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Research Article

Keywords: Vapor–liquid equilibria, Alcohol-based fuels, Cubic-Plus-Association equation of state, Binary mixtures, Thermodynamic modeling

Posted Date: September 3rd, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-10706044/v1>

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Additional Declarations: No competing interests reported.

Hydrogen Bonding Governs Vapor–Liquid Equilibria in Alcohol-Based Fuels: A Thermodynamic Equation-of-State Approach

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Abstract

Accurate description of vapor–liquid equilibria in alcohol-based fuels requires a thermodynamic framework that accounts for hydrogen bonding and the effects of molecular structure on association behavior. In this work, a unified Cubic-Plus-Association equation-of-state framework is developed for the vapor–liquid equilibria of isobutanol, 1-butanol, and 2-ethyl-1-hexanol mixtures. A two-site association scheme is applied to all three primary alcohols, while the steric hindrance in 2-ethyl-1-hexanol is represented through adjusted association parameters, yielding a lower association energy than those of 1-butanol and isobutanol. Pure-component parameters regressed from saturated vapor pressure and liquid density data give average absolute deviations of 0.2%–1.9% and 0.1%–1.0%, respectively. Cross-association is described using the Wolbach–Sandler combining rule without additional adjustable parameters. A single temperature-independent binary interaction parameter is sufficient for the isobutanol + 1-butanol and isobutanol + 2-ethyl-1-hexanol systems, whereas the 1-butanol + 2-ethyl-1-hexanol system requires a temperature-dependent parameter, ($k_{ij} = 0.00012 - 6.6/T$), with (T) in K. The model reproduces the experimental vapor–liquid equilibria with average absolute deviations in liquid mole fraction of 2.8%, 1.9%, and 2.3%, respectively. These results demonstrate that hydrogen bonding and molecular-structure effects can be captured within a unified thermodynamic framework using a limited number of physically interpretable parameters, providing a practical basis for the thermodynamic design of separation processes involving alcohol-based fuels.

Key words: Vapor–liquid equilibria; Alcohol-based fuels; Cubic-Plus-Association equation of state; Binary mixtures; Thermodynamic modeling

1. Introduction

Isobutanol and 1-butanol have attracted considerable attention in recent years as fuel additives and as potential alternatives to fossil fuels [1]. Compared with ethanol, isobutanol offers higher energy density, lower oxygen content, and reduced hygroscopicity, making it an attractive gasoline blending component. Beyond fuel applications, both alcohols serve as organic solvents, extracting agents, and reactants in the production of butylated amino resins, butyl acrylate, and high-grade epoxy resins.

2-Ethyl-1-hexanol is an essential chemical intermediate widely used in the manufacture of ester plasticizers, particularly dioctyl phthalate (DOP) and di(2-ethylhexyl) phthalate (DEHP), which are employed in producing flexible polyvinyl chloride. It also finds applications in coatings, adhesives, lubricants, and as a solvent for resins, disinfectants, and detergents [2].

The coexistence of these alcohols in industrial streams is not uncommon. In the recovery of 2-ethyl-1-hexanol from a DOP production plant, the recovered mixture contains isobutanol and 1-butanol as "light products" in a typical proportion of 3 mass%. These light components, if not adequately separated, are responsible for increasing the color index of the synthesized DOP when the recovered 2-ethyl-1-hexanol is returned to manufacturing. The separation of these alcohols by distillation requires reliable vapor-liquid equilibrium (VLE) data over wide temperature and pressure ranges, yet such data are notably scarce in the open literature.

Despite their industrial significance, VLE data for the binary systems involving these three alcohols remain limited and incomplete. For the isobutanol + 1-butanol system, the earliest measurements date back to Kay and Donham [3], who reported data in the pressure range of 2757.9-4136.9 kPa and temperature range of 518.92-558.58 K. Tamir and Wisniak [4] later provided data at atmospheric pressure between 381.52 and 388.72 K. These sources are several decades old and do not report uncertainty values. For the 1-butanol + 2-ethyl-1-hexanol system, Ghanadzadeh et al. [5] measured isobaric VLE data at atmospheric pressure in the temperature range of 392-458.15 K; subsequent studies employed artificial neural networks to estimate VLE data for this binary [6, 7]. The common shortcomings of these literature data are evident: narrow temperature and pressure ranges, sparse data points, and in several cases, complete absence of uncertainty estimates.

Fendu and Pricop-Nicolae recently reported experimental p - T - x VLE data for these three binary systems using a static equilibrium apparatus [8], covering temperature ranges of 305.15-388.15 K for isobutanol + 1-butanol, 305.15-455.15 K for isobutanol + 2-ethyl-1-hexanol, and 320.15-455.15 K for 1-butanol + 2-ethyl-1-hexanol, with pressures up to 99.779 kPa. These data were regressed using the NRTL model, but the binary interaction parameters obtained are specific to the activity-coefficient model and thus are not transferable to equation-of-state frameworks.

The Cubic-Plus-Association (CPA) Equation of State [9] combines the Soave-Redlich-Kwong cubic equation with Wertheim's association theory, providing a robust engineering tool for the accurate prediction of phase equilibria and density of hydrogen-bonding fluids. Unlike activity-coefficient models, CPA retains a physical basis for molecular interactions through its association term, and it has been successfully applied to a wide range of alcohol-containing systems. However, CPA has not yet been applied to the specific binary combinations of isobutanol, 1-butanol, and 2-ethyl-1-hexanol. Given that experimental VLE data are now available for these systems, a systematic CPA modeling effort is both timely and necessary.

The objective of this study is to apply the CPA Equation of State to model the VLE behavior of the three binary systems: isobutanol + 1-butanol, isobutanol + 2-ethyl-1-hexanol, and 1-butanol + 2-ethyl-1-hexanol. Pure-component parameters for the three alcohols are regressed from saturated vapor pressure and liquid density data. Binary VLE data reported by Fendu and Pricop-Nicolae are then used to determine the binary interaction parameters for each system. The modeling results are compared with the experimental data, and the performance of CPA is assessed against the NRTL model results from the same experimental dataset, as well as against predictions from the UNIFAC and IDEAL models. The final set of pure-component and binary parameters is intended for use in process simulation for the design and optimization of distillation operations involving these alcohol mixtures.

2. Thermodynamic Framework

2.1. The CPA Equation of State

The CPA Equation of State [9] couples Wertheim's association theory with the SRK cubic Equation of State [10], serving as a robust engineering tool for the accurate prediction of thermodynamic properties-including phase equilibria and density-of fluids that exhibit hydrogen bonding, such as alcohols and water.

In CPA, the residual Helmholtz energy is given by:

$$A^r = A^{SRK} + A^{ASSOC} \quad (1)$$

The residual Helmholtz energy for the cubic Soave-Redlich-Kwong EOS [10] is calculated from:

$$A^{SRK} = nRT \left[-\ln \left(1 - \frac{b}{v} \right) - \frac{a(T)}{bRT} \ln \left(1 + \frac{b}{v} \right) \right] \quad (2)$$

where n is the total number of moles, T is the temperature, R is the gas constant, v is the molar volume, and b and $a(T)$ are the co-volume parameter and the temperature dependent energy parameter of the mixture, respectively.

$$b = \sum_i x_i b_i \quad (3)$$

where b_i is the pure co-volume parameter and x_i is the mole fraction of component i .

For the binary system, the classical one-fluid mixing rule is used for $a(T)$ [11].

$$a(T) = \sum_i \sum_j x_i x_j \sqrt{a_i(T) a_j(T)} (1 - k_{ij}) \quad (4)$$

The temperature dependent component specific parameter $a_i(T)$ is given by:

$$a_i = a_{0i} \left(1 + c_{1i} (1 - \sqrt{T_{ri}}) \right)^2 \quad (5)$$

where T_{ri} is the reduced temperature of component i , defined as $T_{ri} = T/T_{ci}$, T_{ci} is the critical temperature of component i .

The residual Helmholtz energy for association A^{ASSOC} is based on the formulation of Wertheim's association theory [12, 13] and can be found from the solution of the constrained optimization problem [14] given by:

$$A^{assoc} = RT \left[\sum_i n_i \sum_{A_i} \left(\ln X_{A_i} - \frac{1}{2} X_{A_i} + \frac{1}{2} \right) \right] \quad (6)$$

$$\frac{1}{X_{A_i}} = 1 + \sum_j \rho_j \sum_{B_i} X_{B_j} \Delta_{A_i B_j} \quad (7)$$

where n_i is the number of moles of component i , X_{A_i} is the fraction of site A on component i that is not bonded to any other site, ρ_j is the density of component j , and

$\Delta_{A_i B_j}$ is the association strength, which is calculated from:

$$\Delta_{A_i B_j} = g(\rho) \left[\exp \left(\frac{\varepsilon^{A_i B_j}}{k_B T} \right) - 1 \right] b_{ij} \beta^{A_i B_j} \quad (8)$$

where the two association parameters are the association volume, $\beta^{A_i B_j}$, and the association energy, $\varepsilon^{A_i B_j}$, while b_{ij} is given by $b_{ij} = (b_i + b_j)/2$. The simplified radial distribution function is expressed as: $g(\rho) = (1 - 1.9\eta)^{-1}$, and the packing fraction η is equal to $b/4v$.

2.2. Parameter Regression and Error Definition

The pure-component parameters for each alcohol - b_i , c_{1i} (or equivalently a_{0i}), $\varepsilon^{A_i B_i} / k_B$, and $\beta^{A_i B_i}$ - are obtained by minimizing the sum of squared relative deviations between calculated and experimental saturated vapor pressure (P_{sat}) and saturated liquid density (ρ_{sat}^L). The objective function for pure-component regression is defined as:

$$S_{pure} = \sum_{k=1}^{N_P} \left(\frac{P_{sat,k}^{calc} - P_{sat,k}^{expt}}{P_{sat,k}^{expt}} \right)^2 + \sum_{k=1}^{N_\rho} \left(\frac{\rho_{sat,k}^{calc} - \rho_{sat,k}^{expt}}{\rho_{sat,k}^{expt}} \right)^2 \quad (9)$$

where N_P and N_ρ are the numbers of experimental data points for vapor pressure and liquid density, respectively. The experimental data for saturated vapor pressure and liquid density are taken from literatures.

The quality of the pure-component parameter regression is evaluated using the average absolute deviation (AAD) defined as:

$$AAD(P_{sat}) = \frac{100}{N_P} \sum_{k=1}^{N_P} \left| \frac{P_{sat,k}^{calc} - P_{sat,k}^{expt}}{P_{sat,k}^{expt}} \right| \quad (10)$$

$$AAD(\rho_{sat}^L) = \frac{100}{N_\rho} \sum_{k=1}^{N_\rho} \left| \frac{\rho_{sat,k}^{calc} - \rho_{sat,k}^{expt}}{\rho_{sat,k}^{expt}} \right| \quad (11)$$

For binary mixtures, the binary interaction parameter k_{ij} in Eq. (4) is determined by fitting the experimental $p - T - x$ VLE data. The regression minimizes the sum of squared relative deviations between calculated and experimental pressures:

$$S_{binary} = \sum_{m=1}^N \left(1 - \frac{P_m^{calc}}{P_m^{expt}} \right)^2 \quad (12)$$

where N is the number of experimental VLE data points for the given binary system, P_m^{calc} is the bubble-point pressure calculated from the CPA equation at the experimental temperature T_m and liquid composition $x_{1,m}$, and P_m^{expt} is the experimental pressure. Convergence is achieved when the objective function value falls below a tolerance of $1e - 6$.

For systems where a single temperature-independent k_{ij} is insufficient to describe the VLE data across the entire temperature range, a temperature-dependent form is employed:

$$k_{ij}(T) = k_{ij}^{(0)} + k_{ij}^{(1)}T + \frac{k_{ij}^{(2)}}{T} \quad (13)$$

where $k_{ij}^{(0)}$, $k_{ij}^{(1)}$ and $k_{ij}^{(2)}$ are adjustable coefficients.

The quality of the binary VLE correlation is evaluated using the average absolute deviation in the liquid-phase mole fraction of the most volatile component:

$$AAD(x_1) = \frac{100}{N} \sum_{m=1}^N |x_{1,m}^{calc} - x_{1,m}^{expt}| \quad (14)$$

3. Pure-Component Parameters and Association Scheme

3.1. Critical Properties

The critical properties and acentric factors for isobutanol, 1-butanol, and 2-ethyl-1-hexanol are listed in Table 1. These values are required as input to the SRK part of the CPA equation.

Table 1. Pure Component Critical Properties and Acentric Factors [15].

Component	CAS	T_c [K]	P_c [kPa]	ω	M [kg/mol]
Isobutanol	78-83-1	549.792	4395.01	0.579201	74.12
1-Butanol	71-36-3	564.86	4506.18	0.585728	74.12
2-Ethyl-1-hexanol	104-76-7	645.622	3303.35	0.578977	130.23

The molecular structures of the three alcohols and the selection of an appropriate association scheme are discussed in the following section.

3.2. Selection and Justification of the 2B Association Scheme

All three alcohols studied in this work - isobutanol, 1-butanol, and 2-ethyl-1-hexanol - are primary alcohols containing a single terminal hydroxyl group. Each molecule thus provides one proton donor site (the hydroxyl hydrogen) and one proton acceptor site (the lone electron pairs on the hydroxyl oxygen). Within the framework of statistical associating fluid theory, this donor-acceptor stoichiometry directly corresponds to the 2B association scheme, in which each molecule carries one donor site and one acceptor site.

The use of the 2B scheme for 1-butanol is standard practice in CPA and PC-SAFT modeling, and it has been shown to accurately correlate saturated vapor pressure, liquid density, and enthalpy of vaporization simultaneously. For isobutanol, the methyl branches are located at the β -carbon, remote from the hydroxyl group, and their influence on hydrogen-bonding accessibility is negligible. The 2B scheme is

therefore equally appropriate for isobutanol, as has been widely adopted in thermodynamic modeling of butanol isomers [16].

2-Ethyl-1-hexanol requires closer examination. The hydroxyl group is attached to a primary carbon, but the β -carbon bears both an ethyl and a n-butyl substituent, resulting in significantly greater steric hindrance in the vicinity of the hydroxyl group than in either butanol isomer. It must be emphasized, however, that steric hindrance only weakens the average hydrogen-bonding strength; it does not alter the donor-acceptor stoichiometry of the hydroxyl group. The molecule still provides one hydroxyl hydrogen as a donor, and the lone pairs on the hydroxyl oxygen can only accept one proton donor chemically; they cannot simultaneously participate in two independent hydrogen bonds. A 3B scheme - one donor and two independent acceptors - would imply that the two lone pairs on oxygen can form two hydrogen bonds concurrently, which is inconsistent with the electronic structure of primary alcohols and with spectroscopic evidence. A 1A scheme, on the other hand, would permit only dimer formation and would fail to produce chain-like multimers, contradicting the actual association cluster distribution in primary alcohol liquids. The 2B scheme is therefore retained for 2-ethyl-1-hexanol. The reduction in hydrogen-bonding strength due to steric hindrance is fully absorbed by adjusting the association energy parameter (ε^{AiBi}/k_B) and the association volume parameter (β^{AiBi}) during pure-component regression.

This treatment is consistent with the modeling practice documented in the literature for 2-ethyl-1-hexanol and its mixtures using PC-SAFT and CPA, where the 2B scheme has been shown to reproduce pure-component properties and binary phase equilibria accurately over wide temperature and pressure ranges.

With the association scheme established, the pure-component parameters were regressed and the resulting properties are presented in the following section.

3.3. Pure-Component Property Prediction

The CPA pure-component parameters for each alcohol - b_0 , c_1 (or equivalently Γ), ε^{AiBi}/k_B , and β^{AiBi} - were obtained by fitting saturated vapor pressure and saturated liquid density data from the literatures [3, 8, 17-25], following the regression procedure described in Section 2.3.1.

Table 2 summarizes the resulting parameters, Table 3 summarizes the resulting performances,

Table 2. Pure-Component Parameters for.

Isobutanol	b_0 [L/mol]	T [K]	c_1 [-]	$1000 \times \beta^{A_i B_j}$	$\epsilon^{A_i B_j}$
Isobutanol	81.01	2378.79	1.32	50.07	1360.52
1-Butanol	81.29	2417.11	1.43	50.21	1288.46
2-Ethyl-1-hexanol	143.38	2804.85	1.42	51.01	1262.31

Association scheme: 2B

Table 3. Modeling Performance for pure component

Isobutanol	T	AAD	P_{sat}	T	AAD ρ_{sat}^L
Isobutanol [3, 8, 17-19]	305.15-539.35	1.9%	326.5-547.65	1.0%	
1-Butanol [8, 20-24]	320.15-390.53	0.2%	278.15-343.15	0.1%	
2-Ethyl-1-hexanol [8, 24, 25]	370.15-457.44	1.0%	278.15-363.15	0.6%	

The parameter values in Table 2 provide quantitative support for the interpretation discussed in Section 3.2: the association energy for 2-ethyl-1-hexanol ($\epsilon/k_B =$

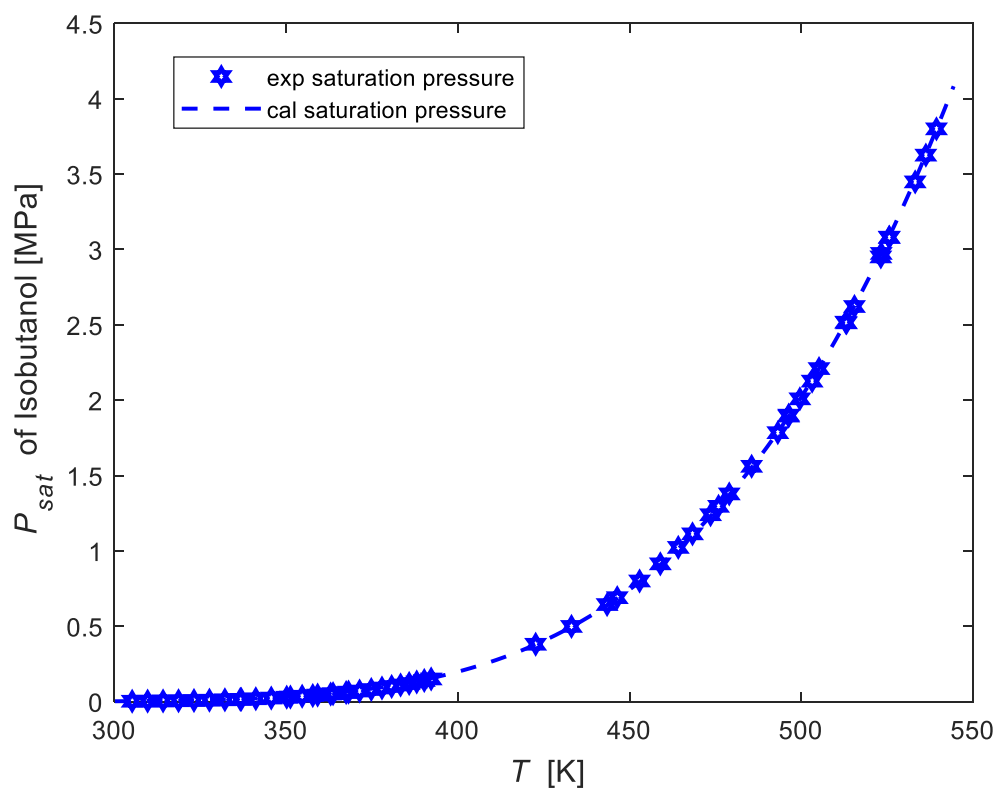
1262.31 K) is lower than that for 1-butanol (1288.46 K) and isobutanol (1360.52 K). This trend is consistent with the expected weakening of hydrogen-bonding strength caused by steric hindrance at the β -carbon, though the differences among the three alcohols are relatively modest.

Figures 1 and 2 compare the CPA-calculated values with experimental data for saturated vapor pressure and saturated liquid density, respectively, over the temperature ranges of the available experimental data.

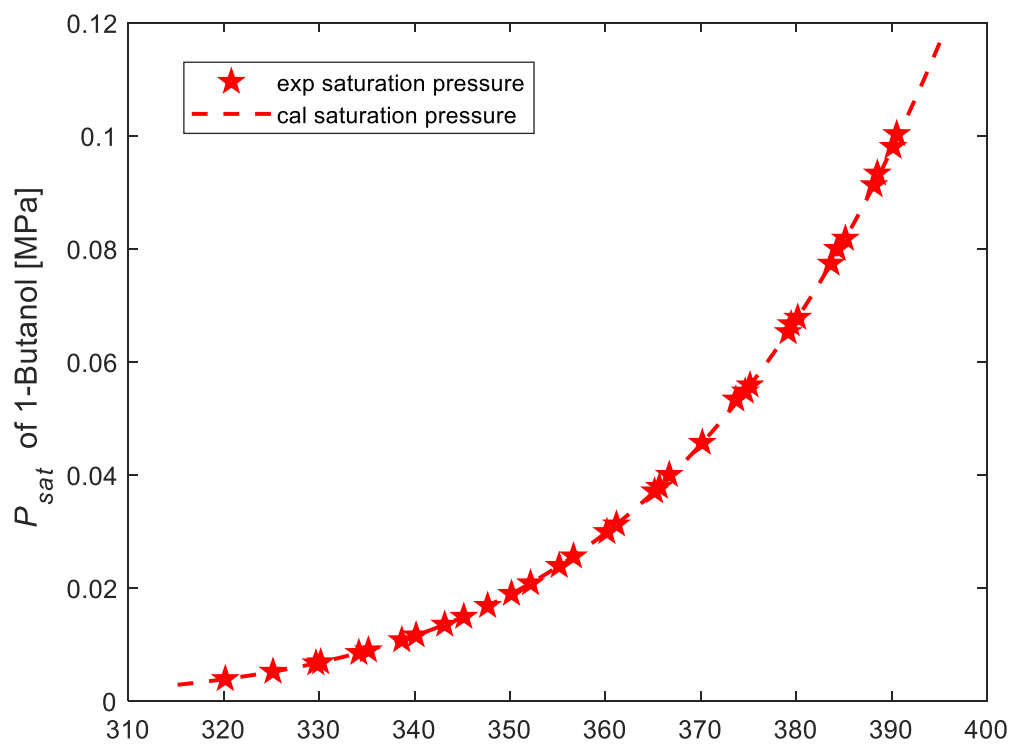
The CPA model accurately correlates the saturated properties of all three alcohols over their respective experimental temperature ranges. For isobutanol, the *AADs* are 1.9% for vapor pressure (305.15-539.35 K) and 1.0% for liquid density (326.50-547.65 K). For 1-butanol, the corresponding *AADs* are 0.2% and 0.1% (over 320.15-390.53 K and 278.15-343.15 K, respectively), confirming the well-established performance of the 2B scheme for this compound. For 2-ethyl-1-hexanol, despite its larger molecular size and steric hindrance, the *AADs* are 1.0% and 0.6% (over 370.15-457.44 K and 278.15-363.15 K, respectively). These deviations are well within the typical tolerance for engineering calculations. The fitted association energies follow the expected steric trend (isobutanol > 1-butanol > 2-ethyl-1-hexanol), as discussed in Section 3.2.

Over the temperature ranges examined, the CPA-calculated values remain in good agreement with the experimental data for all three alcohols. The overall *AAD* values for vapor pressure range from 0.2% to 1.9%, and for liquid density from 0.1% to 1.0%. These are well within the typical tolerance for thermodynamic models used in process simulation and distillation design. The slightly higher deviations observed for isobutanol (particularly in the high-temperature region) and for 2-ethyl-1-hexanol are consistent with the greater molecular complexity of these compounds compared to linear 1-butanol. Nevertheless, the results validate the pure-component parameters presented in Table 2 and demonstrate that the 2B association scheme, with appropriate parameter adjustments, can represent the pure-component properties of the three primary alcohols investigated in this work.

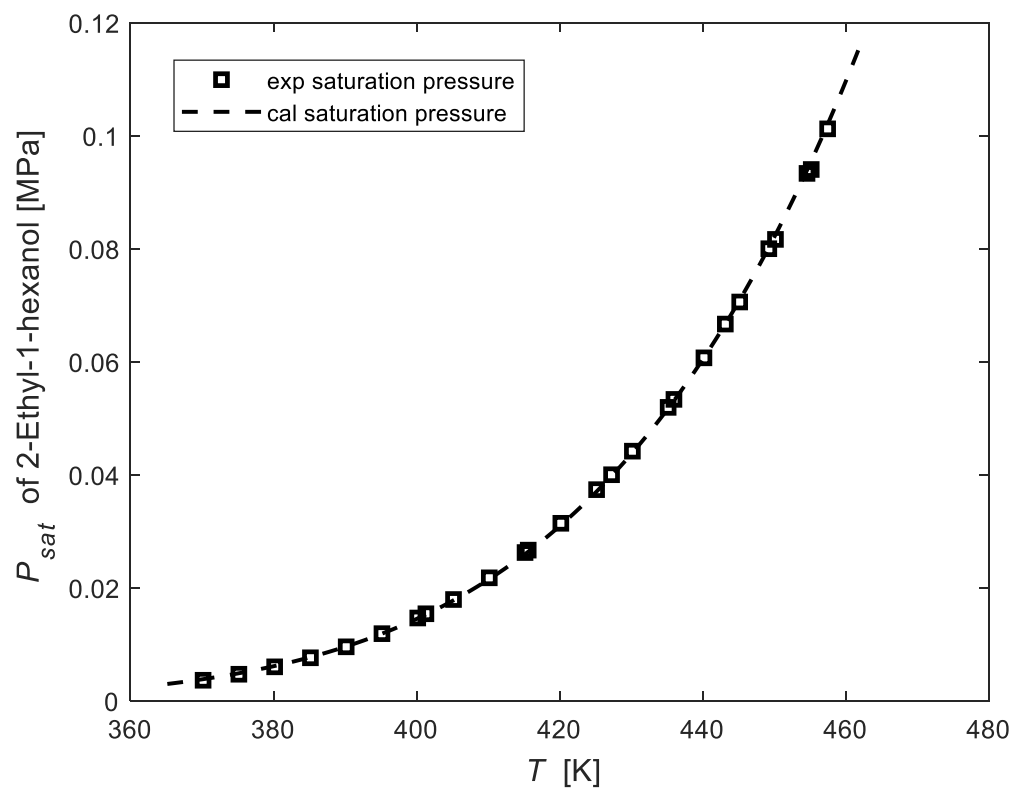
The pure-component parameters established in this section serve as the basis for the extension of the CPA model to binary mixtures, which is discussed in Section 4.



(a) [3, 8, 17-19]



(b) [8, 20-24]



(c) [8, 24, 25]

Figure 1. Pure component saturated vapor pressures: comparison between experimental data and predictions. (a) Isobutanol; (b) 1-Butanol; (c) 2-Ethyl-1-hexanolIsobutanol.

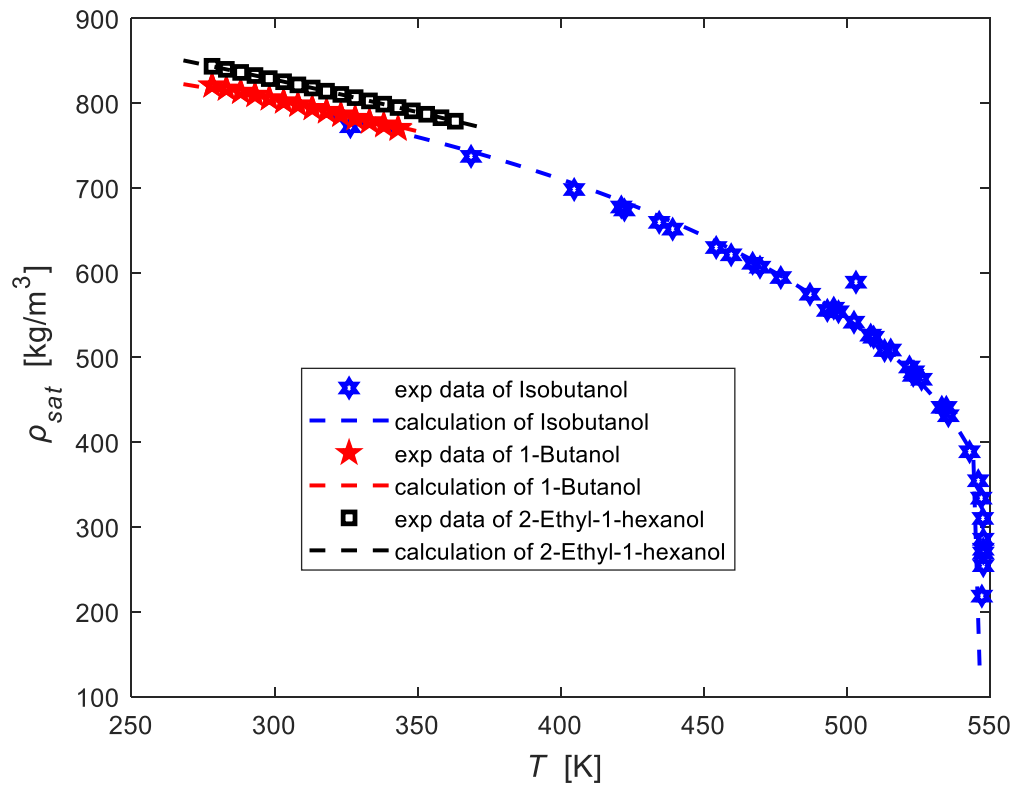


Figure 2. Pure component saturated liquid density: comparison between experimental data and predictions. [3, 8, 17-25]

4. VLE Modeling for Binary Mixtures

4.1. Cross-Association Treatment

In the 2B association scheme adopted in this work, each molecule carries one donor site (D, the hydroxyl hydrogen) and one acceptor site (A, the lone electron pairs on the hydroxyl oxygen). The subscripts 1, 2, and 3 denote isobutanol, 1-butanol, and 2-ethyl-1-hexanol, respectively. A notation such as $D_1 \leftrightarrow A_2$ thus represents a hydrogen bond formed between the donor site of isobutanol and the acceptor site of 1-butanol [9, 16].

In binary mixtures, each component retains the 2B association scheme defined in Section 3.2. For the three systems investigated in this work - isobutanol (1) + 1-butanol (2), isobutanol (1) + 2-ethyl-1-hexanol (3), and 1-butanol (2) + 2-ethyl-1-hexanol (3) - both self-association and cross-association occur simultaneously. For each binary mixture, both self-association and all possible cross-association hydrogen bonds between the donor (D) and acceptor (A) sites of the two components are accounted for within the 2B scheme [9, 16].

In the CPA framework, the cross-association energy parameters are determined from the pure-component self-association energies using the Wolbach-Sandler combining rule (CR-1 rule) [18]. Specifically, the cross-association energy is calculated as the geometric mean of the self-association energies of the two components: $\varepsilon^{A_i B_j} = \sqrt{\varepsilon^{A_i B_i} \cdot \varepsilon^{A_j B_j}}$. No additional adjustable parameters are introduced for cross-association.

Since the three alcohols share chemically similar hydroxyl groups, the pure-component association parameters fully determine the cross-association behavior in the binary mixtures. In the present systems, the non-ideality arising from hydrogen-bond network reorganization can be described without introducing extra adjustable parameters for cross-association.

4.2. Binary Interaction Parameter Regression

Using the pure-component parameters established in Section 3, the CPA model was extended to the three binary mixtures. The binary interaction parameter k_{ij} in Eq. (4) was determined by fitting the experimental $p - T - x$ VLE data reported by Fendu and Pricop-Nicolae [8], following the regression procedure described in Section 2.3.2. The temperature and pressure ranges of the experimental data are: (305.15-388.15) K

and (2.284-99.779) kPa for isobutanol + 1-butanol, (305.15-455.15) K and (2.284-99.779) kPa for isobutanol + 2-ethyl-1-hexanol, and (320.15-455.15) K and (3.635-98.039) kPa for 1-butanol + 2-ethyl-1-hexanol.

Table 4 summarizes the optimized k_{ij} values for each binary system, together with the average absolute deviations in the liquid-phase mole fraction of the most volatile component ($AAD(x_1)$).

Table 4. Optimized Binary Interaction Parameters and Composition Deviations.

Binary System	k_{ij}	T [K]	P [kPa]	$AADx_1$
Isobutanol (1) + 1-Butanol (2)	-0.0012	305.15- 389.15	2.284 99.779	2.8%
Isobutanol (1) + 2-Ethyl-1-hexanol (2)	-0.0083	305.15- 455.15	2.284 98.320	1.9%
1-Butanol (1) + 2-Ethyl-1-hexanol (2)	0.00012-6.6/ T	320.15- 455.15	3.635 98.039	2.3%

For the isobutanol + 1-butanol and isobutanol + 2-ethyl-1-hexanol systems, a single temperature-independent k_{ij} is sufficient to correlate the VLE data across the entire temperature range. For the 1-butanol + 2-ethyl-1-hexanol system, however, a temperature-dependent k_{ij} is required. The fitted form $k_{ij} = 0.00012 - 6.6/T$ (with T in K) reflects the fact that the molecular size difference between the two components ($M = 74.12$ g/mol vs. 130.23 g/mol) and the associated differences in association strength become more pronounced at lower temperatures, where hydrogen bonding is stronger. A single temperature-independent k_{ij} is insufficient to capture this varying non-ideality across the full experimental temperature range.

4.3. Modeling Results for the Three Binary Systems

The vapor pressure curves as functions of temperature for each binary system are presented in Figures 3-5. In these figures, experimental data points for each liquid composition (x_1) are plotted with their standard uncertainties in pressure, and the

solid lines represent CPA calculations using the parameters listed in Table 2.

It should be noted that the experimental data presented in the $P - T$ diagrams are not isobaric measurements. For each liquid composition, measurements were taken across the accessible temperature range of the static equilibrium apparatus, with the equilibrium pressure evolving as the temperature increased. Consequently, the number of data points sharing identical pressure values across different compositions is limited. This is a characteristic feature of static equilibrium apparatus measurements: for each composition, the temperature is raised incrementally and the corresponding equilibrium pressure is recorded, yielding a $P - T$ trajectory rather than discrete isobaric data points. The comparison between calculated and experimental values is therefore made based on the $P - T$ relationship for each fixed composition, and the model's performance is assessed by the deviations between the calculated and experimental pressures over the entire data set, as quantified by the $AAD(x_1)$ values in Table 3. The error bars shown in the figures correspond to the standard uncertainties in pressure reported in the original experimental study.

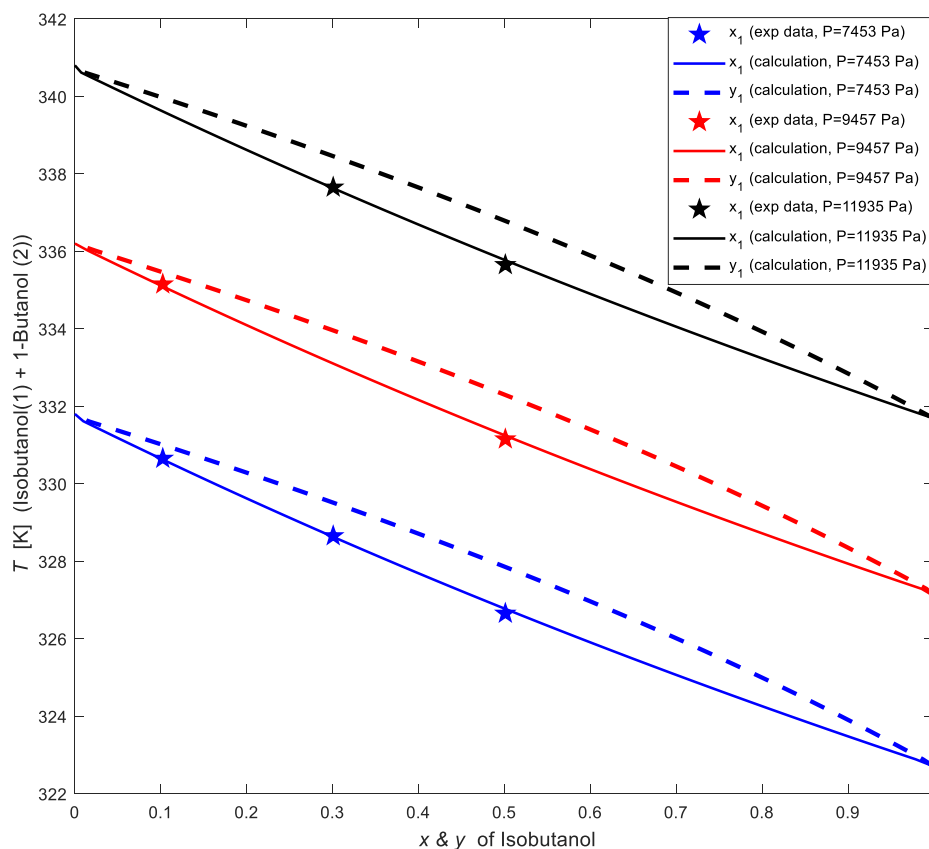


Figure 3. Modeling performance for VLE for Isobutanol (1) + 1-Butanol (2) at different pressures.

Figure 3 presents the vapor pressure curves as a function of temperature for the isobutanol + 1-butanol binary system at five different liquid compositions, together with the pure-component curves. The experimental data cover the temperature range of 305.15-388.15 K and pressures from 2.284 to 99.779 kPa. The CPA model reproduces the experimental data with an $AAD(x_1)$ of 2.8%. Both components are butanol isomers of identical molar mass, with closely similar association energies ($\varepsilon/k_B = 1360.52$ K for isobutanol vs. 1288.46 K for 1-butanol). The required k_{ij} is accordingly small (-0.0012), indicating that the physical contribution to the excess free energy requires only minor adjustment. The agreement between the calculated and experimental vapor pressures is consistent across the entire composition and temperature ranges.

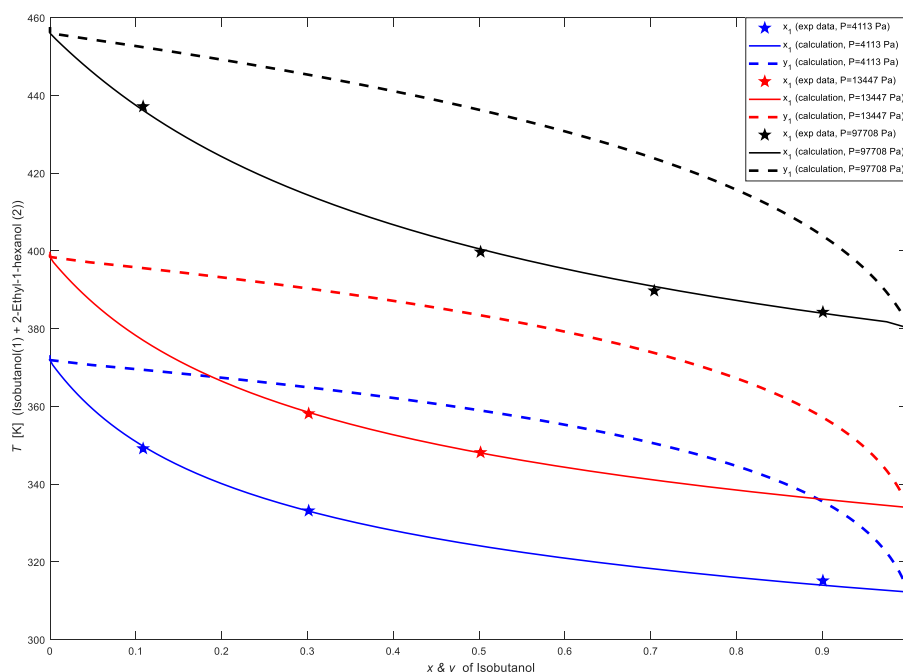


Figure 4. modeling performance for VLE for Isobutanol (1) + 2-Ethyl-1-hexanol (2) at different pressures.

Figure 4 displays the vapor pressure curves for the isobutanol + 2-ethyl-1-hexanol system at six liquid compositions, together with the pure-component curves, covering 305.15-455.15 K and 2.284-99.779 kPa. The CPA model yields an $AAD(x_1)$ of 1.9%, the lowest among the three systems. The molecular size difference between the two components is substantial ($M = 74.12$ vs. 130.23 g/mol), and the association energies

also differ (1360.52 vs. 1262.31 K). Despite these differences, the 2B association scheme, combined with the Wolbach-Sandler combining rule for cross-association, captures the non-ideal behavior accurately with a single temperature-independent k_{ij} of -0.0083. The negative sign indicates a slight attractive departure from the geometric combining rule.

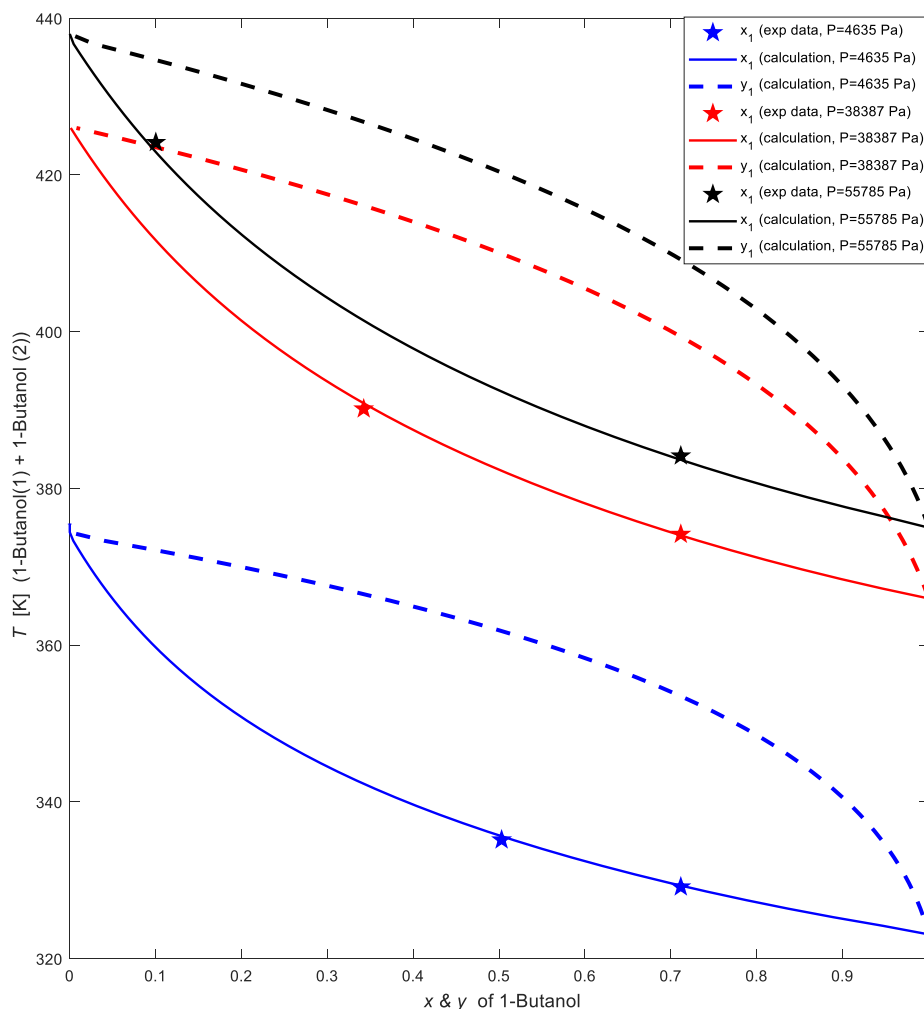


Figure 5. modeling performance for VLE for 1-Butanol (1) + 2-Ethyl-1-hexanol (2) at different pressures.

Figure 5 shows the vapor pressure curves for the 1-butanol + 2-ethyl-1-hexanol system at six liquid compositions, together with the pure-component curves, across 320.15-455.15 K and 3.635-98.039 kPa. The CPA model gives an $AAD(x_1)$ of 2.3% with the temperature-dependent k_{ij} defined in Table 3. This system exhibits the greatest non-ideality of the three investigated, attributable to the combination of a significant molecular size disparity and the structural asymmetry introduced by the β -

carbon substituents of 2-ethyl-1-hexanol. The temperature dependence of k_{ij} captures the enhanced hydrogen-bonding interactions at lower temperatures, where the steric hindrance of 2-ethyl-1-hexanol has a more pronounced effect on the hydrogen-bond network of the mixture.

Over the entire composition and temperature ranges examined, the CPA-calculated vapor pressures are in good agreement with the experimental data for all three binary systems. The deviations remain consistent across both low- and high-pressure ranges, confirming that the model parameters are robust and suitable for process simulation applications. The overall $AAD(x_1)$ values of 1.9%-2.8% are within the accuracy required for engineering design of distillation columns.

The pure-component and binary parameters obtained in this work can be used in process simulation software for the design and optimization of distillation operations involving these alcohol mixtures, including the recovery of 2-ethyl-1-hexanol from DOP production streams and the separation of butanol isomers from mixed alcohol raffinates.

5. Model Comparison and Applicability Analysis

5.1. Comparison with NRTL, UNIFAC, and IDEAL Models

For context, the NRTL model is a semi-empirical activity-coefficient model that requires system-specific fitted parameters; UNIFAC is a purely predictive group-contribution method; and the IDEAL model assumes ideal behavior. The following comparison highlights the differences in parameter efficiency, physical basis, and predictive capability among these approaches.

Parameter efficiency and fitting accuracy. In the NRTL regression of the same experimental data by Fendu and Pricop-Nicolae [8], the eight-parameter version yields maximum relative deviations in liquid-phase composition of -6.64% for isobutanol + 2-ethyl-1-hexanol and -6.91% for 1-butanol + 2-ethyl-1-hexanol, with average relative deviations of about 1.27% and 1.59%, respectively. For the CPA model, the average absolute deviations in mole fraction are 1.9%-2.8% using only one or two adjustable binary parameters. A direct numerical comparison between these values is not strictly meaningful, because NRTL reports relative deviations (normalized by the experimental value) while CPA reports absolute deviations in mole fraction. Nevertheless, both models provide accuracy well within the tolerance required for distillation design. The principal advantage of the CPA approach lies in its significantly fewer adjustable parameters and the physical interpretability of its association parameters.

Physical basis and parameter interpretability. The NRTL parameters are regression coefficients obtained by fitting experimental data. Although the NRTL model is grounded in the local composition concept and the non-randomness assumption, the numerical values of its parameters are system-specific and are less directly interpretable in terms of molecular-level interactions. Moreover, NRTL parameters cannot be reliably transferred between different systems or extrapolated beyond the temperature range of the data used for regression without risking significant loss of accuracy. The CPA parameters, by contrast, are more directly interpretable. The association energy ($\varepsilon^{A_i B_i}/k_B$) corresponds to the hydrogen-bonding strength, and the association volume ($\beta^{A_i B_i}$) reflects the steric availability of the bonding sites. The association energies follow a consistent trend across the three alcohols: isobutanol (1360.52 K) > 1-butanol (1288.46 K) > 2-ethyl-1-hexanol (1262.31 K), which correlates with the steric environment of the hydroxyl group. This physical basis

provides additional confidence in the model's behavior within the range of conditions for which the parameters were regressed.

Predictive capability versus correlative flexibility. The UNIFAC model is entirely predictive and does not require system-specific parameters. However, the $T - x - y$ diagrams reported in [8] show that the bubble-point and dew-point curves predicted by UNIFAC differ significantly from those obtained with NRTL (fitted to experimental data), particularly in the concentration range of 0-0.5 for isobutanol + 2-ethyl-1-hexanol and 0-0.9 for 1-butanol + 2-ethyl-1-hexanol at 20 kPa. The differences become more pronounced at 80 kPa. The IDEAL model deviates even more substantially, as it neglects all molecular interactions. The CPA model occupies an intermediate position between these extremes. Like UNIFAC, it contains a predictive element through the Wolbach-Sandler combining rule for cross-association, which is determined entirely from pure-component parameters. Like NRTL, it can be adjusted to experimental data through one or two binary parameters. This combination of predictive capability and adjustable flexibility makes CPA particularly suitable for systems where experimental data are limited but pure-component properties are available.

Non-ideality and azeotropy. All three binary systems exhibit significant non-ideal behavior due to hydrogen bonding between the alcohol molecules. However, none of the systems form azeotropes under the studied conditions. This is consistent with the relatively close boiling points and association strengths of the components. The CPA model, with its physically based association term, captures this non-ideal but non-azeotropic behavior without requiring the large number of adjustable parameters that an activity-coefficient model would need.

5.2. Applicability and Limitations of the CPA Model

The results presented in Sections 3 and 4 demonstrate that the CPA Equation of State with the 2B association scheme can represent both pure-component properties and binary VLE behavior for the three alcohol systems investigated. The following advantages and limitations are identified.

Advantages. First, the model achieves high accuracy with minimal parameterization. The pure-component properties are reproduced with *AAD* values of 0.2%-1.9% for vapor pressure and 0.1%-1.0% for liquid density. The binary VLE is correlated

with $AAD(x_1)$ values of 1.9%-2.8% using only one temperature-independent k_{ij} for two of the systems and a temperature-dependent k_{ij} for the third. This parameter economy is a distinct advantage over activity-coefficient models such as NRTL, which require three to eight adjustable parameters for comparable accuracy.

Second, the model parameters retain physical meaning and consistency. The association energies decrease with increasing steric hindrance at the hydroxyl-bearing carbon: isobutanol (1360.52 K) > 1-butanol (1288.46 K) > 2-ethyl-1-hexanol (1262.31 K). This trend is consistent with the molecular structures of the three alcohols and provides confidence that the model captures the underlying physics of hydrogen bonding.

Third, the cross-association treatment through the Wolbach-Sandler combining rule allows the model to predict binary mixture behavior from pure-component parameters alone, requiring only a small adjustment through k_{ij} . This is particularly valuable for systems where experimental VLE data are scarce or unavailable.

Limitations. For the 1-butanol + 2-ethyl-1-hexanol system, a temperature-dependent k_{ij} was required. This suggests that the single-parameter version of CPA, while capturing the general trend, does not fully account for the temperature variation of non-ideality in this system. The molecular size disparity and the steric effects of 2-ethyl-1-hexanol may introduce complexities that exceed the capacity of the one-parameter physical-term correction. Extension to a temperature-dependent k_{ij} provides the necessary flexibility, but at the cost of additional parameterization.

The CPA model, like all cubic equations of state, has limitations in the near-critical region. The CPA model, like all cubic equations of state, shows slightly larger deviations at higher reduced temperatures. For isobutanol, the deviations above 450 K are somewhat larger than those at lower temperatures. This is a common feature of the SRK-based association model, rather than a specific near-critical effect, and the overall accuracy remains within engineering tolerance for subcritical applications. For process simulation applications in the subcritical region, however, the accuracy is sufficient.

Finally, the model's performance at elevated pressures beyond the experimental range has not been validated. While the CPA Equation of State is generally applicable at higher pressures, the parameters regressed in this work were optimized for the sub-

atmospheric to atmospheric range. Users should exercise caution when extrapolating to significantly higher pressures.

Despite these limitations, the CPA model with the parameters presented in this work provides a reliable and efficient tool for the thermodynamic modeling of the three binary alcohol systems. The model is suitable for use in process simulation software for the design and optimization of distillation operations, including the recovery of 2-ethyl-1-hexanol from DOP production streams and the separation of butanol isomers from mixed alcohol raffinates.

6. Conclusion

This study addresses the lack of a unified and physically interpretable thermodynamic description of alcohol-based fuel mixtures that simultaneously accounts for hydrogen bonding and molecular-structure effects. The Cubic-Plus-Association equation of state with the two-site association scheme captures the weaker association of sterically hindered 2-ethyl-1-hexanol through a reduced association energy relative to 1-butanol and isobutanol, while retaining a compact parameter framework.

Pure-component parameters reproduce saturated vapor pressures and liquid densities with average absolute deviations of 0.2%–1.9% and 0.1%–1.0%, respectively. For binary mixtures, the Wolbach–Sandler combining rule describes cross-association without additional adjustable parameters. A single temperature-independent binary interaction parameter is sufficient for isobutanol + 1-butanol and isobutanol + 2-ethyl-1-hexanol, whereas 1-butanol + 2-ethyl-1-hexanol requires ($k_{ij} = 0.00012 - 6.6/T$), with (T) in K. The experimental vapor–liquid equilibria are reproduced with average absolute deviations in liquid mole fraction of 2.8%, 1.9%, and 2.3%, respectively.

Overall, the results demonstrate that hydrogen bonding, steric effects, and molecular-size disparity can be represented within a unified equation-of-state framework using a limited number of physically interpretable parameters. The resulting model provides a practical thermodynamic basis for phase-equilibrium prediction and separation-process design of alcohol-based fuel blends.

Acknowledgments

This work is supported by Startup Foundation for Young Teachers of Shanghai Ocean University, Project No. A2-2006-26-200311. The authors also acknowledge the support by the College of Food Science and Technology, Shanghai Ocean University, and School of Electrical and Power Engineering, Hohai University.

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