

Surface Tension of Heptane, Decane, Hexadecane, Eicosane, and Some of Their Binary Mixtures

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Surface tension measurements were performed by the Wilhelmy plate method. Measured systems included pure heptane, decane, hexadecane, eicosane, and some of their binary mixtures at temperatures from 293.15 K to 343.15 K with an average absolute deviation of 1.6%. The results were compared with a new corresponding states model. The average absolute deviation was found to be 1.0%.

1. Introduction

The study of surfaces has received increasing attention in many scientific areas such as chemistry and chemical engineering, environmental sciences, material sciences, physics, and electronics. The thermophysical property that has been most widely used to characterize surfaces is the surface tension.

Surface tension plays a significant role in several industries, such as paints, detergents, agrochemicals, and petroleum. In extraction processes, oil has to travel through capillary channels, and this type of flow is strongly dominated by surface tension effects.

Although there is a large databank of surface tension for the pure *n*-alkanes below hexadecane, data for their mixtures and the heavier members of the series are scarce.

The main objective of this work was to determine surface tension of some pure and mixed *n*-alkanes, not available in the literature or for which the reported data was incomplete. The first results, reported in this paper, show the ability of our equipment to measure surface tension accurately with an average absolute deviation (eq 1) of 1.6%. Measurements for two of the four studied binary systems were considerably extended.

These data, together with some previous collected results and future measurements, should provide a comprehensive database from which a model for the surface tension of heavy hydrocarbons and their mixtures can be developed. In this paper, a new corresponding states model recently developed for the prediction of the surface tension of pure *n*-alkanes up to dotriacontane¹ was tested for the prediction of the mixture data reported in this work.

2. Experimental Methods

The chemicals used in the measurements were heptane (Riedel de Haën, 99%), decane (Aldrich, 99%), hexadecane (Sigma, 99%), and eicosane (Sigma, 99%). These chemicals were dried over molecular sieves. No further purification was performed.

A NIMA DST 9005 tensiometer from NIMA Technology, Ltd. was used in these measurements. This tensiometer is

based on force measurements, for which it has a precision balance able to measure to within 10^{-6} mN. It can operate with a Wilhelmy plate or a DuNouy ring. The plate perimeter and ring diameter and thickness were measured within ± 10 μm and are introduced in the control program that automatically returns surface tension values. The dimensions of the platinum Wilhelmy plate were 20.20 mm width and 0.18 mm thickness. This tensiometer can also be used to measure force, contact angles, and dynamic surface tension. Several measurement parameters can be easily changed, giving this equipment considerable versatility.

The sample (approximately 50 cm³) was introduced in a thermostatic glass vessel, on whose walls thermostatic water circulated. Temperature control was maintained by the use of an external Pt100 probe directly immersed in the solution. This probe was connected to an HAAKE F6 circulator that can control temperature within 0.01 K. The ability of this system to measure temperature accurately was guaranteed by calibration against a certified Thermometrics S10 thermistor. After calibration, the average absolute deviation (eq 1) was smaller than 0.04 K with a maximum deviation of -0.07 K at 319.72 K.

During the measurements the platinum plate was immersed and detached. Surface tension was determined from the maximum value of the plot of surface tension versus immersion depth while the plate was detached.

Mixtures were carefully prepared in a Mettler Toledo AB204 analytical balance (± 0.0001 g). The uncertainty in the mole fraction was calculated to be less than 2×10^{-5} .

Special precautions were taken to avoid evaporation of the more volatile components during measurement. For that, the tensiometer was hermetically closed, and a small portion of the more volatile component was introduced inside the tensiometer to saturate the air. Humidity control was also reached with the use of dried silica gel. Before the measurements, the glass vessel was carefully cleaned with water and detergent to completely remove that previous sample. After that, the vessel was washed with plenty of distilled water to remove detergent. In the end, it was flushed with pure acetone and dried before use. Surfactant-free paper was used for cleaning purposes.

Before each measurement the platinum plate was flame cleaned in a Bunsen burner to eliminate contaminants. The

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Table 1. Pure Component Data and Comparison with Literature

<i>n</i> -alkane	<i>T</i> /K	$\gamma/\text{mN}\cdot\text{m}^{-1} \pm 0.02 \text{ mN}\cdot\text{m}^{-1}$					
		this work	Jasper ³	McLure ⁴	Jasper ⁵	Koefoed ⁶	Águila-Hernandez ⁷
<i>n</i> -C ₇ H ₁₆	293.15	20.53	20.28	20.21	20.14	20.30	
	303.15	19.49	19.27	19.17	19.17	19.31	
	313.15	18.50	18.25	18.19	18.18		
	323.15	17.44	17.24	17.18	17.20		
	333.15	16.50	16.22	16.19	16.22		
<i>n</i> -C ₁₀ H ₂₂	293.15	24.47	23.89		23.83		
	303.15	23.35	22.98		22.91		
	313.15	22.45	22.06		21.99		
	323.15	21.55	21.14		21.07		
	333.15	20.60	20.22		20.15		
	343.15	19.70			19.23		
	293.15	28.12	27.64		27.47	27.40	
<i>n</i> -C ₁₆ H ₃₄	303.15	27.05	26.79		26.62	26.63	
	313.15	26.26	25.95		25.76		
	323.15	25.30	25.11		24.91		25.08
	333.15	24.40	24.27		24.06		24.25
	343.15	23.51	23.42		23.20		23.38
<i>n</i> -C ₂₀ H ₄₂	313.15	27.62			27.21		
	323.15	26.74			26.38		26.52
	333.15	25.96			25.54		25.58
	343.15	25.09			24.71		24.71

sample surface was also cleaned before measurement by aspiration with a Pasteur pipet and discarded. This allows the removal of some surface active contaminants and the formation of a new and clean surface.

Tensiometer and balance calibrations were made against masses provided by the manufacturers.

3. Results and Discussion

The Wilhelmy plate method was used for all the reported results. This method is independent of the sample liquid density, which gives it an advantage over some of the other common methods, which rely on sample densities to obtain surface tension values².

Data were taken from 293.15 K up to 343.15 K in temperature intervals of 10 K.

Each sample was measured in at least five sets of three immersion/detachment cycles each, thus giving a minimum of 15 surface tension values, from which an average was taken.

Results are compared with available experimental data using percent average absolute deviations (% AAD):

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

where *n* is the number of data points, *X* is the studied property (surface tension), and the subscript *a* stands for the accepted value.

Pure component results and comparison with literature values^{3–7} are provided in Table 1. The reported uncertainty ($\pm 0.02 \text{ mN}\cdot\text{m}^{-1}$) is the highest uncertainty found from all the data points. It is a combined standard uncertainty calculated using the law of propagation of uncertainty in which temperature, force, and plate dimensions were considered. An overall average absolute deviation (eq 1) of 1.6% was found, corresponding to 1.5% for heptane, 2.1% for decane, 1.3% for hexadecane, and 1.4% for eicosane. The maximum absolute deviation was 2.7%, found for decane at 293.15 K, compared with Jasper⁵ data. As can be seen in Table 1, some discrepancies can be found among data from other authors, from which we can conclude that our equipment is able to measure surface tension with a good accuracy.

Average mixture data are presented in Tables 2–5, and comparison with reported values from Pandey and Pant,⁸

Table 2. Surface Tension of the Binary Mixture Heptane (1) + Decane (2)

<i>x</i> (2)	$\gamma/\text{mN}\cdot\text{m}^{-1} \pm 0.03 \text{ mN}\cdot\text{m}^{-1}$				
	293.15 K	303.15 K	313.15 K	323.15 K	333.15 K
0.000	20.53	19.49	18.50	17.44	16.50
0.251	21.68	20.72	19.75	18.85	17.91
0.501	22.73	21.57	20.67	19.80	18.96
0.752	23.47	22.46	21.49	20.62	19.78
1.000	24.47	23.35	22.45	21.55	20.60

Table 3. Surface Tension of the Binary Mixture Heptane (1) + Hexadecane (2)

<i>x</i> (2)	$\gamma/\text{mN}\cdot\text{m}^{-1} \pm 0.04 \text{ mN}\cdot\text{m}^{-1}$				
	293.15 K	303.15 K	313.15 K	323.15 K	333.15 K
0.000	20.53	19.49	18.50	17.44	16.50
0.200	22.36	21.44	20.61	19.71	19.03
0.500	24.76	23.78	22.95	22.06	21.31
0.800	26.83	25.88	25.28	24.63	23.80
1.000	28.12	27.05	26.26	25.30	24.40

Table 4. Surface Tension of the Binary Mixture Decane (1) + Hexadecane (2)

<i>x</i> (2)	$\gamma/\text{mN}\cdot\text{m}^{-1} \pm 0.03 \text{ mN}\cdot\text{m}^{-1}$				
	293.15 K	303.15 K	313.15 K	323.15 K	333.15 K
0.000	24.47	23.35	22.45	21.55	20.60
0.250	25.29	24.37	23.54	22.60	21.67
0.500	26.20	25.48	24.76	23.71	22.87
0.752	27.18	26.17	25.46	24.65	23.72
1.000	28.12	27.05	26.26	25.30	24.40

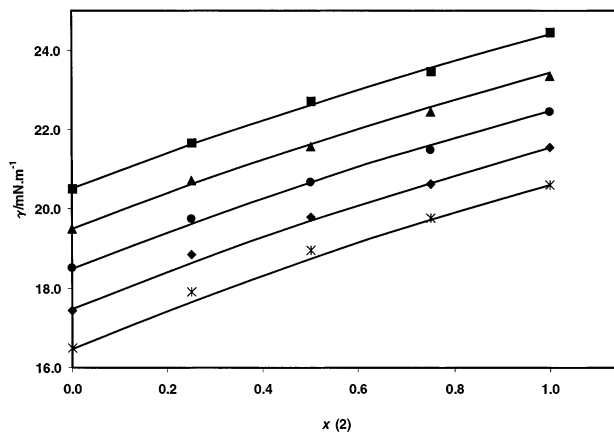
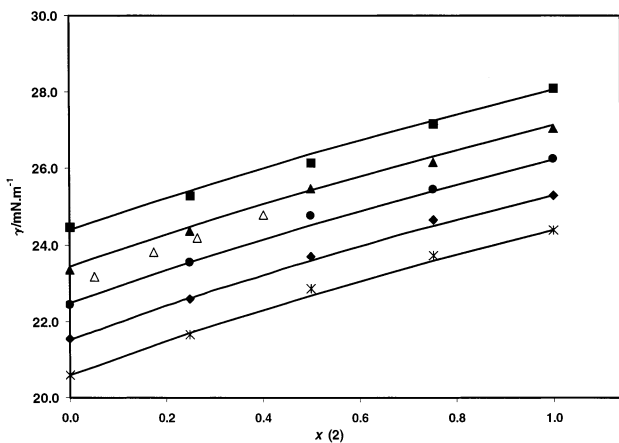
Koefoed and Villadsen,⁶ Águila-Hernandez,⁷ and Pugachevich et al.⁹ can be found graphically in Figures 2–4. Pandey and Pant⁸ reported four mixture data points ($0.05 < x(n\text{-C}_{16}\text{H}_{34}) < 0.40$) for the system decane + hexadecane at 303.16 K. Koefoed and Villadsen⁶ and Pugachevich et al.⁹ presented data for the mixture heptane + hexadecane at 293.15 K, 303.15 K, 333.15 K, and 373.15 K. Águila-Hernandez⁷ presented full composition data for the mixture hexadecane + eicosane from 323.15 K up to 353.15 K.

Calculated uncertainties are reported on each table heading and represent the highest uncertainty found from all the mixture points. The proceeding is the same used for the pure components, this time including also the uncertainty due to mixture preparation.

Because no mixture data were measured by us and the other authors under the same conditions, visual inspection

Table 5. Surface Tension of the Binary Mixture Hexadecane (1) + Eicosane (2)

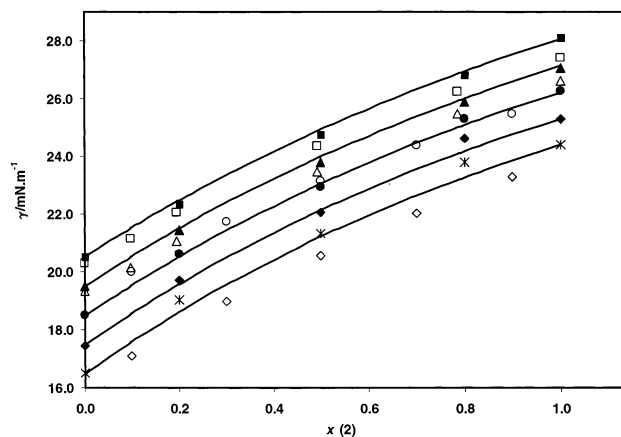
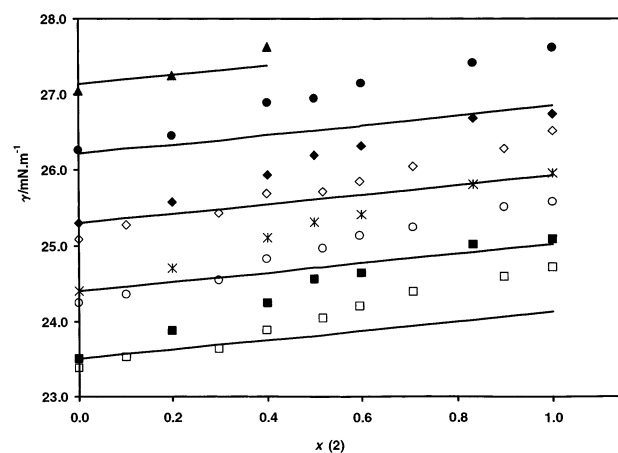
$x(2)$	$\gamma/\text{mN}\cdot\text{m}^{-1} \pm 0.01 \text{ mN}\cdot\text{m}^{-1}$				
	303.15 K	313.15 K	323.15 K	333.15 K	343.15 K
0.000	27.05	26.26	25.30	24.40	23.51
0.200	27.25	26.45	25.58	24.70	23.87
0.400	27.63	26.89	25.94	25.11	24.25
0.500		26.95	26.19	25.31	24.56
0.600		27.15	26.32	25.41	24.64
0.833		27.42	26.69	25.81	25.02
1.000		27.62	26.74	25.96	25.09

**Figure 1.** Surface tension of $n\text{-C}_7\text{H}_{16}$ (1) + $n\text{-C}_{10}\text{H}_{22}$ (2): ■, 293.15 K; ▲, 303.15 K; ●, 313.15 K; ◆, 323.15 K; *, 333.15 K; —, model.**Figure 2.** Surface tension of $n\text{-C}_{10}\text{H}_{22}$ (1) + $n\text{-C}_{16}\text{H}_{34}$ (2): ■, 293.15 K; ▲, 303.15 K; ●, 313.15 K; ◆, 323.15 K; *, 333.15 K; △, ref 8, 303.16 K; —, model.

has to be used to demonstrate that although our equipment seems to give systematically higher values than those reported in the literature, small deviations can be observed, which can guarantee that our measurements should have considerable accuracy. It should also be noted that, for the system heptane + hexadecane, data reported by Koefoed and Villadsen⁶ for hexadecane presented the highest deviation from our data, as can be seen in Table 1. Data from Pugachevich et al.⁹ are systematically lower than those reported either in this work or by Koefoed and Villadsen.⁶

For the mixture hexadecane–eicosane, our data are somewhat higher than those reported by Águila-Hernández,⁷ but small deviations are observed. Average absolute deviations (eq 1) for the pure components are 0.7% and 1.3%, respectively, for hexadecane and eicosane.

No mixture information was found in the literature for the system heptane–decane.

**Figure 3.** Surface tension of $n\text{-C}_7\text{H}_{16}$ (1) + $n\text{-C}_{16}\text{H}_{34}$ (2): ■, 293.15 K; ▲, 303.15 K; ●, 313.15 K; ◆, 323.15 K; *, 333.15 K; □, ref 6, 293.15 K; △, ref 6, 303.15 K; ○, ref 9, 303.15 K; ◇, ref 9, 333.15 K; —, model.**Figure 4.** Surface tension of $n\text{-C}_{16}\text{H}_{34}$ (1) + $n\text{-C}_{20}\text{H}_{42}$ (2): ▲, 303.15 K; ●, 313.15 K; ◆, 323.15 K; *, 333.15 K; ■, 343.15 K; ◇, ref 7, 323.15 K; ○, ref 7, 333.15 K; □, ref 7, 343.15 K; —, model.

4. Modeling

Mixture data were predicted using a corresponding states model¹ recently proposed. This model is based only on pure component properties: critical temperature, critical volume, Pitzer acentric factor, and surface tension of the three chosen reference fluids, which in this case were the three lower n -alkanes selected for this work—heptane, decane, and hexadecane. Relevant equations are presented below:

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

$$\gamma_r = \gamma_{r_1} + D_1(\omega_j - \omega_1) + D_2(\omega_j - \omega_1)(\omega_j - \omega_2) \quad (3)$$

$$D_1 = \frac{\gamma_{r_2} - \gamma_{r_1}}{\omega_2 - \omega_1} \quad D_2 = \frac{\frac{\gamma_{r_3} - \gamma_{r_1}}{\omega_3 - \omega_1} - \frac{\gamma_{r_2} - \gamma_{r_1}}{\omega_2 - \omega_1}}{\omega_3 - \omega_2} \quad (4)$$

where γ is the surface tension, V_c is the critical volume, T_c is the critical temperature, ω is the Pitzer acentric factor, x is the mole fraction, and the subscripts r , j , 1 , 2 , and 3 refer to reduced property, target fluid, and each one of the three reference fluids, respectively.

Table 6. Prediction of Mixture Data with the Corresponding States Model

system	% AD	% AAD
$n\text{-C}_7\text{H}_{16} + n\text{-C}_{16}\text{H}_{34}$	-0.28	0.85
$n\text{-C}_{10}\text{H}_{22} + n\text{-C}_{16}\text{H}_{34}$	-0.05	0.44
$n\text{-C}_7\text{H}_{16} + n\text{-C}_{10}\text{H}_{22}$	-0.28	0.55
$n\text{-C}_{16}\text{H}_{34} + n\text{-C}_{20}\text{H}_{42}$	-2.06	2.06
average	-0.67	0.97

This model, previously presented for pure fluids, is here extended to mixtures by considering the mixture as a pseudopure fluid, characterized by pseudovalues of the critical temperature and volume and Pitzer acentric factor. The mixing and combining rules used are described by eqs 5–9:

$$\omega_m = \sum_i X_i \omega_i \quad (5)$$

$$V_{cm} = \sum_i \sum_j X_i X_j V_{cij} \quad (6)$$

$$T_{cm} V_{cm} = \sum_i \sum_j X_i X_j T_{cij} V_{cij} \quad (7)$$

$$V_{cij} = \frac{1}{8} (V_{ci}^{1/3} + V_{cj}^{1/3})^3 \quad (8)$$

$$T_{cij} V_{cij} = (T_{ci} V_{ci} T_{cj} V_{cj})^{1/2} \quad (9)$$

The indexes i and j in the equations represent pure components.

Results are reported in Table 6 and presented in Figures 1–4. An average absolute deviation of 1.0% was found for the 67 mixture data points measured in this work.

Higher deviations were found for the mixture hexadecane–eicosane, but one should remember that an extrapolation of the model is required using the reference system heptane–decane–hexadecane. Better results shall be expected if eicosane is selected as one of the reference fluids.

Still, the results show that using only five to six pure component surface tension values from each reference fluid, one is able to estimate all the corresponding mixture data points with a very small deviation. Extrapolation of the model is valid, but higher deviations should be expected.

These results clearly show that the proposed model is adequate for the surface tension modeling of hydrocarbon mixtures.

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