Suggestion of mixing rule for parameters of $PR\mu$ model for light liquid hydrocarbon mixtures

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Abstract–Our aim is to improve the predictions for the viscosities of selected light liquid hydrocarbon mixtures by using a reliable model based on Peng-Robinson equation of state (PR EOS). Therefore, a viscosity model on the basis of the similarity between PvT and $T\mu$ (viscosity) P has been applied. Based on the volume-translated Peng-Robinson equation of state (VTPR EOS), a correction has been used for viscosity to improve the results of model. The viscosity model can be extended to mixtures by using an appropriate mixing rule for the parameters of the PR model. For a better description of viscosity and improvement of some calculation results, a mixing rule has been proposed for the parameters of the model. The results of the model show that the agreement between experimental and the calculated viscosities is reasonably good and noticeable improvements can be seen in the results of some calculations.

Keywords: Viscosity, Equation of State, PRµ Model, Hydrocarbon Mixtures

INTRODUCTION

The thermodynamic and transport properties of fluids are essential for engineering applications such as design or analysis of chemical processes, heat and mass transfer and numerical analysis of fluid flow. Among these properties, liquid viscosity emerges as one of the key transport properties required in petrochemical, petroleum, and chemical industries, including fluid transport, mixing, agitation, filtration, heat exchange, or concentration. It is also the most important property in polymer processing. In addition, the thickness and uniformity of a coating layer on a wafer depends on the viscosity of photoresistant. In the design, operation, and optimization of separation equipment, it is important to determine the precise values of liquid viscosity over wide ranges of temperature and pressure [1,2]. The viscosity of n-alkane mixtures is a main parameter in modeling underground oil flow and other applications of chemical engineering such as oil processes, process equipment in the oil and gas industries and oil recovery technology [3]. The accuracy of hydrodynamic process modeling in different applications depends on the reliability of the dynamic viscosity determination for the working media in the liquid and vapor states [4].

Reliable viscosity data are measured by experimental methods, but it is almost impossible to measure the viscosities of all mixtures with experimental methods. Although viscosity data are abundant in the atmosphere, the experimental viscosity data at high pressures are considered a restriction; therefore, fluid viscosities should be described at high pressures by applying a reliable model [2].

Several models have been proposed for the calculation of fluid viscosity. Among these, the correlation of Lohrenz et al. [5,6] and the viscosity model based on the corresponding states theory suggested by Pedersen and Fredenslund [7] are currently applied in the petroleum industry. Three main problems hinder their application: (1) limited application range and accuracy, (2) the viscosity of liquid and gas phases are calculated by using different correlations, so a smooth transition in the near-critical region is a problem, and (3) density is needed for calculation of the fluid viscosity, so that a different density correlation is required [8].

First, Philips [9] indicated the similarity between the PíT and $T\mu$ (viscosity) P relationships in 1912. Little and Kennedy [10] developed the first viscosity model based on the van der Waals EOS. Lawal [11] suggested a viscosity model on the basis of the four-parameter Lawal-Lake-Silberberg EOS that could be applied to pure hydrocarbons and their mixtures. In 1997, Guo et al. [12] recommended two viscosity models, respectively based on the Petal-Teja EOS and the PR EOS. In 1998, Guo reformulated the viscosity model based on the PR EOS and the prediction accuracy was improved [13]. Lee et al. [14] proposed a viscosity model based on the Eyring's absolute rate theory. They estimated the excess activation free energy of flow, $G^{\neq E}$, in Eyring's theory by using the Patel-Teja equation of state [15]. Lee and Lee [16] applied two-parameter van der Waals equations of state in combination with Eyring kinematic viscosity model to study the effect of the selected mixing rule on the viscosity computations of binary nonaqueous mixtures. Cao et al. [17] developed a "viscosity-thermodynamic" model (UNIMOD) to correlate the viscosity and VLE data by the UNIQUAC model. They also applied the same interaction energy parameters. Martins et al. [18] applied the model based on Eyring absolute rate theory for liquid viscosity. The viscosity of the system was described by a combination of a reference term and a deviation contribution. They calculated the residual Helmholtz free energy of the system by using reliable equations of state, including Peng-Robinson [19], Soave-Redlich-Kwong [20] and Peng-Robinson-Stryjek-Vera [21].

The major advantages of applying the viscosity model based on an equation of state are: (1) the viscosity of gas and liquid phases can be determined by a single model, achieving smooth transition of liquid/gas viscosity in the near-critical region, (2) both high and

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low pressure data can be correlated, and no involvement of density exists in computing the fluid viscosity [8].

In this paper, $PR\mu$ model [8] is used for determining the viscosities of light liquid hydrocarbon mixtures. Based on applying mixing rule for determining parameters of the model, the model is applicable for liquid hydrocarbon mixtures. The aim of this work is to improve some of the results obtained from the work of Fan and Wang [8] and properly predict the viscosities of liquid hydrocarbon mixtures. Compared with the work of Fan and Wang [8], different mixing rule is applied for model parameters. This method is also applied for more hydrocarbon mixtures and the results are compared with experimental data from the other works.

MODEL DESCRIPTION

1. PR_{µ0} Model

On the basis of the similarities between PvT and $T\mu P$ relationships, by changing the positions of T and P in the PR EOS, v is substituted with μ and gas constant R is substituted with R' (defined subsequently) [8]. The PR viscosity equation is described as follows:

$$T' = \frac{R'P}{\mu - b} - \frac{a}{\mu^2 + 2\mu b - b^2}$$
(1)

where a presumptive temperature T' is expressed by following expressions:

$$T'=T-T_d$$
(2)

$$T_d = 0.45 T_c$$
 (3)

In Eq. (1), P represents pressure in bar, T the temperature in K, μ the viscosity, 10⁻⁷ Pa s and subscript c shows critical state. In addition, T_d is also necessary for correction of the calculated viscosities. Based on a minimum of deviation of the calculated results from the experimental data, coefficient 0.45 is selected for T_d.

The parameters of the equation can be expressed by following expressions:

Applying the similarities between the PvT and $T\mu P$ diagrams, the critical isobar of the $T\mu P$ diagram has a horizontal inflection point at the critical point [8]. For this critical point, the equation can be written as follows:

$$(\mu - \mu_c)^3 = 0$$
 (4)

Eq. (4) can be expanded as follows:

$$\mu^{3} - 3\mu_{c}\mu^{2} + 3\mu_{c}^{2}\mu - \mu_{c}^{3} = 0$$
⁽⁵⁾

At the critical point ($R'=r_c$), Eq. (1) is expressed as follows:

$$\mu^{3} - \left(\frac{r_{c}P_{c}}{T_{c}'} - b\right)\mu^{2} + \left(\frac{a}{T_{c}'} - \frac{2br_{c}}{T_{c}'} - 3b^{2}\right)\mu - b\left(\frac{a}{T_{c}'} - \frac{br_{c}}{T_{c}'} - b^{2}\right) = 0 \quad (6)$$

By equalizing the coefficients of Eqs. (5) and (6), the following equations are obtained:

$$3\mu_c = \frac{\mathbf{r}_c \mathbf{P}_c}{\mathbf{T}_c'} - \mathbf{b} \tag{7}$$

$$3\mu_c^2 = \frac{a}{T_c'} - \frac{2br_c}{T_c'} - 3b^2$$
(8)

$$\mu_c^3 = b \left(\frac{a}{T_c'} - \frac{br_c}{T_c'} - b^2 \right)$$
(9)

By solving Eqs. (7)-(9), the coefficients a, b and Z_c are obtained:

$$a = 0.45724 \frac{(r_c P_c)^2}{T'_c}$$
(10)

$$b = 0.0778 \frac{r_c P_c}{T'_c}$$
(11)

$$Z_c = \frac{\mu_c T_c'}{r_c P_c} = 0.3074$$
(12)

According to Eq. (12):

$$r_{c} = \frac{\mu_{c} T_{c}'}{0.3074 P_{c}}$$
(13)

The critical viscosity μ_c can be determined by empirical correlation. Applying Uyehara and Watson [22] empirical correlation, the critical viscosity μ_c can be calculated by applying the following equation as a function of critical temperature (T_c), critical pressure (P_c) and molecular mass (M_W).

$$\mu_c = 7.7 T_c^{-1/6} M_W^{1/2} P_c^{2/3}$$
(14)

where μ_c is in micropoise.

In Eq. (1), R' can be calculated from:

$$\mathbf{R}' = \boldsymbol{\beta}(\mathbf{P})\mathbf{r}_c \tag{15}$$

 β (P) is a pressure-dependent parameter whose value is 1 at critical pressure. The following generalized expression is applied for determining this parameter.

$$\beta(\mathbf{P}) = \mathbf{e}_0 (1 - \mathbf{P}_r^{-1}) - 0.02715 \mathbf{P}_r^{-1} ((\mathbf{P}_r + 0.25)^{-1} - 0.8) + \mathbf{P}_r^{-1}$$
(16)

where

$$e_0 = 0.03192 - 3.3125 \times 10^{-4} M_w \omega \tag{17}$$

2. Liquid Viscosity Correction

The above viscosity model developed from PR EOS is named the PR μ_0 model. The viscosity of liquid calculated based on the PR μ_0 model is poorly represented; therefore, a correction of the viscosity should be used.

Based on the volume-translated PR equation of state (VTPR EOS), a correction of viscosity is required. This correction can be expressed as the following:

$$\mu = \mu^{PR} + c_0 + c \tag{18}$$

where μ^{PR} is the viscosity computed from Eq. (1), c_0 is a function of reduced pressure.

$$c_0 = 6.714(P_r - 1) - 127.8((P_r + 1)^{-1} - 0.5)$$
(19)

In Eq.(18), c depends on μ^{PR} and can be computed from Eq. (21).

$$\mu_r = \frac{\mu^{PR}}{\mu_c} \tag{20}$$

$$c=e_{3} \ln \mu_{+}+e_{4}(\mu_{-}-1)+e_{5}((\mu_{+}+1.25)^{-1}-0.4444)$$
(21)

The coefficients of e3, e4 and e7 depend on molecular weight, and

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(22)

the acentric factor and can be calculated from:

e=3337.201-717.955M

$$e_5=3337.201-717.955M_M \omega \quad \omega < 0.3$$
 (22)
 $e_5=17000 \quad \omega \ge 0.3$ (23)

$$e_3 = 216.643 + 0.231e_5 \quad \omega < 0.3$$
 (24)

$$e_3 = 4130.636 \qquad \omega \ge 0.3$$
 (25)

$$e_4 = \left(\frac{e_5}{\left(e_7 + 1.25\right)^2} - \frac{e_3}{e_7}\right)$$
(26)

Coefficient of e_7 depends on the acentric factor and can be obtained from:

$$\mathbf{e}_{7} = 1.767 + 18.384\omega - 32.728\omega^{2} + 80.299\omega^{3} \tag{27}$$

This viscosity correction model is named the $PR\mu$ model. An example of the detailed calculations is also given in [8].

3. Extension of Model to Hydrocarbon Mixtures

Based on the work of Fan and Wang [8], the viscosity model is extended to mixtures by using the following mixing rules:

$$\mathbf{z}_m = \sum_{i} \mathbf{z}_i \mathbf{x}_i \quad \mathbf{z} = \mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{r}_c, \mathbf{T}_d \text{ and } \boldsymbol{\beta}$$
(28)

In Eq. (28), subscript m shows mixture.

In this work, these mixing rules are suggested for the purpose of extending viscosity model to light liquid hydrocarbon mixtures.

$$\mathbf{z}_m = \sum_i \sum_j \mathbf{z}_{ij} \mathbf{x}_i \mathbf{x}_j \quad \mathbf{z} = \mathbf{a}, \mathbf{b}, \mathbf{r}_c, \mathbf{T}_d \text{ and } \boldsymbol{\beta}$$
(29)

$$\mathbf{c}_m = \sum_i \mathbf{c}_i \mathbf{x}_i$$

Where

$$\mathbf{z}_{ij} = \sqrt{\mathbf{z}_i \mathbf{z}_j} \tag{31}$$

CALCULATION RESULTS

1. Binary Mixtures

The binary mixtures of heptane (1)-octane (2) are first considered. These mixtures contain (28.08 mole% heptane+71.92 mole% octane), (54.27 mole% heptane+45.73 mole% octane) and (79.06 mole% heptane+20.94 mole% octane). The experimental viscosity data of these mixtures are taken from Abdulagatov and Azizov [3], who reported experimental data for 122 points in the temperature range of 298.39-472.52 K and three isobars: 0.1, 5 and 10 MPa. The experimental data, the results computed by $PR\mu$ model and comparisons with the experimental data are summarized in Tables 1-3. The average absolute deviations (AAD%) are also illustrated in Tables 1-3. The average absolute deviations viscosity data defined by:

$$AAD\% = \frac{1}{N} \sum_{i=1}^{N} \frac{\mu_{exp} - \mu_{calc}}{\mu_{exp}} \times 100$$
(32)

In Eq. (32), N represents the number of experimental points. Tables 1-3 show that the overall absolute deviations of the $PR\mu$ model in combination with the suggested mixing rule are 4.16%, 4.36% and 4.33% for these three binary mixtures, respectively. So, the results of $PR\mu$ model in combination with the proposed mixing rules have a reasonable agreement with experimental data of heptane (1)-octane (2) mixtures in the given temperature range, three isobars and three different compositions. The viscosities of these three systems are also modeled by using Eq. (28). The AADs% are 4.6%, 4.86% and 4.76% for these three binary mixtures, respectively. According to the Abdulagatov and Azizov [3], the AAD for the method of Huber et al. [23] is 0.45%; therefore, the applied model performs relatively well for these three systems.

2. Ternary Mixtures

The viscosities of five ternary mixtures at different pressures and

Table 1. Experimental data and calculated values for viscosities of heptane (1)-octane (2) hydrocarbon mixture (x_1 =28.08 mole%, x_2 = 71.92 mole%) [3]

(30)

μ (mPa·s)									
T (K)	P=0.1 MPa		P=5 MPa				P=10 MPa		
	$\mu_{\scriptscriptstyle calc}$	$\mu_{\scriptscriptstyle exp}$	AAD%	$\mu_{\scriptscriptstyle calc}$	$\mu_{\scriptscriptstyle exp}$	ADD%	$\mu_{\scriptscriptstyle calc}$	$\mu_{\scriptscriptstyle exp}$	AAD%
298.39	0.445	0.467	4.71	0.484	0.493	1.82	0.496	0.521	4.80
303.85	0.418	0.441	5.21	0.458	0.465	1.50	0.471	0.492	4.27
312.71	0.379	0.400	5.25	0.421	0.424	0.71	0.434	0.446	2.69
321.71	0.344	0.362	4.97	0.387	0.384	0.78	0.400	0.405	1.23
333.54	0.304	0.322	5.59	0.348	0.341	2.05	0.362	0.360	0.55
344.39	0.273	0.291	6.18	0.317	0.306	3.59	0.331	0.325	1.85
354.08	0.248	0.267	7.12	0.293	0.283	3.53	0.307	0.299	2.67
363.71	0.225	0.245	8.16	0.271	0.261	3.83	0.285	0.276	3.26
373.51				0.251	0.241	4.15	0.265	0.255	3.92
382.99				0.233	0.223	4.48	0.247	0.237	4.22
393.49				0.215	0.206	4.37	0.229	0.220	4.09
413.6				0.186	0.178	4.49	0.200	0.191	4.71
432.62				0.162	0.156	3.85	0.176	0.168	4.61
455.63				0.138	0.133	3.76	0.152	0.145	4.82
473.46				0.122	0.118	3.39	0.136	0.130	4.61
Average			5.90			3.09			3.50
Over all					4.16				

μ (mPa·s)									
T (K)	P=0.1 MPa		P=5 MPa				P=10 MPa		
	$\mu_{\scriptscriptstyle calc}$	$\mu_{\scriptscriptstyle exp}$	AAD%	$\mu_{\scriptscriptstyle calc}$	μ_{exp}	ADD%	$\mu_{\scriptscriptstyle calc}$	μ_{exp}	AAD%
298.15	0.415	0.436	4.81	0.453	0.461	1.73	0.465	0.487	4.51
303.29	0.391	0.414	5.56	0.431	0.435	0.92	0.443	0.459	3.48
312.74	0.353	0.374	5.61	0.395	0.396	0.25	0.408	0.419	2.62
321.21	0.323	0.338	4.44	0.365	0.359	1.67	0.379	0.380	0.26
333.73	0.284	0.300	5.33	0.327	0.319	2.51	0.341	0.338	0.89
344.4	0.255	0.273	6.59	0.299	0.290	3.10	0.313	0.307	1.95
352.62	0.235	0.255	7.84	0.279	0.270	3.33	0.293	0.286	2.44
363.74	0.211	0.232	9.05	0.256	0.247	3.64	0.270	0.260	3.85
373.97				0.236	0.227	3.96	0.250	0.240	4.17
383.18				0.220	0.212	3.77	0.234	0.224	4.46
394.51				0.202	0.195	3.59	0.216	0.206	4.85
403.23				0.189	0.183	3.27	0.204	0.193	5.70
415.96				0.173	0.167	3.59	0.187	0.177	5.65
424.55				0.163	0.158	3.16	0.177	0.167	5.99
433.62				0.153	0.148	3.38	0.166	0.158	5.06
452.73				0.133	0.129	3.10	0.147	0.140	5
463.18				0.124	0.120	3.33	0.138	0.131	5.34
473.10				0.116	0.112	3.57	0.129	0.123	4.87
Average			6.15			2.88			3.95
Over all					4.33				

Table 2. Experimental data and calculated values for viscosities of heptane (1)-octane (2) hydrocarbon mixture (x_1 =54.27 mole%, x_2 = 45.73 mole%) [3]

 Table 3. Experimental data and calculated values for viscosities of heptane (1)-octane (2) hydrocarbon mixture (x1=79.06 mole%, x2= 20.94 mole%) [3]

μ (mPa · s)									
T (K)	P=0.1 MPa		P=5 MPa				P=10 MPa		
	$\mu_{\scriptscriptstyle calc}$	$\mu_{\scriptscriptstyle exp}$	AAD%	$\mu_{\scriptscriptstyle calc}$	$\mu_{\scriptscriptstyle exp}$	ADD%	$\mu_{\scriptscriptstyle calc}$	$\mu_{\scriptscriptstyle exp}$	AAD%
298.22	0.387	0.408	5.14	0.425	0.435	2.30	0.437	0.459	4.79
305.74	0.357	0.379	5.80	0.396	0.402	1.49	0.409	0.425	3.76
312.75	0.331	0.352	5.96	0.372	0.373	0.26	0.385	0.395	2.53
323.82	0.295	0.314	6.05	0.337	0.334	0.90	0.350	0.353	0.85
335.62	0.262	0.281	6.76	0.304	0.298	2.01	0.318	0.316	0.63
344.21	0.240	0.260	7.69	0.283	0.276	2.54	0.297	0.292	1.71
353.20	0.220	0.239	7.95	0.263	0.255	3.14	0.277	0.270	2.59
364.62	0.197	0.216	8.79	0.240	0.232	3.44	0.254	0.246	3.25
373.19				0.225	0.217	3.69	0.239	0.230	3.91
384.55				0.206	0.198	4.04	0.220	0.211	4.26
395.52				0.190	0.183	3.82	0.204	0.195	4.61
407.72				0.174	0.167	4.19	0.188	0.180	4.44
424.45				0.154	0.149	3.35	0.168	0.160	5
435.62				0.142	0.138	2.90	0.156	0.149	4.70
455.30				0.124	0.120	3.33	0.138	0.132	4.54
472.52				0.110	0.107	2.80	0.124	0.118	5.08
Average			6.77			2.76			3.54
Over all					4.36				

temperatures are presented. First, the viscosity behavior of ternary mixtures of heptane (1)-octane (2)-nonane(3) is considered. It is the mixture of three paraffins containing 28.70 mole% heptane, 20.80

mole% octane and 50.50 mole% nonane. Based on the work of Barrufet et al. [24], the range of temperature was nearly (293 to 313) K at the isobar of 1 bar for the experimental viscosities. The viscosi-



Fig. 1. Calculated and experimental viscosities for 28.70 mole% heptane, 20.80 mole% octane and 50.50 mole% nonane: (■) experimental data; (■) calculated results [23].



Fig. 2. Calculated and experimental viscosities of 75.07 mole% pentane (1), 10.01 mole% octane (2) and 14.92 mole% decane (3) at different pressures and temperatures. Experimental data: (■) T=313.05 K; (◆) T=328.05 K; (▲) T=343.15 K; (-) T=358.25 K; (●) T=373.25 K; (■) calculated results [24].

ties have been computed for this mixture at 1 bar for pressures ranging from 290-315 K. Fig. 1 presents a comparison of the calculated viscosities of this mixture and experimental data. The mean absolute deviation from experimental data is about 3.1%. By using Eq. (28), the AAD% of this system is 8.25%. So, the proposed mixing rule performs well for this system.

The second example of ternary system, represented in Fig. 2, illustrates the viscosities of the system containing 75.07 mole% pentane, 10.01 mole% octane and 14.92 mole% decane at different pressures and temperatures. The experimental data were measured at 313.05, 328.05, 343.15, 358.25 and 373.25 K in the range of 0 bar to 250 bar and they are given from [25]. The maximum deviation of the prediction is for 313.15 K. The mean absolute error for all experimental data is about 2.47%, so that reasonable agreement between modeling results and experimental data can be seen for these two ternary systems. By using Eq. (28) in combination with the PR μ

Table 4. Experimental data [26] and calculated values for viscosities for ternary hydrocarbon mixtures

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P (bar)	T (K)	$\mu_{exp} (\mathrm{mPa} \cdot \mathrm{s})$	$\mu_{calc} (\mathrm{mPa} \cdot \mathrm{s})$
30.26 mole% l	heptane+64.02	mole% octane +5.71	mole% hexyl benzene
1	293.15	0.5163	0.4986
1	298.15	0.4870	0.4700
1	303.15	0.4604	0.4436
1	308.15	0.4368	0.4191
1	313.15	0.4144	0.3964
27.62 mole% l	neptane +63.86	mole% nonane+8.52	mole% hexyl benzene
1	293.15	0.6188	0.6282
1	298.15	0.5811	0.5867
1	303.15	0.5470	0.5495
1	308.15	0.5162	0.5159
1	313.15	0.4871	0.4855
56.38 mole%	octane +34.48 n	nole% nonane +9.14	mole% hexyl benzene
1	293.15	0.6375	0.6392
1	298.15	0.5966	0.5901
1	303.15	0.5611	0.5525
1	308.15	0.5294	0.5185
1	313.15	0.5006	0.4879
AAD%		1.98	

model, the AAD% of this system is 10.48%. So, the applied method performs well for this ternary system.

The third, fourth and fifth ternary systems contain (30.26 mole% heptane +64.02 mole% octane +5.71 mole% hexyl benzene), (27.62 mole% heptane +63.86 mole% nonane +8.52 mole% hexyl benzene) and (56.38 mole% octane +34.48 mole% nonane +9.14 mole% hexyl benzene), respectively. The experimental data are given from [26]. All experimental data ranged (293 to 313) K at the isobar of 1 bar. Table 4 illustrates the experimental data and the modeling results. One can see that very good agreement exists between experimental data and modeling results. According to [26], The AAD% of PR μ model in combination with Eq. (28) is 6.44%. Also, according to [26], the AADs% of the Sastri-Rao Method (S-R) [27], the Przezdiecki-Sridhar Method (P-S) [27], and the Dymond-Assael Hard Sphere Model (D-A) [27,28] are 3.66, 22.11 and 2.24, respectively. This comparison shows the advantages of the proposed mixing rule for these three ternary systems

3. Quaternary Mixtures

The viscosity data of two quaternary mixtures containing butane (1)-hexane (2)-decane (3)-carbon dioxide (4) at isobars of 25.14 and 49.28 bar and five different temperatures are listed in Table 5. The calculated results of this work and the work of Fan and Wang [8] and their comparison with experimental data from the literature [25] are also illustrated in Table 5. For the first system (x_1 =15 mole%, x_2 =15 mole%, x_3 =47.6 mole%) the mean deviation from experimental data is 19.33% and 3.94%, respectively, for the work of Fan and Wang [8] and this work, so noticeable improvement is seen in predicting the viscosity of this mixtures in this work (To our knowledge, Fan and Wang [8] used Eq. (28) to predict the viscosity.). For the second quaternary mixture (x_1 =17.7 mole%, x_2 =17.7 mole%, x_3 =56 mole%) the mean deviation from experimental data are 6.06% and 5.61%, respectively, for work of Fan and Wang [8] and this work of Fan and Wang [8] and this work of Fan and Wang [8] and this work of Fan and Wang [8] and the viscosity.).

			Fan and Wang [8]	This work	Fan and Wang [8]	This work		
T (K)	P (bar)	μ_{exp} (×10 ⁻⁷ Pas)	μ_{calc} (×10 ⁻⁷ Pas)	μ_{calc} (×10 ⁻⁷ Pas)	AAD%	AAD%		
Butane (1)+hexane (2)+decane (3)+carbon dioxide (4): $x_1=0.15$, $x_2=0.15$, $x_3=0.476$								
324.26	49.28	3040	3575	3080	17.60	1.31		
342.04	49.28	2790	3165	2685	13.44	3.76		
359.82	49.28	2440	2820	2360	15.57	3.28		
377.59	49.28	2160	2525	2089	16.90	3.29		
395.37	49.28	1720	2290	1859	33.14	8.08		
Average	-	-	-	-	19.33	3.94		
	Bı	atane (1)+hexane (2)+	decane (3)+carbon diox	xide (4): $x_1 = 0.177, x_2 =$	=0.177, x ₃ =0.56			
324.26	25.14	3500	3825	3489	9.28	0.31		
342.04	25.14	3070	3320	3001	8.14	2.24		
359.82	25.14	2750	2922	2606	6.25	5.24		
377.59	25.14	2500	2574	2278	2.96	8.89		
395.37	25.14	2320	2287	2004	1.42	13.6		
Average	-	-	-	-	5.61	6.06		
Pentane (1)+hexane(2)+heptane(3)+decane(4)+carbon dioxide(5): $x_1=0.075$, $x_2=0.0225$, $x_3=0.08$, $x_4=0.397$								
359.82	49.28	2430	2790	2383	14.81	1.97		
377.59	49.28	2190	2505	2108	14.38	3.74		
383.15	49.28	1970	2420	2031	22.84	3.10		
395.37	49.28	1720	2260	1874	31.39	8.95		
Average	-	-	-	-	20.85	4.44		
	Pentane (1)+h	nexane(2)+heptane(3)-	+decane(4)+carbon dio	xide(5): $x_1 = 0.088$, $x_2 =$	$= 0.264, x_3 = 0.094, x_4 = 0.4$	167		
359.82	25.14	2780	2877	2631	3.49	5.36		
377.59	25.14	2520	2541	2300	0.83	8.73		
383.15	25.14	2310	2448	2207	5.80	4.45		
395.37	25.14	2090	2257	2070	7.99	0.96		
Average	-	-	-	-	4.52	4.87		
Over all	-	-	-	-	12.58	4.83		

 Table 5. Experimental data and calculated values for viscosities of hydrocarbon mixtures [8]

so the work of Fan and Wang [8] has better predictions. For the first three data improvements can be noticed, but the last two predictions of the Fan and Wang [8] are much better than this work.

4. Five-component Mixtures

The viscosities of two complex mixtures' normal paraffins with carbon dioxide are presented in Table 5. The experimental data are given from the literature [24]. They contain Pentane (1), hexane(2), heptane (3), decane(4) and carbon dioxide(5). For the first one (x_1 = 7.5 mole%, x_2 =2.25 mole%, x_3 =8 mole%, x_4 =39.7 mole%), predictions are improved from 20.85% in the work of Fan and Wang [8] to 4.44% in this work. Applying PR μ model with the proposed mixing rules also improves the viscosity calculation from 12.58% in the work of Fan and Wang [8] to 4.83% in this work for the second five-component mixture (x_1 =8.8 mole%, x_2 =2.64 mole%, x_3 =9.4 mole%, x_4 =46.7 mole%). As mentioned before, Fan and Wang [8] used Eq. (28) to predict the viscosity. So the applied model improves the performance of the viscosity predictions for these two mixtures.

CONCLUSIONS

On the basis of similarity between PvT and T μ (viscosity) P, the PR μ model has been applied for calculating the viscosities of liquid hydrocarbons. By using a mixing rule for the parameters of the model,

this model is applicable for hydrocarbon mixtures. A mixing rule is also suggested for determination of $PR\mu$ model parameters. The model adequately describes the viscosities of the selected liquid hydrocarbon mixtures. The following conclusions can be drawn from this work:

• For binary mixtures of heptane (1)-octane (2), which are considered in this work, the AADs% are 4.16%, 4.36% and 4.33%. So, there is a reasonable agreement between calculated results and experimental data.

• For ternary mixtures of this work the AADs% are 3.10%, 2.47% and 1.98%. So, the combination of PR μ model and suggested mixing rule has been successfully applied for these two ternary mixtures. Also, the applied model performs better than the Sastri-Rao Method (S-R) [27], the Przezdiecki-Sridhar Method (P-S) [27], and the Dymond-Assael Hard Sphere Model (D-A) [27,28].

• For two quaternary mixtures selected for this work, the AADs% are 3.94% and 6.06%. According to Fan and Wang [8], the AAD% for the first one is 19.33%. In comparison with Fan and Wang [8], noticeable improvement can be seen in the calculation results for the first sample.

• For two five-component mixtures AADs% are 4.44% and 4.83%. Based on the work of Fan and Wang [8], the AADs% are 20.85% and 12.48%. So, much better predictions are seen for these

LIST OF SYMBOLS

- a : energy parameter for PR equation of state; $PR\mu$ model parameter
- b : volumetric parameter for PR equation of state; $PR\mu$ model parameter
- c, c_0 : parameters of viscosity
- e : parameters in Eqs. (15) and (18)
- M_w : molecular mass [g/mol]
- P : pressure [bar]
- \mathbf{r}_c : parameter of the PR μ model
- R : generalized gas constant
- R' : parameter of the PR μ model
- T : temperature [K]
- T_d : a specific temperature for correction of the calculated viscosities
- T' : a presumptive temperature
- v : molar volume [l/mol]
- x : liquid mole fraction

Greek Letters

- $\alpha(T)$: temperature dependent function
- $\beta(P)$: pressure dependent function in PR μ model
- μ : dynamic viscosity [×10⁷ Pa s]
- ω : acentric factor

Subscripts

- c : critical property
- m : mixture property
- r : reduced property

Superscripts

 $PR \quad : calculated \ by \ PR\mu_0 \ model$

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