



Experimental data and modeling of viscosities and densities of pyrene + toluene + heptane mixtures at $T = (293.15 \text{ to } 343.15) \text{ K}$



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ABSTRACT

Oil mixtures are a complex system that remains unclear. Its study is particularly challenging due to the many variables involved in their properties. These include, for instance, the compositions of the mixture and the nature of their compounds. To simplify the study of these systems, it is proposed to model them with simpler mixtures, as in the case of using hydrocarbon mixtures to describe the behavior of crude oil. Two mixtures have been prepared; the one hand, a binary mixture of pyrene in toluene, and on the other hand, a ternary mixture of pyrene in toluene/heptane has been prepared. Their densities and dynamic and kinematic viscosities have been measured from (293.15 to 343.15) K at atmospheric pressure. The compositions of binary and ternary systems are 1.0, 2.5, 5.0, 7.5, 10.0, 12.5, and 15.0 % weight fraction of pyrene. In the case of ternary systems, several toluene/heptane mass ratios have been studied, from 0.1 to 10. This article presents new experimental results of density and viscosity for the mixtures studied.

Therefore, a theoretical study has been carried out to describe experimental data. Viscosity models, such as Ideal, Refutas, Ratcliff, UNIFAC-Visco, and Krieger, have been checked and, in some cases, have been modified to analyze the dependence of viscosity on temperature, composition, and possible association of pyrene. Standard deviations for each model and system have been calculated. Modified Ratcliff and Krieger models presented an excellent agreement with experiments.

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1. Introduction

Crude oil is classified as light or heavy based on different physical properties, such as molecular weight, viscosity, density, and API gravity [1]. Viscosity is an important physical property in crude oil mixtures since high viscosity values can cause significant problems during oil production and transport, and it plays a crucial role in reservoir evaluation, performance calculation, reservoir simulation, forecasting production, and designing production facilities, as well as planning thermal enhanced oil recovery methods. Understanding the viscosity of crude oil systems under production and transportation conditions is a significant advantage in successful exploitation strategy and production design [2]. The viscosity of crude oils is highly affected by operating pressure and temperature and their composition in terms of asphaltene, wax, resin, and aromatics. The high viscosity of crude oil mixtures is usually due to the presence of solid particles forming emulsions related to heavy asphaltene components [3], whose presence results in some undesirable problems in the petroleum industry field [4]. Several aspects influence the size of the aggregates generated [5], such

as the oil's pressure and temperature, and the medium's composition [6]. There is no direct relation to the amount of asphaltene, but additional structural effects such as the structure of the asphaltene molecule, the π - π interaction, the branching of aliphatic chains, and the degree of aggregation determine the stability and size of aggregates.

The viscosities of crude oil mixtures are commonly estimated by empirical correlations, usually from very scarce information related to the density of the mixture and the operating temperature. Generally, poor results are obtained, and their improvement requires additional information related to the fluid's composition, especially asphaltene and similar complex aromatic systems [4].

The high number of components in petroleum mixtures makes difficult the application of such methods, and the study of mixtures formed by a few components representatives of the petroleum composition can give some view of the limitations of proposed models. The viscosity of simpler mixtures with few components is also essential for detailed design and optimizing industrial processes, such as heat and mass transfer, separation processes, and reaction engineering [7,8], and these values are significant in elucidating the behavior of liquids and their mixtures [9–11].

Unfortunately, viscosity is a complex property, and even for much simpler systems, there is not a helpful model able to predict

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its viscosity in a wide range of conditions. Roelands proposed an empirical equation to characterize the viscosity variation of mineral oils with temperature [12]. The review [13] is focused on the viscosity of pure components; it applies seven different theoretical models, showing their limitations in the range of pressure and temperature. Numerous molecular modeling methods have been reported in the literature for viscosity calculations for simple molecules such as water [14] and complex systems such as asphaltenes [15]. These methods include quantitative structure-property relationships (QSPR), equations of state (EOS), group contribution (GC), and molecular dynamics (MD) simulations [16].

Extension to mixtures requires introducing mixing rules to describe the composition effect, and reference [17] classifies mixing rules into two main groups: pure mixing rules, including those based on the viscosity blending index [18], and mixing rules with additional binary parameters, including those with a named excess function [19]. Arrhenius, and Grunberg, and Nissan model described the viscosity for the ideal mixtures, Redlich–Kister extension included non-idealities [20], Chevalier *et al.* [21] proposed a method of predicting a liquid-phase mixture's kinematic viscosity from the pure components' known viscosity and included the deviation to ideality determined by a group contribution method, the UNIFAC-Visco model. Ratcliff and Khan predicted the viscosity for multicomponent systems using a viscosity deviation function to account for deviation from ideality [17]. The viscosity models of a colloidal suspension or macromolecular solution introduce volume fractions and parameters that provide some view into the inter-particle interactions and the interactions with the continuous phase. The Einstein model and their modifications, Pal-Rhodes, Mooney, Eiler and Krieger and Dougherty models [22], determine the relative viscosity as a function of solvent viscosity and intrinsic viscosity.

This work aims to provide a comprehensive set of experimental values for density and viscosity for mixtures formed by pyrene + toluene + heptane, covering from (293.15 to 343.15) K at atmospheric pressure and several compositions: 1.0, 2.5, 5.0, 7.5, 10.0, 12.5 and 15.0 % mass fraction of pyrene. Several models proposed to describe viscosity will be checked and modified to introduce additional effects, such as temperature or association. Several kinds of models were considered, including some with predictive mixing rules ideal [17], Refutas [17], the Ratcliff [17] model with deviation function including interaction parameters, the UNIFAC-Visco [21] as a predictive model based on group contribution, and the Krieger [22] as representative of dispersion models.

2. Experimental section

2.1. Materials

Chemicals used in this work are listed in Table 1 next to CAS N°, supplier, and mass fraction purity. The supplier specified purities, and all chemicals were used without further purifications.

2.2. The samples preparation and injection method

The binary and ternary mixtures were prepared in the composition range: 1.0, 2.5, 5.0, 7.5, 10.0, 12.5, and 15.0 w % of pyrene. To

prepare binary mixtures, pyrene and toluene were weighed at room temperature and atmospheric pressure using a Sartorius balance (Model: 15205974) with an accuracy of ± 0.0001 g and added to a glass 100 ml vial with a Teflon magnetic bar. The mixtures were kept at a constant temperature (303.15 K) and stirred in a silicon bath for 2 h to ensure that a homogeneous mixture was obtained. The ternary mixtures were prepared at the same composition range of polyaromatic compound: 1.0, 2.5, 5.0, 7.5, 10.0, 12.5, and 15.0 w % of pyrene, and for each of these pyrene compositions, the mass ratios of solvents toluene/heptane, r (g/g), were: 0.1, 0.5, 1.0, 5.0 and 10.0. In a previous work [23], a similar approach was described to prepare the samples, firstly, pyrene was dissolved in toluene at 313.15 K, and then a corresponding amount of heptane was added. The ternary mixtures were stirred at 323.15 K for 12 h. Those mixtures with a higher concentration of pyrene and heptane could not be measured because the pyrene did not completely dissolve. The standard deviation in the composition for the samples was 0.1 %.

After the preparation of the solutions, the correct preparation of the samples for density and viscosity measurements was carried out according to the following temperature profile:

- The sample was heated at 323.15 K in a silicon bath to completely dissolve the possible solid phase.
- Sample was injected using a syringe previously heated at 323.15 K.
- Measurement cell was kept at 323.15 K after the sample was injected, then heated to 343.15 K.
- Viscosity and density measurements were made in a cooling ramp from 343.15 K to 293.15 K at a 5 K interval.

2.3. Viscometer

The dynamic viscosity and density measurement for the different samples was performed using a viscometer Stabinger SVM 3001/G2 [24] at several temperatures. Kinematic viscosity was computed. The temperature was determined with an integrated Pt100 sensor. The temperature in the cell was controlled to ± 0.0 1 K. In addition, a standard type APS3, Lot. No.: 3200405, supplied by the manufacturer (Anton Parr), has been chosen to measure its density and viscosity from 293.15 K to 343.15 K. The expanded uncertainty providing a level of confidence of approximately 95 % for density is $1 \cdot 10^{-1}$ kg·m⁻³ and for kinematic and dynamic viscosity is $7.0 \cdot 10^{-4}$ mm²·s⁻¹ and $7.0 \cdot 10^{-4}$ mPa·s, respectively. The data obtained in this work were compared to certificate of calibration and the expanded uncertainties reported were estimated at: $1 \cdot 10^{-1}$ kg·m⁻³ for density, $5.0 \cdot 10^{-4}$ mm²·s⁻¹ for kinematic viscosity and $4.0 \cdot 10^{-4}$ mPa·s for dynamic viscosity.

3. Calculation section

Analysis of viscosity versus temperature curves requires the use of well-known viscosity models (Arrhenius, Fulcher, Walther, Geniesse, Crouch, Roelands, Wright, Manning [25,26]). The composition effect is considered through mixing rules. Reference [17] classifies mixing rules into two main groups: pure mixing rules, including those based on the viscosity blending index, and mixing rules with

Table 1
Chemicals used in this work.

Name	CASR No.	Formula	Supplier	Mass fraction purity
heptane	142–82-5	C ₇ H ₁₆	Scharlau	99 %
toluene	108–88-3	C ₇ H ₈	Scharlau	99.9 %
pyrene	129–00-0	C ₁₆ H ₁₀	Alfa Aesar	99 %

additional binary parameters, including those with an excess function.

Table 2 describes all the viscosity models used in this work. Some modifications were introduced to properly describe the experimental behavior. In this work, the Roelands model [27] was used to describe pure component viscosity of pyrene as a function of temperature. Refutas model [28] is widely used due to similarity to ASTM 341 [29], but it is easier to be applied on multicomponent mixtures.

Ratcliff and Khan model [30] obtains mixture viscosity from pure component values and a deviation function, $\Delta(\ln v)$, that includes interaction parameters and represents the ideality deviation. Deviation function is clear for binary mixtures, $\Delta(\ln v)_b$, but two options will be checked in this work for ternary systems, $\Delta(\ln v)_{t1}$ and, $\Delta(\ln v)_{t3}$. To improve obtained results, and include the temperature effect, a linear dependence was added to $\Delta(\ln v)_{t1}$, $a_{123} = a_{123,0} + a_{123,1}T$, and similarly could be done for the binary parameters in $\Delta(\ln v)_{t3}$.

UNIFAC-Visco model for viscosity predictions [31], contains the well-known combinatorial and residual contributions of the UNIFAC model to the excess Gibbs energy, $G^{E,C}$ and $G^{E,R}$, and the binary interaction parameters, a_{nm} , between groups n and m , involved in the residual term, are introduced through the interaction parameter-temperature function Ψ_{nm} . Where, as described in Gaston-Bonhomme et al. [32], the value for temperature T is replaced by the reference value 298 K. Consequently, the temperature effect is not introduced through the model but by the pure component properties (viscosity, molar volume) and by the mixture molar volume.

UNIFAC-Visco can describe viscosities for systems with components very different in size and multicomponent hydrocarbon mixtures [33]. However, the available interaction parameters are very scarce and were less studied than those for activity coefficients.

A simplified method to quantify an possible association process due to the π - π interaction of pyrene molecules was carried out through the UNIFAC method. When two pyrene molecules are associated, they can be considered a supra-molecular species where the number of UNIFAC groups, molecular structural parameters, r and q , and molecular weight are double values. Still, consequently, the mole fraction is half value.

An association factor, f_a , was introduced according to $n_k^{(1)} = f_a n_k^{(1,0)}$, where $n_k^{(1,0)}$ represents the number of k -groups in component 1 (pyrene) as a single molecule, if association occurs

Table 2
Viscosity models.

Model	Equation	Parameters	Composition	Ref.
Roelands	$\ln(\ln(\eta + 4.2)) = -S_0 \cdot \ln(1 + \frac{T}{135}) + \ln(G_0)$	S_0, G_0	-	[27]
Refutas	$VBI_i = 23.097 + 33.469 \log(\log(v_i + 0.8))$ $VBI_m = \sum w_i VBI_i$ $v_m = 10^{10 \left(\frac{VBI_m - 23.097}{33.469} \right)} - 0.8$		w_i	[28]
Ideal	$\ln v_m^{id} = \sum \varphi_i \ln v_i$		φ_i	
Ratcliff	$\ln v_m = \ln v_m^{id} + \Delta(\ln v)$ $\Delta(\ln v)_b = a_{ij} w_i w_j$ $\Delta(\ln v)_{t1} = a_{123} w_1 w_2 w_3$ $\Delta(\ln v)_{t3} = a_{12} w_1 w_2 + a_{13} w_1 w_3 + a_{23} w_2 w_3$	$a_{123} = a_{123,0} + a_{123,1}T$ a_{ij}	w_i	[30]
UNIFAC-Visco	$\ln \eta_m = \sum x_i \ln \left(\eta_i \frac{v_i}{v_m} \right) + \frac{G^{E,C}}{RT} - \frac{G^{E,R}}{RT}$ $\Psi_{nm} = \exp\left(-\frac{a_{nm}}{298}\right)$ $n_k^{(1)} = f_a n_k^{(1,0)}$; $f_a = 1 + a_{tol} w_{tol}^2 + a_{c7} w_{c7}^2$	a_{nm} a_i	x_i	[31]
Krieger	$v_r = \frac{v_m}{v_{m1}}$; $v_r = \left(1 - \frac{\varphi}{\varphi_m}\right)^{-[\eta] \cdot \varphi_m}$ $v_m = v_m^{id} \left(\frac{\varphi_m - \varphi}{\varphi_m - \varphi^{id}} \right)^{-[\eta] \cdot \varphi_m}$ $\frac{\varphi_m - \varphi}{\varphi_m - \varphi^{id}} = 1 + b_{tol} \varphi_{tol}^2 + b_{c7} \varphi_{c7}^2$	$[\eta]: \varphi_m$ $b_i = b_{i,0} + b_{i,1}T$	φ_i	[34]

η : dynamic viscosity, v : kinematic viscosity, T : temperature, w : mass fraction, φ : volume fraction, x : mole fraction, VBI : viscosity blending index, v : molar volume, G^E : excess Gibbs energy, Ψ_{nm} : interaction parameter-temperature UNIFAC function, subscript i and j refers to components i and j , and m to the mixture.

and $f_a > 1$ the number of groups increases to $n_k^{(1)}$, from that change, values for r , q , and M_w will be further changed.

The association factor was assumed composition-dependent, depending on both the toluene and heptane content. Several forms were tested and optimal was that given by $f_a = 1 + a_{tol} w_{tol}^2 + a_{c7} w_{c7}^2$.

Specific models can be used for a mixture that can be considered as a dispersed system. Relative viscosity is defined as the relation between experimental kinematic viscosity and those for a liquid in absence of dispersed phase, $v_r = \frac{v_m}{v_{m1}}$.

In this work, the model of Krieger-Dougherty [34] was supposed to describe the variation of viscosity with the volume fraction, φ , of the dispersed phase over a wide range. Involved parameters are the maximum volume fraction of the dispersed phase for which the fluid can flow, φ_m , and the intrinsic viscosity, $[\eta]$. This model does not consider particle interaction but assumes a hard-sphere suspension with random packing in a Newtonian fluid [35].

Combining the definition of ideal viscosity and the Krieger model, and assuming that nonidealities affect only φ but not φ_m and $[\eta]$, the following expression can be obtained:

$$v_m = v_m^{id} \left(\frac{\varphi_m - \varphi}{\varphi_m - \varphi^{id}} \right)^{-[\eta] \cdot \varphi_m}$$

The ratio $\frac{\varphi_m - \varphi}{\varphi_m - \varphi^{id}}$ account the difference in aggregates fraction between the actual solution and that with ideal behavior. A value higher than 1 is due to $\varphi < \varphi^{id}$; this represents a disaggregation process. The meaning of such an equation is that deviation from ideal behavior is due to the change in the association between molecules that changes the magnitude φ ; in this work, it was assumed that pyrene is responsible for such change.

Such ratio was correlated against composition of toluene and heptane similarly to f_a in UNIFAC-Visco model, $\frac{\varphi_m - \varphi}{\varphi_m - \varphi^{id}} = 1 + b_{tol} \varphi_{tol}^2 + b_{c7} \varphi_{c7}^2$.

To improve obtained results and include the temperature effect, a linear dependence was added to a_i parameters, $b_i = b_{i,0} + b_{i,1}T$. Where subscript i apply both for toluene and heptane.

4. Results and discussion

4.1. Experimental data

Viscosities and densities of pure liquid components, toluene, and heptane, listed in Table 3, were measured at a temperature

Table 3

Comparison of the experimental density (ρ), dynamic viscosity (η), and kinematic viscosity (ν) of pure liquids at T = (293.15 to 343.15) K and atmospheric pressure (P = 101.6 kPa) with literature values.

Compound	T/K	$\rho/(10^3 \text{ kg}\cdot\text{m}^{-3})$	$\eta/(\text{mPa}\cdot\text{s})$	$\nu/(\text{mm}^2\cdot\text{s}^{-1})^*$	$\rho/(10^3 \text{ kg}\cdot\text{m}^{-3})$ lit.	$\eta/(\text{mPa}\cdot\text{s})$ lit.	
Toluene	293.15	0.8659	0.5338	0.6165	0.8657 ^c , 0.86684 ^d , 0.86689 ^e	0.587 ^c , 0.58714 ^e	
	298.15	0.8612	0.5043	0.5856	0.8623 ^b , 0.86224 ^e	0.55 ^b , 0.55220 ^e	
	303.15	0.8565	0.4769	0.5568	0.85752 ^d , 0.85757 ^e	0.5260 ^a , 0.52050 ^e	
	308.15	0.8518	0.4531	0.5319	0.8528 ^a , 0.85289 ^e	0.4972 ^a , 0.49164 ^e	
	313.15	0.8470	0.4310	0.5089	0.8480 ^a , 0.84820 ^e	0.4710 ^a , 0.46530 ^e	
	318.15	0.8423	0.4106	0.4875	0.8433 ^a , 0.84349 ^e	0.4475 ^a , 0.44116 ^e	
	323.15	0.8374	0.3913	0.4673	0.8385 ^a , 0.83869 ^d , 0.83876 ^e	0.4256 ^a , 0.41900 ^e	
	328.15	0.8339	0.3746	0.4492	0.83400 ^e	0.39859 ^e	
	333.15	0.8292	0.3573	0.4309	0.82916 ^d , 0.82923 ^e	0.37975 ^e	
	338.15	0.8244	0.3428	0.4158	0.82443 ^e	0.36231 ^e	
	343.15	0.8193	0.3296	0.4023	0.81953 ^d , 0.81961 ^e	0.34614 ^e	
	Heptane	293.15	0.6841	0.3981	0.5819	0.68385 ^d , 0.68385 ^e	0.410 ^d , 0.41229 ^e
		298.15	0.6795	0.3811	0.5609	0.67961 ^d , 0.67961 ^e	0.3960 ^b , 0.389 ^d , 0.39014 ^e
		303.15	0.6752	0.3619	0.5360	0.6749 ^a , 0.67535 ^d , 0.67535 ^e	0.3730 ^a , 0.368 ^b , 0.36973 ^e
		308.15	0.6709	0.3428	0.5110	0.67105 ^d , 0.67106 ^e	0.349 ^e , 0.35087 ^e
313.15		0.6666	0.3253	0.4880	0.66673 ^d , 0.66675 ^e	0.33341 ^e	
318.15		0.6622	0.3090	0.4666	0.66238 ^d , 0.66240 ^e	0.315 ^d , 0.31719 ^e	
323.15		0.6579	0.2927	0.4449	0.65799 ^d , 0.65803 ^e	0.300 ^d , 0.30209 ^e	
328.15		0.6536	0.2667	0.4080	0.65357 ^d , 0.65362 ^e	0.284 ^d , 0.28801 ^e	
333.15		0.6490	0.2558	0.3941	0.64911 ^d , 0.64918 ^e	0.271 ^d , 0.27484 ^e	
338.15		0.6446	0.2216	0.3438	0.64460 ^d , 0.64470 ^e	0.26250 ^e	
343.15		0.6401	0.1996	0.3118	0.64017 ^d	0.25091 ^e	

*Values of kinematic viscosity were calculated. Standard uncertainties (u), are: u(T) = 0.01 K, u(P) = 0.05 kPa, u(ρ) = 1.0·10⁻¹ kg·m⁻³, u(η) = 4.0·10⁻⁴ mPa·s, u(ν) = 5.0·10⁻⁴ mm²·s⁻¹. ^a Reference [9]; ^b Reference[38]; ^c Reference[16]; ^d Reference[40]; ^e Reference[39].

range from 293.15 K to 343.15 K at a 5 K interval. For pure pyrene, the viscosities at these temperatures were extrapolated by the Roelands model, and the densities were calculated considering a linear density-temperature relationship, using data obtained from Hind et al. [36,37]. The viscosity and the density values obtained in this work have been compared with the data obtained in the literature (Table 3) [9,16,38–40]. The density values show slight differences, while the deviations between viscosity values measured and reported are more significant.

Experimental and calculated data of pure toluene, heptane, and pyrene were used to fit the models described in the calculation section.

The viscosity and density of binary mixtures of pyrene + toluene experimental results for each composition (1.0, 2.5, 5.0, 7.5, 10.0, 12.5, and 15.0 w % of pyrene) at different temperatures are presented in Table 4. Also, these data are shown in Figs. 1 and 2. As expected, the values for the viscosity and the density increase as pyrene concentration increases at the same temperature. On the other hand, the viscosity and the density decrease nonlinearly and linearly, respectively, as the temperature increases for each binary mixture at the same composition. At 293.15 K for a mixture with 15.0 w % of pyrene, solid phase formation was observed, and the viscosity value was more significant than expected for the homogeneous liquid mixture. Still, it has been considered that the value does not formally correspond to the mixture studied at that temperature. Thus, density and viscosity values are not given in Table 4.

For the ternary systems, pyrene + toluene + heptane, the measured densities and dynamic viscosities and calculated kinematic viscosity from (293.15 to 343.15) K and atmospheric pressure over the composition range studied are given in Tables 5–9. Due to the low viscosity and density values of the mixtures studied, some measurements could not be performed, the rotor of the instrument was forced to rotate, and the viscosity measurements provided are unreliable since they do not present adequate accuracy. [41] It has

been considered not to include these measurements in the data tables. Experimental data show that the densities and viscosities for all ternary mixtures decrease with a temperature rise.

For a given pyrene composition higher content of heptane in the mixture, density, and viscosity values decrease. High heptane content in some ternary mixtures causes the appearance of a solid phase at the lowest temperatures studied: 293.15 K, 298.15 K, and 303.15 K. This occurs for the mixture of 7.5 % pyrene and mass ratio toluene/heptane of 0.5 (Table 8) and, also, similar to what was observed for a binary mixture of 15% of pyrene + toluene, for the ternary mixtures: 15 % of pyrene and mass ratio toluene/heptane 5.0 and 10.0, solids were formed inside viscometer cell (Table 9).

Viscosity changes widely with composition and temperature, and to detect more minor additional effects, the viscosity deviation was used according to $\Delta(\ln \nu) = \ln \nu_m - \ln \nu_m^{id}$.

Most data in this work, 85 %, displays negative values for $\Delta(\ln \nu)$, ranging from -0.07 to 0.07 and highly dependent on temperature and compositions. Similar conclusions could be obtained from the relative deviation between viscosity and ideal viscosity, $\Delta \nu = \frac{\nu_m - \nu_m^{id}}{\nu_m}$.

For example, Fig. 3 shows the temperature effect on $\Delta(\ln \nu)$ for 4 of the systems studied. For each system, a clear trend can be detected, but this trend is not the same for all of them, and sometimes it is just the opposite, showing a complex behavior depending on the composition of pyrene and the ratio of toluene/heptane.

This temperature effect is relevant for the model's application because such opposite effects often lead to parameters insensitive to temperature due to the averaging effect on temperature during the fitting process.

Similar to the composition effect, Fig. 4 shows $\Delta(\ln \nu)$ for all the determined data at 293.15 K and 333.15 K as a function of toluene volume fraction. For binary systems pyrene + toluene, simple trends can be detected, but the presence of heptane introduces more complex composition dependence.

Table 4

Experimental density (ρ) and dynamic viscosity (η), and kinematic viscosity (ν) of binary system pyrene (1) + toluene (2) at T= (293.15 to 343.15) K, and atmospheric pressure (101.6 kPa).

T/K	w ₁ /%	$\rho/(10^3 \text{ kg}\cdot\text{m}^{-3})$	$\eta/(\text{mPa}\cdot\text{s})$	$\nu/(\text{mm}^2\cdot\text{s}^{-1})^b$	w ₁ /%	$\rho/(10^3 \text{ kg}\cdot\text{m}^{-3})$	$\eta/(\text{mPa}\cdot\text{s})$	$\nu/(\text{mm}^2\cdot\text{s}^{-1})^b$
293.15	1.0	0.8691	0.5397	0.6210	10.0	0.8914	0.6398	0.7177
298.15		0.8643	0.5098	0.5898		0.8867	0.6029	0.6799
303.15		0.8596	0.4824	0.5612		0.8821	0.5681	0.6440
308.15		0.8549	0.4566	0.5341		0.8776	0.5366	0.6114
313.15		0.8503	0.4336	0.5099		0.8730	0.5081	0.5820
318.15		0.8456	0.4135	0.4890		0.8684	0.4812	0.5541
323.15		0.8409	0.3946	0.4693		0.8638	0.4583	0.5306
328.15		0.8362	0.3773	0.4512		0.8592	0.4358	0.5072
333.15		0.8314	0.3610	0.4342		0.8546	0.4137	0.4841
338.15		0.8266	0.3471	0.4199		0.8500	0.3928	0.4621
343.15		0.8219	0.3325	0.4046		0.8453	0.3722	0.4403
293.15	2.5	0.8731	0.5566	0.6375	12.5	0.8990	0.6910	0.7686
298.15		0.8685	0.5246	0.6040		0.8945	0.6486	0.7251
303.15		0.8639	0.4958	0.5739		0.8900	0.6110	0.6865
308.15		0.8592	0.4704	0.5475		0.8854	0.5762	0.6508
313.15		0.8546	0.4468	0.5228		0.8809	0.5454	0.6191
318.15		0.8499	0.4245	0.4995		0.8763	0.5165	0.5894
323.15		0.8452	0.4048	0.4789		0.8715	0.4913	0.5637
328.15		0.8405	0.3861	0.4594		0.8664	0.4680	0.5402
333.15		0.8357	0.3683	0.4407		0.8613	0.4462	0.5181
338.15		0.8307	0.3513	0.4229		0.8565	0.4267	0.4982
343.15		0.8256	0.3363	0.4073		0.8519	0.4094	0.4806
293.15	5.0	0.8797	0.5794	0.6586	15.0	a	a	a
298.15		0.8750	0.5505	0.6291		0.9024	0.6855	0.7596
303.15		0.8703	0.5212	0.5989		0.8980	0.6446	0.7178
308.15		0.8657	0.4888	0.5646		0.8935	0.6082	0.6807
313.15		0.8611	0.4644	0.5393		0.8890	0.5754	0.6472
318.15		0.8565	0.4415	0.5155		0.8845	0.5448	0.6159
323.15		0.8518	0.4168	0.4893		0.8800	0.5177	0.5883
328.15		0.8472	0.3940	0.4651		0.8754	0.4932	0.5634
333.15		0.8425	0.3719	0.4414		0.8709	0.4672	0.5365
338.15		0.8378	0.3509	0.4188		0.8663	0.4392	0.5070
343.15		0.8331	0.3334	0.4002		0.8615	0.4174	0.4845
293.15	7.5	0.8853	0.6026	0.6807				
298.15		0.8806	0.5680	0.6450				
303.15		0.8760	0.5332	0.6087				
308.15		0.8714	0.5017	0.5757				
313.15		0.8668	0.4730	0.5457				
318.15		0.8622	0.4488	0.5205				
323.15		0.8576	0.4244	0.4949				
328.15		0.8530	0.4033	0.4728				
333.15		0.8484	0.3834	0.4519				
338.15		0.8436	0.3646	0.4322				
343.15		0.8390	0.3481	0.4149				

^a Solid phase was formed into viscometer cell.

^b Values of kinematic viscosity are calculated. Standard uncertainties (u), are: u(T) = 0.01 K, u(P) = 0.05 kPa, u(ρ) = 1.0·10⁻¹ kg·m⁻³, u(η) = 4.0·10⁻⁴ mPa·s, u(ν) = 5.0·10⁻⁴ mm²·s⁻¹, u(w₁) = 0.001.

4.2. Viscosity models

The performance of several viscosity models described above was checked according to standard deviation and percent relative absolute deviation:

$$\sigma = \left(\frac{1}{N-1} \sum_{i=1}^{i=N} (v_{i,\text{exp}} - v_{i,\text{cal}})^2 \right)^{1/2} \quad (1a)$$

$$\Delta(\%) = \left(\frac{1}{N} \sum_{i=1}^{i=N} \frac{|v_{i,\text{exp}} - v_{i,\text{cal}}|}{v_{i,\text{exp}}} \right) \cdot 100 \quad (1b)$$

Where subscript exp and cal refer to experimental and calculated values, sums are extended over all the experimental data, N, or over data for specific systems to detect systematic errors for the several models. Optimizing the values for parameters in some of the models considered was also done by minimizing the values for standard deviation and percent relative absolute deviation. Table 10 lists the obtained parameters for all the viscosity models used in this work.

The numerical values of each model's standard deviation for all studied systems are listed in Table 11. Overall values for σ and Δ (%) of each model are also included.

The performance of the models will not be checked only by overall deviations of Eqs. (1a) and (1b), as in some cases, very disperse distribution for the specific systems is considered, and the standard deviation of the particular deviations is also listed.

All the magnitudes from pure components (viscosities, densities) were experimental values at the same temperature, except pyrene, as previously noted. The mixture density required for volume fraction calculation was also an experimental value.

Ideal model. The first model considered was the ideal mixture. Overall values listed in Table 11, $\sigma = 0.031 \text{ mm}^2\cdot\text{s}^{-1}$ and $\Delta(\%) = 5.0$, can be regarded as accurate and compare favorably with more complex models. This can be related to the low viscosity values of the involved solvents (toluene, heptane). However, when individual systems are analyzed, a non-uniform distribution is obtained, as can be checked in Fig. 5.

Thus, showing a very different accuracy for systems depending on their composition.

Table 5

Experimental density (ρ) and dynamic viscosity (η) and kinematic viscosity (ν) of ternary mixture: 1.0 w % of pyrene (1) in toluene (2) and heptane (3) at different mass ratio, r (g/g), toluene/heptane, at T= (293.15 to 343.15) K, and atmospheric pressure (101.6 kPa).

T/K	r/(g/g)	$\rho/(10^3 \text{ kg}\cdot\text{m}^{-3})$	$\eta/(\text{mPa}\cdot\text{s})$	$\nu/(\text{mm}^2\cdot\text{s}^{-1})^b$	r/(g/g)	$\rho/(10^3 \text{ kg}\cdot\text{m}^{-3})$	$\eta/(\text{mPa}\cdot\text{s})$	$\nu/(\text{mm}^2\cdot\text{s}^{-1})^b$		
293.15	0.1	0.7004	0.4011	0.5727	5.0	0.8323	0.4585	0.5509		
298.15		0.6961	0.3801	0.5460		0.8278	0.4411	0.5329		
303.15		0.6918	0.3602	0.5207		0.8231	0.4183	0.5082		
308.15		0.6875	0.3416	0.4969		0.8185	0.3970	0.4850		
313.15		0.6832	0.3240	0.4742		0.8139	0.3777	0.4641		
318.15		0.6788	0.3079	0.4536		0.8092	0.3588	0.4434		
323.15		0.6744	0.2928	0.4342		0.8046	0.3428	0.4260		
328.15		0.6699	0.2793	0.4169		0.8000	0.3279	0.4099		
333.15		0.6654	0.2657	0.3993		0.7953	0.3118	0.3921		
338.15		0.6608	0.2540	0.3844		-	-	-		
343.15		0.6559	0.2494	0.3802		-	-	-		
293.15		0.5	0.7379	0.4027		0.5457	10.0	0.8489	0.5092	0.5998
298.15			0.7334	0.3814		0.5200		0.8443	0.4825	0.5715
303.15			0.7290	0.3623		0.4970		0.8396	0.4588	0.5465
308.15			0.7246	0.3443		0.4752		0.8349	0.4357	0.5219
313.15	0.7202		0.3281	0.4556	0.8303	0.4161		0.5011		
318.15	0.7158		0.3142	0.4389	0.8256	0.3961		0.4798		
323.15	0.7113		0.3021	0.4247	0.8210	0.3795		0.4622		
328.15	0.7068		0.2772	0.3922	0.8163	0.3644		0.4464		
333.15	0.7024		0.2684	0.3821	0.8116	0.3467		0.4272		
338.15	0.6978		0.2602	0.3729	0.8069	0.3326		0.4122		
343.15	0.6932		0.2467	0.3559	0.8022	0.3182		0.3967		
293.15	1.0		0.7680	0.4032	0.5250					
298.15			0.7634	0.3896	0.5103					
303.15			0.7589	0.3756	0.4949					
308.15			0.7545	0.3596	0.4766					
313.15		0.7500	0.3438	0.4584						
318.15		0.7455	0.3291	0.4414						
323.15		0.7410	0.3093	0.4174						
328.15		0.7365	0.2909	0.3950						
333.15		0.7319	0.2784	0.3804						
338.15		0.7273	0.2654	0.3649						
343.15		0.7226	0.2498	0.3457						

^b Values of kinematic viscosity are calculated. Standard uncertainties (u), are: u(T) = 0.01 K, u(P) = 0.05 kPa, u(ρ) = $1.0\cdot 10^{-1} \text{ kg}\cdot\text{m}^{-3}$, u(η) = $4.0\cdot 10^{-4} \text{ mPa}\cdot\text{s}$, u(ν) = $5.0\cdot 10^{-4} \text{ mm}^2\cdot\text{s}^{-1}$, u(w_1) = 0.001, u(r) = 0.002.

Refutas model. As a purely predictive model widely used for more complex systems, its performance is expected to be similar to ideal mixtures. Overall values listed in Table 11, $\sigma = 0.032 \text{ mm}^2\cdot\text{s}^{-1}$ and $\Delta(\%) = 5.0$, confirm such point, and analysis for specific systems leads to similar conclusions.

Ratcliff model. According to the experimental section's discussion, the deviation function's fit should improve results. However, when $\Delta(\ln \nu)_{11}$ is used, the only parameter for the deviation function includes the averaged effect of the composition of all the components. The obtained value was $a_{123,0} = -0.070$, and overall deviation values, $\sigma = 0.031 \text{ mm}^2\cdot\text{s}^{-1}$ and $\Delta(\%) = 4.9$, reveal that description is similar to that obtained by the ideal model. Thus, a one-parameter model cannot reproduce the complexity of the mixtures.

When temperature dependence is included, obtained values were $a_{123,0} = 0.315$ and $a_{123,1} = -0.0091$; however, the overall deviation got, those listed in Table 11, $\sigma = 0.031 \text{ mm}^2\cdot\text{s}^{-1}$ and $\Delta(\%) = 4.9$, represent a negligible improvement, thus confirming that because the complex temperature effect described for deviation function, the fitting of parameters for temperature dependence, only slightly improve calculated values because the average temperature effect is not enough.

The second version for this model, given by $\Delta(\ln \nu)_{13}$ requires 3 parameters, obtained values were $a_{12} = 0.115$, $a_{13} = 0.937$, $a_{23} = -0.544$. Overall deviation values in Table 11, $\sigma = 0.015 \text{ mm}^2\cdot\text{s}^{-1}$ and $\Delta(\%) = 2.5$, represent an important reduction for the deviations. According to previous experience with $\Delta(\ln \nu)_{11}$, no temperature effect was checked.

Fig. 6 represents deviations for individual systems for the Ratcliff model with the three forms for deviation function. When $\Delta(\ln \nu)_{11}$ or $\Delta(\ln \nu)_{11T}$ are used, it is possible to check that, despite

similar overall deviation to the ideal solution, individual systems are not equally described. Higher deviations for some systems (central part of the Figure) are reduced, and the overall performance can be considered improved.

UNIFAC-Visco model. According to the model description, the UNIFAC-Visco model is a predictive model with interaction parameters available in the literature. Table 12 lists the original UNIFAC-Visco structural and interaction parameters required for hydrocarbon (aliphatic + aromatic) systems. However, the property description of the systems included in this work requires the AC group (aromatic carbon non-linked to hydrogen, by analogy to activity coefficients groups). Consequently, the following inadequate description was considered pyrene = 18 ACH groups, toluene = 6 ACH + 1 CH₂ groups.

Deviations in Table 11, $\sigma = 0.048 \text{ mm}^2\cdot\text{s}^{-1}$ and $\Delta(\%) = 6.5$, are less accurate than the ideal visco model, probably due to the deficient description of the involved mixtures.

To improve the model description and check the ability of the UNIFAC-Visco model to describe those mixtures, a new aromatic group was introduced (AC, aromatic carbon without hydrogen). Next definition was improved: pyrene = 12 ACH + 6 AC groups, toluene = 5 ACH + 1 AC + 1 CH₃ groups. As in the UNIFAC model for activity coefficients, R and Q values were the same, and ACH and AC were the same main group with the same interaction parameter as other groups. To adopt such a new description, only one binary interaction was recalculated; in this work, it was assumed that CH₂-ACH has the biggest effect, and it was fitted. Table 13 lists the final UNIFAC-Visco structural and interaction parameters. Deviations in Table 11, $\sigma = 0.039 \text{ mm}^2\cdot\text{s}^{-1}$ and $\Delta(\%) = 5.6$, represent an improvement compared to original the UNIFAC-Visco, but they are less accurate than the ideal visco model.

Table 6

Experimental density (ρ) and dynamic viscosity (η) and kinematic viscosity (ν) of ternary mixture: 2.5 w % of pyrene (1) in toluene (2) and heptane (3) at different mass ratio, r (g/g), toluene/heptane, at $T=$ (293.15 to 343.15) K, and atmospheric pressure (101.6 kPa).

T/K	$r/(g/g)$	$\rho/(10^3 \text{ kg}\cdot\text{m}^{-3})$	$\eta/(\text{mPa}\cdot\text{s})$	$\nu/(\text{mm}^2\cdot\text{s}^{-1})^b$	$r/(g/g)$	$\rho/(10^3 \text{ kg}\cdot\text{m}^{-3})$	$\eta/(\text{mPa}\cdot\text{s})$	$\nu/(\text{mm}^2\cdot\text{s}^{-1})^b$
293.15	0.1	0.7052	0.4090	0.5800	5.0	0.8361	0.4752	0.5684
298.15		0.7008	0.3916	0.5588		0.8314	0.4529	0.5447
303.15		0.6965	0.3726	0.5350		0.8268	0.4327	0.5233
308.15		0.6922	0.3520	0.5085		0.8223	0.4104	0.4991
313.15		0.6879	0.3284	0.4774		0.8177	0.3913	0.4785
318.15		0.6835	0.3086	0.4515		0.8130	0.3710	0.4563
323.15		0.6791	0.2917	0.42965		0.8084	0.3519	0.4353
328.15		0.6747	0.2776	0.4114		0.8038	0.3361	0.4181
333.15		0.6702	0.2560	0.3820		0.7991	0.3206	0.4012
338.15		0.6655	0.2370	0.3561		0.7944	0.3069	0.3863
343.15		0.6610	0.1912	0.2893		0.7897	0.2913	0.3689
293.15	0.5	-	-	-	10.0	0.8533	0.5159	0.6046
298.15		-	-	-		0.8486	0.4906	0.5781
303.15		0.7343	0.3652	0.4973		0.8440	0.4650	0.5509
308.15		0.7298	0.3490	0.4782		0.8393	0.4414	0.5259
313.15		0.7253	0.3312	0.4566		0.8347	0.4201	0.5033
318.15		0.7209	0.3145	0.4363		0.8301	0.3989	0.4805
323.15		0.7164	0.2978	0.4157		0.8255	0.3801	0.4604
328.15		0.7120	0.2788	0.3916		0.8208	0.3535	0.4307
333.15		0.7074	0.2706	0.3825		0.8161	0.3310	0.4056
338.15		0.7029	0.2542	0.3616		0.8114	0.3085	0.3802
343.15		0.6984	-	-		0.8066	0.2980	0.3694
293.15	1.0	0.7711	0.4076	0.5286				
298.15		0.7664	0.3936	0.5136				
303.15		0.7620	0.3703	0.4860				
308.15		0.7575	0.3691	0.4873				
313.15		0.7531	0.3504	0.4653				
318.15		0.7486	0.3335	0.4455				
323.15		0.7441	0.3185	0.4280				
328.15		0.7395	0.3018	0.4081				
333.15		0.7349	0.2846	0.3873				
338.15		0.7303	0.2673	0.3660				
343.15		0.7257	0.2550	0.3514				

^b Values of kinematic viscosity are calculated. Standard uncertainties (u), are: $u(T) = 0.01$ K, $u(P) = 0.05$ kPa, $u(\rho) = 1.0 \cdot 10^{-1}$ kg·m⁻³, $u(\eta) = 4.0 \cdot 10^{-4}$ mPa·s, $u(\nu) = 5.0 \cdot 10^{-4}$ mm²·s⁻¹, $u(w_1) = 0.001$, $u(r) = 0.002$.

Table 7

Experimental density (ρ) and dynamic viscosity (η) and kinematic viscosity (ν) of ternary mixture: 5.0 w % of pyrene (1) in toluene (2) and heptane (3) at different mass ratio, r (g/g), toluene/heptane, at $T=$ (293.15 to 343.15) K, and atmospheric pressure (101.6 kPa).

T/K	$r/(g/g)$	$\rho/(10^3 \text{ kg}\cdot\text{m}^{-3})$	$\eta/(\text{mPa}\cdot\text{s})$	$\nu/(\text{mm}^2\cdot\text{s}^{-1})^b$	$r/(g/g)$	$\rho/(10^3 \text{ kg}\cdot\text{m}^{-3})$	$\eta/(\text{mPa}\cdot\text{s})$	$\nu/(\text{mm}^2\cdot\text{s}^{-1})^b$
293.15	0.5	-	-	-	5.0	0.8434	0.4978	0.5902
298.15		-	-	-		0.8388	0.4687	0.5588
303.15		0.7419	0.3812	0.5138		0.8342	0.4419	0.5297
308.15		0.7374	0.3669	0.4976		0.8297	0.4184	0.5043
313.15		0.7329	0.3501	0.4777		0.8251	0.3978	0.4821
318.15		0.7285	0.3332	0.4574		0.8205	0.3773	0.4598
323.15		0.7240	0.3153	0.4355		0.8160	0.3603	0.4415
328.15		0.7196	0.2963	0.4118		0.8113	-	-
333.15		0.7151	0.2763	0.3864		0.8067	-	-
338.15		0.7106	0.2620	0.3687		-	-	-
343.15		0.7060	0.2507	0.3551		-	-	-
293.15	1.0	0.7792	0.4278	0.5490	10.0	0.8584	0.5413	0.6306
298.15		0.7747	0.4087	0.5276		0.8537	0.5131	0.6010
303.15		0.7702	0.3900	0.5064		0.8491	0.4867	0.5732
308.15		0.7658	0.3756	0.4905		0.8447	0.4601	0.5447
313.15		0.7614	0.3549	0.4661		0.8400	0.4361	0.5192
318.15		0.7569	0.3380	0.4466		0.8354	0.4136	0.4951
323.15		0.7524	0.3226	0.4288		0.8308	0.3923	0.4723
328.15		0.7479	0.3087	0.4128		0.8261	0.3735	0.4521
333.15		0.7434	0.2934	0.3947		0.8215	0.3552	0.4324
338.15		0.7389	-	-		0.8168	0.3430	0.4199
343.15		0.7341	-	-		0.8121	0.3287	0.4047

^b Values of kinematic viscosity are calculated. Standard uncertainties (u), are: $u(T) = 0.01$ K, $u(P) = 0.05$ kPa, $u(\rho) = 1.0 \cdot 10^{-1}$ kg·m⁻³, $u(\eta) = 4.0 \cdot 10^{-4}$ mPa·s, $u(\nu) = 5.0 \cdot 10^{-4}$ mm²·s⁻¹, $u(w_1) = 0.001$, $u(r) = 0.002$.

The introduction of the simplified method to account for the eventual association of pyrene led to more accurate viscosity predictions, from Table 11, $\sigma = 0.024$ mm²·s⁻¹ and $\Delta(\%) = 3.8$. Obtained parameters were $a_{\text{tol}} = -0.6$ and $a_{\text{c7}} = 2.3$, representing

that toluene leads to a reduction in association and the opposite for heptane. It is important to note that systems with high toluene content, due to the negative a_{tol} value, lead to senseless $f_a < 1$ values, representing a high trend to reduce pyrene association.

Table 8

Experimental density (ρ) and dynamic viscosity (η) and kinematic viscosity (ν) of ternary mixture: 7.5 w % of pyrene (1) in toluene (2) and heptane (3) at different mass ratio, r (g/g), toluene/heptane, at $T = (293.15 \text{ to } 343.15) \text{ K}$, and atmospheric pressure (101.6 kPa).

T/K	$r(\text{g/g})$	$\rho/(10^3 \text{ kg}\cdot\text{m}^{-3})$	$\eta/(\text{mPa}\cdot\text{s})$	$\nu/(\text{mm}^2\cdot\text{s}^{-1})^b$	$r(\text{g/g})$	$\rho/(10^3 \text{ kg}\cdot\text{m}^{-3})$	$\eta/(\text{mPa}\cdot\text{s})$	$\nu/(\text{mm}^2\cdot\text{s}^{-1})^b$
293.15	0.5	<i>a</i>	<i>a</i>	<i>a</i>	5.0	0.8497	0.5515	0.6490
298.15		<i>a</i>	<i>a</i>	<i>a</i>		0.8451	0.5209	0.6164
303.15		<i>a</i>	<i>a</i>	<i>a</i>		0.8405	0.4948	0.5887
308.15		0.7491	0.3871	0.5167		0.8360	0.4699	0.5621
313.15		0.7448	0.3696	0.4962		0.8315	0.4473	0.5379
318.15		0.7404	0.3533	0.4772		0.8269	0.4282	0.5178
323.15		0.7359	0.3370	0.4579		0.8214	0.4060	0.4943
328.15		0.7315	0.3220	0.4402		0.8165	0.3859	0.4726
333.15		0.7270	0.3086	0.4245		0.8135	0.3671	0.4512
338.15		0.7224	0.2959	0.4096		0.8087	0.3513	0.4344
343.15		0.7174	0.2843	0.3963		0.8040	0.3358	0.4177
293.15	1.0	0.7868	0.4595	0.5840	10.0	0.8656	0.5779	0.6676
298.15		0.7824	0.4378	0.5596		0.8610	0.5455	0.6336
303.15		0.7780	0.4172	0.5362		0.8565	0.5166	0.6031
308.15		0.7736	0.3986	0.5152		0.8520	0.4897	0.5748
313.15		0.7692	0.3812	0.4956		0.8474	0.4654	0.5492
318.15		0.7647	0.3640	0.4760		0.8428	0.4427	0.5253
323.15		0.7602	0.3487	0.4587		0.8382	0.4216	0.5030
328.15		0.7557	0.3327	0.4402		0.8336	0.4022	0.4825
333.15		0.7511	0.3174	0.4226		0.8289	0.3844	0.4637
338.15		0.7466	0.3019	0.4044		0.8242	0.3680	0.4465
343.15		0.7418	0.2893	0.3900		0.8192	0.3546	0.4329

^a Solid phase was formed into viscometer cell.

^b Values of kinematic viscosity were calculated. Standard uncertainties (u), are: $u(T) = 0.01 \text{ K}$, $u(P) = 0.05 \text{ kPa}$, $u(\rho) = 1.0 \cdot 10^{-1} \text{ kg}\cdot\text{m}^{-3}$, $u(\eta) = 4.0 \cdot 10^{-4} \text{ mPa}\cdot\text{s}$, $u(\nu) = 5.0 \cdot 10^{-4} \text{ mm}^2\cdot\text{s}^{-1}$, $u(w_1) = 0.001$, $u(r) = 0.002$.

Table 9

Experimental density (ρ) and dynamic viscosity (η) and kinematic viscosity (ν) of ternary mixture: 10.0 w %, 12.5 w % and 15.0 w % of pyrene (1), in toluene (2) and heptane (3) mixture at different mass ratio, r (g/g), toluene/heptane, at $T = (293.15 \text{ to } 343.15) \text{ K}$, and atmospheric pressure (101.6 kPa).

T/K	$w_1/\%$	$r(\text{g/g})$	$\rho/(10^3 \text{ kg}\cdot\text{m}^{-3})$	$\eta/(\text{mPa}\cdot\text{s})$	$\nu/(\text{mm}^2\cdot\text{s}^{-1})^b$	$r(\text{g/g})$	$\rho/(10^3 \text{ kg}\cdot\text{m}^{-3})$	$\eta/(\text{mPa}\cdot\text{s})$	$\nu/(\text{mm}^2\cdot\text{s}^{-1})^b$
293.15	10.0	5.0	0.8569	0.5795	0.6763	10.0	0.8722	0.6028	0.6911
298.15			0.8522	0.5478	0.6428		0.8673	0.5742	0.6620
303.15			0.8477	0.5194	0.6127		0.8627	0.5452	0.6320
308.15			0.8434	0.4931	0.5847		0.8582	0.5167	0.6021
313.15			0.8387	0.4706	0.5611		0.8537	0.4901	0.5741
318.15			0.8342	0.4486	0.5378		0.8491	0.4654	0.5481
323.15			0.8296	0.4287	0.5168		0.8446	0.4430	0.5245
328.15			0.8251	0.4089	0.4956		0.8400	0.4224	0.5029
333.15			0.8205	0.3911	0.4767		0.8354	0.4033	0.4828
338.15			0.8159	0.3739	0.4583		0.8308	0.3852	0.4636
343.15			0.8113	0.3578	0.4410		0.8261	0.3685	0.4461
293.15	12.5	5.0	0.8629	0.5990	0.6942	10.0	0.8788	0.6434	0.7321
298.15			0.8585	0.5655	0.6587		0.8743	0.6055	0.6925
303.15			0.8540	0.5344	0.6258		0.8698	0.5726	0.6583
308.15			0.8495	0.5063	0.5960		0.8654	0.5402	0.6242
313.15			0.8450	0.4805	0.5686		0.8608	0.5119	0.5947
318.15			0.8405	0.4557	0.5422		0.8563	0.4866	0.5683
323.15			0.8360	0.4347	0.5200		0.8518	0.4625	0.5430
328.15			0.8314	0.4174	0.5020		0.8472	0.4404	0.5198
333.15			0.8270	0.4002	0.4839		0.8425	0.4207	0.4993
338.15			0.8223	0.3834	0.4662		0.8379	0.4018	0.4795
343.15			0.8174	0.3688	0.4512		0.8333	0.3834	0.4601
293.15	15.0	5.0	<i>a</i>	<i>a</i>	<i>a</i>	10.0	<i>a</i>	<i>a</i>	<i>a</i>
298.15			<i>a</i>	<i>a</i>	<i>a</i>		<i>a</i>	<i>a</i>	<i>a</i>
303.15			<i>a</i>	<i>a</i>	<i>a</i>		<i>a</i>	<i>a</i>	<i>a</i>
308.15			0.8571	0.5427	0.6332		0.8725	0.5701	0.6534
313.15			0.8527	0.5156	0.6047		0.8680	0.5401	0.6222
318.15			0.8482	0.4898	0.5774		0.8635	0.5124	0.5934
323.15			0.8437	0.4665	0.5529		0.8590	0.4871	0.5670
328.15			0.8392	0.4442	0.5293		0.8545	0.4632	0.5421
333.15			0.8347	0.4237	0.5076		0.8500	0.4381	0.5154
338.15			0.8300	0.4051	0.4881		0.8454	0.4160	0.4921
343.15			0.8251	0.3886	0.4710		0.8404	0.3975	0.4730

^a Solid phase was formed into viscometer cell.

^b Values of kinematic viscosity were calculated. Standard uncertainties (u), are: $u(T) = 0.01 \text{ K}$, $u(P) = 0.05 \text{ kPa}$, $u(\rho) = 1.0 \cdot 10^{-1} \text{ kg}\cdot\text{m}^{-3}$, $u(\eta) = 4.0 \cdot 10^{-4} \text{ mPa}\cdot\text{s}$, $u(\nu) = 5.0 \cdot 10^{-4} \text{ mm}^2\cdot\text{s}^{-1}$, $u(w_1) = 0.001$, $u(r) = 0.002$.

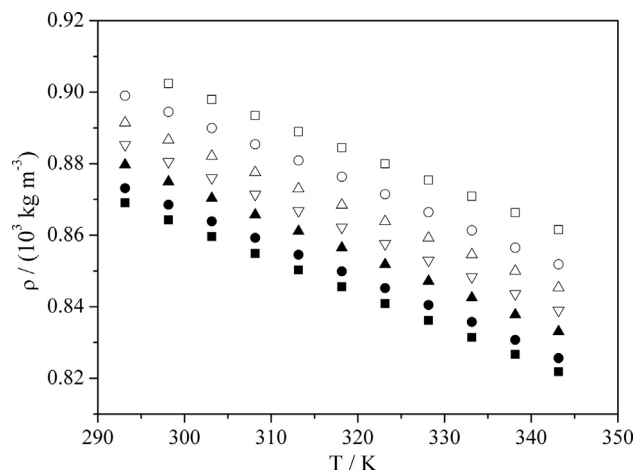


Fig. 1. Density as a function of temperature for binary mixtures pyrene (1) + toluene (2). (■) 1.0 w %; (●) 2.5 w %; (▲) 5.0 w %; (▽) 7.5 w %; (△) 10.0 w %; (○) 12.5 w %; (□) 15.0 w % of pyrene.

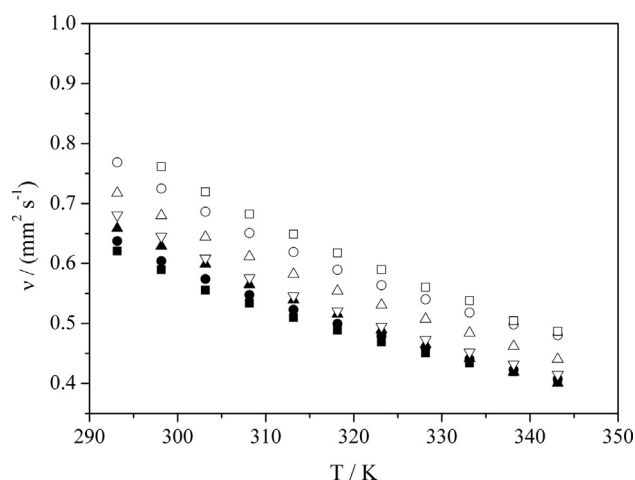


Fig. 2. Kinematic viscosity as a function of temperature for binary mixtures pyrene (1) + toluene (2). (■) 1.0 w %; (●) 2.5 w %; (▲) 5.0 w %; (▽) 7.5 w %; (△) 10.0 w %; (○) 12.5 w %; (□) 15.0 w % of pyrene.

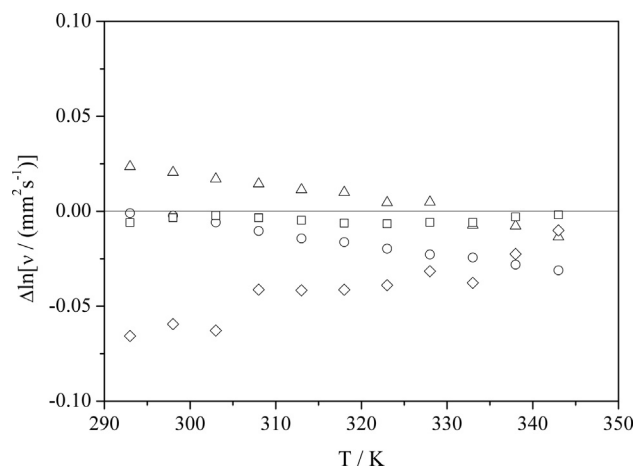


Fig. 3. Temperature effect on viscosity $\Delta(\ln\nu)$ of binary mixtures: (△) 15 w % of pyrene + toluene; (○) 7.5 w % of pyrene + toluene; and ternary mixtures: (◇) 2.5 w % of pyrene + toluene/heptane mass ratio: 1.0; (□) 10 w % of pyrene + toluene/heptane mass ratio: 10.

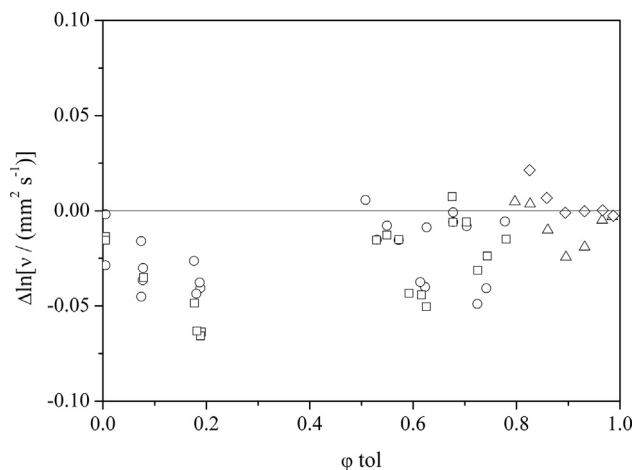


Fig. 4. Composition effect on viscosity $\Delta(\ln\nu)$ of all data of binary mixtures pyrene + toluene at: (△) 333.15 K; (◇) 293.15 K; and ternary mixtures pyrene + toluene + heptane at: (○) 333.15 K; and (□) 293.15 K.

Table 10
Viscosity model parameters.

Model	Parameters
Roelands (pyrene)	$S_0 = 0.729$ $G_0 = 4.964$
Ratcliff, $\Delta(\ln \nu)_{T1}$, T independent	$a_{123,0} = -0.070$
Ratcliff, $\Delta(\ln \nu)_{T1T}$, T dependent	$a_{123,0} = 0.315$ $a_{123,1} = -0.0091$
Ratcliff, $\Delta(\ln \nu)_{T3}$, T independent	$a_{12} = 0.115$ $a_{13} = 0.937$ $a_{23} = -0.544$
UNIFAC-Visco	$a_{tol} = -0.6$ $a_{C7} = 2.3$
Krieger	$[\eta] = 0.253$ $\varphi_m = 0.526$ $b_{tol} = 0.263$ $b_{C7} = 1.48$

Subscript: 1 pyrene, 2 toluene, 3 heptane.

Fig. 7 represents deviations for individual systems for three UNIFAC-Visco model versions. The original model and that with the fitted parameter is less accurate than an ideal model, and, as can be checked in Fig. 7, it is due to the high deviations found for some specific mixtures. For most systems, results are very similar with all the versions, and the reduction in the standard deviation is more related to the improvement in specific systems whose description by the original UNIFAC-Visco is poorly described. The understanding including association leads to better description and a qualitative improvement for systems with higher deviation in previous versions.

Krieger model. From the fitting process, a value of $\varphi_m = 0.526$ was obtained, in agreement with the value proposed by Leighton-Acrivos ($\varphi_m = 0.58$) [42] considered for the maximum volume fraction of the dispersed phase in this work. Intrinsic viscosity has a low value, $[\eta] = 0.253$, which can be assumed due to the tiny size of the eventually associated species and the low viscosity of the solvent [43]. Values for $b_{tol} = 0.263$ and $b_{C7} = 1.48$ are both positive; thus, $\varphi < \varphi^{id}$ represents a disaggregation process, and in this case, both components produce the same effect and are even stronger for heptane than for toluene. Results from Table 11, $\sigma = 0.026 \text{ mm}^2 \cdot \text{s}^{-1}$ and $\Delta(\%) = 4.0$, can be considered accurate and represent improvement versus the ideal model.

When temperature dependence is included, the overall deviation obtained in Table 11 $\sigma = 0.025 \text{ mm}^2 \cdot \text{s}^{-1}$ and $\Delta(\%) = 3.5$, representing a negligible improvement, again confirming that temperature dependence is not the main factor (Fig. 8).

Table 11
Standard deviations, σ (mm^2s^{-1}), of all mixtures and all models, and overall deviations.

	System	Ideal	Refutas	Ratcliff $\Delta(\ln v)_{T1}$	Ratcliff $\Delta(\ln v)_{TT}$	Ratcliff $\Delta(\ln v)_{T3}$	UNIFAC-Visco Table 12	UNIFAC-Visco Table 13	UNIFAC-Visco with f_a	Krieger	Krieger T dep.
Binary mixtures	1 % py + tol	0.004	0.003	0.004	0.004	0.005	0.002	0.001	0.007	0.018	0.015
	2.5 % py + tol	0.005	0.003	0.004	0.003	0.006	0.010	0.009	0.010	0.018	0.015
	5 % py + tol	0.016	0.012	0.015	0.012	0.018	0.022	0.020	0.022	0.017	0.013
	7.5 % py + tol	0.022	0.014	0.019	0.017	0.025	0.028	0.024	0.029	0.012	0.008
	10 % py + tol	0.011	0.012	0.011	0.003	0.014	0.056	0.050	0.015	0.020	0.016
	12.5 % py + tol	0.019	0.031	0.023	0.020	0.013	0.091	0.082	0.019	0.037	0.034
Ternary mixtures	15 % py + tol	0.021	0.035	0.026	0.024	0.015	0.105	0.095	0.026	0.038	0.036
	1 % py r0.1	0.027	0.028	0.027	0.027	0.027	0.026	0.025	0.025	0.076	0.073
	2.5 % py r0.1	0.025	0.025	0.025	0.025	0.016	0.011	0.012	0.011	0.058	0.067
	1 % py r0.5	0.042	0.043	0.042	0.042	0.024	0.016	0.025	0.024	0.028	0.024
	2.5 % py r0.5	0.049	0.050	0.049	0.049	0.010	0.010	0.025	0.020	0.014	0.012
	5 % py r0.5	0.044	0.044	0.043	0.043	0.013	0.015	0.012	0.012	0.020	0.014
	7.5 % py r0.5	0.034	0.036	0.034	0.034	0.025	0.043	0.031	0.043	0.040	0.023
	1 % py r1	0.053	0.054	0.053	0.053	0.016	0.012	0.032	0.031	0.017	0.009
	2.5 % py r1	0.054	0.055	0.054	0.054	0.017	0.015	0.030	0.028	0.020	0.010
	5 % py r1	0.068	0.068	0.068	0.068	0.017	0.008	0.027	0.021	0.025	0.018
	7.5 % py r1	0.048	0.048	0.047	0.048	0.018	0.037	0.016	0.021	0.019	0.006
	1 % py r5	0.053	0.053	0.053	0.053	0.016	0.011	0.040	0.044	0.032	0.033
	2.5 % py r5	0.045	0.044	0.045	0.045	0.012	0.004	0.027	0.034	0.026	0.027
	5 % py r5	0.065	0.061	0.064	0.065	0.032	0.005	0.028	0.043	0.043	0.044
	7.5 % py r5	0.019	0.014	0.018	0.018	0.009	0.055	0.026	0.007	0.004	0.004
	10 % py r5	0.016	0.011	0.015	0.016	0.010	0.074	0.044	0.020	0.008	0.008
	12.5 % py r5	0.025	0.016	0.024	0.024	0.009	0.079	0.049	0.020	0.009	0.009
	15 % py r5	0.012	0.024	0.012	0.013	0.030	0.110	0.081	0.060	0.029	0.028
	1 % py r10	0.013	0.013	0.013	0.013	0.011	0.016	0.006	0.010	0.010	0.010
	2.5 % py r10	0.034	0.032	0.034	0.034	0.016	0.013	0.017	0.029	0.016	0.017
5 % py r10	0.026	0.021	0.026	0.026	0.009	0.026	0.007	0.017	0.007	0.009	
7.5 % py r10	0.010	0.005	0.010	0.010	0.006	0.054	0.032	0.004	0.010	0.009	
10 % py r10	0.007	0.004	0.006	0.006	0.006	0.072	0.049	0.012	0.013	0.011	
12.5 % py r10	0.005	0.013	0.006	0.005	0.013	0.090	0.067	0.021	0.022	0.020	
15 % py r10	0.007	0.011	0.007	0.006	0.005	0.098	0.074	0.027	0.013	0.012	
Overall	σ (mm^2s^{-1})	0.031	0.032	0.031	0.031	0.015	0.048	0.039	0.024	0.026	0.025
	$\Delta(\%)$	5.0	5.0	4.9	4.9	2.5	6.5	5.6	3.8	4.0	3.5
	σ (σ)	0.019	0.019	0.019	0.019	0.007	0.034	0.024	0.012	0.016	0.016

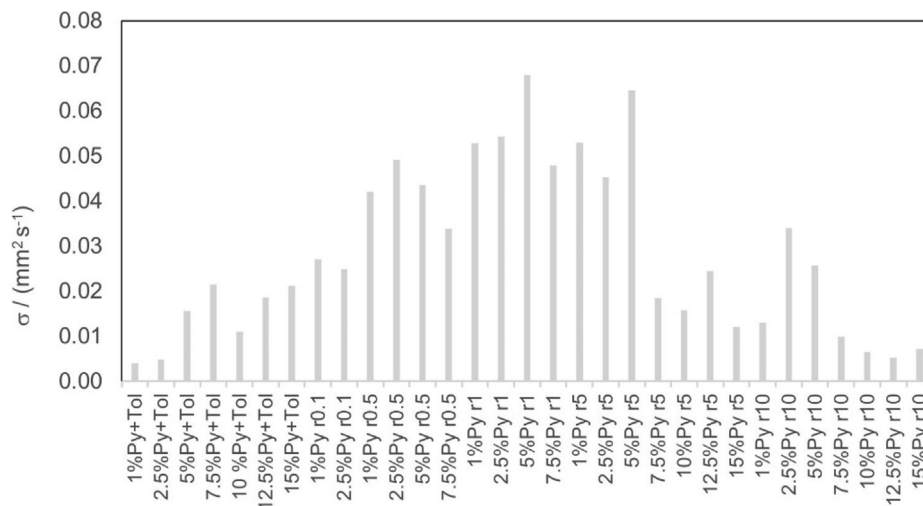


Fig. 5. Standard deviations, σ , for all the systems studied using the ideal solution model.

5. Conclusions

In this work, two relevant properties have been measured and calculated, a static and a dynamic property, density and viscosity, respectively. The density and the viscosity of binary and ternary mixtures pyrene, toluene and heptane were measured at temperatures from 293.15 to 343.15 K over a wide composition range at atmosphere pressure. Experimentally, for binary systems viscosities and densities decrease with temperature increases, and those mixtures with higher pyrene content are more viscous. Viscosities

and densities are highly dependent on temperature and composition for ternary mixtures. Most data in this work exhibit negative values for viscosity deviation, ranging from -0.07 to 0.07 .

The performance of several viscosity models is checked according to overall standard deviation and for the specific systems since there is very disperse distribution in some systems. The ideal and Refutas models present similar deviation values, $\sigma = 0.031 \text{ mm}^2\text{s}^{-1}$ and $\sigma = 0.032 \text{ mm}^2\text{s}^{-1}$, respectively, and the deviations exhibit non-uniform distribution for some specific systems. Ratcliff's model using only one parameter does not improve deviations

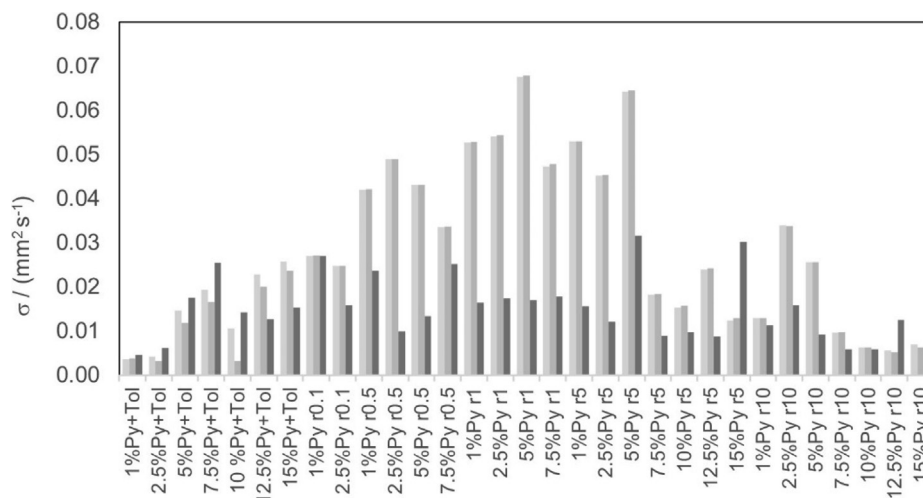


Fig. 6. Standard deviations, σ , for all the systems studied using the Ratcliff model: (light grey) $\Delta(\ln v)_{11}$, (grey) $\Delta(\ln v)_{11t}$, (dark grey) $\Delta(\ln v)_{13}$.

Table 12
Structural and binary interaction parameters for the original UNIFAC-Visco model.

	R	Q	a_{nm}		
			CH2	CH3	ACH
CH2	0.674	0.540	0.00	66.53	406.70
CH3	0.901	0.848	-709.50	0.00	-119.50
ACH	0.531	0.400	-623.70	237.20	0.00

Table 13
Structural and binary interaction parameters for the UNIFAC-Visco model with fitted parameters.

	R	Q	a_{nm}			
			CH2	CH3	ACH	AC
CH2	0.674	0.540	0.00	66.53	630.00	630.00
CH3	0.901	0.848	-709.50	0.00	-119.50	-119.50
ACH	0.531	0.400	-540.00	237.20	0.00	0.00
AC	0.365	0.120	-540.00	237.20	0.00	0.00

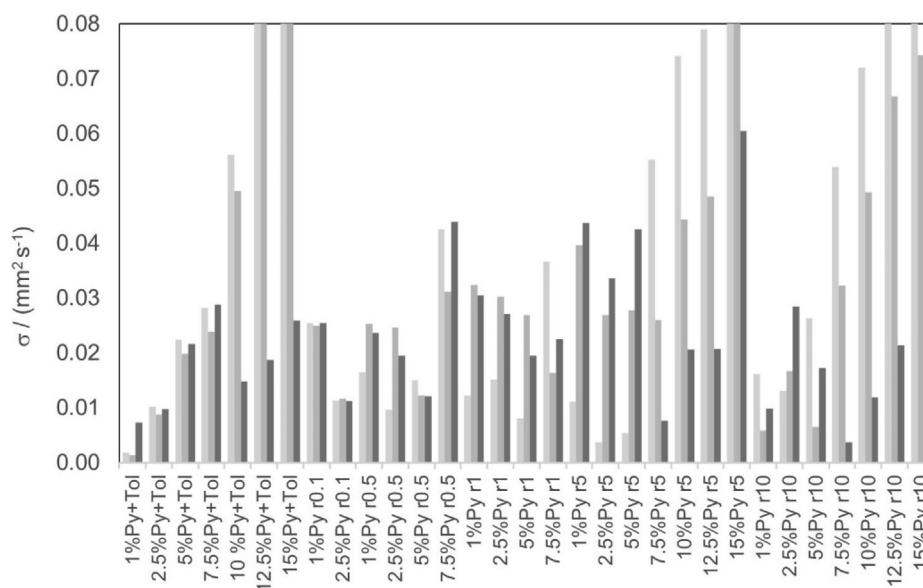


Fig. 7. Standard deviations, σ , for all the systems studied using the UNIFAC-Visco model: (light grey) Original model; (grey) New group AC and fitted parameters; (dark grey) New group AC and fitted parameters and association.

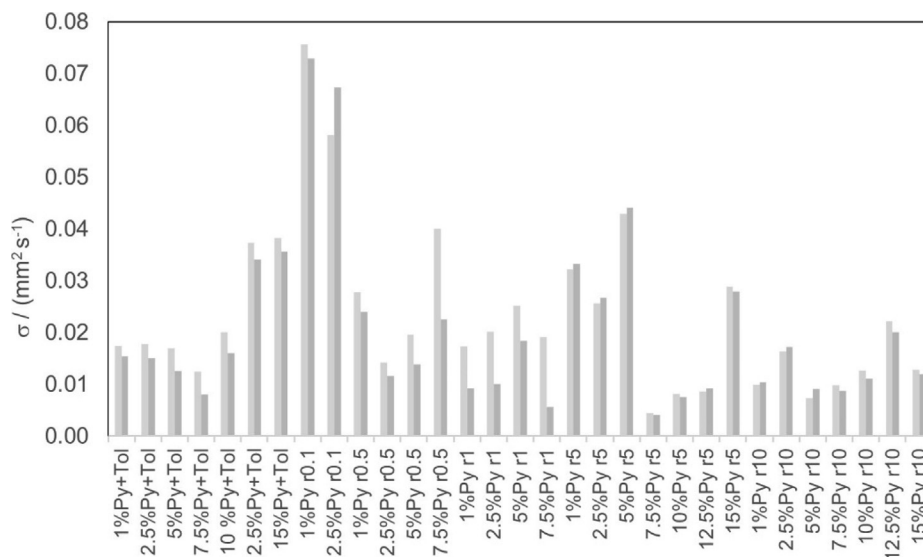


Fig. 8. Standard deviations, σ , for all the systems studied using the Krieger model: (light grey) Krieger model, (grey) Krieger model with temperature dependence.

obtained by ideal and Refutas models. However, introducing 3 interaction parameters, the Ratcliff model presents an important reduction of deviations, and the overall deviation is $\sigma = 0.015 \text{ mm}^2 \cdot \text{s}^{-1}$. Three UNIFAC-Visco model versions are considered. The original model ($\sigma = 0.048 \text{ mm}^2 \cdot \text{s}^{-1}$) and that with the fitted parameter ($\sigma = 0.039 \text{ mm}^2 \cdot \text{s}^{-1}$) are less accurate than the ideal model. The third version of the UNIFAC-Visco model introduces the possibility of pyrene association. In this case, more accurate viscosity predictions are obtained with a standard deviation of $\sigma = 0.024 \text{ mm}^2 \cdot \text{s}^{-1}$. The reduction in the standard deviation is related to improving specific systems whose description by the original UNIFAC-Visco is poor. Finally, the Krieger model considers the eventual association of pyrene and the temperature dependence, it can be considered accurate ($\sigma = 0.025 \text{ mm}^2 \cdot \text{s}^{-1}$) and represent improvement versus the ideal model.

In conclusion, the model of Ratcliff, with the deviation function $\Delta(\ln v)_{13}$ including three binary interaction parameters, is the recommended model as it yields the lowest overall deviations with simple parameters.

CRedit authorship contribution statement

Maria José Tenorio: Methodology, Validation, Investigation, Writing – original draft, Writing – review & editing. **Inmaculada Suárez:** Conceptualization, Methodology, Formal analysis, Writing – original draft. **Julia D. Magdaleno:** Methodology, Investigation. **Miguel A. González:** Validation, Writing – original draft, Writing – review & editing. **Baudilio Coto:** Conceptualization, Data curation, Software, Funding acquisition, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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