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Flash point prediction of binary partially and totally miscible alcohol-water mixtures by various equation of states and experimental validation

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Abstract

In the present article, the experimental flash points (FPs) of partially miscible and non-ideal mixtures including 3-pentanol+water, 2-pentanol+water, and 1-hexanol+water are reported for the first time. The measured FPs were predicted based on the vapor pressure concept and thermodynamic equilibrium. The cubic-plus-association (CPA) equation of state (EoS) along with the CR-1 combining rule and Elliot combining rule (ECR) were used to investigate the non-ideality of investigated systems. In the following, the same method was used with the Soave-Redlich-Kwong (SRK) and Peng-Robinson (PR) EoSs to evaluate whether simpler EoSs can accurately predict the FPs of non-ideal mixtures. Therefore, in addition to 3-pentanol+water, 2-pentanol+water, and 1-hexanol+water, numerous totally and partially miscible aqueous-organic systems containing 1-pentanol, isobutanol, 2-butanol, 1-butanol, isopropanol, propanol, ethanol, and methanol were studied in terms of FP prediction. The findings indicated that SRK is marginally more effective than PR. Moreover, SRK EoS was almost as effective as the CPA EoS with the CR-1 combining rule. The CPA EoS that used ECR, on the other hand, was far superior to the SRK and PR EoSs. To the best of our knowledge, CPA parameters for 2-pentanol, 3-pentanol, and 1-hexanol were calculated and reported for the first time.

Keywords: Flash point; partially miscible; vapor pressure-based model; Cubic EoSs; CPA EoS; aqueous-organic systems.

1. Introduction

Aqueous-organic mixtures are frequently used in a variety of industries. A technique known as a water-methanol injection, for instance, involves mixing methanol and water and injecting the mixture into high-performance diesel and gasoline engines to boost power and lower intake air temperature (Rogóż et al., 2022). In many industries, such as the cooling of microelectronics, pesticide spray, and ink-jet printing applications, the presence of ethanol and water mixture is crucial (Ozturk and Erbil, 2020). Additionally, adding 1-butanol and 1-pentanol to water can drastically alter the droplet impact, a significant phenomenon in laser equipment, direct fuel injection, the erosion of steam turbine blades, and other similar applications (Cai et al., 2021). As a result, it is essential to have information about aqueous-organic mixtures, particularly concerning their safety.

One of the vital safety characteristics of flammable liquids is their flash point (FP). At FP, an ignitable liquid releases sufficient vapor to develop an ignitable combination with ambient air. FP is the temperature of a combustible material (mostly liquid) which is considered a significant property from a safety point of view (Di Benedetto et al., 2018a, b; Gaudin et al., 2015; Lakzian et al., 2020). According to the definition, transporting, processing, and storing a flammable liquid must be done below the FP temperature to avoid specific hazards such as explosions and fire. A flammable liquid can be either pure or a mixture. There are generally two procedures for determining the experimental FP of combustible liquids, denominated open-cup and closed-cup (Álvarez et al., 2019; Jalaei Salmani et al., 2018; Torabian and Sobati, 2019). The experimental data determined by the closed-cup approach is more reliable and consistent, particularly when addressing multicomponent mixtures. Experimental data are preferred to model-calculated ones; however, modeling would significantly save cost and time. Accordingly, various

predictive/correlative models were developed in all engineering disciplines (Jalaei Salmani et al., 2022a; Jalaei Salmani et al., 2022b; Jalaei Salmani et al., 2018, 2019, 2020; Lakzian et al., 2020; Lakzian and Jalaei Salmani, 2021; Mansouri et al., 2022; Pourabadeh et al., 2020). There are several closed-cup predictive categories; the models based on the vapor pressure of ignitable liquids with a rich theoretical background can reliably predict the FP of numerous kinds of combustible liquid mixtures. In this approach, the FP is calculated based on the combining rule of Le Chatelier (Le Chatelier, 1891) and a vapor-liquid equilibrium (VLE) model (Jalaei Salmani et al., 2018; Phoon et al., 2014). Indeed, it is presumed that the liquid and the produced vapor phase above it are in thermodynamic equilibrium. It is worth noting that the non-ideality of the studied ignitable mixtures should be considered to achieve satisfactory results (Jalaei Salmani et al., 2018). Affens and McLaren (Affens and McLaren, 1972), White et al. (White et al., 1997), Lee and Ha (Lee and Ha, 2003), and Hanley (Hanley, 1998) proposed certain predictive models which are suitable for almost ideal liquid mixtures. If the established VLE model considers the non-ideality of flammable liquid properly, the final model would satisfactorily predict the FP. There are typically two methods for developing a VLE model, which are $\varphi - \varphi$ and γ-φ (Jalaei Salmani et al., 2018; Lakzian et al., 2020). In the γ-φ approach, an equation of state (EoS) is used to simulate the vapor phase of a system, whereas an activity coefficient model is employed to describe the liquid phase, e.g., the NRTL (Renon and Prausnitz, 1968), Wilson (Wilson, 1964), and UNIQUAC (Abrams and Prausnitz, 1975). However, in the φ-φ approach, an EoS is used to describe both the behavior of liquid and vapor phases (Jalaei Salmani et al., 2018; Lakzian et al., 2020). Liaw and his team developed a well-known model based on the γ-φ approach and using various activity coefficient models by which the FPs of numerous non-ideal flammable solutions were properly predicted. In their works, the non-ideality of the ignitable blend was studied by the

applied activity coefficient models while assuming an ideal behavior for the vapor phase (Lakzian and Liaw, 2021, 2022; Liaw and Yang, 2020). Besides, Jalaei et al. (Jalaei Salmani et al., 2018) proposed a model based on the vapor pressure of the blend to anticipate the FP of water-alcohol and alkane-alkane systems where the φ-φ approach was the basis of VLE calculation; similar to the works of Liaw and his co-workers, the produced vapor phase at the top of the ignitable liquid blend was considered as an ideal gas, while an EoS was utilized to handle the non-ideality of flammable liquid mixture. The applied EoS can compute pure compounds' vapor pressure, eliminating the Antoine equation requirement, whereas the Liaw model needs the Antoine equation vitally. Moreover, Jalaei et al. proposed an approach in which one experimental FP data is needed to acquire binary adjustable parameters (BAPs) and, contrary to Liaw's model, there is no longer a need for binary VLE data (Jalaei Salmani et al., 2018). Furthermore, typically fewer BAPs are required than under Liaw's model (Jalaei Salmani et al., 2018). In their work, the cubic plus association (CPA) EoS (Kontogeorgis et al., 1996) could correctly predict the FP of non-ideal and ideal mixtures alone, whereas several activity coefficient models should be examined to achieve satisfactory results in Liaw's model. Recently, Lakzian et al. applied Jalaei's model to a wide range of alcohol + water mixtures. They also evaluated the effectiveness of two various combining rules, i.e. CR-1 combining rule and Elliot combining rule (ECR). Satisfactory outcomes were acquired by CPA EoS, especially with the aid of ECR for all studied mixtures (Lakzian et al., 2020).

As mentioned, the proposed approach by Jalaei et al. has several advantages, while the applied CPA EoS is somewhat complicated. Experimental saturation liquid density and vapor pressure data of pure compounds are needed as well to obtain the five constants of CPA EoS. It would be more advantageous if the approach produces reasonable results with simpler EoSs. Cubic EoSs

such as Soave-Redlich-Kwong (SRK) (Soave, 1972) and Peng-Robinson (PR) (Peng and Robinson, 1976), besides their simplicity, are capable of describing different thermodynamic systems properly; their parameters (a_0, b, c) are easily obtained by critical properties of pure compounds. Therefore, this study is conducted to implement that approach using SRK and PR EoSs for predicting the FP of numerous water-alcohol solutions, including methanol + water, ethanol + water, propanol + water, isopropanol + water, 1-butanol + water, 2-butanol + water, isobutanol + water, and 1-pentanol + water. Accordingly, the effect of applied EoS on the quality of obtained results by the proposed approach is revealed. In the following, the FPs of the 2-pentanol + water and 3-pentanol+water binary mixture are experimentally measured in this study. Moreover, the obtained FPs are also modeled by SRK, PR, and CPA EoSs utilizing the proposed method.

2. Experimental

2.1. Materials

2-pentanol (98%), 3-pentanol (98%), and 1-hexanol (99%) were purchased from Acros Organics (Geel, Belgium), Tokyo Chemical Industry (TCI, Tokyo, Japan), and Alfa Aesar (Kandel, Germany), respectively.

2.2. Methods

The FPs of three aqueous mixtures were measured experimentally in this study: 3-pentanol + water, 2-pentanol + water, and 1-hexanol + water. The HFP 362-Tag device (Walter Herzog, Germany) was used in the closed-cup FP measurement (Liaw et al., 2022). The measurement method followed the American Society for Testing and Materials D56 (ASTM D56) standard ((ASTM), 2005). The operating setups have been employed in some studies (Lakzian and Liaw,

2021, 2022) in which the heating rate for ignitable liquids with FPs greater than 60 °C was 3 °C/min, while for ignitable liquids with FPs less than or equal to 60 °C was 1 °C/min. Furthermore, ASTM D56 presented two test intervals (test interval-1: for ignitable liquids with FPs less than or equal to 60 °C and test interval-2: for ignitable liquids with FPs greater than 60 °C), with the values of interval-1 and interval-2 being 0.5 and 1.0 °C, respectively. The start-test value was 5 °C lower than expected, and the end-of-test value was 20 °C higher than expected. The expected temperature was obtained based on the literature. The sample volume was 50 mL for the measurement of every composition of mixtures. The FP of each composition was measured 10 times. The weight of each sample was measured (AY-220 Shimadzu digital mass balance; capacity: 220 ± 0.0001 g) and stirred (Harmony Hotplate Stirrer: HTS-1003; the speed of 60-1500 rpm) for 15 minutes before FP measurements.

The maximum standard uncertainty of the calculated mole fractions, u(x_1), for all of the measured mixtures (i.e., 2-pentanol + water, 3-pentanol + water, and 1-hexanol + water) was ± 1×10^{-4}. The maximum combined expanded uncertainty in FP, U(*FP*), for 2-pentanol + water, 3-pentanol + water, and 1-hexanol + water was ± 0.22, ± 0.46, and ± 0.75 K, respectively, with a confidence level of %95 (k ≈ 2).

3. Modeling

The SRK EoS is given as follows (Soave, 1972):

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

where *P*, *T*, *v*, and *R* are pressure (Pa), temperature (K), molar volume ($m^3.mol^{-1}$), and the universal gas constant (= 8.314 $J.mol^{-1}.K^{-1}$). And:

$$a = a_0 \left[1 + c\left(1 - \sqrt{\frac{T}{T_c}}\right)\right]^2 \quad (2)$$

The SRK parameters (a_0, b, and c) are defined in terms of critical pressure (P_c), critical temperature (T_c), and acentric factor (ω):

$$a_0 = 0.42747 \left(\frac{R^2 T_c^2}{P_c}\right) \quad (3)$$

$$b = 0.08664 \left(\frac{RT_c}{P_c}\right) \quad (4)$$

$$c = 0.480 + 1.574\omega - 0.176\omega^2 \quad (5)$$

The PR EoS is written in the following form (Peng and Robinson, 1976):

$$P^{PR} = \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)} \quad (6)$$

where its parameters are defined as follows:

$$a = a_0 \left[1 + c\left(1 - \sqrt{\frac{T}{T_c}}\right)\right]^2 \quad (7)$$

$$a_0 = 0.45724 \left(\frac{R^2 T_c^2}{P_c}\right) \quad (8)$$

$$b = 0.0778 \left(\frac{RT_c}{P_c}\right) \quad (9)$$

$$c = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (10)$$

In CPA EoS, an association term that considers the effect of hydrogen bonding is combined with a simple EoS such as SRK EoS (Soave, 1972). The pressure for CPA EoS is provided by Eq. (11) (Kontogeorgis and Folas, 2009):

$$P^{CPA} = P^{SRK} + P^{Association} = \left(\frac{RT}{v-b} - \frac{a}{v(v+b)}\right) + \left(-\frac{1}{2}\frac{RT}{v}\left(1 + \rho\frac{\partial \ln g}{\partial \rho}\right)\sum_i x_i \sum_{A_i}\left(1 - X_{A_i}\right)\right) \quad (11)$$

In Eq. (11), ρ is the molar density (*=1/v*), and *b*, *T*, and *R* are the co-volume parameter ($m^3.mol^{-1}$), temperature (K), and universal gas constant (=8.314 $J.mol^{-1}.K^{-1}$), respectively. The attractive parameter *a* ($Pa.m^6.mol^{-2}$) is related to the critical temperature (T_c) as follows:

$$a = a_0\left[1 + c\left(1 - \sqrt{\frac{T}{T_c}}\right)\right]^2 \quad (12)$$

X_{Ai} is the mole fraction of molecule *i* which does not develop hydrogen bonds at site *A*, which is defined by Eq. (13):

$$X_{A_i} = \left(1 + \rho\sum_j x_j \sum_{B_j} X_{B_j} \Delta^{A_i B_j}\right)^{-1} \quad (13)$$

The association strength Δ^{AiBj} is computed by Eq. (14):

$$\Delta^{A_i B_j} = g\left[exp\left(\frac{\varepsilon}{RT} - 1\right)\right] b_{ij}\beta \quad (14)$$

where β and ε are the "association volume" and "association energy", respectively. g is the simplified radial distribution function which is computed by Eq. (15):

$$g = \frac{1}{1-1.9\eta} \quad (15)$$

and:

$$b_{ij} = \frac{b_i + b_j}{2} \quad (16)$$

In Eq. (15), η is defined by the following expression (Eq. (17)):

$$\eta = \frac{1}{4} b\rho \quad (17)$$

In Eqs. (11) and (13), the summations ($\sum_{Ai}$ and $\sum_{Bi}$) are done only over the sites. According to Eqs. (11) to (14), for a pure associating component, CPA EoS has five adjustable parameters (a_0, b, c, ε, and β), which are typically established by using data fitting on liquid density and vapor pressure obtained experimentally. An associating compound is a compound that contains hydrogen bonds.

Developing an EoS for a mixture is done by applying the mixing rules; in the current study, the conventional van der Waals one-fluid ones are employed:

$$b_{mix} = \sum_i x_i b_i \tag{18}$$

$$a_{mix} = \sum_i \sum_j x_i x_j a_{ij} \tag{19}$$

$$a_{ij} = \sqrt{a_i a_j}\left(1 - k_{ij}\right) \tag{20}$$

where k_{ij} is the binary interaction parameter (BIP) which is obtained by one empirical FP value (Jalaei Salmani et al., 2018), and x_i is the mole fraction of constituent i in the ignitable mixture. It is worth noting that k_{ij} is symmetric, i.e., $k_{ij} = k_{ji}$ and $k_{ii} = k_{jj} = 0$.

When working with mixtures that contain multiple associating compounds, such as 2-propanol + water and 3-propanol + water, the combining rules should be applied in light of CPA EoS. The capabilities of two popular combining rules, Elliot and CR-1, were examined in this study; the CR-1 combining rule is given by Eqs. (21) and (22) (Kontogeorgis and Folas, 2009):

$$\varepsilon_{associating1-associating2} = \varepsilon = \frac{\varepsilon_{associating1} + \varepsilon_{associating2}}{2} \tag{21}$$

$$\beta_{associating1-associating2} = \beta = \sqrt{\beta_{associating1} \times \beta_{associating2}} \tag{22}$$

and Elliot combining rules (ECR) is defined by Eq. (23) (Kontogeorgis and Folas, 2009):

$$\Delta^{A_iB_j} = \sqrt{\Delta^{A_iB_i}\Delta^{A_jB_j}} \quad (23)$$

To construct a VLE computation by the φ-φ approach the fugacity of component *i* in the mixture (f_i) and the fugacity of the pure compound (f) are needed:

$$ln\,\phi = ln\left(\frac{f}{P}\right) = \frac{1}{RT}\int_V^\infty \left[\frac{P}{n_i} - \frac{RT}{V}\right] dV - ln\,Z + (Z-1) \quad (24)$$

$$ln\,\phi_i = ln\left(\frac{f_i}{x_i P}\right) = \frac{1}{RT}\int_V^\infty \left[\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j} - \frac{RT}{V}\right] dV - ln\,Z \quad (25)$$

In Eqs. (24) and (25), Z, φ, and φ_i are the compressibility factor, pure compound fugacity coefficient, and the fugacity coefficient of constituent *i* in the mixture, respectively. It is worth mentioning that the details about VLE computation can be found elsewhere (Matsoukas, 2013).

For a binary ignitable mixture, Le Chatelier's rule is given by Eq. (26):

$$\sum \frac{y_i}{LFL_i} = \frac{y_1}{LFL_1} + \frac{y_2}{LFL_2} = 1 \quad (26)$$

where y_i refers to the mole fraction of the flammable constituent *i* in the vapor phase while LFL_i is its lower flammable limit (LFL) that is linked to ambient pressure (P):

$$LFL_i = \frac{P_{i,sat}^{fp}}{P} \quad (27)$$

where $P_{i,sat}^{fp}$ is the vapor pressure of component *i* at its FP; the y_i value is obtained by VLE calculations (fugacity equality within adjacent phases):

$$f_i^l = f_i^v \quad (28)$$

$$x_i\phi_i^l P = y_i\phi_i^v P; x_i\phi_i^l = y_i\phi_i^v \quad (29)$$

From a thermodynamic perspective, a vapor phase at atmospheric pressure (1 atm) is essentially regarded as an ideal gas. Hence:

$$\phi_i^v = 1 \Rightarrow x_i \phi_i^l = y_i \tag{30}$$

Combining Eqs. (26), (27), and (30) resulted in the final expression of FP:

$$P\left(\sum \frac{x_i \phi_i^l}{P_{i,sat}^{fp}}\right) = 1 \tag{31}$$

Eq. (31) is satisfied by the FP temperature. It must be noted that only ignitable compounds are included in the summation in Eq. (31).

4. Results and discussion

The predictive method proposed by Jalaei et al. (Jalaei Salmani et al., 2018) and followed by Lakzian et al. (Lakzian et al., 2020) that was described in the previous section was applied to compute the FP of methanol + water, ethanol + water, propanol + water, isopropanol + water, 1-butanol + water, 2-butanol + water, isobutanol + water, 1-pentanol + water, 2-pentanol + water, 3-pentanol + water, and 1-hexanol + water using SRK and PR EoS. For this purpose, critical temperature and pressure of pure compounds, along with their acentric factors, are required, where **Table 1** provides such information. The FPs of 2-pentanol + water and 3-pentanol + water binary mixtures are also studied by CPA EoS, while the CPA parameters are required to model the mixtures; **Table 2** gives the CPA parameters of water, 2-pentanol, 3-pentanol, and 1-hexanol.

To assess the difference between empirical data and those predicted by the model, two statistical parameters of average absolute deviation (ADD) as well as root mean square deviation (RMSD) were employed as given by Eqs. (32) and (33), respectively:

$$RMSD = \sqrt{\frac{1}{n_p}\sum_{i=1}^{n_p}\left(T_i^{exp} - T_i^{calc}\right)^2} \quad (32)$$

$$AAD = \sum_{i=1}^{n_p}\frac{\left|T_i^{exp} - T_i^{calc}\right|}{n_p} \quad (33)$$

where T_i^{exp} and T_i^{calc} refer to the empirical and the predicted FP temperature, respectively; n_p denotes the number of mole fractions through the entire composition range (Lakzian et al., 2020).

In Jalaei et al., (Jalaei Salmani et al., 2018), it was mentioned that for the calculation of k_{ij} in Eq. (20) one experimental FP data is required. This value was the FP at a mixture when the mole fraction of the alcohol is equal to 0.1. The BIP, k_{ij} in Eq. (20), was modified via a simple optimization to achieve a zero deviation between the experimental and predicted FP data (at alcohol mole fraction 0.1). Other mole fractions' FP temperatures were then predicted using the obtained BIP.

The obtained results are available in **Tables S1 to S11 (Supplementary material)** and **Figs. 1 to 3**. In each Table, the experimental FP, the deviation between experimental data and model-anticipated ones by SRK and PR EoSs, along with the obtained (optimized) BIPs (k_{ij}) are given. For further evaluation of SRK and PR EoSs potential in anticipating the FP of studied mixtures, the results of CPA EoS by CR-1 and ECR combining rules obtained by Jalaei et al. (Jalaei Salmani et al., 2018) and Lakzian et al. (Lakzian et al., 2020) with the same approach are also provided. Additionally, overall performance is presented in **Table 3** for better comprehension. It can be seen that the obtained results using SRK are slightly more satisfactory than those calculated using PR. It can also be seen that the optimized BIPs (k_{ij}) are almost the same for both EoSs for each binary mixture (**Tables S1 to S11**). As the alcohol becomes heavier, its mixture

with water becomes more non-ideal; the separation of phases occurs in a mixture of butanol and heavier alcohols with water. Actually, the partial miscibility is due to the high non-ideality of the system. According to the results, the performance of both SRK and PR EoSs is not satisfactory over the whole concentration addressing partially miscible water-alcohol mixtures; because conventional cubic EoSs such as SRK and PR are generally not sufficiently effective in handling non-ideal thermodynamic systems. As mentioned, partially miscible mixtures (1-pentanol + water, 2-pentanol + water, 3-pentanol + water, 1-hexanol + water, isobutanol + water, 1-butanol + water, and 2-butanol + water) are more non-ideal compared to totally miscible mixtures (isopropanol + water, propanol + water, ethanol + water, and methanol + water). Regarding **Table 3**, it can be said that SRK EoS is almost as effective as the CPA EoS along with the CR-1 combining rule. However, the CPA EoS using ECR is completely superior to SRK and PR EoSs. It is worth noting that CPA EoS was essentially developed to describe non-ideal systems, especially those with hydrogen bond compounds such as water-alcohol mixtures. As can be seen in **Figs. 1(c) and 1(d)**, and in all graphs in **Figs. 2 and 3**, both SRK and PR EoSs overpredicted the FP of studied systems which is challenging from the safety point of view. However, according to all figures, the trend of experimental data is almost correctly described by them. Additionally, it should be mentioned that these EoSs are simple to be implemented and their parameters (a_0, b, c) are easily obtained by critical properties, while five constants of CPA EoS require experimental saturation vapor pressure and liquid density data.

Consider modeling new experimental FP data (2-pentanol + water, 3-pentanol + water, and 1-hexanol + water), CPA EoS using ECR predict the FPs accurately whereas the performance of SRK and PR EoSs is not satisfactory. Overall, the RMSD and ADD of the results of SRK and PR for all mixtures under study were less than 5.5 and 8.0 K, respectively.

5. Conclusion

The FPs of 1-pentanol + water, isobutanol + water, 2-butanol + water, 1-butanol + water, isopropanol + water, propanol + water, ethanol + water, and methanol + water mixtures were anticipated by a vapor pressure-based model. The current model is based on the vapor-liquid equilibrium (VLE) where the φ-φ approach using Soave-Redlich-Kwong (SRK) and Peng-Robinson (PR) equation of states (EoSs) were utilized. The employed model has advantages such as simplicity, requiring no experimental VLE data, and reliance on the fewest number of adjustable parameters (only a BIP, i.e., k_{ij}). Comparisons were made between the current results and those found in the literature as well as those obtained by the same approach using cubic-plus-association (CPA) EoS with the aid of the CR-1 combining rule and Elliot combining rule (ECR).

In the following, the FPs of 3-pentanol + water, 2-pentanol + water, and 1-hexanol + water binary mixture were experimentally determined for the first time in this study; the obtained experimental data were then predicted using the model applying SRK, PR, and CPA EoSs. The new experimental FPs were accurately predicted utilizing CPA EoS by ECR, whereas the accuracy of SRK and PR EoSs was not satisfactory.

Regarding all studied mixtures, as the alcohol becomes heavier, its mixture with water becomes more non-ideal; the separation of phases occurs in a mixture of butanol and heavier alcohols with water. The partial miscibility is due to the high non-ideality of the system (1-hexanol + water, 3-pentanol + water, 2-pentanol + water, 1-pentanol + water, isobutanol + water, 2-butanol + water, 1-butanol + water). The accuracy of SRK and PR EoSs is decreased as the non-ideality of the studied system is increased. Overall, RMSD and ADD of SRK and PR results for all studied

mixtures were less than 5.5 and 8.0 K, respectively. The findings also revealed that SRK is slightly more effective than PR; the trend of experimental data is almost correctly described by both EoSs. Moreover, SRK EoS was nearly as effective as the CPA EoS with CR-1 combining rule. The CPA EoS that used ECR, on the other hand, was far superior to the SRK and PR EoSs. It is worth mentioning that pure-component parameters are required to predict the FP of studied mixtures by CPA EoS. However, to the best of our knowledge, these parameters for 2-pentanol, 3-pentanol, and 1-hexanol are not available in the literature while they were calculated and reported for the first time in this study.

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Statements and Declarations

The authors have no conflict of interest to declare.

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Table 1
Physical properties of studied pure compounds (Jalaei Salmani et al., 2019; Poling et al., 2001)

Compound	Critical temperature (T_c/K)	Critical pressure (P_c/bar)	Acentric factor (ω)
water	647.13	220.6	0.344
methanol	512.64	80.9	0.565
ethanol	514.00	61.4	0.644
propanol	536.78	51.7	0.629
isopropanol	508.30	47.6	0.665
1-butanol	563.05	44.2	0.590
2-butanol	536.05	41.8	0.574
isobutanol	547.78	43.0	0.590
1-pentanol	588.15	39.09	0.579
2-pentanol	560.30	36.75	0.561
3-pentanol	559.60	37.14	0.514
1-hexanol	611.40	35.10	0.573

Table 2
CPA parameters of some associating components

Component	a_0 ($Pa.m^6.mol^{-2}$)	$b \times 10^5$ ($m^3.mol^{-1}$)	c (unitless)	ε ($Pa.m^3.mol^{-1}$)	$\beta \times 10^3$ (unitless)	Ref.
2-Pentanol	2.17146	10.21111	0.96309	21186	3.4	this study
3-Pentanol	2.09540	9.97296	1.03586	20015	3.4	this study
1-Hexanol	2.64139	11.37941	0.95868	24104	2.6	this study
Water	0.12277	1.4515	0.67359	16655	69.2	(Kontogeorgis and Folas, 2010)

Table 3

The comparison between different EoSs in predicting the FPs of all studied mixtures by the applied approach

System	Alcohol mole fraction	The calculated statistical parameters by CPA EoS **(Jalaei Salmani et al., 2018; Lakzian et al., 2020)** and this study				The calculated statistical parameters by cubic EoSs (this study)			
		AADs		**RMSDs**		**AADs**		**RMSDs**	
		ECR	CR-1	ECR	CR-1	SRK	PR	SRK	PR
Methanol + water	0.1-1.0	0.72	0.79	0.87	0.92	0.63	0.60	0.87	0.87
Ethanol + water	0.1-1.0	0.32	0.77	0.43	0.99	1.05	1.19	1.52	1.68
Propanol + water	0.1-1.0	0.87	2.51	1.15	2.97	3.01	3.19	3.64	3.86
Isopropanol + water	0.1-1.0	0.42	2.05	0.53	2.64	2.47	2.65	3.53	3.57
1-Butanol + water	0.1-1.0	0.26	2.17	0.36	2.92	2.97	3.19	4.20	4.46
2-Butanol + water	0.1-1.0	0.88	1.20	1.18	1.53	2.70	2.90	3.67	3.92
Isobutanol + water	0.1-1.0	0.64	1.33	0.80	1.87	3.04	3.25	4.33	4.58
1-Pentanol + water	0.1-1.0	0.29	3.04	0.39	4.06	3.88	4.12	5.62	5.91
2-Pentanol + water	0.1-1.0	0.53	3.09	0.69	4.22	4.39	4.61	6.26	6.53
3-Pentanol + water	0.1-1.0	0.65	3.28	0.96	4.32	5.16	5.34	7.02	7.29
1-Hexanol + water	0.1-1.0	1.39	4.06	1.84	5.32	5.24	5.41	7.27	7.58
Average		0.63	2.21	0.84	2.89	3.14	3.31	4.36	4.57

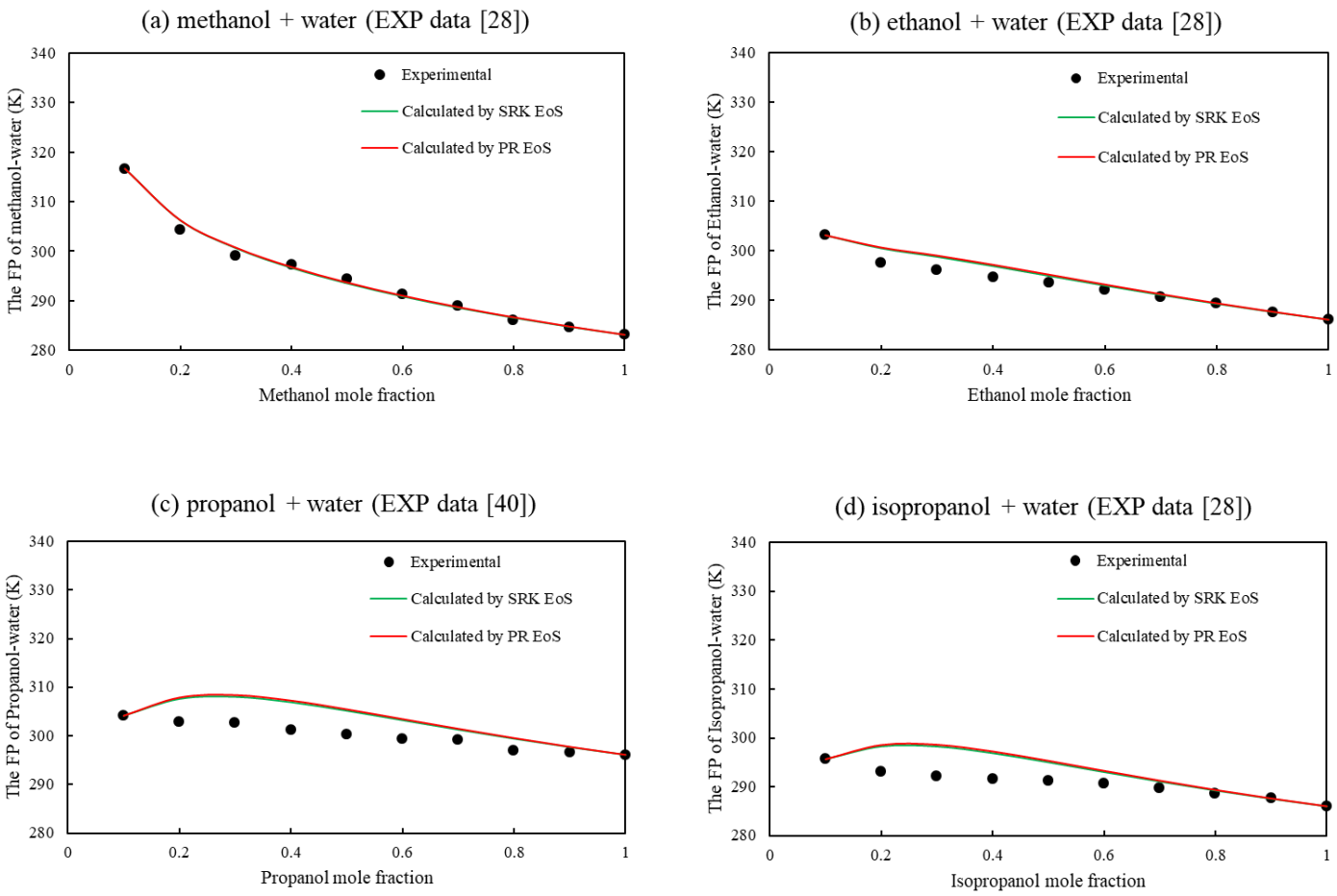

Fig. 1. FPs prediction results by SRK and PR EoSs for totally miscible alcohols + water mixtures; (a) methanol + water, (b) ethanol + water, (c) propanol + water, and (d) isopropanol + water (The Supplementary Materials contain the large-scale graphics; **Figs. S1 and S4**).

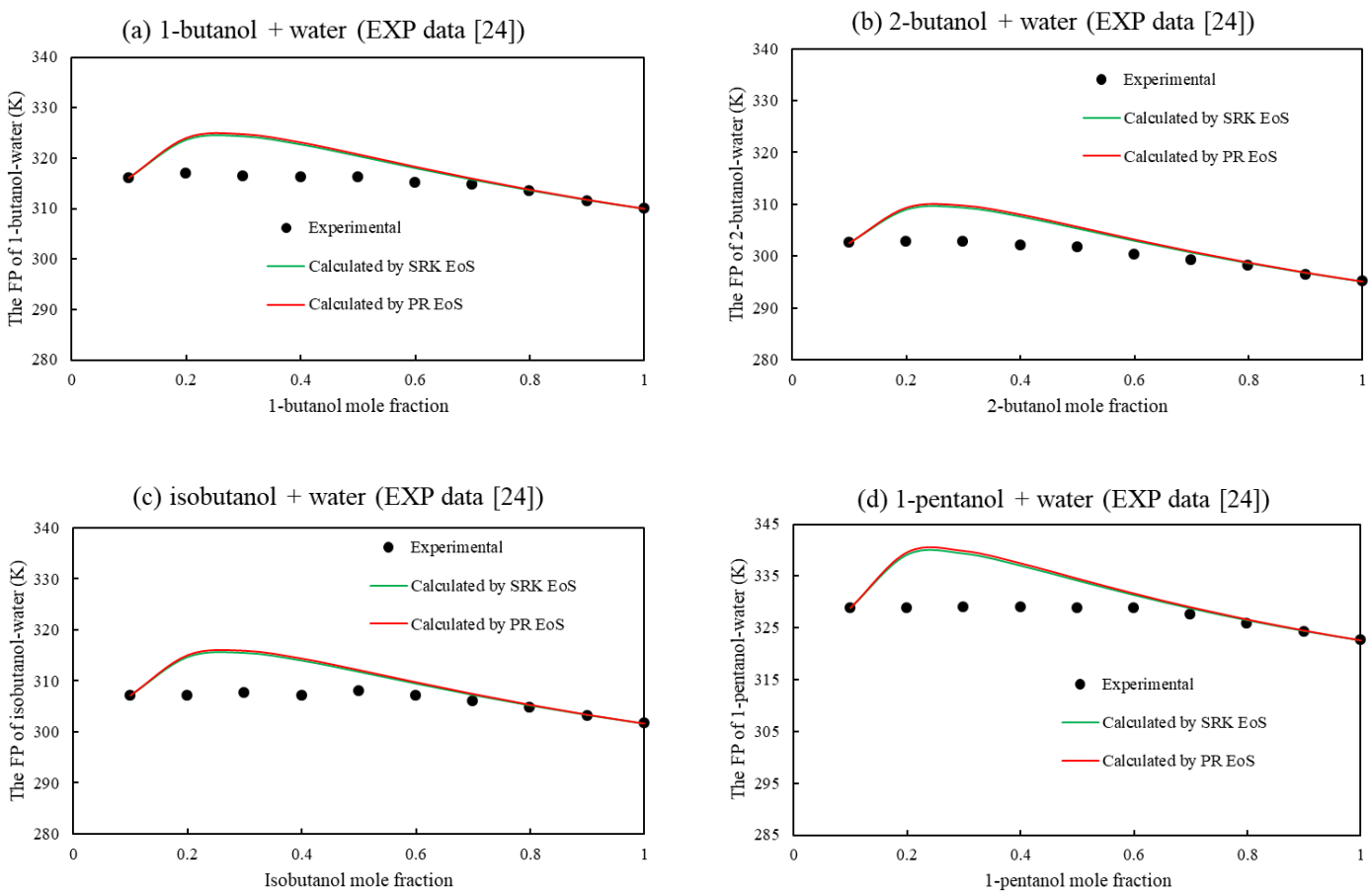

Fig. 2. FPs prediction results by SRK and PR EoSs for partially miscible alcohols + water mixtures; (a) 1-butanol + water, (b) 2-butanol + water, (c) isobutanol + water, and (d) 1-pentanol + water (The Supplementary Materials contain the large-scale graphics; **Figs. S5 and S8**).

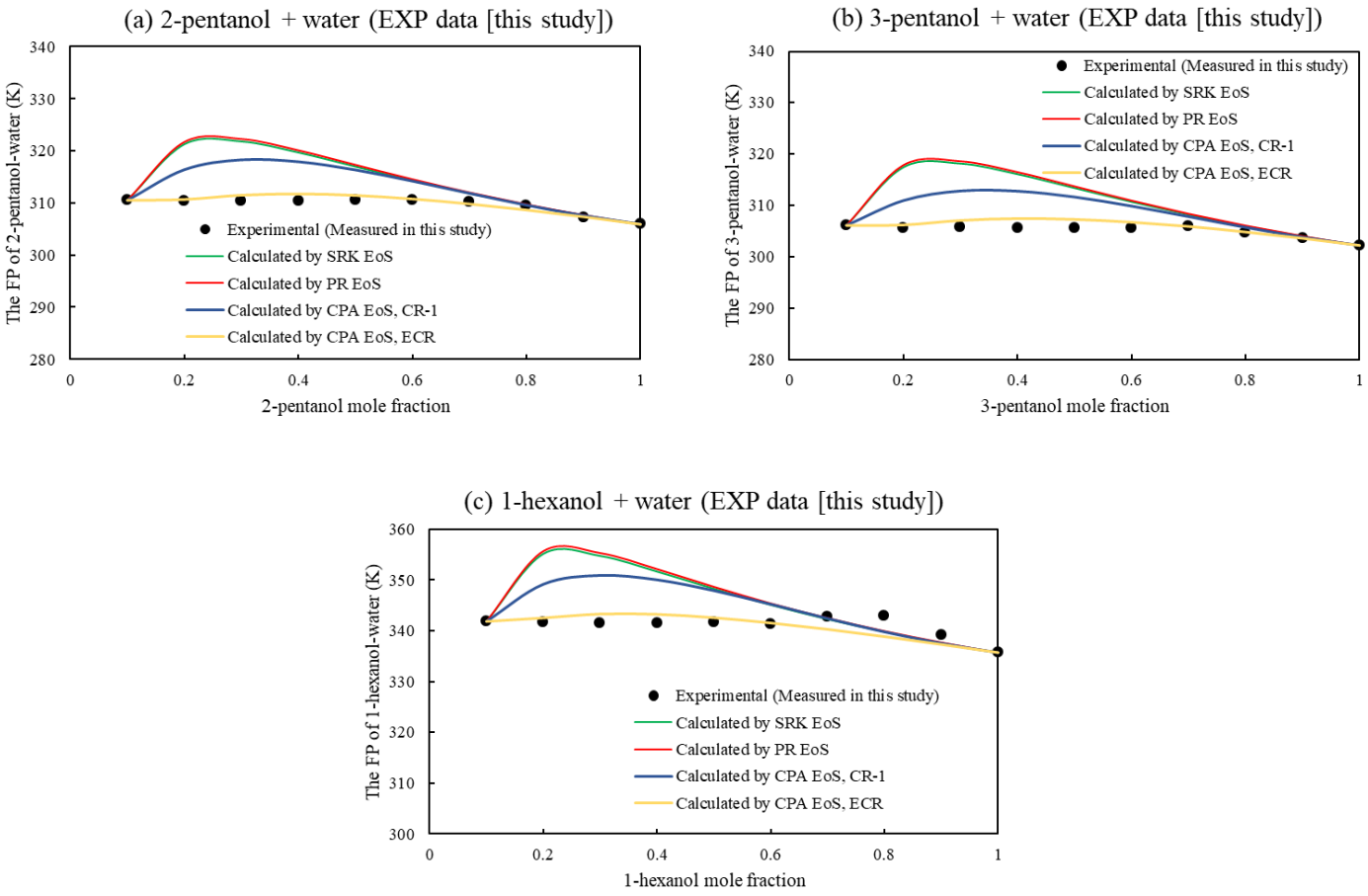

Fig. 3. FPs prediction results by SRK, PR, and CPA EoSs for partially miscible alcohols + water mixtures; (a) 2-pentanol + water, (b) 3-pentanol + water, and (c) 1-hexanol + water (The Supplementary Materials contain the large-scale graphics; **Figs. S9 and S11**).