

Measurement and modeling of surface tensions of asymmetric systems: heptane, eicosane, docosane, tetracosane and their mixtures

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Abstract

To extend the surface tension database for heavy or asymmetric *n*-alkane mixtures, measurements were performed using the Wilhelmy plate method. Measured systems included the binary mixtures heptane + eicosane, heptane + docosane and heptane + tetracosane and the ternary mixture heptane + eicosane + tetracosane at temperatures from 313.15 K (or above the melting point of the mixture) up to 343.15 K. All the measurements were performed at atmospheric pressure.

Using these data, along with data previously measured by us and collected from the literature, a recently proposed corresponding states model was assessed. It is shown that using a new generalized combining rule for the critical temperature, the data can be described with deviations of about 1% that is within the experimental uncertainty of the measurements.

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1. Introduction

The continuous demand for new products has been moving the chemical industry towards the production of a broad range of chemicals. Thermophysical properties are frequently required both for product and process design, and in many cases these are scarce or unavailable. Although several models have been proposed, it is still essential to carry out experimental measurements to assess their limitations and provide a basis for the development of improved models.

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One of the most well-documented families of chemicals is that of the *n*-alkanes. Many of the measurements available so far were done due to the importance that alkanes have in the petroleum industry. In the past, the focus has been on light oils and for this reason, data for compounds above hexadecane (C₁₆H₃₄) are scarce.

Advances in the extraction technology, founded on the progressive reservoir depletion, are enabling the additional recovery of heavier oils, rising oil lifetime. The mixture of heavier and lighter components makes the new oils more asymmetric, and thus, the interest in heavier and asymmetric *n*-alkane mixtures is raising.

The importance of interfacial tension for the petroleum industry extends far beyond the extraction processes, when oil has to travel through capillary channels and where this type of flow is strongly dominated by surface tension effects. Other operations such as adsorption, distillation or extraction are also dependent on this property. Outside the refinery, the environmental concerns about oil spills, both on sea and fresh waters, are a field where the study of the oil–water interface can provide information on how the oil will spread over the water.

With the growing importance of the heavy oils, new data and models able to describe systems containing large hydrocarbons are required.

The main objective of this work was to determine liquid–vapor surface tension of *n*-alkanes, with a special emphasis on asymmetric mixtures, and develop a model for its description. Some data previously reported [1] showed the ability of our equipment to measure surface tension accurately with an average absolute deviation of 1.6%.

Results for three binary and one ternary mixtures of eicosane, docosane and tetracosane mixed with heptane are presented. These new data, together with other collected results, should provide a database from which a model for the surface tension of heavy hydrocarbons and their mixtures can be developed and evaluated.

A recently proposed corresponding states model [1] is used for the modeling of the reported data. To improve the description of asymmetric mixtures, such as studied in this work, a general combining rule for the critical temperature is employed, allowing for deviations within the uncertainty of the experimental results.

2. Experimental methods

All chemicals were commercial products with a stated purity of at least 99%. Eicosane (Sigma), docosane (Sigma) and tetracosane (Fluka) were used without further purification. Heptane (Riedel de Haën) was dried over molecular sieves before use.

A NIMA DST 9005 tensiometer from NIMA Technology, Ltd., incorporating a microbalance able to read force within 10⁻⁶ mN, was operated on the Wilhelmy plate method. A platinum plate of 20.20 mm width and 0.18 mm thickness was employed. From the force measurements and the plate dimensions, this tensiometer automatically returns surface tension values.

For the measurement, approximately 50 cm³ of the solution was introduced in a thermostatic glass vessel, located inside the tensiometer chamber. Temperature is controlled within 0.01 K by an external Pt100 probe directly immersed in the solution and connected to an HAAKE F6 circulator. The accuracy of this temperature measuring system (±0.04 K) was assured by calibration against a certified *Thermometrics S10 thermistor*. Other details about the measuring apparatus and procedure can be found elsewhere [1].

Mixtures were carefully prepared by weighting the components in a *Mettler Toledo AB204* analytical balance (± 0.0001 g). Uncertainty in mole fraction was calculated to be less than 1×10^{-5} .

To avoid heptane evaporation during the measurement, a small portion was introduced inside the tensiometer chamber to saturate the gas phase. Humidity was removed from the gas phase using dried silica gel.

Before each run, the platinum plate was flamed in a Bunsen burner to eliminate contaminants. The sample surface was cleaned by suction with a Pasteur pipette and discarded. This allows the removal of some surface-active contaminants and the formation of a new and clean surface.

Balance and tensiometer were calibrated with masses provided by the manufacturers.

3. Results and discussion

Pure component surface tension was measured from 273.15 K (or above the melting point) up to 343.15 K in temperature intervals of 10 K. The surface tension of binary mixtures heptane + eicosane, heptane + docosane and heptane + tetracosane and the ternary mixture heptane + eicosane + tetracosane were measured above 313.15 K.

For each liquid, at least 15 surface tension values were recorded, from which an average was taken.

Deviations were calculated using *percent average absolute deviation* (%AAD):

$$\% \text{AAD} = \frac{1}{n} \sum \left| \frac{\gamma - \gamma_a}{\gamma_a} \right| \times 100 \quad (1)$$

where n is the number of data points, γ is the surface tension and the subscript 'a' stands for the accepted value.

In Table 1 pure component surface tensions are presented and compared with literature values [2–7]. The uncertainty reported in this table heading ($\pm 0.03 \text{ mN m}^{-1}$) is the maximum uncertainty found from all data. This was evaluated using the law of propagation of uncertainty in which force, plate dimensions and temperature were considered.

An average absolute deviation of 1.1% was found for heptane, eicosane and docosane. No literature data was found for tetracosane. The maximum deviation found was 1.8% for heptane at 293.15 K, compared with the data of Jasper [4]. A graphical comparison with literature data is presented in Fig. 1 for heptane, where data from Grigoryev et al. [8] taken at different temperatures from our measurements, are also included. The measured data agrees with the data previously reported as much as the different sets of data agree between themselves.

It should be noted that for docosane and tetracosane, at the lowest temperatures, surface tension decreases with decreasing temperature, an opposite trend to what is generally found. This phenomenon is particular of some heavy n -alkanes with chain length $14 < n \leq 50$, some alcohols and liquid crystals are ascribed to surface freezing, where the surface presents solid ordering before the bulk liquid does, around 3 K above the melting point [9–11].

Mixture data are presented in Table 2 and plotted as isotherms in Figs. 2 and 3 as a function of composition. Reported uncertainty corresponds, again, to the maximum uncertainty found from all the mixture points. The calculation procedure was the same used for the pure components, this time also including the uncertainty due to mixture preparation. No data was previously available for any of the mixtures reported in this work.

Table 1
Pure component surface tension of *n*-alkanes and comparison with literature

<i>n</i> -Alkane	<i>T</i> (K)	γ (mN m ⁻¹)						
		This work ^a	Jasper et al. [2]	McLure et al. [3]	Jasper [4]	Koefoed and Villadsen [5]	Águila-Hernandez [6]	Jasper and Kring [7]
<i>n</i> -C ₇ H ₁₆	273.15	22.28	22.31					22.10
	283.15	21.37	21.30		21.12			
	293.15	20.50	20.28	20.21	20.14	20.30		
	303.15	19.47	19.27	19.17	19.17	19.31		
	313.15	18.42	18.25	18.19	18.18			
	323.15	17.41	17.24	17.18	17.20			
	333.15	16.42	16.22	16.19	16.22			
	343.15	15.32			15.24			
<i>n</i> -C ₂₀ H ₄₂	313.15	27.58			27.21			
	323.15	26.67			26.38		26.52	
	333.15	25.85			25.54		25.58	
	343.15	25.01			24.71		24.71	
<i>n</i> -C ₂₂ H ₄₆	318.15	26.72 ^b						
	323.15	27.42					27.15	
	333.15	26.60					26.25	
	343.15	25.79					25.54	
<i>n</i> -C ₂₄ H ₅₀	323.15	26.67 ^b						
	333.15	27.05						
	343.15	26.22						

^a Uncertainty: ± 0.03 mN m⁻¹.

^b Measured at temperatures where surface crystallization is known to occur.

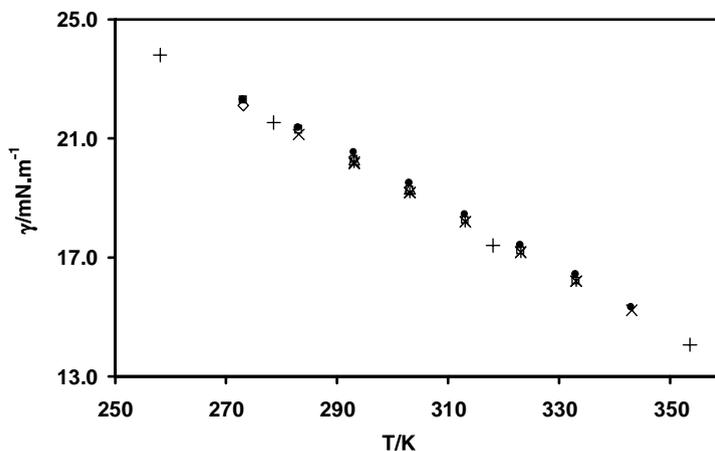


Fig. 1. Surface tension of *n*-C₇H₁₆: (●), this work; (□), [3]; (×), [4]; (×), [5]; (Δ), [6]; (◇), [8]; (+), [9].

Table 2
Surface tension of *n*-alkane mixtures (uncertainty: $\pm 0.07 \text{ mN m}^{-1}$)

System	$x(1)$	$x(2)$	$x(3)$	$\gamma \text{ (mN m}^{-1}\text{)}$			
				313.15 K	323.15 K	333.15 K	343.15 K
Heptane (1) + eicosane (2)	0.750	0.250		21.29	20.53	19.68	18.60
	0.500	0.500		23.76	22.87	22.19	21.57
	0.251	0.749		25.83	25.06	24.28	23.58
Heptane (1) + docosane (2)	0.750	0.250		21.55	20.81	20.03	19.15
	0.500	0.500		23.99	23.49	22.74	22.02
	0.250	0.750		25.93	25.54	24.92	24.27
Heptane (1) + tetracosane (2)	0.750	0.250		21.71	20.85	20.20	19.63
	0.500	0.500			23.76	23.17	22.66
	0.250	0.750			26.04	25.44	24.81
Heptane (1) + eicosane (2) + tetracosane (3)	0.000	0.500	0.500		27.27	26.51	25.69
	0.200	0.401	0.399		25.87	25.08	24.46
	0.404	0.298	0.298		24.44	23.41	22.71
	0.499	0.250	0.251	24.07	23.34	22.73	21.99
	0.602	0.199	0.199	23.15	22.34	21.57	21.13
	0.785	0.107	0.108	21.22	20.33	19.40	18.70
	0.800	0.100	0.100	20.78	20.03	19.17	18.52

The curvature presented as a function of composition, where the mixture surface tension is higher than the corresponding mole fraction average, is typical of *n*-alkane mixtures. The opposite trend is commonly observed in mixtures containing other families of fluids. These differences are the consequence of the different surface compositions that will result in the minimum free energy of the system.

The ternary mixture heptane+eicosane+tetracosane was studied at equimolar compositions of eicosane and tetracosane to allow for a comparison of this ternary data with that of the binary mixture heptane + docosane. Both systems are plotted in Fig. 3 as a function of heptane mole fraction. As can be seen from this figure and Table 2, it seems that the binary data resembles that of the equivalent ternary mixture

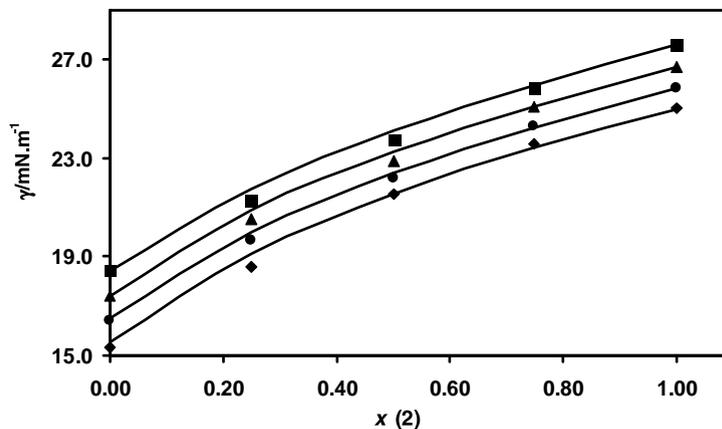


Fig. 2. Surface tension of *n*-C₇H₁₆ (1) + *n*-C₂₀H₄₂ (2): (■), 313.15 K; (▲), 323.15 K; (●), 333.15 K; (◆), 343.15 K; (—), model.

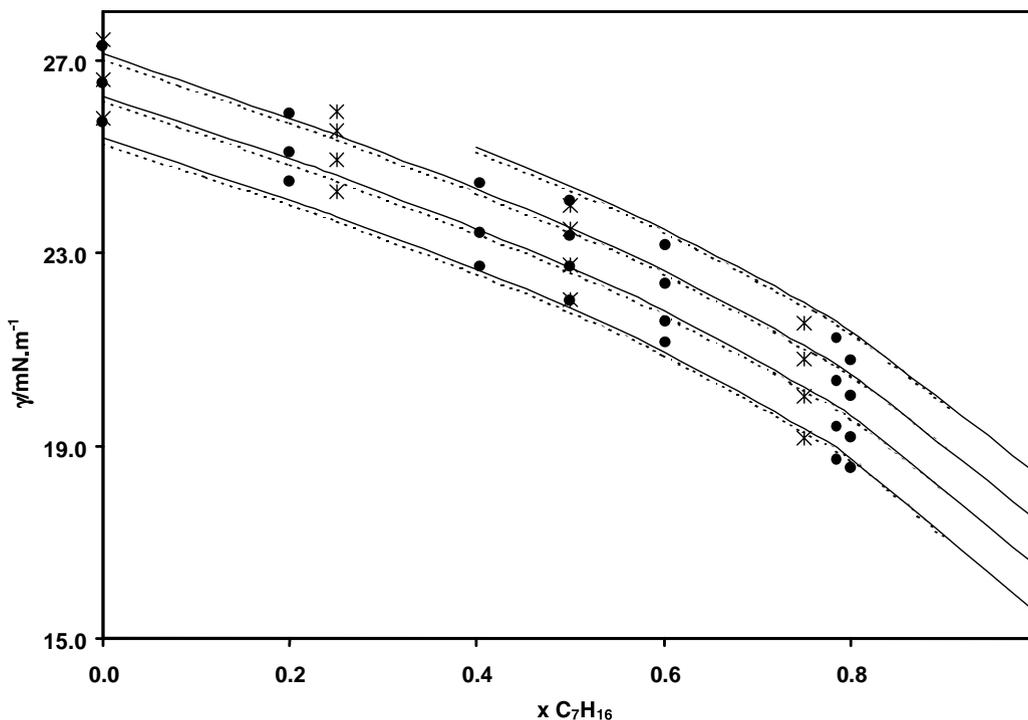


Fig. 3. Surface tension of $n\text{-C}_7\text{H}_{16}$ (1) + $n\text{-C}_{24}\text{H}_{50}$ (2), (*); $n\text{-C}_7\text{H}_{16}$ (1) + $n\text{-C}_{20}\text{H}_{42}$ (2) + $n\text{-C}_{24}\text{H}_{50}$ (3), (●); and model (—).

heptane + docosane + tetracosane. It is interesting to note that the equimolar ($x = 0.5$) mixture of eicosane and tetracosane presents surface tension values quite close to those of pure docosane, although systematically lower. A study on several other pure, binary and ternary data [1–7,12,13] showed that for n -alkanes with the same average chain length, surface tension slightly decreases with the increase on the number of components, as observed in this work.

4. Modeling

The application of *corresponding states* models extends from equilibrium properties such as vapor pressure [14–18], liquid density [14,17,19,20] or surface tension [14,21–23] to transport properties such as viscosity [14,24–27] and thermal conductivity [14]. In spite of this versatility, and the small amount of experimental information required, *corresponding states* models can return very accurate estimates of thermophysical properties.

In its original form, the *corresponding states principle*, as proposed by van der Waals, expressed the reduced compressibility factor (Z_r) in terms of a universal function of two parameters, the dimensionless temperature (T_r) and molar volume (V_r) (or pressure, P_r).

Experimental evidence has, however, shown that this two-parameter *corresponding states* approach was limited to the noble gases and nearly spherical molecules such as nitrogen, oxygen and methane. One of the adopted approaches to extend this theory to a broader range of fluids, was the introduction

of a third parameter, the Pitzer acentric factor (ω), which accounts for the non-conformalities. A Taylor series expansion of the property of interest is performed about this third parameter, with the series being usually truncated beyond the first derivative. With the advent of cheaper and faster computers, Lee and Kesler [28] suggested replacing the derivative in the Taylor series with its finite difference:

$$Z_{rj}(T_r, P_r, \omega) = Z_{r0}(T_r, P_r) + \frac{\omega_j}{\omega_1} [Z_{r1}(T_r, P_r) - Z_{r0}(T_r, P_r)] \quad (2)$$

$$Z_r = \frac{P_r V_r}{T_r} \quad (3)$$

$$T_r = \frac{T}{T_c}, \quad P_r = \frac{P}{P_c}, \quad V_r = \frac{V}{V_c} \quad (4)$$

where Z is the compressibility factor, PV/RT , ω is the Pitzer acentric factor and the subscripts 'r' and 'c' stand for reduced and critical property and j and 0 for target and spherical reference fluid, respectively. Subscript 1 represents a non-spherical reference fluid ($\omega > 0$).

Following Teja and coworkers [17,19,21–24,29,30] the spherical reference in Eq. (2) was abandoned. Therefore, both reference fluids could be similar to the evaluating fluid, reducing the errors due to large interpolations/extrapolations. Several thermophysical properties were estimated according to this new framework with very good predictive results:

$$X_r = X_{r1} + \frac{\omega - \omega_1}{\omega_2 - \omega_1} (X_{r2} - X_{r1}) \quad (5)$$

where X_r stands for the reduced property to be evaluated and subscripts 1 and 2 for the two reference fluid properties at the same reduced conditions as those of the target fluid.

Recently, Queimada et al. studying surface tension [23], viscosity, vapor pressure and liquid density [31] of the series of the n -alkanes showed that, if instead of truncating the Taylor series expansion beyond the first derivative, the second derivative is also taken into account, better results are obtained, especially if heavy components are to be considered. A third reference fluid is introduced with the advantage that no change in the reference system has to be done if one wants to study a large range of fluids or an asymmetric system. If instead, the Teja approach is adopted for asymmetric systems with a single reference system, considerable deviations resulting from the interpolations/extrapolations may result [23,31].

The three-fluids corresponding states model for surface tensions can be written as:

$$\gamma_r = \gamma_{r1} + D_1(\omega_j - \omega_1) + D_2(\omega_j - \omega_1)(\omega_j - \omega_2) \quad (6)$$

$$D_1 = \frac{\gamma_{r2} - \gamma_{r1}}{\omega_2 - \omega_1}, \quad D_2 = \frac{(\gamma_{r3} - \gamma_{r1})/(\omega_3 - \omega_1) - (\gamma_{r2} - \gamma_{r1})/(\omega_2 - \omega_1)}{\omega_3 - \omega_2} \quad (7)$$

$$\gamma_r = \gamma \times \frac{V_c^{2/3}}{T_c} \quad (8)$$

where γ represents surface tension, mN m^{-1} , and subscript j stands for the evaluating fluid.

Mixtures are evaluated using the *one-fluid theory* with the following mixing and combining rules for the pseudocritical parameters:

$$\omega_m = \sum_i x_i \omega_i \quad (9)$$

$$V_{cm} = \sum_i \sum_k x_i x_k V_{cik} \quad (10)$$

$$T_{cm} V_{cm} = \sum_i \sum_k x_i x_k T_{cik} V_{cik} \quad (11)$$

$$V_{cik} = \frac{1}{8} (V_{ci}^{1/3} + V_{ck}^{1/3})^3 \quad (12)$$

$$T_{cik} = \sqrt{T_{ci} T_{ck}} \left(\frac{V_{ci} V_{ck}}{V_{cik}} \right)^{(n/3)-1} \quad (13)$$

In the above equations indexes i and k represent pure components and x mole fraction. For the use with Eqs. (6)–(13), experimental critical properties were collected from the literature, when available [32]. Correlations were considered for those n -alkanes for which there were no experimental information. Critical temperature was calculated from the correlation of Tsonopoulos [33], critical pressure from that of Magoulas and Tassios [34], critical volume from Marano and Holder [35] and the Pitzer acentric factor from Han and Peng [36].

Following Coutinho et al. [37] a more general combining rule for the cross-critical temperature, T_{cik} , was adopted (Eq. (13)). If n is taken equal to 6, this equation reduces to the combining rule used in our previous work [1]. Coutinho et al. [37] show that for phase equilibrium calculations, this combining rule progressively deteriorates with component asymmetry, with the value of n approaching 3 for extremely asymmetric systems, such as those involving some polymer solutions.

Other combining rules can be derived from this expression setting different values of the parameter n . Setting $n = 3$, one obtains the geometric combining rule. Plöcker et al. [30] used $n = 3.75$ for calculating vapor–liquid equilibria of asymmetric systems. Other values of n between 3 and 7.5 can also be found [37]. The n parameter can thus be fitted or used as variable with the system asymmetry, and thus no binary interaction parameters are required while using this approach.

The optimum value of n to be used with Eq. (13) was estimated from the data measured in this work and data from literature for binary systems [1,6,9,10,38].

The following objective function was used within a least-squares fit:

$$F_{obj} = \left(\gamma_{m,exp} - \sum_i x_i \times \gamma_{i,exp} \right) - \left(\gamma_{m,model} - \sum_i x_i \times \gamma_{i,model} \right) \quad (14)$$

where subscript ‘m’ denotes mixture and ‘exp’ for experimental value.

While using this objective function, we consider that our model returns the correct values for the pure components and that only the curvature of the surface tension data versus composition has to be corrected.

An n value of 4.6 was obtained from this overall fit.

To show how this model can represent mixture data using a small amount of experimental information, heptane, decane and eicosane were selected as reference fluids, and only our measurements were selected: heptane and eicosane from this work, and decane data from [38]. For each reference fluid, surface tension was fitted to a two-parameter equation:

Table 3

Estimation of the surface tension of *n*-alkane mixtures for different values of *n* (Eq. (13)) with the corresponding states model

System	Reference	%AAD	
		<i>n</i> = 6.0	<i>n</i> = 4.6
<i>n</i> -C ₆ H ₁₄ + <i>n</i> -C ₈ H ₁₈	[10]	1.49	1.57
<i>n</i> -C ₇ H ₁₆ + <i>n</i> -C ₁₀ H ₂₂	[1]	0.73	0.57
<i>n</i> -C ₆ H ₁₄ + <i>n</i> -C ₁₀ H ₂₂	[9]	0.80	1.28
<i>n</i> -C ₁₆ H ₃₄ + <i>n</i> -C ₂₀ H ₄₂	[1]	0.52	0.52
<i>n</i> -C ₁₆ H ₃₄ + <i>n</i> -C ₂₀ H ₄₂	[6]	1.36	1.44
<i>n</i> -C ₁₆ H ₃₄ + <i>n</i> -C ₂₂ H ₄₆	[6]	0.80	0.92
<i>n</i> -C ₈ H ₁₈ + <i>n</i> -C ₁₄ H ₃₀	[10]	2.52	2.93
<i>n</i> -C ₁₀ H ₂₂ + <i>n</i> -C ₁₆ H ₃₄	[1]	0.50	0.48
<i>n</i> -C ₁₀ H ₂₂ + <i>n</i> -C ₁₆ H ₃₄	[9]	0.82	1.19
<i>n</i> -C ₆ H ₁₄ + <i>n</i> -C ₁₄ H ₃₀	[10]	3.43	4.48
<i>n</i> -C ₇ H ₁₆ + <i>n</i> -C ₁₆ H ₃₄	[1]	0.65	0.82
<i>n</i> -C ₇ H ₁₆ + <i>n</i> -C ₁₆ H ₃₄	[5]	1.33	2.12
Average		1.25	1.53
Asymmetric systems			
<i>n</i> -C ₇ H ₁₆ + <i>n</i> -C ₂₀ H ₄₂	This work	0.86	0.82
<i>n</i> -C ₇ H ₁₆ + <i>n</i> -C ₂₂ H ₄₆	This work	1.78	1.01
<i>n</i> -C ₇ H ₁₆ + <i>n</i> -C ₂₄ H ₅₀	This work	2.95	1.50
<i>n</i> -C ₇ H ₁₆ + <i>n</i> -C ₂₀ H ₄₂ + <i>n</i> -C ₂₄ H ₅₀	This work	2.11	1.07
<i>n</i> -C ₁₀ H ₂₂ + <i>n</i> -C ₂₀ H ₄₂	[38]	1.22	0.57
<i>n</i> -C ₁₀ H ₂₂ + <i>n</i> -C ₂₂ H ₄₆	[38]	2.15	1.38
<i>n</i> -C ₁₀ H ₂₂ + <i>n</i> -C ₂₄ H ₅₀	[38]	2.86	1.70
<i>n</i> -C ₁₀ H ₂₂ + <i>n</i> -C ₂₀ H ₄₂ + <i>n</i> -C ₂₄ H ₅₀	[38]	1.45	0.59
Average		1.92	1.08

$$\gamma = A \left(1 - \frac{T}{T_c} \right)^B \quad (15)$$

which gives the reference fluid surface tension as a function of the dimensionless temperature.

Deviations presented by this model for 18 binary and two ternary *n*-alkane mixtures are compared in Table 3 using *n* = 4.6 and 6.0 in Eq. (13). As can be seen, for low asymmetries the best choice is to use *n* = 6.0, while for the most asymmetric mixtures, deviations can be reduced to half of its value if we select *n* = 4.6.

A comparison between the model using *n* = 4.6 and experimental data reported in this work is shown in Figs. 2 and 3. An average absolute deviation of 1.1% was found for the 59 mixture data points measured in this work. Using *n* = 6 in Eq. (13), an average absolute deviation about 80% higher is obtained.

With respect to the comparison between the binary mixture heptane + docosane and the ternary mixture heptane + eicosane + tetracosane, very small deviations are observed using this model, in agreement with the experimental results. Binary data calculated from the model are, in average, 0.3% higher than that of the ternary mixture. Similar results can be obtained from the experimental values.

Results show that using only four to eight pure component surface tension values from each reference fluid, one is able to estimate all the corresponding mixture data with a very small deviation. These results clearly show that the proposed model is adequate to the surface tension modeling of hydrocarbon mixtures.

5. Conclusions

Surface tension measurements on three new binary and one ternary *n*-alkane mixtures were reported. The accuracy of the measuring system was assured by comparison of the measured pure component data with values reported on literature. An average absolute deviation of 1.1% was obtained. No literature data was found for tetracosane or any of the mixture points.

Surface tension of the binary mixture heptane + docosane was compared with those of the ternary mixture heptane + eicosane + tetracosane. Although it seems that an agreement between both systems exists, it is evident that the surface tension of the binary mixture is somewhat higher than the corresponding ternary data. The model presented in this work is able to describe these very small differences.

A corresponding states model was evaluated for the estimation of the measured data. It was shown that the use of simple mixing rules can return accurate surface tension values, but particularly for asymmetric systems, an improvement can be obtained if a more general expression is adopted for the cross-critical temperature. With this formalism, average absolute deviations can be quite close to the accuracy of the experiments.

List of symbols

A, B	correlation parameters in Eq. (15)
%AAD	percent average absolute deviation (Eq. (1))
n	parameter in Eq. (13)
P	pressure (bar)
T	absolute temperature (K)
V	molar volume ($\text{cm}^3 \text{mol}^{-1}$)
x	mole fraction
X	thermophysical property
Z	compressibility factor

Greek symbols

γ	surface tension (mN m^{-1})
ω	Pitzer acentric factor

Subscripts

0	spherical reference fluid
1, 2, 3	non-spherical reference fluids
a	accepted value
c	critical property
exp	experimental value
i, k	pure component indexes in Eqs. (9)–(13)

<i>j</i>	target fluid
<i>m</i>	mixture property
<i>r</i>	reduced property

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