

Assessment and modeling of the isobaric vapor-liquid-liquid equilibrium for water + cyclopentyl methyl ether + alcohol (ethanol or propan-1-ol) ternary mixtures

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Abstract

The three-phase equilibria of water + cyclopentyl methyl ether (CPME) + ethanol or propan-1-ol ternary mixtures are explored from experimental determinations and theoretical modeling at a constant pressure (101.3 kPa), and over 350 K to 356 K. Experimental measurements are performed in a modified Gillespie phase equilibria dynamic cell, which includes an ultrasonic homogenizer. The reliability of the measure three-phase equilibria is validated by employing the Wisniak's L/W thermodynamic consistency test. The measured vapor-liquid-liquid equilibria (VLLE) data at 101.3 kPa are accurately predicted from the phase stability restriction coupled with the multiphase equilibrium criteria. The application of this combined approach is showcased as a thermodynamical tool to explore all possible phase equilibria regions (*i.e.*, one-, two-, and three-phase), providing a robust representation of the multiphase equilibria. Both phase stability and the corresponding multiphase equilibria are calculated using the SAFT-VR-Mie EoS model (statistical associating fluid theory of variable range employing a Mie potential equation of state), where the association and polar nature of pure components and their binary interactions are explicitly considered.

No ternary azeotropy is detected within the experimental range of stable VLLE for the water + CPME + ethanol ternary mixture, although the theoretical extrapolation of the experimental conditions using the SAFT-VR-Mie EoS its existence. For the case of the water + CPME + propan-1-ol ternary mixtures, a stable VLLE with a heterogeneous ternary azeotrope is detected from the interpolation of the experimental determinations.

The predicted heterogeneous ternary azeotrope supports use of CPME as a potential entrainer candidate for dehydration of bio-alcohols (*e.g.*, ethanol or propan-1-ol) as well as the distillate products, bio-alcohols (ethanol or propan-1-ol)+ CPME mixtures can be directly used as a renewable fuel without the need of additional separation stages.

Keywords: vapor-liquid-liquid equilibria, cyclopentyl methyl ether, ethanol, propan-1-ol, water,

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1. Introduction

Renewable (bio or synthetic) fuels are lauded as a potential mid-term alternative to substitute partially or totally traditional fossil fuels.[1, 2] These carbon-neutral (or negative) fuels can be used directly in traditional engines with minimal modifications while offering technical benefits such the increasing the octane ratio and engine efficiency.[1, 2] Complementary, renewable fuels can also be used in short-term period as renewable alternatives to oxygenate additives for traditional gasoline reducing the human and environmental impact indexes caused by the unburned hazardous components.

Over the past decades, one of the most successful examples of renewable fuels pertains to bio-alcohols (*e.g.*, low molecular weight alcohols ranging from methanol to pentanol and their isomers), which can be obtained from ecologically sustainable and fully fossil-free routes such as microbiological or fermentation processes of natural products and organic waste materials (*e.g.*, root vegetables, algae, food crops, fruits, wastes from wood, vegetables, and forest waste, cellulose, among others) [1, 2, 3, 4, 5, 6] as well as from biocatalytic synthesis [7], among others. Bio-alcohols play a central role in producing other bio-fuels, such as bio-diesel and bio-ether. Specifically, bio-diesel can be produced from the chemical reaction of bio-alcohols with triglycerides obtained from animal fat and vegetable oil. [1, 2, 4, 5] In contrast, bio-ethers can be synthesized from sugar beet, wheat, or alternatively using waste glycerol obtained from bio-diesel production.[1, 2, 4]

Despite their potential use as alternative renewable fuels and the broad spectrum of alternative sources for their production, one of the main limitations of using raw bio-alcohols as fuel or oxygenate additives for gasoline engines, is that they are usually produced in aqueous media. Therefore, the incorporation of bio-alcohols as a renewable fuel implies not only their obtention but also their dehydration to reach technically acceptable levels of water content (*i.e.*, $\leq 1\%$ v/v). One of the most advantageous dehydration techniques for this purpose is the heterogeneous azeotropic distillation. [8, 9, 10] In this distillation unit operation, a light entrainer is aggregated to the aqueous-alcoholic feed to enhance the separation by modifying the fluids relative volatilities at the azeotropic condition. The selection of entrainer is restricted to those that form a ternary heterogeneous azeotrope.[9, 10] According to Brits, [11] most of the entrainers that have been considered and characterized are fossil-based components. Specifically, some alkanes (*e.g.*, hexane, isooctane, cyclohexane),[12, 13, 14, 15, 16, 17, 18] aromatics (*e.g.*, toluene, and 1,4-dimethylbenzene), [19, 20] acetates (*e.g.*, n-propyl acetate),[21, 22, 23] and ethers (methyl tert-butyl ether and diisopropyl ether) [14, 24, 25] exhibit ternary heterogeneous azeotropy and fulfill the adequate thermodynamical conditions to carry out heterogeneous azeotropic distillation separation.

32 There is a need to develop and study eco-friendly and fossil-free entrainers to produce and be able to
 33 label bio-alcohols as fully renewable fuels. One alternative is to use synthetic fuels compatible with tradi-
 34 tional engines, which reduces additional separation stages in the bio-alcohol production. Two remarkable
 35 and eco-friendly synthetic fuels are 2,5-dimethylfuran (2,5-DMF) and cyclopentyl methyl ether (CPME).
 36 Specifically, 2,5-DMF can be synthesized from fructose using a catalytic biomass-to-liquid process,[26]
 37 and displays excellent thermophysical properties to be used in gasoline blending and biofuels [27, 28, 29].
 38 CPME can be produced through a green pathway by methylation of cyclopentanol or by adding methanol
 39 to cyclopentene.[30] The toxicology, environmental and technical evaluations,[30, 31, 32] of CPME suggest
 40 that it can be cataloged as a feasible new renewable additive for oxygenate gasoline due to it exhibiting low
 41 volatility (high boiling point), moderate toxicity, low hydrophobicity, low peroxide formation rate, easy
 42 separation and recovery from water, among other properties. Additionally, CPME shows high compatibil-
 43 ity with hydrocarbons and other additives for fossil fuels as well as excellent thermodynamical properties
 44 to be directly used as fuel or oxygenate additives for gasoline, as was described in our previous works
 45 ([33, 34, 35, 36, 37, 38, 39] and references therein) making it as an ideal component for bio-gasoline blend
 46 employed in ground transportation as well as providing alternatives for sustainable aviation fuels (SAF).
 47 [40, 41, 42]

48 Following our previous reports on 2,5-DMF, [27, 28, 29] and CPME,[33, 34, 35, 36, 37, 38, 39] this
 49 contribution aims to explore the potential applications of CPME as an eco-friendly entrainer for dehydra-
 50 tion of two important bio-alcohols, namely ethanol and propan-1-ol, where also the dehydrated mixtures
 51 (*i.e.*, CPME + ethanol and CPME + propan-1-ol) can potentially be used directly as biofuel. Specifi-
 52 cally, this work is focused on the experimental determinations as well as the theoretical predictions of the
 53 vapor – liquid – liquid equilibria (VLLE) formed by these two aqueous ternary mixtures (*i.e.*, water +
 54 CPME + ethanol, and water + CPME + propan-1-ol). The experimental measurements are carried out
 55 by using a modified Gillespie-type dynamic equilibrium cell, which includes an ultrasonic homogenizer.
 56 The reliability of the VLLE experimental data will be validated by employing the Wisniak’s L/W ther-
 57 modynamic consistency point-point test. Theoretical predictions are conducted by using the statistical
 58 associating fluid theory of variable range employing a Mie potential equation of state (SAFT-VR-Mie
 59 EoS),[43] extended for associating Mie fluids,[44] and polar fluids [45]. The latter extensions provide a
 60 molecular-based model to describe pure fluids and mixtures, taking into account the attraction, repulsion,
 61 chain, association, and polar nature of pure fluids and their binary interactions. The theoretical predic-
 62 tions are based on a phase stability criteria [46] coupled with a multiphase flash algorithm, [47] which
 63 provides a route to detect all possible (one, two, and three) coexisting phases.

2. Experimental Section

2.1. Chemical Reagents

Cyclopentyl methyl ether (CPME) was obtained from Sigma-Aldrich, whereas the other reagents (*i.e.*, water, ethanol, and propan-1-ol) were obtained from Merck. The reagents were used here as they were received. Table 1 summarizes the technical specification of the reagents reported by the suppliers, as well as our gas chromatography (GC) verification using a Perkin-Elmer gas chromatograph (Model Clarus 580), which uses a Thermal Conductivity Detector (TCD) with a a packed column (Porapak Q 80/100) of 0.3 cm in diameter and 2.0 m long. The GC thermal conditions are 493.15 K for the detector, 483.15 K for the injector, and 473.15 K for the column. The GC test permits to confirm the purity of the chemical indicated by the manufacturers.

Table 1: Technical specification for the used chemicals.

Chemical Name	CAS	Supplier	Mass fraction purity (stated by the supplier)	Purification method	Mass fraction purity (detected by GC)
Cyclopentyl methyl ether (CPME)	5614-37-9	Sigma-Aldrich	0.999	none	0.999
Ethanol	64-17-5	Merck	0.999	none	0.999
Propan-1-ol	71-23-8	Merck	0.995	none	0.998
Ultrapure water	7732-18-5	Merck	—	none	—

2.2. Measurements of purity indicators for pure fluids.

Three different indicators are used to certificate the purity of the reagents used here (*i.e.*, water, CPME, ethanol, and propan-1-ol). Specifically, a Bellingham and Stanley Multiscale Automatic Refractometer (model RFM 81, England) is employed for measuring the refractive indexes, n_D , at the Na D line, within a standard uncertainty of 10^{-5} . An Anton Paar densimeter (model DMA 5000, Austria) is employed for the liquid mass densities determinations, ρ , within a standard uncertainty of $4 \times 10^{-4} g cm^{-3}$. A Fischer Labor and Verfahrenstechnik cell (model VLE/VLLE 602, Germany) is used to measure the normal boiling points (T_b). The general technical details of this equilibrium cell have been described in our previous work, [48] and some specific details are given in the following section. Table 2 collects the corresponding determinations of n_D , and ρ at 101.3 kPa, and 298.15 K, as well as the T_b at 101.3 kPa. In Table 2 reference values are also included for comparison.[49] The experimental values of n_D , ρ , and T_b in Table 2 agree the reference values and also agree to our previous measurements,[33, 34, 35, 36, 37, 38, 39, 48]

and certify that the purity of the chemicals (CMPE, ethanol, propan-1-ol, and water) is adequate to carry out VLLE measurements.

Table 2: Experimental determinations and reference values of the refractive indexes at Na D line, (n_D), liquid mass densities, (ρ), and normal boiling points (T_b) of the reagents used in this work measured at 298.15 K and 101.3 kPa ^{a, b}

Component	n_D		$\rho / g\ cm^{-3}$		T_b / K	
	<i>Exp.</i>	<i>Lit.</i>	<i>Exp.</i>	<i>Lit.</i>	<i>Exp.</i>	<i>Lit.</i>
CPME	1.41976	1.42060	0.85823	0.85790	378.32	378.60
Ethanol	1.36068	1.36068	0.78507	0.78506	351.44	351.44
Propan-1-ol	1.38333	1.38370	0.79954	0.79960	370.30	370.30
Water	1.33374	1.33288	0.99670	0.99707	373.09	373.17

^a The standard uncertainties considering a 0.68 level of confidence are: $u(T) = 0.1\ K$, $u(T_b) = 0.1\ K$, $u(P) = 0.3\ kPa$ for T_b , $u(n_D) = 4 \times 10^{-4}$. Relative standard uncertainty for pressure: $u(P) = 1\%$. The combined expanded uncertainties calculated by using a 0.95 level of confidence ($k = 2$) are: $U(\rho) = 1.0 \times 10^{-3}\ gcm^{-3}$. ^b The reference values are taken from NIST – TDE database.[49]

2.3. Vapor – liquid – liquid equilibrium determinations

The Vapor-Liquid-Liquid Equilibria (VLLE) is measured at 101.3 kPa by using a commercial VLLE cell (Fischer Labor and Verfahrenstechnik, LABODEST cell model VLE/VLLE 602, Germany). This VLLE cell incorporates an ultrasonic probe inside its boiling chamber to increase the homogenization of the mixture and allows us to measure mixtures with limited miscibility. This modified phase equilibria cell was initially designed by Gomis et al. [50] and used in a broad spectrum of the mixtures (see for instances Refs. [50, 13, 51, 52]). In this work, we followed a similar experimental procedure described in depth in our previous work.[48], where all technical details can be found.

Briefly, a mixture with a known global liquid concentration is placed into the chamber of the VLLE cell. Then, the experimental pressure is fixed at 101.3 kPa with an estimated overall instrument accuracy of 0.1 kPa using a vacuum pump and nitrogen simultaneously. Once the experimental pressure is reached, the mixture is simultaneously mixed with a magnetic stirrer and heated to its boiling point by an immersion heater. Once the mixture starts boiling, the ultrasonic device is used to promote the homogenization of the partly miscible liquid phases. The boiling mixture flows through a Cottrell pump, which increases mass transfer and equilibria among the phases, then the mixture passes through a separation compartment. The separated fluids pass through condensers and return to the VLLE chamber, where the mixture is stirred, and then the mixture is transported again to the immersion heater. On average, the mixture boils and circulates for 3 to 4 hours to reach the thermal equilibrium. In this device, the temperature is measured

with an estimated accuracy of 0.1 K and a resolution of 0.01 K. Once the thermal equilibrium is attained, the vapor is transferred using a heated line to the GC oven where a UW 10-port valve allows the splitting of the vapor to the GC column and the other portion returns to the VLLE cell. The composition in the vapor phase is measured several times until it reaches a constant value. Once the temperature and vapor compositions reach at stationary condition, the mixture is assumed to be in phase equilibrium, and liquid phase sample is extracted from the VLLE cell. This liquid sample is maintained at the boiling equilibrium temperature using a dry bath and rested until the LLE is observed. From the LLE, samples are taken from both liquid phases (*i.e.*, the aqueous rich phase and the organic rich phase) and immediately mixed with an internal standard to avoid further separation. The mole fractions determinations are carried by using GC, where the peak area ratio is transformed to the mole fraction employing the external (vapor phase) and internal (liquid phases) standard methods. Each calibration curve is fitted to a linear function with a $R^2 \geq 0.99$, and the mole fraction is measured within 0.001. This work, propan-1-ol is utilized as a standard for the case of water + CPME + ethanol mixture, whereas ethanol is utilized for water + CPME + propan-1-ol mixture.

3. Theoretical Section

3.1. Thermodynamic consistency test for VLLE measurements.

The measurements of VLLE at 101.3 kPa for ternary mixtures provide the equilibrium state variables, namely: the equilibrium temperature (T), and the equilibrium mole fractions for the two liquids phases, namely: the aqueous bulk phase (*i.e.*, x_1^w, x_2^w, x_3^w), and the organic bulk phase (*i.e.*, x_1^o, x_2^o, x_3^o), and the equilibrium mole fractions for the vapor bulk phase (*i.e.*, y_1, y_2, y_3). The data is validated using the Wisniak's L/W thermodynamic consistency point-point test.[53] This consistency test consists of evaluating the L_k/W_k ratio for every measure point (k) at each liquid-vapor pair ($L_j - V$). Considering that the vapor phase can be assumed as a perfect gas and that the effect of the pressure of the liquid phase fugacity can be neglected, L_k/W_k ratio can be expressed as:[53]

$$\left(\frac{L_k}{W_k}\right)^{L_j-V} = \frac{\left(\frac{\sum_{i=1}^3 x_i \Delta h_i^0}{\sum_{i=1}^3 x_i \Delta h_i^0 / T_i^0} - T\right)}{\left(\frac{RT}{\sum_{i=1}^3 x_i \Delta h_i^0 / T_i^0}\right) \left(\sum_{i=1}^3 x_i \ln \left(\frac{y_i P}{x_i P_i^0}\right) - \sum_{i=1}^3 x_i \ln \left(\frac{y_i}{x_i}\right)\right)} \quad (1)$$

In Eq. 1, R symbolizes the universal gas constant, P, T, x_i, y_i represents the equilibrium conditions of pressure, temperature, and mole fractions for component i in the liquid and the vapor phase, respectively, for the $L_j - V$ equilibrium. T_i^0 denotes the boiling temperature of pure fluid i at the experimental isobaric condition, here T_i^0 corresponds to the normal boiling temperature (the numerical values are included in Table 2). Δh_i^0 represents the pure fluid i vaporization enthalpy at the isobaric condition, which can be

135 taken from experimental databases. Here, the NIST – TDE database, [49] is used here to obtain the values
 136 of Δh_i^0 , which are included in Table 3. P_i^0 represents the vapor pressure of pure component i evaluated
 137 at T . $P_i^0(T)$ has been experimentally determined in our previous works using the same equilibrium cell
 138 for ethanol and CPME [33], propan-1-ol [37], and water [48]. The Antoine equation is used to correlate
 139 $P_i^0(T)$:

$$\log(P_i^0/kPa) = A_i - \frac{B_i}{(T/K) + C_i} \quad (2)$$

140 In 2 A_i , B_i , and C_i symbolizes constants for the the Antoine equation, whose numerical values are
 141 collected in Table 3.

Table 3: Enthalpy of vaporization (Δh_i^0) and Antoine constants (A_i, B_i, C_i) for the pure components

Component	$\Delta h_i^0 / kJ mol^{-1}$	A_i	B_i	C_i
CPME ^{a, b}	32.900	6.5772	1536.3534	– 20.3705
Ethanol ^{a, b}	38.936	7.1687	1551.6458	– 50.9050
Propan-1-ol ^{a, c}	41.665	7.0071	1517.6000	– 66.8030
Water ^{a, d}	40.799	7.2398	1761.2550	– 36.5881

^a Δh_i^0 values are taken from NIST – TDE database.[49] The Antonine constants are taken from: ^b Mejía and Cartes [33], ^c Mejía et al. [37], ^d Mejía et al. [48].

142 Using the experimental measurements (P, T, x_i, y_i) , and the values of Δh_i^0 and $P_i^0(T)$, the L_k/W_k
 143 ratio can be evaluated from Eq. 1. The theoretical value for this ratio is one for each experimental
 144 point (k) at each biphasic pair $L_j - V$. The deviations from unity quantify the apparent inaccuracy of a
 145 given data point in the context of the data set. An acceptable range for experimental determinations is
 146 $0.9 < (L_k/W_k) < 1.10$.[53]

147 3.2. Thermodynamical Modeling for VLLE

148 The thermodynamical conditions for a vapor - liquid - liquid equilibrium (VLLE) are given by the
 149 following set of equations:[54, 55]

$$P^w = P^o = P^v = P^{VLLE} \quad (3a)$$

$$T^w = T^o = T^v = T^{VLLE} \quad (3b)$$

$$\mu_i^w = \mu_i^o = \mu_i^v = \mu_i^{VLLE}; i = 1, 2, 3 \quad (3c)$$

150 In Eqs. (3), P represents the absolute pressure, T symbolizes the absolute temperature, and μ_i
 151 represents the chemical potential of component i . The superscripts w, o, v represent the aqueous, the

organic, and the common vapor bulk phases, respectively. Finally, the superscript VLLE denotes the phase equilibrium condition. Both the P and μ_i are related to the Helmholtz energy density, a : [54, 55]

$$P = \rho \left(\frac{\partial a}{\partial \rho} \right)_T - a \quad (4a)$$

$$\mu_i = \left(\frac{\partial a}{\partial \rho_i} \right)_{T, V, \rho_j} \quad (4b)$$

where ρ symbolizes the molar density of the mixture, and ρ_i is the molar density of species i . Both densities are directly related to the mole fraction, x_i : $x_i = \rho_i / \rho$.

In this work, a is described by the statistical associating fluid theory of variable range employing a Mie potential equation of state (*a.k.a.*, SAFT-VR-Mie EoS) [43, 45, 44], whose main expression and the corresponding parameters are summarized in Sec. 3.2.1.

It is important to point out that one of the main hurdles to calculate VLLE from Eqs. 3a to 3c is the identification of the stable phases at a given condition, especially where the phase equilibrium displays ternary heteroazeotropy. In order to overcome this difficulty, the VLLE calculations must be coupled with sophisticated algorithms [56] and/or a stability analysis of the possible phases. [46, 57, 58] In this work, the latter approach is coupled with phase equilibrium calculations to obtain reliable VLLE. The specific details of this combined approach are given in Sec. 3.2.2.

3.2.1. Statistical Associating Fluid Theory of Variable Range employing a Mie potential (SAFT-VR-Mie)

The Helmholtz energy density, a , for the SAFT-VR-Mie EoS is given by the expression: [43, 44, 45]

$$a = a^{IG} + a^R = a^{IG} + a^{MONO} + a^{CHAIN} + a^{ASSOC} + a^{POL} \quad (5)$$

In the latter expression, a^{IG} denotes the ideal gas reference, and a^R represents the residual Helmholtz energy density. a^R is formed by the sum of the follow four terms: a^{MONO} is the monomer (unbounded) contribution, a^{CHAIN} represents the contribution for chain molecules formation, a^{ASSOC} symbolizes the contribution of the intermolecular association and a^{POL} accounts for the contribution of polar interactions. The full equations for these contributions are included in the supplementary information of our previous work, [59] or alternatively these equations can be found in the original references [43, 44, 45].

Considering the SAFT-VR-Mie model, the pure fluids are described by up to ten parameters, namely: m_{si} (number of spherical segments that form the chain of component i), σ_{ii} (effective segment diameter for component i), ε_{ii} (the potential well depth for component i), $\lambda_{a,ii}$ and $\lambda_{r,ii}$ (attraction and repulsion exponents of the intermolecular Mie potential for component i , respectively), ε_{ii}^{AB} (site-site interaction energy for association for component i), $r_{c,ii}^{AB}$ (association range for component i), $r_{d,ii}^{AB}$ (distance between

the associating site for component i), μ_{ii} (dipolar moment for component i) and $n_{p,ii}$ (number of polar sites for component i). In this EoS model, it is also necessary to stipulate the scheme of association, which can be defined three parameters: $[B, P, N]$, where (B) denotes the number of bipolar sites, (P) represents the number of positive sites, and (N) describes the number of negative sites. This information yields a way to consider the cross-associating of the fluid mixtures. [60, 61]

The molecular parameters for the pure fluids have been tabulated for several fluids (*e.g.*, Refs. [43, 45, 44, 62]) otherwise, their numerical values can be acquired by the minimization of an objective function that incorporates the model predictions and experimental data, as was described in the original SAFT-VR-Mie manuscripts. [43, 45, 44]. For computation purposes, a python code to solve the SAFT-VR-Mie model is provided elsewhere.[59]. Alternatively, the molecular parameters for the pure fluids can be obtained by applying the principle of corresponding states.[63, 64, 65] For the pure fluids involved here, the molecular parameters are already available, and their values are collected in Table 4. In all cases, $\lambda_a = 6$, [63] and $r_d^{AB}/\sigma = 0.4$. [66]

Table 4: SAFT-VR-Mie EoS parameters for pure fluids.^{a, b}

Component	m_{si}	$\sigma_{ii}/\text{\AA}$	$\varepsilon_{ii}/k_B/K$	$\lambda_{r,ii}$	$\varepsilon_{ii}^{AB}/k_B/K$	$r_{c,ii}^{AB}/\sigma$	μ_{ii}/D	$n_{p,ii}$	$[B, P, N]$
CPME ^c	2.3250	4.1360	343.91	14.155	—	—	1.27	1.919	[0, 0, 1]
Ethanol ^{c, d}	1.7728	3.5592	224.50	11.319	3018.05	0.3547	—	—	[1, 0, 1]
Propan-1-ol ^{c, d}	2.2513	3.6008	253.45	11.960	2794.88	0.3481	—	—	[1, 0, 1]
Water ^{c, d}	1.7311	2.4539	110.85	8.3080	1991.07	0.5624	—	—	[0, 2, 2]

^a m_{si} is the number of spherical segments that form the chain of component i ; σ_{ii} is the effective segment diameter for component i ; ε_{ii} is the potential well depth for component i ; $\lambda_{a,ii}$ and $\lambda_{r,ii}$ are the attraction and repulsion exponents of the intermolecular Mie potential for component i , respectively; ε_{ii}^{AB} is the site-site interaction energy for association for component i ; $r_{c,ii}^{AB}$ is the association range for component i ; $r_{d,ii}^{AB}$ is the distance between the associating site for component i ; μ_{ii} is the dipolar moment for component i ; $n_{p,ii}$ is the number of polar sites for component i ; (B) is the number of bipolar sites; (P) is the number of positive sites; (N) is the number of negative sites. ^b λ_a and r_d^{AB}/σ are fixed for all pure fluids to 6 and 0.4, respectively. The values of the others SAFT-VR-Mie parameters are taken from: ^c Chaparro [67], ^d

Cripwell et al. [62]

In this work, the SAFT-VR-Mie model is extended to mixtures employing mixing rules where the pure fluid parameters are replaced by cross parameters. In the case of Mie exponents ($\lambda_{a,ij}$ and $\lambda_{r,ij}$), size (σ_{ij}), energy (ε_{ij}), association energy (ε_{ij}^{AB}), association range ($r_{c,ij}^{AB}$), and distance between the associating site ($r_{d,ij}^{AB}$), the following mixing rules are used:

$$(\lambda_{k,ij} - 3) = \sqrt{(\lambda_{k,ii} - 3)(\lambda_{k,jj} - 3)}; k = a, r \quad (6a)$$

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \quad (6b)$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}} \frac{\sqrt{\sigma_{ii}^3 \sigma_{jj}^3}}{\sigma_{ij}^3} (1 - k_{ij}) \quad (6c)$$

$$\varepsilon_{ij}^{AB} = \sqrt{\varepsilon_{ii}^{AB} \varepsilon_{jj}^{AB}} (1 - l_{ij}) \quad (6d)$$

$$r_{c,ij}^{AB} = \frac{r_{c,ii}^{AB} + r_{c,jj}^{AB}}{2} \quad (6e)$$

$$r_{d,ij}^{AB} = \frac{r_{d,ii}^{AB} + r_{d,jj}^{AB}}{2} \quad (6f)$$

In Eqs. (6c) and (6d), k_{ij} , and l_{ij} are interaction binary parameters which can be found by fitting the phase equilibria experimental data of the binary mixture with the SAFT-VR-Mie EoS predictions. Finally, for components without self-association, $\varepsilon_{ii}^{AB} = 0$, but for those that associate with other species that form the mixture (*i.e.*, water + CPME and alcohols + CPME), the unlike association energy (ε_{ij}^{AB}) is equal to half self-associating molecule (*i.e.*, water or alcohol), and the interaction site, ($r_{c,ij}^{AB}$) will be fitted from experimental data.

Here, k_{ij} , l_{ij} , and $r_{c,ij}^{AB}$ are taken from previous works, [67] where these parameters were fitted to available experimental determinations. Specifically, the two aqueous binary mixtures (*i.e.*, ethanol + water, propan-1-ol + water) and CPME + alcohol (*i.e.*, ethanol or propan-1-ol) binary mixtures, k_{ij} , l_{ij} , and $r_{c,ij}^{AB}$ were obtained from vapor - liquid equilibria. For the case of CMPE + water, the k_{ij} , and $r_{c,ij}^{AB}$ values were obtained from liquid-liquid equilibrium. (see details in Ref.[67])

In Table 5, the numerical values of the unlike parameters of the binary mixtures involved in this work are reported. Examples of phase equilibria determinations involving the optimization of cross parameters are extensively described by Michelsen and Mollerup [68] and Gmehling et al., [69] textbooks or alternatively by Mejía et al. [59] where a Python code is freely available for download.

k_{ij} , l_{ij} , and $r_{c,ij}^{AB}$

3.2.2. Stability Analysis and Phase Equilibria Calculations for VLLE

The VLLE predictions are carried out in two steps, as described before. Firstly, the stability analysis of the phases is performed, and then the possible stable phases are used to initialize the VLLE calculation. In general terms, the stability analysis of the phases brings a route forth to explore the entire composition space of a ternary mixture at a given pressure, temperature, and global composition. This stability analysis allows assessing if the ternary mixture would remain as a bulk single-phase mixture or if it would split into two phases (*i.e.*, VLE or LLE) or three phases (VLLE). In the framework of analysis of the

Table 5: Interaction parameters for binary fluid mixtures.^a

Mixture				
i	j	k_{ij}	l_{ij}	$r_{c,ij}^{AB}$
CPME	Ethanol	0.01015	0	2.23150
CPME	Propan-1-ol	0.01053	0	2.20879
CPME	Water	-0.01606	0	2.64636
Ethanol	Water	-0.00699	-0.01518	0
Propan-1-ol	Water	0.00729	-0.01100	0

^a k_{ij} is the interaction parameter for the potential well depth; l_{ij} is the interaction parameter for the site-site interaction energy for association; $r_{c,ij}^{AB}$ is the interaction parameter for the association range. The numerical values of the interaction parameters are taken from Chaparro [67].

phase stability, the Gibbs tangent plane criterion (*tpd*) for a given P , T , and global composition ($\mathbf{z}$) is calculated from the following expression:[46]

$$tpd(\mathbf{w}) = \sum_{i=1}^c w_i \left[\ln w_i + \ln \hat{\phi}_i(\mathbf{w}) - \ln z_i - \ln \hat{\phi}_i(\mathbf{z}) \right] \quad (7)$$

In Equation 7, $\mathbf{w}$ and $\mathbf{z}$ are the trial phase and global composition molar fraction vectors, respectively. c denotes the components (here $c = 3$). $\hat{\phi}_i$ symbolizes the effective fugacity coefficient of component i in the mixture, which is computed here from the SAFT-VR-Mie EoS by using the equation:[55, 68]

$$RT \ln \hat{\phi}_i = \frac{1}{\rho} \left\{ \left(\frac{\partial a^R}{\partial x_i} \right)_{T, \rho, x_j \neq i} - \sum_{j=1}^c \left[x_j \left(\frac{\partial a^R}{\partial x_j} \right)_{T, \rho, x_j \neq i} \right] \right\} + \left(\frac{\partial a^R}{\partial \rho} \right)_T - \ln \left\{ \frac{1}{RT} \left(\left(\frac{\partial a^R}{\partial \rho} \right)_T - \frac{a^R}{\rho} \right) + 1 \right\} \quad (8)$$

By employing the stability analysis,[46] Eq. 7 provides a route to evaluate a trial phase ($\mathbf{w}$) at T and P . If there exists a $\mathbf{w}$ for which the *tpd* function is negative, then the Gibbs free energy of the system would decrease if this phase were to be present in the system. Hence, the original global mixture ($\mathbf{z}$) is unstable at those conditions of P and T .

Here, we analyze the minima value of the *tpd* function with a negative *tpd* value to detect the possible stable phases at given conditions. If all the founded minima have a positive *tpd* value, then the mixture is said to be stable. If only two minima are found, the mixture is likely to split into VLE if one of the minima is a liquid-like trial phase and the other is a vapor-like trial phase. Similarly, the system is likely to split into LLE if both minima are liquid-like trial phases. Finally, if one finds two liquid-like trial phases and a vapor-like trial phase, the system might split into VLLE.

233 Once plausible regions where VLLE is bracketed, the three-phase equilibrium is computed using a
 234 modified multiphase flash algorithm that computes phase equilibria and tests the stability simultaneously.
 235 Mathematically, the modified Rashford-Rice multiphase flash objective function provides a solution to the
 236 numerical problem:[47]

$$\sum_{i=1}^c \frac{z_i (K_{ik} \exp(\theta_i) - 1)}{1 + \sum_{j=1, j \neq r}^{\pi} \beta_j (K_{ij} \exp(\theta_j) - 1)} = 0 \quad ; \quad k = 1, \dots, \pi, k \neq r \quad ; \quad \text{subject to: } \beta_k \theta_k = 0 \quad (9)$$

237 In Eqs. 9, z_i denotes the global mole fraction of species i , $K_{ij} = x_{ij}/x_{ir} = \hat{\phi}_{ir}/\hat{\phi}_{ij}$ is the equilibrium
 238 constant for component i in the bulk phase j with respect to the reference bulk phase r . θ_j , and β_j
 239 represent the stability variable, and the bulk phase fraction of the phase j , respectively. The stability
 240 variables are zero for stable phases and positive for unstable phases.

241 Finally, the capability to predict ternary mixtures at VLLE from their binary contributions will be
 242 evaluated by computing the statistics deviation of VLLE only using binary interaction parameters. The
 243 global absolute average deviation will be calculated by using the expression:

$$GAAD\% = \frac{100}{3N} \sum_{j=1}^N \left[\sum_{i=1}^2 \left[\left(x_{i,j}^{o,cal} - x_{i,j}^{o,exp} \right)^2 + \left(x_{i,j}^{w,cal} - x_{i,j}^{w,exp} \right)^2 + \left(y_{i,j}^{cal} - y_{i,j}^{exp} \right)^2 \right] \right] \quad (10)$$

244 Particular details of calculations and illustrations of VLLE including stability analysis are described
 245 in Ref. [59] where Python notebooks are freely available for download.

246 4. Results

247 The experimental measurements of the three-phase equilibria (VLLE) at the isobaric condition of
 248 101.3 kPa for two aqueous ternary mixtures formed with CPME, and an alcohol (ethanol or propan-1-ol)
 249 are collected in Tables 6 and 7, respectively.

250 The reliability of the experimental VLLE summarized in Tables 6, and 7 is assessed using the L/W
 251 thermodynamic consistency test. Figure 1 displays the thermodynamic consistency test results for the
 252 explored ternary mixtures. It is found that the VLLE data meet the consistency criteria and they do
 253 not exhibit substantial deviations along the experimental range. Analysis of Figure 1 suggests the L/W
 254 interval cover the range 0.95 to 0.98 for water + CPME + ethanol ternary mixture, whereas the 0.97 to
 255 0.98 is the interval range for the water + CPME + propan-1-ol ternary mixture. Thus, the experimental
 256 determinations of the VLLE fulfill the consistency criterion.

257 The reported VLLE data for the ternary mixtures (*cf.* Table 6, and Table 7) have been modeled
 258 applying the SAFT-VR-Mie EoS. As described in the Sec. 3.2, the SAFT-VR-Mie EoS allows predicting
 259 the VLLE using only the constitutive sub-binary mixture information. For the water + CPME + ethanol

Table 6: Vapor-liquid-liquid equilibria experimental determinations for the water (1) + CPME (2) + ethanol (3) ternary mixture at 101.3 kPa.^{a, b}

T/K	Organic Phase		Aqueous Phase		Vapor Phase	
	x_1^o	x_2^o	x_1^w	x_2^w	y_1	y_2
350.37	0.3033	0.4350	0.8832	0.0082	0.3633	0.3227
350.45	0.2708	0.4897	0.8631	0.0340	0.3732	0.3266
350.85	0.1810	0.6431	0.9219	0.0080	0.3788	0.3423
351.74	0.1320	0.7461	0.9439	0.0056	0.3984	0.3661
352.31	0.1065	0.8019	0.9449	0.0159	0.4044	0.4009
352.65	0.1528	0.7707	0.8850	0.0834	0.4083	0.3994
353.07	0.1296	0.8064	0.8842	0.0848	0.4481	0.3828
354.95	0.0620	0.9211	0.9797	0.0110	0.4635	0.4893
356.05	0.0525	0.9475	0.9738	0.0262	0.5451	0.4549

^a T symbolizes the equilibrium temperature; x_i denotes the equilibrium liquid mole fraction of specie i , and y_i represents the equilibrium vapor mole fraction of specie i . ^b The standard uncertainties for pressure, temperature and mole fractions are

$$u(P) = 0.1 \text{ kPa}, u(T) = 0.06 \text{ K}, \text{ and } u(x_1) = u(y_1) = 0.001.$$

mixture, the EoS model considers three binary mixtures: water + ethanol and CPME + ethanol at VLE and water + CPME at LLE. For the water + CPME + propan-1-ol mixture, the corresponding binaries are water + propan-1-ol and CPME + propan-1-ol at VLE and water + CPME at LLE. Therefore, the VLLE calculations from the SAFT-VR-Mie EoS are predictions for both ternary systems.

As described in Sec.3.2.2, reliable VLLE predictions need to be accompanied by a stability phase analysis of the entire composition space at a given pressure and temperature conditions. The stability test and phase equilibrium calculation are carried out as follows: *a.* A liquid-like global composition is tested against vapor-like trial phases to check for possible VLE; *b.* A vapor-like global composition is tested against liquid-like trial phases to check for possible VLE; *c.* A liquid-like global composition is tested against liquid-like trial phases to check for possible LLE. The *tpd* minima are obtained, possible duplicated minima are disregarded, and the *tpd* values are sorted. From the stability test one can establish if the mixture at the given global composition will remain as a bulk phase (no negative *tpd* values) or if it is likely to split into VLE (one vapor and one liquid compositions with negative *tpd* values), LLE (two liquid compositions with negative *tpd* values) or VLLE (one vapor and two liquid compositions with negative *tpd* values). Then, it is necessary to perform the actual phase equilibria calculation to check which phases will be present. This is done by solving the modified multi-phase flash, Eq. 9, that checks for equilibrium and stability simultaneously. The phase equilibrium calculation is initialized using the

Table 7: Vapor-liquid-liquid equilibria experimental determinations for the water (1) + CPME (2) + propan-1-ol (3) ternary mixture at 101.3 kPa.^a

T/K	Organic Phase		Aqueous Phase		Vapor Phase	
	x_1^o	x_2^o	x_1^w	x_2^w	y_1	y_2
354.80	0.1420	0.6674	0.9586	0.0202	0.4998	0.3739
354.82	0.2206	0.5244	0.9783	0.0002	0.4972	0.3488
354.90	0.2750	0.4292	0.9747	0.0001	0.5004	0.3335
354.92	0.1302	0.7583	0.9887	0.0002	0.5113	0.3982
354.99	0.3076	0.3763	0.9557	0.0094	0.4889	0.3216
355.08	0.0881	0.8195	0.9908	0.0001	0.4874	0.4278
355.22	0.0797	0.8522	0.9927	0.0001	0.5380	0.4033
355.31	0.4064	0.2498	0.9643	0.0007	0.5183	0.2776
355.52	0.4835	0.1707	0.9564	0.0016	0.5296	0.2642
355.88	0.0926	0.9074	0.9838	0.0162	0.5204	0.4796
356.19	0.6210	0.0844	0.9311	0.0005	0.5819	0.2019

^a see footnote of Table 6

minima from the *tpd* test as initial guesses.

To illustrate the stability analysis and phase equilibria calculation, we selected the mixture formed by water (1) + CPME (2) + ethanol (3) at 349.5 K and 101.3 kPa, and the following global trial compositions, $z = [0.5, 0.4, 0.1]$ and $z = [0.4, 0.3, 0.3]$. The stability test results are displayed in Figure 2. The color map of this figure refers to the *tpd* results where there is a likelihood of having a bulk phase (ocean blue), VLE (dark turquoise), LLE (turquoise) or VLLE (lime green). In this figure, the trial global compositions are denoted by a red circle. Additionally, the true VLLE compositions at the given temperature and pressure are represented by the black squares, while the dashed lines represent the respective tie lines. Only if a global composition lies inside the triangle enclosed by the tie lines then the mixture would split into VLLE. In Figure 2a, the global composition $z = [0.5, 0.4, 0.1]$ lies in the region where the *tpd* test suggested VLLE; however, this point converges to a LLE, with a vapor phase fraction equal to zero, and its stability variable is positive. This global composition lies outside the region enclosed by the tie lines. On the other hand, in Figure 2b, the multiphase flash for the global compositions $z = [0.4, 0.3, 0.3]$ detects two stable liquids and one stable vapor, *i.e.*, all the phase fractions are greater than zero and the stability variable results are equal to zero; in this latter case the system is in VLLE. This global composition lies inside the region enclosed by the tie lines. In the supporting information section, a python notebook is available to reproduce this phase stability exploration.

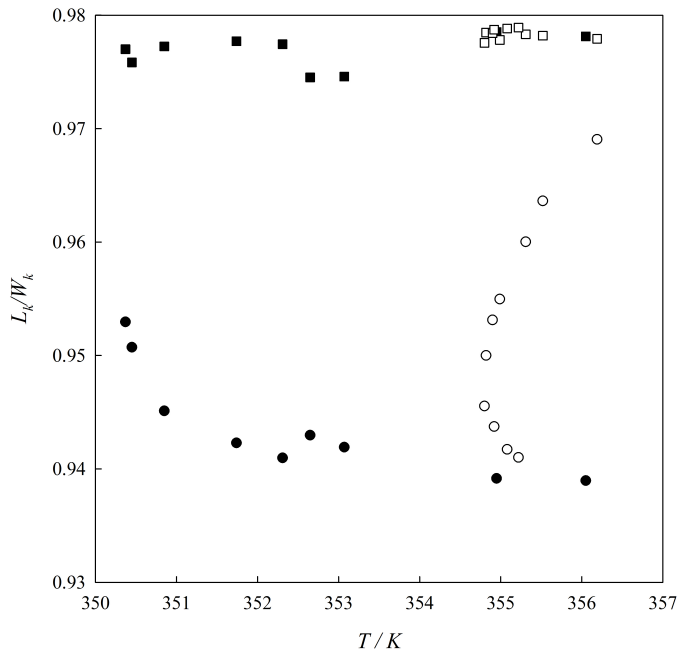


Figure 1: The L/W thermodynamic consistency test. (L_k/W_k) vs. experimental temperature, T . water + CPME + ethanol mixture: $\bullet$: L^oV (organic liquid phase and vapor), $\blacksquare$: L^wV (aqueous liquid phase and vapor). water + CPME + propan-1-ol mixture: $\circ$: L^oV (organic liquid phase and vapor), $\square$: L^wV (aqueous liquid phase and vapor)

Considering the stability test results and using the modified multiphase flash (Eq. 9), the isobaric VLLE for the explored ternary mixtures are fully predicted. Figure 3 shows the nonisothermal binodal curve ($x^w - x^o$) and y projection, and Figure 4 displays the VLLE diagrams in $T - x^w - x^o - y$ projection for the explored ternary aqueous mixtures at 101.3 kPa. Figures 4 include the measured data points, the experimental tie lines, and the corresponding SAFT-VR-Mie EoS predictions. In the supporting information section, a python notebook is available to reproduce the VLLE predictions for the case of water (1) + CPME (2) + ethanol (3) ternary mixture.

In order to compare experimental determinations with the corresponding theoretical predictions, Table 8 summarizes the absolute average deviation (AAD) in mole fractions in detail. The predictions of VLLE display relatively low AADs in mole fractions, showing the appropriateness of the selected molecular based equation of state to model these systems. Additionally, Table 9 reports the calculated global absolute average deviation (GAAD) (see Eq. 10), where it is feasible to state that the SAFT-VR-Mie EoS calculations based only on binary contributions (binary interaction parameters) can accurately predict the VLLE for water + CPME + ethanol or propan-1-ol mixtures in the whole experimental range.

From the latter results, ones can state that the SAFT-VR-Mie model predicts the main phase equilibrium characteristic within an acceptable deviation. These results are very useful for increasing the precision of designing and modeling suitable column sequences to remove water from alcohols through

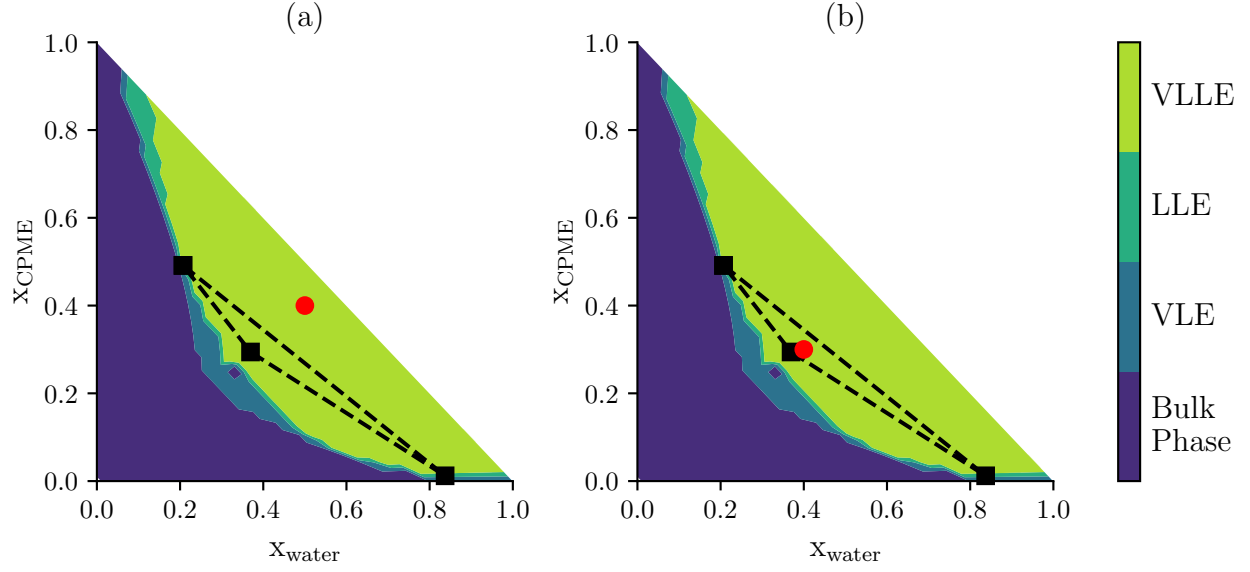


Figure 2: Illustration of the phase stability test results for the ternary mixture formed by water, CPME, and ethanol at 101.3 kPa and 349.5 K. ● Global trial composition: (a) $z = [0.5, 0.4, 0.1]$; (b) $z = [0.4, 0.3, 0.3]$, ■ — ■ true phase composition. The color map refers to the possible types of phase equilibrium obtained from the *tpd* test.

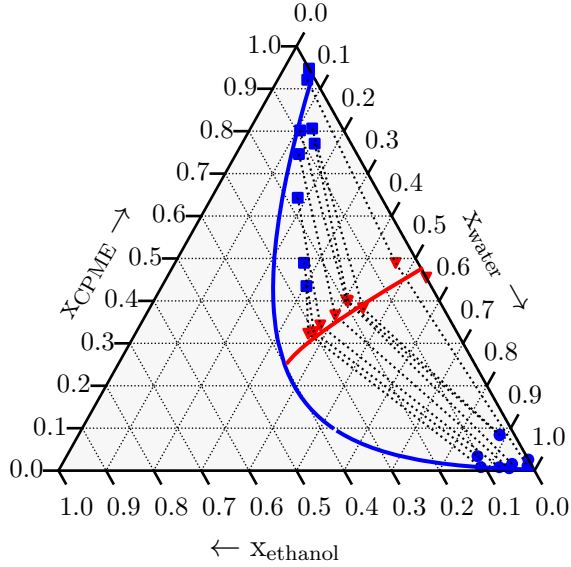
Table 8: Absolute Average Deviation (AAD) for the VLLE predictions for the two ternary systems formed by water, CPME, and an alcohol at 101.3 kPa. ^a

Alcohol	$\% \Delta x_i^o$	$\% \Delta x_j^o$	$\% \Delta x_k^o$	$\% \Delta x_i^w$	$\% \Delta x_j^w$	$\% \Delta x_k^w$	$\% \Delta y_i$	$\% \Delta y_j$	$\% \Delta y_k$
Ethanol	0.595	1.124	0.090	0.172	0.162	0.007	0.075	0.032	0.066
Propan-1-ol	0.504	0.596	0.767	0.023	0.005	0.014	0.083	0.098	0.204

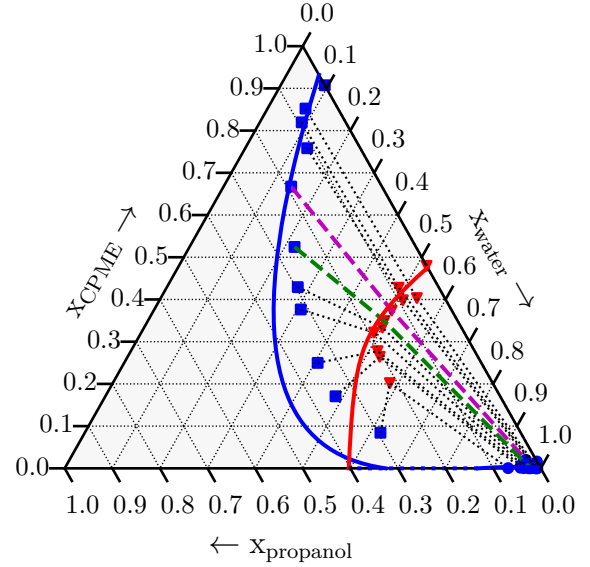
^a $\% \Delta \vartheta^\delta = (100/N) \sum_{i=1}^N |\vartheta_i^{exp} - \vartheta_i^{cal}|$ with $\vartheta^\delta = x^o$ (organic phase); x^w (aqueous phase) and y (vapor phase).

heterogeneous distillation using a process systems simulator. For example, gProms [70] with the g-SAFT module [71] can directly use the values of molecular parameters of the pure fluids and binary parameters to design and simulate this unit operation.

With the aim of evaluating the feasibility of the CPME begin used as an entrainer for ethanol and propan-1-ol, it is mandatory to explore the VLLE behavior in depth. In the first VLLE case (water + CPME + ethanol), experimental measurements (see Table 6, and Figures 3a and 4a) report no ternary heterogeneous azeotropy within the experimental range. In fact, the experimental tie line shows that the vapor corresponding to the LLE is always above the single line that connects both liquid phases. However, the theoretical predictions provide a robust route to extrapolate the experimental range. It is possible to observe that this mixture can form a ternary heterogeneous azeotrope near the LLE'S upper critical solution temperature (UCST). Table 10 summarizes the corresponding theoretical heteroazeotropic coordinates. Unfortunately, this behavior is difficult to verify from experimental determination due to



(a) water (1) + CPME (2) + ethanol (3)



(b) water (1) + CPME (2) + propan-1-ol (3)

Figure 3: Nonisothermal VLLE in $x^w - x^o - y$ projection at 101.3 kPa for the ternary mixtures. Measured points: $\blacktriangledown$: vapor; $\blacksquare$: liquid 1; $\bullet$: liquid 2. $\cdots$: experimental tie lines. $-$: SAFT-VR-Mie EoS predictions.

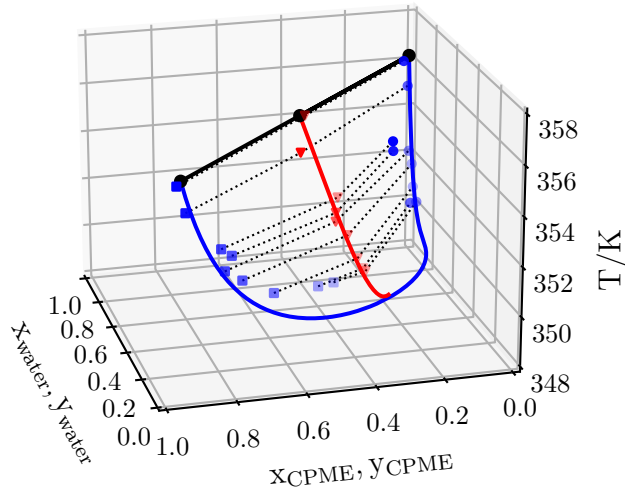
Table 9: Global Absolute Average Deviation (GAAD) obtained from SAFT-VR-Mie EoS for water (1) + CPME (2) + alcohol (3) mixtures.^a

Alcohol (3)	$\% \Delta x^o$	$\% \Delta x^w$	$\% \Delta y$	$\% GAAD$
Ethanol	0.603	0.144	0.058	0.774
Propan-1-ol	0.623	0.014	0.128	0.765

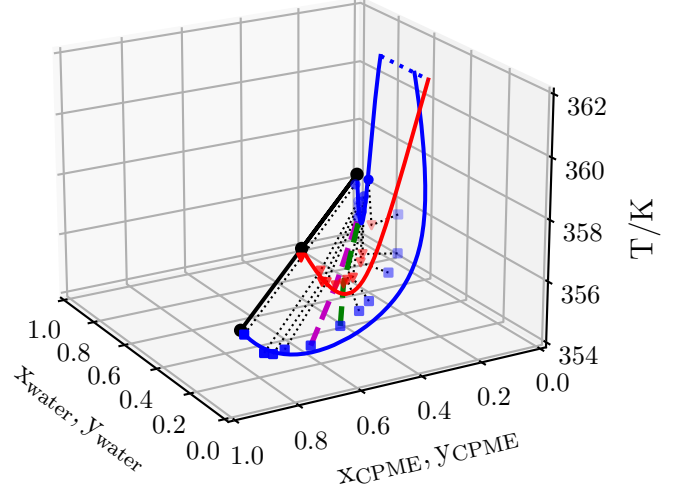
^a $\% \Delta \vartheta^\delta = \frac{100}{3N} \sum_{j=1}^N \sum_{i=1}^3 [\vartheta_{i,j}^{exp} - \vartheta_{i,j}^{cal}]^2$ with the terms defined in Table 8. GAAD is given by Eq. 10.

the proximity of the UCST. For the second VLLE case (water + CPME + propan-1-ol), the experimental determinations (see Table 7, and Figures 3b and 4b) suggest that points of the vapor are above the corresponding LLE at low propan-1-ol mole fraction until the ternary mixture reaches a condition where these points are approximately connected by a straight line (see the pink line in Figure 3b). By increasing the propan-1-ol mole fraction; it is possible to observe that the vapor is below the LLE, as illustrated by the green line displays in Figure 3b. The tie line transition denotes the existence of a ternary heterogenous azeotrope, whose coordinates are located between the pink and green tie lines. The latter behavior is also confirmed by the SAFT-VR-Mie EoS predictions. Table 10 summarizes both experimental and theoretical coordinates for the ternary heterozeotropic state.

Comparing the phase equilibria obtained from both ternary mixtures, one can propose the CPME as an appropriate entrainer for propan-1-ol, and suggest its use to design and model advanced distillation protocols. On the other hand, CPME may be used as an entrainer for ethanol, but its use is restricted to



(a) water (1) + CPME (2) + ethanol (3)



(b) water (1) + CPME (2) + propan-1-ol (3)

Figure 4: VLLE in $T - x^w - x^o - y$ projection at 101.3 kPa for the ternary mixtures. Measured points: $\blacktriangledown$: vapor; $\blacksquare$: liquid 1; $\bullet$: liquid 2. $\cdots$: experimental tie lines. $-$: SAFT-VR-Mie EoS predictions.

Table 10: Ternary heterozeotropic coordinates at 101.3 kPa for two ternary mixtures formed by water, CPME, and an alcohol.^a

Alcohol	Method	T/K	x_1^o	x_2^o	x_1^w	x_2^w	y_1	y_2
Ethanol	SAFT-VR-Mie	349.277	0.310	0.303	0.742	0.026	0.358	0.26
Propan-1-ol	Experimental	354.692	0.159	0.610	0.977	0.006	0.486	0.375
	SAFT-VR-Mie	354.515	0.167	0.577	0.970	0.003	0.483	0.347

^a T is the heterozeotropic temperature; x_i are the heterozeotropic liquid mole fractions of specie i ; y_i are the heterozeotropic vapor mole fractions of specie i . The superscripts o and w represent the organic and aqueous phases, respectively.

extremal conditions.

5. Conclusion

This contribution reports thermodynamically consistent measurements and accurate modeling of the three-phase equilibria (VLLE) for two ternary mixtures formed by water, CPME, and an alcohol (*i.e.*, ethanol or propan-1-ol) at atmospheric pressure. Both mixtures are accurately estimated using the SAFT-VR-Mie EoS using only pure fluids and binary sub-systems information. These results provide a secure route to interpolate experimental information to other conditions as well as to use their input parameters in an equilibrium-model-based simulation program (*i.e.*, gProms with gSAFT) to calculate residual curves, and to design a heterogeneous distillation operation unit.

344 According to the experimental evidence and theoretical modeling, the ternary mixture formed by
345 water, CPME, and propan-1-ol shows ternary heterogeneous azeotropy. In contrast, the ternary hetero-
346 geneous azeotrope for the water + CPME + ethanol mixture is only observed theoretically, we conclude
347 that CPME is a suitable candidate as an entrainer for the dehydration of biopropan-1ol.

348 **Supporting Information Available**

349 The corresponding python notebooks for the phase stability exploration and VLLE calculations for
350 the ternary mixture formed by water, CPME, and ethanol are available at
351 <https://github.com/gustavoehm/VLLE-Water-CPME-Alcohol>

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356 **CRedit authorship contribution statement**

357 **Andrés Mejía:** Conceptualization (lead), Investigation (lead), Writing – original draft (lead), Method-
358 ology (equal), Formal analysis (lead), Validation (equal), Funding acquisition (lead). **Marcela Cartes:**
359 Conceptualization (lead), Formal analysis (equal), Investigation (equal), Data curation (lead), Methodol-
360 ogy (equal), Validation (equal), Funding acquisition (lead), Writing – review & editing (equal). **Gustavo**
361 **Chaparro:** Data curation (equal), Investigation (Equal), Methodology (equal), Formal analysis (equal),
362 Validation (equal), Software (lead), Writing – review & editing (equal). **Erich A. Müller:** Formal
363 analysis (equal), Investigation (equal), Validation (equal), Writing – review & editing (equal).

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