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Modeling associating hydrocarbon + alcohol mixtures using the Peng-Robinson equation of state and the Wong-Sandler mixing rules

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ABSTRACT

The main objective of the study is the accurate modeling of the bubble pressure and of the vapor phase concentration in associating hydrocarbon + alcohol mixtures and the correct comparison with results from the literature. A relatively simple equation of state is used and comparison is done considering various factors that affect the accuracy of the results, so fair and correct conclusions can be drawn. The mathematical complexity of the model, the type and amount of basic properties and the number of adjustable parameters used by the model, among other factors are discussed. The Peng-Robinson equation of state including the Wong-Sandler mixing rules was used. This combination of equations of state and mixing rules have not yet been applied in a systematic way to alcohol + hydrocarbon mixtures at low and moderate pressure, as done in this work, although other complex equation of state models have been used for some selected systems. It is concluded that simple and well-founded models can correlate equilibrium data in these complex mixtures with similar accuracy than other more sophisticated models.

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1. Introduction

Accurate prediction of thermodynamic properties of fluids and phase equilibrium in mixtures is required for the design and simulation of industrial processes. In particular, processes involved in petroleum production from natural hydrocarbon reserves require good representation of the phase behavior in different type of mixtures. In describing phase equilibrium, equations of state (EoS) have been commonly employed and numerous models are available in the literature [1]. In specific applications, however, some EoS are not of sufficient accuracy, mainly because of inadequate use of the mixing rules [1–3]. That is mainly the reason of the very limited use of EoS for describing properties of mixtures containing polar substances that

self-associate through hydrogen bonding (such as water or alcohols).

Kretschmer and Wiebe [4] presented an interesting study on the thermodynamics of alcohol + hydrocarbon mixtures but they did not discuss the vapor-liquid equilibrium (VLE) in these mixtures. For VLE calculations, several approaches have been proposed to account for the association in this type of mixtures. Hanks et al. [5] used the continuous linear association model (CLAM) to predict vapor-liquid equilibrium of thirty-five binary mixtures alcohol + aromatic hydrocarbons. The authors found that the model properly represented the large deviations from ideal solutions that arise from alcohol association. Yakoumis et al. [6] used the so-called Cubic-Plus-Association equation of state (CPA-EoS) to study binary systems containing one associating compound (alcohol) and an inert one (hydrocarbon). The CPA-EoS combines the Soave-Redlich-Kwong equation (SRK) for the physical part with an association term based on perturbation theory. The authors found better results than those obtained by the

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SRK equation and its performance was similar to that of other association models, such as the Anderko EoS, and the more complex SAFT and Simplified SAFT-EoS. Pires et al. [2] considered an EoS formed by two contributions (physical and chemical) as proposed by Anderko [7], and correlated bubble point pressure data for binary water + hydrocarbon and alcohol + hydrocarbon systems. The results obtained were in reasonable agreement with the experimental data. Li and Englezos [8] employed the SAFT-EoS to correlate phase equilibrium in systems containing alcohols, water, carbon dioxide and hydrocarbons. They considered eighteen systems of which six are alcohol + hydrocarbon mixtures. Good results were found for the vapor phase concentration but higher deviations were found for the bubble pressure. Dell' Era et al. [9] determined VLE data for the systems butane + alcohols and used several liquid phase models and COSMO-RS for correlating the experimental data. Al-Saifi et al. [10] applied the dipolar PC-SAFT to correlate and predict phase equilibrium of alcohol + hydrocarbon mixtures using three dipolar terms. The results were in good agreement with experimental data, although for several systems the authors did not report deviations for the vapor phase concentrations.

Most of the models presented above require several pure component parameters that are obtained by fitting experimental data (usually vapor pressure data) and also contain some binary interaction parameters obtained from binary VLE data. This makes the models more difficult to use in comparison with classical EoS in which the critical properties, easily found in the open literature, are usually employed. For instance, the application of the complex EoS for associating fluids presented by Pires et al. [2] requires the energy and entropy of vaporization of each component in the mixture, values determined by fitting vapor pressure and liquid density data. Also, other parameters claimed by the authors to be available are not easily found for many substances (characteristic temperature of intermolecular interactions, characteristic molar volume and external degrees of freedom of a molecule). Additionally, the model requires three adjustable parameters for binary mixtures. Al-Saifi et al. [10] applied the dipolar PC-SAFT claiming that good results were found with no adjustable parameters for binary mixtures. However, they had to fit six pure component parameters for each of the component in the mixture (12 parameters per binary mixture) to get the alleged good results. Yakoumis et al. [6] use the CPA equation of state with five adjustable parameters for each component in the mixture (10 parameters per binary mixture).

To correlate VLE data for this type of mixtures, classical equations of state with modern mixing rules usually require few adjustable parameters. Among the several models of this type available in the literature the Peng-Robinson EoS with the Wong-Sandler mixing rules including the van Laar model for the activity coefficient (PR/WS/VL model with three adjustable parameters) have demonstrated to have the necessary flexibility for representing in acceptable form the phase behavior of complex mixtures [11]. It seems that the three adjustable parameters of the PR/WS/VL model are able to take into account all the different factors that affect phase behavior in these

types of mixtures. To the best of the authors' knowledge this is the first time that a systematic study on the application of the PR/WS/VL model to associating alcohol + hydrocarbon mixtures has been successfully done.

The Table 1 shows the characteristics of several models that have been applied to alcohols + hydrocarbons mixtures. The very different characteristics of the various models should be considered when the goodness of a model is compared with the results of other researchers that use models with different characteristics. The following factors must be considered to decide which is the best model for a given application:

- the mathematical complexity of the model;
- the type and amount of basic properties used by the model;
- the number of adjustable pure component parameters;
- the number of adjustable binary interaction parameters;
- the physical meaning of the parameters;
- the range of applicability (pressure and temperature) and;
- the generalization of the model (type of fluids and mixtures).

The best model should be that which appropriately compensates physical foundation, accuracy of the results and mathematical simplicity. These concepts are applied in this paper to compare the results of the model employed with other results from the literature.

2. The thermodynamic model

Of the many equations of state nowadays available, the so-called cubic equations derived from van der Waals proposal such as the Peng-Robinson EoS [12], are widely used to treat a wide variety of mixtures. The EoS proposed by Peng and Robinson can be written in a general form as follows:

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b) + b(V-b)} \quad (1)$$

In this equation, a and b are parameters, specific for each substance, determined using the critical properties, T_c and P_c , and the temperature for "a". Commonly $a = a_c \alpha(T_R)$.

$$b = 0.077796 \frac{RT_c}{P_c}$$

$$a_c = 0.457235 \frac{R^2 T_c^2}{P_c}$$

$$a = a_c \alpha(T_R) \quad (2)$$

$$\alpha(T_R) = \left[1 + F(1 - T_R^{0.5}) \right]^2$$

$$F = 0.37464 + 1.54226 \omega - 0.26992 \omega^2$$

For mixtures the EoS parameters (a and b) are replaced by mixtures parameters (a_m y b_m):

$$P = \frac{RT}{V-b_m} - \frac{a_m}{V(V+b_m) + b_m(V-b_m)} \quad (3)$$

Table 1

Main characteristics of various models presented in the literature for correlating VLE data of alkane + alcohol mixtures.

Author/model	Mixtures studied	Pure component parameters	Interaction parameters	Objective function	Comments
Yakoumis et al. (1997) [6] CPA-EoS	Alcohols + hydrocarbons	5 (adjustable)	1 (adjustable from VLE data)	$F = \sum_{i=1}^N \left(\frac{p_i^{\text{exp}} - p_i^{\text{cal}}}{p_i^{\text{exp}}} \times 100 \right)^2$	The five pure component parameters for each compound in the mixture are determined from regression of vapor pressure and density data
Pires et al. (2001) [2] Anderko-EoS	Alcohols + hydrocarbons	6 (3 adjustable and 3 from literature)	1 (adjustable from VLE data)	$F = \frac{\sum_{i=1}^N \left[\left \frac{V_i^{\text{exp}} - V_i^{\text{cal}}}{V_i^{\text{exp}}} \right + \left \frac{p_i^{\text{exp}} - p_i^{\text{cal}}}{p_i^{\text{exp}}} \right \right]}{2N}$	Two of the pure component parameters for each compound in the mixture are determined from regression of vapor pressure and density data. The other parameters are claimed to be found in the literature but are not readily available
Li and Englezos (2004) [8] SAFT-EoS	Alcohols, water, carbon dioxide with hydrocarbons	5 for alcohols components and 3 for hydrocarbons (all adjustable)	2 (adjustable from VLE data)	Not reported	Five pure component parameters for alcohols components and three parameters for hydrocarbons are required. These parameters are estimated by regression of saturated vapor pressure and liquid density data
Al-Saifi et al. (2008) [10] PC-SAFT-JC	Water + alcohols, hydrocarbons; alcohols + alcohols, hydrocarbons.	6 (adjustable)	None	Not reported	PC-SAFT-JC requires six adjustable parameters when considering associating components determined by regression of vapor pressure and liquid density
This Work PR/WS/VL EoS	Alcohols + hydrocarbons	3 (from the literature)	3 (adjustable from VLE data)	$F = \sum_{i=1}^N \left \frac{p_i^{\text{cal}} - p_i^{\text{exp}}}{p_i^{\text{exp}}} \right $	The three pure component parameters (critical temperature, critical pressure and acentric factor) are readily available in the open literature. The three parameters for the mixture are obtained from VLE data

In this work, the Wong-Sandler (WS) mixing rules has been used to express the dependency of the parameters a_m y b_m on concentration. The WS mixing rules for the Peng-Robinson EoS can be summarized as follows [13]:

$$b_m = \frac{\sum_i^N \sum_j^N x_i x_j \left(b - \frac{a}{RT} \right)_{ij}}{1 - \sum_i^N \frac{x_i a_i}{b_i RT} - \frac{A_\infty^E(X)}{\Omega RT}} \quad (4)$$

$$\left(b - \frac{a}{RT} \right)_{ij} = \frac{1}{2} [b_i + b_j] - \frac{\sqrt{a_i a_j}}{RT} (1 - K_{ij})$$

$$a_m = b_m \left(\sum_i^N \frac{x_i a_i}{b_i} + \frac{A_\infty^E(x)}{\Omega} \right)$$

In these equations, k_{ij} is an interaction parameter, $\Omega = -0.62323$ for the Peng-Robinson EoS, and $A_\infty^E(y)$ is calculated assuming that $A_\infty^E(y) \approx A_0^E(y) \approx g_0^E$, being g_0^E the excess Gibbs free energy. For g_0^E several models have been used in the literature. In this work g_0^E has been calculated using the van Laar model:

$$\frac{g_0^E}{RT} = \frac{(A_{12}/RT)x_1 x_2}{X_1(A_{12}/A_{21}) + X_2} \quad (5)$$

In the equations (4) and (5) “x” represents the mole fraction in the liquid phase when the fugacity coefficient

for the components in the liquid phase is determined, and “x” represents the mole fraction in the vapor phase when the fugacity coefficient for the components in the vapor phase is calculated.

For a binary mixture the WS mixing rule includes one adjustable binary interaction parameter k_{12} for $(b-a/RT)_{ij}$, besides the two parameters, A_{12} and A_{21} , included in the g_0^E model. These three adjustable parameters for each of the mixtures have been determined using experimental phase equilibrium data at constant temperature, available in the literature. In summary, the thermodynamic model used in this work includes the Peng-Robinson equation of state, the Wong-Sandler mixing rule, and the van Laar model for g_0^E in the mixing rules, and contains three adjustable parameters. The model is designated as PR/WS/VL in the rest of the paper.

3. Mixtures Studied

Twenty-four binary alcohol + hydrocarbon mixtures were considered in this study. The alcohols included in the mixtures are: methanol, ethanol, 1-propanol, 2-propanol and 2-butanol and the hydrocarbons considered are: methane, ethane, propane, n-butane, n-pentane, n-hexane and n-heptane. Table 2 shows pure component properties for all the substances involved in this study. In the table, M is the molecular

Table 2
Properties for all substances involved in this study.

Components	M (kg/kg mol)	T _b (K)	T _c (K)	P _c (bar)	V _c (m ³ /kmol)	ω
Alkanols						
methanol	32.0	337.85	512.65	80.84	0.117	0.5659
ethanol	46.1	351.45	513.95	61.37	0.168	0.6436
1-propanol	60.1	370.35	536.75	51.69	0.218	0.6204
2-propanol	60.1	355.41	508.30	47.64	0.222	0.6669
2-butanol	74.1	372.70	536.20	42.02	0.269	0.5768
Hydrocarbons						
methane	16.0	111.66	190.56	45.99	0.099	0.0116
ethane	30.1	184.55	305.32	48.72	0.146	0.0995
propane	44.1	231.11	369.83	42.48	0.200	0.1523
n-butane	58.1	272.65	425.12	37.96	0.255	0.2002
n-pentane	72.2	309.22	469.70	33.70	0.313	0.2515
n-hexane	86.2	341.88	507.60	30.25	0.371	0.3013
n-heptane	100.2	371.58	540.20	27.40	0.428	0.3495

mass, T_b is the normal boiling temperature, T_c is the critical temperature, P_c is the critical pressure, V_c is the critical volume and ω is the acentric factor. The values for these properties were obtained from Daubert et al. [14].

Table 3 gives some details on the experimental data used in the study including the literature source for each data set. In this table, T is the temperature (expressed in kelvin), n is the number of experimental data, x₁ is the liquid mole fraction for component 1, y₁ is the vapor mole fraction for component 1 and P is the pressure (expressed in bars). As seen in Table 3, data for 70 isotherms with a total of 700 data points were considered. The temperature ranges from 298 to 523 K and the pressure from about 0.5 to 105 bars.

Bubble pressure calculations for binary mixtures were performed using the PR/WS/VL model. The adjustable parameters of the model (k₁₂, A₁₂, A₂₁) were determined by optimization of the objective function given by eqn. (6). The program designed considers the use of the Levenberg-Marquardt algorithm as the optimization method [35]. The objective function was defined as the relative error between calculated and experimental values of the pressure:

$$F = \sum_{i=1}^N \left| \frac{p_i^{cal} - p_i^{exp}}{p_i^{exp}} \right| \quad (6)$$

In this equation N is the number of points in the experimental data set and P is the bubble pressure.

4. Results and discussion

Table 4 shows the optimum binary interaction parameters in the Wong-Sandler mixing rule at all temperatures studied and the results for the pressure P and the vapor mole fraction y₁ for the 24 binary mixtures. This table shows the average-absolute deviations for the pressure %ΔP|, and the average-absolute deviations and average-relative deviations for the concentration of component 1 in the vapor phase %Δy_{1|and %Δy₁,}

respectively. For a set of N data these deviations are defined as follows:

$$\begin{aligned} |\% \Delta P| &= \frac{100}{N} \sum \left| \frac{P^{cal} - P^{exp}}{P^{exp}} \right|_i \\ |\% \Delta y_1| &= \frac{100}{N} \sum \left| \frac{y_1^{cal} - y_1^{exp}}{y_1^{exp}} \right|_i \\ \% \Delta y_1 &= \frac{100}{N} \sum \left[\frac{y_1^{cal} - y_1^{exp}}{y_1^{exp}} \right]_i \end{aligned} \quad (7)$$

As seen in Table 4, the PR/WS/VL model reproduces the bubble pressures of these binary mixtures with mean absolute deviations less than 5.3% for any temperature. The pressure was calculated with deviations between 0.3% and 5.2%. Of the seventy studied isotherms, 27 are reproduced with deviations less than 1%, 31 with deviations from 1.0% to 3.0%, 7 with deviations from 3.1% to 4.0%, and 5 with deviations from 4.1% to 5.2%.

With respect to the hydrocarbon concentration in the vapor phase y₁, this quantity is predicted in all cases with average-absolute deviations from 0.3% to 9.2%. Of the seventy studied isotherms, 21 are reproduced with deviations less than 1%, 38 with deviations from 1.0% to 4.0%, 5 with deviations from 4.1% to 6.0%, 5 with deviations from 6.1% to 8.0%, and 1 with the maximum deviation found (9.2%). The average-relative deviations vary between -3.8% and 9.1%.

The Table 5 shows results for similar mixtures presented by Yakoumis et al. [6], Pires et al. [2], Li and Englezos [8] and Al-Saifi et al. [10] with the models described in Table 1 and with results of Soo et al. [16] and Courtial et al. [22] who used the PR equation of state with the Wong-Sandler mixing rules but including the NRTL model for the excess Gibbs free energy instead of the van Laar model used in the present paper (PR/WS/NRTL). In the overall, results are similar. Thus, by only analyzing the average deviations, none of the models shows superiority over the others. In the average, the complex literature models correlate pressure with 2.1% absolute deviations and our model with 2.4%. The concentration of the

Table 3

Details on the phase equilibrium data for the systems considered in this study. In the table the temperature values have been rounded to the closest integer.

Systems	References	T (K)	N	Range of data		
				Range of x_1	Range of y_1	Range of P (bar)
Methanol (2) + Ethane (1)	Ishira et al. [21] Courtial et al. [22] Dell Era et al. [9]	298	7	0.053–0.988	0.959–0.998	9.63–41.55
		323	11	0.069–0.973	0.841–0.938	3.37–5.28
		364	25	0.009–0.999	0.268–0.968	3.69–14.41
Propane (1)	Leu et al. [23]	311	11	0.016–0.984	0.822–0.980	2.12–13.43
		352	8	0.020–0.975	0.660–0.966	5.60–31.73
		393	8	0.027–0.589	0.502–0.764	14.46–57.32
		474	6	0.028–0.173	0.146–0.274	53.01–86.63
n-Butane (1)	Courtial et al. [22]	373	13	0.018–0.988	0.368–0.965	5.72–17.20
		403	11	0.019–0.992	0.248–0.982	11.75–30.91
		423	7	0.019–0.713	0.226–0.735	19.64–43.74
		433	11	0.009–0.424	0.103–0.615	20.82–48.45
		443	7	0.011–0.369	0.067–0.504	24.54–54.34
		470	5	0.008–0.261	0.039–0.261	40.11–69.17
n-Pentane (1)	Wilsak et al. [24]	373	9	0.012–0.956	0.224–0.795	4.51–8.46
		398	9	0.045–0.975	0.298–0.888	10.44–15.12
		423	9	0.033–0.940	0.187–0.819	16.91–25.28
Ethanol (2) + Methane (1)	Suzuki et al. [15]	313	5	0.021–0.107	0.989–0.994	18.08–100.73
		333	5	0.028–0.105	0.977–0.989	25.94–104.64
Ethane (1)	Suzuki et al. [15]	313	5	0.078–0.602	0.984–0.992	13.65–54.14
		333	9	0.057–0.567	0.958–0.981	13.07–78.97
Propane (1)	Zabaloy et al. [17]	325	6	0.169–0.881	0.974–0.988	9.74–18.00
		350	5	0.160–0.858	0.935–0.973	13.57–29.60
		375	5	0.171–0.837	0.874–0.943	20.19–43.81
n-Butane (1)	Soo et al. [16]	323	9	0.193–0.974	0.919–0.970	3.81–5.03
		353	9	0.109–0.962	0.782–0.952	5.61–10.34
		373	12	0.025–0.976	0.428–0.965	4.26–15.72
		403	10	0.035–0.973	0.353–0.965	9.51–20.73
		423	14	0.027–0.975	0.210–0.973	13.25–38.00
n-Pentane (1)	Seo et al. [18]	423	9	0.059–0.904	0.242–0.840	12.79–19.68
		465	13	0.079–0.979	0.172–0.974	31.00–41.45
		500	5	0.018–0.120	0.033–0.120	50.30–57.19
n-Hexane (1)	Seo et al. [19]	473	12	0.013–0.959	0.025–0.887	20.16–34.79
		483	11	0.032–0.951	0.046–0.880	23.76–40.99
		493	10	0.025–0.937	0.026–0.902	28.13–48.85
		503	5	0.016–0.954	0.018–0.954	31.04–55.61
n-Heptane (1)	Seo et al. [20]	483	10	0.051–0.896	0.059–0.793	17.20–36.77
		508	11	0.027–0.859	0.030–0.753	26.17–56.58
		523	5	0.721–0.910	0.721–0.852	27.95–37.72
1-Propanol (2) + Methane (1)	Suzuki et al. [15]	313	5	0.036–0.141	0.996–0.998	21.65–100.79
		333	5	0.020–0.130	0.985–0.994	14.10–101.97
Ethane (1)	Suzuki et al. [15]	313	5	0.106–0.547	0.994–0.996	13.47–51.11
		333	6	0.080–0.503	0.971–0.991	13.56–67.42
Propane (1)	Jiménez-Gallegos et al. [26]	318	9	0.139–0.665	0.988–0.995	5.75–13.14
		324	8	0.111–0.871	0.983–0.994	5.28–15.71
		349	8	0.097–0.940	0.948–0.989	5.40–26.41
n-Butane (1)	Panasen et al. [25]	330	24	0.012–0.988	0.631–0.994	0.47–5.90
n-Pentane (1)	Jung et al. [27]	468	15	0.020–0.948	0.064–0.946	16.79–33.52
		483	13	0.026–0.592	0.072–0.592	22.39–40.29
		498	10	0.020–0.415	0.042–0.415	28.64–44.45
		513	7	0.025–0.245	0.047–0.245	37.26–48.24
2-Propanol (2) + Ethane (1)	Kodama et al. [28]	308	9	0.260–0.990	0.990–0.996	21.91–49.90
		313	8	0.336–0.978	0.984–0.996	31.69–53.57
Propane (1)	Zabaloy et al. [30]	333	8	0.094–0.902	0.920–0.994	5.70–19.82
n-Butane (1)	Moilanen et al. [29]	323	23	0.031–0.986	0.713–0.986	0.81–4.95
n-Hexane (1)	Seo et al. [31]	483	14	0.029–0.904	0.042–0.878	24.31–33.76
		493	18	0.040–0.935	0.045–0.924	26.80–39.85
		503	9	0.022–0.973	0.027–0.970	29.45–45.46
		483	11	0.039–0.908	0.039–0.853	15.14–31.21
		498	11	0.039–0.882	0.039–0.806	19.70–40.21
n-Heptane (1)	Oh et al. [32]	508	7	0.410–0.892	0.410–0.837	22.45–39.67
		523	6	0.725–0.898	0.725–0.848	26.79–34.17
		328	11	0.286–0.995	0.987–0.999	10.10–18.97
2-Butanol (2) + Propane (1)	Gros et al. [33]	348	11	0.286–0.995	0.973–0.998	13.65–28.24

Table 3 (Continued)

Systems	References	T (K)	N	Range of data		
				Range of x_1	Range of y_1	Range of P (bar)
n-Butane (1)	Moilanen et al. [29]	368	11	0.274–0.995	0.946–0.997	17.03–40.82
		323	23	0.027–0.99	0.797–0.997	0.52–4.92
n-Pentane (2)	Kim et al. [34]	364	25	0.016–0.989	0.399–0.995	1.24–12.74
		468	12	0.064–0.977	0.147–0.977	15.88–32.72
		483	11	0.042–0.706	0.097–0.706	19.39–36.80
		498	9	0.033–0.495	0.060–0.495	25.01–39.06
		513	6	0.049–0.301	0.079–0.301	31.62–40.94

Table 4

Optimum binary interaction parameter and van Laar constants in the Wong-Sandler mixing rules at all temperatures studied and average deviations for the pressure and vapor mole fraction of component (1), using the PR/WS/VL model.

Systems	T (K)	A_{12}	A_{21}	k_{12}	[% ΔP]	[% Δy_1]	[% Δy_1]
Methanol (2) + Ethane (1)	298	1.5133	1.4666	0.1079	2.3	0.7	0.5
Propane (1)	311	1.4379	0.4262	0.5323	5.1	1.7	1.7
	352	1.2473	0.4211	0.5154	4.9	2.3	2.3
	393	1.8014	0.7234	0.4019	2.5	6.6	2.2
	474	2.5750	2.1315	0.1336	0.4	1.2	0.4
	323	2.6762	3.6923	0.0514	4.9	1.6	0.6
n-Butane (1)	364	2.5154	3.9707	0.0882	3.8	2.6	–0.9
	373	2.3601	3.0773	0.2148	4.5	2.4	1.7
	403	1.9084	2.3213	0.3157	2.8	1.8	0.6
	423	2.0916	1.2503	0.3562	3.7	3.4	2.0
	433	2.3232	1.5134	0.3081	2.8	2.8	< 0.1
	443	2.3487	3.9115	0.1396	2.5	6.5	–4.0
	470	2.6143	2.4354	0.1624	0.7	1.6	< 0.1
	373	2.7736	3.6646	0.1569	3.8	6.5	–4.7
n-Pentane (1)	398	2.3332	3.5473	0.1894	1.7	2.9	–1.1
	423	1.6295	3.2400	0.3209	1.1	4.2	0.4
Ethanol (2) + Methane (1)	313	0.9632	1.3324	0.0339	0.7	0.3	–0.3
	333	0.9312	1.4921	0.0886	0.3	0.4	–0.4
Ethane (1)	313	1.3525	1.1306	0.1385	3.6	1.9	–1.9
	333	1.3535	1.1249	0.1585	2.5	0.7	–0.7
Propane (1)	325	1.1841	3.6667	0.1274	3.6	0.9	–0.9
	350	1.0263	3.8665	0.1266	3.1	1.6	–1.6
	375	1.0471	3.2831	0.1235	2.6	3.8	–3.8
n-Butane (1)	323	1.77830	3.7293	0.0581	2.6	0.6	–0.4
	353	2.0813	3.7653	0.0109	1.6	0.9	–0.6
	373	2.1273	3.7560	0.0064	2.5	1.6	< 0.1
	403	2.0774	3.3002	0.0491	1.4	1.4	0.7
	423	2.0032	3.2235	0.0704	1.1	3.4	–1.9
n-Pentane (1)	423	2.0574	2.5842	0.1176	0.4	1.3	0.4
	465	2.1698	3.0782	0.0496	0.9	1.9	–1.0
	500	1.7118	1.5856	0.1850	0.5	2.7	–2.5
n-Hexane (1)	473	1.6305	1.5880	0.2202	0.4	3.9	3.7
	483	0.9195	1.6116	0.2855	1.4	3.6	3.5
	493	0.1563	0.1008	0.2154	1.9	2.3	1.5
	503	0.9101	0.8509	0.2405	1.1	2.0	1.5
n-Heptane (1)	483	2.3865	2.1708	0.1194	1.0	4.0	–2.5
	508	1.4868	1.5011	0.2698	0.8	1.6	–1.3
	523	0.4651	2.2526	0.3496	0.8	1.0	–0.6
1-Propanol (2) + Methane (1)	313	0.5417	2.4752	0.0952	2.8	0.2	–0.2
	333	0.6396	1.0645	0.1599	0.7	0.3	–0.3
Ethane (1)	313	0.8963	1.5307	0.0709	0.4	0.3	–0.3
	333	0.9330	1.4436	0.0739	0.2	0.6	–0.6
	318	0.8108	0.6629	0.2771	0.8	0.4	–0.4
Propane (1)	324	0.7694	0.5676	0.2983	0.8	0.5	–0.5
	349	0.2286	0.2342	0.3253	2.0	0.7	–0.7
	330	1.4574	3.2947	0.0410	2.3	1.0	–1.0
n-Butane (1)	468	1.1738	2.0650	0.1053	1.5	6.8	6.5
n-Pentane (1)	483	1.0540	1.9969	0.1227	1.2	2.8	1.0
	498	1.2374	1.2503	0.1217	0.6	5.8	3.8
	513	1.0424	1.3454	0.1526	0.5	1.4	–0.3

Table 4 (Continued)

Systems	T (K)	A ₁₂	A ₂₁	k ₁₂	%ΔP	%Δy ₁	%Δy ₁
2-Propanol (2) + Ethane (1)	308	2.0846	−0.1849	0.1715	1.1	0.7	−0.6
	313	1.4134	−0.2152	0.1600	2.3	0.5	−0.3
Propane (1)	333	1.8783	0.2539	0.3968	3.4	0.6	0.1
n-Butane (1)	323	1.4622	3.1920	0.0427	2.2	1.0	−0.6
	483	0.8971	1.0537	0.1867	0.3	3.1	−1.1
n-Hexane (1)	493	1.4450	1.3889	0.0829	0.6	2.1	0.8
	503	0.1437	2.3500	0.3168	0.7	2.8	0.4
n-Heptane (1)	483	1.5888	1.7465	0.0855	1.3	5.0	−2.5
	498	1.1498	1.0290	0.1707	0.3	4.2	−1.5
	508	1.3576	0.8700	0.1741	0.7	2.4	−2.2
	523	1.3850	0.7724	0.1767	1.0	0.6	−0.4
2-Butanol (2) + Propane (1)	328	1.2356	0.3856	0.3182	0.9	0.2	−0.1
	348	1.1224	0.4155	0.2730	0.5	0.2	−0.1
	368	0.7374	0.4868	0.2165	0.2	0.1	< 0.1
n-Butane (1)	323	1.2424	2.8698	0.0128	1.6	1.1	−1.1
	364	1.1162	2.5751	0.0289	1.1	1.0	−0.9
	468	1.2446	1.4554	0.0084	1.0	9.2	9.1
n-Pentane (2)	483	1.0224	1.5354	0.0255	0.9	5.8	3.2
	498	−0.0624	−0.0940	0.1535	5.2	7.9	3.4
	513	0.5970	2.8956	0.1002	0.6	1.3	0.4

Table 5

Comparison between this work and results from the literature for same alcohol + hydrocarbon mixtures using different models. The indexes a y b indicate that the values were determined using other deviations definitions as given at end of the table.

Mixture	References/model	T (K)	%ΔP	%Δy ₁	This work	
					[%ΔP]	[%Δy ₁]
Butane (1) + ethanol (2)	Yakoumis et al. [6]/CPA Li and Englezos [8]/SAFT Al-Saifi et al. [10]/PC-SAFT Seo et al. [16]/PR/WS/NRTL	323	2.0	---	2.6	0.6
			19.9 ^a	0.0082 ^b		
			2.1	---		
		353	---	0.2	1.6	0.9
			373	---	1.2	2.5
			403	---	1.5	1.4
423	---	6.7	1.1	3.4		
n-pentane (1) + methanol (2)	Yakoumis et al. [6]/CPA	373	2.0	1.7	3.8	6.5
		398	1.8	1.7	1.7	2.9
		423	2.2	1.3	1.1	4.2
Butane (1) + methanol (2)	Pires et al. [2]/Anderko EoS Courtial et al. [22]/PR/WS/NRTL	323	4.2	11.3	4.9	1.6
			---	0.6		
			---	1.6		
		373	---	1.6	4.5	2.4
			403	---	2.5	2.8
			423	---	4.8	3.7
433	---	9.2	2.8	2.8		
443	---	16.1	2.5	6.5		
n-Pentane (1) + methanol (2)	Wilsak et al. [24]	373	2.9	6.8	3.8	6.5
		398	1.0	5.5	1.7	2.9
		423	0.6	4.0	1.3	3.3
n-pentane (1) + methanol (2)	Al-Saifi et al. [10]/PC-SAFT	373	2.3	1.1	3.8	6.5
		398	2.5	0.7	1.7	2.9
		423	2.8	0.4	1.3	3.3
n-pentane (1) + ethanol (2)	Soo et al. [18]	423	1.7	0.2	0.4	1.3
		465	1.0	0.1	0.9	1.9
Propane (1) + ethanol (2)	Li and Englezos [8]/SAFT	325	12.2 ^a	0.0176 ^b	3.6	0.9
		350	14.6 ^a	0.0221 ^b	3.1	1.6

Note: deviations in some cases were defined in a different way:

$$^a (P)(\%) = 100 \sqrt{\sum_{i=1}^N (P_i^{cal} - P_i^{exp})^2} / (N - 1).$$

$$^b (y) = \sqrt{\sum_{i=1}^N (y_i^{cal} - y_i^{exp})^2} / (N - 1).$$

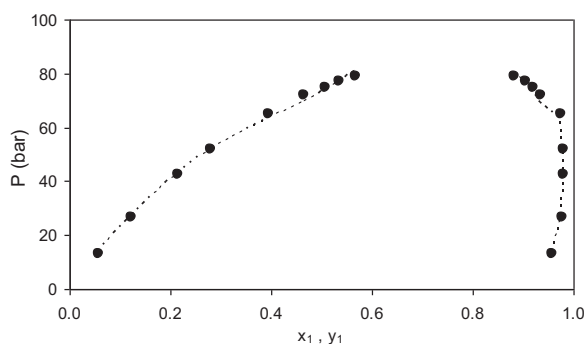


Fig. 1. Experimental (●) and calculated values (–) of bubble pressure P vs.- liquid mole fraction x_1 and vapor mole fraction y_1 for the system ethane (1) + ethanol (2) at $T = 333$ K. Experimental data are from Suzuki et al. [15].

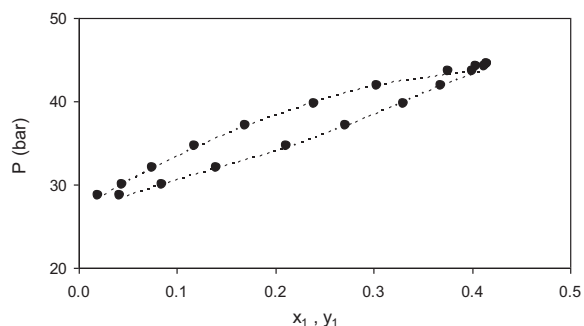


Fig. 2. Experimental (●) and calculated values (–) of bubble pressure P vs.- liquid mole fraction x_1 and vapor mole fraction y_1 for the system n-pentane (1) + 1-propanol (2) at $T = 498$ K. Experimental data are from Jung et al. [27].

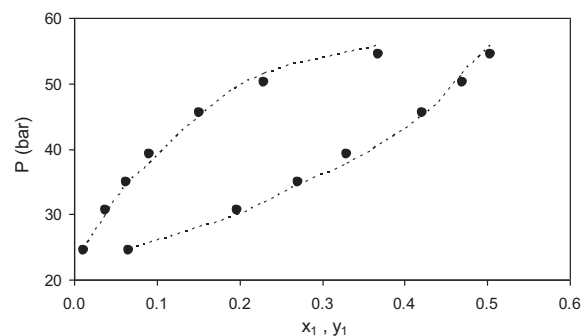


Fig. 3. Experimental (●) and calculated values (–) of bubble pressure P vs.- liquid mole fraction x_1 and vapor mole fraction y_1 for the system n-butane (1) + methanol (2) at $T = 443$ K. Experimental data are from Courtial et al. [22].

hydrocarbon in the gas phase is correlated with other models with average-absolute deviations of 3.5% while the PR/WS/VL model gives a little lower value (3.0% in the average).

As explained in the Introduction section comparison between different models must considered several factors besides its accuracy. Considering the characteristics of the PR/WS/VL model such as: the number and availability of basic properties used by the model (critical properties and acentric factor only), the number of adjustable parameters

for the mixtures (three for binary mixtures), the wide range of applicability (pressure and temperature), the equations used in this work represents an acceptable model giving results with accuracy similar to more sophisticated equations that use several pure component properties that are frequently not available.

As additional examples of the results provided by the PR/WS/VL model, the Figs. 1–3 show the bubble pressure versus concentration for three mixtures with different behavior. The Fig. 1 shows results for the mixture ethane (1) + ethanol (2) at 333 K, in which one of the components is much more volatile than the other so the concentration of component 1 in the vapor phase is much higher than in the liquid phase especially at low pressures. The Fig. 2 shows results for the mixture n-pentane (1) + 1-propanol (2) at 498 K, in which both components have similar volatilities so the concentration of component 1 in the vapor phase is similar to that of the liquid phase at all pressures. The Fig. 3 shows results for the mixture n-butane (1) + methanol (2) at 443 K, which shows an intermediate behavior as those presented in Figs. 1 and 2. In the figures, the symbol (●) represents the experimental data and the dashed line (–) represents the calculated values. It can be seen that there is good agreement between model estimates and experimental data in both cases, showing the versatility of the model.

5. Conclusions

Vapor-liquid equilibrium in mixtures alcohol + hydrocarbon at low and moderate pressures has been modeled using the EoS method (Peng-Robinson + Wong-Sandler + van Laar, PR/WS/VL) and appropriate comparison with other results from the literature using similar and more complex models have been done. The study and the results allow obtaining three main conclusions:

- various factors must be considered when comparing results provided by different models;
- the main factors are: the mathematical complexity of the model, the type and amount of basic properties and the number of adjustable parameters used by the model;
- the equation of state method using appropriate mixing rules such as the one of Wong and Sandler can be used to model low and moderate pressure complex mixtures;
- bubble pressures can be obtained with good accuracy with the PR/WS/VL model, giving absolute-average deviations below 5.3% for each isothermal data set and the overall absolute-average deviations is 1.7%;
- the concentration in the vapor phase y_1 can be obtained with good accuracy, giving absolute-average deviations below 9.3% for each isothermal data set and the overall absolute-average deviations and relative-average deviations are 2.3% and 0.08%, respectively.

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Glossary

Notation

Symbols

- A_{ij} : parameter in the van Laar model
 a_c , b : parameter in the PR EOS
 a_m , b_m : interaction parameters in the mixing rules
 g^E : excess Gibbs free energy
 k_{ij} : binary interaction parameter
 P : pressure
 P_c : critical pressure
 R : ideal gas constant
 T : temperature
 T_c : critical temperature
 T_R : reduced temperature
 V : volume
 y_i : mole fraction of congener in the vapor phase (component 1)
 y_i^{calc} : calculated mole fraction in the vapor phase
 y_i^{exp} : experimental mole fraction in the vapor phase
 x_i : experimental mole fraction in the liquid phase (component i)

Abbreviations

- CPA: Cubic-Plus-Association
 EoS: equation of state
 NRTL: Non-random two-liquid model
 PR: Peng-Robinson
 PR/WS/VL: Peng-Robinson + Wong-Sandler + van Laar model
 SAFT: Statistical associating fluid theory
 PC-SAFT: Perturbed-Chain-SAFT
 VL: van Laar
 WS: Wong-Sandler mixing rule

Greek letters

- Δ : deviation
 $\alpha(T)$: temperature function in the PR EoS
 ω : acentric factor

Super/subscripts

- cal: calculated
 exp: experimental
 i, j: components i and j