

Surface Tension of Decane Binary and Ternary Mixtures with Eicosane, Docosane, and Tetracosane

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A tensiometer operating on the Wilhelmy plate method was employed to measure liquid–vapor interfacial tensions of three binary mixtures and one ternary mixture of decane with eicosane, docosane, and tetracosane. Tensions of binary mixtures $n\text{-C}_{10}\text{H}_{22} + n\text{-C}_{20}\text{H}_{42}$, $n\text{-C}_{10}\text{H}_{22} + n\text{-C}_{22}\text{H}_{46}$, and $n\text{-C}_{10}\text{H}_{22} + n\text{-C}_{24}\text{H}_{50}$ and the ternary $n\text{-C}_{10}\text{H}_{22} + n\text{-C}_{20}\text{H}_{42} + n\text{-C}_{24}\text{H}_{50}$ were measured from 293.15 K (or above the solution melting temperature) up to 343.15 K. An average absolute deviation of 1.3% was obtained in comparison with pure component literature data. No mixture information for the reported systems was found in the literature. Results were modeled with a recently proposed corresponding states model. The average absolute deviation was found to be 1.2%.

1. Introduction

The continuous demand for new products has been moving the chemical industry toward the production of a broad range of chemicals. Thermophysical properties are frequently required for both product and process design, and in many cases, these are scarce or unavailable.

One of the most well documented families of chemicals is that of the n -alkanes. Many of the data appeared because alkanes are important in the petroleum industry. Because data availability decreases as we progress through the homologous series, many of the heavier n -alkanes still remain to be studied. In fact, above eicosane ($n\text{-C}_{20}\text{H}_{42}$) there is a considerable lack of data for many of the most important thermophysical properties such as vapor pressure, liquid density, viscosity, thermal conductivity, and interfacial tension.

Some recent advances in oil extraction technology made possible the recovery of several heavier oil fractions.¹ The mixture of heavier and lighter components also made the new oils more asymmetric, thus there is emerging interest in heavier and asymmetric n -alkane mixtures.

The importance of interfacial tension for the petroleum industry extends far beyond the extraction process, when oil has to travel through capillary channels and where this type of flow is strongly dominated by interfacial tension effects. In fact, it is not unusual in the extraction of crudes to add surfactants to modify the interfacial properties between crude oil and the geological reservoir.¹ Other operations such as multiphase transport in pipelines, adsorption, distillation, or extraction also rely on this property. Outside the refinery, environmental concerns about oil spills, both in seawater and freshwater, is a field where the study of the oil–water interface can provide important information because it can determine the path, transport mechanisms, and fate of organic pollutants in the environment. Other industries where interfacial ten-

sions arising from long alkyl chains are important are those producing coatings, paints, detergents, cosmetics, and agrochemicals. Although literature data have substantially increased over the last few decades, information about asymmetric or heavy systems is still scarce.

The main objective of this work was to determine liquid–vapor interfacial tensions of pure and mixed n -alkanes, with a special interest in the measurement of some pure heavier members and some of their mixtures with a lighter one. Our first results, reported elsewhere,^{2,3} showed the ability of our equipment to measure interfacial tension accurately with an average absolute deviation (eq 1) of 1.3%.

This work presents liquid–vapor interfacial tensions of three binary mixtures and one ternary mixture of eicosane, docosane, and tetracosane mixed with decane.

Because the experimental measurement of thermophysical properties is an expensive and time-consuming procedure, the alternative is to select models from which the desired properties can be obtained within the required accuracy. Although several models have been proposed, it is still essential to carry out some experimental measurements on new systems of interest to assess their limitations and provide a basis for the development of improved models.

These measurements, together with other collected results, have already provided an extensive database from which a model for the liquid–vapor interfacial tension of heavy hydrocarbons and their mixtures was developed and evaluated.^{2–4}

In this paper, the modeling results of the reported systems are also presented and discussed.

2. Experimental Methods

The chemicals used in the measurements were decane (Aldrich, $\geq 99\%$), eicosane (Sigma, $\geq 99\%$), docosane (Sigma, $\geq 99\%$), and tetracosane (Fluka, $\geq 99\%$). Decane was dried over molecular sieves. No further purification was performed.

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A NIMA DST 9005 tensiometer from NIMA Technology, Ltd., able to read force⁵ to within 10^{-6} mN, was operated on the basis of the Wilhelmy plate method.⁶ Dimensions of the platinum plate were 20.20 mm width and 0.18 mm thickness (± 0.01 mm). The sample was introduced in a thermostatic glass vessel whose temperature was controlled to within ± 0.01 K by an external Pt100 probe directly immersed in the solution and connected to a HAAKE F6 circulator. The accuracy of this temperature measuring system was assured by calibration against a certified Thermometrics S10 thermistor (± 0.0015 K). The average absolute deviation (eq 1) was smaller than 0.04 K with a maximum deviation of -0.07 K at 319.72 K. Other details about the measuring apparatus and procedure can be found elsewhere.²

Mixtures were prepared with a Mettler Toledo AB204 analytical balance (± 0.0001 g). The mole fraction uncertainty was calculated to be less than 1×10^{-5} .

Special precautions were taken to avoid the evaporation of decane during the measurements. For that, a small portion of decane was introduced inside the tensiometer to saturate the air. Humidity control was reached with the use of dried silica gel.

Before the measurements, the glass vessel was carefully cleaned with water and detergent to remove the previous sample completely. After that, the vessel was washed with plenty of distilled water and dried before use. The glass vessel was regularly soaked in $5 \text{ mol}\cdot\text{L}^{-1}$ nitric acid to remove any extra contaminant. 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 sample interface 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 interface.

The tensiometer and balance were calibrated with masses provided by the manufacturers.

3. Results and Discussion

Data were taken from 293.15 K (or above the fluid melting point) up to 343.15 K in temperature intervals of 10 K. Each sample was measured using at least 4 sets of 5 cycles of immersion/detachment each, thus giving a minimum of 20 interfacial tension values, from which an average was taken.

Results are compared with available experimental data using the percent average absolute deviation (% 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 (interfacial tension), and the subscript a stands for the accepted value.

Pure component results and comparison with literature values⁷⁻⁹ are provided in Table 1. The estimated uncertainty ($\pm 0.03 \text{ mN}\cdot\text{m}^{-1}$) is the highest uncertainty found from all of the data points. It is a combined standard uncertainty estimated using the law of propagation of uncertainty in which temperature, force, and plate dimensions were considered.¹⁰

An overall average absolute deviation (eq 1) of 1.3% was found, corresponding to 1.5% for decane and 1.1% for eicosane and docosane. No literature data were found for tetracosane. The maximum absolute deviation was 2.2%, found for decane at 343.15 K and compared with Jasper⁸

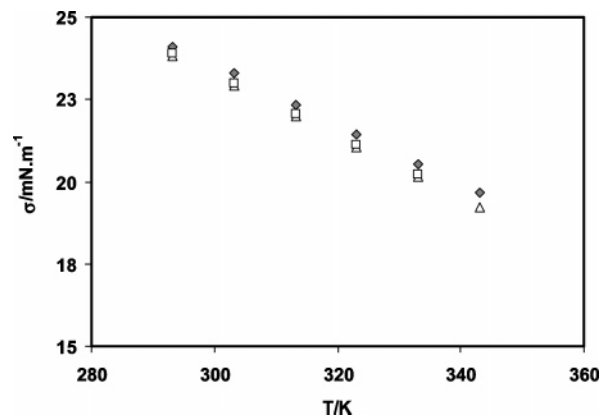


Figure 1. Vapor-liquid interfacial tension of $n\text{-C}_{10}\text{H}_{22}$: \diamond , this work; \triangle , Jasper;⁸ \square , Jasper et al.⁷

Table 1. Pure Component Liquid-Vapor Interfacial Tension Data and Comparison with Literature

<i>n</i> -alkane	<i>T</i> /K	$\sigma/\text{mN}\cdot\text{m}^{-1}$				% AAD
		this work	ref 7	ref 8	ref 9	
<i>n</i> -C ₁₀ H ₂₂	293.15	24.09	23.89	23.83		1.5
	303.15	23.29	22.98	22.91		
	313.15	22.33	22.06	21.99		
	323.15	21.43	21.14	21.07		
	333.15	20.54	20.22	20.15		
	343.15	19.66		19.23		
<i>n</i> -C ₂₀ H ₄₂	313.15	27.58		27.21		1.1
	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	323.15	27.42			27.15	1.1
	333.15	26.60			26.25	
	343.15	25.79			25.54	
<i>n</i> -C ₂₄ H ₅₀	333.15	27.05				
	343.15	26.22				
		% AAD	1.3	1.5	1.0	1.3

Table 2. Interfacial Tension of the Binary Mixtures

mixture	x_2	293.15	303.15	313.15	323.15	333.15	343.15
		K	K	K	K	K	K
<i>n</i> -C ₁₀ H ₂₂ (1) + <i>n</i> -C ₂₀ H ₄₂ (2)	0.200	$\sigma \pm 0.02/\text{mN}\cdot\text{m}^{-1}$					
		25.45	24.59	23.70	22.71	21.83	20.96
	0.400		25.77	24.86	24.04	23.11	22.18
	0.499		26.45	25.50	24.69	23.60	22.80
	0.600			26.00	25.25	24.34	23.60
<i>n</i> -C ₁₀ H ₂₂ (1) + <i>n</i> -C ₂₂ H ₄₆ (2)	0.799			27.13	26.16	25.40	24.53
	0.200			23.39	22.67	22.13	21.51
	0.400			25.36	24.29	23.49	22.87
	0.499			26.08	25.01	24.18	23.39
	0.600			26.67	25.57	24.78	23.94
<i>n</i> -C ₁₀ H ₂₂ (1) + <i>n</i> -C ₂₄ H ₅₀ (2)	0.800				26.68	26.05	25.22
	0.200			24.07	23.13	22.24	21.42
	0.401				24.64	23.84	22.96
	0.495				25.29	24.48	23.55
	0.600				25.99	25.04	24.10
0.796				27.14	26.27	25.35	

data. A graphical comparison of decane measured data with literature data is presented in Figure 1. Small deviations are observed in this Figure and also in Table 1. Similar discrepancies were found before for other *n*-alkanes^{2,3} and also among different authors, from which we can conclude that our equipment is able to measure interfacial tension with a good accuracy.

Average mixture data are presented in Tables 2 and 3 and plotted in Figures 2 to 3 as a function of composition.

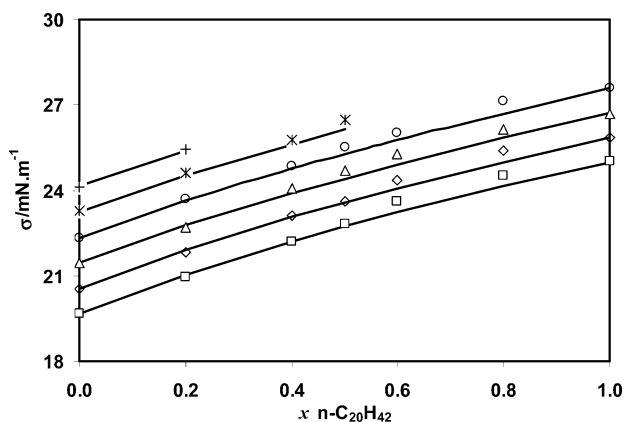


Figure 2. Vapor-liquid interfacial tension of $n\text{-C}_{10}\text{H}_{22}$ (1) + $n\text{-C}_{20}\text{H}_{42}$ (2): +, 293.15 K; *, 303.15 K; ○, 313.15 K; △, 323.15 K; ◇, 333.15 K; □, 343.15 K; —, model.

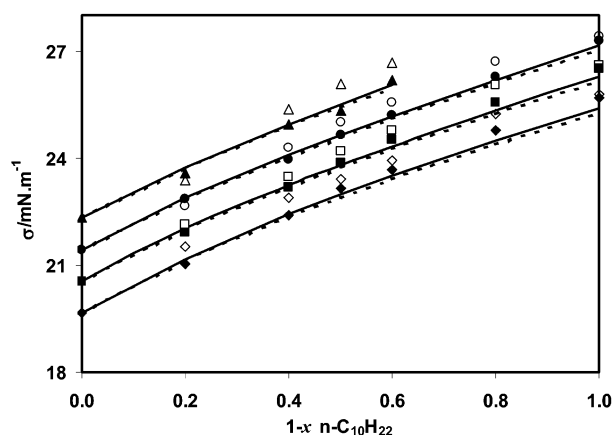


Figure 3. Vapor-liquid interfacial tension of $n\text{-C}_{10}\text{H}_{22}$ (1) + $n\text{-C}_{20}\text{H}_{42}$ (2) + $n\text{-C}_{24}\text{H}_{50}$ (3) (filled symbols) and $n\text{-C}_{10}\text{H}_{22}$ (1) + $n\text{-C}_{22}\text{H}_{46}$ (2) (open symbols): triangles, 313.15 K; circles, 323.15 K; squares, 333.15 K; diamonds, 343.15 K. —, Model, binary mixture; - - - model, ternary mixture.

Table 3. Interfacial Tension of the Ternary Mixture Decane (1) + Eicosane (2) + Tetracosane (3)

x_1	x_2	313.15 K	323.15 K	333.15 K	343.15 K
$\sigma \pm 0.03/\text{mN}\cdot\text{m}^{-1}$					
0.000	0.500		27.27	26.51	25.69
0.201	0.400		26.26	25.56	24.77
0.400	0.300	26.16	25.20	24.52	23.67
0.500	0.250	25.33	24.65	23.85	23.16
0.600	0.200	24.93	23.96	23.17	22.38
0.800	0.100	23.56	22.86	21.92	21.02

Estimated uncertainties are reported in each Table heading and represent the highest uncertainty found from all of the mixture points. The estimation procedure is the same as that used for the pure components, this time also including the uncertainty due to mixture preparation.¹⁰

No mixture information was found for any of the mixtures reported in this work.

4. Modeling

Mixture data were predicted using a recently proposed corresponding states model.²⁻⁴ This model is based on pure component properties: critical temperature, critical volume, Pitzer acentric factor, and the interfacial tensions of the three chosen reference fluids—heptane, decane and eicosane—the same as those used before in a previous paper.³ Experimental critical properties and Pitzer acentric factors were used when available.^{11,12} Correlations were

Table 4. Pure Component Reference Fluid Properties

reference fluid	T_c/K	$V_c/\text{cm}^3\cdot\text{mol}^{-1}$	ω	$A/\text{mN}\cdot\text{m}^{-1}$	B
$n\text{-C}_7\text{H}_{16}$	540.2	428	0.350	53.83	1.25
$n\text{-C}_{10}\text{H}_{22}$	617.7	624	0.490	55.44	1.31
$n\text{-C}_{20}\text{H}_{42}$	768	1340	0.891	58.32	1.45

Table 5. Prediction Capacity of the Mixture Data with the Corresponding States Model

system	% AD	% AAD
$n\text{-C}_{10}\text{H}_{22} + n\text{-C}_{20}\text{H}_{42}$	-0.7	0.8
$n\text{-C}_{10}\text{H}_{22} + n\text{-C}_{22}\text{H}_{46}$	-1.4	1.7
$n\text{-C}_{10}\text{H}_{22} + n\text{-C}_{24}\text{H}_{50}$	-2.0	2.0
$n\text{-C}_{10}\text{H}_{22} + n\text{-C}_{20}\text{H}_{42} + n\text{-C}_{24}\text{H}_{50}$	-0.5	0.7
average	-1.1	1.2

assessed for those n -alkanes for which there were no experimental data. The critical temperature was obtained from the correlation of Tsonopoulos;¹³ the critical volume, from Marano and Holder;¹⁴ and the Pitzer acentric factor, from Han and Peng.¹⁵

Relevant model equations are presented below

$$\sigma_r = \sigma \times \frac{V_c^{2/3}}{T_c} \quad (2)$$

$$\sigma_r = \sigma_{r1} + D_1(\omega_j - \omega_1) + D_2(\omega_j - \omega_1)(\omega_j - \omega_2) \quad (3)$$

$$D_1 = \frac{\sigma_{r2} - \sigma_{r1}}{\omega_2 - \omega_1} \quad D_2 = \frac{\frac{\sigma_{r3} - \sigma_{r1}}{\omega_3 - \omega_1} - \frac{\sigma_{r2} - \sigma_{r1}}{\omega_2 - \omega_1}}{\omega_3 - \omega_2} \quad (4)$$

where σ is the interfacial tension, V_c is the critical volume, T_c is the critical temperature, ω is the Pitzer acentric factor, and subscripts $r, j, 1, 2,$ and 3 refer to the reduced property, target fluid, and each of the three reference fluids, respectively.

Reference fluid data were correlated as a function of temperature according to eq 5

$$\sigma = A \times (1 - T_r)^B \quad (5)$$

where A and B are correlating parameters. These are presented in Table 4, together with the required critical properties and Pitzer acentric factors.

Mixing and combining rules are described below

$$\omega_m = \sum_i x_i \omega_i \quad (6)$$

$$V_{cm} = \sum_i \sum_j x_i x_j V_{cij} \quad (7)$$

$$T_{cm} V_{cm} = \sum_i \sum_j x_i x_j T_{cij} V_{cij} \quad (8)$$

$$V_{cij} = \frac{1}{8} (V_{ci}^{1/3} + V_{cj}^{1/3})^3 \quad (9)$$

$$T_{cij} = \sqrt{T_{ci} T_{cj}} \left(\frac{\sqrt{V_{ci} V_{cj}}}{V_{cij}} \right)^{(n/3) - 1} \quad (10)$$

where x is the mole fraction, indexes i and j represent pure components, and m represents the mixture property.

Following Coutinho et al.,¹⁶ a more general combining rule for the cross-critical temperature, T_{cij} , was adopted in this work (eq 10). This equation reduces to the combining rule used in our previous work² if the parameter n is set

equal to 6. For the purposes of this report and following previous results for other asymmetric mixtures,³ the n parameter was set equal to 4.6.

Modeling results are reported in Table 5 and presented in Figures 2 and 3 together with the experimental measurements. An average absolute deviation of 1.2% was found for the 81 mixture data points measured in this work. As seen in Figure 3, the model is able to distinguish the higher interfacial tensions of the binary n -C₁₀H₂₂ + n -C₂₂H₄₆ from the slightly lower values obtained for the equivalent ternary mixture n -C₁₀H₂₂ + n -C₂₀H₄₂ + n -C₂₄H₅₀ (containing equal mole fractions of the lighter n -C₂₀H₄₂ and heavier n -C₂₄H₅₀).

The results show that by using only five to six pure component interfacial tension values from each reference fluid one is able to estimate all of the corresponding mixture data points with a very small deviation. These results clearly show that the proposed model is adequate for the liquid–vapor interfacial tension modeling of hydrocarbon mixtures.

5. Conclusions

Liquid–vapor interfacial tensions were reported for three binary mixtures and one ternary mixture containing decane and heavy n -alkanes (eicosane, docosane, and tetracosane). Measurements were taken from 293.15 K (or above the fluid melting point) up to 343.15 K. Comparison with the available pure component literature data showed that an average deviation close to 1% was obtained. For the mixture data reported in this work no literature data were found.

Mixture results were modeled with a new corresponding states model able to deal with lighter and heavier n -alkanes and their asymmetric mixtures. Deviations below 2% were obtained for all of the reported mixtures, showing the adequacy of using this model to estimate interfacial tensions of these systems.

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