils and bitumens, in which a similar idea is developed.

Table-I: Coefficients values for the self-referencing model (Faustian 3)

(Equation 3)									
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							

#### B. Association of the self-referencing method and mixing rules:

The objective of the mixing rules is to account for the viscosity of the mixture from knowledge of viscosities of pure substances, their molar fractions, with, where appropriate, specific interaction parameters. In particular, we have used the conventional formulations below (equations 1 and 2) which have proved effective in different cases. Recall that a large number of mixing laws have been proposed and studied by KANTI et al and by ourselves [10][13][12][14] on a set of pure substances and binaries whose experimentation has been done in our laboratory and it is not a question here to make an exhaustive review. The reader may possibly refer to the work of KANTI et al [12] for a larger review.

$$\eta^{1/3} = \sum_{i=1}^{N} (x_i \eta i^{1/3})$$
 (4)  
 
$$\ln \eta = \sum_{i=1}^{N} x_i \ln \eta i$$
 (5)

$$\ln \eta = \sum_{i=1}^{N} x_i \ln \eta i \tag{5}$$

Equation 1 had been postulated previously by KENDALL and MONROE [17] and equation 2 by GRUNBERG and NISSAN [18]. 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 [19] which has a more physical basis, has been justified theoretically, and it may be thought more representative of an ideal behaviour. It is expressed in the form:

 $\ln \eta V = \sum_{i=1}^{N} x_i \ln \eta i V i$  (6) in which V and Vi are molar volumes.

In order to asses and compare the performance of various References, we defined the following quantities:

$$Dev(i) = 100 x (\eta exp - \eta cal) / \eta exp$$
 (7)

$$Devabs(i) = |Dev(i)| \ge 0 \tag{8}$$

$$AAD = I/Nb \ x \sum_{i=Nb}^{i} (Devabs(i))$$
 (9)

$$Bias = 1/Nb \ x \sum_{i=Nb}^{i} (Dev(i)) \ (10)$$

Where Nb is the number of experimental points, nexp the measured viscosity value and ncal the value calculated using a given reference. The quantity AAD (Average Absolute Deviation) indicates how close the calculate curves are to the experimental curves and the quantity Bias indicates how good the experimental points are distributed to either side of the calculated curves.





Finally DM characterizes the maximum error that can be

#### III. DISCUSSION AND ANALYSIS OF THE RESULTS

As previously mentioned, this procedure developed by KANTI M. et al (1989) has already been described in papers published during the preliminary discussion of contrasting pure and binary substances whose experimental measurements were made by KANTI M. et al and by ourselves [10][13][12][14]. Initially this method was performed to model the behavior of oil cuts but preliminary results obtained by Mr. KANTI then those obtained by us in connection with our experiences have prompted us to test more fully with our database of more than 15000 experimental points. It is therefore used for pure substances and mixtures diverse equation 3 with the coefficient values provided in Table I. In the case of mixtures we also tested the skills of self-reference after coupling model with the mixing rules without adjustable parameters, which combines simplicity and predictive, the power law 1/3 (equation 4) and the additivity law on logarithms (equation 5). However, it must be emphasized here that the method only applies to homogeneous liquid systems. Also in the following we excluded from the verification the pure substances and systems presenting data in the gaseous state.

#### A. Analysis of the results for pure substances:

The coefficients of equation 3 (Table I) were originally adjusted to pure substances with at least 7 carbons. At first we limited the checks to pure components of the base whose carbon number is greater than or equal to 6. The results are

generated using a given reference.

shown in Table II which has two parts. The first is associated with the measurements made at  $P \le 1000$  bars (because the initial calibration of the coefficients respected this constraint). The second concerns all the experimental data without pressure limitation. In the latter case the maximum value of the pressure is indicated (for example 5055 bars for the octane). It may happen, for some substances, that it has no modification compared to the first part of the table because  $P_{max} \le 1000$  bar (for example for heptane).

In the second part of the table, with the extension in pressure there is of course a slight overall deterioration of the prediction which remains nevertheless quite satisfactory. Figure 1 illustrates the comparisons undertaken. If in some cases (for example  $C_{18}$  or cyclopentane where a respective extension is recorded at 3600 and 4000 bar) the extension slightly modifies the mean deviation (ADD), in other cases (for example cis and trans-decalin where is recorded for both an extension at 3600 bar) the disturbance is wider. We can also note the very good representation by this method of substances such as benzene and cyclohexane. Finally, for all the points, the maximum deviation is 47.8% in the case of  $P \le 1000$  bar; it increases to 75.4% when there is no restriction ( $P_{max} = 5188$  bar).

Performance was also examined for low carbon substances. It follows from Table III that, with respect to the latter, the results become unsatisfactory, a phenomenon undoubtedly related to the calibration basis of the coefficients of equation3.

Table-II: Results obtained on pure substances with carbon number  $\geq 6$ 

	The said of the sa			00 bars		P≤P <sub>max</sub> bars				
Component	Reference	$Nb_1$	ADD	BIAS	DM	$Nb_2$	ADD	BIAS	DM	$P_{max}$
n-Hexane	[20]-[21]-[22]	48	7.2	-15.1	34.8	81	15.7	-15.1	75.4	5000
n-Heptane	[12]	17	5.3	-5.2	11.6	17	5.3	-5.2	11.6	1000
n-Octane	[20]-[23]-[24]	28	4.1	3.3	15.0	81	9.5	3.3	44.0	5055
n-Decane	[25]-[[33]]-[12]-[27]-[28]	264	6.3	-2.4	31.9	264	6.3	-2.4	31.9	1000
n-Dodecane	[27]-[29]-[23]-[24]-[30]	87	3.1	7.4	17.4	188	8.9	7.4	41.5	5016
n-Tetradecane	[12]-[27]	44	2.7	0.1	6.5	44	2.7	0.1	6.5	1000
n-Pentadecane	[29]-[27]-[30]	57	3.8	6.2	9.8	115	9.0	6.2	27.1	3200
n-Hexadecane	[31]-[27]-[24]	41	5.0	-3.1	18.8	47	4.9	-3.1	18.8	1505
n-Octadecane	[30]-[27]-[29]	49	4.1	3.1	11.9	97	6.7	3.1	24.7	3600
Heptamethylnonane	[10]	29	19.4	19.0	40.3	29	19.4	19.0	40.3	1000
Pristane	[10]	28	17.1	-17.1	27.5	28	17.1	-17.1	27.5	1000
Methycyclohexane	[20][10]	31	5.5	9.5	9.4	37	10.2	9 .5	53.8	4000
Cyclohexane	[32]-[24]-[22]	51	5.1	0.1	17.6	52	5.1	0.1	17.6	2000
Cyclopentane	[20]	6	1.9	-2.8	2.0	8	3.7	-2.8	6.9	4000
Toluene	[33]-[34][10]	73	12.2	-12.2	29.4	97	14.8	-14.1	36.5	5188
m-Xylene	[10]	23	11.9	11.8	25.9	23	11.9	11.8	25.9	1000
p-Xylene	[34][10]	36	11.4	-11.4	30.0	36	11.4	-11.4	30.0	1000
o-Xylene	[10]	29	7.3	-7.3	15.4	29	7.3	-7.3	15.4	1000
Benzene	[35]-[32]-[34]	54	10.2	-10.2	29.9	72	14.5	14.5	43.0	4022
n-Buthylbenzene	[27]-[12]	46	4.6	0.9	9.8	46	4.6	0.9	9.8	1000
Hexylbenzene	[27]	29	2.6	1.6	7.2	29	2.6	1.6	7.2	1000
Octylbenzene	[27]	29	4.1	1.6	9.8	29	4.1	1.6	9.8	1000
Nonylbenzene	[12]	17	2.8	-2.6	8.4	17	2.8	-2.6	8.4	1000
Cis-Decalin	[29]	14	8.3	8.3	21.5	48	31.3	31.3	70.6	3600
trans-Decalin	[29]	17	10.2	10.2	20.3	50	26.7	26.7	57.6	3600
1-Methylnaphtalene	[10]	29	11.4	-11.2	26.2	29	11.4	-11.2	26.2	1000
Naphtalene	[36]	17	13.6	-13.6	25.3	22	16.4	-16.4	31.4	1013
Phenantrene	[36]	14	28.1	-28.1	47.8	18	33.2	-33.2	55.2	1013
Phenyldodecane	[10]	29	8.3	-8.2	20.5	29	8.3	-8.2	20.5	1000
Total		1232	7.3	-3.1	47.8	1662	10.5	1.0	75.4	5188

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Table III: Results obtained on pure substances with carbon number  $\leq 5$ 

		P≤1000 bars				P≤P <sub>max</sub> bars					
Component	Reference	$Nb_1$	ADD	BIAS	DM	$Nb_2$	ADD	BIAS	DM	P <sub>max</sub>	
n-Pentane	[20]-[32]	7	17.9	-17.9	34.7	25	37.9	-37.9	79.9	5000	
n-Butane	[37]	61	59.1	58.3	92.8	61	59.1	58.3	92.8	341	
i-Butane	[37]	118	78.5	77.2	99.9	118	78.5	77.2	99.9	341	

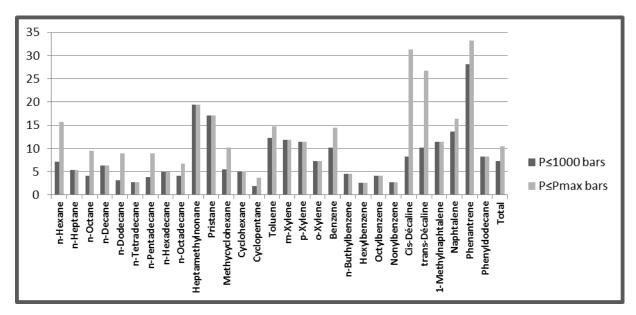


Fig.1. Mean deviation (ADD) for pure substances with carbon number  $\geq 6$ 

#### B. Analysis of the results for pure mixtures:

Given the fact that it is sufficient to know the viscosity at 1 bar and a temperature T<sub>0</sub> we have incorporated in addition to synthetic mixtures, the oil cuts previously studied by KANTI et al [35] [14], which form very complex mixtures. Let us already indicate that for 216 experimental points relating to 8 different sections we obtain 3.0% mean deviation (ADD), 1.6 average deviation (BIAS) and 12.7 maximum deviation. The  $C_1 + CO_2$  or  $C_1 + C_2$  binaries, in which certain experimental points correspond to the gaseous state, are excluded from the verification field. Indeed, we have verified that the values of the adjustment coefficients are only significant for liquid mixtures.

Regarding the performances on all the data of the mixtures considered, we have shown in Table IV four significant lines because we should not give too much weight to the binary C<sub>1</sub>+ C<sub>10</sub> (586 experimental points). Thus the "Total 1" line includes the  $C_1 + C_{10}$  binary but not the oil cuts, the "Total 2" line excludes the  $C_1+C_{10}$  binary and the cuts, the "Total 3" line considers the cuts but not the C<sub>1</sub>+C<sub>10</sub> binary, the "Total 4" line finally covers all the mixtures. It appears that the use of the method at all pressures is not followed by a pronounced increase in mean deviation (ADD). For example for the cyclohexane + hexane binary, extending the field of study to 5000 bar, the average deviation from 9.2% to 12.7%. For the octane + dodecane binary, the average deviation increases from 1.7% to 11.0%, but the latter value remains satisfactory, the pressure range extending to 5055 bar (the maximum deviation increases from 4.7 to 31.1%. Figure 2 relates to these results. Note that if we exclude the  $C_1 + C_{10}$  binary (whose methane element contains less than 6 carbon atoms) and if we restrict ourselves to  $P \le 1000$  bar, we place ourselves in the conditions of adjustment of the coefficients of the equation 3; an average deviation of 5% and a maximum deviation of 33.3% are observed, interesting performances, indicating that the coefficients are of general use and that, in a certain way, the viscosity at the pressure P<sub>0</sub> and temperature T<sub>0</sub> contains information specific to the studied system.

Table-IV: Results obtained on mixtures

		P≤1000 bars				P≤P <sub>max</sub> bars				
Mixtures	Reference	$Nb_1$	ADD	BIAS	DM	$Nb_2$	ADD	BIAS	DM	P <sub>max</sub>
Toluene+Hexane	[33]	50	7.8	-6.8	23.6	117	14.7	-12.3	53.9	5055
Toluene+Pristane	[10]	86	4.6	-3.1	10.5	86	4.6	-3.1	10.5	1000
Toluene+Heptamethylnonane	[10]	87	6.6	-0.2	21.1	87	6.6	-0.2	21.1	1000
Toluene+Methylnaphtalene	[10]	87	9.4	-6.7	22.8	87	9.4	-6.7	22.8	1000
n-Buthylbenzene+	[12]	119	2.5	1.1	5.8	119	2.5	1.1	5.8	1000
n-Tetradecane										
Cyclohexane+n-Hexane	[22]	44	9.2	-8.1	28.8	79	12.7	-9.5	50.2	5000
Cyclohexane+n-Octane	[24]	72	2.7	-0.8	7.9	108	3.2	0.5	12.6	1630
Cyclohexane+n-Dodecane	[24]	53	3.7	2.7	10.7	89	6.8	5.9	17.5	2002
Cyclohexane+n-Hexadecane	[24]	48	4.2	3.2	33.3	68	6.5	5.6	33.3	1808
n-Hexane+n-Dodecane	[23]	6	6.6	0.4	18.1	22	11.2	8.1	31.5	4551
n-Octane+n-Dodecane	[23]	10	1.7	0.5	4.7	36	11.0	10.5	31.1	5055
n-Decane+n-Heptane	[27]	11	3.8	-2.3	6.2	11	3.8	-2.3	6.2	1000

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n-Decane+n-Tetradecane	[12]	119	4.7	3.8	12.3	119	4.7	3.8	12.3	1000
n-Decane+n-Hexadecane	[27]	51	2.7	1.0	6.8	51	2.7	1.0	6.8	1000
Nonylbenzene+Heptane	[12]	119	3.0	1.3	10.0	119	3.0	1.3	10.0	1000
n-Octane+n-Heptane	[38]	168	11.6	-11.5	33.3	168	11.6	-11.5	33.3	491
n-Decane+n-Tetradecane+	[12]	85	1.4	0.3	4.3	85	1.4	0.3	4.3	1000
n-Buthylbenzene										
n-Decane+n-Dodecane+	[27]	115	2.9	-0.4	12.1	115	2.9	-0.4	12.1	1000
n-Tétradécane+n-Hexadecane										
Methane+n-Decane	[25]-[28]	586	11.6	-11.0	79.9	586	11.6	-11.0	79.9	689
petroleum cuts	[12]	216	3.0	1.6	12.7	216	3.0	1.6	12.7	1000
Total 1:		1916	7.2	-4.7	79.9	2152	8.0	-4.3	79.9	5055
with C <sub>1</sub> +C <sub>10</sub> & without cuts										
Total 2:		1330	5.3	-1.9	33.3	1566	6.7	-1.8	53.9	5055
without C <sub>1</sub> +C <sub>10</sub> & without cuts										
Total 3:		1546	5.0	-1.4	33.3	1782	6.3	-1.4	53.9	5055
without $C_1+C_{10}$ & with cuts										
Total 4:		2132	6.8	-4.1	79.9	2368	7.5	-3.4	79.9	5055
with C <sub>1</sub> +C <sub>10</sub> & with cuts										

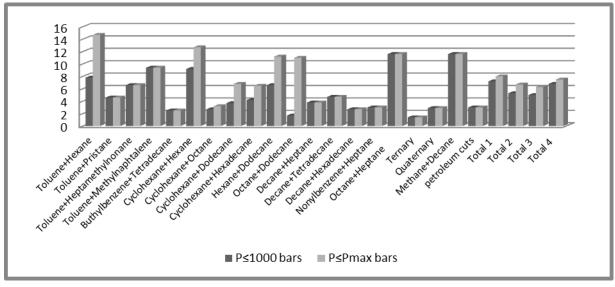


Fig.2. Mean deviation (ADD) for mixtures

#### C. Association of the self-referencing method and mixing rules:

The mixing rules chosen for the coupling are rules without an adjustable parameter. This is the rule in power 3 (Law 1: Equation 4) and the logarithmic additive rule (Law 2: Equation 5). All the preceding mixtures, with the exception of the petroleum fractions (for which the composition is not known), were taken back for the tests. The coupling method requires generating the value of the viscosity of the pure substances from the known values for the pressure P<sub>0</sub> and the temperature T<sub>0</sub> and a table V shows the values used. For all pure bodies  $P_0=1$  bar has been adopted. On the other hand,  $T_0$ corresponds to the minimum temperature for which the database provides the experimental viscosity at  $P_0$ . The results are given in Table VI. The  $C_1 + C_{10}$  binary has, as before, been

On the one hand, there is a restriction or not on the pressure, that the two rules induce very satisfactory results, the law 2 being generally better. Examination of Table VI shows that, component by component, it is sometimes law 1, sometimes

Table-V: Values of  $T_0$  and  $\eta_0$  (at  $P_0 = 1$ bar) used to generate the viscosity of pure substances

Component	T <sub>0</sub> °K	η <sub>0</sub> (P,
		T <sub>0</sub> ) Cp
n-Hexane	273.1	0.38
	5	1
n-Heptane	313.1	0.34

law 2 which provides the best representation. Taking into account the C1 + C10 binary causes a deterioration of the results and it is curious to note that the generated values are more in agreement with the experimental data of the bibliographic reference [[28]] than with those of the reference [25]. For this binary, Law 1 is clearly more appropriate than Law 2.

On the other hand, it is interesting to note that the coupling method does not introduce very large differences compared to the values obtained without coupling. On the "Total 2" line of Table IV (no cut no binary  $C_1 + C_{10}$ ) one can read the following deviations: 5.3%, -1.9%, 33.3% while the coupling with the law 2 provides under similar conditions: 8.0%, -0.5%, 44.2%, this if P  $\leq$  1000 bar. Without restriction on the pressure one observes 6.7%, -1.8%, 53.9% in the first case, and 9.3%, -1.0%, 56.6% in the second case. The maximum deviation as well as the average deviation across all systems is almost the same in both procedures. Figures 3 and 4 show the various performances. It can be seen that even the cyclohexane binaries are now correctly described.

	5	0
n-Octane	273.1	0.71
	5	2
n-Decane	293.1	0.92
	5	0
n-Dodecane	293.1	0.15
	5	0

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n-Tetradecane	293.1	2.33
	5	0
n-Hexadécane	298.1	3.06
	5	1

Toluene	298.1	0.56
	5	1
n-Buthylbenzene	293.1	1.07
-	5	0
Nonylbenzene	313.1	2.09
	5	0
1-Methylnaphtalen	298.1	2.94

e	5	8
Pristane	298.1	6.78
	5	1
Heptamethylnonan	298.1	3.29
e	5	9
Cyclohexane	298.1	0.89
	5	2
Methane	103.1	0.14
	5	4

Table-VI: Results obtained on the mixtures after coupling with the two laws of mixtures: Law 1:  $\mathbf{\eta}^{1/3} = \sum_{i=1}^{N} (\mathbf{x}_i \mathbf{\eta} \mathbf{i}^{1/3})$  Law 2:  $\ln \mathbf{\eta} = \sum_{i=1}^{N} \mathbf{x}_i \ln \mathbf{\eta} \mathbf{i}$ 

		— 1≡I′ '		00 bars	P≤P <sub>max</sub> bars					
Mixtures	Reference	Nb <sub>1</sub>	ADD	BIAS	DM	Nb <sub>2</sub>	ADD	BIAS	DM	P <sub>max</sub>
Toluene+Hexane	[33]	53	12.9	-12.9	25.3	120	19.6	-18.9	56.9	5055
	[22]		11.8	-11.8	24.4		18.8	-18.0	56.6	
Toluene+Pristane	[10]	89	13.3	-13.2	38.2	89	13.3	-13.2	38.2	1000
	[,]	-	6.2	4.5	16.1		6.2	4.5	16.1	
Toluene+Heptamethylnonane	[10]	90	12.0	-11.0	27.9	90	12.0	-11.0	27.9	1000
1			7.3	-2.2	22.0		7.3	-2.2	22.0	
Toluene+1-Methylnaphtalene	[10]	90	23.4	-23.6	59.5	90	23.4	-23.6	59.5	1000
, , , , , , , , , , , , , ,			15.0	-14.8	41.8		15.0	-14.8	41.8	
n-Buthylbenzene+	[12]	126	3.8	0.5	10.2	126	3.8	0.5	10.2	1000
n-Tetradecane	,		3.7	1.9	9.4		3.7	1.9	9.4	
Cyclohexane+n-Hexane	[22]	48	20.9	-20.9	31.9	83	23.3	-22.8	57.0	5000
•			17.5	-17.5	30.3		20.3	-19.7	55.9	
Cyclohexane+n-Octane	[24]	76	8.5	-8.5	17.7	112	7.4	-7.2	17.7	1630
•			7.5	-7.5	16.4		6.4	-6.1	16.4	
Cyclohexane+n-Dodecane	[24]	57	3.6	3.0	10.8	93	6.8	6.1	17.8	2002
•			4.0	3.5	11.2		7.2	6.6	18.5	
Cyclohexane+n-Hexadecane	[24]	52	12.1	12.1	41.5	72	13.9	13.8	41.5	1808
•			16.0	16.0	44.2		17.7	17.7	44.2	
n-Hexane+n-Dodecane	[23]	7	1.7	1.4	3.7	23	4.3	2.4	15.9	4551
			6.9	6.9	10.2		7.8	7.8	19.5	
n-Octane+n-Dodecane	[23]	11	2.7	2.7	5.1	37	11.1	10.7	30.4	5055
			5.9	5.9	7.4		13.7	13.6	32.3	
n-Decane+n-Heptane	[27]	12	8.6	-8.6	12.2	12	8.6	-8.6	12.2	1000
			6.2	-6.2	10.0		6.2	-6.2	10.0	
n-Decane+n-Tetradecane	[12]	126	5.3	5.0	11.2	126	5.3	5.0	11.2	1000
			6.9	6.9	12.5		6.9	6.9	12.5	
n-Decane+n-Hexadecane	[27]	54	3.0	3.0	6.4	54	3.0	3.0	6.4	1000
			7.3	7.3	11.9		7.3	7.3	11.9	
Nonylbenzene+Heptane	[12]	126	3.6	-2.5	13.3	126	3.6	-2.5	13.3	1000
			6.9	6.4	15.0		6.9	6.4	15.0	
n-Octane+n-Heptane	[38]	172	9.9	-9.7	38.9	172	9.9	-9.7	38.9	491
			9.9	-9.6	38.8		9.9	-9.6	38.8	
n-Decane+n-Tetradecane+	[12]	90	3.1	-1.6	8.2	90	3.1	-1.6	8.2	1000
n-Buthylbenzene			2.7	-0.3	7.1		2.7	-0.3	7.1	
n-Decane+n-Dodecane+	[27]	120	4.4	4.0	8.8	120	4.4	4.0	8.8	1000
n-Tétradécane+n-Hexadecane			6.6	6.6	11.2		6.6	6.6	11.2	
Total 1 : without $C_1+C_{10}$		1399	8.6	4.8	59.5	1635	9.8	-5.0	59.0	5055
			8.0	-0.5	44.2		9.3	-1.0	56.6	
Methane+n-Decane	[28]	96	14.6	11.2	25.5	586	14.6	11.2	25.5	420
			34.4	34.1	56.6		34.4	34.1	56.6	
Methane+n-Decane	[25]	502	22.9	22.9	45.0	586	22.9	22.9	45.0	689
			37.4	37.4	66.5		37.4	37.4	66.5	
Methane+n-Decane	[25]-[28]	598	21.6	21.0	45.0	586	21.6	21.0	45.0	689
			36.9	36.9	66.5		36.9	36.9	66.5	
Total 2 : with $C_1+C_{10}$		1997	12.5	2.9	59.5	2233	13.0	2.0	59.5	5055
			16.7	10.7	66.5		16.7	9.2	66.5	

Note: In table VI there are more points than in table IV. Indeed, for the coupling, it is enough to know the viscosities of the pure bodies and no point of the mixture serves as a reference. On the other hand, without coupling (Table IV), it is necessary for each composition a point of reference of the mixture.





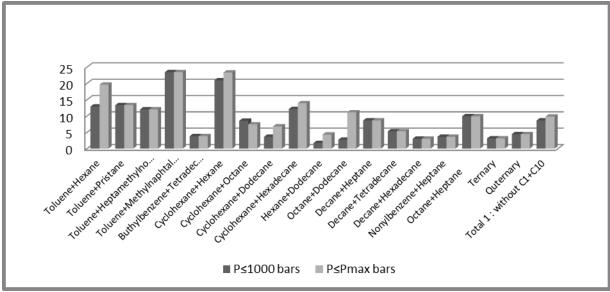


Fig.3. Mean deviation (ADD) obtained on the mixtures after coupling with the law 1

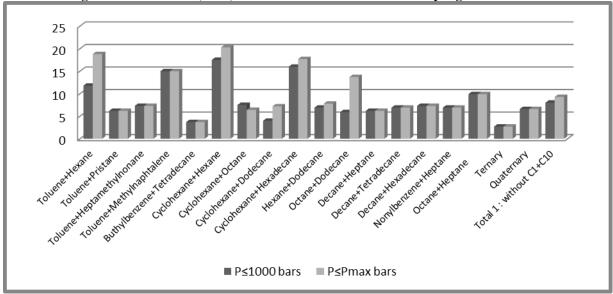


Fig.4. Average deviation (ADD) obtained on the mixtures after coupling with the law 2:

#### IV. CONCLUSION

In this article we have just examined the possibilities of restitution of the viscosity offered by the model of self-reference. Obviously, from the above data, it appears that the self-reference model can be applied successfully to both pure substances and mixtures and that it can be used for mixtures of unknown composition. In the case of mixtures of known composition it lends itself well to a coupling with the weighting laws. This model does not require adjustment but only to have information relating to the viscosity at 1 bar and the reference temperature T<sub>0</sub>. For mixtures, in the case of coupling, it is sufficient to know the viscosities of the pure substances at  $T_0$  and  $P_0$ . Examination of the preceding tables shows that this method effectively characterizes the behavior of the property in a range of extended pressure (up to 5000 bars and perhaps more). Its only disadvantage is that it is only suitable for systems in the liquid state. Since the coefficients were initially adjusted to moderately heavy substances, it might be interesting to resume the calibration procedure by including lighter substances. Finally, let us insist on the fact that it is a simple model to handle in practice and under equal conditions, it is more performant compared to various models tested in the literature.

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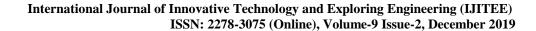
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- -Coordinator of the Professional Licensing Program "Instrumentation and Biomedical Maintenance" (since 2014) "Maintenance of Scientific Equipment" (since 2015)
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