Study of the viscosity of hydrocarbon mixtures under pressure and temperature: A critical model of the corresponding states to double reference in the modeling domain.

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Abstract. The studied predictive model of behavior viscometric is the model of K.A. Petersen [1]. The dominant idea of this method is to characterize the viscosity of a fluid from two models taken as a reference in passing through a reduced pressure. The method is corresponding state with two references. This study shows that this method is dependent on the choice of reference and for each of the possibilities of C10/C6H6 and C1/C10 references. The results were investigated for four different weight ratios. It shows that the introduction of an adjusted coefficient does not improve significantly compared to results without adjustment factor, which appears to be the best choice. Regarding the influence of the choice of references, generally the two couples appear suitable but we noted that the choice is not necessary. In the case of mixtures containing at least one aromatic, the results are correct, especially if one takes the ratio of adjustment and our ratio without adjustment compared to that of K. A. PETERSEN[1]. The experimental results of the viscosity exhibit a good agreement with the calculated values. We can predict that the relative improvement is the finding that the introduction of the second body of reference (C10) from the model states corresponding to a reference (C1) of the authors.

1. Introduction

A more sophisticated variant of the model states corresponding to a reference [1] does not introduce the form factor and which retains the powers of critical viscosity \( \eta_c = C T_{c1}^{1/6} M^{1/2} P_{c1}^{-2/3} \) is the model of corresponding states to double reference. It was initially proposed by A. S. Teja and P. Ricz (1981) [2] and taken up by K. Aasberg-Pedersen (1991) [3]. In order to experiment properly and to test this model and critique their performance on mixtures of hydrocarbons, we used the experimental database (15000 points) that we created [4] on the viscosity and the density, depending on the pressure and temperature, light and heavy hydrocarbons, and their mixtures.

2. Methods

Four our study, we selected viscosity data on pure substances and mixtures of hydrocarbons of known compositions. For the latter, it is important to know precisely the composition of mixtures because the critical viscosity \( \eta_{cm} = C T_{cm}^{1/6} M_{m}^{-1/2} P_{cm}^{-2/3} \) involved the terms \( M_m, P_{cm}, T_{cm} \). Considering the results of the literature, we chose three rules of mixtures, PEDERSEN [3], ETTAHIR [5] and WONG [6]. Recall here that the rules of PEDERSEN and WONG lead to the same \( T_{cm} \) and \( P_{cm} \) values and differ
only for oc. But with the rule PEDERSEN, we adopt the definition of Mm proposed by K. AASBERG-PEDERSEN (1991) [2], [3] explained by the following equation:

\[ Mm = 8.67358 \times 10^3 (\text{MW}^{0.36079} - \text{MN}^{0.36079}) + \text{MN} ; \]

\[ \text{MW} = \sum_{i} \text{Mi}^2 / \sum_{i} \text{Mi} \text{et} \quad \text{Mn} = \sum_{i} \text{Mi} \]

For rules of WONG-ETTAHIR we used the classical linear law: \( \text{Mm} = \sum_{i} \text{Mi} \).

In addition, we have considered two possibilities of double reference, first methane (C1) and decane (C10), on the other decane (C10) and benzene (C6H6). In the latter case, we check if it is possible to facilitate the return of the viscosity of heavy compounds like alkanes or aromatic, given the references adopted.

Finally, we wanted to test several distinct definitions of the factor K involved in the equation below, rather than limiting itself to theacentric factor (\( \omega \)) as in the literature. K. AASBERG-PEDERSEN (1991) [2], [3] admit the neighboring relation:

\[ \ln \eta(P,T) = \ln \eta_1(P_1,T_1) + K \ln (\eta_2(P_2,T_2) / \eta_1(P_1,T_1)) \quad \text{avec} \quad K = (\text{IP1} - \text{IP2}) / (\text{IP1} - \text{IP2}) \]

Where IP denotes an arbitrary prior parameter which is used to characterize the weighting between two references. Initially this parameter corresponds to IP = \( \omega \) and the last authors proposed to use IP = M (Molar mass). Since \( \eta = \eta / \eta_2 \) we can finally write:

\[ \eta(P,T) = \eta_c \cdot \eta_1(P_1, T_1) / \eta_2(P_2, T_2) \cdot \eta_1 / \eta_2(P_1, T_1) \cdot \eta_2 \]

Where \( \eta_1 \) and \( \eta_2 \) are evaluated under the conditions corresponding to the temperature and the reduced pressure of the system studied, that is to say: \( T_i = Tc_i / Tc \) et \( P_i = Pci / Pc \) \( (i=1,2) \). The indices 1 and 2 are relative to the two reference bodies of which the characteristics are known and K is a weighting factor. One of the major disadvantages of the method is clear: it is linked to the fact that its use is a priori limited by the reduced pressure and temperature domain common to the two references: indeed, \( \eta, \eta_1 \) and \( \eta_2 \) must be evaluated for Same temperatures and pressures. So, and from our database of references we have limited ourselves to the following areas of use:

- 0.476 ≤ Tr ≤ 2.740 \quad \text{Pr} ≤ 15.0 \quad \text{Methane}
- 0.395 ≤ Tr ≤ 0.773 \quad \text{Pr} ≤ 49.6 \quad \text{Decane}
- 0.395 ≤ Tr ≤ 0.664 \quad \text{Pr} ≤ 20.4 \quad \text{Benzene}

As mentioned above we opted for a comparative study of the factor K according to the following four weights:

- \( K_\omega = (\omega - \omega_1) / (\omega_2 - \omega_1) \) \quad \text{(Eq 1)}
- \( K_M = (M - M_1) / (M_2 - M_1) \) \quad \text{(Eq 2)}
- \( K_\Lambda = (A_0 K_\omega + A M K_M + A P K_P + A T K_T) / 4 \) \quad \text{(Eq 3)}
- \( K_{\text{total}} = (K_\omega + K_M + K_P + K_T) / 4 \) \quad \text{(Eq 4)}

The weighting factors \( K_{\text{total}} \) and \( K_\Lambda \) have been introduced of kinds to better differentiate two neighboring systems, for example two isomers which necessarily admit the same \( K_M \). Indeed, it is intuitive to think that one of the four quantities \( \omega, M, Pc, Tc \) is in itself sufficiently characteristic of the system studied. As regards the use of \( K_M \), the comparison of the results obtained with this report only reflects the evaluation difference of Mm since for the two rules WONG and ETTAHIR Tm and Pcm are identical. At the end \( K_\Lambda \) the coefficients \( A_0, A M, A P, A T \) are adjustable quantities. For the latter weighting coefficient and for each of the two possibilities of double reference C1/C10 and C10/C6H6 we have chosen the same pure bodies to constitute an adjustment basis, but taking into account the overlap constraint the number of points retained By body changes from one reference torque to the other. For the C1/C10 pair, 18 pure bodies and 280 experimental points are involved, whereas for C10/C6H6 there are 15 pure bodies and 168 experimental points. The values of the coefficients obtained after numerical adjustment are:

Reference C1/C10:
In order to assess and compare the performance of various References, we defined the following quantities:

\[
\text{Dev}(i) = 100 \times \frac{\eta_{\text{exp}} - \eta_{\text{cal}}}{\eta_{\text{exp}}} \quad \text{Dev abs}(i) = \left| \text{Dev}(i) \right| \geq 0 \quad \text{DM} = \text{Max}(\text{Dev abs}(i))
\]

\[
\text{AAD} = \frac{1}{\text{Nb}} \sum_{i=1}^{\text{Nb}} \text{Dev abs}(i)
\]

\[
\text{Bias} = \frac{1}{\text{Nb}} \sum_{i=1}^{\text{Nb}} \text{Dev abs}(i)
\]

In which \(\text{Nb}\) is the number of experimental points, \(\eta_{\text{exp}}\) the measured viscosity value and \(\eta_{\text{cal}}\) 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 well the experimental points are distributed to either side of the calculated curves. Finally DM characterizes the maximum error that can be generated using a given reference.

### Table 1. Comparison of results obtained based on coefficients \(K_A\) adjustment.

| Reference     | \(K_M\) | \(K_o\) | \(K_A\) | \(K_{Total}\) |
|---------------|---------|---------|---------|---------------|
| \(C_1/C_{10}\)| AAD     | 13.8    | 9.9     | 7.4           | 10.3          |
|               | Bias    | -11.0   | -4.5    | -0.1          | -5.5          |
|               | DM      | 40.6    | 43.0    | 28.5          | 38.7          |
| \(C_{10}/C_6H_6\)| AAD     | 19.1    | 20.5    | 15.7          | 19.8          |
|               | Bias    | -16.1   | -16.2   | -14.0         | -16.2         |
|               | DM      | 63.4    | 63.3    | 60.5          | 64.2          |

There is in both cases an improvement on all tree features of the adjustment relating to \(K_A\) and the improvement is very clear in the case of the couple \(C_1/C_{10}\).

### 3. Discussion of results

#### 3.1. Results obtained for the whole of the base in the field of Recovery:

The application of the method of double reference to the determination of the viscosity of mixtures requires the prior definition of pseudo-critical coordinates. The given results are demonstrated by using the residual viscosity correlation \([7] [8] [9] [10]\). We restricted to the three rules of mixtures PEDERSEN, WONG and ETTHAHR. The presented results are obtained on a set of mixtures of hydrocarbons derived from our database in the area of recovery.

Initially we used the couple \(C_1/C_{10}\) as double reference. The mixtures were in turn separated into two main groups. The first included five binary containing \(CO_2\) and \(C_1\) or the second group consists of 16 binary, ternary and quaternary one containing neither \(C_1\) nor \(CO_2\). Table 2 shows the values of mean deviation and we can see that the mixing rule ETTHAHR was less well for the return of mixtures with \(C_1\) and \(CO_2\). For mixtures without \(C_1\) or \(CO_2\), the results are similar for all three rules. It appears that the best relationships are \(K_A\) and \(K_{Total}\). These results are in the same way as for pure substances \([5]\). Table 3 provides detailed results of all the mixes for the average deviation. We noticed that the binary cyclohexane are the least represented. Figure 1 shows the average deviation of mixing, obtained with the rule of Pedersen and weight \(K_{Total}\). We also noted that the maximum deviations are relatively low except for binaries consisting of cyclohexane.

In a second step, we have taken the couple \(C_1/Benzene\) as a double reference. Note that no point has been upheld in our database for the mixture \(C_1+C_4\) and ethanol+toluene \([11]\) due to the constraints collection already exposed. In this case the maximum deviation (51.7\%) is obtained for the mixture of \(C_7+C_8\) when it was observed for the binary cyclohexane+C8 with other references. The results of both
groups are provided in table 4. For all data, the report $K_{\text{Total}}$ (combined with the rule and Pedersen WONG) leads to the smallest average deviation. With this couple C1/Benzen, binaries cyclohexane containers are represented better with the couple C1/C10 (see figure 1 and 2). With the exception of this class of mixtures, the pair definitely needed C1/C10 similarly to the case of pure [5]. This confirms once more that the representativeness of the model is of benefit conditional on the adoption of remote references by their chain length rather than the nature of chemical families (see figure 2). With this pair the viscosity of mixtures of light paraffin in the various possible phases as well as mixtures of heavy bodies is described correctly (see figure 1-off). A wider use of the procedure with respect to natural gas or petroleum fractions, system more complex than synthetic blends taken into account in the database, may be feasible if the pseudo-critical parameters are accessible.

**Table 2.** Average deviation for the reference C1/C10 (Application of all the 2 groups without extrapolation).

| Group                  | Nb | Rule | KM | $K_0$ | KA | $K_{\text{Total}}$ |
|------------------------|----|------|----|-------|----|---------------------|
| (Mixture without C1 and CO2) | 520 | 2    | 12.1 | 13.0  | 10.5 | 11.1                |
| (mixture with C1 and CO2)  | 149 | 2    | 12.9 | 10.5  | 13.2 | 11.1                |

With the exception of this class of mixture, the number of points used in the field of recovery (without extrapolation) is described correctly (see figure 1 and 2).

**Table 3.** Mean deviation for the reference C1/C10.

| Mixture                  | Reference | Nb | Rule | KM | $K_0$ | KA | $K_{\text{Total}}$ |
|--------------------------|-----------|----|------|----|-------|----|---------------------|
| Toluene+n-Hexane         | [12]      | 32 | 1    | 3.9| 3.0  | 4.0 | 5.0                 |
| Toluene+Pristane         | [13]      | 32 | 1    | 4.3| 3.4  | 3.9 | 5.5                 |
| Toluene+Heptamethyleneonane | [13]      | 30 | 1    | 11.2| 9.1 | 5.3 | 7.4                 |
| Toluene+1-Methylnaphthalene | [13]    | 38 | 3    | 8.3| 18.5 | 14.1| 12.9                |
| n-Butylbenzene+n-Tetradecane | [14]   | 30 | 1    | 15.5| 6.0 | 4.5 | 7.0                 |
| n-Decane+n-Tetradecane   | [14]      | 30 | 2    | 14.2| 7.3 | 3.9 | 6.9                 |
| Nonylbenzene+n-Heptane   | [14]      | 30 | 2    | 12.7| 39.5| 5.9 | 13.9                |
| n-Decane+n-Tetradecane+  | [14]      | 34 | 3    | 12.1| 43.4| 10.7| 20.8                |
| n-Butylenbenzene         | [15]      | 26 | 1    | 23.4| 16.1| 22.4| 20.3                |
| Cyclohexane+n-Hexane     | [15]      | 28 | 3    | 7.3 | 3.2 | 4.8 | 7.7                 |
| Cyclohexane+n-Octane     | [16]      | 51 | 1    | 22.1| 23.8| 23.8| 20.8                |
| Cyclohexane+n-Dodecane   | [16]      | 25 | 1    | 29.5| 34.6| 32.9| 31.1                |
| n-Hexane+n-Dodecane      | [16]      | 25 | 2    | 31.2| 33.0| 34.3| 31.5                |
| n-Octane+n-Dodecane      | [17]      | 26 | 3    | 36.2| 39.8| 38.3| 37.2                |

1: Rule PEDERSEN; 2: Rule WONG, 3: Rule ETTAHIR; Nb: Number of points used in the field of recovery (without extrapolation)
| n-Decane+n-Heptane  | [18] | 4   | 1   | 5.9 | 8.0 | 7.6 | 9.4 |
| n-Decane+n-Hexadecane | [18] | 14  | 1   | 5.7 | 3.7 | 4.6 | 5.2 |
| n-Decane+n-Dodecane+ | [18] | 32  | 1   | 5.0 | 3.3 | 5.1 | 5.4 |
| n-Tetradecane+n-Hexadecane | 32  | 2   | 4.3 | 3.3 | 5.7 | 5.6 |
| n-Octane+n-Heptane   | [19] | 90  | 1   | 4.5 | 6.0 | 5.3 | 6.6 |
| Methane+n-Decane     | [20][21] | 242 | 1   | 15.4 | 16.9 | 14.5 | 14.8 |
| Methane+Propane      | [21][24] | 76  | 1   | 9.4  | 6.7  | 13.0 | 8.6  |
| Methane+n-Butane     | [21]  | 16  | 1   | 5.3  | 2.8  | 6.3  | 2.9  |
| Methane+Ethane       | [22]  | 112 | 1   | 4.6  | 6.4  | 4.8  | 4.3  |
| n-Decane+CO2         | [24]  | 53  | 1   | 4.7  | 3.4  | 6.4  | 4.2  |

Table 4. Mean deviation for the reference C10/Benzene (Application of all the 2 groups without extrapolation).

| Group                     | Nb | Rule | KM  | K0  | Kα  | KTotal |
|---------------------------|----|------|-----|-----|-----|--------|
| Group 1: Mixture without C1 and CO2 | 315 | 1   | 15.3 | 15.9 | 15.6 |
| Group 2: mixture with C1 and CO2  | 215 | 1   | 16.7 | 19.2 | 36.7 |
| Group 1 + Group 2           | 530 | 1   | 15.9 | 17.2 | 23.3 |
|                           | 530 | 2   | 16.4 | 17.3 | 23.8 |
|                           | 545 | 3   | 20.0 | 21.6 | 29.6 |

Figure 1. Average deviations obtained for PEDERSEN’s rule and report of KTotal for mixtures without extrapolation:

- ■ Reference C1/C10
- ○ Reference C10/Benzene
3.2. Results obtained on the entire base after extrapolation outside the area of recovery:

As before we used the couple of references \( C_{1}/C_{10} \) by extrapolating from the base to field \( 0476 \leq Tr \leq Pr \leq 2.74 \) and 100, so with 4712 pairs \( P, T \) instead of 1007 without extrapolation. The results are provided in Table 5 do not show an overall deterioration in respect to the average deviation. Therefore, for the areas studied \( Pr \) and \( Tr \), stress recovery can be lifted without difficulty. These good results by using the parameters \( KA \) and \( K_{Total} \) deserve to be highlighted. Figure 3 is typical of the average deviation found with the rule of Pedersen and the weight \( K_{Total} \) and warrants that the results obtained with an extrapolation compare favorably to those in the absence of extrapolation.

Table 5: Average deviation for the reference \( C_{10}/Benzene \) (Application of the 2 groups together with extrapolation).

|                | Nb  | Rule | K\(_M\) | K\(_w\) | K\(_A\) | K\(_Total\) |
|----------------|-----|------|---------|---------|---------|-------------|
| Group 1 :      |     |      |         |         |         |             |
| Mixture without C1 and CO2 | 1328 | 1    | 14.4    | 15.1    | 12.2    | 12.6        |
|                 | 1328 | 2    | 13.6    | 15.2    | 12.6    | 12.7        |
|                 | 1379 | 3    | 14.5    | 17.4    | 14.5    | 15.0        |
| Group 2 :      |     |      |         |         |         |             |
| Mixture with C1 and CO2 | 3384 | 1    | 9.7     | 11.5    | 8.2     | 10.0        |
|                 | 3384 | 2    | 9.5     | 11.3    | 8.3     | 9.8         |
|                 | 3271 | 3    | 12.5    | 12.8    | 12.1    | 12.6        |
| Group 1 + Group 2 |     |      |         |         |         |             |
|                 | 4712 | 1    | 11.0    | 12.5    | 9.3     | 10.7        |
|                 | 4712 | 2    | 10.7    | 12.4    | 9.5     | 10.6        |
|                 | 4650 | 3    | 13.1    | 14.2    | 12.8    | 13.3        |

1: Rule PEDERSEN, 2: Rule WONG, 3: Rule ETTAHIR, Nb: Number of points used in the field of recovery (without extrapolation)

Figure 3. Average deviations obtained for PEDERSEN’s rule and report of \( K_{Total} \): Case of mixture (with and without extrapolation) and reference \( C_{1}/C_{10} \):

- without extrapolation
- with extrapolation
4. Conclusion

We examined the performance of the model states corresponding to double references. The results show that the introduction of the adjusted coefficients in the ratio of KA does not improve significantly compared with KTotal and it seems to be the best choice. The Reports ω, KM and K, were easy but they presented not good results compared to KA and KTotal. This finding is confirmed for the pure body in our work presented in ETTAHIR thesis. About the influence of the choice of references, we found that the two sets of references appear proper, but we note that the choice is not indifferent by using the C10/Benene and occurs cyclohexane and minimizes the maximum deviation from the couple Cl/C10. This generates the highest average deviation for this group of mixtures, regardless of gear choice K. However, only the two lends itself to an extension beyond the field of recovery, outlook favorable for lifting the restriction of the constraint method. In addition, analysis of results indicates that the rules are those WONG PEDERSEN and to be given priority, the rule is less effective ETTAHIR although its average deviation (13.3%) on the field compared with the extrapolated KTotal is very respectable. But the other two rules are better, approaching 10%.

Note that the performance of this predictive model vis-à-vis other elements that ring, are much more convincing because the deviations observed are considerably reduced compared to those induced by other models tested, such as the model of residual viscosity and the model states corresponding to a reference, especially in the case of liquid mixtures and heavy bodies. Small deviations were also found for the mixture CO2+C10, despite a high concentration of CO2 (greater than 50%), promising results on the ability of the model to simulate the influence of CO2 on the viscosity of fluids in reservoirs.

The viscosities calculated for the quaternary C10+C12+C14+C16+C10 butylbenzene the ternary C14 and other heavy components in mixtures, are very close to experimental results, unlike the case of model states corresponding to a reference. The marked improvement of the representation is undoubtedly the introduction of the second reference (C10), which promotes long carbon chains. With the single reference model (C1), only lights paraffin were well represented. These performances suggest therefore predict potential capabilities of the model to be extended to heavy oil.

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