Research Article

Empirical Correlations for K-Values of Crude Oils

Jose V. Flores-Cano, 1 Carlos G. Aguilar-Madera, 1 Erik C. Herrera-Hernández, 2 G. Espinosa-Paredes, 3 Jose P. Ruelas-Leyva, 4 Victor Matías-Pérez, 1 and Jorge A. Briones-Carrillo 1

1 Universidad Autónoma de Nuevo León, Facultad de Ciencias de la Tierra, Carretera a Cerro Prieto Km. 8, C.P. 67700, Linares, Mexico
2 Centro de Investigación y Estudios de Posgrado, Facultad de Ciencias Químicas, Universidad Autónoma de San Luis Potosí, Av. Dr. Manuel Nava 6, Zona Universitaria 78210, San Luis Potosí, Mexico
3 Área de Ingeniería en Recursos Energéticos, Universidad Autónoma Metropolitana-Iztapalapa, CDMX 09340, Mexico
4 Universidad Autónoma de Sinaloa, Facultad de Química, Blvd. Miguel Tamayo Espinosa de los Monteros S/n, Col. Desarrollo Urbano Tres Ríos, C.P. 80050, Culiacán, Mexico

Correspondence should be addressed to G. Espinosa-Paredes; gepe@xanum.uam.mx

Received 2 May 2022; Accepted 21 July 2022; Published 5 August 2022

Academic Editor: Pedro Castano

Copyright ©2022 Jose V. Flores-Cano et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Based on the Soave–Redlich–Kwong equation of state, empirical correlations for the K-values of N₂, CO₂, H₂S, C₁, and C₂ are proposed. Complementarily, the binary interaction coefficients involving the plus fraction, C₇⁺, were optimized by fitting into 131 experimental data from the literature. The criterion to select the form of the empirical correlations was based on the identification of the major dependencies of the equilibrium constants on the system variables (e.g., pressure, temperature, and composition). For most of the experimental data, the saturation pressure calculated via the empirical correlations is in excellent agreement with those reported from the laboratory. The empirical correlations cover a variety of temperatures (128–314 °F), pressures (313–6880 psi), and compositions (N₂: 0.0–1.67%; CO₂: 0.0–9.11%; H₂S: 0.0–3.68%; C₁: 5.63–74.18%; C₂: 0.84–12.45%; C₇⁺: 10.72–83.2%). The proposed correlations are useful for rapid vapor-liquid equilibrium calculations during the compositional modeling of petroleum reservoirs.

1. Introduction

In petroleum-related studies, variables such as bubble point pressure, oil density, crude oil gravity, gas gravity, gas/oil ratio, gas and oil formation volume factors, among others, are of great interest. In particular, equilibrium ratios or K-values are required in the design for the separation of crude oil-natural gas mixtures and gas condensates. Moreover, pipeline design strongly depends on the K-values, which need to be determined under several operating conditions [1]. The K-values also take importance in the numerical simulation of petroleum reservoirs when a compositional approach is required, for instance, during the simulation of enhanced oil recovery.

The K-values can be obtained by means of analyzing a representative sample of crude oils or by theoretical determination using an empirically derived correlation or equation of state. The first requires several experiments, resulting in expensive and time-consuming procedures, whereas the last is more accessible through simulations. Despite simulations being more accessible, when predicting K-values, special attention is needed to avoid large calculation times or calculation failures due to the lack of convergence [2].

The conventional way to estimate the K-values is through empirical correlations. In this regard, several correlations have been proposed for predicting the equilibrium ratios of hydrocarbon mixtures. These correlations range from a simple mathematical expression to complicated formulations containing several composition-dependent variables. Some of these correlations are Wilson’s [3], and Standing’s correlations [4], the convergence pressure [5] method, and...
the Whitson and Torp equation [6]. Detailed descriptions of these correlations are available by Ahmed [7].

Nung and Tsai [8] calculated the vapor-liquid equilibrium for mixtures of carbon dioxide with hydrocarbons at temperatures ranging from 193 to 511 K and pressures up to 170 atm. The researchers correlated successfully by using the corresponding state principle in combination with classical mixing rules using the optimum binary interaction parameters $k_{ij}$ and the universal constant $\eta = 0.35$. The method was verified using data from the literature.

In more recent times, Vatandoost et al. [9] developed a model for the prediction of $K$-values for heavy fractions in hydrocarbon systems ($C_{11}$ to $C_{20}$s). The proposed correlation considers the effects of mixture composition and binary interaction parameters on $K$-values in terms of temperature within the Peng–Robinson equation of state (PR EOS) [10]. The proposed correlation shows a better agreement with the PR EOS results than the methods of Whitson and Torp [6], Rashidi and Valeh-e-Sheyda [2], and Ghafoori et al. [11].

Ahmadi et al. [12] developed a predictive model to determine the thermodynamic equilibrium constant for hydrocarbon systems (C11 to C20s). The proposed correlation considers the effects of mixture composition and binary interaction parameters on $K$-values in terms of temperature within the Peng–Robinson equation of state (PR EOS) [10]. The proposed correlation shows a better agreement with the PR EOS results than the methods of Whitson and Torp [6], Rashidi and Valeh-e-Sheyda [2], and Ghafoori et al. [11].

Ahmadi et al. [12] developed a predictive model to determine the thermodynamic equilibrium constant for hydrocarbon systems (C11 to C20s). The proposed correlation considers the effects of mixture composition and binary interaction parameters on $K$-values in terms of temperature within the Peng–Robinson equation of state (PR EOS) [10]. The proposed correlation shows a better agreement with the PR EOS results than the methods of Whitson and Torp [6], Rashidi and Valeh-e-Sheyda [2], and Ghafoori et al. [11].

Ahmadi et al. [12] developed a predictive model to determine the thermodynamic equilibrium constant for hydrocarbons and nonhydrocarbons of 10 different crude oils (20–40°API) within a temperature range of 600–1212°R and a pressure range of 14.7–7000 psi. Their proposed model was a hybrid model of LSSVM (least squares support vector machine) and GA (genetic algorithm) and led to predictions with good agreement of the experimental data.

On one hand, the literature is vast in terms of non-conventional computational theories to predict crude oil properties. For instance, Ansari and Gholami [13] focused on the design of a smart model fusing a support vector regression model and an optimization technique for learning the relationship between the saturation pressure and compositional data like temperature, hydrocarbon, and non-hydrocarbon compositions of crudes, and $C_{7+}$ specifications. In another case, Ahmadi et al. [14] worked on a method involving swarm intelligence and artificial neuronal networks as a robust and effective method to determine the bubble point pressure of crude oil samples. A more elaborated theory was formulated by Fang and Lei [15] by applying a continuous thermodynamic correlation with the Gaussian distribution function to correlate the experimental vapor pressure data of four different crude oils. The vapor and liquid phase distribution functions of the fuel fractions and their vapor-liquid equilibrium constants were calculated with satisfactory results. Continuous thermodynamics has proved to be an efficient way to quantitatively calculate the thermodynamic properties and the vapor-liquid equilibrium behavior of multicomponent systems, such as fuel fractions.

On the other hand, the equations of state are widely used by engineers and scientists due to their versatility and accuracy for different hydrocarbon mixtures. Among these equations, the Soave–Redlich–Kwong equation of state (SRK EOS) [16] has been extensively applied by petroleum companies [17], and it is stated to be one of the most popular equations of state currently used in simulations needing thermodynamics and vapor-liquid equilibrium properties [18]. Other specific applications of SRK include, for instance, the description of the Brazil nut oil/carbon dioxide considered as a pseudobinary system [19], and it has also been employed to predict changes in viscosities with temperature and pressure for light hydrocarbons, $\text{CO}_2$, and $\text{N}_2$ [20].

In this contribution, simple correlations for $K$-values in crude oils are proposed. The accuracy of these correlations is evaluated by comparing the prediction of pressure saturation with over 131 crude oils from the literature, ranging over a variety of pressures, temperatures, and compositions. We found excellent agreement when the SRK EOS is employed with optimized binary interaction coefficients related to the fraction $C_{7+}$. The main purpose of this work is to avoid tedious empirical correlations with a lot of coefficients without sacrificing precision.

2. Mathematical Statements

2.1. The Soave–Redlich–Kwong Equation of State (SRK EOS). In this work, we employ the SRK EOS [16], which in terms of compressibility $Z$ is as follows:

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0,$$

(1)

with

\[ A = \frac{p_{cm}}{R^2 T_0}, \]

\[ B = \frac{p_{cm}}{RT_0}, \]

\[ a_m = \sum_{i=1}^{n_c} x_i \Psi_i, \]

\[ b_m = \sum_{i=1}^{n_c} x_i b_i, \]

\[ \Psi_i = \sum_{j=1}^{n_c} x_j a_{ij}, \quad i, j = 1, 2, \ldots, n_c, \]

\[ a_{ij} = \sqrt{a_i a_j (1 - k_{ij})}, \]

\[ a_i = \Omega_i R^2 \frac{T_{ci}^2}{P_{ci}}, \]

\[ b_i = \Omega_i R \frac{T_{ci}}{P_{ci}}, \]

\[ \alpha_i = \left[ 1 + m_i \left( 1 - \sqrt{T_{ri}} \right) \right]^2, \]

\[ T_{ri} = \frac{T}{T_{ci}}, \]

\[ m_i = 0.480 + 1.574 \omega_i - 0.176 \omega_i^2. \]

The coefficients $\Omega_i$, and $\Omega_i$ are 0.427480 and 0.08664, respectively. In the above equations, $T_{ci}$ and $P_{ci}$ are the critical temperature and pressure for each chemical
component, respectively; \( \omega_i \) is the acentric factor; \( k_{ij} \) represents the binary interaction coefficients. \( P \) is the pressure system, \( T \) is the temperature, \( R \) is the ideal gas constant, \( n_i \) is the number of chemical components, \( x_i \) represents the molar fraction of component \( i \) in the liquid phase, and analogously \( y_i \) is the molar fraction in the gas phase. Once the cubic equation (1) is solved and the correct roots are chosen (real, positive, and minimum root for the liquid; real, positive, and largest root for the gas), then the fugacity (\( f_i^L \)) and fugacity coefficient (\( \Phi_i^L \)) are calculated as

\[
f_i^L = x_i P \Phi_i^L,
\]

\[
\ln \Phi_i^L = \frac{b_i}{b_m} (Z_i^L - 1) - \ln (Z_i^L - B) - \frac{A}{B} \left( \frac{2W_i}{a_m} - \frac{b_i}{b_m} \right) \ln \left( \frac{Z_i^L}{Z_i^L + B} \right).
\]

In all of the above equations, some mathematical expressions are written for the liquid, and the analogous expressions are easily obtained for the gas phase doing \( Z_i^G \) instead of \( Z_i^L \) and \( y_i \) instead of \( x_i \), wherever appropriate.

2.2. Ancillary Information. Although critical properties and the acentric factor of pure components are reported in the literature, these must be estimated for the \( C_7 \) fraction since it is a pseudo-component in the compositional modeling. The critical properties of \( C_7 \) are estimated by Jamialahmadi et al. [21], as shown in the following equation:

\[
P_{c_{C_7}} \text{[atm]} = 36.02 \exp (-0.01323 M_{C_7}) + 26.12 \exp (-0.002561 M_{C_7}). \tag{4}
\]

\[
T_{c_{C_7}} \text{[K]} = 239.4 \ln (M_{C_7}) - 555.3.
\]

In the same way, the boiling point temperature is computed with

\[
T_{b_{C_7}} \text{[K]} = 0.0004989 T_{c_{C_7}}^2 + 0.3639 T_{c_{C_7}} + 20.92. \tag{5}
\]

With this, the acentric factor for \( C_7 \) is calculated via Edmister’s rule, which is as follows:

\[
\omega_{C_7} = \frac{3 \log (P_{C_7} \text{[atm]})}{7 \left( \frac{T_{c_{C_7}}}{T_{b_{C_7}}} - 1 \right)} - 1. \tag{6}
\]

The binary interaction coefficients are employed as reported in the Peng–Robinson equation of state [7]; nevertheless, as shown in Table 1, the corresponding coefficients interacting with \( C_7 \) remain unknown at this point, and they need to be optimized to fit with the experimental data.

2.3. The Rachford–Rice Equation and Equilibrium. The Rachford–Rice equation represents the combination of molar balances for the hydrocarbon mixture and individual components in terms of just 1 mole of the mixture (\( n = 1 \)), it is given by

\[
\sum_{i=1}^{n} \frac{z_i (K_i - 1)}{1 + n_y (K_i - 1)} = 0. \tag{7}
\]

With \( n_y \) being the moles of the gas phase \( n_y = 1 - n_i \), \( n_i \) are the moles in the liquid, \( K_i \) is the equilibrium coefficient, \( K_i = y_i/x_i \), and \( z_i \) is the global fraction mole of the component \( i \) in the hydrocarbon mixture. As in this work, we use the experimental values of the pressure saturation as a means to validate the SRK results, then the Equation (7) is forced to satisfy \( n_y = 0 \) leading to

\[
\sum_{i=1}^{n} z_i (K_i - 1) = 0. \tag{8}
\]

We note, additionally, that in the bubble point, the global composition equals that of the liquid, i.e., \( z_i = x_i \).

At equilibrium, the fugacity for each component is equal between liquid and gas

\[
f_i^L = f_i^V. \tag{9}
\]

This expression needs to be verified in the solution of the SRK model. It can be straightforwardly demonstrated that the pressure saturation can be computed once the fugacity and fugacity coefficient are available, which is as follows:

\[
P_{\text{sat}} = \sum_{i=1}^{n} \frac{n_i f_i^L}{\Phi_i^L}. \tag{10}
\]

3. Results and Discussion

3.1. Estimated Binary Interaction Coefficients for the Plus Fraction. The saturation pressure calculated via Equation (10) was compared against the experimental data collected in the work of Elsharkawy [22], where 56 crude oils from the Middle East and other 75 oils from the literature are summarized. These laboratory experiments ranged over a variety of pressures (313–6880 psi), temperatures (128–314°F), and compositions (\( N_2: 0.0–1.67\%; CO_2: 0.0–9.11\%; H_2S: 0.0–3.68\%; C_1: 5.63–74.18\%; C_2: 0.84–12.45\%; C_7+: 10.72–83.2\%) . Inspecting the SRK model and the ancillary expressions in the previous section, it is noted that the binary interaction coefficients involving the plus fraction are the unique degrees of freedom. Thus, those parameters were tuned through one evolutive computational algorithm where various combinations of parameters are evaluated with the error, as shown in the following equation:

\[
\text{error} = \left( P_{\text{exp}} - P_{\text{SRK}} \right)^2. \tag{11}
\]

The computational objective is to find the optimum coefficients \( k_{iC_7} \) minimizing such an error. In Equation (11), \( P_{\text{exp}} \) is the experimental measurement of saturation pressure for a given experiment and \( P_{\text{SRK}} \) is the saturation pressure calculated with the SRK equation of state. The iterative procedure needs to know a priori of the equilibrium constants, and then, they are recalculated through the ratio of the fugacity coefficients.
Table 1: Binary interaction coefficients $k_{ij}$. Here, $k_{ij} = k_{ji}$.

<table>
<thead>
<tr>
<th></th>
<th>CO$_2$</th>
<th>N$_2$</th>
<th>H$_2$S</th>
<th>C$_1$</th>
<th>C$_2$</th>
<th>C$_3$</th>
<th>nC$_4$</th>
<th>nC$_5$</th>
<th>nC$_6$</th>
<th>C$_7+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.135</td>
<td>0.105</td>
<td>0.130</td>
<td>0.125</td>
<td>0.115</td>
<td>0.115</td>
<td>0.115</td>
<td>??</td>
</tr>
<tr>
<td>N$_2$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.130</td>
<td>0.025</td>
<td>0.010</td>
<td>0.090</td>
<td>0.095</td>
<td>0.100</td>
<td>0.110</td>
<td>??</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>0.0</td>
<td>0.070</td>
<td>0.085</td>
<td>0.080</td>
<td>0.075</td>
<td>0.070</td>
<td>0.070</td>
<td>0.070</td>
<td>0.070</td>
<td>??</td>
</tr>
<tr>
<td>C$_1$</td>
<td>0.0</td>
<td>0.005</td>
<td>0.010</td>
<td>0.025</td>
<td>0.025</td>
<td>0.025</td>
<td>0.030</td>
<td>0.030</td>
<td>0.030</td>
<td>??</td>
</tr>
<tr>
<td>C$_2$</td>
<td>0.0</td>
<td>0.005</td>
<td>0.010</td>
<td>0.025</td>
<td>0.025</td>
<td>0.025</td>
<td>0.030</td>
<td>0.030</td>
<td>0.030</td>
<td>??</td>
</tr>
<tr>
<td>C$_3$</td>
<td>0.0</td>
<td>0.000</td>
<td>0.000</td>
<td>0.015</td>
<td>0.015</td>
<td>0.015</td>
<td>0.015</td>
<td>0.015</td>
<td>0.015</td>
<td>??</td>
</tr>
<tr>
<td>nC$_4$</td>
<td>0.0</td>
<td>0.005</td>
<td>0.005</td>
<td>0.005</td>
<td>0.005</td>
<td>0.005</td>
<td>0.005</td>
<td>0.005</td>
<td>0.005</td>
<td>??</td>
</tr>
<tr>
<td>nC$_5$</td>
<td>0.0</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>??</td>
</tr>
<tr>
<td>nC$_6$</td>
<td>0.0</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>??</td>
</tr>
<tr>
<td>C$_7+$</td>
<td>0.0</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
</tbody>
</table>

\[ K_i = \frac{\Phi_i^L}{\Phi_i^F}. \] (12)

As initial $K$-values, we use Wilson's correlation [3].

We note that there is not a unique combination of binary coefficients, and they vary for each petroleum sample. In Figure 1, we plotted in the left column the computed binary coefficients $k_{N_2,C_1}$, $k_{CO_2,C_1}$, $k_{H_2S,C_1}$, $k_{C_1,C_2}$, and $k_{C_2,C_3}$, while in the right column, we calculated the frequency histograms, intending to identify one representative value for all oil samples. The binary coefficients do not follow a Gaussian distribution; instead, they appear to be a Hyper-Pascal-type distribution for most of the coefficients. Based on the distributions plotted in Figure 1, in Table 2, we summarize the mean, mode, and standard deviations for each binary coefficient. According to the shape of the frequency histograms, the mode is a more representative value for the binary interaction coefficients associated with the fraction plus. In general, the binary coefficients related to $N_2$ and $CO_2$ are one order of magnitude larger than the other components.

3.2. Determining the Significant Interdependency Variables. The equilibrium constants depend on the variables such as the pressure and temperature, as well as the composition of the hydrocarbon mixture and the individual critical properties of the chemical components. This can be elucidated from the equation of state described above. Aiming to develop empirical correlations, we now focus to find the significant dependencies of $K$-values with the system variables. Once the equilibrium constants are determined, they are correlated with the hydrocarbon composition, pressure, temperature, molecular mass, and relative gravity of the plus fraction. The degree of correlation was quantitatively measured with the $R^2$ coefficient corresponding to the best possible fitting function (i.e., logarithmic, exponential, potential, linear, etc.). To decide if one correlation is significant or not, we adopted the following degree of correlation:

(i) Weak correlation, $R^2 \leq 0.2$
(ii) Intermediate correlation, $0.2 < R^2 \leq 0.6$
(iii) Strong correlation, $0.6 < R^2$

Based on this classification, we present graphically in Figure 2 the main correlations of equilibrium constants regarding the system variables. The equilibrium constants presenting the major dependencies are those related to lighter molecules, for instance, nitrogen and methane. The dominant variables are $C_1$, $C_2$, and $C_7+$ compositions and pressure. Among these dominant variables, the methane content and pressure stand out as they are the unique two variables manifesting strong correlations with the $K$-values of nitrogen and methane.

3.3. Empirical Correlations of Equilibrium Constants. On the basis of the correlation matrix depicted in Figure 2, a multivariable fitting process was performed aiming to find the best form of the empirical equations. The method of Nelder–Mead was programmed into Octave language to find the coefficients of equations. These empirical equations are the following, where the minimum error is also reported.

Equilibrium constant for $N_2$ is as follows:

\[
K_{N_2} = -2.7038 \ln(z_{C_1} \%) + 17.8008(z_{C_1} \%)^{-0.8381} \\
+ 11.4078e^{-0.0227z_{C_1} \%} - 5.4213 \ln(P[\text{psi}]) + 46.9978,
\] error = 552.68.

Equilibrium constant for $CO_2$ is as follows:

\[
K_{CO_2} = 16.5406(z_{C_1} \%)^{-0.9460} \\
+ 2.2757(z_{C_1} \%)^{-0.6357} \\
+ 48.0488(z_{C_2} \%)^{-0.0057} - 0.4710 \ln(P[\text{psi}]) - 43.2289,
\] error = 52.269.

Equilibrium constant for $H_2S$ is as follows:

\[
K_{H_2S} = 18.4386(z_{C_1} \%)^{-0.9601} \\
- 1.8661 \times 10^{-5}(z_{C_1} \%)^{-67.2352} \\
- 1038.6926(P[\text{psi}])^{-233.2401},
\] error = 50.180.

Equilibrium constant for $C_1$ is as follows:
$K_{C_1} = -0.3095 \ln(z_{C_1} \%)$
\[+ 1.8861 + 0.2125(z_{C_1} \%)^{-14.9070}
+ 836.5233 \exp(-5.3164z_{C_1} \%)
+ 4298.0248(P[psi])^{-1.05204},
\]
error = 28.065.

Equilibrium constant for $C_2$ is as follows:

$K_{C_2} = -0.3798 \ln(z_{C_2} \%)$
\[+ 45.7672 + 2.3878(z_{C_2} \%)^{-0.2846}
+ 46.8008 \exp(-0.0002z_{C_2} \%)
+ 17.2059(P[psi])^{-0.4566},
\]
error = 15.652.

Equilibrium constant for $C_7^+$ is as follows:

\[\text{Figure 1: Examples of estimated binary interaction coefficients related to the plus fraction. Graphics in the right column are the corresponding frequency histograms.}\]
In this case, the error is defined as
\[
error = \sum_i \left( K_i^{\text{exp}} - K_i^{\text{corr}} \right)^2 ,
\]
where \( K_i^{\text{exp}} \) is the experimental value, while \( K_i^{\text{corr}} \) is the equilibrium constant computed from the empirical equation.

The equilibrium constants for medium-weight components from \( C_3 \) to \( C_6 \) present weak correlations with the variable systems. For this reason, we do not report any empirical correlation for \( K \)-values of those components, and instead, we collect the mean value and the standard deviation in Table 3. The user can take the mean value as a rapid estimation of the equilibrium constant, but assuming that as long as the standard deviation increases, then the correct value can be more deviated. It is worth to stress that, at least for the range of temperatures occurring in the experimental set-up, the equilibrium constants performed a weak dependency on the temperature, while other variables significantly dominated the degree of correlation (see Figure 2).

### Table 2: Summary of binary interaction coefficients involving the \( C_7+ \) fraction.

<table>
<thead>
<tr>
<th>Binary interaction coefficient</th>
<th>Mean</th>
<th>Mode</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_{N_2,C_7+} )</td>
<td>0.140</td>
<td>0.175</td>
<td>0.099</td>
</tr>
<tr>
<td>( k_{CO_2,C_7+} )</td>
<td>0.108</td>
<td>0.066</td>
<td>0.095</td>
</tr>
<tr>
<td>( k_{H_2S,C_7+} )</td>
<td>0.063</td>
<td>0.078</td>
<td>0.038</td>
</tr>
<tr>
<td>( k_{C_1,C_7+} )</td>
<td>0.078</td>
<td>0.014</td>
<td>0.060</td>
</tr>
<tr>
<td>( k_{C_2,C_7+} )</td>
<td>0.072</td>
<td>0.014</td>
<td>0.061</td>
</tr>
<tr>
<td>( k_{C_3,C_7+} )</td>
<td>0.078</td>
<td>0.019</td>
<td>0.078</td>
</tr>
<tr>
<td>( k_{C_4,C_7+} )</td>
<td>0.079</td>
<td>0.016</td>
<td>0.073</td>
</tr>
<tr>
<td>( k_{C_5,C_7+} )</td>
<td>0.088</td>
<td>0.016</td>
<td>0.069</td>
</tr>
</tbody>
</table>

### Table 3: Mean value and standard deviation for uncorrelated equilibrium constants.

<table>
<thead>
<tr>
<th>( K_i )</th>
<th>Mean value</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_3 )</td>
<td>0.9037</td>
<td>0.3875</td>
</tr>
<tr>
<td>( C_4 )</td>
<td>0.7258</td>
<td>0.8379</td>
</tr>
<tr>
<td>( C_5 )</td>
<td>0.5422</td>
<td>0.5557</td>
</tr>
<tr>
<td>( C_6 )</td>
<td>0.5633</td>
<td>0.9208</td>
</tr>
</tbody>
</table>

It does not mean that the temperature was not considered in our theoretical development.

### 3.4. Comparison of Results

To finalize, we compared our results against pertinent experimental data. First, in Figure 3, we plot the saturation pressure computed with the SRK EOS employing the optimum binary interaction coefficients (some of them are plotted in the left column of Figure 1). Besides, the experimental measurements published by Jamialahmadi et al. [21] are included to validate the numerical estimations of the SRK EOS. It is clear that the SRK EOS predicts remarkably well the experimental saturation pressure, and only for 4 crude oils, there are appreciable deviations. This validated SRK EOS allows the computation of all equilibrium constants for each crude oil sample through all the theories described in the Mathematical Statements section of this paper. Thus, we can think about such \( K \)-values as true values for each crude oil. What follows is the comparison of the equilibrium constants calculated with the SRK EOS against the simple correlations derived here. Figure 4 presents the \( K \)-values for \( N_2 \) and \( C_1 \) by way of examples. There are some crude oil samples where the equilibrium constant prediction is excellent, but there are
also cases with large deviations. In general, the major trend is captured by the simple empirical correlations, and they can be easily used by reservoir engineers as needed. As mentioned before, the reliable empirical correlations for $K$-values are useful for compositional modeling, avoiding the need for solving iterative state equations.

4. Conclusions

Simple correlations for $K$-values in crude oils were proposed using equilibrium constants computed from the Soave–Redlich–Kwong equation of state. The new correlations constitute a direct calculation tool with excellent predictions. According to the methodology followed for the development of simple correlations, it is important to highlight the main findings:

(i) The corresponding binary coefficients interacting with $C_7+$ are unknown, and they were optimized to fit the experimental data.

(ii) There is not a unique combination of binary coefficients, and they vary for each petroleum sample. In general, the binary coefficients related to $N_2$ and $CO_2$ are one order of magnitude larger than those for the other components (Figure 1 and Table 2).

(iii) The equilibrium constants presenting the major dependencies on the system variables are those related to the lighter molecules ($N_2$, $CO_2$, $H_2S$, $C_1$, and $C_2$) (see Figure 2). The equilibrium constant for the plus fraction presents a moderate dependency on the pressure and its own composition.

(iv) The degree of correlation of equilibrium constants with the system variables is crucial to finding the best form of empirical equations. Following this idea, we propose a new empirical correlation for $K$-values, Equations (13)–(18).

(v) The saturation pressure calculated with the empirical correlations was compared against 131 experimental data of crude oil (Figure 3), and only for 4 cases, there were appreciable deviations.

In principle, the empirical correlations for $K$-values of crude oils developed here can be reliably and straightforwardly used to compute thermodynamic properties for vapor-liquid equilibrium.

Abbreviations

$f_i$: Fugacity of $i$-component
$K_i$: Equilibrium ratio
$k_{ij}$: Binary interaction parameters
$n_i$: Number of chemical components
$n_{li}$: Moles of the liquid phase
$n_g$: Moles of the gas phase
$P$: Pressure system
$P_{sat}$: Pressure saturation
$P_{ci}$: Critical pressure for each chemical component
$P_{sat,exp}$: Experimental measurement of saturation pressure
$P_{ri}$: Reduced pressure for each chemical component
$P_{sat,SRK}$: Saturation pressure calculated with the Soave–Redlich–Kwong equation of state (SRK EOS)
$R$: Ideal gas constant
$T$: Temperature system
$T_{ci}$: Critical temperature for each chemical component
$T_{ri}$: Reduced temperature for each chemical component
$x_i$: Molar fraction of component $i$ in the liquid phase
$y_i$: Molar fraction of component $i$ in the gas phase
$Z$: Gas deviation factor or compressibility factor

Greek Symbols

$\phi_i$: Fugacity coefficient
$\omega_i$: Acentric factor.

Data Availability

The data used to support this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

References


general physical data calculations,” *Annual AIChE National
Meeting*, Cleveland, OH, USA, 1968.


Book. Volume II*, Section 25: Equilibrium Ratio K Data, Gas
Processors Association, Tulsa, AK, USA, 1974.


equilibrium for systems of carbon dioxide + hydrocarbons by
the corresponding-states principle,” *Chemical Engineering

Dehghani, “A new approach for predicting equilibrium ratios
of hydrocarbon heavy fractions: focus on the effect of mixture

of state,” *Industrial & Engineering Chemistry Fundamentals*,

empirical K-value equation for reservoir fluids,” *Fuel*, vol. 98,

ratio of hydrocarbons and non-hydrocarbons at reservoir
conditions: experimental and modeling study,” *Fuel*, vol. 210,

regression model for estimation of saturation pressure of

connectionist model for predicting bubble point pressure of
 crude oils: application of artificial intelligence,” *Petroleum*,

and calculation of vapor pressure and vapor–liquid equilib-
rium constant of hydrocarbon fuel fractions,” *Fluid Phase

[16] G. Soave, “Equilibrium constants from a modified Redlich-
Kwong equation of state,” *Chemical Engineering Science*,
vol. 27, no. 6, pp. 1197–1203, 1972.

interaction parameters (kij) of the Peng-Robinson and those
of the Soave-Redlich-Kwong equations of state: application to
the definition of the PR2SRK model,” *Fluid Phase Equilibria*,

“Updated versions of the generalized Soave α-function suit-
able for the Redlich-Kwong and Peng-Robinson equations of

N. T. Machado, “Phase equilibrium measurements of Brazil
nut (*Bertholletia excelsa*) oil in supercritical carbon

Soave-Redlich-Kwong equation of state,” *Fluid Phase Equi-

generalized set of correlations for plus fraction character-

saturation pressures of crude oils,” *Journal of Petroleum