

Investigation of the Low-Pressure Phase Behavior and SAFT Modeling of 1-Alcohol and n-Alkane Binary Systems

du Plessis, Susanna H.; Smith, Sonja A.M.; Latsky-Galloway, Carla; Schwarz, Cara E.

Published in: Journal of Chemical and Engineering Data

Link to article, DOI: 10.1021/acs.jced.3c00346

Publication date: 2024

Document Version Publisher's PDF, also known as Version of record

Link back to DTU Orbit

Citation (APA):

du Plessis, S. H., Smith, S. A. M., Latsky-Galloway, C., & Schwarz, C. E. (2024). Investigation of the Low-Pressure Phase Behavior and SAFT Modeling of 1-Alcohol and *n*-Alkane Binary Systems. *Journal of Chemical and Engineering Data*, *69*, 623-638. https://doi.org/10.1021/acs.jced.3c00346

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.

- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Article

Investigation of the Low-Pressure Phase Behavior and SAFT Modeling of 1-Alcohol and *n*-Alkane Binary Systems

Susanna H. du Plessis, Sonja A. M. Smith, Carla Latsky-Galloway, and Cara E. Schwarz*

Cite This: J. Chem. Eng. Data 2024, 69, 623–638



ACCESS	III Metrics & More		E Article Recommendations		3 Supporting Information
ABSTRACT: The	low-pressure phase behavior	of 1-alc and the	ohol + <i>n</i> -alkane systems is investig ability of SAFT models to predic	gated t the	

ABSTRACT: The low-pressure phase behavior of 1-alcohol + *n*-alkane systems is investigated by considering trends in the experimental data and the ability of SAFT models to predict the data. Data for four new isobaric binary 1-alcohol + *n*-alkane systems at 40 kPa are presented in this study, including 1-heptanol + *n*-octane, 1-octanol + *n*-nonane, 1-nonanol + *n*-decane, and 1-decanol + *n*-undecane. These systems were not azeotropic, although positive deviations from ideality were observed. The $C_nOH + C_{n+1}$ data were compared to the previously measured data for the $C_nOH + C_{n+2}$, $C_nOH + C_{n+3}$, and $C_nOH + C_{n+4}$ systems, and trends and observations were elucidated. It was concluded that the azeotropic composition could be predicted for other systems not considered in these studies based on the available data. Finally, the modeling of the available *n*-alkane and 1-alcohol data was considered using the PC-SAFT and SAFT-VR-Mie models, and SAFT-VR-Mie consistently outperformed PC-SAFT.



1. INTRODUCTION

Mixtures of alcohols and alkanes can be readily produced by Fischer–Tropsch synthesis, depending on the reaction conditions used such as the catalyst type, temperature, and pressure.^{1,2} The hydrocarbons produced by the Fischer– Tropsch process can be used as fuel sources and, depending on the carbon number of the product, can also be used as precursors in a variety of industries such as the surfactant and detergent, plasticizer, foodstuff, or pharmaceutical industries. The alcohols and alkanes are, however, required with reasonable purity in order to be used for further processing in these industries.

The separation of alcohol and alkane mixtures has been increasingly researched for industrial application.²⁻⁶ The separation of these mixtures is made difficult by the presence of crossover boiling and melting points,⁷ as well as nonideal phase behavior, and therefore, traditional separation methods are ineffective. In order to better understand the nonideal phase behavior observed, a systematic study into the phase behavior of various alkane + alcohol mixtures was conducted. Previously, experimental data for alkane + alcohol mixtures, where the carbon chains differed by two,⁸ three,⁹ and four¹⁰ carbon atoms, were measured and interpreted at 40 kPa. These series of systems were specifically chosen to evaluate a large variety of industrially relevant systems but to also allow a structured investigation into the phase behavior of 1-alcohol + n-alkane containing systems. Further, it is in these series of systems where crossover boiling points and azeotropic behavior is present. A pressure of 40 kPa was chosen to ensure that the saturation temperature of the pure components was reduced sufficiently below the 523.15 K maximum of the experimental setup and

decomposition of compounds did not occur, while also greatly improving operability of the setup. Additionally, the data are further useful to improve current extractive distillation processes which is used to separate detergent range 1-alcohols and *n*alkanes, which is operated under vacuum conditions.¹¹

The aim of this study is to present an investigation of the phase behavior of 1-alcohol + *n*-alkane systems, where the *n*alkane has between 1 and 4 carbon atoms more than the 1alcohol. This investigation was conducted by first presenting new experimental data for four new experimental vapor-liquid equilibrium data sets at 40 kPa, including 1-heptanol + n-octane, 1-octanol + n-nonane, 1-nonanol + n-decane, and 1-decanol + nundecane. Second, the phase behavior for 1-alcohol + n-alkane systems was analyzed considering four series of systems including the $C_nOH + C_{n+1}$, $C_nOH + C_{n+2}$, $C_nOH + C_{n+3}$, and $C_nOH + C_{n+4}$ series to elucidate trends within and between the various homologous series. Third, the thermodynamic modeling was conducted on the experimental data using the statistical associating fluid theory (SAFT) type models as, although experimental work is necessary to understand the phase behavior properties of mixtures, a suitable thermodynamic model is further required to aid in the design of industrial processes. To this end, the mixtures investigated in this work are also modeled with the PC-SAFT and SAFT-VR Mie equations

Special Issue: In Honor of Gabriele Sadowski Received: June 9, 2023

Accepted: August 4, 2023 Published: August 15, 2023





pubs.acs.org/jced

Article

Table 1. Supplier and Product Information, CAS Numbers, Chemical Purities as Indicated by the Supplier, and Water Content for All Chemicals Used in the Experimental Measurements^a

Component	CAS number	Supplier	Product number	Purity ^b	Water content ^c
methanol	67-56-1	Sigma-Aldrich	34860	≥0.99	0.0005
2-pentanol	31087-44-2	Fluka	76942	≥0.98	0.0011
1-heptanol	111-70-6	Sigma-Aldrich	10214549	≥0.99	0.0009
1-octanol	111-87-5	Sigma-Aldrich	102152069	≥0.99	0.0003
1-nonanol	143-08-8	Sigma-Aldrich	102087521	≥0.99	0.0008
1-decanol	112-30-1	Sigma-Aldrich	10104222	≥0.99	0.0006
<i>n</i> -octane	111-65-9	Sigma-Aldrich	102161762	≥0.99	0.0008
<i>n</i> -nonane	111-84-2	Sigma-Aldrich	102148072	≥0.99	0.0002
<i>n</i> -decane	124-18-5	Sigma-Aldrich	1002940415	≥0.99	0.0002
<i>n</i> -undecane	1120-21-4	Sigma-Aldrich	102145685	≥0.99	0.0002
		-			

^aPurities and water content indicated as mass fraction. ^bChemical purities (mass fraction) as stated by the supplier and confirmed by GC-MS. ^cWater content (mass fraction) determined by Karl Fischer titrations.

of state, models which take nonidealities in both the vapor and the liquid phase into account.

2. EXPERIMENTAL DATA FOR THE C_NOH + C_{N+1} SYSTEMS

2.1. The Experimental Setup and Procedure. A Pilodist VLE100 model all-glass dynamic recirculating still was used to measure the isobaric T-xy data presented in this study. A detailed schematic of the still and a description of the still operation are provided in previous publications.^{12,13}

In order to generate a single vapor-liquid equilibrium data point, the still is charged with a binary alkane + alcohol mixture through the feed buret into the mixing chamber. The still is sealed off from the atmosphere, after which the vacuum pump and immersion heater are turned on. The subatmospheric pressure set point is maintained by manually throttling the vacuum pump using a needle valve, ensuring that the set point is maintained to within 0.2 kPa. The mixing chamber is connected to the boiling chamber, which contains the immersion heater that partially vaporizes the mixture. The vaporization forces the two-phase mixture through the Cottrell tube, where contact between the phases takes place and equilibrium is attained. From the Cottrell tube, the two-phase mixture pushes into the equilibrium chamber, and the phases are separated. The liquid phase is recirculated from the bottom of the equilibrium chamber into the mixing chamber. The vapor phase is recirculated from the top of the equilibrium chamber, where it is condensed and also recirculated into the mixing chamber. A magnetic stir bar ensures that the mixture is sufficiently mixed in the mixing chamber, and recirculation of the phases continues.

A Pt-100 probe that measures the equilibrium temperature is situated in the equilibrium chamber and is in contact with both phases as they exit the Cottrell tube. After the mixture has recirculated for approximately 1 h, the vapor and liquid phases are sampled through the sampling ports by briefly opening the solenoid valves. The equilibrium temperature of the mixture and pressure of the still are noted as the stable values observed in the 10 min prior to sampling.

The vapor and liquid samples are subsequently prepared for gas chromatography analysis by adding 30 μ L of both samples and internal standard (2-pentanol) to separate 1.5 mL vials. The sample and internal standard are weighed accurately to 0.00001 g. The 1.5 mL vial is filled with the gas chromatography solvent (methanol), after which 100 μ L of the sample was diluted in 1.4 mL of methanol. The gas chromatograph used for the analyses

Table 2. Experimental VLE Data for the 1-Heptanol $(1) + n$ -
Octane (2) System at Pressure $p = 40$ kPa, Given at
Temperature T, Liquid Mole Fraction x_1 , and Vapor Mole
Fraction y_i^a

T/K	$x_1/\text{mol}\cdot\text{mol}^{-1}$	$y_1/\text{mol}\cdot\text{mol}^{-1}$
368.55	0.000	0.000
368.72	0.016	0.009
368.54	0.029	0.015
369.02	0.037	0.018
369.06	0.043	0.020
369.05	0.044	0.021
369.67	0.097	0.034
369.93	0.123	0.038
370.31	0.158	0.043
370.61	0.180	0.044
371.18	0.239	0.049
371.72	0.283	0.054
371.99	0.302	0.055
372.44	0.339	0.059
373.09	0.378	0.065
374.14	0.443	0.072
374.75	0.465	0.077
376.00	0.515	0.090
377.99	0.602	0.107
381.62	0.686	0.137
388.38	0.798	0.221
393.83	0.854	0.279
396.32	0.875	0.322
397.69	0.882	0.344
400.37	0.901	0.399
404.25	0.925	0.483
408.59	0.950	0.590
409.42	0.953	0.605
412.04	0.965	0.695
415.17	0.979	0.791
419.08	0.996	0.949
420.52	1.000	1.000

^{*a*}Uncertainties were calculated for each individual point, and for each data point, the combined standard uncertainties are no larger than u(T) = 0.31 K, $u(x_1) = 0.008$ mol·mol⁻¹, $u(y_1) = 0.008$ mol·mol⁻¹, and u(P) = 0.2 kPa. Individual data point uncertainties are provided in the Supporting Information in Table S.18.

was an Agilent 7890B model and was equipped with either Agilent DB-FFAP or Agilent HP-5 columns.

Table 3. Experimental VLE Data for the 1-Octanol (1) + *n*-Nonane (2) System at Pressure p = 40 kPa, Given at Temperature *T*, Liquid Mole Fraction x_1 , and Vapor Mole Fraction y_1^a

T/K	$x_1/\text{mol}\cdot\text{mol}^{-1}$	$y_1/mol \cdot mol^{-1}$
392.08	0.000	0.000
392.26	0.018	0.011
392.54	0.039	0.022
393.29	0.099	0.046
394.44	0.200	0.073
395.56	0.274	0.089
396.79	0.354	0.111
397.32	0.382	0.110
398.40	0.447	0.122
399.02	0.471	0.133
401.74	0.581	0.166
403.75	0.641	0.193
404.55	0.658	0.202
405.76	0.689	0.215
407.89	0.731	0.249
409.39	0.756	0.270
410.53	0.775	0.288
413.94	0.824	0.352
414.91	0.837	0.367
416.98	0.858	0.401
419.46	0.879	0.460
421.27	0.898	0.502
423.88	0.919	0.566
427.43	0.943	0.657
429.83	0.959	0.733
431.46	0.968	0.785
432.19	0.973	0.811
435.63	0.991	0.932
435.93	0.993	0.942
437.68	1.000	1.000

"Uncertainties were calculated for each individual point, and for each data point, the combined standard uncertainties are no larger than u(T) = 0.26 K, $u(x_1) = 0.010$ mol·mol⁻¹, $u(y_1) = 0.009$ mol·mol⁻¹, and u(P) = 0.18 kPa. Individual data point uncertainties are provided in the Supporting Information in Table S.19.

2.2. Materials. The materials used in this study were the same as those used in the previous studies.^{8,9} Table 1 presents the list of chemicals that were relevant for the systems presented in this study, including the chemical supplier, CAS numbers, indicated purity, and water content. GC-mass spectrometry (GC-MS) was used to ensure negligible contamination of the chemicals and adherence to the purities indicated by the suppliers. Furthermore, Karl Fischer titrations were performed to ensure that the water content of the chemicals was negligible prior to using it for experimentation.

Pure component vapor pressure curves were also generated prior to experimentation and compared to the literature as additional confirmation of the chemical purities. These data, along with the experimental pure component boiling temperatures, were provided in previous studies and showed good agreement with literature data.^{8,9}

2.3. Uncertainty. The uncertainties associated with the temperature, pressure, and composition measurements that are reported were determined by using the recommendations in the Evaluation of Measurement Data—Guide to Expression of Uncertainty in Measurement (GUM).¹⁴ All uncertainties that

^{*a*}Uncertainties were calculated for each individual point, and for each data point, the combined standard uncertainties are no larger than u(T) = 0.27 K, $u(x_1) = 0.008$ mol·mol⁻¹, $u(y_1) = 0.007$ mol·mol⁻¹, and u(P) = 0.18 kPa. Individual data point uncertainties are provided in the Supporting Information in Table S.20.

are reported were determined as the combined standard uncertainties, taking all of the uncertainty contributions into account in accordance with the law of uncertainty propagation. The contributions that were taken into account for each of the measurements are provided in the Supporting Information, along with the individual uncertainties that were calculated for each of the experimental data points.

2.4. Thermodynamic Consistency. Although the reliability of the newly measured experimental data was ensured by verifying the equipment and procedure in our previous work,^{8,9} and by conducting uncertainty analysis, the thermodynamic consistency of the newly measured data must also be ensured. To this end, the newly measured data were tested for thermodynamic consistency by means of the L/W Wisniak,^{15,16} McDermott–Ellis,¹⁷ and Fredenslund¹⁸ consistency tests as recommended by Wisniak et al.¹⁹ Information on these tests and pure component parameters used, as well as the point-to-point consistency results for the L/W Wisniak and McDermott–Ellis tests and the Fredenslund test results, is provided in the Supporting Information.

pubs.acs.org/jced

T/K	$x_1/\text{mol}\cdot\text{mol}^{-1}$	$y_1/\text{mol}\cdot\text{mol}^{-1}$
414.07	0.000	0.000
414.44	0.021	0.013
415.14	0.073	0.040
415.78	0.126	0.062
416.63	0.195	0.083
417.47	0.244	0.102
418.15	0.287	0.113
419.94	0.393	0.144
421.91	0.483	0.175
422.05	0.490	0.178
422.41	0.504	0.182
422.58	0.510	0.186
424.48	0.589	0.220
426.31	0.634	0.249
427.61	0.672	0.278
428.34	0.689	0.287
428.35	0.692	0.287
431.02	0.750	0.336
431.58	0.758	0.346
435.20	0.819	0.425
436.48	0.837	0.455
438.15	0.857	0.494
440.86	0.888	0.566
442.54	0.906	0.607
442.92	0.911	0.617
446.56	0.944	0.721
449.63	0.968	0.833
451.21	0.981	0.891
453.32	0.996	0.974
454.00	1.000	1.000

Table 5. Experimental VLE Data for the 1-Decanol (1) + n-Undecane (2) System at Pressure p = 40 kPa, Given at Temperature *T*, Liquid Mole Fraction x_1 , and Vapor Mole Fraction y_1^a

T/K	$x_1/\text{mol}\cdot\text{mol}^{-1}$	$y_1/mol \cdot mol^{-1}$
434.70	0.000	0.000
435.04	0.024	0.013
435.05	0.024	0.014
436.26	0.108	0.055
436.80	0.159	0.076
437.03	0.170	0.077
438.41	0.266	0.112
441.17	0.414	0.175
441.52	0.437	0.180
442.86	0.486	0.216
444.37	0.549	0.249
446.17	0.605	0.286
446.30	0.618	0.286
446.77	0.629	0.295
446.77	0.630	0.298
448.12	0.663	0.324
451.38	0.744	0.400
456.23	0.832	0.522
456.78	0.846	0.539
460.97	0.901	0.660
463.71	0.938	0.753
466.24	0.962	0.844
468.43	0.984	0.927
470.29	1.000	1.000

"Uncertainties were calculated for each individual point, and for each data point, the combined standard uncertainties are no larger than u(T) = 0.32 K, $u(x_1) = 0.007$ mol·mol⁻¹, $u(y_1) = 0.006$ mol·mol⁻¹, and u(P) = 0.2 kPa. Individual data point uncertainties are provided in the Supporting Information in Table S.21.



Figure 1. Temperature, *T*, versus experimental liquid mole fraction, x_1 , and experimental vapor mole fraction, y_1 , at pressure p = 40 kPa for 1-heptanol (1) + *n*-octane (2) (blue markers), 1-octanol (1) + *n*-nonane (2) (red markers), 1-nonanol (1) + *n*-decane (2) (gray markers), and 1-decanol (1) + *n*-undecane (2) (green markers).



Figure 2. Vapor mole fraction, y_1 , versus liquid mole fraction, x_1 , at pressure p = 40 kPa for 1-heptanol (1) + *n*-octane (2) (blue markers), 1-octanol (1) + *n*-nonane (2) (red markers), 1-nonanol (1) + *n*-decane (2) (gray markers), and 1-decanol (1) + *n*-undecane (2) (green markers).



Figure 3. Experimentally calculated excess molar Gibbs energy, G_{mv}^E vs liquid mole fraction, x_1 , for 1-heptanol (1) + *n*-octane (2) (blue markers), 1-octanol (1) + *n*-nonane (2) (red markers), 1-nonanol (1) + *n*-decane (2) (gray markers), and 1-decanol (1) + *n*-undecane (2) (green markers). The numerical values for the excess molar Gibbs energy are provided in the Supporting Information in Tables S.18–S.21.

2.5. Experimental Data. The experimental T-xy data are provided in Tables 2–5 for 1-heptanol + *n*-octane, 1-octanol + *n*-nonane, 1-nonanol + *n*-decane, and 1-decanol + *n*-undecane, respectively, while the data are provided graphically in Figure 1.

From Figure 1, it is clear that, as the carbon number of the molecules increases, the size of the phase envelope decreases. This is due to the difference in the pure component saturation temperatures of the system decreasing as the molecule size increases, therefore decreasing the relative volatility of the system.

The reduction in the relative volatility is also evidenced in Figure 2 where the systems with smaller molecules have an xy

graph that is further away from the x = y line, while the *xy* graphs tend toward the x = y line as the molecule size increases.

From Figure 1 and Figure 2, it is clear that the systems investigated do not present azeotropy, as no temperature minimum is observed in Figure 1 and none of the *xy* graphs intersect the x = y line. The systems did, however, display positive deviations from ideality, which is evident from Figure 3, as each of the systems exhibited molar excess Gibbs energies which were greater than zero. These experimental molar excess Gibbs energies were calculated from eq 1 where *R* refers to the universal gas constant, *T* refers to the experimental temperature, x_i refers to the experimental mole fraction, and γ_i refers to the experimentally determined activity coefficient:

$$G_{\rm m}^{\rm E} = RT \sum_{i}^{n} x_i \ln \gamma_i \tag{1}$$

From Figure 3, it is surmised that, as the carbon chain of the *n*-alkane and 1-alcohol increased, the deviation from ideality decreased.

In contrast to the temperature–composition and composition plots provided in Figure 1 and Figure 2, respectively, the molar excess Gibbs energy plot shows some scatter. This is purely because the difference in the saturation temperatures of the pure components is significant; therefore, the equilibrium temperature measured fluctuated up to 0.2 K. As the molar excess Gibbs energy is a strong function of temperature, these fluctuations increased the scatter of the G_m^E plots over the compositional spectrum.

3. COMPARISON OF HOMOLOGOUS SERIES

Four series of binary 1-alcohol + *n*-alkane data sets have been systematically measured, including $C_nOH + C_{n+1}$, $C_nOH + C_{n+2}$, $C_nOH + C_{n+3}$, and $C_nOH + C_{n+4}$ systems where the *n*-alkanes ranged from *n*-octane to *n*-tetradecane and the 1-alcohol ranged from 1-pentanol to 1-decanol.⁸⁻¹⁰ Each of the data sets in the previous and present studies were measured at a constant pressure of 40 kPa, in order to investigate trends within each of these series (with increasing molecular size) and between series (as the alkane or alcohol remains constant and the other molecule changes).

3.1. Effect of Molecular Size. The previous studies by Schwarz and co-workers⁸⁻¹⁰ investigated the effect of molecule size (that is, the effect of the increasing carbon number) within the series where the *n*-alkane molecule was 2, 3, and 4 carbon atoms larger than the 1-alcohol. Table 6 provides the azeotropic temperature, azeotropic composition, and saturation temperature difference for each series of systems considered.

Based on the data provided in Table 6 and the discussions provided by Schwarz and co-workers, $^{8-10}$ the trends that were observed were similar in each of these series and can be summarized as follows:

- As the molecular size of the 1-alcohol and *n*-alkane increased, the azeotrope shifted toward the 1-alcohol-rich side of the compositional spectrum. This could be attributed to the saturation temperature of the *n*-alkanes increasing more with molecular size than the 1-alcohols thus reducing the difference in the saturation temperature between the two pure components, as the molecule sizes increase.
- As the molecular size of the 1-alcohol and n-alkane increased, the deviation from ideality decreased, with the smallest systems showing the largest deviation and

Table 6. Experimental Azeotropic Temperature, $T_{azeotrope}$, Azeotropic Mole Fraction in Terms of the 1-Alcohol, $x_{1,azeotrope}$, and the Experimental Difference between the Pure Component Saturation Temperatures of the 1-Alcohol and *n*-Alkane $T_{sat,difference}^{a}$ for the $C_nOH + C_{n+2}$, $C_nOH + C_{n+3}$, $Q_nOH + C_{n+3}$ and $C_nOH + C_{n+4}$ Systems at p = 40 kPa

System	$T_{ m azeotrope}/{ m K}$	$x_{1,azeotrope}/mol\cdot mol^{-1}$	$T_{\rm sat, difference}^{a}/{ m K}$
	$C_nOH + C_{n+}$	2	
1-hexanol + <i>n</i> -octane	368.2	0.060	34.0
1-heptanol + <i>n</i> -nonane	391.9	0.069	28.5
1-octanol + <i>n</i> -decane	414.0	0.072	23.5
1-nonanol + <i>n</i> -undecane	434.5	0.081	19.1
1-decanol + <i>n</i> -dodecane	453.8	0.083	16.3
	$C_nOH + C_{n+}$	3	
1-pentanol + <i>n</i> -octane	364.8	0.226	16.5
1-hexanol + <i>n</i> -nonane	387.7	0.288	10.6
1-heptanol + <i>n</i> -decane	409.3	0.353	6.7
1-octanol + <i>n</i> -undecane	429.3	0.409	2.8
1-nonanol + <i>n</i> -dodecane	448.3	0.473	0.2
1-decanol + <i>n</i> -tridecane	466.0	0.528	-1.5
	$C_nOH + C_{n+}$	4	
1-pentanol (1) + <i>n</i> -nonane (2)	378.0	0.538	-7.7
1-hexanol (1) + <i>n</i> -decane (2)	398.5	0.598	-11.8
1-heptanol (1) + <i>n</i> -undecane (2)	416.8	0.690	-15.1
1-octanol (1) + <i>n</i> -dodecane (2)	435.3	0.721	-17.3
1-decanol (1) + <i>n</i> -tetradecane (2)	468.7	0.888	-19.9

 ${}^{a}T_{\text{sat,difference}} = T_{\text{sat,1-alcohol}} - T_{\text{sat,n-alkane}}$



Figure 4. Temperature, *T*, versus experimental liquid mole fraction, x_1 , and experimental vapor mole fraction, y_1 , at pressure p = 40 kPa for 1-octanol (1) + *n*-nonane (2) (\triangle), 1-octanol (1) + *n*-decane (2)⁸ (\bigcirc), 1-octanol (1) + *n*-decane (2)¹⁰ (\bigcirc), and 1-octanol (1) + *n*-dodecane (2)¹⁰ (\diamondsuit).

maxima on the molar excess Gibbs energy plots. The degree of nonideality is thus dependent on the carbon chain length of the pure components. This trend may be explained by the fact that, as the molecular size increases,



Figure 5. Vapor mole fraction, y_1 , vs liquid mole fraction, x_1 , at pressure p = 40 kPa for 1-octanol (1) + *n*-nonane (2) (\triangle), 1-octanol (1) + *n*-decane (2)⁸ (\bigcirc), 1-octanol (1) + *n*-undecane (2)⁹ (\square), and 1-octanol (1) + *n*-dodecane (2)¹⁰ (\diamondsuit).



Figure 6. Experimentally calculated molar Gibbs energy, G_m^E , vs liquid mole fraction, x_1 , for 1-octanol (1) + *n*-nonane (2) (\triangle), 1-octanol (1) + *n*-decane (2)⁸ (\bigcirc), 1-octanol (1) + *n*-undecane (2)⁹ (\square), and 1-octanol (1) + *n*-dodecane (2)¹⁰ (\diamondsuit).

the hydroxyl groups become more diluted and thus the molecules become more similar with respect to molecular interactions.

These observations were generally true for the data presented in this study, where the *n*-alkane chain was one carbon longer than the 1-alcohol. However, the systems presented in this study did not display azeotropy. It is postulated that the magnitude of the difference between the pure component saturation temperature for the $C_nOH + C_{n+1}$ systems is too great, and therefore, the increase in the vapor pressure of the mixture due to the hydrogen bonding between the self-associating 1-alcohols is not significant enough to give cause to a minimum boiling azeotrope.

3.2. Effect of Changing *n***-Alkane.** The effect of changing the *n*-alkane in systems with the 1-alcohol was considered by



Figure 7. Azeotropic composition, $x_{azeotrope}$ in terms of the 1-alcohol mole fraction plotted against the carbon number of the *n*-alkane in the system. Colors indicate the 1-alcohol in the systems: 1-decanol (green), 1-nonanol (gray), 1-octanol (red), 1-heptanol (blue), 1-hexanol (orange), and 1-pentanol (purple). Circle markers are used to indicate the $C_nOH + C_{n+2}$ series of systems,⁹ square markers are used for the $C_nOH + C_{n+3}$ systems,⁹ and diamond markers are used for the $C_nOH + C_{n+4}$ systems.¹⁰

Table 7. Results Obtained for the Linear Regression of the Azeotropic Composition as a Function of the Carbon Number of the *n*-Alkane for the $C_nOH + C_{n+2}$, $C_nOH + C_{n+3}$, and $C_nOH + C_{n+4}$ Systems, Including the Slope and Intercept Parameters, as Well as the R^2 Value That Was Obtained for Each Series of Systems

Series of systems	Slope parameter	Intercept parameter	R^2 value
$C_nOH + C_{n+2}$	0.0058	0.015	0.9611
$C_nOH + C_{n+3}$	0.0602	-0.2538	0.9995
$C_nOH + C_{n+4}$	0.0691	-0.0869	0.9881

plotting the T-xy and xy data for systems with the same 1alcohol in one figure. The data for 1-octanol are presented in this section and are given in Figure 4 and Figure 5. Similar trends are observed for other alcohols considered in this work. It is evident that there is a clear progression in the phase behavior as the carbon number of the *n*-alkane carbon increased from C_9 to C_{12} .

The azeotropic composition shifted in the direction of the 1alcohol-rich region as the difference in the size of the carbonchain length of the *n*-alkane increased. This can be seen clearly from Figure 5 as the intersection of each of the *xy* graphs with the x = y line shifts toward the 1-alcohol-rich side of the compositional spectrum as the molecular size increases and 1octanol changes from being the less volatile component to being the more volatile component.

The molar excess Gibbs energy functions of each of the 1octanol systems are further considered, to evaluate the degree of nonideality observed in each of the series $(C_nOH + C_{n+1}, C_nOH + C_{n+2}, C_nOH + C_{n+3}, \text{ and } C_nOH + C_{n+4})$. Figure 6 indicates the molar excess Gibbs energy of the 1-octanol systems as a function of the liquid composition.

As is evidenced from Figure 6, the deviation from ideality is similar for each of the systems and does not change significantly between series as the *n*-alkane increases in size.

370

0.0

0.2



 $x_1, y_1 \ / \ \mathrm{mol} \cdot \mathrm{mol}^-$ **Figure 8.** Temperature, *T*, versus experimental liquid mole fraction, x_1 , and experimental vapor mole fraction, y_1 , at pressure p = 40 kPa for liquid mole fraction, x_1 , and experimental vapor mole fraction, y_1 , at pressure p = 40 kPa for 1-octanol (1) + *n*-nonane (2) (red \triangle), 1heptanol (1) + *n*-nonane (2)⁸ (blue \bigcirc), 1-hexanol (1) + *n*-nonane (2)⁹ (orange \Box), and 1-pentanol (1) + *n*-nonane (2)¹⁰ (purple \diamondsuit).

0.6

0.8

1.0

0.4



Figure 9. Vapor mole fraction, y_1 , versus liquid mole fraction, x_1 , at pressure p = 40 kPa for 1-octanol (1) + *n*-nonane (2) (red \triangle), 1heptanol (1) + n-nonane $(2)^8$ (blue \bigcirc), 1-hexanol (1) + n-nonane $(2)^9$ (orange \Box), and 1-pentanol (1) + *n*-nonane (2)¹⁰ (purple \diamondsuit).

Finally, in Figure 7 the azeotropic compositions for the systems that displayed azeotropy $(C_nOH + C_{n+2}, C_nOH + C_{n+3})$ and $C_nOH + C_{n+4}$) were plotted as a function of the carbon number of the *n*-alkane. For each series considered (indicated by the different markers), it is evident that a linear relationship is observed. It would therefore be possible to extrapolate the linear function to higher and lower carbon numbers in each series and subsequently estimate the azeotropic composition of systems not considered here. Table 7 provides the result of the linear regression that was performed for each of the series of systems. The reported R^2 values indicate that the linear model is able to describe 96.11%, 99.95%, and 98.81% of the variability in the



Figure 10. Difference in the pure component saturation temperature between the 1-alcohol and *n*-alkane, $\Delta T^{
m saturaton}$, determined as $\Delta T^{
m saturation}$ = $T^{
m saturation}_{
m 1-alcohol}$ - $T^{
m saturation}_{
m alkane}$ versus the azeotropic composition, x_{azeotrope}, in terms of the 1-alcohol composition: 1-decanol (green), 1nonanol (gray), 1-octanol (red), 1-heptanol (blue), 1-hexanol (orange), and 1-pentanol (purple). Circle markers are used to indicate the $C_nOH + C_{n+2}$ series of systems,⁸ square markers are used for the $C_nOH + C_{n+3}$ systems,⁸ and diamond markers are used for the $C_nOH + C_nOH$

0.6

/ mol·mol

0.8

1.0

0.4

 $x_{azeotrope}$

-40 0.0

0.2



Figure 11. Ratio of the pure component saturation temperatures $\frac{1}{T^{sat2}}$ versus the azeotropic composition, $x_{azeotrope}$, in terms of the 1-alcohol composition: 1-decanol (green), 1-nonanol (gray), 1-octanol (red), 1heptanol (blue), 1-hexanol (orange), and 1-pentanol (purple). Circle markers are used to indicate the $C_nOH + C_{n+2}$ series of systems, square markers are used for the $C_nOH + C_{n+3}$ systems, and diamond markers are used for the $C_nOH + C_{n+4}$ systems. All data are from Schwarz and co-workers,⁸⁻¹⁰ except the 1-pentanol + *n*-heptane data were obtained from Mohsen-Nia and Memarzadeh.²⁰

data for the $C_nOH + C_{n+2}$, $C_nOH + C_{n+3}$, and $C_nOH + C_{n+4}$ series, respectively. Furthermore, it is evident that the slopes for the $C_nOH + C_{n+3}$ and $C_nOH + C_{n+4}$ systems are greater than those of the $C_nOH + C_{n+2}$ systems, and therefore, the azeotropic composition changes more drastically for the former two systems than the latter as the carbon number changes.



Figure 12. Ratio of the azeotropic temperature and the saturation temperatures of component 1, $\frac{T^{\text{sull}}}{T^{\text{sull}}}$, versus the azeotropic composition, $x_{\text{azeotrope}}$, in terms of the 1-alcohol composition: 1-decanol (green), 1-nonanol (gray), 1-octanol (red), 1-heptanol (blue), 1-hexanol (orange), and 1-pentanol (purple). Circle markers are used to indicate the $C_nOH + C_{n+2}$ series of systems, square markers are used for the $C_nOH + C_{n+3}$ systems, and diamond markers are used for the $C_nOH + C_{n+4}$ systems.

Considering Figure 4, it is seen that the size of the phase envelope decreases as the *n*-alkane number increases, from *n*nonane to *n*-undecane, but then increases for the 1-octanol + *n*dodecane combination. Finally, from Figure 5, it is seen that the azeotrope shifts toward the 1-octanol-rich side as the *n*-alkane carbon number increases. These observations are attributed to the change in the difference of the pure component saturation temperature and the size of the *n*-alkane, as larger *n*-alkanes contribute to more steric hindrance and therefore inhibit the self-associating 1-octanol from forming multimers more readily. **3.3. Effect of Changing 1-Alcohol.** This section investigates the effect of changing the 1-alcohol while keeping the *n*-alkane constant. The data for *n*-nonane are plotted in Figure 8 and Figure 9, and similar to the previous data shown for the 1-octanol systems in Figure 4 and Figure 5, clear progression of the phase behavior is observed as the carbon number of the 1-alcohol increases from C_5 to C_8 .

The observations are similar to the previous section; however, here the azeotropic composition shifts toward the 1-alcohol-rich side as the 1-alcohol carbon number increases. This is again attributed to the larger 1-alcohol molecule contributing to more steric hindrance, since the larger carbon chain of the alcohol molecule inhibits the terminal hydroxyl group from selfassociating.

3.4. Effect of Saturation Temperature. When considering the azeotropic composition as a function of the difference in the pure component saturation temperatures ($T^{\text{saturation}}$), two observations can be made:

- For systems where the difference in the pure component saturation temperature is small, the azeotropic composition is close to equimolar.
- When $T_{alkane}^{saturation} > T_{alcohol}^{saturation}$, the azeotropic composition is in the 1-alcohol-rich region, while the azeotropic composition was in the *n*-alkane-rich region when $T_{alkane}^{saturation} < T_{alcohol}^{saturation}$.

These observations are evident from Figure 10.

From Figure 10, it can be seen that there is a negative relationship between the azeotropic composition and the difference in the pure component saturation temperature for the 1-alcohol + *n*-alkane systems. This is shown by the negative slope of the trendlines included in Figure 10, which indicates that, as the difference in the pure component saturation temperatures approaches zero, the azeotropic composition shifts toward the middle of the compositional spectrum. Furthermore, the azeotropic composition is concentrated in the 1-alcohol-rich region ($x_{1-alcohol} > 0.5$) for systems where the *n*-alkane saturation temperature is higher than the 1-alcohol, and similarly, the azeotropic composition lies in the *n*-alkane-rich

Table 8. Pure Component Parameters for PC-SAFT Used in This Work^a

						%AA	RD	
Component	σ (Å)	т	$\varepsilon/k_{\rm B}$ (K)	$\varepsilon^{\rm AB}/k_{\rm B}$ (K)	κ^{AB}	p^{sat}	$ ho^{ m sat}$	ref.
n-pentane	3.7729	2.6896	231.20			0.250	1.292	31
<i>n</i> -hexane	3.7983	3.0576	236.77			0.641	0.619	31
n-heptane	3.8049	3.4831	238.40			0.255	0.874	31
<i>n</i> -octane	3.8373	3.8176	242.78			0.435	0.757	31
<i>n</i> -nonane	3.8448	4.2079	244.51			0.524	0.592	31
<i>n</i> -decane	3.8384	4.6627	243.87			0.940	0.555	31
<i>n</i> -undecane	3.8893	4.9082	248.82			1.130	0.646	31
<i>n</i> -dodecane	3.8959	5.3060	249.21			0.874	0.718	31
n-tridecane	3.9143	5.6877	249.78			1.435	1.066	31
n-tetradecane	3.9396	5.9002	254.21			2.207	0.755	31
1-pentanol	3.4508	3.6260	247.28	2252.10	0.01032	0.747	0.363	32
1-hexanol	3.6735	3.5146	262.32	2538.90	0.00575	1.747	0.499	32
1-heptanol	3.5450	4.3985	253.46	2878.50	0.00116	2.169	2.114	32
1-octanol	3.7145	4.3555	262.74	2754.80	0.00220	3.416	0.552	32
1-nonanol	3.7292	4.6839	263.64	2941.90	0.00143	1.628	0.985	32
1-decanol	3.8627	4.7230	267.92	2811.02	0.00330	1.177	0.477	57

"All alcohols are modeled with the 2B association scheme. ^b%AARD = $100/N_X \sum_i^{N_X} |X_i^{calc} - X_i^{exp}|/X_i^{exp}$, where X is the property, N_X is the number of data points of X, and the superscript "calc" refers to calculated values and the superscript "exp" refers to 30 equidistant points calculated from DIPPR⁵⁸ correlations in the range 0.5 < T_r < 0.9.

- 1-

Table 9. Pure Component Parameters for SAFT-VR Mie Used in This	Work","
---	---------

								%AARD ^c	
Component	$\sigma\left(\mathrm{\AA}\right)$	т	$\varepsilon/k_{\rm B}$ (K)	$\lambda^{ m r}$	$\varepsilon^{\mathrm{AB}}/k_{\mathrm{B}}$ (K)	$r_{ m c}^{ m AB}/\sigma$	$p^{\rm sat}$	$p^{\rm sat}$	ref.
<i>n</i> -pentane	4.3759	1.8594	336.74	16.438			0.232	0.272	59
<i>n</i> -hexane	4.2969	2.2549	321.81	15.069			1.231	0.073	59
n-heptane	4.5427	2.2413	381.42	18.252			0.462	0.109	59
<i>n</i> -octane	4.5708	2.4777	391.87	18.654			0.386	0.139	59
<i>n</i> -nonane	4.6236	2.6665	404.83	19.116			0.587	0.140	59
<i>n</i> -decane	4.5727	3.0058	396.17	18.403			0.838	0.163	59
<i>n</i> -undecane	4.6328	3.1753	414.49	19.551			0.417	0.289	this work
n-dodecane	4.7430	3.2483	438.20	20.872			0.629	0.237	59
n-tridecane	4.7279	3.5050	437.24	20.634			1.390	0.799	this work
n-tetradecane	4.7156	3.7825	437.42	20.660			0.764	0.476	this work
1-pentanol	4.0140	2.4568	308.76	12.633	2632.72	0.34110	0.269	0.168	60
1-hexanol	4.4996	2.0859	377.99	14.000	3180.89	0.27399	0.600	0.170	this work
1-heptanol	4.3650	2.6310	378.89	15.513	3034.79	0.28448	0.295	0.802	this work
1-octanol	4.5181	2.6382	400.23	16.173	2959.50	0.29947	0.111	0.120	61
1-nonanol	4.9736	2.2449	459.01	17.089	3456.94	0.26445	0.276	0.237	61
1-decanol	5.0310	2.4250	478.59	18.915	3197.07	0.28719	0.124	0.152	61

^{*a*} For all molecules, $\lambda^{a} = 6$. ^{*b*} All alcohols are modeled with the 2B association scheme. ^{*c*}%AARD = $100/N_{X} \sum_{i}^{N_{X}} |X_{i}^{calc} - X_{i}^{exp}|/X_{i}^{exp}$, where X is the property, N_{X} is the number of data points of X, the superscript "calc" refers to calculated values, and "exp" refers to 30 equidistant points calculated from DIPPR⁵⁸ correlations in the range $0.5 < T_{r} < 0.9$.

region $(x_{1-\text{alcohol}} < 0.5)$ for systems where the 1-alcohol saturation temperature is higher than the *n*-alkane.

Although the phase behavior analysis performed up until now only regarded data measured at 40 kPa under isobaric conditions, it is also necessary to evaluate data measured under other conditions. Since both the pure component saturation temperatures and azeotropic temperature and composition are a function of the system pressure, the ratio of the pure component saturation temperatures as a function of the azeotropic temperature was evaluated including literature data for 1-pentanol + *n*-heptane at 53.3 and 91.3 kPa²⁰ (Figure 11). The remaining literature data for 1-alcohols ranging from C₅ to C₁₀ and *n*-alkanes ranging from C₈ to C₁₄ were either isothermal or only *T*–*x* data were available from which the azeotropic composition cannot be easily determined and was therefore not considered.

Figure 11 allows the azeotropic composition to be evaluated as a function of a dimensionless variable which makes it possible to consider systems at pressures other than 40 kPa. From Figure 11, the same conclusions that were made for Figure 10 are observed. Thus, when the pure component saturation temperatures approach equality (thus, when the ratio of the pure component saturation temperatures approach 1, as observed for the $C_nOH + C_{n+3}$ systems), the azeotropic composition tends to equimolar. Furthermore, for the systems where the ratio is larger than 1, as observed for the $C_nOH + C_{n+2}$ systems (thus, when the saturation temperature for component 1 is larger than that for component 2), the azeotropic composition is concentrated in the component-2-rich region, while the opposite is true when the ratio is smaller than 1, as observed for the $C_nOH + C_{n+4}$ systems.

3.5. Temperature Dependence of the Azeotrope. Finally, the temperature dependence of the azeotrope is considered. The dimensionless variable $\frac{T^{\text{sat1}}}{T^{\text{sat2}}}$ is thus plotted against the azeotropic composition in Figure 12.

From Figure 12, it is seen that, as the ratio of the azeotropic composition to the saturation temperature of component 1 increases, the azeotropic composition shifts toward the

component-1-rich side of the compositional spectrum. This is observed within the series of systems considered, as each of the series display positive slopes, and is also observed between the three series considered.

4. THERMODYNAMIC MODELING WITH SAFT MODELS

The statistical associating fluid theory, or SAFT, is a family of equations of state that finds its roots in statistical mechanics and

Table 10.	Deviation	Values for	the Binary	VLE Investigated
in This W	ork Using	PC-SAFT	and SAFT-	VR Mie

	PC-SAFT			SAFT-VR Mie						
system	Δy^{a}	Δp^{b}	$\Delta T^{c}/K$	Δy^{a}	$\Delta p^{\mathbf{b}}$	$\Delta T^{c}/\mathrm{K}$	refs.			
(n + 1)	3.78	8.23	2.93	2.28	4.02	1.47	65-72			
(<i>n</i> + 2)	3.42	9.42	2.67	1.73	3.58	1.03	8, 20, 63–65, 69, 73–77			
(<i>n</i> + 3)	4.28	10.39	2.35	2.30	3.43	0.82	9, 62, 65, 69, 74, 78			
(n + 4)	6.33	6.15	3.87	4.15	1.53	1.85	10, 65, 74			
${}^{a}\Delta y = AADy = 100/N \sum_{i}^{N} y_{i}^{calc} - y_{i}^{exp} $. ${}^{b}\Delta p = \%AARD = 100/N \sum_{i}^{N} p_{i}^{calc} - p_{i}^{exp} /p_{i}^{exp}$; calculated for the isothermal systems. ${}^{c}\Delta T = AADT$										
= $1/N \sum_{i}^{N} T_{i}^{\text{calc}} - T_{i}^{\text{exp}} $; calculated for the isobaric systems. N is the										
number o	f data p	oints, an	d the sup	perscript	ts "calc'	' and "ex	p" refer to			
calculated and experimental values, respectively.										

can account for deviations from ideality in both the vapor and the liquid phases. The theory is derived from the first-order perturbation theory of Wertheim,^{21–24} which was extended by Chapman and co-workers^{25,26} to develop the following Helmholtz free energy expansion:

$$\frac{A^{\rm r}}{N_{\rm A}k_{\rm B}T} = \left(\frac{A^{\rm hs}}{N_{\rm A}k_{\rm B}T} + \frac{A^{\rm disp}}{N_{\rm A}k_{\rm B}T}\right)^{\rm seg} + \frac{A^{\rm chain}}{N_{\rm A}k_{\rm B}T} + \frac{A^{\rm assoc}}{N_{\rm A}k_{\rm B}T}$$
(2)



Figure 13. T-xy plots of the (n + x) systems measured at p = 40 kPa: (a) (n + 1); (b) (n + 2); (c) (n + 3); (d) (n + 4). Predictions were obtained with PC-SAFT (solid lines) and SAFT-VR Mie (dashed lines). In all graphs, the alkanol is component 1. Colors are used to identify the alkanol: 1-pentanol (purple); 1-hexanol (orange); 1-heptanol (blue); 1-octanol (red); 1-nonanol (gray); 1-decanol (green). Data are from this work and from Schwarz and co-workers.⁸⁻¹⁰

The residual Helmholtz free energy A^r is calculated as the sum of the following contributions: a reference system (seg) that contains hard spheres (hs) to which dispersion forces (disp) are added, the formation of chain molecules (chain), and hydrogen bonding, or association (assoc), where such forces are present.

The choice of reference fluid and the addition of terms accounting for other interactions, among other things, have led to the development of many different versions of SAFT models. The successes and limitations of SAFT are discussed in many good review articles.^{27–29} In this contribution, we chose to work with two versions of SAFT:

- PC-SAFT,³⁰⁻³² which has been used to describe the properties of a wide range of systems, including polymers,^{33,34} biofuels,^{35,36} and pharmaceuticals;^{37,38}
 SAFT-VR Mie,³⁹⁻⁴¹ which is a more advanced version of
- SAFT-VR Mie, ³⁹⁻⁴¹ which is a more advanced version of SAFT than PC-SAFT. SAFT-VR Mie has been used to describe the properties of, among others, hydro-

carbons,^{42–44} flue gas components,^{44–48} and associating molecules.^{49–53}

4.1. PC-SAFT. The perturbed-chain SAFT equation of state (PC-SAFT), developed by Gross and Sadowski, 30-32 introduces a fundamental difference to eq 2, that is, that a reference fluid of hard chains, rather than hard spheres, is considered. This requires a reformulation of eq 2:

$$\frac{A^{\rm r}}{N_{\rm A}k_{\rm B}T} = \left(\frac{A^{\rm hs}}{N_{\rm A}k_{\rm B}T} + \frac{A^{\rm chain}}{N_{\rm A}k_{\rm B}T}\right)^{\rm hc} + \frac{A^{\rm disp}}{N_{\rm A}k_{\rm B}T} + \frac{A^{\rm assoc}}{N_{\rm A}k_{\rm B}T}$$
(3)

Once the reference chain is formed, dispersion forces are added to each chain, rather than each segment. In this way, the chain length dependence of the dispersion energy is taken into account, which is not the case when molecules are formed via eq 2.



Figure 14. (y - x) vs *x* plots of the systems measured at p = 40 kPa: (a) (n + 1); (b) (n + 2); (c) (n + 3); (d) (n + 4). Predictions obtained with PC-SAFT (solid lines) and SAFT-VR Mie (dashed lines). In all graphs, the alkanol is component 1. Colors are used to identify the alkanol: 1-pentanol (purple); 1-hexanol (orange); 1-heptanol (blue); 1-octanol (red); 1-nonanol (gray); 1-decanol (green). Data are from this work and from Schwarz and co-workers.^{8–10}

PC-SAFT further makes use of the modified square-well potential function of Chen and Kreglewski.⁵⁴ This simple function introduces a soft repulsion to the potential function which is important to the behavior of real molecules. More details on the development of PC-SAFT can be found in the original manuscripts.^{30–32} The PC-SAFT parameters used in this work are shown in Table 8.

4.2. SAFT-VR Mie. The SAFT with variable range Miepotential³⁹⁻⁴¹ (SAFT-VR Mie) describes the interaction between molecules using the Mie-potential u^{Mie} .⁵⁵

$$u^{\text{Mie}}(r) = C_{ij} \varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{\lambda_{ij}^{r}} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{\lambda_{ij}^{s}} \right]$$
(4)

$$C_{ij} = \frac{\lambda_{ij}^{r}}{\lambda_{ij}^{r} - \lambda_{ij}^{a}} \left(\frac{\lambda_{ij}^{r}}{\lambda_{ij}^{a}} \right)^{\lambda_{ij}^{a} / (\lambda_{ij}^{r} - \lambda_{ij}^{a})}$$
(5)

Here σ is the temperature independent segment diameter, ε is the Mie-potential well-depth and is also called the dispersion energy, and r is the distance between two segments. λ^{a} and λ^{r} are the attractive and repulsive potential range parameters, respectively. For most fluids, λ^{a} is set equal to the London dispersion value of 6.⁵⁶

SAFT-VR Mie expands the dispersion term up to third-order, a feature that allows for improved description of pure component behavior in the near-critical region. Details about the model development can be found in Lafitte et al.⁴¹ The





Figure 15. Azeotropic composition, $x_{azeotrope}$, in terms of the 1-alcohol mole fraction plotted against the carbon number of the *n*-alkane in the system. Colors indicate the 1-alcohol in the systems: 1-decanol (green), 1-nonanol (gray), 1-octanol (red), 1-heptanol (blue), 1-hexanol (orange), and 1-pentanol (purple). Circle markers are used to indicate the $C_nOH + C_{n+2}$ series of systems, square markers are used for the $C_nOH + C_{n+3}$ systems, and diamond markers are used for the $C_nOH + C_{n+4}$ systems. Solid lines are PC-SAFT predictions, while dashed lines are SAFT-VR Mie predictions.

SAFT-VR Mie parameters used in this work are shown in Table 9.

4.3. Modeling Results. The deviation results for the systems investigated in this work are shown in Table 10 with further details provided in the Supporting Information. Here we attempt to show the predictive capabilities of the two models; therefore, no binary interaction parameters are used, i.e., all $k_{ij} = 0$.

Overall, the predictions obtained with SAFT-VR Mie are much better than those obtained with PC-SAFT. This is observed in both the deviations presented in Table 10, as well as the T-xy plots in Figure 13. PC-SAFT offers a good description of the vapor phase boundaries in only the (n + 1) systems and is not able to describe the liquid phase boundaries in any of the investigated systems. SAFT-VR Mie, on the other hand, offers excellent descriptions of the VLE in these systems and is especially well-suited to describe the very narrow phase envelopes observed in the (n + 3) systems (Figure 13c). Both models offer a good qualitative description of the x-yrelationship, as evidenced in Figure 14. However, apart from the SAFT-VR Mie description for the 1-pentanol + n-nonane mixture, neither model is able to describe the x-y relationship in the (n + 4) systems. This is also observed as an increase in the AADy as the systems become more asymmetric, as shown in Figure 16. Of the investigated mixtures, the (n + 4) systems are the most asymmetric and are also the most nonideal (see section 3.1). This could explain why both models have difficulty describing the observed phase behavior.

The azeotropic composition of the investigated mixtures is predicted in Figure 15. Here it is shown that SAFT-VR Mie also outperforms PC-SAFT. PC-SAFT does not predict an azeotrope in the $C_nOH + C_{n+2}$ systems and only predicts an azeotrope for the lowest $C_nOH + C_{n+4}$ systems. SAFT-VR Mie, on the other hand, is able to predict the azeotrope in almost all the mixtures where an azeotrope is present, and predicts the azeotropic



Figure 16. Average deviations obtained with PC-SAFT (blue) and SAFT-VR Mie (red) for all systems investigated: (a) absolute average deviation in vapor mole fraction (AADy); (b) percentage absolute average relative deviation in pressure (%AARDP); (c) absolute average deviation in temperature (AADT).

composition accurately for both the $C_nOH + C_{n+2}$ and $C_nOH + C_{n+3}$ systems.

One could argue that the better descriptions obtained by SAFT-VR Mie are due to the additional degree of freedom offered by the additional parameter that is varied during parameter regressions (λ^r) and that a fairer comparison of the model performances could be obtained by fitting PC-SAFT to the binary VLE through $k_{ij} \neq 0$. The repulsive range parameter, along with the stronger fundamental foundation of SAFT-VR Mie, certainly offers an improved description of the pure component behavior, as evidenced by the deviations obtained for pure component properties (see Table 9). However, λ^r is



Figure 17. Predictions obtained with PC-SAFT (solid lines) and SAFT-VR Mie (dashed lines) for (a) 1-pentanol + *n*-nonane at p = 26.66 kPa,⁶² p = 40 kPa,¹⁰ p = 53.33 kPa,⁶² p = 79.99 kPa,⁶² and p = 101.32 kPa;⁶² (b) 1-octanol + *n*-decane at T = 353.15 K,⁶³ T = 373.15 K,⁶⁴ T = 383.15 K,⁶⁴ T = 383.15 K,⁷⁵ and T = 353.15 K,⁶⁵ and T = 353.15 K,⁶⁵ methods.

only determined once per molecule and its effect on mixture behavior is transferred, whereas system-specific k_{ij} s will likely need to be determined to obtain improved descriptions with PC-SAFT.

We also investigated the models' performance over extended temperature and pressure ranges. Shown in Figure 17 are predictions for (a) 1-pentanol + n-nonane and (b) 1-octanol + n-decane over a range of conditions. As is clear from these figures, the prediction quality for the models remains constant over the range of conditions.

5. CONCLUSIONS

Isobaric data were presented for four binary 1-alcohol + *n*-alkane systems, where the *n*-alkane was 1 carbon atom larger than the 1alcohol, including 1-heptanol + *n*-octane, 1-octanol + *n*-nonane, 1-nonanol + *n*-decane, and 1-decanol + *n*-undecane. Each of the systems was measured at 40 kPa using a verified dynamic recirculating still and was shown to be thermodynamically consistent. None of the systems presented in this study were azeotropic, in contrast to each of the previously measured series for the $C_nOH + C_{n+2}$, $C_nOH + C_{n+3}$, and $C_nOH + C_{n+4}$ systems, which all presented azeotropy. These systems, however, still presented positive deviations from ideality.

The newly measured data were also considered in conjunction with previously measured data for $C_nOH + C_{n+2}$, $C_nOH + C_{n+3}$, and $C_nOH + C_{n+4}$ systems, which were also measured at 40 kPa in order to elucidate trends and observations within and between a series of systems. For each series, the deviation from ideality was a maximum for the smallest system, while the C_nOH + C_{n+4} series presented the largest deviations from ideality. It is postulated that the former is due to the increased polarity of the smaller 1-alcohol molecules, while the latter is due to the size asymmetry of the molecules, which is a maximum for the C_nOH + C_{n+4} series. Additionally, it was observed that, when considering the azeotropic composition as a function of carbon number while keeping either the 1-alcohol or *n*-alkane constant, an approximately linear trend was observed. Therefore, it could be possible to predict the azeotropic composition for mixtures not considered here by extrapolating to other members of the homologous series using the linear function determined for the $C_nOH + C_{n+2}$, $C_nOH + C_{n+3}$, and $C_nOH + C_{n+4}$ series.

Finally, the phase behavior was modeled predictively with PC-SAFT and SAFT-VR Mie. In all systems, SAFT-VR Mie outperformed PC-SAFT in its description of the VLE, offering better predictions, especially of the liquid phase boundaries. No temperature dependence of the predictions was observed when investigating extended temperature and pressure ranges.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jced.3c00346.

The detailed uncertainty calculations that were conducted for the experimental temperature, pressure, and composition measurements and also subsequently the uncertainties that were determined for each individual measurement; information pertaining to the consistency test utilized and the individual point-to-point consistency results provided for each measurement; and details regarding the deviations of the thermodynamic model prediction from the experimental data (PDF)

AUTHOR INFORMATION

Corresponding Author

Cara E. Schwarz – Department of Chemical Engineering, Stellenbosch University, Banghoekweg, Stellenbosch 7600, South Africa; orcid.org/0000-0001-5513-2105; Email: cschwarz@sun.ac.za

Authors

- Susanna H. du Plessis Department of Chemical Engineering, Stellenbosch University, Banghoekweg, Stellenbosch 7600, South Africa
- Sonja A. M. Smith Department of Chemical Engineering, Stellenbosch University, Banghoekweg, Stellenbosch 7600,

South Africa; Department of Chemistry, Center for Energy Resources Engineering (CERE), Technical University of Denmark, DK-2800 Lyngby, Denmark; orcid.org/0000-0002-5963-5858

Carla Latsky-Galloway – Department of Chemical Engineering, Stellenbosch University, Banghoekweg, Stellenbosch 7600, South Africa; Orcid.org/0000-0003-1416-579X

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jced.3c00346

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

PC-SAFT calculations were conducted using the FeO_{s}^{79} package in Python.

REFERENCES

(1) Qian, W.; Zhang, H.; Ying, W.; Fang, D. Product Distributions of Fischer–Tropsch Synthesis over Co/AC Catalyst. J. Nat. Gas Chem. **2011**, 20 (4), 389–396.

(2) Li, S.; Tang, Z.; Zhou, F.; Li, W.; Yuan, X. Separation of Primary Alcohols and Saturated Alkanes from Fischer–Tropsch Synthesis Products. *Chin. J. Chem. Eng.* **2014**, *22* (9), 980–983.

(3) Schwarz, C. E.; Bonthuys, G. J. K.; Van Schalkwyk, R. F.; Laubscher, D. L.; Burger, A. J.; Knoetze, J. H. Separation of Alkanes and Alcohols with Supercritical Fluids. Part II. Influence of Process Parameters and Size of Operating Range. *J. Supercrit. Fluids* **2011**, 58 (3), 352–359.

(4) Bonthuys, G. J. K.; Schwarz, C. E.; Burger, A. J.; Knoetze, J. H. Separation of Alkanes and Alcohols with Supercritical Fluids. Part I: Phase Equilibria and Viability Study. *J. Supercrit. Fluids* **2011**, *57* (2), 101–111.

(5) Chaitanya, K. V.; Krishna, Ch.; Beebi, Sk.; Divya, K. Supercritical Fluid Extraction of Functional Ingredients From Plants: A Review. *Curr. Biochem. Eng.* **2015**, *2* (1), 24–32.

(6) Mathys, R. G.; Heinzelmann, W.; Witholt, B. Separation of Higher Molecular Weight Organic Compounds by Pervaporation. *Chem. Eng. J.* **1997**, 67 (3), 191–197.

(7) *Perry's Chemical Engineers' Handbook*, 8th ed.; Green, D. W., Perry, R. H., Eds.; McGraw-Hill: New York, 2008.

(8) Du Plessis, S. H.; Latsky-Galloway, C.; Schwarz, C. E. Low-Pressure Phase Equilibrium Data for Binary Systems of 1-Alcohols (C n OH) and n -Alkanes (C n + 2). *J. Chem. Eng. Data* **2023**, DOI: 10.1021/ acs.jced.3c00026.

(9) Du Plessis, S. H.; Latsky-Galloway, C.; Schwarz, C. E. Experimental Measurement and PSRK and NRTL Modeling of Binary 1-Alcohol (Cm) + N-Alkane (Cm+3) Vapor-Liquid Equilibrium Data. *J. Chem. Eng. Data* **2022**, *67* (8), 1915–1931.

(10) Ferreira, M.; Schwarz, C. E. Low-Pressure VLE Measurements and Thermodynamic Modeling, with PSRK and NRTL, of Binary 1-Alcohol + n-Alkane Systems. *J. Chem. Eng. Data* **2018**, *63* (12), 4614–4625.

(11) Crause, J. C.; Greager, I. P. Production of Detergent Range Alcohols. US 7728178 B2, 2010.

(12) Cripwell, J. T.; Schwarz, C. E.; Burger, A. J. Vapor-Liquid Equilibria Measurements for the Nine N -Alkane/Ketone Pairs Comprising 2-, 3-, and 4-Heptanone with n -Octane, n -Nonane, and n -Decane. *J. Chem. Eng. Data* **2015**, *60* (3), 602–611.

(13) Pienaar, C.; Schwarz, C. E.; Knoetze, J. H.; Burger, A. J. Vapor-Liquid-Liquid Equilibria Measurements for the Dehydration of Ethanol, Isopropanol, and n-Propanol via Azeotropic Distillation Using DIPE and Isooctane as Entrainers. *J. Chem. Eng. Data* **2013**, 58 (3), 537–550.

(14) Bureau International des Poids et Mesures. Evaluation of Measurement Data—Guide to the Expression of Uncertainty in Measurement. *Joint Committee for Guides in Metrology*. **2008**; p 134.

(15) Wisniak, J. A New Test for the Thermodynamic Consistency of Vapor-Liquid Equilibrium. *Ind. Eng. Chem.* **1993**, *32*, 1531–1533.

(16) Wisniak, J. Herington Test for Thermodynamic Consistency 1994, 33, 177–180.

(17) McDermott, C.; Ellis, S. R. M. A Multicomponent Consistency Test. Chem. Eng. Sci. **1965**, 20, 293–296.

(18) Fredenslund, A.; Gmehling, J.; Rasmussen, P. Vapor-Liquid Equilib Using UNIFAC a Group-Contribution Method, 1st ed.; Elsevier B.V.: Amsterdam, The Netherlands, 1977.

(19) Wisniak, J.; Ortega, J.; Fernández, L. A Fresh Look at the Thermodynamic Consistency of Vapour-Liquid Equilibria Data. *J. Chem. Thermodyn.* **2017**, *105*, 385–395.

(20) Mohsen-Nia, M.; Memarzadeh, M. R. Isobaric Vapor-Liquid Equilibria of Heptane + 1-Butanol and Heptane + 1-Pentanol Systems at (53.3 and 91.3) KPa. *J. Chem. Eng. Data* **2010**, *55*, 2140–2144.

(21) Wertheim, M. S. Fluids with Highly Directional Attractive Forces. I. Statistical Thermodynamics. J. Stat. Phys. **1984**, 35 (1-2), 19-34.

(22) Wertheim, M. S. Fluids with Highly Directional Attractive Forces. II. Thermodynamic Perturbation Theory and Integral Equations. *J. Stat. Phys.* **1984**, 35 (1-2), 35–47.

(23) Wertheim, M. S. Fluids with Highly Directional Attractive Forces. III. Multiple Attraction Sites. J. Stat. Phys. **1986**, 42 (3–4), 459–476.

(24) Wertheim, M. S. Fluids with Highly Directional Attractive Forces. IV. Equilibrium Polymerization. *J. Stat. Phys.* **1986**, *42* (3–4), 477–492.

(25) Chapman, W. G.; Gubbins, K. E.; Jackson, G.; Radosz, M. New Reference Equation of State for Associating Liquids. *Ind. Eng. Chem. Res.* **1990**, *29* (8), 1709–1721.

(26) Chapman, W. G.; Gubbins, K. E.; Jackson, G.; Radosz, M. SAFT: Equation-of-State Solution Model for Associating Fluids. *Fluid Phase Equilib.* **1989**, *52* (C), 31–38.

(27) Müller, E. A.; Gubbins, K. E. Molecular-Based Equations of State for Associating Fluids: A Review of SAFT and Related Approaches. *Ind. Eng. Chem. Res.* **2001**, *40* (10), 2193–2211.

(28) Economou, I. G. Statistical Associating Fluid Theory: A Successful Model for the Calculation of Thermodynamic and Phase Equilibrium Properties of Complex Fluid Mixtures. *Ind. Eng. Chem. Res.* **2002**, *41* (5), 953–962.

(29) McCabe, C.; Galindo, A. Chapter 8: SAFT Associating Fluids and Fluid Mixtures. In *Applied Thermodynamics of Fluids*; Goodwin, A. R., Sengers, J., Peters, C. J., Eds.; The Royal Society of Chemistry: 2010; pp 215–279.

(30) Gross, J.; Sadowski, G. Application of Perturbation Theory to a Hard-Chain Reference Fluid: An Equation of State for Square-Well Chains. *Fluid Phase Equilib.* **2000**, *168* (2), 183–199.

(31) Gross, J.; Sadowski, G. Perturbed-Chain SAFT: An Equation of State Based on a Perturbation Theory for Chain Molecules. *Ind. Eng. Chem. Res.* **2001**, *40* (4), 1244–1260.

(32) Gross, J.; Sadowski, G. Application of the Perturbed-Chain SAFT Equation of State to Associating Systems. *Ind. Eng. Chem. Res.* **2002**, *41* (22), 5510–5515.

(33) Tumakaka, F.; Gross, J.; Sadowski, G. Modeling of Polymer Phase Equilibria Using Perturbed-Chain SAFT. *Fluid Phase Equilib.* **2002**, 194–197, 541–551.

(34) Chmelař, J.; Smolná, K.; Haškovcová, K.; Podivinská, M.; Maršálek, J.; Kosek, J. Equilibrium Sorption of Ethylene in Polyethylene: Experimental Study and PC-SAFT Simulations. *Polymer* **2015**, *59*, 270–277.

(35) Rodriguez, G.; Beckman, E. J. Modelling Phase Behavior of Biodiesel Related Systems with CO2 Using a Polar Version of PC-SAFT. *Fluid Phase Equilib.* **2019**, *485*, 32–43.

(36) Corazza, M. L.; Fouad, W. A.; Chapman, W. G. Application of Molecular Modeling to the Vapor-Liquid Equilibrium of Alkyl Esters (Biodiesel) and Alcohols Systems. *Fuel* **2015**, *161*, 34–42.

(37) Lehmkemper, K.; Kyeremateng, S. O.; Heinzerling, O.; Degenhardt, M.; Sadowski, G. Long-Term Physical Stability of PVP- and PVPVA-Amorphous Solid Dispersions. Mol. Pharmaceutics 2017, 14 (1), 157-171.

(38) Dohrn, S.; Luebbert, C.; Lehmkemper, K.; Kyeremateng, S. O.; Degenhardt, M.; Sadowski, G. Phase Behavior of Pharmaceutically Relevant Polymer/Solvent Mixtures. *Int. J. Pharm.* **2020**, *577*, 119065.

(39) Lafitte, T.; Bessieres, D.; Piñeiro, M. M.; Daridon, J. L. Simultaneous Estimation of Phase Behavior and Second-Derivative Properties Using the Statistical Associating Fluid Theory with Variable Range Approach. J. Chem. Phys. **2006**, 124 (2), 024509.

(40) Lafitte, T.; Piñeiro, M. M.; Daridon, J.-L.; Bessières, D. A Comprehensive Description of Chemical Association Effects on Second Derivative Properties of Alcohols through a SAFT-VR Approach. J. Phys. Chem. 2007, 111 (13), 3447–3461.

(41) Lafitte, T.; Apostolakou, A.; Avendaño, C.; Galindo, A.; Adjiman, C. S.; Müller, E. A.; Jackson, G. Accurate Statistical Associating Fluid Theory for Chain Molecules Formed from Mie Segments. *J. Chem. Phys.* **2013**, *139* (15), 154504.

(42) Aimoli, C. G.; Maginn, E. J.; Abreu, C. R. A. Force field comparison and thermodynamic property calculation of supercritical CO_2 and CH_4 using molecular dynamics simulations. *Fluid Phase Equilib.* **2014**, *368*, 80–90.

(43) Dufal, S.; Lafitte, T.; Galindo, A.; Jackson, G.; Haslam, A. J. Developing Intermolecular-Potential Models for Use with the SAFT-VR Mie Equation of State. *AIChE J.* **2015**, *61* (9), 2891–2912.

(44) Nikolaidis, I. K.; Franco, L. F. M.; Vechot, L. N.; Economou, I. G. Modeling of physical properties and vapor-liquid equilibrium of ethylene and ethylene mixtures with equations of state. *Fluid Phase Equilib.* **2018**, 470, 149–163.

(45) Cárdenas, H.; Mejía, A. Phase behaviour and interfacial properties of ternary system $CO_2 + n$ -butane + n-decane: coarsegrained theoretical modelling and molecular simulations. *Mol. Phys.* **2016**, 114 (18), 2627–2640.

(46) Perez, A. G.; Coquelet, C.; Paricaud, P.; Chapoy, A. Comparative study of vapour-liquid equilibrium and density modelling of mixtures related to carbon capture and storage with the SRK, PR, PC-SAFT and SAFT-VR Mie equations of state for industrial uses. *Fluid Phase Equilib.* **2017**, *440*, 19–35.

(47) Aimoli, C. G.; Maginn, E. J.; Abreu, C. R. A. Thermodynamic Properties of Supercritical Mixtures of Carbon Dioxide and Methane: A Molecular Simulation Study. *J. Chem. Eng. Data* **2014**, *59* (10), 3041– 3054.

(48) Nascimento, F. P.; Paredes, M. L. L.; Bernardes, A. P. D.; Pessoa, F. L. P. Phase behavior of $CO_2/toluene$, CO_2/n -decane and $CO_2/toluene/n$ -decane: Experimental measurements and thermodynamic modeling with SAFT-VR Mie equation of state. *J. Supercrit. Fluids* **2019**, *154*, 104634.

(49) Dufal, S.; Lafitte, T.; Haslam, A. J.; Galindo, A.; Clark, G. N. I.; Vega, C.; Jackson, G. The A in SAFT: developing the contribution of association to the Helmholtz free energy within a Wertheim TPT1 treatment of generic Mie fluids. *Mol. Phys.* **2015**, *113* (9–10), 948–984.

(50) Cripwell, J. T.; Smith, S. A. M.; Schwarz, C. E.; Burger, A. J. SAFT-VR Mie: Application to Phase Equilibria of Alcohols in Mixtures with *n*-Alkanes and Water. *Ind. Eng. Chem. Res.* **2018**, *57* (29), 9693–9706.

(51) Cripwell, J. T.; Kruger, F. J.; Burger, A. J. Accounting for cross association in non-self-associating species using a physically consistent SAFT-VR Mie approach. *Fluid Phase Equilib.* **2019**, *483*, 1–13.

(52) Smith, S. A.; Cripwell, J. T.; Schwarz, C. E. A Quadrupolar SAFT-VR Mie Approach to Modeling Binary Mixtures of CO_2 or Benzene with *n*-Alkanes or 1-Alkanols. *J. Chem. Eng. Data* **2020**, 65 (12), 5778– 5800.

(53) Smith, S. A. M.; Schwarz, C. E.; Burger, A. J.; Cripwell, J. T. Accounting for Cross-Association in Nonself-Associating Species Using SAFT-VR Mie: Application to Mixtures with Esters. *Fluid Phase Equilib.* **2023**, *569*, 113775.

(54) Chen, S. S.; Kreglewski, A. Applications of the Augmented van Der Waals Theory of Fluids.: I. Pure Fluids. *Berichte Bunsenges. Für Phys. Chem.* **1977**, *81* (10), 1048–1052.

(55) Mie, G. Zur Kinetischen Theorie Der Einatomigen Körper. *Ann. Phys.* **1903**, *316* (8), 657–697.

(56) Eisenschitz, R.; London, F. Über Das Verhältnis Der van Der Waalsschen Kräfte Zu Den Homöopolaren Bindungskräften. Z. Für Phys. **1930**, 60 (7–8), 491–527.

(57) Grenner, A.; Kontogeorgis, G. M.; von Solms, N.; Michelsen, M. L. Modeling Phase Equilibria of Alkanols with the Simplified PC-SAFT Equation of State and Generalized Pure Compound Parameters. *Fluid Phase Equilib.* **2007**, 258 (1), 83–94.

(58) Wilding, W. V.; Knotts, T. A.; Giles, N. F.; Rowley, R. L. DIPPR Data Compilation of Pure Chemical Properties, Design Institute For Physical Properties; AIChE: New York, 2020.

(59) Dufal, S.; Lafitte, T.; Galindo, A.; Jackson, G.; Haslam, A. J. Developing Intermolecular-Potential Models for Use with the SAFT-VR Mie Equation of State. *AIChE J.* **2015**, *61* (9), 2891–2912.

(60) Cripwell, J. T.; Smith, S. A. M.; Schwarz, C. E.; Burger, A. J. SAFT-VR Mie: Application to Phase Equilibria of Alcohols in Mixtures with n-Alkanes and Water. *Ind. Eng. Chem. Res.* **2018**, *57* (29), 9693–9706.

(61) Smith, S. A.; Cripwell, J. T.; Schwarz, C. E. A Quadrupolar SAFT-VR Mie Approach to Modeling Binary Mixtures of CO2 or Benzene with n-Alkanes or 1-Alkanols. *J. Chem. Eng. Data* **2020**, *65*, 5778–5800.

(62) Kirss, H.; Siimer, E.; Kuus, M. Isobaric Vapor-Liquid Equilibria of the Ternary System Methylbutyl Ketone + 1-Pentanol + Nonane. J. Chem. Eng. Data 2006, 51 (1), 153–156.

(63) Van Pham, S. Investigations of the Phase Equilibria Liquid-Liquid and Liquid-Vapor in Binary and Ternary Model Experiments with the Solvent Dimethyl Formamide; Leipzig University: 1983.

(64) Plesnar, Z.; Gierycz, P.; Gregorowicz, J.; Bylicki, A. Vapour-Liquid Equilibrium and Solid-Solid Equilibrium in the System Formed by Octan-1-Ol and n-Decane: Measurement and Calculation. *Thermochim. Acta* **1989**, *150* (1), 101–109.

(65) Schmelzer, J.; Taummler, H. Binary VLE Data of 1-Alcohol+ Alkane Systems; Karl Marx University: 1984.

(66) Linek, J.; Wichterle, I. Isobaric Vapor-Liquid Equilibria in Binary Mixtures Containing Hexane+ a Pentanol Isomer at 27, 53, and 93 KPa. *ELDATA Int. Electron J. Phys-Chem. Data* **1995**, *1*, 265–274.

(67) Ovejero, G.; Romero, M. D.; Díez, E.; Lopes, T.; Díaz, I. Isobaric Vapor-Liquid Equilibrium for the Binary Systems 1-Pentanol + Cyclohexane and 1-Pentanol + n-Hexane at Low Alcohol Compositions. J. Chem. Eng. Data 2007, 52 (5), 1984–1987.

(68) Byer, S. M.; Gibbs, R. E.; Van Ness, H. C. Vapor-Liquid Equilibrium: Part II. Correlations from P-x Data for 15 Systems. *AIChE J.* **1973**, *19* (2), 245–251.

(69) Oracz, P. Recommendations for VLE Data on Binary 1-Alkanol+ n-Alkane Systems; Warsaw University: 1976.

(70) Ronc, M.; Ratcliff, G. R. Measurement of Vapor-Liquid Equilibria Using a Semi-Continuous Total Pressure Static Equilibrium Still. *Can. J. Chem. Eng.* **1976**, *54* (4), 326–332.

(71) Sayegh, S. G.; Ratcliff, G. A. Excess Gibbs Energies of Binary Systems of Isopentanol and N-Pentanol with Hexane Isomers at 25° C: Measurement and Prediction by Analytical Group Solution Model. *J. Chem. Eng. Data* **1976**, *21* (1), 71–74.

(72) Rao, R.; Chiranjivi, C.; Dasarao, C. J. Vapour-liquid Equilibria Systems: Hexane-hexylalcohol and Heptane-hexylalcohol. *J. Appl. Chem.* **1968**, *18* (6), 166–168.

(73) Tai, T. B.; Ramalho, R. S.; Kaliaguine, S. Application of Wilsonés Equation to Determination of Vapor-liquid Equilibrium Data and Heats of Mixing for Non-ideal Solutions. *Can. J. Chem. Eng.* **1972**, *50* (6), 771–776.

(74) Treszczanowicz, A. J.; Treszczanowicz, T. Vapor-liquid Equilibriums of Nonelectrolyte Mixtures. Part III. Vapor-liquid-Phase Equilibriums of Binary Systems Formed by 1-Pentanol and Alkanes. *Bull. Acad. Pol. Sci.-Chim.* **1979**, *27* (9), 689–695.

(75) Máchová, I.; Linek, J.; Wichterle, I. Vapour-Liquid Equilibria in the Heptane - 1-Pentanol and Heptane - 3-Methyl-1-Butanol Systems at 75, 85 and 95 °C. *Fluid Phase Equilib.* **1988**, *41* (3), 257–267.

(76) Zielkiewicz, J. (Vapor + Liquid) Equilibria in (Heptane + Propan-2-Ol or Butan-1-Ol or 2- Methhylporpan-1-Ol or 2-

Methylpropan-2-Ol or Pentan-1-Ol) at the Temperature 313.15 K. J. Chem. Thermodyn **1994**, 26, 919–923.

(77) Rhodes, J. M.; Bhethanabotla, V. R.; Campbell, S. W. Total Vapor Pressure Measurements for Heptane + 1-Pentanol, + 2-Pentanol, + 3-Pentanol, + 2-Methyl-1-Butanol, + 2-Methyl-2-Butanol, + 3-Methyl-1-Butanol, and + 3-Methyl-2-Butanol at 313.15 K. *J. Chem. Eng. Data* **1997**, 42 (4), 731–734.

(78) Cova, D. R.; Rains, R. K. Vapor-Liquid Equilibria in Hydrocarbon-Alcohol Systems n-Decane-1-Heptanol and n-Decane-2-Methyl-1-Hexanol. J. Chem. Eng. Data 1974, 19 (3), 251–253.

(79) Rehner, P.; Bauer, G.; Gross, J. FeOs: An Open-Source Framework for Equations of State and Classical Density Functional Theory. *Ind. Eng. Chem. Res.* **2023**, *62* (12), 5347–5357.