PERFORMANCE OF PREDICTIVE APPROACHES FOR THE VISCOSITY OF BINARY LIQUID MIXTURES OF 1-ALCOHOLS

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Abstract - The objective of this study is to evaluate the predictive performance of three semi-theoretical approaches for modeling viscosity of binary liquid mixtures composed of 1-alcohols. For the mixtures that contain 1-alcohols with a similar number of carbon atoms, three schemes including the Rough Hard-Sphere model, the McAllister model, and UNIFAC-VISCO were demonstrated to be able to reproduce the mixture viscosity with an average deviation of 5%. For highly asymmetrical mixtures without the presence of small molecules, only McAllister-type model successfully reproduced the experimental values. The prediction done by the Rough Hard-Sphere model on the basis of using simple mixing rules for characteristic parameters indicated that this model should be further modified to improve its predictive capability.

Key words - Viscosity; Rough Hard-Sphere; McAllister; UNIFAC-VISCO; 1-alcohols

1. Introduction

Viscosity of 1-alcohol based mixtures is a thermophysical property that plays an important role in many industrial applications involving the fluid flow [1], [2]. Alcohols are used as solvents in many industrial extraction processes or in many synthesis processes for other compounds. In the context of the depletion of fossil energetic resources and global heating, an interest in the utilization of 1-alcohols as additives into gasoline or diesel is increasing [3] - [5]. The design of chemical processes which can be used to produce alcohol species from the so-called second-generation biofuels, the demand in an efficient utilization of alcohol-mixed fuels, *etc*, always require a reliable knowledge of thermophysical properties including the viscosity of fluids under consideration. However, accurate values of viscosity are not always obtained by experimental means. This becomes more challenging when the viscosity measurements are carried out at extreme conditions (high temperature and high pressure) and for industrial fluids, primarily complicated mixtures, *e.g.* alcohol-mixed fuels. In this case, the data is usually supplemented by using predictive approaches that can estimate the viscosity of fluids in a broad range of temperature, pressure and composition.

In literature, numerous approaches from purely empirical and correlative to semi-theoretical are reported for the purpose of modeling the viscosity of mixtures. A critical review of these models is well presented in references [6], [7]. For the objective of this study, attention is paid only on the semi-theoretical models, which are developed in combination of an underlying theory, resulting in the assurance of the predictive power of the models. Successful viscosity approaches have been proposed based on the corresponding-states theory [8], free-volume concept [9], the friction theory [10], [11], the relationship with residual entropy [12], density scaling [13], hard-sphere type models [14], [15], McAllister type models [16], UNIFAC-VISCO [17]. These models were developed and validated against a large experimental data set including different chemical families. However, none of these models are found to be tested systematically for mixtures containing only alcohols. Therefore, the objective of this work is to evaluate the predictive performance of models for the viscosity of liquid mixtures of 1-alcohols.

Three predictive models are selected in this work including (i) the so-called Rough Hard Sphere model (RHS), first proposed by Assael and Dymond [14], [18], (ii) the McAllister type model, first proposed by [16], and (iii) an industrially practical model called UNIFAC-VISCO [17]. The choice of three models is based on the fact that *(i)* all three models are preferably used by many investigators who wanted to validate their viscosity measurement, *(ii)* the uncertainty in predicting the viscosity of mixtures given by all three models is usually within 5%. More details about three models are presented in Section 3 of this report.

2. Database

As mentioned in the Introduction section, this work will be focused on the evaluation of predictive capability of approaches for the viscosity of binary liquid mixtures containing only species of 1-alcohol chemical family. To that end, a database of 57 mixtures with number carbon ranging from Ethanol to 1-Dodecanol was collected from literature. The available data set consists of 1863 data points covering a range of temperature (283.15 – 338.15K) and atmospheric pressure. The majority of the measurements have been reported at atmospheric pressures and near room temperature. The measurement uncertainty for viscosity and density is reported within 1 or 2 %. Table 1 showed the summary of the data set collected from literature for binary mixtures containing 1-alcohols. Literature search indicated that the viscosity of binary 1-alcohols mixtures has been measured for at least 57 different systems, providing ample data for the evaluation purpose in this work. It should be noted that only measured values including viscosity and density were collected in this database.

3. Predictive approaches

In this work, three semi-theoretical approaches are utilized to estimate the viscosity values of binary mixtures containing only 1-alcohols. The choice of these methods for this study is mainly based on its predictive capability, claimed by the developers, for associating mixtures such as ones containing 1-alcohols. In this section, three approaches will be briefly highlighted with essential features. The reader is referred to the original publications for more details.

***Table 1.** Summary of binary liquid mixtures containing 1-alcohols, used for the evaluation purpose*

Mixtures*	N. of data	Range of T, K	Range of P, MPa	Ref.
c2ol + c3ol	72	293 – 328	0.1	[21]
c2ol + c4ol	117	283 – 328	0.1	[21], [22]
c2ol + c5ol	117	283 – 328	0.1	[21], [22]
c2ol + c6ol	72	293 – 328	0.1	[23]
c2ol + c7ol	117	283 – 328	0.1	[22], [23]
c2ol + c8ol	45	283 – 313	0.1	[22]
c2ol + c9ol	45	283 – 313	0.1	[22]
c2ol + c10ol	45	283 – 313	0.1	[22]
c3ol + c4ol	24	293 – 313	0.1	[24], [25]
c3ol + c5ol	42	293 – 313	0.1	[24]–[26]
c3ol + c7ol	18	293 – 298	0.1	[26]
c3ol + c9ol	18	293 – 298	0.1	[26]
c3ol + c11ol	18	293 – 298	0.1	[26]
c4ol + c5ol	24	293 – 313	0.1	[24], [25]
c4ol + c9ol	24	293 – 313	0.1	[24], [25]
c4ol + c10ol	24	293 – 313	0.1	[24], [25]
c5ol + c7ol	18	293 – 298	0.1	[26]
c5ol + c8ol	24	293 – 313	0.1	[24], [25]
c5ol + c9ol	18	293 – 298	0.1	[26]
c5ol + c11ol	18	293 – 298	0.1	[26]
c6ol + c7ol	25	298 – 338	0.1	[27]
c6ol + c8ol	25	298 – 338	0.1	[27]
c6ol + c9ol	25	298 – 338	0.1	[27]
c6ol + c10ol	25	298 – 338	0.1	[27]
c6ol + c11ol	25	298 – 338	0.1	[27]
c6ol + c12ol	25	298 – 338	0.1	[27]
c7ol + c8ol	49	293 – 338	0.1	[24], [25], [27]
c7ol + c9ol	43	293 – 338	0.1	[26], [27]
c7ol + c10ol	25	298 – 338	0.1	[27]
c7ol + c11ol	43	298 – 338	0.1	[27]
c7ol + c12ol	25	298 – 338	0.1	[27]
c8ol + c9ol	88	283 – 338	0.1	[27], [28]
c8ol + c10ol	88	283 – 338	0.1	[27], [28]
c8ol + c11ol	70	293 – 338	0.1	[27], [28]
c8ol + c12ol	25	298 – 338	0.1	[27]
c9ol + c10ol	100	283 – 338	0.1	[24], [27], [28]
c9ol + c11ol	88	293 – 338	0.1	[26]–[28]
c9ol + c12ol	25	298 – 338	0.1	[27]
c10ol + c11ol	94	293 – 338	0.1	[24], [25], [27], [28]
c10ol + c12ol	25	298 – 338	0.1	[27]
c11ol + c12ol	25	298 – 338	0.1	[27]

(*) *c2ol: Ethanol, c3ol: 1-Propanol, c4ol: 1-Butanol, c5ol: 1-Pentanol, c6ol: 1-Hexanol, c7ol: 1-Heptanol, c8ol: 1-Octanol, c9ol: 1-Nonanol, c10ol: 1-Decanol, c11ol: 1-Undecanol, c12ol: 1-Dodecanol.*

3.1. Rigid Hard-sphere model (RHS model)

First proposed by J.H. Dymond [18] and then refined into a practical predictive approach by Assael *et al.* [14], the kinetic-theory-of-hard-sphere based model was applied to estimate the viscosity of pure liquids by assuming that the reduced viscosity, η^*, is a universal function of the reduced molar volume, $V^* = V_m/V_o$, as shown in Eqs. (1) & (2). This scheme was claimed to be able to reproduce the viscosity of pure fluids within an uncertainty of approximately 5% [14], [19], [20].

$$log\left(\frac{\eta^*}{R_\eta}\right) = \sum_{i=0}^{7} a_{\eta i}\,(V^*)^i \tag{1}$$

$$\eta^* = \frac{16}{5}(2N_A)^{1/3}\left(\frac{\pi}{MRT}\right)^{1/2}\frac{V_m^{2/3}}{R_\eta}\eta \tag{2}$$

Where, V_m, V_o, M, R, T, R_η and η respectively corresponds to the molar volume, the molar core volume, the molar mass, the universal gas constant, the temperature, the roughness factor, and the dynamic viscosity. The universal coefficients $a_{\eta i}$ in Eq. (1) can be found in the original work of Assael *et al.* [14]. In this scheme, V_o and R_η are two main parameters characterizing specific chemical families and determined by adjustments to experimental data of viscosity. Equations (3) and (4) represent the correlations for molar core volume and roughness factor for pure 1-alcohols that depend upon temperature T and carbon number C_n of pure species of interest.

$$V_o = \sum_{i=0}^{1} b_i T^{-i/2} + \sum_{i=0}^{4} d_i C_n^{(i+2)/2} + \sum_{i=0}^{5} g_i (C_n T)^{(i+1)/2} \tag{3}$$

$$\begin{aligned} R_\eta &= \sum_{i=0}^{2} h_i T^i \ \ for\ CH_3OH \div 1 - C_5H_{11}OH \\ R_\eta &= 38.22 - 16.071C_n + 2.353C_n^2 - 0.1088C_n^3 \\ &\quad for\ 1 - C_6H_{13}OH \div 1 - C_{10}H_{21}OH \end{aligned} \tag{4}$$

The parameters including b_i, d_i, g_i in Eq. (3) and h_i in Eq. (4) can be found in the original work by Assael *et al.* [20].

The so-called RHS model can be extended into predicting the viscosity of mixtures by applying simple mixing rules for two characteristic parameters, as described in Eqs. (5) & (6):

$$V_{o,mix} = \sum_{i=0}^{N} x_i V_{o,i} \tag{5}$$

$$R_{\eta,mix} = \sum_{i=1}^{N} x_i R_{\eta,i} \tag{6}$$

Based on the vast literature research, it is worth noting that this scheme has not been extensively evaluated for mixtures containing only 1-alcohols. The reason is partly due to the lack of the measured data for this kind of mixtures. However, the predictive performance of this scheme for mixtures containing species other than 1-alcohols was reported to be within 5% of uncertainty for mixtures such as n-alkanes – n-alkanes [29], n-alkanes – aromatics [30].

3.2. The three-body interaction model (McAllister model)

Based on Eyring's reaction rate theory, R.A. McAllister developed a so-called three-body interaction model for correlating the viscosity of binary mixtures [16]. This model was then further developed for ternary mixtures by several investigators [31], [32] and for multi-component mixtures [33]. Although the McAllister-type model is considered to be one of the best correlative techniques for the viscosity of binary liquid mixtures [34], its major drawback lies in estimating the values of interaction parameters of the model, which are usually adjusted against a relatively large experimental database. For the prediction purpose, Asfour and co-workers modified the McAllister model by using the molecular parameters and the viscosities of pure components to predict the values of the interaction parameters [35]. Their scheme for the kinematic viscosity ν_m of a binary liquid mixture is described in Eqs. (7 – 9) as follows:

$$\ln(\nu_m) = \sum_{i=1}^{n} x_i^3 \ln(\nu_i M_i) + 3\sum_{i=1}^{n}\sum_{j=1}^{n} x_i^2 x_j \ln(\nu_{ij} M_{ij}) - \ln(M_{avg}) \quad (7)$$

Where, x_i, ν_i, M_i respectively correspond to molar fraction, kinematic viscosity, molar mass of component i constituting the mixture; M_{avg} the average molar mass of the mixture; ν_{ij}, M_{ij} binary interaction parameters which are estimated by using following relationships:

$$\frac{\nu_{ij}}{(\nu_i^2 \nu_j)^{1/3}} 1 + 0.044 \frac{(N_j - N_i)^2}{(N_i^2 N_j)^{1/3}} \quad (8)$$

$$M_{ij} = \frac{2M_i + M_j}{3} \quad (9)$$

Where, N_i is the carbon number of species i. The kinematic viscosity estimated from Eq. (7) can be converted into the dynamic viscosity by multiplying with the mixture density.

It is interesting to notice that although being successfully tested on binary liquid mixtures of n-alkanes, this scheme was also demonstrated to be suitable for estimating the viscosity of binary liquid mixtures containing 1-alcohols. Hussein *et al.* reported the prediction performance for these mixtures with an overall deviation of 1.2% [26]. The scheme is therefore included in this study for comparison purpose.

3.3. UNIFAC-VISCO model

Chevalier *et al.* [17], [36] developed a group contribution model, called UNIFAC-VISCO, for estimating the viscosity of liquid mixtures. This model is founded on the theory of Eyring and the UNIFAC group contribution concept, originally proposed by Fredenslund *et al.* [37] for predicting thermodynamic equilirium properties. In this model, the dynamic viscosity of a mixture is calculated by using Eq. (10):

$$ln(\eta_m) = \sum_{i=1}^{n} x_i \ln\left(\eta_i \frac{V_i}{V_m}\right) + \frac{\Delta^* g^{EC}}{RT} + \frac{\Delta^* g^{ER}}{RT} \quad (10)$$

The combinatorial term, $\Delta^* g^{EC}/RT$, accounting for differences in size and shape of species constituting the mixture under consideration, is calculated by:

$$\frac{\Delta^* g^{EC}}{RT} = \sum_{i=1}^{n} x_i ln\frac{\phi_i}{x_i} + 5\sum_{i=1}^{n} q_i x_i ln\frac{\theta_i}{\phi_i} \quad (11)$$

Where, ϕ_i and θ_i are the molecular surface area fraction and molecular volume fraction, respectively.

The residual term, $\Delta^* g^{ER}/RT$, accouting for the energy interaction between structural groups contained in the molecules constituting the mixture of interest, is calculated by using Eq. (12).

$$\frac{\Delta^* g^{ER}}{RT} = -\sum_{i=1}^{n} x_i \ln(\gamma_i^{*R}) \quad (12)$$

Where, γ_i^{*R} is assumed to be the difference between the sum of the individual contributions of each group k in the mixture and the sum of the individual contributions in the pure component environment. For Eqs. (10-12), the molecular parameters and group parameters are estimated by using the group contribution method. The calculation procedure with this model is detailed in the reference [34].

The UNIFAC-VISCO model was applied to correlate and predict the viscosity of many binary systems involving 1-alcohols [38], [39]. There is only one study which systematically evaluated the prediction performance of this scheme for binary liquid mixtures composed of 1-alcohols ranging from 1-hexanol to 1-dodecanol [27]. The predictive results reported within this study were very encouraging.

4. Results and discussion

In this section, the results of using three approaches for predicting the viscosity of binary liquid mixtures of 1-alcohols will be presented and discussed. The analysis is quantified by the average absolute deviation (AAD) between predicted values (η_{pred}) and measured values (η_{exp}), which is averaged over the number of data points n of a mixture considered, as shown in Eq. (13).

$$AAD = \frac{1}{n}\sum_{i=1}^{n} \frac{|\eta_{pred} - \eta_{exp}|}{\eta_{exp}} \times 100 \quad (13)$$

In order to help with the analysis, the discussion will be separated into two different parts. The first part is for binary liquid mixtures containing molecules of the carbon number smaller than 10 while the second one is for the rest of the database considered in this work (see Table 1). This is due to the fact that the RHS model was only developed for 1-alcohols ranging from methanol to 1-decanol, resulting in the unavailability of the characteristic parameters for V_o and R_η for species of the carbon number greater than 10.

4.1. Mixtures containing species of the carbon number smaller than 10

Table 2 summarizes AAD and MD (maximum deviation) for the prediction of the viscosity of binary mixtures of the carbon number smaller than 10 by using three models including the RHS, McAllister and UNIFAC-VISCO models. As shown in Table 2, the McAllister (with AAD of 1.26%) and UNIFAC-VISCO (with AAD of 2.00%) models are observed to give a better prediction compared to the RHS model (with AAD of 4.10%).

Table 2. *Comparison of the prediction of the viscosity of binary mixtures of the carbon number smaller than 10, by means of three models including RHS, McAllister, UNIFAC-VISCO*

Mixtures	RHS$^{(*)}$	McAllister$^{(*)}$	UNIFAC-VISCO$^{(*)}$
c2ol + c3ol	4.64 / 6.67	0.78 / 1.90	0.70 / -1.98
c2ol + c4ol	2.88 / 5.42	1.57 / -8.48	1.10 / 4.11
c2ol + c5ol	2.83 / 5.56	0.92 / 4.27	1.16 / -2.72
c2ol + c6ol	2.60 / 4.92	0.85 / 2.18	2.46 / -5.21
c2ol + c7ol	2.24 / -6.15	1.44 / 4.31	3.16 / -7.20
c2ol + c8ol	1.11 / -5.28	1.86 / -4.57	6.21 / -9.59
c2ol + c9ol	4.97 / -7.36	4.58 / -10.1	9.41 / -14.7
c2ol + c10ol	5.07 / -9.72	6.51 / -12.5	11.8 / -17.8
c3ol + c4ol	1.31 / 2.45	0.35 / 0.68	0.27 / -0.57
c3ol + c5ol	2.41 / 6.22	0.84 / 4.73	0.48 / -3.17
c3ol + c7ol	1.73 / -4.50	0.75 / 2.36	1.75 / -3.17
c3ol + c9ol	4.11 / -9.88	1.11 / -2.97	4.32 / -7.06
c4ol + c5ol	3.14 / -5.59	0.57 / 0.91	0.45 / 0.83
c4ol + c9ol	4.14 / -7.36	0.98 / -2.14	1.29 / -3.76
c4ol + c10ol	3.94 / -6.72	0.54 / -1.70	2.53 / -5.27

c5ol + c7ol	4.74 / -5.71	0.43 / -1.04	0.70 / -1.39
c5ol + c8ol	4.45 / -5.91	1.05 / 2.67	0.38 / 1.65
c5ol + c9ol	6.09 / -9.76	0.63 / 1.42	1.15 / -2.54
c6ol + c7ol	2.51 / -5.79	2.09 / 4.50	2.00 / 4.46
c6ol + c8ol	3.72 / -6.91	0.53 / 1.19	0.27 / 1.06
c6ol + c9ol	3.00 / -7.69	0.98 / 2.12	0.32 / 1.38
c6ol + c10ol	4.19 / -6.72	0.82 / 1.52	0.44 / -1.34
c7ol + c8ol	5.81 / -7.69	0.32 / 0.65	0.29 / -0.71
c7ol + c9ol	5.29 / -9.74	1.47 / 4.50	1.22 / 4.38
c7ol + c10ol	6.09 / -7.23	0.89 / 1.29	0.32 / 1.06
c8ol + c9ol	6.41 / -8.53	0.55 / -2.64	0.58 / -2.67
c8ol + c10ol	6.15 / -8.63	0.87 / 4.65	0.97 / 4.51
c9ol + c10ol	6.57 / -8.92	0.47 / 1.83	0.48 / 1.74
Average	***4.10 / -9.88***	***1.26 / -12.5***	***2.00 / -17.8***
(*) The first value in the column is AAD (%) and the second maximum deviation MD (%).			

Figure 1 presented an example of the viscosity calculation of the 1-Nonanol + 1-Decanol mixture by using three models. It showed that RHS underestimates the viscosity in comparison with the other two models which almost gave the same results. The high deviation when using the RHS model can be attributed to the use of simple mixing rules for the two characteristic parameters (V_o, R_η), which did not take into account the intermolecular interaction such as the hydrogen-bonding effects occurring in the studied mixtures. The same observation in the cases of using McAllister and UNIFAC-VISCO for the prediction purpose is partly due to the fact that the underlying theory used to develop these models is based on Eyring's reaction rate theory.

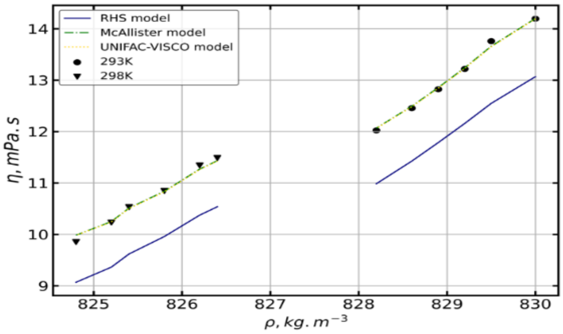

Figure 1. *Viscosity calculation for the 1-Nonanol + 1-Decanol mixture by using three models. The measured data are collected from reference [25]*

Figures 2 and 3 presented the deviation in predicting the viscosity by means of RHS and McAllister, respectively. As shown in Figure 3, it is worth noting that McAllister successfully represented the viscosity for mixtures of which ΔC is smaller than 7, with the estimated uncertainty of 4.2% and bias of -0.02%. It is interesting to note that the deviation produced by this model is weakly dependent upon the asymmetry of the mixtures. In contrast, the calculation with RHS do not follow the same pattern (see. Figure 2). The unexpectedly high deviations (outside 5% range) are observed for mixtures containing long-chain molecules such as 1-Hexanol, 1-Heptanol, 1-Octanol, 1-Nonanol, and 1-Decanol. Nevertheless, the prediction within the RHS scheme is generally very encouraging because the model is purely predictive with the use of only molecular properties of 1-alcohols. Unlike McAllister and UNIFAC-VISCO, there is no need of using the viscosity values of pure species as an input in the RHS scheme.

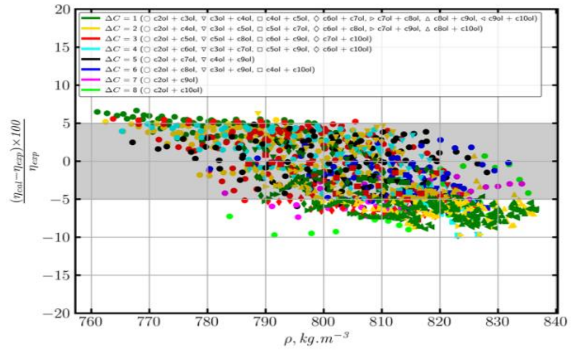

Figure 2. *Deviation of the experimental data from the calculated values by means of the RHS model. ΔC is the difference in carbon number of two species in mixtures considered*

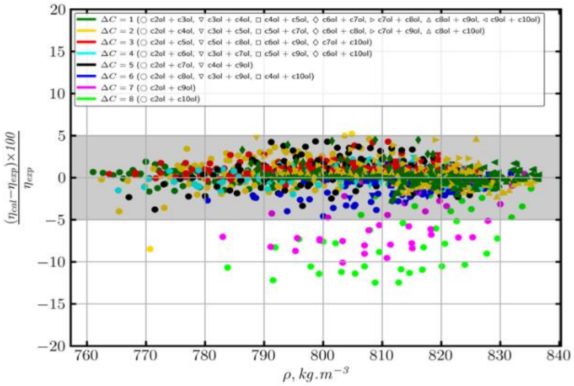

Figure 3. *Deviation of the experimental data from the calculated values by means of the McAllister model. ΔC is the difference in carbon number of two species in mixtures considered*

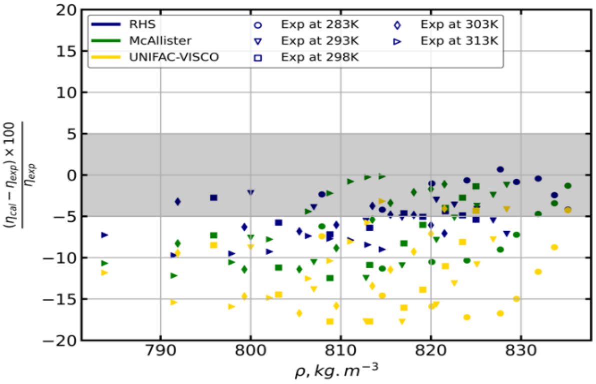

Figure 4. *Deviations in predicting the viscosity of the Ethanol + 1-Decanol mixture by using models including RHS, McAllister, and UNIFAC-VISCO*

With regard to $\Delta C > 7$, namely highly asymmetrical mixture, both models (RHS and McAllister) exhibit the same behavior for the mixtures including Ethanol + 1-Nonanol, Ethanol + 1-Decanol, as demonstrated in Figures 2 and 3. Similarly, UNIFAC-VISCO also failed to reproduce the viscosity of highly asymmetrical mixtures, as depicted in Figure 4. The RHS model performs rather better than the other two models, namely, McAllister and UNIFAC-VISCO, with AAD of 5% and MD of 10% which were also reported for this scheme being applied for n-alkane systems [40]. It is also interesting to note that as of this mixture the RHS model performs better at low molar fraction of small molecule like Ethanol.

4.2. Mixtures containing species of the carbon number greater than 10

Table 3. *Comparison of the prediction of the viscosity of binary mixtures of the carbon number greater than 10, by means of McAllister and UNIFAC-VISCO*

Mixtures	McAllister$^{(*)}$	UNIFAC-VISCO$^{(*)}$
c3ol + c11ol	3.60 / -6.91	7.85 / -10.7
c5ol + c11ol	1.92 / -4.77	3.4 / -6.13
c6ol + c11ol	1.95 / 4.89	1.18 / 4.41
c6ol + c12ol	0.57 / 1.87	1.41 / -3.11
c7ol + c11ol	2.35 / 6.41	2.19 / 6.04
c7ol + c12ol	1.77 / 5.58	1.42 / 5.10
c8ol + c11ol	1.36 / 5.67	1.56 / 5.43
c8ol + c12ol	1.13 / 3.76	0.84 / 3.07
c9ol + c10ol	0.50 / 1.25	0.51 / 1.21
c9ol + c11ol	0.87 / -3.96	0.88 / -4.30
c9ol + c12ol	0.32 / 0.67	0.22 / -0.55
Average	***1.13 / -6.91***	***1.30 / -10.7***

(*) The first value in the column is AAD (%) and the second maximum deviation MD (%).

As previously mentioned, RHS cannot be extended for species of the carbon number greater than 10. The analysis is hence performed only for McAllister and UNIFAC-VISCO in this section. Table 3 summarized the results in calculating the viscosity of mixtures containing species of the carbon number greater than 10. It can be seen that both models worked very well for calculating the viscosity of the mixtures considered, except for the mixture of 1-Propanol and 1-Undecanol in the case of using UNIFAC-VISCO. The estimated uncertainty and bias are respectively 4.02% and 0.15% for the McAllister model, 5.05% and -0.6% for the UNIFAC-VISCO model.

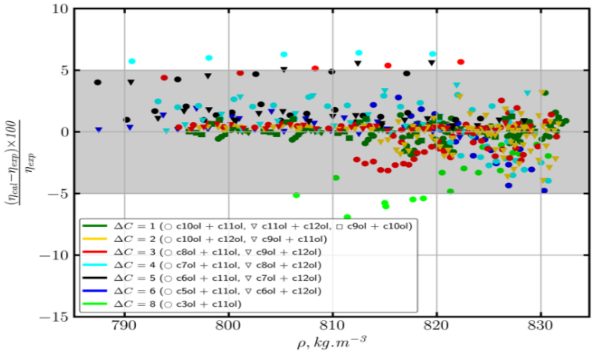

Figure 5. *Percentage deviation of the experimental data from the calculated values by means of the McAllister model. ΔC is the difference in carbon number of two species in mixtures considered*

As shown in Figure 5, the McAllister model reproduced with a good agreement the viscosity of mixtures where the difference in carbon number is smaller than 7. Unlike the previous observation for Ethanol + 1-Decanol, the model can capture well the measured viscosity of the mixture of 1-Propanol + 1-Undecanol (at the same value of $\Delta C = 8$). This results in the need of improving the scheme to take into consideration the presence of small molecules like Ethanol.

Also observed in Figure 5, the McAllister model resulted in high deviations for the 1-Heptanol + 1-Undecanol mixture (outside 5% range) measured by Pinto *et al.* [27]. In order to verify the quality of the measured viscosity for this system, the viscosities measured by Pinto *et al.* was replaced the ones measured by Hussein *et al.* [26] at the similar conditions of the measurements (*i.e.*, temperature, pressure, composition). Because of lacking the experimental data at other conditions, only measurements at 298.15K were evaluated in this section. The new calculation was presented in Figure 6.

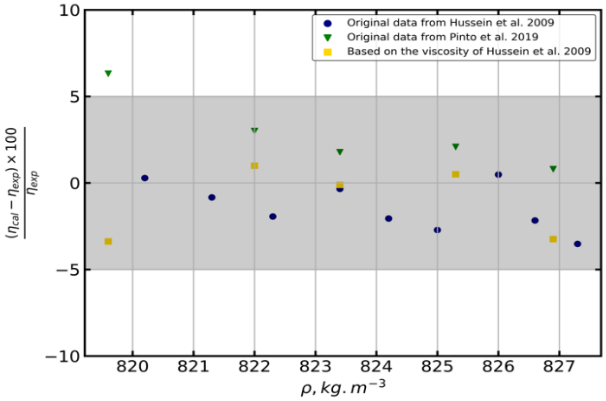

Figure 6. *Viscosity prediction for the mixture of 1-Heptanol + 1-Undecanol by using the McAllister model, with various measured values*

As clearly shown on Figure 6, the deviation from new measured values for this mixture was much improved, with the new AAD of 1.65% (yellow squares) compared to the value of 2.8% (green triangles) based on the original data published by Pinto *et al.* [27].

5. Conclusion

The main objective of this work is to evaluate the predictive capabilities of three semi-theoretical models for the viscosity of binary liquid mixtures containing only 1-alcohols. Regarding the mixtures where the difference in carbon number is not very large ($\Delta C \leq 8$) the McAllister model is highly recommended for predicting the viscosity of binary mixtures, with AAD of 1.23%. The prediction should be taken carefully with mixtures containing small molecules like Ethanol. In the same way as the McAllister model showed, the prediction with the use of UNIFAC-VISCO is also very encouraging, with AAD of 1.82%. The application of the group contribution concept in predicting the viscosity is considered a promising method for characterizing complex industrial fluids of which the composition is very often ill-defined. It should be noted as of using these two models that the quality of the prediction strongly depends on the quality of viscosity values of pure components at the same condition. One of the main advantages of the RHS model in predicting the viscosity of the mixtures lies in the fact that there is no need of pure component information as the other two models do. The results produced by this scheme in this study is also very promising. The prediction could be much improved if the mixing rules for characteristic parameters of this scheme will be further considered in future.

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REFERENCE

[1] E. Hendriks *et al.*, “Industrial Requirements for Thermodynamics and Transport Properties”, *Ind. Eng. Chem. Res.*, vol. 49, no. 22, pp. 11131–11141, Nov. 2010, doi: 10.1021/ie101231b.

[2] M. J. Assael, A. R. H. Goodwin, V. Vesovic, and W. A. Wakeham, *Experimental Thermodynamics Series, Vol. IX. Advances in Transport Properties.* Cambridge: The Royal Society of Chemistry, 2014.

[3] M. Lapuerta, J. Rodríguez-Fernández, R. Patiño-Camino, A. Cova-Bonillo, E. Monedero, and Y. M. Meziani, “Determination of optical and dielectric properties of blends of alcohol with diesel and biodiesel fuels from terahertz spectroscopy”, *Fuel*, vol. 274, p. 117877, 2020, doi: https://doi.org/10.1016/j.fuel.2020.117877.

[4] L. T. Vargas-Ibáñez, G. A. Iglesias-Silva, J. J. Cano-Gómez, C. Escamilla-Alvarado, and M. A. Berrones-Eguiluz, “Densities and Viscosities for Binary Liquid Mixtures of Biodiesel + 1-Pentanol, 2-Pentanol, or 2-Methyl-1-Butanol from (288.15 to 338.15) K at 0.1 MPa”, *J. Chem. Eng. Data*, vol. 63, no. 7, pp. 2438–2450, Jul. 2018, doi: 10.1021/acs.jced.7b00996.

[5] A. Moreau, M. Sobrino, J. Zambrano, J. J. Segovia, M. A. Villamañán, and M. Carmen Martín, “Viscosities and densities of different alcohols (1-propanol, 2-propanol, 1-pentanol and 2-pentanol) at high pressures”, *J. Mol. Liq.*, vol. 344, p. 117744, 2021, doi: https://doi.org/10.1016/j.molliq.2021.117744.

[6] W. D. Monnery, W. Y. Svrcek, and A. K. Mehrotra, “Viscosity: A critical review of practical predictive and correlative methods”, *Can. J. Chem. Eng.*, vol. 73, no. 1, pp. 3–40, Feb. 1995, doi: https://doi.org/10.1002/cjce.5450730103.

[7] D. S. Viswanath, T. K. Ghosh, D. H. L. Prasad, N. V. K. Dutt, and K. Y. Rani, “THEORIES OF VISCOSITY BT - Viscosity of Liquids: Theory, Estimation, Experiment, and Data”, D. S. Viswanath, T. K. Ghosh, D. H. L. Prasad, N. V. K. Dutt, and K. Y. Rani, Eds. Dordrecht: Springer Netherlands, 2007, pp. 109–133.

[8] A. J. Queimada, L. I. Rolo, A. I. Caco, I. M. Marrucho, E. H. Stenby, and J. A. P. Coutinho, “Prediction of Viscosities and Surface Tensions of Fuels Using a New Corresponding States Model”, *Fuel*, vol. 85, pp. 874–877, 2006.

[9] F. Llovell, R. M. Marcos, and L. F. Vega, “Transport Properties of Mixtures by the soft-SAFT + Free-Volume Theory: Application to Mixtures of n-Alkanes and Hydrofluorocarbons”, *J. Phys. Chem. B*, vol. 117, pp. 5195–5205, 2013.

[10] S. E. Quinones-Cisneros, C. K. Zeberg-Mikkelsen, and E. H. Stenby, “Friction Theory Prediction of Crude Oil Viscosity at Reservoir Conditions Based on Dead Oil Properties”, *Fluid Phase Equilib.*, vol. 212, pp. 233–243, 2003.

[11] S. E. Quinones-Cisneros and U. K. Deiters, “Generalization of the Friction Theory for Viscosity Modeling”, *J. Phys. Chem. B*, vol. 110, no. 25, pp. 12820–12834, 2006.

[12] Y. Rosenfeld, “Relation between the Transport Coefficients and the Internal Entropy of Simple Systems”, *Phys. Rev. A.*, vol. 15, p. 2545, 1977.

[13] E. R. Lopez, A. S. Pensado, M. J. P. Comunas, A. A. H. Padua, and J. Fernandez, “Density Scaling of the Transport Properties of Molecular and Ionic Liquids”, *J. Chem. Phys.*, vol. 134, vol. 14, p. 144507, 2011.

[14] M. J. Assael, J. H. Dymond, M. Papadaki, and P. M. Patterson, “Correlation and prediction of dense fluid transport coefficients. I. n-alkanes”, *Int. J. Thermophys.*, vol. 13, no. 2, pp. 269–281, 1992.

[15] V. Vesovic and W. A. Wakeham, “Prediction of the Viscosity of Fluid Mixtures over Wide Ranges of Temperature and Pressure”, *Chem. Eng. Sci.*, vol. 44, no. 10, pp. 2181–2189, 1989.

[16] R. A. McAllister, “The viscosity of liquid mixtures”, *AIChE J.*, vol. 6, no. 3, pp. 427–431, 1960, doi: https://doi.org/10.1002/aic.690060316.

[17] J. L. Chevalier, P. Petrino, and Y. Gaston-Bonhomme, “Estimation method for the kinematic viscosity of a liquid-phase mixture”, *Chem. Eng. Sci.*, vol. 43, no. 6, pp. 1303–1309, 1988, doi: https://doi.org/10.1016/0009-2509(88)85104-2.

[18] J. H. Dymond, “The interpretation of transport coefficients on the basis of the Van der Waals model. I dense fluids”, *Physica*, vol. 75, no. 1, pp. 100–114, 1974, doi: 10.1016/0031-8914(74)90294-8.

[19] M. J. Assael, J. H. Dymond, and P. M. Patterson, “Correlation and prediction of dense fluid transport coefficients. V. Aromatic hydrocarbons”, *Int. J. Thermophys.*, vol. 13, no. 5, pp. 895–905, 1992, doi: 10.1007/BF00503914.

[20] M. J. Assael, J. H. Dymond, and S. K. Polimatidou, “Correlation and prediction of dense fluid transport coefficients. VI.n-alcohols”, *Int. J. Thermophys.*, vol. 15, no. 2, pp. 189–201, 1994, doi: 10.1007/BF01441581.

[21] J. J. Cano-Gómez, G. A. Iglesias-silva, M. Ramos-estrada, and K. R. Hall, “Densities and Viscosities for Binary Liquid Mixtures of Ethanol + 1-Propanol, 1-Butanol, and 1-Pentanol from (293.15 to 328.15)K at 0.1 MPa”, *J. Chem. Eng. Data*, vol. 57, no. 9, pp. 2560–2567, 2012.

[22] M. A. F. Faria, R. J. Martins, M. J. E. M. Cardoso, and O. E. Barcia, “Density and viscosity of the binary systems ethanol + butan-1-ol, + pentan-1-ol, + heptan-1-ol, + octan-1-ol, nonan-1-ol, + decan-1-ol at 0.1 mpa and temperatures from 283.15 K to 313.15 K.”, *J. Chem. Eng. Data*, vol. 58, no. 12, pp. 3405–3419, 2013, doi: 10.1021/je400630f.

[23] J. J. Cano-Gómez, G. A. Iglesias-Silva, E. O. Castrejón-González, M. Ramos-Estrada, and K. R. Hall, “Density and Viscosity of Binary Liquid Mixtures of Ethanol + 1-Hexanol and Ethanol + 1-Heptanol from (293.15 to 328.15) K at 0.1 MPa”, *J. Chem. Eng. Data*, vol. 60, no. 7, pp. 1945–1955, 2015, doi: 10.1021/je501133u.

[24] Z. Shan and A. F. A. Asfour, “Viscosities and densities of eight binary 1-alkanol systems at 308.15 and 313.15 K”, *Fluid Phase Equilib.*, vol. 143, no. 1–2, pp. 253–262, 1998, doi: 10.1016/s0378-3812(97)00267-7.

[25] Z. Shan and A. F. A. Asfour, “Viscosities and densities of nine binary 1-alkanol systems at 293.15 K and 298.15 K”, *J. Chem. Eng. Data*, vol. 44, no. 1, pp. 118–123, 1999, doi: 10.1021/je980177x.

[26] N. M. Hussein and A. F. A. Asfour, “Densities and kinematic viscosities of ten binary 1-alkanol liquid systems at temperatures of (293.15 and 298.15) K”, *J. Chem. Eng. Data*, vol. 54, no. 10, pp. 2948–2952, 2009, doi: 10.1021/je800497u.

[27] C. N. Pinto, G. Z. Frugoli, P. M. Florido, G. V. Atzingen, C. E. C. Rodrigues, and C. B. Gonçalves, “Viscosities and Densities of Fatty Alcohol Mixtures from 298.15 to 338.15 K: Estimation by Kay’s Rule and Prediction by the UNIFAC-VISCO and GC-UNIMOD Group Contribution Methods”, *J. Chem. Eng. Data*, vol. 64, no.5, pp. 1937–1947, 2019, doi: 10.1021/acs.jced.8b00992.

[28] M. A. França Faria *et al.*, “Measurement of density and viscosity of binary 1-alkanol systems (C 8-C11) at 101 kPa and temperatures from (283.15 to 313.15) K”, *J. Chem. Eng. Data*, vol. 50, no. 6, pp. 1938–1943, 2005, doi: 10.1021/je050200w.

[29] M. J. Assael, J. H. Dymond, M. Papadaki, and P. M. Patterson, “Correlation and Prediction of Dense Fluid Transport Coefficients. III. n-Alkane Mixtures”, *Int. J. Thermophys.*, vol. 13, pp. 659–669, 1992.

[30] M. J. Assael, A. E. Kalyva, K. E. Kakosimos, and K. D. Antoniadis, “Correlation and Prediction of Dense Fluid Transport Coefficients. VIII. Mixtures of Alkyl Benzenes with Other Hydrocarbons”, *Int. J. Thermophys.*, vol. 30, no. 6, p. 1733, 2009, doi: 10.1007/s10765-009-0682-3.

[31] V. V. Chandramouli and G. S. Laddha, “Viscosity of ternary liquid mixtures”, *Indian J. Technol.*, vol. 1, no. 5, pp. 199–203, 1963.

[32] R. Kalidas and G. S. Laddha, “Viscosity of Ternary Liquid Mixtures.”, *J. Chem. Eng. Data*, vol. 9, no. 1, pp. 142–145, Jan. 1964, doi: 10.1021/je60020a048.

[33] J. Wu and A. F. A. Asfour, “Viscometric Properties of n-Alkane Liquid Mixtures”, *Fluid Phase Equilib.*, vol. 76, pp. 283–294, 1992.

[34] B. E. Poling, J. M. Prausnitz, and J. P. O’Connell, *The properties of gases and liquids*, 5th ed. New York SE - 1 volume (various pagings) : illustrations ; 24 cm: McGraw-Hill New York, 2001.

[35] A. F. A. Asfour, E. F. Copper, J. Wu, and R. R. Zahran, “Prediction of the McAllister model parameters from pure component properties for liquid binary n-alkane systems”, *Ind. Eng. Chem. Res.*, vol. 30, no. 7, pp. 1666–1669, Jul. 1991, doi: 10.1021/ie00055a040.

[36] Y. Gaston-Bonhomme, P. Petrino, and J. L. Chevalier, “UNIFAC—VISCO group contribution method for predicting kinematic viscosity: extension and temperature dependence”, *Chem. Eng. Sci.*, vol. 49, no. 11, pp. 1799–1806, 1994, doi: https://doi.org/10.1016/0009-2509(94)80065-0.

[37] A. Fredenslund, R. L. Jones, and J. M. Prausnitz, “Group-contribution estimation of activity coefficients in nonideal liquid mixtures”, *AIChE J.*, vol. 21, no. 6, pp. 1086–1099, Nov. 1975, doi: https://doi.org/10.1002/aic.690210607.

[38] A. Rodríguez, J. Canosa, A. Domínguez, and J. Tojo, “Viscosities of dimethyl carbonate with alcohols at several temperatures: UNIFAC-VISCO interaction parameters (-OCOO-/alcohol)”, *Fluid Phase Equilib.*, vol. 216, no. 1, pp. 167–174, 2004, doi: 10.1016/j.fluid.2003.10.014.

[39] B. González, N. Calvar, Á. Domínguez, and J. Tojo, “Dynamic viscosities of binary mixtures of cycloalkanes with primary alcohols at T = (293.15, 298.15, and 303.15) K: New UNIFAC-VISCO interaction parameters”, *J. Chem. Thermodyn.*, vol. 39, no. 2, pp. 322–334, 2007, doi: 10.1016/j.jct.2006.06.008.

[40] T.-B. Nguyen, N. Riesco, and V. Vesovic, “Predicting the viscosity of n-alkane liquid mixtures based on molecular description”, *Fuel*, vol. 208, pp. 363–376, 2017.