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Modeling the thermodynamic properties of cyclic alcohols with the SAFT- γ Mie approach: application to cyclohexanol and menthol systems

Thomas Bernet, Shubhani Paliwal, Ahmed Alyazidi, Riccardo Standish, Andrew J. Haslam, Claire S. Adjiman, George Jackson and Amparo Galindo

Department of Chemical Engineering, Sargent Centre for Process Systems Engineering, Institute for Molecular Science and Engineering, Imperial College London, London, UK

ABSTRACT

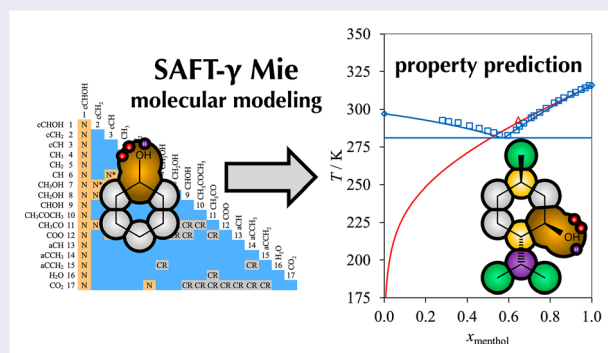
Cyclic alcohols are commonly found in natural and synthetic products and are involved in many biological processes. An ability to model their thermodynamic properties is of interest in food, flavouring, and pharmaceutical manufacturing, particularly for mixtures for which available experimental data are limited. Good examples are mixtures including menthol, a naturally occurring cyclic alcohol widely used in the food and pharmaceutical industries, well-known for its cooling-sensation properties and its role in the discovery of the TRPM8 receptor. Here, we extend the SAFT- γ Mie group-contribution method to model cyclic alcohols, by introducing a new cCHOH group (c for cyclic) composed of two identical Mie segments. Three association sites (two electronic sites of type e and one hydrogen site of type H) are also included to mediate hydrogen bonding. New parameters that characterise the group interactions (one new like interaction and 26 new unlike interactions) are developed and are employed to determine the thermophysical properties (vapour pressure, saturation density, vaporisation enthalpy, and second-order thermodynamic derivative properties) of pure cyclic alcohols, and mixture properties (vapour–liquid equilibria, liquid–liquid equilibria, solid–liquid equilibria, density, and excess enthalpy) of cyclic alcohols in several solvents. The quality of the model is evaluated by comparing predictive calculations with experimental data of 76 systems: six pure fluids and 70 binary mixtures, selected from a large range of solvent families: cyclic, linear, and branched alkanes, 1-alcohols, 2-alcohols, 2-ketones, esters, aromatic compounds, water, and carbon dioxide. Very good overall agreement is found, including for the prediction of solid–liquid solubility, which confirms the transferability of the new group parameters. Together with previously developed parameters, these open the way for the prediction of the thermodynamic properties of further complex mixtures.

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Statistical associating fluid theory (SAFT); menthol; group contribution; phase equilibria; thermodynamic properties



1. Introduction

Cyclic alcohols are secondary alcohols comprising the functional group $-\text{CH}(\text{OH})-$, in which the carbon atom is a member of a molecular cycle. The chemical formula of the simplest cyclic alcohols is $\text{C}_n\text{H}_{2n-1}\text{OH}$, where n is number of carbon atoms in the cycle, e.g. $n = 5$

for cyclopentanol, and $n = 6$ for cyclohexanol. Many molecules containing a cyclic alcohol group are found in natural products, as well as in synthetic compounds, or are known to be involved in biological mechanisms. For instance, cholesterol, testosterone, ergocalciferol (vitamin D_2), and related sterols are cyclic alcohols.

CONTACT Amparo Galindo  a.galindo@imperial.ac.uk  Department of Chemical Engineering, Sargent Centre for Process Systems Engineering, Institute for Molecular Science and Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, UK

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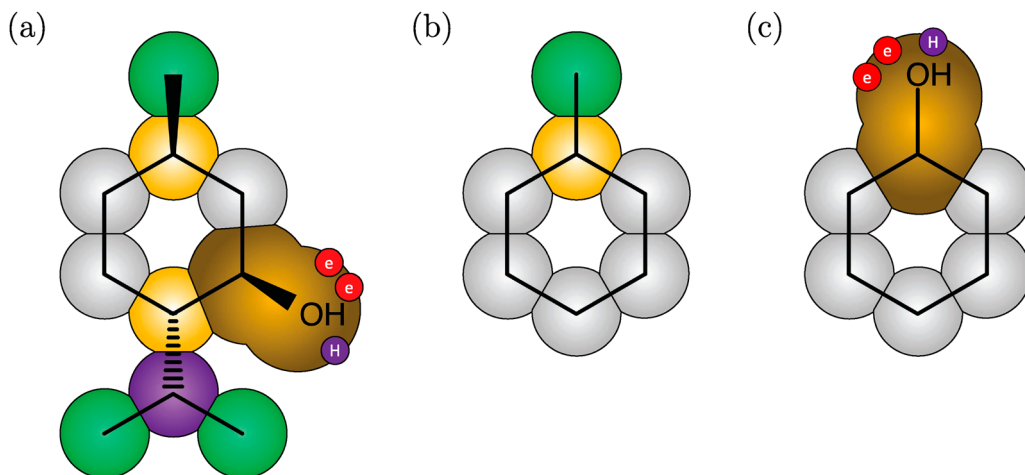


Figure 1. Molecular representation and SAFT- γ Mie molecular model of: (a) menthol, (b) methylcyclohexane, and (c) cyclohexanol. The rings of these molecules are modelled with the cCH₂ group (in grey). The new cCHOH group (in brown) is decorated with association sites denoted by the smaller circles, labelled e for electronegative (acceptor) sites and H for hydrogen (donor) sites. The side chains are modelled with CH (in purple) and CH₃ (in green) groups. The branch carbon participating in the ring and side chain is modelled with the cCH group (in yellow).

Menthol (C₁₀H₁₉OH) in particular is one of the simplest cyclic alcohols found in nature – mostly in mints – and is widely used in the food, flavour, cosmetic, and pharmaceutical industries [1,2]. It is also known for its low toxicity and its biological properties, including as a cooling agent. In 2002, Julius and Patapoutian used menthol to identify the TRPM8 receptor [3,4], involved in the perception of cold, and were awarded the Nobel Prize in Physiology or Medicine in 2021 ‘for their discoveries of receptors for temperature and touch’ [5]. Other studies on transient receptor potential (TRP) channels related to cold, warm, and pain perceptions have followed, based on the use of menthol [6–9]. The natural and most common stereoisomer of menthol found in nature is (–)-menthol, but seven other stereoisomers can be defined: (+)-menthol, (–)-isomenthol, (+)-isomenthol, (–)-neomenthol, (+)-neomenthol, (–)-neoisomenthol, and (+)-neoisomenthol [1]. In our current work, we consider only (–)-menthol (represented in Figure 1(a)), and we refer to the compound simply as ‘menthol’ (CAS number: 1490-04-6). Beyond its cooling properties, knowledge of the thermodynamic properties of menthol – including its miscibility and solubility with other compounds, and its hydrophobicity – are relevant for the design of sustainable eutectic solvents [10], and for the extraction of peppermint oil with supercritical carbon dioxide [11]. The phase behaviour of menthol in solvents has been studied with several approaches, including COSMO-RS [12–19], COSMO-SAC [20,21], NRTL model [15,16,19–21], UNIFAC [12,14,18,22], as well as PC-SAFT [12,13,17,22–24].

The statistical associating fluid theory (SAFT) is an equation of state [25,26] based on statistical mechanics,

that can be used to determine the thermodynamic properties of real compounds from an appropriate molecular model. Molecules are described as combinations of spherical monomers that interact through an intermolecular potential, can form chains of monomers (in order to model non-spherical compounds), and can form hydrogen bonds or other directional interactions, referred to as association interactions [27,28]. The SAFT-VR versions of the equation have been developed explicitly incorporating intermolecular potentials of variable range, e.g. the original SAFT-VR equation [29] for the square-well potential, and the later SAFT-VR Mie version [30–32] for the Mie (generalized Lennard-Jones) potential. These SAFT approaches can be applied to accurately model a wide range of thermodynamic properties of simple or complex fluids, including, e.g. polymers and electrolytes [33–35]. The SAFT- γ Mie group contribution method [31,32,36,37] considered in our current work was developed to extend the predictive capability of the SAFT-VR Mie approach for mixture thermodynamic properties. As a consequence, the SAFT- γ Mie model parameters specify interactions between groups (corresponding to functional groups or combinations of functional groups), rather than to interactions between molecules.

The thermodynamic properties of several families of complex fluids have been studied with SAFT- γ Mie, including deep-eutectic solvents and ionic liquids [38], pharmaceutical compounds (e.g. mefenamic acid [39], ibuprofen and ketoprofen [40–42]), lactones [43], polymers (e.g. polyethylene [44] and polyethylene glycol [45]), and carbon-capture systems [46–48]. Recently, an alternative group-contribution treatment for branched

compounds, the *s*-SAFT- γ Mie version [49–52], has also been presented. For neutral species, SAFT- γ Mie provides a formulation for the residual free energy of fluid mixtures as a sum of three contributions: monomer, chain, and association [37]. Other single-phase and equilibrium properties are obtained from standard thermodynamic relations and allow for the determination of phase diagrams with calculations for vapour–liquid equilibria (VLE), liquid–liquid equilibria (LLE), and solid–liquid equilibria (SLE).

In our current work, we aim to provide reliable predictions of the thermophysical properties of menthol in a range of solvents using the SAFT- γ Mie approach. A new cCHOH group is defined (i.e. a ‘cyclic CHOH’ group), that must be appropriate for menthol as well as for other cyclic alcohols, e.g. cyclohexanol. Additional non-alcoholic compounds are used to characterise the required group parameters, following the group-contribution method. In particular, methylcyclohexane is considered because menthol contains hydrocarbon side chains. The parameters characterised using methylcyclohexane and cyclohexanol are expected to be transferable for the prediction of the properties of menthol, given the molecular structure of these compounds (cf. Figure 1). The cCHOH group is composed of two fused spherical Mie segments, with two association sites of type e and one hydrogen association site of type H included to mimic the hydrogen bonds that cyclic alcohols can establish with other associating groups. The chirality of menthol cannot be accounted for using SAFT- γ Mie (as it is a first-order group-contribution approach), and no distinction between stereoisomers can be drawn. This is not, however, a crucial limitation for our work, as the thermophysical properties considered here are similar for all the stereoisomers, and because (–)-menthol is by far the most common form of natural menthol [1].

We briefly outline the SAFT- γ Mie group-contribution model and approach in Section 2. Results are analysed for pure cyclic alcohols and binary mixtures of cyclic alcohols + cyclic alkanes (Section 2.1), linear alkanes (Section 2.2), branched compounds (Section 2.3), primary alcohols (Section 2.4), linear secondary alcohols (Section 2.5), secondary ketones (Section 2.6), esters (Section 2.7), aromatic compounds (Section 2.8), water (Section 2.9), and carbon dioxide (Section 2.10). Predictions of fluid-phase diagrams for binary mixtures that contain menthol are presented in Section 3, and an analysis of the accuracy of our results is provided in Section 4 for all the systems and properties considered. Conclusions and additional comments are given in Section 5.

2. SAFT- γ Mie model and development for fluid and solid phase equilibria

In the SAFT- γ Mie approach [36,53] molecules are modeled as associating heteronuclear chains of fused spherical segments that interact through Mie potentials of variable range, while hydrogen bonding and strong polar interactions are added by embedding square-well association sites on a given segment [31,32,54]. It is assumed that the properties of a given molecule (or mixture) can be obtained by accounting for the appropriate contributions of the groups. The parameters characterising any given group are treated as transferable to other molecules and mixtures that contain the same group. The SAFT- γ Mie representations of menthol, methylcyclohexane, and cyclohexanol can be seen in Figure 1. A given group k incorporates a number ν_k^* of identical spherical segments, and a shape factor S_k ($0 \leq S_k \leq 1$), introduced to characterise the contribution of the segment to the overall properties of the molecule. Interactions between group k and group l are described by the segment diameter σ_{kl} , the depth of the potential well ε_{kl} , and the repulsive and attractive exponents of the Mie potential, λ_{kl}^r and λ_{kl}^a , respectively. Attractive directional interactions are represented by short-ranged square-well association sites placed on the segments. The parameter $N_{ST,k}$ corresponds to the number of association site types in a group k , and $n_{k,a}$ to the number of sites of a given type $a = 1, \dots, N_{ST,k}$. The interaction between a site of type a placed on a segment of type k and a site of type b placed on a segment of type l is described by an association energy $\varepsilon_{kl,ab}^{HB}$ and a bonding volume $K_{kl,ab}^{HB}$, that represent the strength and the range of the association, respectively. The interactions between groups k and l involve unlike parameters, which can be obtained through combining rules (CR) [36] in the first instance. In our current work, however, ε_{kl} , $K_{kl,ab}^{HB}$, and $\varepsilon_{kl,ab}^{HB}$ are systematically estimated by comparing target calculated and experimental thermophysical properties of pure fluids or mixtures in which the functional group is present, and λ_{kl}^r is occasionally estimated for better agreement.

The total Helmholtz free energy A of a fluid mixture of non-ionic species is expressed as the sum of four contributions [31,32,36,53]:

$$A = A^{\text{ideal}} + A^{\text{monomer}} + A^{\text{chain}} + A^{\text{association}}, \quad (1)$$

where A^{ideal} is the ideal free energy of the mixture, A^{monomer} is the contribution accounting for the interactions between Mie segments, A^{chain} is the free energy associated with the formation of chains, and $A^{\text{association}}$ is the contribution to the free energy due to association. The Born and ionic contributions, which appear

in the full SAFT- γ Mie free-energy expression [37], are not included in Equation (1) since we do not consider any ionic species in our current work. Detailed expressions for each contribution can be found in previous work [31,32,36,53]. The equilibrium thermodynamic properties of the fluid with N_c components can be determined from the total Helmholtz free energy A at a temperature T , volume V , and vector N of the number of molecules, composed of elements N_i of each compound i , such that $N = \sum_{i=1}^{N_c} N_i$ is the total number of molecules in the system. The pressure, P , and chemical potential of compound i , μ_i , are obtained from the standard thermodynamic relations of the Helmholtz free energy A , and are used to determine the fluid-phase-equilibrium conditions [37].

The solid–liquid solubility of compound i in a given solvent at a given T and P is obtained by solving the equality between the chemical potential of i in the solid phase, assumed to be pure here, and in the liquid phase. The activity coefficient of i , $\gamma_i(T, P, \mathbf{x}^{\text{sat}})$, is calculated with SAFT- γ Mie, where $\mathbf{x}^{\text{sat}}$ is the mole fraction of the saturated solution, and the solute mole fraction $x_i^{\text{sat}}(T, P, \mathbf{x}^{\text{sat}})$ is determined with the standard solubility equations for eutectic systems [39,55]. The melting temperature, T_i^{fus} , and the molar enthalpy of fusion, $\Delta h_i^{\text{fus}}(T_i^{\text{fus}}, P)$, are taken from experimental data (the values used in our current work are reported in Table 1, together with their corresponding sources [56–60]). The difference at T_i^{fus} between the molar heat capacity of the liquid phase and the molar heat capacity of the solid phase, $\Delta c_{p,i}(T_i^{\text{fus}}, P)$, is however unknown for most of the molecules considered in our work; we thus neglect the contributions of $\Delta c_{p,i}(T_i^{\text{fus}}, P)$. The list of compounds we consider is shown in Table 2, together with their corresponding group description in the SAFT- γ Mie framework.

The parameters characterising the groups are determined by minimising an objective function defined in previous work [43]. The percentage absolute average deviation (%AAD) of a property p for a system s ,

$$\% \text{AAD}_s p = \frac{1}{N_{s,p}^{\text{D}}} \sum_{i=1}^{N_{s,p}^{\text{D}}} \left| \frac{X_{s,p,i}^{\text{exp}} - X_{s,p,i}^{\text{calc}}}{X_{s,p,i}^{\text{exp}}} \right| \times 100, \quad (2)$$

and the absolute average deviation,

$$\text{AAD}_s p = \frac{1}{N_{s,p}^{\text{D}}} \sum_{i=1}^{N_{s,p}^{\text{D}}} |X_{s,p,i}^{\text{exp}} - X_{s,p,i}^{\text{calc}}|, \quad (3)$$

are used as measures of the accuracy of the theoretical description, where $N_{s,p}^{\text{D}}$ is the number of experimental data points for system s and property p (e.g. the number of points used in parameter estimation $N_{s,p}^{\text{est}}$, or the total

Table 1. Molar enthalpy of fusion Δh_i^{fus} and melting temperature T_i^{fus} of compounds used in the SAFT- γ Mie calculations and predictions in the current work.

Compound i	$\Delta h_i^{\text{fus}}(T_i^{\text{fus}}, P = 1 \text{ bar}) / (\text{kJ/mol})$	$T_i^{\text{fus}}/\text{K}$	Ref.
cyclopentanol	1.54	257.4	[59]
cyclohexanol	1.756	298.61	[57]
menthol	12.3	316	[56]
dodecane	35.9	263.6	[56]
2-methylpropane	4.5	113.6	[56]
2-methylbutane	5.2	113.3	[56]
cyclohexane	2.63	279.75	[57]
methylcyclohexane	6.7	146.6	[56]
methanol	3.21	175.49	[58]
ethanol	5.021	158.65	[57]
propan-1-ol	5.195	147.05	[57]
butan-1-ol	9.282	183.35	[57]
pentan-1-ol	9.829	194.25	[57]
heptan-1-ol	18.0	239.1	[56]
dodecan-1-ol	37.7	297.1	[56]
benzene	9.818	278.33	[60]
water	6.0	273.1	[56]
carbon dioxide	7.9	216.6	[56]

number of points $N_{s,p}^{\text{tot}}$, $X_{s,p,i}^{\text{exp}}$ is the i th measured value of property p of system s , and $X_{s,p,i}^{\text{calc}}$ is the corresponding value calculated with SAFT- γ Mie.

We use the gPROMS [61] tools to perform the parameter estimation and calculations. The open-source toolkits SGTPy [62] and Clapeyron.jl [63] can also be used to reproduce the calculations.

2.1. Pure cyclic alcohols and mixtures of cyclic alcohols + cyclic alkanes: cCHOH–cCHOH and cCHOH–cCH₂ interactions

A new SAFT- γ Mie group, denoted as cCHOH and composed of $v_{\text{cCHOH}}^* = 2$ segments, is characterised here. The cCHOH group is decorated by two e sites (labeled e_1) and one H site to model hydrogen bonds between two cCHOH groups, or between a cCHOH group and another group that contains at least one e site and/or one H site. The cCH₂ group, defined in previous work [53], also needs to be considered to model simple cyclic alcohols, e.g. cyclopentanol and cyclohexanol (the molecular structure of cyclohexanol is shown in Figure 1(c)). The following like SAFT- γ Mie group parameters are characterised here: S_{cCHOH} , $\sigma_{\text{cCHOH-cCHOH}}$, $\varepsilon_{\text{cCHOH-cCHOH}}$, $\lambda_{\text{cCHOH-cCHOH}}^{\text{r}}$, $\varepsilon_{\text{cCHOH-cCHOH}, e_1-\text{H}}^{\text{HB}}$, and $K_{\text{cCHOH-cCHOH}, e_1-\text{H}}^{\text{HB}}$. The unlike parameter $\varepsilon_{\text{cCHOH-cCH}_2}$ is also optimised, together with the like parameters. A representation of the SAFT- γ Mie group interactions considered in our current work can be found in Table 3. The corresponding parameter values, characterised in current and previous work, are summarised in Tables 4–6.

For the parameter estimation, we use NIST correlated data [66] as a reference for the vapour pressure, saturation vapour and liquid densities, and vaporisation enthalpy

Table 2. List of compounds considered in our current work, together with the SAFT- γ Mie group representation.

Compound name	CAS number	Molecular formula	SAFT- γ Mie model
cyclopentanol	96-41-3	C ₅ H ₁₀ O	cCH ₂ ($\times 4$), cCHOH
cyclohexanol	108-93-0	C ₆ H ₁₂ O	cCH ₂ ($\times 5$), cCHOH
2-methylcyclohexanol	583-59-5	C ₇ H ₁₄ O	cCH ₂ ($\times 4$), cCH, CH ₃ , cCHOH
menthol	1490-04-6	C ₁₀ H ₂₀ O	cCH ₂ ($\times 3$), cCHOH, cCH ($\times 2$), CH, CH ₃ ($\times 3$)
<i>n</i> -alkanes (ethane, propane, <i>n</i> -butane, etc.)	N/A	C _{<i>n</i>} H _{2<i>n</i>+2}	CH ₃ ($\times 2$), CH ₂ ($\times (n - 2)$) for $n \geq 2$
2-methylpropane	75-28-5	C ₄ H ₁₀	CH ₃ ($\times 3$), CH
2-methylbutane	78-78-4	C ₅ H ₁₂	CH ₃ ($\times 3$), CH ₂ , CH
3-methylpentane	96-14-0	C ₆ H ₁₄	CH ₃ ($\times 3$), CH ₂ ($\times 2$), CH
2,4-dimethylpentane	108-08-7	C ₇ H ₁₆	CH ₃ ($\times 3$), CH ₂ , CH ($\times 2$)
cyclopentane	287-92-3	C ₅ H ₁₀	cCH ₂ ($\times 5$)
methylcyclopentane	96-37-7	C ₆ H ₁₂	cCH ₂ ($\times 4$), cCH, CH ₃
cyclohexane	110-82-7	C ₆ H ₁₂	cCH ₂ ($\times 6$)
methylcyclohexane	108-87-2	C ₇ H ₁₄	cCH ₂ ($\times 5$), cCH, CH ₃
ethylcyclohexane	1678-91-7	C ₈ H ₁₆	cCH ₂ ($\times 5$), cCH, CH ₂ , CH ₃
1-isopropylcyclohexane	696-29-7	C ₉ H ₁₈	cCH ₂ ($\times 5$), cCH, CH, CH ₃ ($\times 2$)
1,3,5-triisopropylcyclohexane	34387-60-5	C ₁₅ H ₃₀	cCH ₂ ($\times 3$), cCH ($\times 3$), CH ($\times 3$), CH ₃ ($\times 6$)
1-methylpropylcyclohexane	7058-01-7	C ₁₀ H ₂₀	cCH ₂ ($\times 5$), cCH, CH, CH ₂ , CH ₃ ($\times 2$)
methanol	67-56-1	CH ₄ O	CH ₃ OH
1-alcohols (ethanol, propan-1-ol, butan-1-ol, etc.)	N/A	C _{<i>n</i>} H _{2<i>n</i>+2} O	CH ₃ , CH ₂ ($\times (n - 2)$), CH ₂ OH for $n \geq 2$
1,2-ethanediol	107-21-1	C ₂ H ₆ O ₂	CH ₂ OH ($\times 2$)
2-methyl-1-propanol	78-83-1	C ₄ H ₁₀ O	CH ₃ ($\times 2$), CH, CH ₂ OH
2-alcohols (propan-2-ol, butan-2-ol, pentan-2-ol, etc.)	N/A	C _{<i>n</i>} H _(2<i>n</i>+2) O	CH ₃ ($\times 2$), CH ₂ ($\times (n - 3)$), CHOH, for $n \geq 3$
acetone	67-64-1	C ₃ H ₆ O	CH ₃ COCH ₃
2-ketones (butanone, pentan-2-one, hexan-2-one, etc.)	N/A	C _{<i>n</i>} H _{2<i>n</i>} O	CH ₃ CO, CH ₂ ($\times (n - 3)$), CH ₃ for $n \geq 4$
methyl acetate	79-20-9	C ₃ H ₆ O ₂	COO, CH ₃ ($\times 2$)
ethyl acetate	141-78-6	C ₄ H ₈ O ₂	COO, CH ₂ , CH ₃ ($\times 2$)
propyl acetate	109-60-4	C ₅ H ₁₀ O ₂	COO, CH ₂ ($\times 2$), CH ₃ ($\times 2$)
butyl acetate	123-86-4	C ₆ H ₁₂ O ₂	COO, CH ₂ ($\times 3$), CH ₃ ($\times 2$)
diethyl butanedioate	123-25-1	C ₈ H ₁₄ O ₄	COO ($\times 2$), CH ₂ ($\times 4$), CH ₃ ($\times 2$)
benzene	71-43-2	C ₆ H ₆	aCH ($\times 6$)
toluene	108-88-3	C ₇ H ₈	aCH ($\times 5$), aCCH ₃
ethylbenzene	100-41-4	C ₈ H ₁₀	aCH ($\times 5$), aCCH ₂ , CH ₃
1,3,5-triethylbenzene	102-25-0	C ₁₂ H ₁₈	aCH ($\times 3$), aCCH ₂ ($\times 3$), CH ₃ ($\times 3$)
propylbenzene	103-65-1	C ₉ H ₁₂	aCH ($\times 5$), aCCH ₂ , CH ₂ , CH ₃
water	7732-18-5	H ₂ O	H ₂ O
carbon dioxide	124-38-9	CO ₂	CO ₂

of pure cyclohexanol. We also consider binary mixture data of cyclohexanol + cyclohexane (also modelled with the cCHOH and cCH₂ groups only), including isobaric VLE [67], isothermal VLE [68], liquid density [69–71], speed of sound [72], and excess molar enthalpy [73] data. Isobaric SLE data are also available [74], however, the binary mixture of cyclohexanol + cyclohexane is a dystetic system that cannot be described by the standard equations for eutectic systems [39] and are hence not used to validate our model. The properties of cyclohexanol can be seen in Figure 2 together with the corresponding SAFT- γ Mie calculations. Selected thermodynamic properties of cyclohexanol + cyclohexane are shown in Figure 3.

The %AADs and AADs calculated for the properties of pure cyclohexanol and mixtures of cyclohexanol + cyclohexane are reported in Table 7 (where the %AADs and AADs for all the systems considered

in our current work are summarised). The agreement between the SAFT- γ Mie calculations and the experimental data is excellent for pure cyclohexanol. For the data points used to characterise the interactions, the %AADs are 5.281% for vapour pressure, 2.807% for saturation vapour density, 1.309% for saturation liquid density, and 5.883% for vaporisation enthalpy, respectively. The critical temperature of cyclohexanol predicted with the model is $T_{c,\text{cyclohexanol}}^{\text{SAFT}} = 643.0$ K, while the reference from NIST [66] is $T_{c,\text{cyclohexanol}}^{\text{NIST}} = 647.1$ K (corresponding to only %AAD = 0.6336%). The SAFT- γ Mie calculations for the mixture of cyclohexanol + cyclohexane are also in excellent agreement with experimental data: the %AADs are 0.3049% for bubble temperature, 1.252% for dew temperature, 2.153% for bubble pressure, 1.523% for dew pressure, 0.5166% for single-phase density, and 7.838% for excess enthalpy (corresponding to a small AAD of 35.60 J/mol).

Table 3. Summary of the group interactions used to model cyclic alcohols in a range of solvents with the SAFT- γ Mie approach.

		cCHOH	cCH ₂	cCH	CH ₃	CH ₂	CH	CH ₃ OH	CH ₂ OH	CHOH	CH ₃ COCH ₃	CH ₃ CO	COO	aCH	aCCH ₃	aCCH ₂	H ₂ O	CO ₂
cCHOH	1	N																
cCH ₂	2	N																
cCH	3	N																
CH ₃	4	N																
CH ₂	5	N																
CH	6	N																
CH ₃ OH	7	N	N*	N*				CR										
CH ₂ OH	8	N	N*	N*				CR										
CHOH	9	N						CR										
CH ₃ COCH ₃	10	N		N*				CR										
CH ₃ CO	11	N	N*	N*				CR	CR	CR	CR							
COO	12	N		N*				CR	CR	CR		CR						
aCH	13	N																
aCCH ₃	14	N																
aCCH ₂	15	N						CR										
H ₂ O	16	N										CR						
CO ₂	17	N					N			CR	CR	CR	CR	CR	CR	CR		

Notes: Blue shading denotes that group interaction parameters have been optimised in previous work. The new (N) optimised parameters developed in our current work are denoted by yellow shading. The asterisk * indicates that the new parameters have been used in a separate recent work [43]. Grey shading denotes that unlike interaction parameters are predicted using combining rules (CR) [36].

Table 4. SAFT- γ Mie like interaction parameters for the groups considered in our current work (excluding association).

k	group	ν_k^*	S_k	$\sigma_{kk}/\text{\AA}$	λ_{kk}^r	λ_{kk}^a	$(\varepsilon_{kk}/k_B)/K$	$n_{k,H}$	$n_{k,e1}$	$n_{k,e2}$	Ref.
1	cCHOH	2	0.68123	2.8134	18.185	6.0000	372.79	1	2	–	*
2	cCH ₂	1	0.24751	4.7852	20.386	6.0000	477.36	–	–	–	[53]
3	cCH	1	0.096100	5.4116	8.0000	6.0000	699.92	–	–	–	[46]
4	CH ₃	1	0.57255	4.0772	15.050	6.0000	256.77	–	–	–	[36]
5	CH ₂	1	0.22932	4.8801	19.871	6.0000	473.39	–	–	–	[36]
6	CH	1	0.07210	5.2950	8.0000	6.0000	95.621	–	–	–	[53]
7	CH ₃ OH	2	0.83517	3.2462	19.235	6.0000	307.69	1	2	–	[53]
8	CH ₂ OH	2	0.58538	3.4054	22.699	6.0000	407.22	1	2	–	[40]
9	CHOH	2	0.18963	4.5381	18.185	6.0000	599.66	1	2	–	[37]
10	CH ₃ COCH ₃	3	0.72135	3.5981	17.433	6.0000	286.02	1	1	1	[53]
11	CH ₃ CO	2	0.54685	3.9112	19.050	6.0000	525.22	–	2	–	[39]
12	COO	1	0.65264	3.9939	31.189	6.0000	868.92	–	2	–	[36]
13	aCH	1	0.32184	4.0578	14.756	6.0000	371.53	–	1	–	[53]
14	aCCH ₃	1	0.31655	5.4874	23.627	6.0000	651.41	–	1	–	[41,64]
15	aCCH ₂	1	0.20859	5.2648	8.5433	6.0000	591.56	–	1	–	[53]
16	H ₂ O	1	1.0000	3.0063	17.020	6.0000	266.68	2	2	–	[31,32]
17	CO ₂	2	0.84680	3.0500	26.408	5.0550	207.89	–	1	1	[64]

Notes: The asterisk * in the Ref. column indicates that the cCHOH group is characterised in the current work.

2.2. Cyclic alcohols + linear alkanes: cCHOH–CH₃, and cCHOH–CH₂ interactions

The SAFT- γ Mie description of linear alkanes consists of two CH₃ groups and an appropriate number of CH₂ groups, which have been previously characterised [36]. We use these groups, together with the cCHOH group, and data of mixtures of cyclohexanol + *n*-alkanes to characterise the $\varepsilon_{\text{cCHOH-CH}_3}$

and $\varepsilon_{\text{cCHOH-CH}_2}$ unlike energy parameters. We consider experimental isobaric VLE [75] data for cyclohexanol + *n*-nonane (at 26.7 kPa, 53.3 kPa, and 80.0 kPa), isobaric SLE [74,76] for cyclohexanol + *n*-dodecane (at atmospheric pressure), and isothermal VLE [77] data for cyclohexanol + *n*-heptane (at 303.15 K, 313.15 K, 323.15 K, 333.15 K, 343.15 K, 353.15 K, 363.15 K, and 373.15 K). Excess molar enthalpies [78–84] are also available for binary mixtures of cyclohexanol + several

Table 5. Unlike group parameters (excluding association) used with the SAFT- γ Mie approach.

k	l	group k	group l	$(\varepsilon_{kl}/k_B)/K$	λ_{kl}^r	Ref.
1	1	cCHOH	cCHOH	372.79	18.185	*
1	2	cCHOH	cCH ₂	377.75	CR	*
1	3	cCHOH	cCH	39.771	CR	*
1	4	cCHOH	CH ₃	281.09	CR	*
1	5	cCHOH	CH ₂	398.89	CR	*
1	6	cCHOH	CH	0.0000	CR	*
1	7	cCHOH	CH ₃ OH	337.57	CR	*
1	8	cCHOH	CH ₂ OH	368.60	CR	*
1	9	cCHOH	CHOH	819.26	CR	*
1	10	cCHOH	CH ₃ COCH ₃	260.43	CR	*
1	11	cCHOH	CH ₃ CO	201.42	CR	*
1	12	cCHOH	COO	340.14	CR	*
1	13	cCHOH	aCH	231.22	8.0000	*
1	14	cCHOH	aCCH ₃	247.30	8.0000	*
1	15	cCHOH	aCCH ₂	355.11	CR	*
1	16	cCHOH	H ₂ O	346.97	CR	*
1	17	cCHOH	CO ₂	320.00	CR	*
2	2	cCH ₂	cCH ₂	477.36	20.386	[53]
2	3	cCH ₂	cCH	321.71	CR	[46]
2	4	cCH ₂	CH ₃	355.95	CR	[53]
2	5	cCH ₂	CH ₂	469.67	CR	[53]
2	6	cCH ₂	CH	570.45	CR	[53]
2	7	cCH ₂	CH ₃ OH	361.42	CR	*
2	8	cCH ₂	CH ₂ OH	424.64	CR	*
2	9	cCH ₂	CHOH	554.50	CR	[37]
2	10	cCH ₂	CH ₃ COCH ₃	352.19	CR	[37]
2	11	cCH ₂	CH ₃ CO	435.86	CR	*
2	12	cCH ₂	COO	498.60	CR	[40]
2	13	cCH ₂	aCH	393.05	15.377	[39]
2	14	cCH ₂	aCCH ₃	540.63	21.082	[39]
2	15	cCH ₂	aCCH ₂	439.78	9.9058	[39]
2	16	cCH ₂	H ₂ O	350.99	28.000	[46]
2	17	cCH ₂	CO ₂	269.68	CR	[47]
3	3	cCH	cCH	699.92	8.0000	[46]
3	4	cCH	CH ₃	690.17	CR	[46]
3	5	cCH	CH ₂	522.57	CR	[46]
3	6	cCH	CH	0.0000	CR	*
3	7	cCH	CH ₃ OH	345.00	CR	*
3	8	cCH	CH ₂ OH	242.45	CR	*
3	9	cCH	CHOH	640.38	CR	[43]
3	10	cCH	CH ₃ COCH ₃	409.28	CR	*
3	11	cCH	CH ₃ CO	265.24	CR	*
3	12	cCH	COO	0.0000	CR	*
3	13	cCH	aCH	377.21	CR	[39]
3	14	cCH	aCCH ₃	792.29	CR	[39]
3	15	cCH	aCCH ₂	162.65	CR	[39]
3	16	cCH	H ₂ O	377.16	22.265	[46]
3	17	cCH	CO ₂	294.99	CR	[47]
4	4	CH ₃	CH ₃	256.77	15.050	[36]
4	5	CH ₃	CH ₂	350.77	CR	[36]
4	6	CH ₃	CH	387.48	CR	[53]
4	7	CH ₃	CH ₃ OH	275.76	15.537	[53]
4	8	CH ₃	CH ₂ OH	333.20	CR	[40]
4	9	CH ₃	CHOH	479.38	CR	[37]
4	10	CH ₃	CH ₃ COCH ₃	233.48	14.449	[53]
4	11	CH ₃	CH ₃ CO	344.57	CR	[39]
4	12	CH ₃	COO	402.75	CR	[36]
4	13	CH ₃	aCH	305.81	CR	[53]
4	14	CH ₃	aCCH ₃	358.58	CR	[40]
4	15	CH ₃	aCCH ₂	396.91	CR	[53]
4	16	CH ₃	H ₂ O	358.18	100.00	[40]
4	17	CH ₃	CO ₂	205.70	CR	[64]
5	5	CH ₂	CH ₂	473.39	19.871	[36]
5	6	CH ₂	CH	506.21	CR	[53]
5	7	CH ₂	CH ₃ OH	341.41	17.050	[53]
5	8	CH ₂	CH ₂ OH	423.17	CR	[40]
5	9	CH ₂	CHOH	517.64	CR	[37]
5	10	CH ₂	CH ₃ COCH ₃	299.48	11.594	[53]
5	11	CH ₂	CH ₃ CO	431.49	CR	[39]
5	12	CH ₂	COO	498.86	CR	[36]

(continued).

Table 5. Continued.

k	l	group k	group l	$(\varepsilon_{kl}/k_B)/K$	λ_{kl}^r	Ref.
5	13	CH ₂	aCH	415.64	CR	[53]
5	14	CH ₂	aCCH ₃	569.18	CR	[40]
5	15	CH ₂	aCCH ₂	454.16	CR	[53]
5	16	CH ₂	H ₂ O	423.63	100.00	[40]
5	17	CH ₂	CO ₂	276.45	CR	[64]
6	6	CH	CH	95.621	8.0000	[53]
6	7	CH	CH ₃ OH	CR	CR	–
6	8	CH	CH ₂ OH	329.22	CR	[41]
6	9	CH	CHOH	0.0000	CR	[37]
6	10	CH	CH ₃ COCH ₃	637.29	CR	[53]
6	11	CH	CH ₃ CO	321.91	CR	[39]
6	12	CH	COO	353.65	CR	[41]
6	13	CH	aCH	441.43	CR	[53]
6	14	CH	aCCH ₃	769.36	8.0000	[39]
6	15	CH	aCCH ₂	65.410	CR	[53]
6	16	CH	H ₂ O	275.75	CR	[41]
6	17	CH	CO ₂	367.86	CR	*
7	7	CH ₃ OH	CH ₃ OH	307.69	19.235	[53]
7	8	CH ₃ OH	CH ₂ OH	CR	CR	–
7	9	CH ₃ OH	CHOH	CR	CR	–
7	10	CH ₃ OH	CH ₃ COCH ₃	CR	CR	–
7	11	CH ₃ OH	CH ₃ CO	CR	CR	–
7	12	CH ₃ OH	COO	CR	CR	–
7	13	CH ₃ OH	aCH	330.19	CR	[39]
7	14	CH ₃ OH	aCCH ₃	405.45	CR	[39]
7	15	CH ₃ OH	aCCH ₂	CR	CR	–
7	16	CH ₃ OH	H ₂ O	278.45	CR	[53]
7	17	CH ₃ OH	CO ₂	157.83	8.3462	[64]
8	8	CH ₂ OH	CH ₂ OH	407.22	22.699	[40]
8	9	CH ₂ OH	CHOH	389.23	CR	[37]
8	10	CH ₂ OH	CH ₃ COCH ₃	338.47	CR	[37]
8	11	CH ₂ OH	CH ₃ CO	CR	CR	–
8	12	CH ₂ OH	COO	CR	CR	–
8	13	CH ₂ OH	aCH	386.05	CR	[41]
8	14	CH ₂ OH	aCCH ₃	486.62	CR	[41]
8	15	CH ₂ OH	aCCH ₂	434.37	CR	[41]
8	16	CH ₂ OH	H ₂ O	353.37	CR	[40]
8	17	CH ₂ OH	CO ₂	312.30	CR	[47]
9	9	CHOH	CHOH	599.66	18.185	[37]
9	10	CHOH	CH ₃ COCH ₃	340.81	CR	[37]
9	11	CHOH	CH ₃ CO	CR	CR	–
9	12	CHOH	COO	CR	CR	–
9	13	CHOH	aCH	512.16	CR	[37]
9	14	CHOH	aCCH ₃	762.86	CR	[37]
9	15	CHOH	aCCH ₂	357.91	CR	[37]
9	16	CHOH	H ₂ O	479.16	CR	[37]
9	17	CHOH	CO ₂	CR	CR	–
10	10	CH ₃ COCH ₃	CH ₃ COCH ₃	286.02	17.433	[53]
10	11	CH ₃ COCH ₃	CH ₃ CO	CR	CR	–
10	12	CH ₃ COCH ₃	COO	547.44	CR	[37]
10	13	CH ₃ COCH ₃	aCH	333.11	CR	[53]
10	14	CH ₃ COCH ₃	aCCH ₃	479.55	35.957	[39]
10	15	CH ₃ COCH ₃	aCCH ₂	394.83	CR	[53]
10	16	CH ₃ COCH ₃	H ₂ O	287.26	CR	[53]
10	17	CH ₃ COCH ₃	CO ₂	CR	CR	–
11	11	CH ₃ CO	CH ₃ CO	525.22	19.050	[39]
11	12	CH ₃ CO	COO	CR	CR	–
11	13	CH ₃ CO	aCH	426.72	18.030	[39]
11	14	CH ₃ CO	aCCH ₃	552.62	36.429	[39]
11	15	CH ₃ CO	aCCH ₂	663.71	30.712	[39]
11	16	CH ₃ CO	H ₂ O	CR	CR	–
11	17	CH ₃ CO	CO ₂	CR	CR	–
12	12	COO	COO	868.92	31.189	[36]
12	13	COO	aCH	534.18	22.088	[39]
12	14	COO	aCCH ₃	595.48	15.874	[39]
12	15	COO	aCCH ₂	265.62	9.3393	[39]
12	16	COO	H ₂ O	396.81	15.140	[65]
12	17	COO	CO ₂	CR	CR	–
13	13	aCH	aCH	371.53	14.756	[53]
13	14	aCH	aCCH ₃	471.23	CR	[64]
13	15	aCH	aCCH ₂	416.69	CR	[53]

(continued).

Table 5. Continued.

<i>k</i>	<i>l</i>	group <i>k</i>	group <i>l</i>	$(\varepsilon_{kl}/k_B)/K$	λ_{kl}^r	Ref.
13	16	aCH	H ₂ O	357.78	38.640	[53]
13	17	aCH	CO ₂	CR	CR	–
14	14	aCCH ₃	aCCH ₃	651.41	23.627	[41,64]
14	15	aCCH ₃	aCCH ₂	CR	CR	–
14	16	aCCH ₃	H ₂ O	360.70	CR	[41]
14	17	aCCH ₃	CO ₂	CR	CR	–
15	15	aCCH ₂	aCCH ₂	591.56	8.5433	[53]
15	16	aCCH ₂	H ₂ O	329.03	CR	[41]
15	17	aCCH ₂	CO ₂	CR	CR	–
16	16	H ₂ O	H ₂ O	266.68	17.020	[31,32]
16	17	H ₂ O	CO ₂	226.38	CR	[64]
17	17	CO ₂	CO ₂	207.89	26.408	[64]

Notes: The asterisk * indicates parameters characterised in our current work.

n-alkanes at 298.15 K and atmospheric pressure. The experimental data are compared to SAFT- γ Mie calculations in Figure 4.

Excellent agreement is obtained for VLE: %AAD = 0.2960% for the bubble temperature of cyclohexanol + *n*-nonane (Figure 4(a)), and %AAD = 3.734% for the bubble pressure of cyclohexanol + *n*-heptane (Figure 4(b)). Good agreement is found for the excess molar enthalpy of cyclohexanol + *n*-alkanes (Figure 4(c)): for a given composition, the excess molar enthalpy increases for longer *n*-alkanes (from *n*-hexane to *n*-dodecane). The corresponding AADs are of the order of a hundred Joules per mole (cf. Table 7).

Isobaric SLE data [74,76] for cyclohexanol + *n*-dodecane (Figure 4(d)) are not used to characterise the cCHOH–CH₃ and cCHOH–CH₂ interactions, but are considered to assess the prediction capability of the SAFT- γ Mie model proposed here. A eutectic point is computed ($T_{\text{eutectic}}^{\text{SAFT}} = 257$ K and $x_{\text{eutectic,cyclohexanol}}^{\text{SAFT}} = 0.84$), in good agreement with experiments [74] ($T_{\text{eutectic}}^{\text{exp}} = 269.45$ K and $x_{\text{eutectic,cyclohexanol}}^{\text{exp}} = 0.8514$).

2.3. Alkylcycloalkanes and cyclic alcohols + branched compounds: cCH–CH, cCHOH–cCH, and cCHOH–CH interactions

The CH group [53] is used to model compounds with linear side chains. Similarly, the cCH group [46] is used to model the junction between a cycle and a side chain in alkylcycloalkanes. The unlike group-interaction parameter $\varepsilon_{\text{cCH–CH}}$ is characterised here by using experimental data for pure 1-isopropylcyclohexane, pure methylpropylcyclohexane, and mixtures of methylcyclohexane + branched alkanes (single-phase liquid densities are also predicted for pure 1,3,5-triisopropylcyclohexane; cf. Table 7). The dispersion energies $\varepsilon_{\text{cCHOH–cCH}}$ and $\varepsilon_{\text{cCHOH–CH}}$ are then characterised to model pure 2-methylcyclohexanol and pure menthol.

Binary mixture data of alkylcycloalkanes + branched alkanes are used for the characterisation of the cCH–CH group interactions, including: isobaric VLE [85] of methylcyclohexane + 3-methylpentane at 101.3 kPa, and isothermal VLE [86] of methylcyclohexane + 2,4-dimethylpentane at 473.15 K and 503.15 K. Vapour pressure [87,88], single-phase density [89], saturation density [90], and vaporisation enthalpy [90] of pure alkylcycloalkanes are also considered for validation (Figure 5). Pure menthol and 2-methylcyclohexanol data are used for the characterisation of the cCHOH–cCH and cCHOH–CH group interactions, including: vapour pressure [66,91], saturation density [66], and vaporisation enthalpy [66,90] (Figure 6). Speed of sound [92] and isobaric heat capacity [90], i.e. second-order thermodynamic derivative properties, are also considered for pure menthol (Figure 7).

The cCH and CH groups are characterised by very small shape factors, which result in a very small contribution to the overall Helmholtz free energy (and the thermodynamic properties), such that it is difficult to characterise precisely (without degeneracy) the unlike dispersion energy between these groups. Initially, the cCH–CH unlike energy parameter $\varepsilon_{\text{cCH–CH}}$ is found to take a value close to zero following the minimisation of the objective function, and following this result, we have assigned it a value of zero in our model. The %AADs related to the systems used to characterise this interaction are very small for the case of methylcyclohexane + 3-methylpentane (1.795% for the bubble temperature and 1.929% for the dew temperature), and somewhat larger for methylcyclohexane + 2,4-dimethylpentane (16.01% for the bubble pressure and 17.83% for the dew pressure). Furthermore, when transferring this interaction for the prediction of the properties of pure 1-isopropylcyclohexane and 1-methylpropylcyclohexane, excellent agreement with the available data is found (Figure 5), suggesting that the small value of this unlike energy is suitable for these compounds.

Vapour-pressure [66,91] and saturation-density [66] data are used for the characterisation of the cCHOH–cCH and cCHOH–CH interactions, and excellent agreement in the description of the pure menthol and 2-methylcyclohexanol properties is found. Predictions of the vaporisation enthalpy of these two compounds are also very good (Figure 6(c)), as are predictions of their critical temperature (with %AAD = 1.110% for menthol, and %AAD = 0.7535% for 2-methylcyclohexanol), and of the second-order thermodynamic derivative properties for pure menthol (%AAD = 2.652% for the liquid-phase speed of sound at 101.3 kPa, and %AAD = 11.45% for the saturated-liquid isobaric heat capacity).

Table 6. Group association parameters used with the SAFT- γ Mie approach.

k	l	group k	site a of group k	group l	site b of group l	$(\epsilon_{kl,ab}^{\text{HB}}/k_{\text{B}})/\text{K}$	$K_{kl,ab}^{\text{HB}}/\text{\AA}^3$	Ref.
1	1	cCHOH	H	cCHOH	e ₁	1743.6	165.51	*
1	7	cCHOH	H	CH ₃ OH	e ₁	1475.0	671.52	*
1	7	cCHOH	e ₁	CH ₃ OH	H	3039.4	0.49675	*
1	8	cCHOH	H	CH ₂ OH	e ₁	2150.1	56.873	*
1	8	cCHOH	e ₁	CH ₂ OH	H	1702.2	134.81	*
1	9	cCHOH	H	CHOH	e ₁	2004.3	36.324	*
1	9	cCHOH	e ₁	CHOH	H	1346.2	560.30	*
1	10	cCHOH	H	CH ₃ COCH ₃	e ₁	2362.9	900.66	*
1	10	cCHOH	e ₁	CH ₃ COCH ₃	H	0.0000	0.0000	*
1	11	cCHOH	H	CH ₃ CO	e ₁	1790.3	752.44	*
1	12	cCHOH	H	COO	e ₁	2151.6	100.00	*
1	16	cCHOH	H	H ₂ O	e ₁	1688.2	162.42	*
1	16	cCHOH	e ₁	H ₂ O	H	1815.9	131.42	*
7	7	CH ₃ OH	H	CH ₃ OH	e ₁	2062.1	106.57	[53]
7	16	CH ₃ OH	e ₁	H ₂ O	H	1993.5	104.11	[53]
7	16	CH ₃ OH	H	H ₂ O	e ₁	1993.5	104.11	[53]
8	8	CH ₂ OH	H	CH ₂ OH	e ₁	2097.9	62.309	[40]
8	9	CH ₂ OH	H	CHOH	e ₁	2500.0	10.444	[37]
8	9	CH ₂ OH	e ₁	CHOH	H	1464.1	591.55	[37]
8	10	CH ₂ OH	e ₁	CH ₃ COCH ₃	H	686.93	585.99	[37]
8	10	CH ₂ OH	H	CH ₃ COCH ₃	e ₁	1844.8	991.95	[37]
8	16	CH ₂ OH	e ₁	H ₂ O	H	2153.2	147.40	[40]
8	16	CH ₂ OH	H	H ₂ O	e ₁	621.68	425.00	[40]
9	9	CHOH	H	CHOH	e ₁	2480.6	8.4740	[37]
9	10	CHOH	e ₁	CH ₃ COCH ₃	H	1186.9	731.08	[37]
9	10	CHOH	H	CH ₃ COCH ₃	e ₁	1323.1	635.37	[37]
9	16	CHOH	e ₁	H ₂ O	H	2140.9	19.478	[37]
9	16	CHOH	H	H ₂ O	e ₁	2289.1	63.813	[37]
10	10	CH ₃ COCH ₃	H	CH ₃ COCH ₃	e ₁	980.20	2865.2	[53]
10	16	CH ₃ COCH ₃	H	H ₂ O	e ₁	1386.8	188.83	[53]
10	16	CH ₃ COCH ₃	e ₁	H ₂ O	H	1588.7	772.77	[53]
10	16	CH ₃ COCH ₃	e ₂	H ₂ O	H	417.24	1304.3	[53]
12	16	COO	e ₁	H ₂ O	H	1245.8	454.98	[65]
13	16	aCH	e ₁	H ₂ O	H	563.56	339.61	[53]
14	16	aCCH ₃	e ₁	H ₂ O	H	563.56	339.61	[41]
15	16	aCCH ₂	e ₁	H ₂ O	H	563.56	339.61	[41]
16	16	H ₂ O	H	H ₂ O	e ₁	1985.4	101.69	[31,32]
16	17	H ₂ O	e ₁	CO ₂	e ₁	1398.1	91.419	[64]

Notes: The asterisk * indicates that the parameters are characterised in our current work.

2.4. Alkylcycloalkanes and cyclic alcohols + 1-alcohols: cCH₂–CH₃OH, cCH₂–CH₂OH, cCH–CH₃OH, cCH–CH₂OH, cCHOH–CH₃OH, and cCHOH–CH₂OH interactions

Primary alcohols are modelled using a CH₃OH group [53] for methanol and a CH₂OH group [40] for longer alcohols (ethanol, propan-1-ol, butan-1-ol, etc.). Both CH₃OH and CH₂OH groups contain two e₁ sites and one H site to model hydrogen bonding. The interaction parameters $\epsilon_{\text{cCH}_2\text{--CH}_3\text{OH}}$ and $\epsilon_{\text{cCH}_2\text{--CH}_2\text{OH}}$ are characterised here for cycloalkanes + 1-alcohols, as well as $\epsilon_{\text{cCH--CH}_3\text{OH}}$ and $\epsilon_{\text{cCH--CH}_2\text{OH}}$ for alkylcycloalkanes + 1-alcohols. Interactions between cyclic alcohols and methanol are described with $\epsilon_{\text{cCHOH--CH}_3\text{OH}}$, $\epsilon_{\text{cCHOH--CH}_3\text{OH},\text{e}_1\text{--H}}^{\text{HB}}$, $K_{\text{cCHOH--CH}_3\text{OH},\text{e}_1\text{--H}}^{\text{HB}}$, $\epsilon_{\text{cCHOH--CH}_3\text{OH},\text{H--e}_1}^{\text{HB}}$, and $K_{\text{cCHOH--CH}_3\text{OH},\text{H--e}_1}^{\text{HB}}$, while interactions between cyclic alcohols and longer 1-alcohols are described with $\epsilon_{\text{cCHOH--CH}_2\text{OH}}$, $\epsilon_{\text{cCHOH--CH}_2\text{OH},\text{e}_1\text{--H}}^{\text{HB}}$, $K_{\text{cCHOH--CH}_2\text{OH},\text{e}_1\text{--H}}^{\text{HB}}$, $\epsilon_{\text{cCHOH--CH}_2\text{OH},\text{H--e}_1}^{\text{HB}}$, and $K_{\text{cCHOH--CH}_2\text{OH},\text{H--e}_1}^{\text{HB}}$.

A large amount of experimental data is available for binary mixtures of cycloalkanes + 1-alcohols and alkylcycloalkanes + 1-alcohols. We select relevant data for isobaric VLE, LLE, and SLE phase diagrams [74,93–113], isothermal VLE [93,114–123], single-phase liquid densities [124–139], and excess molar enthalpies [119,140–156]. Data are also available for cyclohexanol + 1-alcohol mixtures, including isobaric VLE [157–161], isothermal VLE [162], and excess molar enthalpy [83,163,164].

Isobaric phase diagrams for mixtures of cyclohexane + 1-alcohols at atmospheric pressure can be seen in Figure 8. A region of LLE is found for cyclohexane + methanol both from experiments and calculations (Figure 8(a)), while no LLE is found for mixtures of cyclohexane + longer 1-alcohols (Figures 8(b–e)). Eutectic SLE are predicted with SAFT- γ Mie in very good agreement with the experimental data for the systems considered (Figs. 8(a–e)). In addition, azeotropes are found in mixtures of cyclohexane + methanol, ethanol, propan-1-ol, and butanol, while no azeotrope is found

Table 7. Overview of the accuracy of SAFT- γ Mie in the calculation of pure fluid and binary mixture properties: critical temperature T_c , vapour pressure P_{vap} , saturated-vapour density $\rho_{\text{sat}}^{\text{vap}}$, saturated-liquid density $\rho_{\text{sat}}^{\text{liq}}$, vaporisation enthalpy Δh_{vap} , azeotrope temperature T_{az} , bubble temperature T_{bub} , dew temperature T_{dew} , SLE temperature T_{SLE} , bubble pressure P_{bub} , dew pressure P_{dew} , LLE composition x_1^{LLE} , SLE composition (solubility) x_1^{sat} , mixture density ρ , speed of sound u_{sound} , isobaric heat capacity c_p , and excess molar enthalpy Δh_{mix} .

Critical temperature									
System s (pure)	T/K	P	x_1	$N_{s,p}^{\text{nest}}$	$N_{s,p}^{\text{tot}}$	%AAD	AAD/kPa	Ref.	Fig.
cyclohexanol	647.1	–	pure	0	1	0.6336	4.100	[66]	2(a–c)
1-isopropylcyclohexane	632.2	–	pure	0	1	1.091	6.900	[66]	5(a–c)
1-methylpropylcyclohexane	668	–	pure	0	1	0.7934	5.300	[66]	5(a–c)
menthol	694	–	pure	0	1	1.110	7.700	[66]	6(a–c)
2-methylcyclohexanol	637	–	pure	0	1	0.7535	4.800	[66]	6(a–c)
Vapour pressure									
System s (pure)	T/K	P	x_1	$N_{s,p}^{\text{nest}}$	$N_{s,p}^{\text{tot}}$	%AAD	AAD/kPa	Ref.	Fig.
cyclohexanol	299–600	–	pure	15	15	5.281	13.78	[66]	2(a)
1-isopropylcyclohexane	233–452	–	pure	0	22	24.16	4.649	[87]	5(a)
1-methylpropylcyclohexane	364–454	–	pure	0	20	12.56	4.927	[88]	5(a)
menthol	310–500	–	pure	21	21	29.29	5.594	[91]	6(a)
2-methylcyclohexanol	240–600	–	pure	16	19	6.126	33.54	[66]	6(a)
Vapour density									
System s (pure)	T/K	P	x_1	$N_{s,p}^{\text{nest}}$	$N_{s,p}^{\text{tot}}$	%AAD	AAD/(kg/m ³)	Ref.	Fig.
cyclohexanol	519–606	saturation	pure	11	11	2.807	1.059	[66]	2(b)
menthol	559–672	saturation	pure	11	18	18.14	9.058	[66]	6(b)
2-methylcyclohexanol	511–600	saturation	pure	11	16	10.34	4.276	[66]	6(b)
Liquid density									
System s (pure)	T/K	P/kPa	x_1	$N_{s,p}^{\text{nest}}$	$N_{s,p}^{\text{tot}}$	%AAD	AAD/(kg/m ³)	Ref.	Fig.
cyclohexanol	299–600	saturation	pure	15	15	1.309	10.47	[66]	2(b)
1,3,5-triisopropylcyclohexane	278–343	83.0	pure	0	14	1.366	11.16	[89]	–
1-methylpropylcyclohexane	273–448	saturation	pure	0	12	4.931	31.09	[90]	5(b)
1-isopropylcyclohexane	223–423	saturation	pure	0	12	3.904	22.96	[90]	5(b)
menthol	310–660	saturation	pure	17	19	10.53	75.34	[66]	6(b)
2-methylcyclohexanol	240–600	saturation	pure	16	19	3.734	24.98	[66]	6(b)
Vaporisation enthalpy									
System s (pure)	T/K	P	x_1	$N_{s,p}^{\text{nest}}$	$N_{s,p}^{\text{tot}}$	%AAD	AAD/(kJ/mol)	Ref.	Fig.
cyclohexanol	300–600	saturation	pure	14	14	5.883	2.210	[66]	2(c)
1-isopropylcyclohexane	213–573	saturation	pure	0	10	7.227	2.650	[90]	5(c)
1-methylpropylcyclohexane	273–623	saturation	pure	0	11	8.784	3.401	[90]	5(c)
menthol	298–623	saturation	pure	0	12	10.59	5.556	[90]	6(c)
2-methylcyclohexanol	260–600	saturation	pure	0	18	4.555	1.614	[66]	6(c)
Tx diagram									
System s (1 + 2)	T	P/kPa	x_1	$N_{s,p}^{\text{nest}}$	$N_{s,p}^{\text{tot}}$	%AAD	AAD/K	Ref.	Fig.
cyclohexanol + cyclohexane	T_{bub}	101.3	0.11–0.86	7	7	0.3049	1.134	[67]	3(a)
	T_{dew}	101.3	0.01–0.16	7	7	1.252	4.684	[67]	3(a)
cyclohexanol + nonane	T_{bub}	26.7–80.0	0.00–1.00	39	39	0.2960	1.181	[75]	4(a)
cyclohexanol + dodecane	T_{SLE}	101.3	0.00–1.00	0	41	0.4201	1.125	[74,76]	4(d)
methylcyclohexane + 3-methylpentane	T_{bub}	101.3	0.00–1.00	23	23	1.795	6.380	[85]	–
	T_{dew}	101.3	0.00–1.00	23	23	1.929	6.806	[85]	–
cyclohexane + methanol	T_{bub}	101.3	0.00–1.00	14	28	0.4850	1.595	[93,94]	8(a,f)
	T_{dew}	101.3	0.00–1.00	14	28	0.2603	0.8533	[93,94]	8(a,f)
	T_{LLE}	101.3	0.11–0.93	0	86	–	–	[95]	8(a,f)
	T_{SLE}	101.3	0.00–1.00	0	34	1.686	4.592	[95,96]	8(a,f)
cyclohexane + ethanol	T_{bub}	40–150	0.00–1.00	15	83	0.7595	2.555	[97,98]	8(b,f)
	T_{dew}	40–150	0.00–1.00	15	83	0.5656	1.911	[97,98]	8(b,f)
	T_{SLE}	101.3	0.92–1.00	0	9	0.5002	1.388	[99]	8(b,f)
cyclohexane + propan-1-ol	T_{bub}	101.3	0.00–1.00	0	42	0.5411	1.897	[100]	8(c,f)
	T_{dew}	101.3	0.00–1.00	0	42	0.4845	1.702	[100]	8(c,f)
	T_{SLE}	101.3	0.24–1.00	0	16	4.007	10.05	[99]	8(c,f)
cyclohexane + butan-1-ol	T_{bub}	101.3	0.00–1.00	0	16	0.4897	1.778	[101]	8(d,f)
	T_{dew}	101.3	0.00–1.00	0	16	0.2472	0.8986	[101]	8(d,f)
	T_{SLE}	101.3	0.05–1.00	0	15	1.095	2.723	[102]	8(d,f)
cyclohexane + pentan-1-ol	T_{bub}	101.3	0.93–0.99	0	13	0.0224	0.07922	[103]	8(e,f)
	T_{dew}	101.3	0.97–0.99	0	13	0.0539	0.1910	[103]	8(e,f)
	T_{SLE}	101.3	0.35–1.00	0	14	2.155	5.297	[74]	8(e,f)
cyclohexane + octan-1-ol	T_{bub}	101.3	0.94–0.99	0	9	0.0938	0.3328	[104]	–
	T_{dew}	101.3	0.99–1.00	0	9	0.0772	0.2736	[104]	–
methylcyclopentane + methanol	T_{bub}	101.3	0.00–1.00	0	45	0.6997	2.292	[105,106]	–
	T_{dew}	101.3	0.21–0.79	0	12	0.5169	1.705	[106]	–

(continued).

Table 7. Continued.

Tx diagram									
System <i>s</i> (1 + 2)	<i>T</i>	<i>P</i> /kPa	<i>x</i> ₁	<i>N</i> _{<i>s,p</i>} ^{est}	<i>N</i> _{<i>s,p</i>} ^{tot}	%AAD	AAD/K	Ref.	Fig.
methylcyclohexane + methanol	<i>T</i> _{bub}	101.3	0.00–1.00	0	13	0.5989	2.032	[107]	9(a)
	<i>T</i> _{dew}	101.3	0.00–1.00	0	13	1.344	4.514	[107]	9(a)
	<i>T</i> _{LLE}	101.3	0.13–0.87	76	76	–	–	[108,109]	9(a)
methylcyclohexane + ethanol	<i>T</i> _{bub}	101.3	0.00–1.00	12	24	1.349	4.719	[110]	9(a)
	<i>T</i> _{dew}	101.3	0.00–1.00	12	24	1.117	3.891	[110]	9(a)
methylcyclohexane + propan-1-ol	<i>T</i> _{bub}	101.3	0.00–1.00	0	23	1.488	5.381	[111]	9(a)
	<i>T</i> _{dew}	101.3	0.00–1.00	0	23	1.230	4.446	[111]	9(a)
methylcyclohexane + butan-1-ol	<i>T</i> _{bub}	101.3	0.00–1.00	0	27	1.273	4.746	[111]	9(a)
	<i>T</i> _{dew}	101.3	0.00–1.00	0	27	0.9645	3.590	[111]	9(a)
methylcyclohexane + pentan-1-ol	<i>T</i> _{az}	101.3	0.93	0	1	0.8808	3.290	[112]	9(a)
methylcyclohexane + heptan-1-ol	<i>T</i> _{SLE}	101.3	0.00–1.00	0	11	1.363	3.049	[113]	9(b)
cyclohexanol + methanol	<i>T</i> _{bub}	13.3–101.3	0.00–1.00	21	41	0.7236	2.735	[158,161]	12(a)
	<i>T</i> _{dew}	101.3	0.00–1.00	0	20	0.5327	1.949	[161]	12(a)
cyclohexanol + ethanol	<i>T</i> _{bub}	101.3	0.03–0.97	20	20	0.1886	0.7339	[159]	12(a)
	<i>T</i> _{dew}	101.3	0.00–0.72	20	20	0.1807	0.7100	[159]	12(a)
cyclohexanol + butan-1-ol	<i>T</i> _{bub}	97.1–101.3	0.11–0.88	0	25	0.1432	0.5823	[157,160]	12(a)
	<i>T</i> _{dew}	97.1	0.28–0.97	0	16	0.1916	0.7850	[157]	12(a)
cyclohexanol + pentan-1-ol	<i>T</i> _{bub}	101.3	0.10–0.91	0	9	0.1495	0.6308	[160]	12(a)
cyclohexane + butanone	<i>T</i> _{bub}	20–396	0.02–0.98	32	127	0.2141	0.7315	[167]	14(a)
	<i>T</i> _{dew}	20–396	0.06–0.92	32	127	0.1918	0.6502	[167]	14(a)
cyclohexanol + butanone	<i>T</i> _{bub}	96.7	0.14–0.92	16	16	0.6614	2.478	[175]	16(a)
	<i>T</i> _{dew}	96.7	0.01–0.59	16	16	0.8023	3.059	[175]	16(a)
cyclohexanol + hexan-2-one	<i>T</i> _{bub}	26.7–80.0	0.00–1.00	27	27	0.3907	1.556	[176]	16(b)
cyclohexanol + ethyl acetate	<i>T</i> _{bub}	101.3	0.00–1.00	9	19	0.3126	1.250	[181]	18(a)
	<i>T</i> _{dew}	101.3	0.00–1.00	9	19	0.9001	3.458	[181]	18(a)
cyclohexanol + benzene	<i>T</i> _{SLE}	101.3	0.00–1.00	0	41	3.007	7.656	[74]	19(c)
cyclohexanol + propylbenzene	<i>T</i> _{az}	101.3	0.44	0	1	0.0003060	0.001308	[182]	–
cyclohexanol + water	<i>T</i> _{bub}	101.3	0.00–1.00	11	11	0.4622	1.812	[187]	20(a)
	<i>T</i> _{dew}	101.3	0.00–1.00	11	11	0.5773	2.230	[187]	20(a)
	<i>T</i> _{LLE}	101.3	0.01–0.62	0	40	–	–	[188]	20(a)
	<i>T</i> _{SLE}	101.3	0.00–0.01	0	9	0.002595	0.007073	[189]	20(a)
cyclopentanol + water	<i>T</i> _{bub}	101.3	0.00–1.00	11	11	0.4069	1.560	[194]	20(d)
	<i>T</i> _{dew}	101.3	0.00–1.00	11	11	0.2332	0.8891	[194]	20(d)
	<i>T</i> _{LLE}	101.3	0.00–1.00	0	18	–	–	[195]	20(d)
2-methylpropane + carbon dioxide	<i>T</i> _{SLE}	101.3	0.99–1.00	0	2	15.64	18.44	[201]	21(c)
2-methylbutane + carbon dioxide	<i>T</i> _{SLE}	101.3	0.04–1.00	0	20	8.714	13.33	[202]	21(c)
menthol + 2-methyl-1-propanol	<i>T</i> _{bub}	98.3	0.00–0.06	0	6	0.3817	1.454	[206]	23(a)
menthol + ethyl acetate	<i>T</i> _{bub}	97.9	0.01–0.06	0	14	0.4062	1.417	[206]	23(a)
menthol + 1,2-ethanediol	<i>T</i> _{az}	101.3	0.27	0	1	1.035	4.779	[207]	23(b)
menthol + 1,3,5-triethylbenzene	<i>T</i> _{az}	101.3	0.46	0	1	3.276	15.94	[182]	23(b)
menthol + water	<i>T</i> _{LLE}	101.3	0.00016	0	1	–	–	[209]	23(c)
menthol + ethanol	<i>T</i> _{SLE}	101.3	0.65	0	1	0.5992	1.756	[208]	23(d)
menthol + dodecan-1-ol	<i>T</i> _{SLE}	101.3	0.28–0.99	0	24	0.4505	1.328	[12]	23(d)
Px diagram									
System <i>s</i> (1 + 2)	<i>T</i> /K	<i>P</i>	<i>x</i> ₁	<i>N</i> _{<i>s,p</i>} ^{est}	<i>N</i> _{<i>s,p</i>} ^{tot}	%AAD	AAD/kPa	Ref.	Fig.
cyclohexanol + cyclohexane	308–318	<i>P</i> _{bub}	0.00–0.68	23	23	2.153	0.4449	[68]	3(a)
	308–318	<i>P</i> _{dew}	0.00–0.02	23	23	1.523	0.3189	[68]	3(a)
cyclohexanol + heptane	303–373	<i>P</i> _{bub}	0.00–1.00	40	87	3.734	0.7525	[77]	4(b)
methylcyclohexane + 2,4-dimethylpentane	473–503	<i>P</i> _{bub}	0.00–1.00	18	18	16.01	227.0	[86]	–
cyclopentane + methanol	473–503	<i>P</i> _{dew}	0.00–1.00	18	18	17.83	255.2	[86]	–
	288	<i>P</i> _{bub}	0.00–1.00	0	11	21.78	5.011	[114]	–
cyclohexane + methanol	298–328	<i>P</i> _{bub}	0.00–1.00	13	33	3.941	2.433	[93,115]	10(a)
	298–328	<i>P</i> _{dew}	0.00–1.00	13	33	2.266	1.440	[93,115]	10(a)
cyclohexane + ethanol	323–508	<i>P</i> _{bub}	0.02–1.00	13	62	8.929	120.2	[116–118]	10(a)
	323–508	<i>P</i> _{dew}	0.18–1.00	13	62	7.674	102.6	[116–118]	10(a)
cyclohexane + propan-1-ol	298–333	<i>P</i> _{bub}	0.00–1.00	0	68	7.972	3.424	[119,216]	10(a)
	298–333	<i>P</i> _{dew}	0.00–1.00	0	68	7.530	3.358	[119,216]	10(a)
cyclohexane + butan-1-ol	298	<i>P</i> _{bub}	0.05–0.98	0	14	5.459	0.4592	[119]	10(a)
	298	<i>P</i> _{dew}	0.74–0.97	0	14	7.440	0.8435	[119]	10(a)
methylcyclohexane + methanol	333	<i>P</i> _{bub}	0.00–1.00	15	30	8.347	7.605	[120]	10(b)
	333	<i>P</i> _{dew}	0.00–1.00	15	30	9.009	8.559	[120]	10(b)
methylcyclohexane + ethanol	308–328	<i>P</i> _{bub}	0.03–0.95	16	16	16.90	5.691	[121]	–
	308–328	<i>P</i> _{dew}	0.16–0.54	16	16	14.92	5.064	[121]	–
methylcyclohexane + propan-1-ol	333	<i>P</i> _{bub}	0.00–1.00	0	13	16.05	5.728	[122]	10(b)
methylcyclohexane + butan-1-ol	333	<i>P</i> _{dew}	0.00–1.00	0	13	14.31	5.138	[122]	10(b)
	333	<i>P</i> _{bub}	0.00–1.00	0	14	15.05	3.871	[122]	10(b)
	333	<i>P</i> _{dew}	0.00–1.00	0	14	12.05	3.260	[122]	10(b)

(continued).

Table 7. Continued.

<i>Px</i> diagram									
System <i>s</i> (1 + 2)	<i>T</i> /K	<i>P</i>	<i>x</i> ₁	<i>N</i> _{<i>s,p</i>} ^{est}	<i>N</i> _{<i>s,p</i>} ^{tot}	%AAD	AAD/kPa	Ref.	Fig.
ethylcyclohexane + ethanol	298–363	<i>P</i> _{bub}	0.01–0.03	0	22	2.915	2.092	[123]	–
	298–363	<i>P</i> _{dew}	0.02–0.06	0	22	2.810	2.169	[123]	–
cyclohexanol + methanol	293	<i>P</i> _{bub}	0.00–0.80	8	8	4.314	0.3637	[162]	12(b)
cyclohexane + butanone	323	<i>P</i> _{bub}	0.00–1.00	16	32	2.584	1.170	[169]	–
	323	<i>P</i> _{dew}	0.00–1.00	16	32	2.377	1.088	[169]	–
methylcyclohexane + acetone	318	<i>P</i> _{bub}	0.00–1.00	18	19	2.684	1.004	[168]	14(b)
ethylcyclohexane + butanone	298–363	<i>P</i> _{bub}	0.01–0.03	0	12	3.684	1.298	[123]	–
	298–363	<i>P</i> _{dew}	0.00–0.02	0	12	3.683	1.298	[123]	–
cyclohexanol + acetone	298	<i>P</i> _{bub}	0.04–0.95	12	23	1.883	0.2981	[177]	16(c)
	298	<i>P</i> _{dew}	0.00–0.03	12	23	4.430	0.6523	[177]	16(c)
cyclopentanol + acetone	298	<i>P</i> _{bub}	0.06–0.86	0	13	6.340	0.9316	[178]	–
	298	<i>P</i> _{dew}	0.00–0.03	0	13	17.31	3.413	[178]	–
methylcyclohexane	330–350	<i>P</i> _{bub}	0.00–1.00	34	34	7.214	4.165	[180]	17(a)
+ ethyl acetate	330–350	<i>P</i> _{dew}	0.00–1.00	34	34	7.895	4.721	[180]	17(a)
methylcyclohexane	345–365	<i>P</i> _{bub}	0.00–1.00	34	34	8.651	5.444	[180]	17(b)
+ propyl acetate	345–365	<i>P</i> _{dew}	0.00–1.00	34	34	8.340	5.262	[180]	17(b)
methylcyclohexane	350–370	<i>P</i> _{bub}	0.00–1.00	30	30	8.051	4.736	[180]	17(c)
+ butyl acetate	350–370	<i>P</i> _{dew}	0.00–1.00	30	30	7.006	4.257	[180]	17(c)
cyclohexanol + ethyl acetate	293	<i>P</i> _{bub}	0.00–0.80	9	9	1.558	0.09606	[162]	18(b)
2-methylcyclohexanol	288	<i>P</i> _{bub}	0.22–0.67	7	7	7.038	0.2719	[217]	–
+ ethyl acetate									
cyclohexanol + benzene	293	<i>P</i> _{bub}	0.00–0.88	10	10	18.92	0.9074	[162]	19(a)
cyclohexanol + toluene	333–363	<i>P</i> _{bub}	0.00–0.81	15	15	7.825	2.168	[183]	19(b)
	333–363	<i>P</i> _{dew}	0.00–0.23	15	15	5.051	1.458	[183]	19(b)
2-methylcyclohexanol + benzene	293	<i>P</i> _{bub}	0.00–0.80	0	10	6.952	0.5653	[162]	19(a)
cyclohexanol + water	363	<i>P</i> _{bub}	0.00–0.98	13	13	5.724	2.882	[190]	20(b)
	363	<i>P</i> _{dew}	0.02–0.57	13	13	6.893	2.896	[190]	20(b)
2-methylpropane	263–398	<i>P</i> _{bub}	0.12–1.00	10	82	2.624	76.52	[196–198]	21(a)
+ carbon dioxide	263–398	<i>P</i> _{dew}	0.02–1.00	0	82	4.353	150.7	[196–198]	21(a)
2-methylbutane	278–453	<i>P</i> _{bub}	0.00–1.00	0	75	3.056	81.91	[199,200]	21(b)
+ carbon dioxide	278–453	<i>P</i> _{dew}	0.00–1.00	0	75	7.336	200.9	[199,200]	21(b)
cyclohexanol + carbon dioxide	303–453	<i>P</i> _{bub}	0.36–0.98	11	91	31.96	1746	[203–205]	22
cyclohexanol + carbon dioxide	303–453	<i>P</i> _{dew}	0.00–0.16	11	34	12.77	1155	[205]	22
cyclohexanol + carbon dioxide	303–343	<i>P</i> _{LLE}	0.02–0.57	0	37	–	–	[203]	22
menthol + carbon dioxide	303–343	<i>P</i> _{bub}	0.00–0.43	0	126	29.76	3205	[11,210–213]	24
Composition									
System <i>s</i> (1 + 2)	<i>T</i> /K	<i>P</i> /kPa	<i>x</i> ₁	<i>N</i> _{<i>s,p</i>} ^{est}	<i>N</i> _{<i>s,p</i>} ^{tot}	%AAD	AAD/(mol/mol)	Ref.	Fig.
cyclohexanol + dodecane	264–260–298	101.3	<i>x</i> ₁ ^{sat}	0	41	21.69	0.08128	[74,76]	4(d)
cyclohexane + methanol	275–319	101.3	<i>x</i> ₁ ^{LLE}	0	43	325.6	0.5608	[95]	8(a,f)
	175–280	101.3	<i>x</i> ₁ ^{sat}	0	34	244.8	0.3536	[95,96]	8(a,f)
cyclohexane + ethanol	276–280	101.3	<i>x</i> ₁ ^{sat}	0	9	2.192	0.02079	[99]	8(b,f)
cyclohexane + propan-1-ol	228–280	101.3	<i>x</i> ₁ ^{sat}	0	16	23.32	0.1079	[99]	8(c,f)
cyclohexane + butan-1-ol	196–280	101.3	<i>x</i> ₁ ^{sat}	0	15	33.87	0.04326	[102]	8(d,f)
cyclohexane + pentan-1-ol	222–280	101.3	<i>x</i> ₁ ^{sat}	0	14	9.082	0.05064	[74]	8(e,f)
methylcyclohexane + methanol	288–318	101.3	<i>x</i> ₁ ^{LLE}	76	76	27.55	0.1861	[108,109]	9(a)
methylcyclohexane + heptan-1-ol	148–239	101.3	<i>x</i> ₁ ^{sat}	0	11	35.12	0.1520	[113]	9(b)
cyclohexanol + benzene	298–241–279	101.3	<i>x</i> ₁ ^{sat}	0	41	37.60	0.1294	[74]	19(c)
cyclohexanol + water	–	101.3	<i>x</i> ₁ ^{LLE}	0	40	50.81	0.08464	[188]	20(a)
	272–273	101.3	<i>x</i> ₁ ^{sat}	0	9	1.593	7.984 × 10 ^{–5}	[189]	20(a)
cyclopentanol + water	–	101.3	<i>x</i> ₁ ^{LLE}	0	18	100.7	0.02961	[195]	20(d)
2-methylpropane	115–121	101.3	<i>x</i> ₁ ^{sat}	0	2	0.3228	0.003226	[201]	21(c)
+ carbon dioxide									
2-methylbutane	113–216	101.3	<i>x</i> ₁ ^{sat}	0	20	11.34	0.05211	[202]	21(c)
+ carbon dioxide									
menthol + water	310	101.3	<i>x</i> ₁ ^{LLE}	0	1	79.58	0.0001237	[209]	23(b)
menthol + ethanol	293	101.3	<i>x</i> ₁ ^{sat}	0	1	3.681	0.02381	[208]	23(c)
menthol + dodecan-1-ol	297–282–316	101.3	<i>x</i> ₁ ^{sat}	0	24	6.797	0.03018	[12]	23(c)
Density of binary mixture									
System <i>s</i> (1 + 2)	<i>T</i> /K	<i>P</i> /kPa	<i>x</i> ₁	<i>N</i> _{<i>s,p</i>} ^{est}	<i>N</i> _{<i>s,p</i>} ^{tot}	%AAD	AAD/(kg/m ³)	Ref.	Fig.
cyclohexanol + cyclohexane	293–333	101.3	0.00–0.11	60	83	0.5166	4.315	[69–71]	3(c)
cyclohexane + methanol	279–303	101.3	0.00–1.00	23	45	0.6246	4.880	[124,125]	–
cyclohexane + ethanol	293–303	100.0	0.00–1.00	20	39	1.529	11.87	[126]	–
cyclohexane + propan-1-ol	293–303	100.0	0.00–1.00	0	39	1.174	9.236	[126]	–
cyclohexane + butan-1-ol	298	101.3	0.05–0.95	0	23	1.311	10.36	[127,128]	–
cyclohexane + pentan-1-ol	298	101.3	0.05–1.00	0	18	1.137	9.033	[129]	–
cyclohexane + hexan-1-ol	298	101.3	0.05–0.95	0	11	1.131	9.036	[127]	–

(continued).

Table 7. Continued.

Density of binary mixture									
System s (1 + 2)	T/K	P/kPa	x_1	$N_{s,p}^{est}$	$N_{s,p}^{tot}$	%AAD	AAD/(mol/mol)	Ref.	Fig.
cyclohexane + heptan-1-ol	303–306	101.3	0.00–1.00	0	18	0.9637	7.686	[130,131]	–
cyclohexane + octan-1-ol	298	101.3	0.05–0.95	0	13	1.033	8.290	[132]	–
cyclohexane + nonan-1-ol	293–333	101.3	0.88–0.99	0	54	0.1429	1.095	[133]	–
cyclohexane + decan-1-ol	293–333	101.3	0.20–0.99	0	58	0.2514	1.957	[133,134]	–
methylcyclohexane + methanol	303	101.3	0.00–1.00	0	11	0.6873	5.279	[135]	–
methylcyclohexane + ethanol	298–308	101.3	0.00–1.00	17	33	1.199	9.226	[136]	–
methylcyclohexane + propan-1-ol	298–308	101.3	0.00–1.00	0	33	0.5100	3.970	[136]	–
methylcyclohexane + butan-1-ol	298–308	101.3	0.00–1.00	0	33	0.8696	6.822	[136]	–
methylcyclohexane + pentan-1-ol	303	101.3	0.00–1.00	0	8	1.009	7.962	[137]	–
methylcyclohexane + hexan-1-ol	303	101.3	0.00–1.00	0	8	0.9025	7.155	[137]	–
methylcyclohexane + heptan-1-ol	298–303	101.3	0.00–1.00	0	27	0.8449	6.748	[138,139]	–
cyclohexane + butanone	293–303	101.3	0.00–1.00	13	39	0.3045	2.395	[171]	15(a)
cyclohexane + pentan-2-one	293–303	101.3	0.00–1.00	0	39	0.4546	3.586	[171]	15(a)
methylcyclohexane + butanone	298	101.3	0.00–1.00	12	24	0.3554	2.756	[172]	15(a)
methylcyclopentane + acetone	293–303	101.3	0.00–1.00	20	39	0.8612	6.478	[170]	–
cyclohexanol + benzene	293–333	101.3	0.51–1.00	0	72	1.358	11.80	[70]	–
cyclohexanol + toluene	298	101.3	0.00–1.00	0	10	0.7251	6.683	[183]	–
2-methylcyclohexanol + benzene	298	101.3	0.00–0.04	0	4	1.971	17.25	[184]	–
cyclohexanol + water	298	101.3	0.55–1.00	0	21	2.324	22.03	[191]	–
Speed of sound									
System s (1 + 2)	T/K	P/kPa	x_1	$N_{s,p}^{est}$	$N_{s,p}^{tot}$	%AAD	AAD/(m/s)	Ref.	Fig.
cyclohexanol + cyclohexane	298–323	101.3	0.00–1.00	27	27	3.884	50.51	[72]	–
menthol	307–413	101.3	pure	0	6	2.652	29.86	[92]	7(a)
methylcyclopentane + acetone	293–303	101.3	0.00–1.00	20	39	3.467	39.97	[170]	–
Isobaric heat capacity									
System s (1 + 2)	T/K	P	x_1	$N_{s,p}^{est}$	$N_{s,p}^{tot}$	%AAD	AAD/(J/(mol.K))	Ref.	Fig.
menthol	333–633	saturation	pure	0	11	11.45	46.99	[90]	7(b)
Excess molar enthalpy									
System s (1 + 2)	T/K	P	x_1	$N_{s,p}^{est}$	$N_{s,p}^{tot}$	%AAD	AAD/(J/mol)	Ref.	Fig.
cyclohexanol + cyclohexane	298	101.3	0.05–0.97	11	32	7.838	35.60	[73]	3(d)
cyclohexanol + hexane	298–308	100.0	0.05–0.98	18	50	24.30	123.7	[78]	4(c)
cyclohexanol + heptane	298–303	101.3	0.00–0.90	11	31	23.59	111.7	[79–81]	4(c)
cyclohexanol + octane	298	101.3	0.10–0.88	11	11	25.29	152.8	[80]	4(c)
cyclohexanol + nonane	298–318	101.3	0.10–0.93	11	21	25.16	244.9	[82,83]	4(c)
cyclohexanol + decane	298–318	101.3	0.09–0.92	12	23	15.69	135.4	[80,84]	4(c)
cyclohexanol + dodecane	298–308	100.0	0.04–0.98	14	42	13.00	91.70	[78]	4(c)
cyclopentane + methanol	298	101.3	0.07–0.92	0	13	21.68	96.16	[140]	–
cyclohexane + methanol	298–318	101.3	0.01–0.99	21	63	17.90	53.73	[141]	11(a)
cyclohexane + ethanol	283–363	40.0–101.3	0.02–0.97	25	186	15.47	76.12	[140,142–146]	11(a)
cyclohexane + propan-1-ol	288–308	101.3	0.04–0.98	0	162	14.41	57.32	[119,140]	11(a)
								[144–148,165]	
cyclohexane + butan-1-ol	298	101.3	0.05–0.97	0	44	8.984	40.54	[144,149]	11(a)
cyclohexane + pentan-1-ol	298	101.3	0.10–0.90	0	20	8.986	43.69	[150,151]	11(a)
cyclohexane + hexan-1-ol	298	101.3	0.06–0.98	0	34	12.71	58.00	[152,153]	11(a)
cyclohexane + heptan-1-ol	298	101.3	0.13–0.92	0	10	12.69	59.79	[151]	11(a)
cyclohexane + octan-1-ol	298	101.3	0.05–0.98	0	20	13.87	54.98	[144]	11(a)
cyclohexane + nonan-1-ol	298	101.3	0.15–0.94	0	9	15.19	71.37	[151]	11(a)
cyclohexane + decan-1-ol	298	101.3	0.04–0.98	0	32	11.89	51.91	[119,151,165]	11(a)
methylcyclohexane + methanol	298	101.0	0.02–0.97	12	12	54.65	182.2	[154]	11(b)
methylcyclohexane + ethanol	298–318	101.3	0.10–0.90	17	33	24.54	141.3	[155]	11(b)
methylcyclohexane + propan-1-ol	298–313	100.0	0.05–0.95	0	37	13.07	76.38	[148]	11(b)
methylcyclohexane + butan-1-ol	298	101.3	0.06–0.98	0	21	14.95	67.53	[166]	11(b)
methylcyclohexane + pentan-1-ol	323	101.3	0.05–0.95	0	20	9.101	61.88	[156]	–
methylcyclohexane + hexan-1-ol	298	101.3	0.11–0.98	0	34	20.91	92.30	[166]	11(b)
methylcyclohexane + heptan-1-ol	298	101.3	0.08–0.96	0	21	20.30	82.93	[166]	11(b)
methylcyclohexane + octan-1-ol	298	101.3	0.07–0.99	0	23	16.98	63.72	[166]	11(b)
cyclohexanol + methanol	300	101.3	0.07–0.92	10	10	2.678	4.033	[163]	12(c)
cyclohexanol + ethanol	300	101.3	0.09–0.91	10	10	2.758	2.889	[163]	12(c)
cyclohexanol + propan-1-ol	300	101.3	0.08–0.90	11	11	2.198	1.454	[163]	12(c)
cyclohexanol + butan-1-ol	300	101.3	0.10–0.91	0	13	55.37	46.60	[163]	12(c)
cyclohexanol + hexan-1-ol	298–318	101.3	0.16–0.83	0	19	92.84	129.4	[83,164]	–
cyclohexanol + propan-2-ol	300	101.3	0.08–0.91	9	9	36.94	48.62	[163]	13
cyclohexanol + butan-2-ol	300	101.3	0.08–0.92	15	15	17.47	17.99	[163]	13
cyclohexane + butanone	298–318	101.3	0.03–0.97	15	60	12.16	89.93	[167]	15(b)
cyclohexane + pentan-2-one	298	101.0	0.10–0.90	0	10	12.94	110.6	[173]	15(b)
methylcyclohexane + butanone	298	101.3	0.03–0.98	11	21	17.64	110.2	[174]	15(b)
cyclohexanol + acetone	298	101.3	0.03–0.94	10	19	5.918	77.73	[177]	16(d)
cyclohexanol + hexan-2-one	318	101.3	0.18–0.85	10	10	1.641	21.14	[179]	16(d)

(continued).

Table 7. Continued.

Excess molar enthalpy System s (1 + 2)	T/K	P/kPa	x_1	$N_{s,p}^{est}$	$N_{s,p}^{tot}$	%AAD	AAD/(m/s)	Ref.	Fig.
cyclopentanol + acetone	298	101.3	0.07–0.87	0	16	27.04	404.3	[178]	–
cyclohexanol + benzene	298	101.3	0.00–0.97	10	10	10.91	31.57	[185]	19(d)
cyclohexanol + toluene	303–323	101.3	0.03–0.97	24	47	25.34	234.6	[186]	–
cyclohexanol + water	298	101.3	0.10–0.90	17	35	40.71	32.32	[192]	20(c)
cyclopentanol + water	298	101.3	0.00–0.01	5	21	72.14	47.06	[193]	–

Notes: $N_{s,p}^{est}$ is the number of experimental data points used in parameter estimation, and $N_{s,p}^{tot}$ the number of experimental data points used to calculate %AAD, p and AAD, p , for system s and property p .

for cyclohexane + pentan-1-ol (Figure 8(f)). The SAFT- γ Mie calculations are seen to describe this varied phase behaviour in good agreement with the data.

In Figure 9(a), we show the isobaric phase diagrams at atmospheric pressure for mixtures of methylcyclohexane + methanol, ethanol, propan-1-ol, butan-1-ol, and pentan-1-ol. There are azeotropes in the VLE of these mixtures, and LLE in the methylcyclohexane + methanol mixture, as can be seen in the figures. SLE data are available for methylcyclohexane + heptan-1-ol, as shown in Figure 9(b), and excellent agreement is apparent. The corresponding %AAD is 35.12% for the SLE compositions, while the %AAD is only 1.363% for the corresponding SLE temperatures. Such a difference is due to the

shape of the SLE curve in the phase diagram: the variation in temperature is small from $x_{\text{methylcyclohexane}} = 0.0$ to 0.9 (about 19 K, compared with a temperature scale of hundreds of Kelvin), such that a small deviation in temperature (AAD = 3.049 K) corresponds to a large deviation in $x_{\text{methylcyclohexane}}$ (AAD = 0.1520). Isothermal VLE for cyclohexane + 1-alcohols at 298.15 K and methylcyclohexane + 1-alcohols at 333.15 K are shown in Figures 10(a,b), respectively. The agreement between the model prediction and experimental data is very good in terms of the overall shape of the bubble- and dew-pressure curves, as well as in the prediction of the azeotrope compositions and pressures. %AADs are small for the single-phase density of these mixtures (cf.

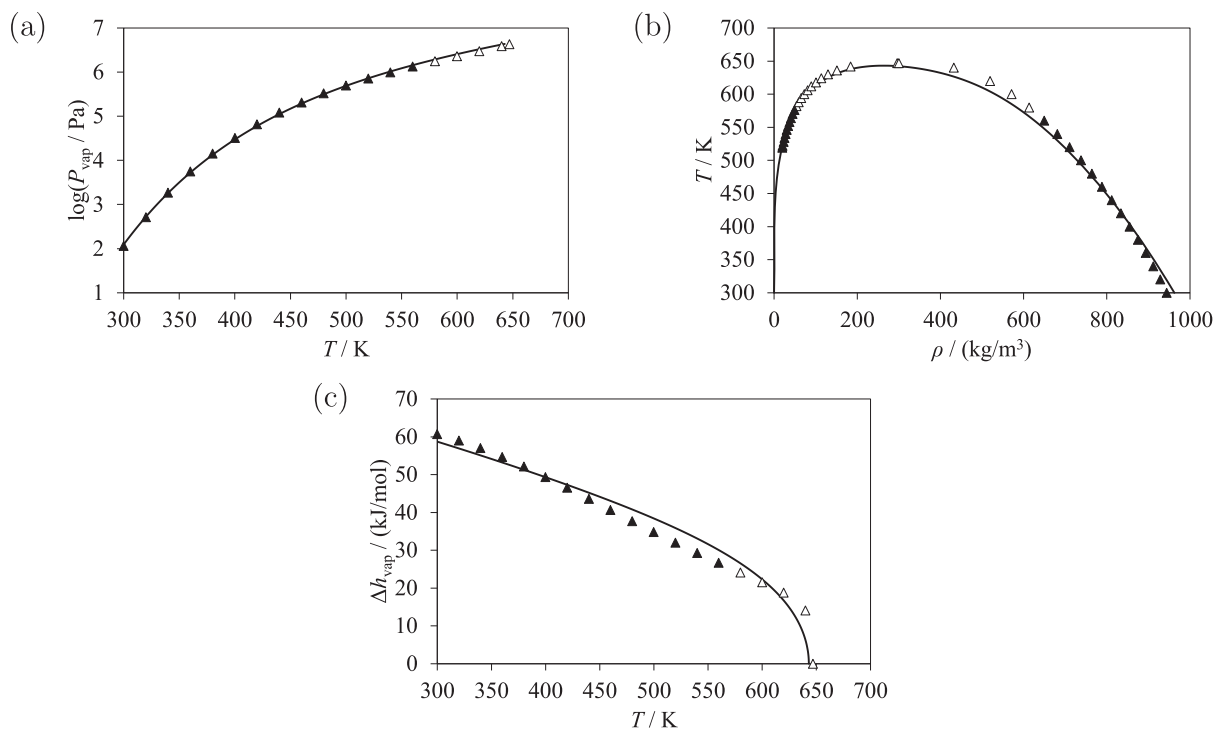


Figure 2. Selected thermodynamic properties of cyclohexanol. The curves represent the calculations with SAFT- γ Mie. NIST correlated experimental data [66] used in the estimation of group-interaction parameters are represented with filled symbols and those not used with open symbols. (a) Vapour pressure. (b) Saturation temperature–density diagram. (c) Vaporisation enthalpy. Thermodynamic conditions and accuracy are detailed in Table 7.

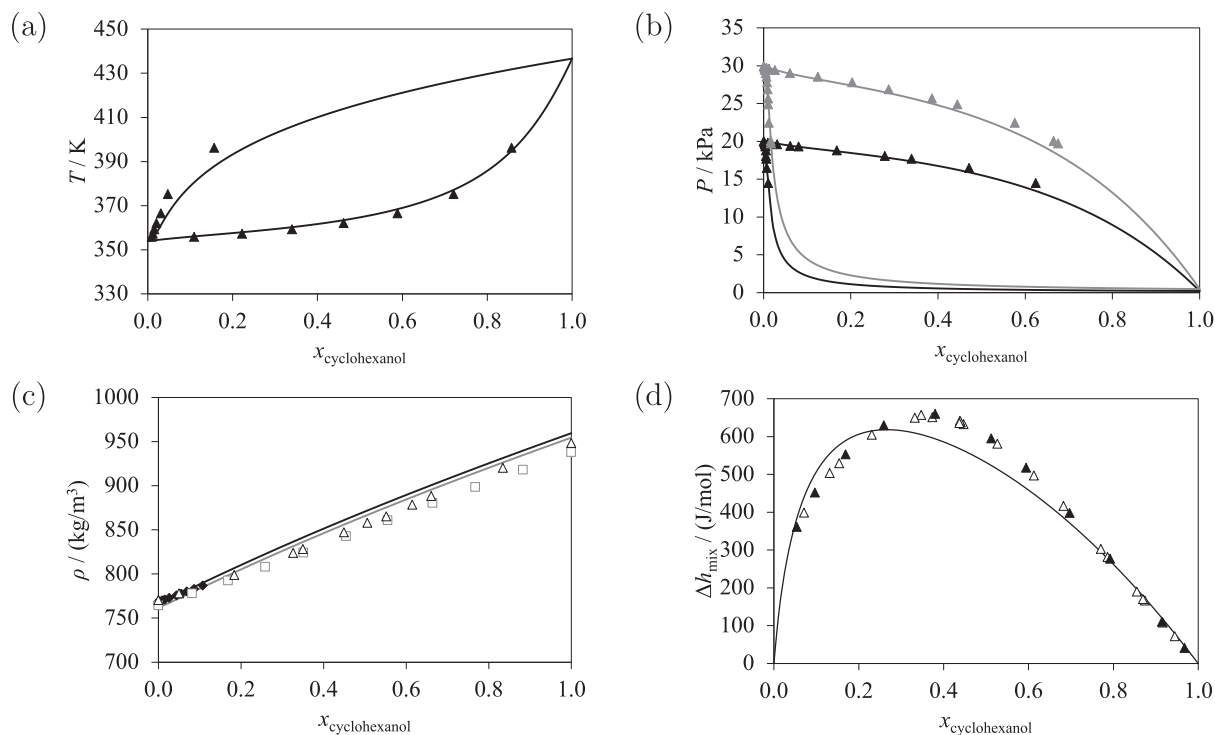


Figure 3. Selected thermodynamic properties of cyclohexanol + cyclohexane. The curves represent the calculations with SAFT- γ Mie. Experimental data used in the estimation of group-interaction parameters are represented with filled symbols and those not used with open symbols. (a) Isobaric vapour–liquid equilibrium at atmospheric pressure, with experimental data for bubble and dew temperatures [67]. (b) Isothermal vapour–liquid equilibria at 308.15 K (black) and 318.15 K (dark grey), with experimental data for bubble and dew pressures [68]. (c) Density at 303.15 K (black) and 308.15 K (dark grey), and at atmospheric pressure, with experimental data represented by triangles [69], diamonds [70], and squares [71]. (d) Excess molar enthalpy at 298.15 K and atmospheric pressure, with experimental data represented with triangles [73]. Thermodynamic conditions and accuracy are detailed in Table 7.

Table 7): the largest deviation is only 1.529% for cyclohexane + ethanol. Many sources report experimental data of excess molar enthalpy for these systems [119,140–156]. We note that the excess molar enthalpy for cyclohexane + 1-alcohols (from methanol to decan-1-ol) is always less than 1 kJ/mol (at 298.15 K and atmospheric pressure), cf. Figure 11(a). Given the scattering of experimental data and the small values of this property, the agreement obtained between calculations and experiments can be deemed very good. Similar features are found for mixtures of methylcyclohexane + 1-alcohols (Figure 11(b)), which also exhibit good overall agreement. The largest %AAD is 54.65% for the case of methylcyclohexane + methanol, which corresponds to an absolute deviation of only 182.2 J/mol.

Comparison between the SAFT- γ Mie calculations and experimental data for mixtures of cyclohexanol + 1-alcohols can be found in Figure 12. As can be seen, excellent agreement is obtained for the isobaric VLE at atmospheric pressure for cyclohexanol + methanol, ethanol, butan-1-ol, and pentan-1-ol (Figure 12(a)), as well as for the bubble pressure at 293.15 K for cyclohexanol + methanol (Figure 12(b)). The corresponding

%AADs are smaller than 1% for the isobaric VLE mentioned, and are only 4.314% for the bubble pressure of cyclohexanol + methanol. No azeotrope is found for these mixtures and excess molar enthalpies are small (less than 250 J/mol, as shown in Figure 12(c)). Excellent agreement is also obtained for the excess molar enthalpy of cyclohexanol + methanol, ethanol, and propan-1-ol (Figure 12(c)). In the case of cyclohexanol + butan-1-ol, the predicted excess enthalpy follows a trend of decreasing value for an increasing chain length of the alcohol, while we note that the experimental data [163] reported for this mixture do not follow this trend. The AADs for cyclohexanol + methanol, ethanol, and propan-1-ol are even smaller: 4.033 J/mol, 2.889 J/mol, and 1.454 J/mol, respectively. The corresponding AAD for cyclohexanol + butan-1-ol is 46.60 J/mol.

2.5. Cyclic alcohols + 2-alcohols: cCHOH-CHOH interactions

The new cCHOH group defined in the current work (for cyclic compounds) and the CHOH group presented in previous work [37] (for secondary alcohols with

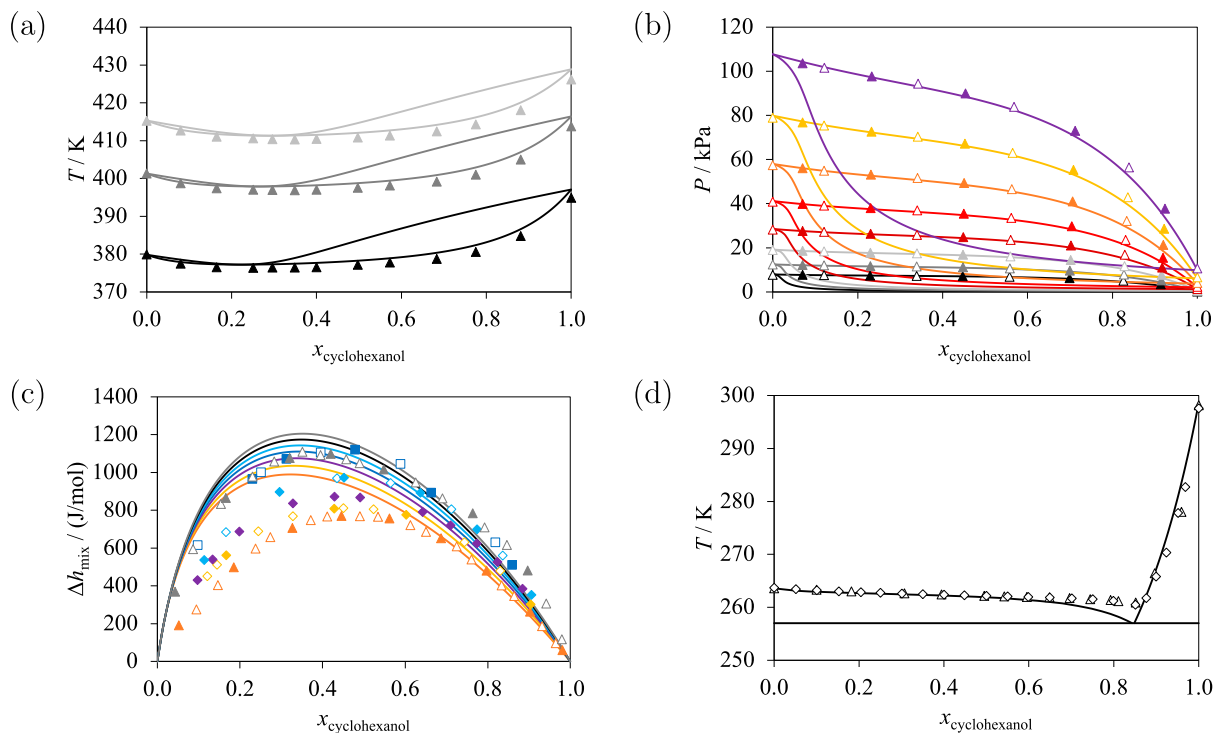


Figure 4. Selected thermodynamic properties of cyclohexanol + *n*-alkanes. The curves represent the calculations with SAFT- γ Mie. Experimental data used in the estimation of group-interaction parameters are represented with filled symbols and those not used with open symbols. (a) Isobaric vapour-liquid equilibria of cyclohexanol + *n*-nonane at 26.7 kPa (black), 53.3 kPa (dark grey), and 80.0 kPa (light grey), with experimental data for bubble temperatures [75]. (b) Isothermal vapour-liquid equilibria cyclohexanol + *n*-heptane at 303.15 K (black), 313.15 K (dark grey), 323.15 K (light grey), 333.15 K (dark red), 343.15 K (red), 353.15 K (orange), 363.15 K (yellow), and 373.15 K (purple), with experimental data for bubble pressures [77]. (c) Excess molar enthalpy at 298.15 K and atmospheric pressure for cyclohexanol + linear alkanes: *n*-hexane (orange), *n*-heptane (yellow), *n*-octane (purple), *n*-nonane (dark blue), *n*-decane (light blue), *n*-undecane (black), and *n*-dodecane (dark grey), with experimental data for *n*-hexane [78], *n*-heptane [80], *n*-octane [80], *n*-nonane [82], *n*-decane [80], and *n*-dodecane [78]. (d) Isobaric solid-liquid equilibria at atmospheric pressure of cyclohexanol + *n*-dodecane, with experimental data represented with triangles [76] and diamonds [74]. Thermodynamic conditions and accuracy are detailed in Table 7.

linear chains joined by the CHOH group) both include two e_1 sites and one H site, but are otherwise modelled with different parameters. We use experimental data to refine the unlike $\varepsilon_{\text{cCHOH-CHOH}}$ energy parameter, and use combining rules for $\varepsilon_{\text{cCHOH-CHOH},e_1-\text{H}}^{\text{HB}}$, $K_{\text{cCHOH-CHOH},e_1-\text{H}}^{\text{HB}}$, $\varepsilon_{\text{cCHOH-CHOH},\text{H}-e_1}^{\text{HB}}$, and $K_{\text{cCHOH-CHOH},\text{H}-e_1}^{\text{HB}}$, due to the limited experimental data available. Only excess molar enthalpy data is found in the literature [163], for cyclohexanol + propan-2-ol and cyclohexanol + butan-2-ol, at 300 K and atmospheric pressure.

Experimental values are small for those two mixtures (Figure 13): the highest value is 194.9 J/mol at $x_{\text{cyclohexanol}} = 0.5462$ for cyclohexanol + propan-2-ol [163]. With SAFT- γ Mie, the excess molar enthalpy is slightly overestimated for cyclohexanol + propan-2-ol (with AAD = 48.62 J/mol) and underestimated for cyclohexanol + butan-2-ol (with AAD = 17.99 J/mol), but with good overall agreement with experiments considering the small range of excess molar enthalpy values.

2.6. Alkylcycloalkanes and cyclic alcohols + 2-ketones: $\text{cCH}_2\text{-CH}_3\text{CO}$, $\text{cCH-CH}_3\text{COCH}_3$, $\text{cCH-CH}_3\text{CO}$, $\text{cCHOH-CH}_3\text{COCH}_3$, and $\text{cCHOH-CH}_3\text{CO}$ interactions

Acetone is represented by a single CH_3COCH_3 molecular group [53], and other 2-ketones are represented by a CH_3CO group [39]. The parameters optimised here are $\varepsilon_{\text{cCH}_2\text{-CH}_3\text{CO}}$ for cycloalkanes + 2-ketones, $\varepsilon_{\text{cCH-CH}_3\text{COCH}_3}$ for alkylcycloalkanes + acetone, and $\varepsilon_{\text{cCH-CH}_3\text{CO}}$ for alkylcycloalkanes + 2-ketones. These parameters are transferred to cyclic alcohols + acetone and cyclic alcohols + 2-ketones, and the related additional parameters characterised here are $\varepsilon_{\text{cCHOH-CH}_3\text{COCH}_3}$, $\varepsilon_{\text{cCHOH-CH}_3\text{COCH}_3,e_1-\text{H}}^{\text{HB}}$, $K_{\text{cCHOH-CH}_3\text{COCH}_3,e_1-\text{H}}^{\text{HB}}$, $\varepsilon_{\text{cCHOH-CH}_3\text{COCH}_3,\text{H}-e_1}^{\text{HB}}$, $K_{\text{cCHOH-CH}_3\text{COCH}_3,\text{H}-e_1}^{\text{HB}}$, $\varepsilon_{\text{cCHOH-CH}_3\text{CO}}$, $\varepsilon_{\text{cCHOH-CH}_3\text{CO},\text{H}-e_1}^{\text{HB}}$, and $K_{\text{cCHOH-CH}_3\text{CO},\text{H}-e_1}^{\text{HB}}$.

For cyclic alkanes + 2-ketones, we consider isobaric-VLE [167], isothermal-VLE [123,168,169], density

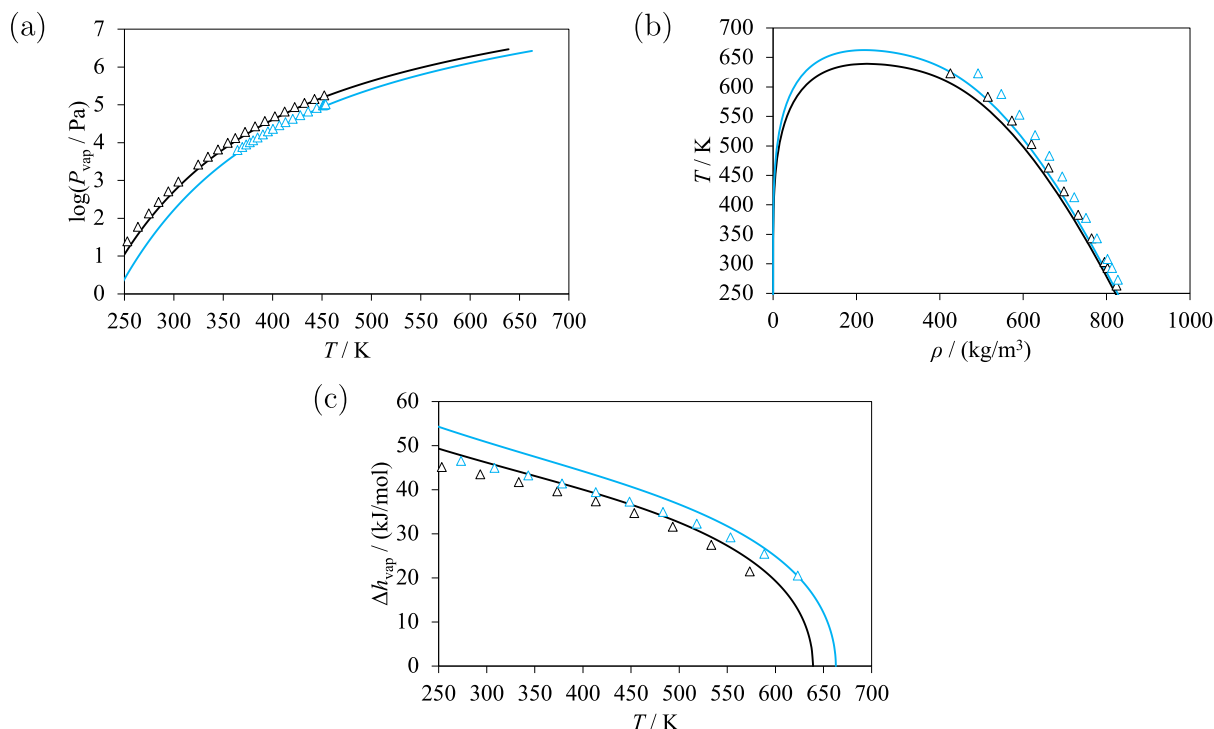


Figure 5. Selected thermodynamic properties of 1-isopropylcyclohexane (black) and 1-methylpropylcyclohexane (blue). The curves represent the calculations with SAFT- γ Mie. Experimental data used in the estimation of group-interaction parameters are represented with filled symbols and those not used with open symbols. (a) Vapour pressure, with experimental data of 1-isopropylcyclohexane [87] and 1-methylpropylcyclohexane [88]. (b) Saturation temperature–density diagram, with experimental data of 1-isopropylcyclohexane [90] and 1-methylpropylcyclohexane [90]. (c) Vaporisation enthalpy, with experimental data of 1-isopropylcyclohexane [90] and 1-methylpropylcyclohexane [90]. Thermodynamic conditions and accuracy are detailed in Table 7.

[170–172], speed-of-sound [170], and excess-molar enthalpy [167,173,174] data. In particular, there are azeotropes in the phase diagrams of cyclohexane + butanone and methylcyclohexane + acetone at the thermodynamic conditions shown in Figure 14. Densities and excess molar enthalpies for cycloalkane + 2-ketone mixtures can be seen in Figure 15. For cyclohexanol + 2-ketone mixtures, we consider isobaric VLE [175,176], isothermal VLE [177,178], and excess molar enthalpy [177–179]; these are illustrated in Figure 16. No azeotrope is found for the cyclohexanol + 2-ketone mixtures.

Overall agreement between SAFT- γ Mie and experiments is excellent for mixtures of cycloalkanes + 2-ketones. For cyclohexane + butanone, azeotropes are predicted accurately; bubble and dew temperatures (Figure 14(a)) are correctly obtained for a large range of pressures (from 20.0 kPa to 395.6 kPa) with %AAD = 0.2141% and 0.1918%, respectively, and bubble and dew pressures at 323.15 K are also in excellent agreement with experiments, with %AAD = 2.584% and 2.377%, respectively. For methylcyclohexane + acetone, the %AAD for bubble pressure at 318.15 K (Figure 14(b)) is 2.684%, and the visual quality of prediction for the

azeotrope pressure and composition can be seen in the inset of Figure 14(b). Density and excess molar enthalpy at 298.15 K and atmospheric pressure for binary mixtures of cyclohexane + butanone, cyclohexane + pentan-2-one, and methylcyclohexane + butanone are shown in Figure 15(a,b). For these mixtures and properties, the trend found is consistent between SAFT- γ Mie calculations and experimental data. The agreement for the density of methylcyclopentane + acetone is found with %AAD = 0.8612% and AAD = 6.478 kg/m^3 , at atmospheric pressure and 293.15 K, 298.15 K, and 303.15 K.

Excellent agreement is also found for mixtures of cycloalkanes + cyclic alcohols. In Figure 16(a), we show the isobaric VLE of cyclohexanol + butanone at 96.7 kPa (%AAD = 0.6614% for bubble temperature and 0.8023% for dew temperature), and in Figure 16(b), we show the isobaric VLE of cyclohexanol + hexan-2-one at 26.7 kPa, 53.3 kPa, and 80.0 kPa (%AAD = 0.3907% for bubble temperature). Isothermal VLE at 298.15 K of cyclohexanol + acetone can be seen in Figure 16(c) (%AAD = 1.883% for bubble pressure and 4.430% for dew pressure). Excess molar enthalpies for mixtures of cyclohexanol + 2-ketones are collected in Figure 16(d)

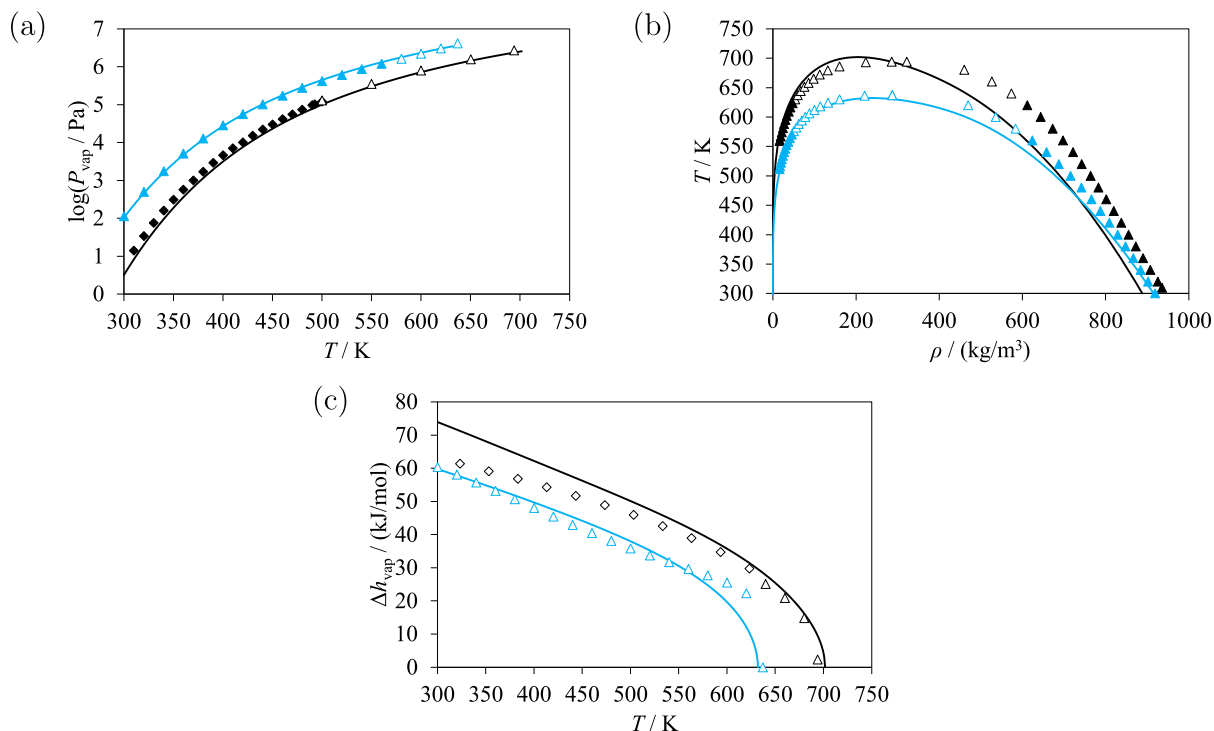


Figure 6. Saturation properties of menthol (black) and 2-methylcyclohexanol (blue). The curves represent the calculations with SAFT- γ Mie. Experimental and NIST correlated experimental data used in the estimation of group-interaction parameters are represented with filled symbols and those not used with open symbols. (a) Vapour pressure, with experimental data for menthol (triangles [66] and diamonds [91]) and 2-methylcyclohexanol [66]. (b) Saturation temperature–density diagram, with experimental data for menthol [66] and 2-methylcyclohexanol [66]. (c) Vaporisation enthalpy, with experimental data for menthol (triangles [66] and diamonds [90]) and 2-methylcyclohexanol [66]. Thermodynamic conditions and accuracy are detailed in Table 7.

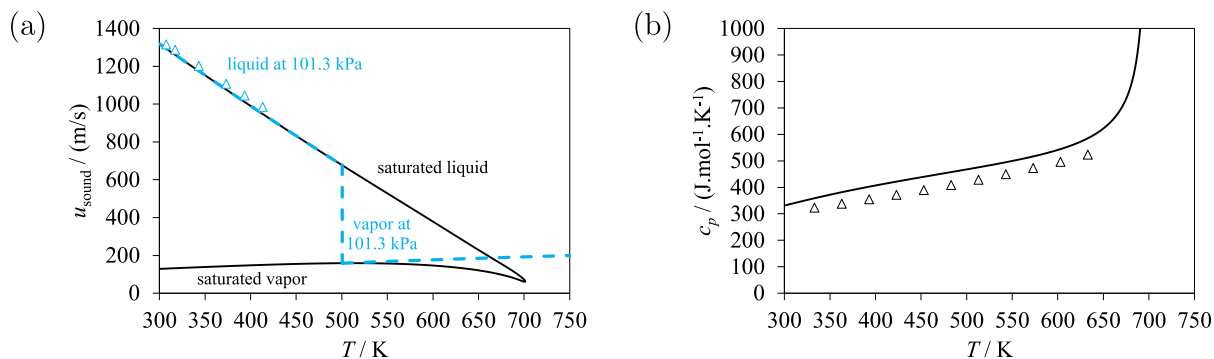


Figure 7. Selected second-order thermodynamic derivative properties of menthol. The curves represent the calculations with SAFT- γ Mie, and the open symbols represent reference data (not used in the estimation of group-interaction parameters). Black continuous curves represent the properties at saturation pressure and blue dashed curves represent the properties at atmospheric pressure. (a) Speed of sound, with experimental data at atmospheric pressure represented with blue triangles [92]. (b) Isobaric heat capacity, with experimental data for the liquid phase at saturation pressure represented with black triangles [90]. Thermodynamic conditions and accuracy are detailed in Table 7.

(the corresponding %AADs for these data are less than 6%).

2.7. Alkylcycloalkanes and cyclic alcohols + esters: $c\text{CH}-\text{COO}$ and $c\text{CHOH}-\text{COO}$ interactions

Linear esters are modelled in the SAFT- γ Mie approach using the COO group [36], which contains two e_1

sites. The $\varepsilon_{c\text{CH}-\text{COO}}$ unlike energy parameter is characterised first by considering mixtures of alkylcycloalkanes + esters. This interaction is then transferred to model mixtures of cyclic alcohols + esters and the additional group interaction parameters needed to model these mixtures ($\varepsilon_{c\text{CHOH}-\text{COO}}$, $\varepsilon_{c\text{CHOH}-\text{COO},\text{H}-e_1}^{\text{HB}}$, and $K_{c\text{CHOH}-\text{COO},\text{H}-e_1}^{\text{HB}}$) are also characterised here.

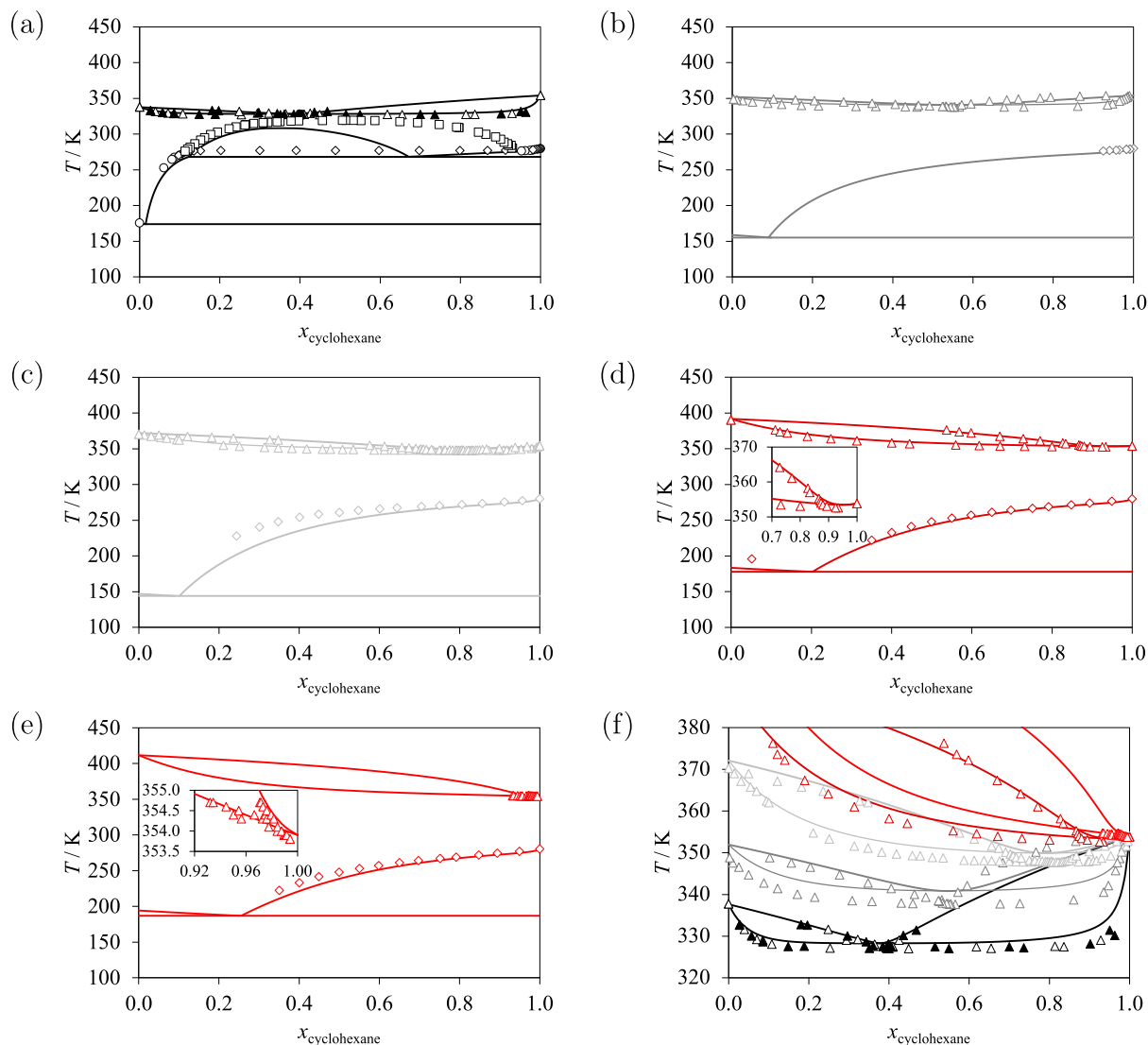


Figure 8. Isobaric phase diagrams of cyclohexane + 1-alcohols: methanol (black), ethanol (dark grey), propan-1-ol (light grey), butan-1-ol (dark red), and pentan-1-ol (red) at atmospheric pressure. The curves represent the calculations with SAFT- γ Mie. Experimental data used in the estimation of group-interaction parameters are represented with filled symbols and those not used with open symbols. (a) Cyclohexane + methanol, with experimental data for VLE (triangles [94]), LLE (squares [95]), and SLE (diamonds [96] and circles [95]). (b) Cyclohexane + ethanol, with experimental data for VLE [98] and SLE [99]. (c) Cyclohexane + propan-1-ol, with experimental data for VLE [100] and SLE [99]. (d) Cyclohexane + butan-1-ol, with experimental data for VLE [101] and SLE [102]. (e) Cyclohexane + pentan-1-ol, with experimental data for VLE [103] and SLE [74]. (f) Superposition of the VLE in (a)–(e) of cyclohexane + 1-alcohols. Thermodynamic conditions and accuracy are detailed in Table 7.

Isothermal VLE data are available for methylcyclohexane + acetates [180], and are used to characterise the cCH–COO interaction. For the temperatures considered, azeotropes are found for methylcyclohexane + ethyl acetate (Figure 17(a)) and methylcyclohexane + propyl acetate (Figure 17(b)), but not for methylcyclohexane + butyl acetate (Figure 17(c)). Data for both isobaric VLE [181] at atmospheric pressure and isothermal VLE [162] at 293.15 K are available for mixtures of cyclohexanol + ethyl acetate (Figure 18(a) and (b), respectively), and are used to characterise the cCHOH–COO interaction. No azeotrope is observed for this mixture.

The SAFT- γ Mie calculations are again found to be in very good agreement with experiments. Azeotropes are correctly obtained from calculations when expected. In particular, the vapour–liquid regions associated with the azeotropic methylcyclohexane + propyl acetate mixture at 345 K and 365 K are very narrow (Figure 17(b)), in very good agreement with experiments. This phase behaviour is difficult to capture and constitutes a stringent test of the model.

The %AADs for the bubble and dew pressures of methylcyclohexane + esters are less than 9% for the thermodynamic conditions considered. For

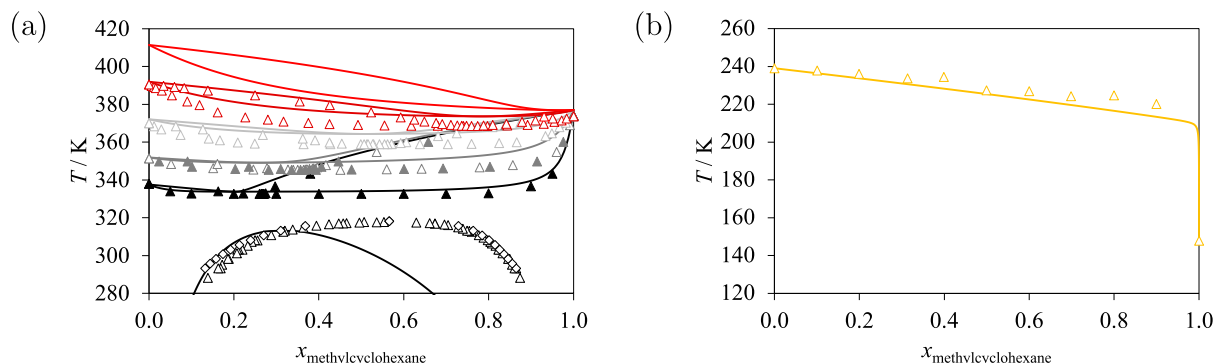


Figure 9. Isobaric phase diagrams at atmospheric pressure of methylcyclohexane + 1-alcohols: methanol (black), ethanol (dark grey), propan-1-ol (light grey), butan-1-ol (dark red), pentan-1-ol (red), and heptan-1-ol (yellow). The curves represent the calculations with SAFT- γ Mie. Experimental data used in the estimation of group-interaction parameters are represented with filled symbols and those not used with open symbols. (a) Vapour-liquid equilibria of methylcyclohexane + 1-alcohols, with experimental data for methanol [107], ethanol [110], propan-1-ol [111], butan-1-ol [111], and pentan-1-ol [112]. Liquid-liquid equilibria of methylcyclohexane + methanol, with experimental data represented by triangles [109] and diamonds [108]. (b) Solid-liquid equilibria of methylcyclohexane + heptan-1-ol, with experimental data represented with triangles [113]. Thermodynamic conditions and accuracy are detailed in Table 7.

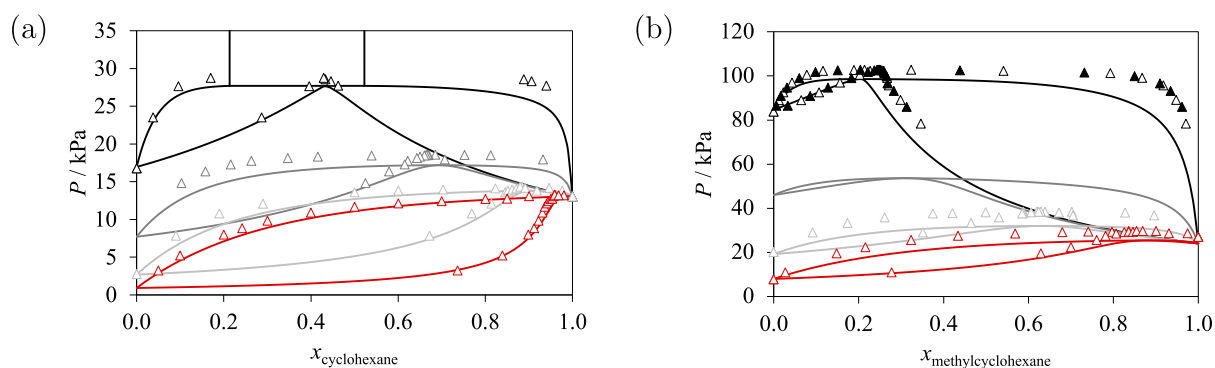


Figure 10. Isothermal vapour-liquid equilibrium of cycloalkanes + 1-alcohols: methanol (black), ethanol (dark grey), propan-1-ol (light grey), and butan-1-ol (dark red). The curves represent the calculations with SAFT- γ Mie. Experimental data used in the estimation of group-interaction parameters are represented with filled symbols and those not used with open symbols. (a) Liquid-liquid equilibrium of cyclohexane + methane at 298.15 K, and bubble and dew pressures of cyclohexane + 1-alcohols at 298.15 K, with experimental data for methanol [115], ethanol [118], propan-1-ol [119], and butan-1-ol [119]. (b) Bubble and dew pressures at 333.15 K of methylcyclohexane + 1-alcohols, with experimental data for methanol [120], propan-1-ol [122], and butan-1-ol [122]. Thermodynamic conditions and accuracy are detailed in Table 7.

cyclohexanol + ethyl acetate, the %AADs are 0.3126% for bubble temperature, 0.9001% for dew temperature, and 1.558% for bubble pressure.

2.8. Cyclic alcohols + aromatic compounds: $c\text{CHOH}-a\text{CH}$, $c\text{CHOH}-a\text{CCH}_3$, and $c\text{CHOH}-a\text{CCH}_2$ interactions

We consider aromatic hydrocarbons composed of the $a\text{CH}$ group [53], the $a\text{CCH}_3$ group [41,64], and the $a\text{CCH}_2$ group [53]. The dispersion contributions to the free energy rely on the parameters $\varepsilon_{c\text{CHOH}-a\text{CH}}$, $\lambda_{c\text{CHOH}-a\text{CH}}^r$, $\varepsilon_{c\text{CHOH}-a\text{CCH}_3}$, $\lambda_{c\text{CHOH}-a\text{CCH}_3}^r$, and $\varepsilon_{c\text{CHOH}-a\text{CCH}_2}$, which are characterised here.

Experimental data for cyclic alcohols + aromatic compounds are available for isobaric SLE [74], isobaric and isothermal VLE [162,182,183], single-phase density [70,183,184], and excess molar enthalpy [185,186]. No azeotrope is found for the isothermal VLE of cyclohexanol + benzene and 2-methylcyclohexanol + benzene at 293.15 K (Figure 19(a)), or for cyclohexanol + toluene at 333.15 K and 363.15 K (Figure 19(b)), while a eutectic point is found for the SLE of cyclohexanol + benzene (Figure 19(c)). Excess molar enthalpies of cyclohexanol + benzene (Figure 19(d)) and cyclohexanol + toluene are smaller than 2 kJ/mol at standard temperature and pressure.

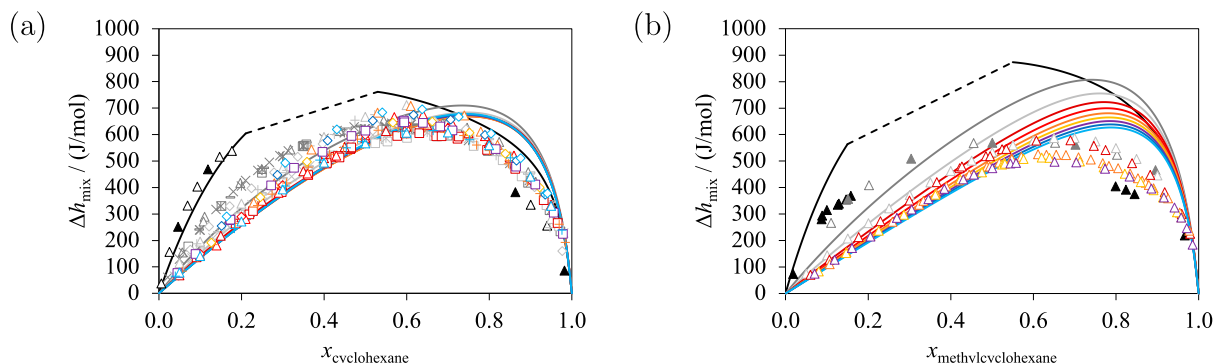


Figure 11. Excess molar enthalpy of binary mixtures at atmospheric pressure of cycloalkanes + 1-alcohols: methanol (black), ethanol (dark grey), propan-1-ol (light grey), butan-1-ol (dark red), pentan-1-ol (red), hexan-1-ol (orange), heptan-1-ol (yellow), octan-1-ol (purple), nonan-1-ol (dark blue), and decan-1-ol (light blue), at atmospheric pressure. The curves represent calculations with SAFT- γ Mie. Continuous and dashed curves correspond to single-phase regions and equilibrium regions of the phase diagram, respectively. Experimental data used in the estimation of group-interaction parameters are represented with filled symbols and those not used with open symbols. (a) Cyclohexane + 1-alcohols at 298.15 K, with experimental data for methanol [141], ethanol (triangles [143], squares [144], times [145], rectangles [140], asterisks [146]), propan-1-ol (squares [144], times [145], rectangles [140], asterisks [146], triangles [119], plus [165], diamonds [147], dash [148]), butan-1-ol (squares [144], triangles [149]), pentan-1-ol (triangles [150], diamonds [151]), hexan-1-ol (triangles [152], plus [153]), heptan-1-ol [151], octan-1-ol [144], nonan-1-ol [151], and decan-1-ol (triangles [119], plus [165], diamonds [151]). (b) Methylcyclohexane + 1-alcohols at 298.15 K, with experimental data for methanol [154], ethanol [155], propan-1-ol [148], butan-1-ol [166], hexan-1-ol [166], heptan-1-ol [166], and octan-1-ol [166]. Thermodynamic conditions and accuracy are detailed in Table 7.

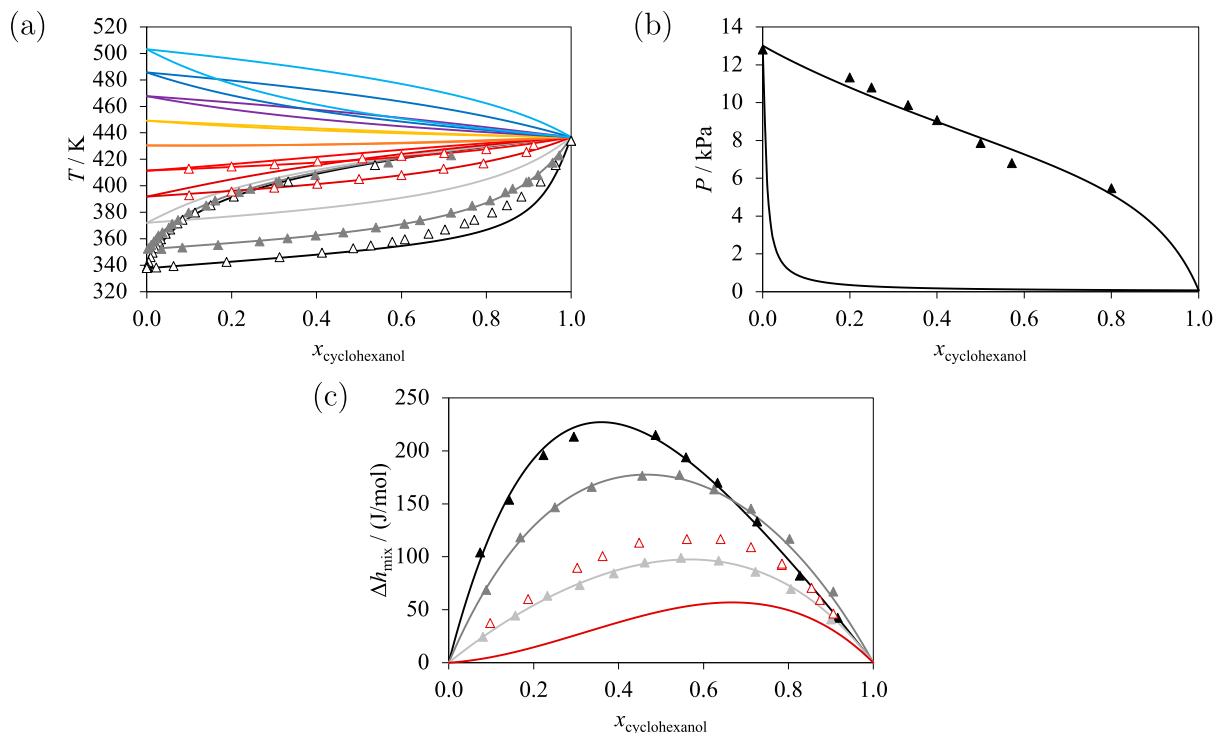


Figure 12. Selected thermodynamic properties of binary mixtures of cyclohexanol + 1-alcohols: methanol (black), ethanol (dark grey), propan-1-ol (light grey), butan-1-ol (dark red), pentan-1-ol (red), hexan-1-ol (orange), heptan-1-ol (yellow), octan-1-ol (purple), nonan-1-ol (dark blue), and decan-1-ol (light blue). The curves represent calculations with SAFT- γ Mie. Experimental data used in the estimation of group-interaction parameters are represented with filled symbols and those not used with open symbols. (a) Isobaric vapour-liquid equilibria at atmospheric pressure for cyclohexanol + 1-alcohols, with experimental data for methanol [158], ethanol [159], butan-1-ol [160], and pentan-1-ol [160]. (b) Isothermal vapour-liquid equilibrium at 293.15 K for cyclohexanol + methanol, with experimental data for bubble pressure [162]. (c) Excess molar enthalpy for cyclohexanol + 1-alcohols at 300 K, with experimental data for methanol [163], ethanol [163], propan-1-ol [163], and butan-1-ol [163]. Thermodynamic conditions and accuracy are detailed in Table 7.

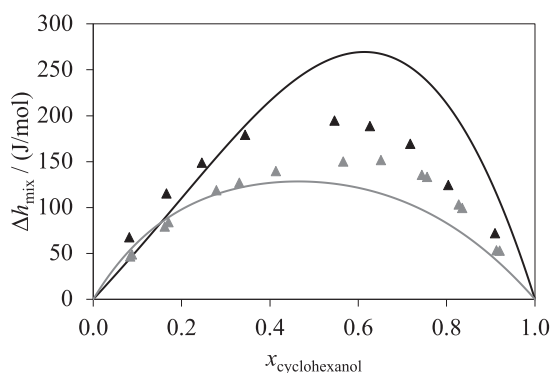


Figure 13. Excess molar enthalpy at 300 K and atmospheric pressure for cyclohexanol + 2-alcohols: propan-2-ol (black) and butan-2-ol (dark grey). The curves represent the calculations with SAFT- γ Mie. Experimental data (used in the estimation of group-interaction parameters) are represented with filled symbols [163]. Thermodynamic conditions and accuracy are detailed in Table 7.

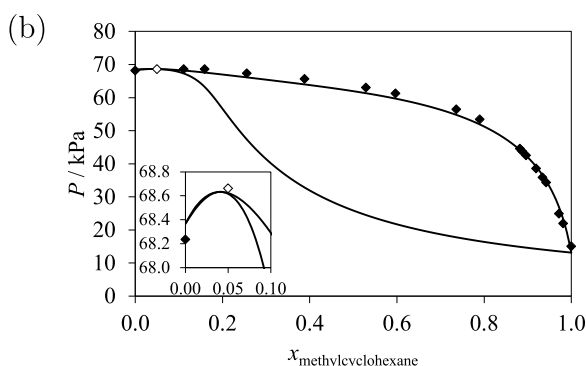
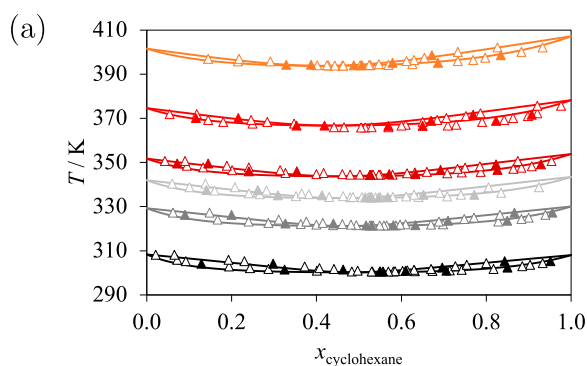


Figure 14. Phase diagrams of cycloalkanes + 2-ketones. The curves represent the calculations with SAFT- γ Mie. Experimental data used in the estimation of group-interaction parameters are represented with filled symbols and those not used with open symbols. (a) Isobaric vapour-liquid equilibria of cyclohexane + butanone at 20.0 kPa (black), 46.7 kPa (dark grey), 73.3 kPa (light grey), 101.3 kPa (dark red), 199.5 kPa (red), and 395.6 kPa (orange), with experimental data for bubble and dew temperatures [167]. (b) Isothermal vapour-liquid equilibrium of methylcyclohexane + acetone at 318.15 K, with experimental data for bubble and azeotrope pressures [168]. Thermodynamic conditions and accuracy are detailed in Table 7.

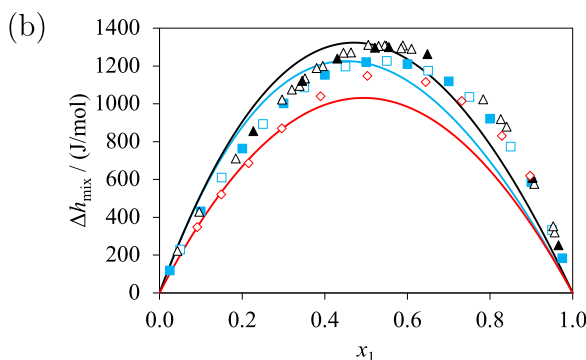
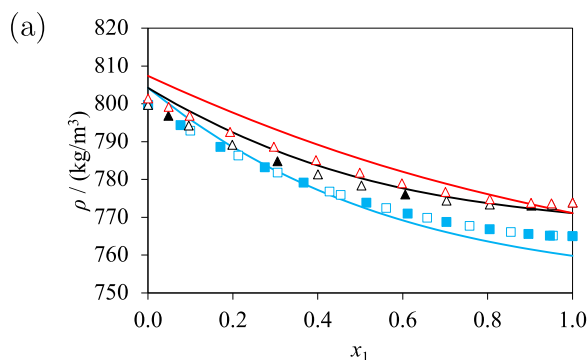


Figure 15. Selected thermodynamic properties of binary mixtures of cycloalkanes (compound 1) + 2-ketones (compound 2). The curves represent calculations with SAFT- γ Mie. Experimental data used in the estimation of group-interaction parameters are represented with filled symbols and those not used with open symbols. (a) Density of cyclohexane + butanone (black), cyclohexane + pentan-2-one (red), and methylcyclohexane + butanone (blue), at 298.15 K and atmospheric pressure, with experimental data represented with triangles [171] and squares [172]. (b) Excess molar enthalpy of cyclohexane + butanone (black), cyclohexane + pentan-2-one (red), and methylcyclohexane + butanone (blue), at 298.15 K and atmospheric pressure, with experimental data represented with triangles [167], diamonds [173], and squares [174]. Thermodynamic conditions and accuracy are detailed in Table 7.

All of these features are obtained with the SAFT- γ Mie approach after characterising the interaction parameters, as can be seen in Figure 19. The %AAD of bubble pressure is smaller for 2-methylcyclohexanol + benzene (6.952%) than for cyclohexanol + benzene (18.92%). For cyclohexanol + toluene, deviations are smaller for the dew pressure (5.051%) than for the bubble pressure (7.825%). Small %AAD values are obtained for the density of cyclohexanol + benzene (1.358%) and for the density of cyclohexanol + toluene (0.7251%). For the molar excess enthalpy, %AADs are reasonably small both for cyclohexanol + benzene and cyclohexanol + toluene (10.91% and 25.34%, respectively), as are the corresponding AADs (31.57 J/mol and 234.6 J/mol, respectively).

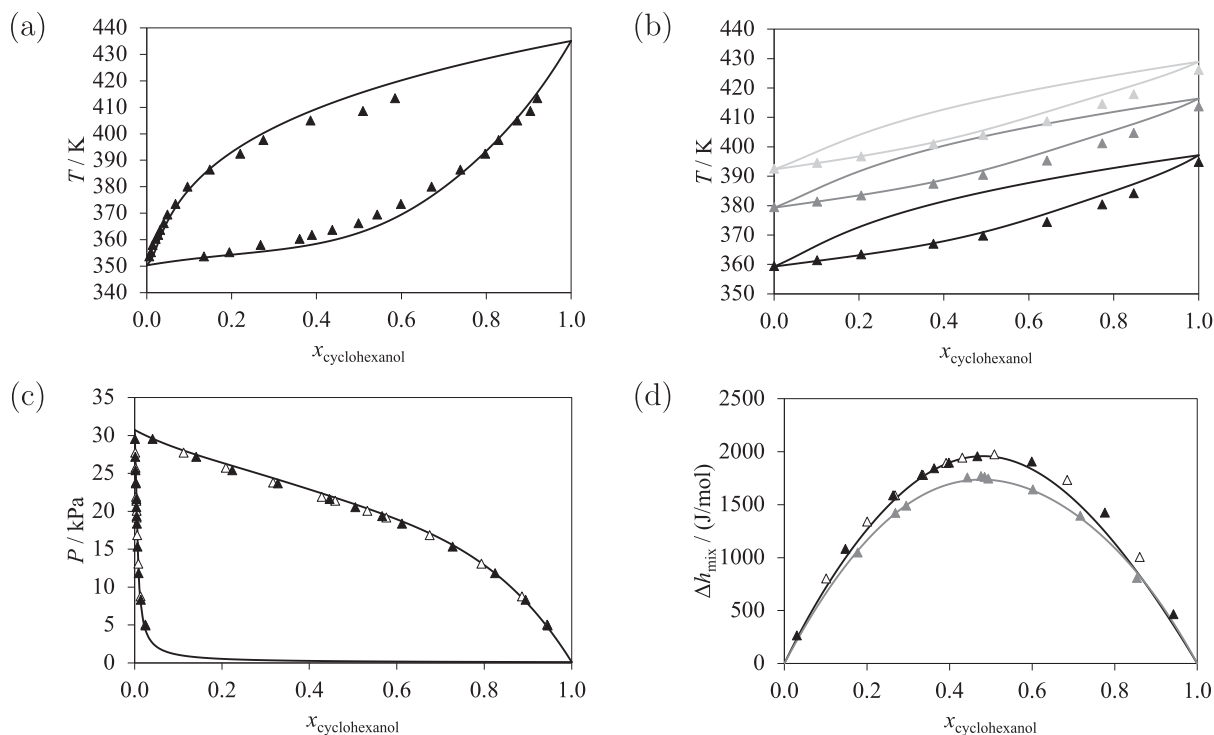


Figure 16. Selected thermodynamic properties of binary mixtures of cyclohexanol + 2-ketones. The curves represent calculations with SAFT- γ Mie. Experimental data used in the estimation of group-interaction parameters are represented with filled symbols and those not used with open symbols. (a) Isobaric vapour-liquid equilibrium of cyclohexanol + butanone at 96.7 kPa, with experimental data for bubble and dew temperatures [175]. (b) Isobaric vapour-liquid equilibrium of cyclohexanol + hexan-2-one at 26.7 kPa (black), 53.3 kPa (dark grey), and 80.0 kPa (light grey), with experimental data for bubble temperatures [176]. (c) Isothermal vapour-liquid equilibrium of cyclohexanol + acetone at 298.15 K, with experimental data for bubble and dew pressures [177]. (d) Excess molar enthalpy of cyclohexanol + acetone at 298.15 K (black) and cyclohexanol + hexan-2-one at 318.15 K (dark grey), at atmospheric pressure, with experimental data for acetone [177] and hexan-2-one [179]. Thermodynamic conditions and accuracy are detailed in Table 7.

2.9. Cyclic alcohols + water: cCHOH-H₂O interactions

A single molecular group, typically denoted as H₂O, is used to represent water in the SAFT- γ Mie approach; here we adopt the spherical water model of Dufal et al. [31,32]. Five parameters are characterised here to model the dispersion and hydrogen bonding interactions between the cCHOH group and H₂O: $\varepsilon_{\text{cCHOH-H}_2\text{O}}$, $\varepsilon_{\text{cCHOH-H}_2\text{O},\text{e}_1-\text{H}}^{\text{HB}}$, $K_{\text{cCHOH-H}_2\text{O},\text{e}_1-\text{H}}^{\text{HB}}$, $\varepsilon_{\text{cCHOH-H}_2\text{O},\text{H}-\text{e}_1}^{\text{HB}}$ and $K_{\text{cCHOH-H}_2\text{O},\text{H}-\text{e}_1}^{\text{HB}}$.

The experimental isobaric phase diagram of cyclohexanol + water at atmospheric pressure is well described by available VLE [187], LLE [188], and SLE [189] data. The LLE region is bounded by a solid-liquid-liquid-equilibrium (SLLE) curve at low temperature ($T_{\text{SLLE}}^{\text{exp}} = 272.5$ K) and by a vapour-liquid-liquid-equilibrium (VLLE) curve at high temperature ($T_{\text{VLLE}}^{\text{exp}} = 371.4$ K). An azeotrope is found along the VLLE, and metastable LLE data, above T_{VLLE} , are also provided [188]. Isobaric VLE [190], density [191], and excess molar enthalpy [192,193] data for cyclohexanol + water are

also available. For cyclopentanol + water, we consider isobaric VLE [194] and LLE [195] data at atmospheric pressure.

We use the VLE and excess-enthalpy data mentioned to characterise the SAFT interaction parameters between the cCHOH and H₂O groups, such that LLE and SLE curves are predicted. Good qualitative agreement is obtained for the isobaric phase diagram of cyclohexanol + water at atmospheric pressure (Figure 20(a)). The LLE region predicted is slightly larger than in the experiments, and the liquid-liquid critical point is overestimated. However, the azeotrope is correctly described with SAFT, as well as the SLLE and VLLE temperatures ($T_{\text{SLLE}}^{\text{SAFT}} = 273$ K and $T_{\text{VLLE}}^{\text{SAFT}} = 371$ K, respectively). The pressure of the three-phase (VLLE) line in the isothermal phase diagram of cyclohexanol + water at 363.15 K is also correctly predicted with SAFT- γ Mie ($P_{\text{VLLE}}^{\text{exp}} = 74.514$ kPa and $P_{\text{VLLE}}^{\text{SAFT}} = 73$ kPa; cf. Figure 20(b)). The excess molar enthalpy of cyclohexanol + water at 298.15 K and atmospheric pressure (Figure 20(c)) exhibits an ‘S’ shape, with negative

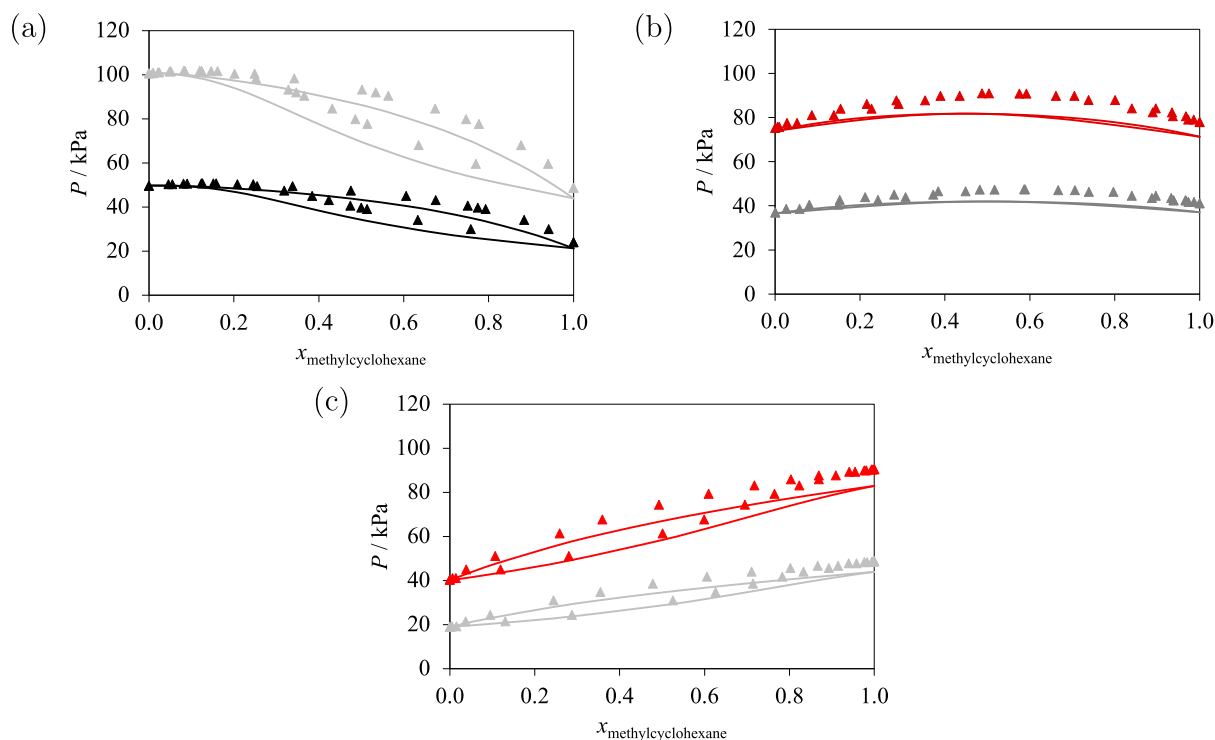


Figure 17. Isothermal vapour–liquid equilibrium of binary mixtures of methylcyclohexane + esters; with experimental data for bubble and dew pressures [180]. The curves represent calculations with SAFT- γ Mie. Experimental data used in the estimation of group-interaction parameters are represented with filled symbols. (a) Methylcyclohexane + ethyl acetate at 330 K (black) and 350 K (light grey). (b) Methylcyclohexane + propyl acetate at 345 K (dark grey) and 365 K (dark red). (c) Methylcyclohexane + butyl acetate at 350 K (light grey) and 370 K (red). Thermodynamic conditions and accuracy are detailed in Table 7.

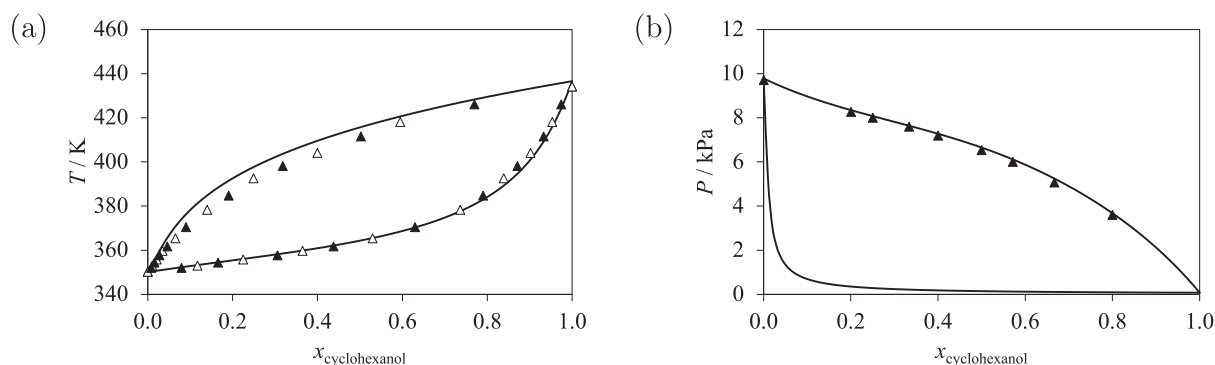


Figure 18. Selected thermodynamic properties of cyclohexanol + ethyl acetate. The curves represent the calculations with SAFT- γ Mie. Experimental data used in the estimation of group-interaction parameters are represented with filled symbols and those not used with open symbols. (a) Isobaric vapour–liquid equilibrium at atmospheric pressure, with experimental data for bubble and dew temperatures [181]. (b) Isothermal vapour–liquid equilibria at 293.15 K, with experimental data for bubble pressures [162]. Thermodynamic conditions and accuracy are detailed in Table 7.

values for $x_{\text{cyclohexanol}} < 0.075$ and positive values for $x_{\text{cyclohexanol}} > 0.075$, as can be seen both from SAFT calculations and experiments. In addition, the VLE and LLE calculations of the isobaric phase diagram of cyclopentanol + water at atmospheric pressure are in very good agreement with the experimental data (Figure 20(d)).

2.10. Branched alkanes + carbon dioxide and cyclic alcohols + carbon dioxide: CH-CO₂ and cCHOH-CO₂ interactions

Carbon dioxide is modelled with a single CO₂ molecular group [64], decorated with one association site of type e_1 and one of type e_2 , which are active in interactions with water or amine [47,48] groups. The unlike

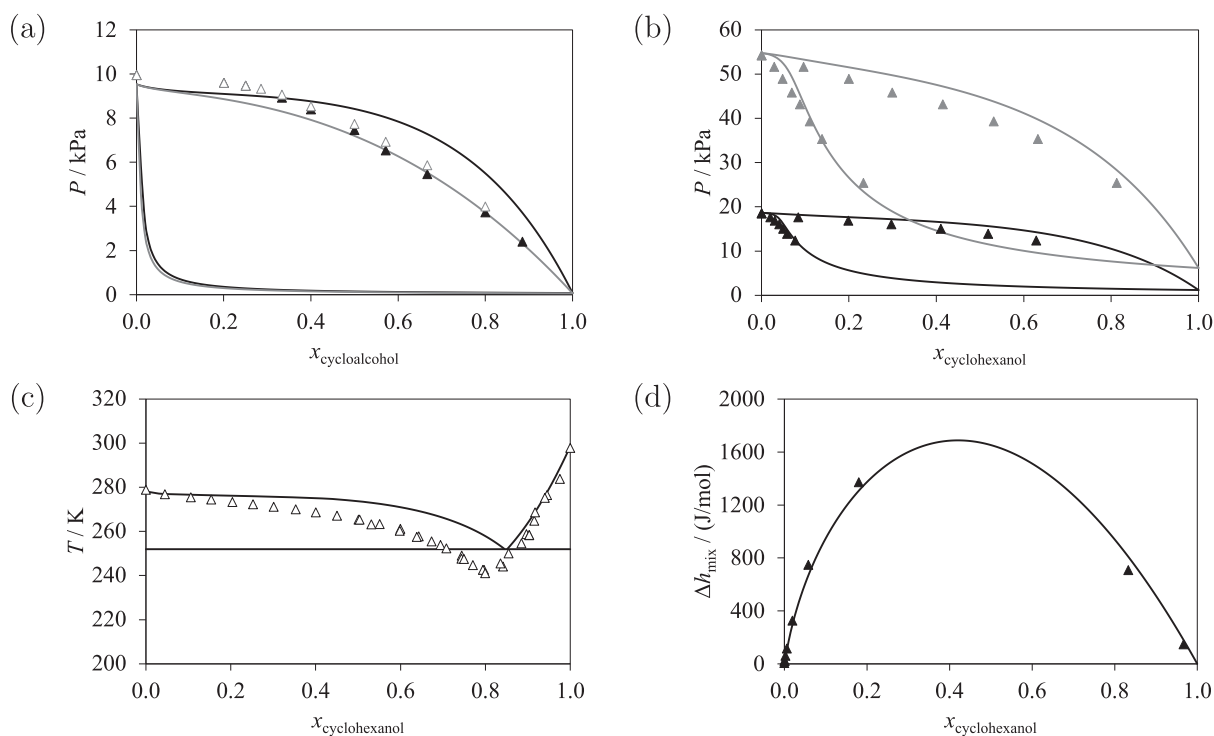


Figure 19. Selected thermodynamic properties of cyclic alcohols + aromatic compounds. The curves represent the calculations with SAFT- γ Mie. Experimental data used in the estimation of group-interaction parameters are represented with filled symbols and those not used with open symbols. (a) Isothermal vapour-liquid equilibria of cyclohexanol + benzene (black) and 2-methylcyclohexanol + benzene (dark grey) at 293.15 K, with experimental data for bubble pressures [162]. (b) Isothermal vapour-liquid equilibria of cyclohexanol + toluene at 333.15 K (black) and 363.15 K (dark grey), with experimental data for bubble and dew pressures [183]. (c) Isobaric solid-liquid equilibrium of cyclohexanol + benzene at atmospheric pressure, with experimental data represented with triangles [74]. (d) Excess molar enthalpy of cyclohexanol + benzene at 298.15 K, with experimental data represented with triangles [185]. Thermodynamic conditions and accuracy are detailed in Table 7.

group parameters we characterise here are $\varepsilon_{\text{CH}-\text{CO}_2}$ and $\varepsilon_{\text{cCHOH}-\text{CO}_2}$ as no cross association is considered between CO_2 and the alkyl and hydroxyl groups.

We consider isothermal fluid-phase equilibria for 2-methylpropane (isobutane) + carbon dioxide [196–198] (Figure 21(a)) and 2-methylbutane (isopentane) + carbon dioxide [199,200] (Figure 21(b)). For these two mixtures, isobaric SLE data are also available [201,202] (Figure 21(c)). Experimental data of isothermal fluid-phase equilibria are also available for cyclohexanol + carbon dioxide [203–205] at several temperatures. In particular, VLE and LLE regions are observed close to the critical point of CO_2 , at 303.15 K, with a three-phase VLLE line at $P_{\text{VLLE}}^{\text{exp}} \approx 6.9$ MPa. At higher temperatures, above the upper critical end point (UCEP), a continuous change from VLE to LLE phase behaviour is reported, without a three-phase line (cf. Figure 22).

The characterisation of the unlike energy parameter $\varepsilon_{\text{CH}-\text{CO}_2}$ is carried out using bubble-pressure data for 2-methylpropane + carbon dioxide at 383.15 K only. Excellent agreement between SAFT predictions

and experiments for bubble and dew pressures is obtained at the other temperatures available for 2-methylpropane + carbon dioxide, as well as for 2-methylbutane + carbon dioxide, as shown in Figure 21(a,b). The corresponding %AADs are 2.624% and 4.353% for the bubble and dew pressures of 2-methylpropane + carbon dioxide, and 3.056% and 7.336% for the bubble and dew pressures of 2-methylbutane + carbon dioxide. Agreement for the isothermal SLE of these mixtures is also very good, as shown in Figure 21(c). For cyclohexanol + carbon dioxide, comparisons between SAFT- γ Mie calculations and experiments are shown in Figure 22 at 303.15 K, 333.15 K, 393.15 K, and 453.15 K. VLLE is predicted with SAFT at 303.15 K, consistent with what is observed from experiments. Excellent agreement is obtained for the pressure of the VLLE, with $P_{\text{VLLE}}^{\text{SAFT}} \approx 7.1$ MPa (compared with $P_{\text{VLLE}}^{\text{exp}} \approx 6.9$ MPa for experiments), while the LLE region above the VLLE pressure is somewhat smaller for our SAFT predictions than for the experimental data (the poor quantitative agreement is related to the difficulty of describing critical points with a

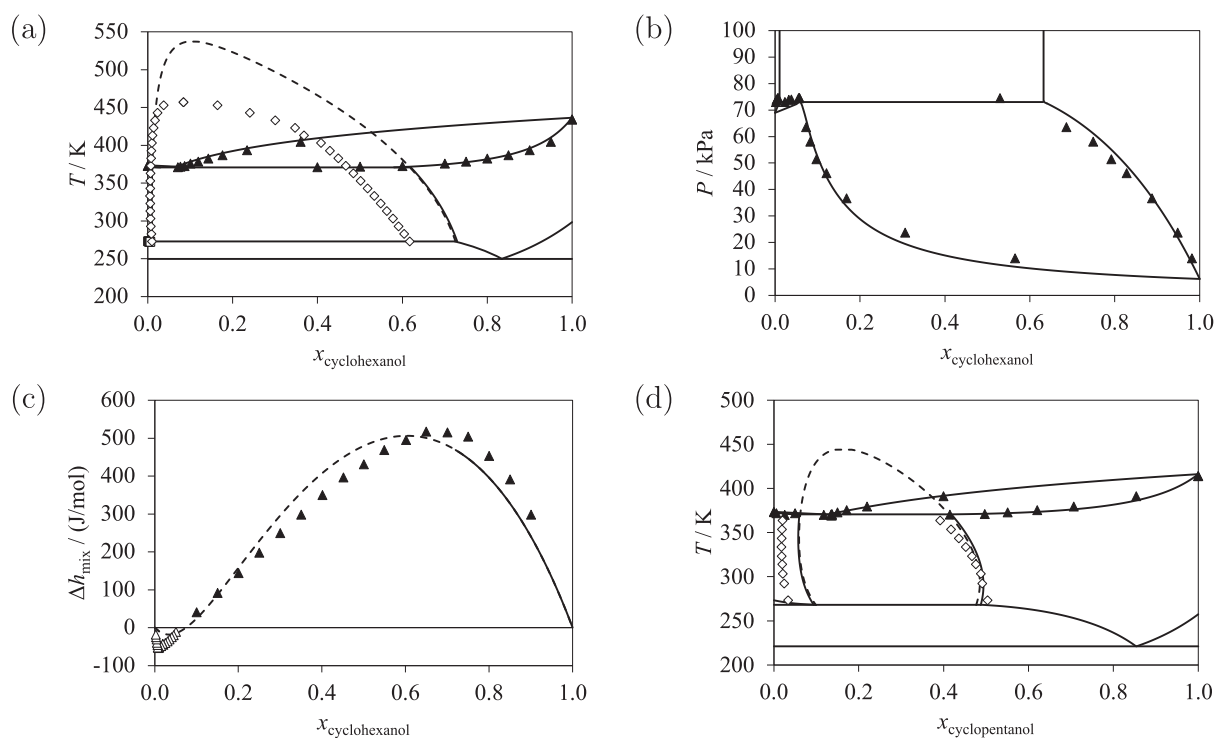


Figure 20. Selected thermodynamic properties of cyclic alcohols + water. The curves represent the calculations with SAFT- γ Mie. Continuous and dashed curves represent stable and metastable states, respectively. Experimental data used in the estimation of group-interaction parameters are represented with filled symbols and those not used with open symbols. (a) Isobaric vapour-liquid, liquid-liquid, and solid-liquid equilibria of cyclohexanol + water at atmospheric pressure, with experimental data for bubble and dew temperatures [187], liquid-liquid equilibrium [188], and solid-liquid equilibrium [189]. (b) Isothermal vapour-liquid equilibria of cyclohexanol + water at 363.15 K, with experimental data for bubble and dew pressures [190]. (c) Excess molar enthalpy of cyclohexanol + water at 298.15 K and atmospheric pressure, with experimental data represented with triangles [192]. (d) Isobaric vapour-liquid, liquid-liquid, and solid-liquid equilibria of cyclopentanol + water at atmospheric pressure, with experimental data for bubble and dew temperatures [194] and liquid-liquid equilibrium [195]. Thermodynamic conditions and accuracy are detailed in Table 7.

thermodynamic perturbation theory). At higher temperatures, however, the fluid-phase equilibria obtained with SAFT- γ Mie are in good quantitative agreement with experiments.

3. Full predictions for binary mixtures with menthol

The availability of experimental data for binary mixtures involving menthol is limited to a few mixtures and properties. In particular, isobaric VLE data [12,91,182,206–209] at atmospheric pressure are available for menthol + ethyl acetate, 2-methyl-1-propanol, 1,2-ethanediol, and 1,3,5-triethylbenzene. An LLE region is found experimentally [209] for menthol + water, and SLE data [12,56,208] are provided for menthol + ethanol and menthol + dodecan-1-ol. More data are available for the isothermal fluid-phase equilibria of menthol + carbon dioxide [11,210–213] at several temperatures.

All the interaction parameters required for the molecular modelling of menthol with the solvents mentioned

above have been characterised in our current work and described in previous sections. As a consequence, the SAFT- γ Mie calculations shown in the current section are fully predictive, and are not refined by additional parameter optimisation. This also means that the agreement between the predictions and experimental data is a

test of the transferability of the parameters already characterised. The VLE for menthol + ethyl acetate and menthol + 2-methyl-1-propanol are shown in Figure 23(a). No azeotrope is predicted, and excellent agreement is found with experiments for the two mixtures (%AAD are 0.4062% and 0.3817%, respectively). In Figure 23(b), azeotropes can be seen both in the SAFT- γ Mie calculations and experiments: a homogeneous azeotrope for menthol + 1,2-ethanediol, and a heterogeneous azeotrope for menthol + 1,3,5-triethylbenzene (a large LLE region is predicted, as well as three-phase VLLE). The %AADs in the azeotrope temperatures are small (1.035% and 3.276%, respectively), although we note that more experimental data are required to assess the quality of the predictions for the entire VLE range. An LLE

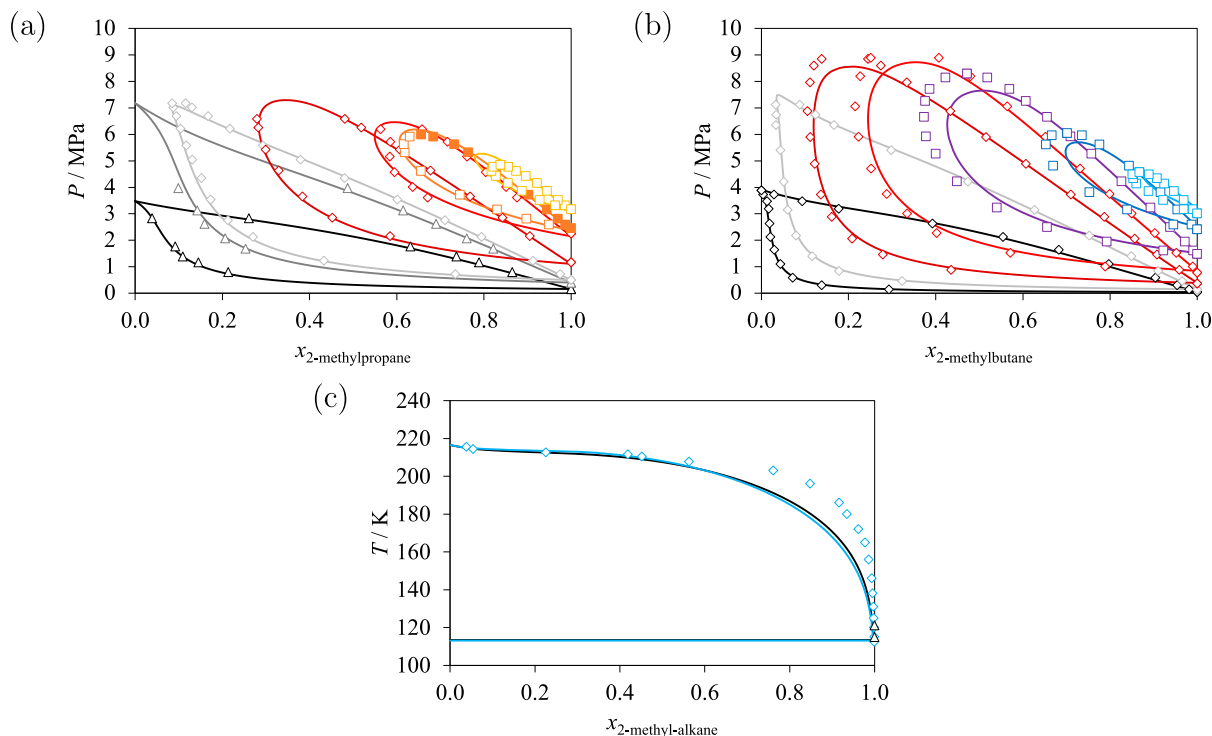


Figure 21. Phase diagrams of branched hydrocarbons (2-methylpropane and 2-methylbutane) + carbon dioxide. The curves represent the calculations with SAFT- γ Mie. Experimental data used in the estimation of group-interaction parameters are represented with filled symbols and those not used with open symbols. (a) Isothermal fluid-phase equilibria of 2-methylpropane + carbon dioxide at 273.15 K (black), 303.15 K (dark grey), 310.93 K (light grey), 344.26 K (dark red), 377.59 K (red), 383.15 K (orange), and 398.15 K (yellow), with experimental data represented with triangles [196], diamonds [197], and squares [198]. (b) Isothermal fluid-phase equilibria of 2-methylbutane + carbon dioxide at 277.59 K (black), 310.93 K (light grey), 344.32 K (dark red), 377.65 K (red), 408.15 K (purple), 438.15 K (dark blue), and 453.15 K (light blue), with experimental data represented with diamonds [199] and squares [200]. (c) Isobaric solid-liquid equilibria of 2-methylpropane + carbon dioxide (black) and 2-methylbutane + carbon dioxide (light blue) at atmospheric pressure, with experimental data represented with triangles [201] and diamonds [202]. Thermodynamic conditions and accuracy are detailed in Table 7.

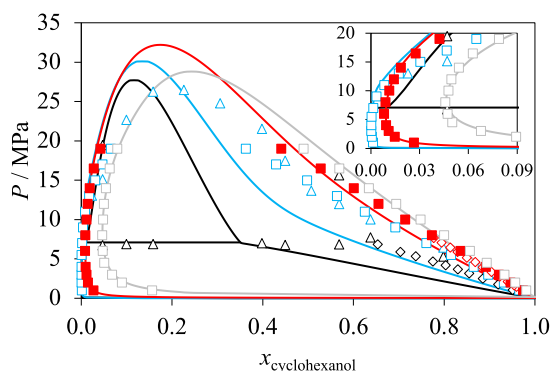


Figure 22. Isothermal fluid-phase equilibria of cyclohexanol + carbon dioxide at 303.15 K (black), 333.15 K (light blue), 393.15 K (red), and 453.15 K (light grey). The curves represent the calculations with SAFT- γ Mie. Experimental data used in the estimation of group-interaction parameters are represented with filled symbols and those not used with open symbols, and are represented by triangles [203], diamonds [204], and squares [205]. Thermodynamic conditions and accuracy are detailed in Table 7.

region is also obtained with SAFT for menthol + water, bounded by VLE and SLE lines in Figure 23(c). A single experimental data point is found for the LLE [209], in good agreement with the SAFT- γ Mie prediction, with $\text{AAD} = 1.237 \times 10^{-4}$ for the LLE composition. In Figure 23(d), we show SAFT predictions and experiments for the SLE at atmospheric pressure of menthol + ethanol and menthol + dodecan-1-ol. The prediction for menthol + ethanol is compared with the single experimental point found in the literature [208]. Excellent agreement is found, with deviations in temperature of $\% \text{AAD} = 0.5992\%$ and $\text{AAD} = 1.756 \text{ K}$, and deviations in composition of $\% \text{AAD} = 3.681\%$ and $\text{AAD} = 0.02381$. A eutectic point is observed both with SAFT and experiments [12] for menthol + dodecan-1-ol, and very good agreement is found for the SLE curve, with $\% \text{AAD} = 0.4505\%$ and $\text{AAD} = 1.328 \text{ K}$ in temperature, and $\% \text{AAD} = 6.797\%$ and $\text{AAD} = 0.03018$ in composition.

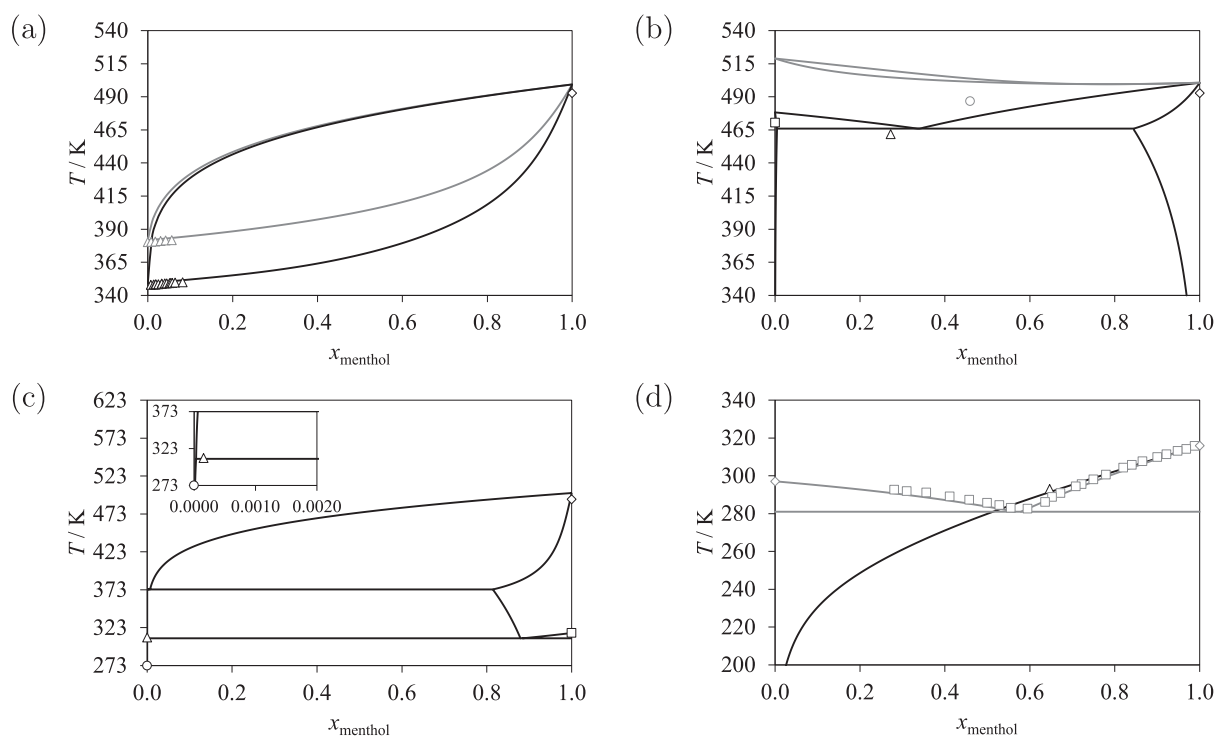


Figure 23. Isobaric phase diagrams at atmospheric pressure of binary mixtures containing menthol, including vapour–liquid, liquid–liquid, or solid–liquid equilibria. The curves represent the predictions with SAFT- γ Mie. Experimental data used in the estimation of group-interaction parameters are represented with filled symbols and those not used with open symbols. (a) Vapour–liquid equilibrium of menthol + ethyl acetate (black) and menthol + 2-methyl-1-propanol (grey), with experimental data for bubble temperatures [206] and boiling temperature of pure menthol [91]. (b) Vapour–liquid and liquid–liquid equilibria of menthol + 1,2-ethanediol (black) and menthol + 1,3,5-triethylbenzene (grey), with experimental data for azeotropes (a triangle [207] and a circle [182]), and boiling temperatures of pure menthol [91] and pure 1,2-ethanediol [215]. (c) Vapour–liquid, liquid–liquid, and solid–liquid equilibria of menthol + water, with experimental data for liquid–liquid equilibrium [209], and melting temperatures of pure menthol [56] and pure water [56]. (d) Solid–liquid equilibrium of menthol + ethanol (black) and menthol + dodecan-1-ol (dark grey), with experimental data represented with a triangle [208], diamonds [56], and squares [12]. Thermodynamic conditions and accuracy are detailed in Table 7.

The high-pressure phase diagram of menthol + carbon dioxide has been studied by Sovová et al. [11] for the extraction of peppermint oil by supercritical carbon dioxide, presenting fluid–fluid and fluid–solid coexistence. The isothermal fluid-phase diagram of menthol + carbon dioxide at 323.15 K is shown in Figure 24, including SAFT calculations, data from Sovová et al. [11], and other experimental data [210–213]. Most of these experiments correspond to bubble-pressure measurements for low concentrations of menthol. At 323.15 K, pure menthol is subcritical, while pure carbon dioxide is supercritical. The shape of the fluid-phase envelope is characteristic of a mixture above a UCEP [214], with continuous change from VLE to LLE phase behaviour as the pressure increases. The CO_2 -rich phase is dense (liquid-like) above 12 MPa, and a change of curvature is observed at this pressure (as can be seen in the inset of Figure 24). This means that the fluid-phase equilibrium has the characteristics of LLE above 12 MPa, and the characteristics

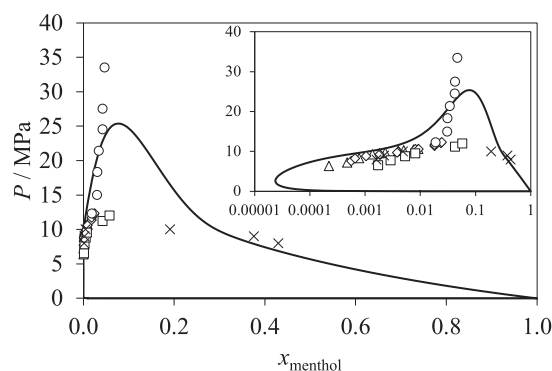


Figure 24. Isothermal fluid-phase equilibria of menthol + carbon dioxide at 323.15 K. The curve represents the predictions with SAFT- γ Mie. Experimental data (not used in the estimation of group-interaction parameters) are represented with triangles [210], diamonds [11], squares [211], circles [212], and cross [213]. Thermodynamic conditions and accuracy are detailed in Table 7.

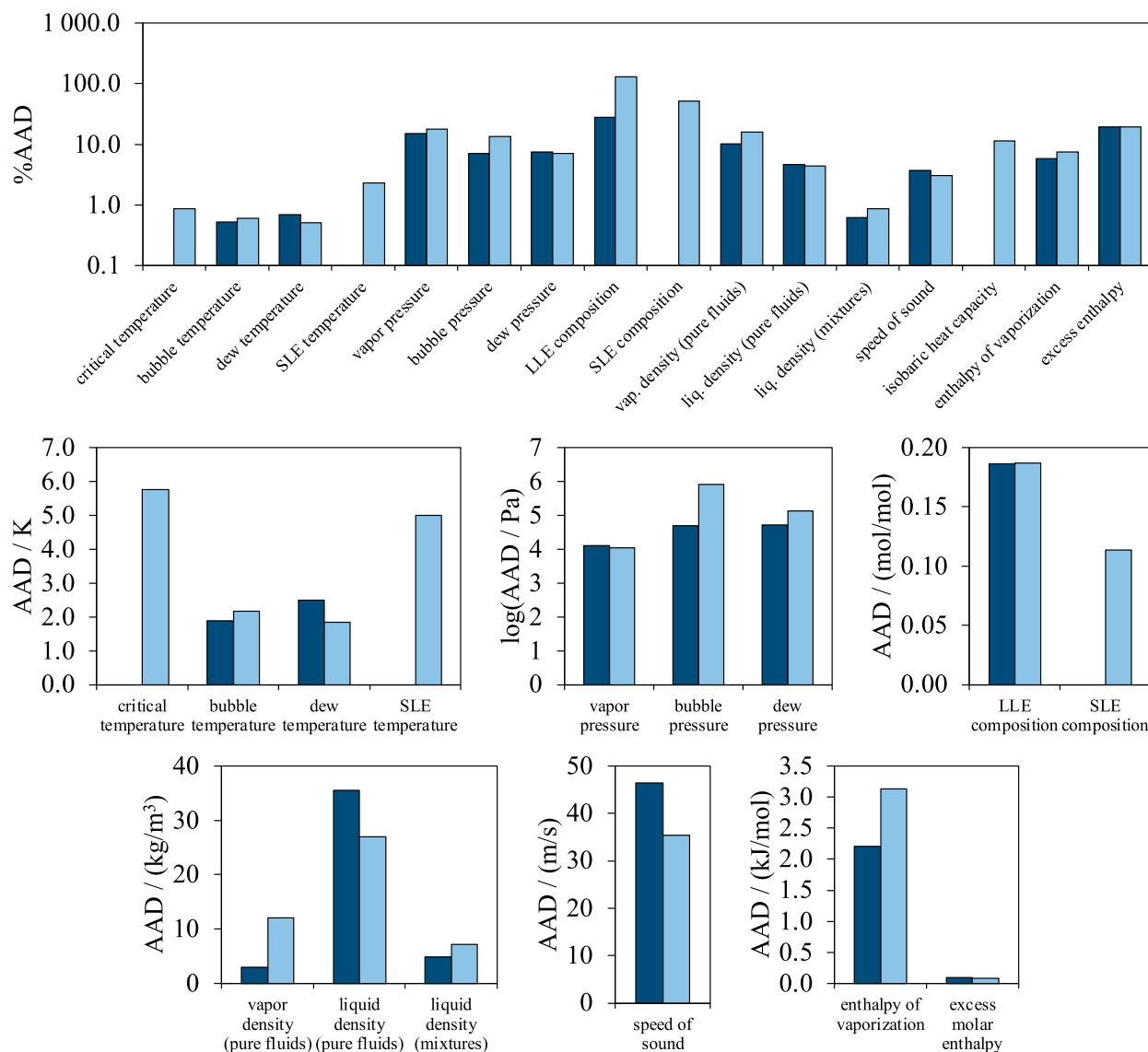


Figure 25. Overall %AAD and AAD for the properties considered in our current work. The results for the data used in parameter estimation are presented in dark blue and the results for the predictions are in pale blue.

of VLE below 12 MPa. However, the change of the curvature of the envelope is continuous, and no VLLE is found, as the phase rich in carbon dioxide is supercritical. This behaviour is seen in the SAFT- γ Mie prediction, with good agreement with the experimental data available.

4. Accuracy of the model

We summarise in Table 7 the accuracy of SAFT- γ Mie, evaluated with %AADs and AADs, for the systems considered in the current work. The properties evaluated for pure fluids are the critical temperature, vapour pressure, saturated vapour and liquid densities, single-phase liquid density, vaporisation enthalpy, speed of sound, and

isobaric heat capacity. For mixtures, the properties are the azeotrope, bubble, dew, and SLE temperatures, bubble and dew pressures, LLE composition, solubility (i.e. the solubility of a solid in a liquid), single-phase density, and excess molar enthalpy. For each system and property, we report the number of experimental points selected for the evaluation of the %AADs and AADs, as well as the thermodynamic conditions used as input in the calculation.

We summarise the %AADs and AADs per property in Table 8 and Figure 25. The values of the %AADs depend mostly on the type of properties and the magnitude of the values rather than particular mixtures or compounds, e.g. we found less than 0.7% for dew temperatures, with $\%AAD^{\text{est}} = 0.6940\%$ (where ‘est’ refers

Table 8. Overview of the accuracy of SAFT- γ Mie calculations for the pure fluids and the binary mixtures considered in our work.

Property p	N_p^{est}	N_p^{pred}	%AAD ^{est}	%AAD ^{pred}	AAD ^{est}	AAD ^{pred}
critical temperature	0	5	–	0.8763	–	5.760 K
bubble temperature	264	458	0.5215	0.6105	1.894 K	2.168 K
dew temperature	170	394	0.6940	0.5173	2.501 K	1.841 K
SLE temperature	0	237	–	2.315	–	4.989 K
vapour pressure	52	45	15.17	17.88	12.86 kPa	10.97 kPa
bubble pressure	365	689	7.168	13.58	50.41 kPa	830.4 kPa
dew pressure	263	447	7.404	7.130	50.69 kPa	131.7 kPa
LLE composition	76	102	27.55	129.6	0.1861	0.1868
SLE composition	0	237	–	51.99	–	0.1136
vapour density (pure fluids)	33	12	10.04	15.95	2.981 kg/m ³	12.06 kg/m ³
liquid density (pure fluids)	48	43	4.706	4.416	35.54 kg/m ³	27.03 kg/m ³
liquid density (mixtures)	165	637	0.6285	0.8682	4.849 kg/m ³	7.130 kg/m ³
speed of sound	47	25	3.738	3.089	46.39 m/s	35.43 m/s
isobaric heat capacity	0	11	–	11.45	–	46.99 J/(mol.K)
enthalpy of vaporisation	14	51	5.883	7.411	2.210 kJ/mol	3.130 kJ/mol
excess molar enthalpy	320	1020	19.11	19.13	0.09232 kJ/mol	0.08305 kJ/mol

Notes: N_p^{est} is the number of experimental data points used in parameter estimation for property p . N_p^{pred} is the number of experimental data points not used in parameter estimation (prediction only) for property p . We calculate the corresponding %AAD^{est}, %AAD^{pred}, AAD^{est}, and AAD^{pred}.

to data used in the estimation of the group parameters) and %AAD^{pred} = 0.5065% ('pred' for predicted data) and about 7% for dew pressure (%AAD^{est} = 7.404% and %AAD^{pred} = 7.130%). The AADs also depend more on the property considered – and its unit – than on the points used for estimation (AAD^{est}) or prediction (AAD^{pred}), which assesses the quality of the model.

5. Conclusions

We have extended the applicability of the SAFT- γ Mie group-contribution approach by introducing a cyclic cCHOH group. In addition to the new cCHOH–cCHOH interaction, 26 unlike group-interactions have been characterised. 76 systems have been used to estimate the parameters or to evaluate the quality of the predictions. Six pure fluids (1-isopropylcyclohexane, 1-methylpropylcyclohexane, 1,3,5-triisopropylcyclohexane, cyclohexanol, 2-methylcyclohexanol, and menthol) and 70 binary mixtures, selected to include a large range of solvent families (cyclic, linear, and branched alkanes, 1-alcohols, 2-alcohols, 2-ketones, esters, aromatic compounds, water, and carbon dioxide) have been considered. Among these systems, mixtures including cyclohexane, methylcyclohexane, or cyclohexanol have been studied in greater detail, as they are representative of small molecules containing the groups of interest.

The transferability of the new parameters has been tested systematically for many mixtures and properties, including solubility, such that the new model can be used to predict the thermodynamic properties of larger molecules. In particular, we predicted the properties of mixtures that contain menthol with very good agreement with the experimental data available. The quality

of the results has been shown in a range of figures and phase diagrams, and a systematic calculation of %AADs and AADs has been performed. The new cCHOH group can be used to model other complex cyclic alcohols with SAFT- γ Mie, which are relevant for many biological and pharmaceutical systems.

The cCHOH group and the associated interaction parameters can be combined with the existing database of SAFT- γ Mie parameters [37], making it possible to predict the thermodynamic properties and phase behaviour of countless new compounds and mixtures across wide range of temperature, pressure, and composition. Such predictive models can support the design of novel molecules, formulations, and processes in sectors as diverse as pharmaceuticals, agrochemicals, chemicals, consumer products, or energy.

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We dedicate this paper to the memory of our good friend and colleague Luis Rull and in honour of José-Luis Abascal and the Statistical Physics community in Spain.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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Data statement

Data underlying this article can be accessed on Zenodo at <https://doi.org/10.5281/zenodo.13464857> and used under the Creative Commons Attribution license.

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