Interfacial Tension of Alkane + Water Systems[†]

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Interfacial tension was measured for hexane + water, heptane + water, octane + water, nonane + water, decane + water, undecane + water, and dodecane + water, using the emergent drop experimental technique with a numerical method based on a fourth degree spline interpolation of the drop profile. The experimental equipment used to generate the drop consists of a cell with a stainless steel body and two Pyrex windows. The inner cell was previously filled with water. A surgical needle (at the bottom of the cell) was used to introduce the organic phase into the cell (forming the emergent drop). Water was used to keep the temperature constant inside the cell (between 10 °C and 60 °C). The cell was illuminated from the back using a fiber optic lamp and a diffuser. A video camera (with a 60 mm microlens and an extension ring) was located at the front window. The emergent drop image was captured and sent to the video recording system. The cell and the optical components were placed on an optical table with vibration isolation legs. A new correlation was found to predict interfacial tension (γ) as a function of temperature (t) and the number of carbon atoms (n) with a deviation of less than 0.05% from experimental values.

1. Introduction

Many investigations have dealt with the characterization of water/oil interfaces because of its relevance in many industrial applications. Although, in the literature, several works can be found with organic + water systems, few of them use the emergent drop method.

The objective of this work was to determine interfacial tension from the emergent drop method and the mathematical model developed by López de Ramos *et al.*[1] for *n*-alkane + water systems. Additionally, a new correlation for interfacial tension as a function of temperature and number of carbon atoms is proposed.

2. Mathematical Model

The shape of liquid drops (pending from a surface) can be described by the Laplace−Young equation. This equation is just a balance between gravity, hydrostatic pressure, and surface tension effects. When drops are axisymmetric, the Laplace−Young equation can be written as

$$\left(\frac{1}{R_1} + \frac{1}{R_2}\right) = -\frac{\Delta\rho gy}{\gamma} + f(R_0) \tag{1}$$

where γ is the surface tension, R_1 and R_2 are the principal radii of curvature, $\Delta\rho$ is the difference in densities of the two fluids, g is the gravitational acceleration, and R_0 is the radius of curvature at $y = 0$ (Figure 1). The term $(1/R_1 + 1/R_2)$ is the mean curvature of the drop; this curvature is a function of the y position and can be expressed using differential geometry as

$$\left(\frac{1}{R_1} + \frac{1}{R_2}\right) = \frac{d^2y/dx^2}{[1 + (dy/dx)^2]^{3/2}} + \frac{dy/dx}{x[1 + (dy/dx)^2]^{1/2}} \tag{2}$$
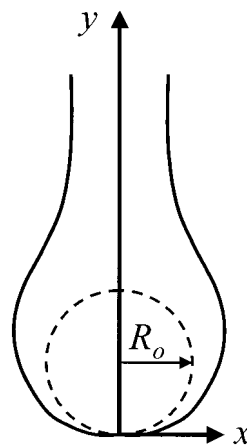
Figure 1. Pendant drop showing the geometrical variables.

Solutions to the Young−Laplace equation for a pendant drop (eq 1) predict a linearly varying curvature as a function of elevation. Plotting the mean curvature of the pendant drop versus the y position (elevation) renders a straight line with slope $-\Delta\rho gy/\gamma$. Computer-generated spline functions[1] were used to represent the experimental data to a prescribed degree of smoothness. In turn, derivatives of the spline functions provide an accurate and reliable way to determine the curvature (eq 2) of the drop image.

This method can be easily adjusted to emergent drops, by just rotating the image 180° before the edge detection process. It is also possible to rewrite eq 1 with a plus sign in front of the gravity term, because in this case the y axis and the gravity have the same direction.

3. Experimental Methods

3.1. Chemicals. Several emergent drop experiments were performed at atmospheric pressure. The organic phase used was hexane (99%, Aldrich), heptane (99%,
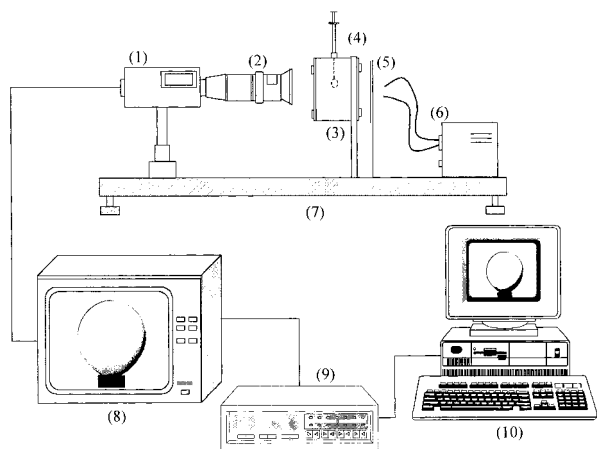
Figure 2. Experimental setup of the equipment used to obtain TGA images from emergent drops: 1, video camera; 2, lenses; 3, visualization cell; 4, syringe; 5, diffuser; 6, fiber optic lamp; 8, high resolution monitor; 9, video recorder; 10, computer with TARGA.

Aldrich), octane (99%, Aldrich), nonane (99%, Aldrich), decane (99+%, Sigma), undecane (99+%, Aldrich), and dodecane (99+%, Aldrich). All organic liquids were distilled in an all-glass apparatus and passed several times through an alumina column to remove any active impurities. Water was also distilled in an all-glass apparatus (three times).

3.2. Equipment. To create drops, a stainless steel cell was designed with two Pyrex windows. These windows are sealed to the cell body through a gasket (grafoil, 0.001 587 5 m of thickness). The liquid phase can be introduced into the cell from the top or from the bottom in order to create pendant or emergent drops. A surgical needle inserted at the top of the cell is used to form pendant drops. A small hole on the bottom surface allows the formation of emergent drops or captive bubbles. There is a thermocouple well in one of the sides. Four channels spanning the width of the cell are used to circulate water, keeping the temperature constant inside the cell. The circulating water temperature is controlled using a constant-temperature bath. Figure 2 is a schematic view of the complete experimental setup.

The cell is illuminated from the back using a fiber optic lamp. A diffuser is placed between the lamp and the rear window. A video camera (CCD-72 from DAGE-MTI Incorporated) is located at the front window. Two lenses can be attached to the video camera through a C connector. One of the lenses is the Nikkon 60 mm micro with a PK-13 extension ring, and the other lens is the D. O. Industries Zoom 6000 Microscopic. The emergent drop image can be captured easily, and it can be sent to the video recording system (Panasonic AG-7300) or to the computer (using the Targa videographic system connected to an Intel 80586-100 MHz CPU with VGA card and monitor). The image visualization equipment is also furnished with a Sony PVM2530 RGB monitor. The cell and the optical components are placed on an optical tubular bench with vibration isolation legs. Figure 3 shows a typical emergent drop image. In Figure 3a the image is presented as a TARGA format. Figure 4b shows the black and white image, and Figure 4c shows the emergent drop outline. From the drop image outline the xy profile is obtained using a program in Visual-Basic. Finally, the interfacial tension can be calculated using a spline method.

3.3. Calibrations. The emergent drop technique used to determine interfacial tension does not really need any correction factors.[2]
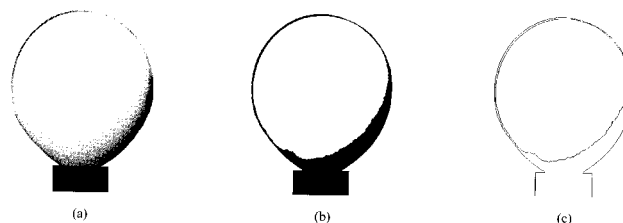
Figure 3. Typical emergent drop: (a) original Targa image; (b) black and white image; (c) drop outline.
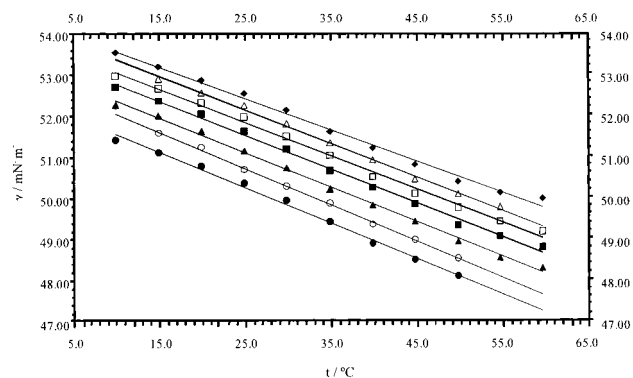
Figure 4. Interfacial tension values as a function of temperature for several n-alkanes: ●, hexane; ○, heptane; ▲, octane; ■, nonane; □, decane; △, undecane; ◆, dodecane.

The mathematical method with the computational program was tested calculating the surface tension for a hypothetical water drop profile. This drop profile was generated from the Laplace–Young equation using a theoretical surface tension value of 72.10 mN·m^{-1}. After using the program, the value of surface tension obtained perfectly matched the theoretical value.

The experimental procedure was previously tested with excellent results.[1,3] The propagation error calculations predict a value of $\Delta\gamma \approx \pm 0.04$ mN·m^{-1}.

3.4. Procedures. After choosing the n-alkane + water system and having the inner cell filled with water, a surgical needle is used to introduce the organic phase into the cell from the bottom (forming the emergent drop). The cell temperature is set between (10 and 60) °C. Then, the drop image is recorded using the video system and the image capture procedure begins. The final result is the xy drop profile.

It is important to allow enough time to achieve stability at the interface. It is not the purpose of this work to compute dynamic interfacial tension.

3.5. Calculation of Interfacial Tension. With the xy profile and the computational program, the interfacial tension value is then calculated from the slope of the plotting of curvature as a function of y.

4. Results and Discussion

In Table 1 are reported all the experimental interfacial tension values for all the n-alkanes + water systems selected. Figure 4 shows the interfacial tension values as a function of temperature for all the system studied. As can be seen, there is a lineal dependence between γ and t. Table 2 presents all the lineal regression equations that fit the experimental data. As the number of carbon atoms increases, interfacial tension decreases. Table 3 compares the experimental values calculated using the lineal equation (Table 2) at 22 °C with those reported at the same temperature by Goebel and Lunkenheimer.[4] Although

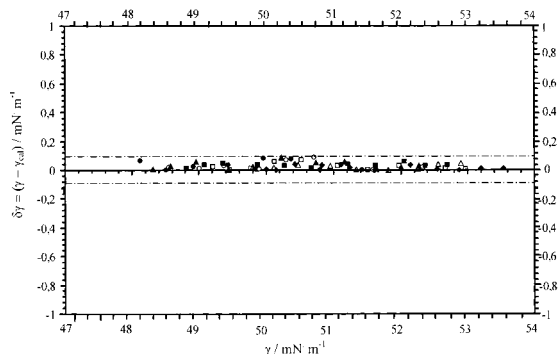**Table 1. Interfacial Tension Experimental Values at Different Temperatures**

	interfacial tension, γ/mN·m^{-1} ± 0.04						
$(t \pm 0.1)$/°C	hexane + water	heptane + water	octane + water	nonane + water	decane + water	undecane + water	dodecane + water
10.0	51.43		52.27	52.69	52.97		53.54
15.0	51.11	51.59	52.01	52.37	52.67	52.90	53.20
20.0	50.80	51.24	51.64	52.06	52.33	52.56	52.87
25.0	50.38	50.71	51.16	51.63	51.98	52.25	52.55
27.5	50.11	50.47	51.00	51.48	51.77	52.10	52.34
30.0	49.96	50.30	50.74	51.21	51.51	51.82	52.14
32.5	49.70	50.12	50.48	50.95	51.26	51.54	51.82
35.0	49.44	49.89	50.22	50.68	51.06	51.35	51.62
37.5	49.18	49.64	50.09	50.54	50.83	51.15	51.43
40.0	48.92	49.38	49.84	50.27	50.53	50.95	51.24
45.0	48.52	49.00	49.45	49.87	50.13	50.47	50.83
50.0	48.13	48.55	48.95	49.36	49.78	50.11	50.43
55.0			48.58	49.09	49.45	49.79	50.15
60.0			48.32	48.82	49.21		50.00

Table 2. Slope (a), Intercept (b), and Correlation Factor R^2 of the Lineal Equation $\gamma = at + b$

	a	b	
system	mN·m^{-1}·°C^{-1}	mN·m^{-1}	R^2
hexane + water	−0.0857	52.432	0.9944
heptane + water	−0.0896	52.99	0.9957
octane + water	−0.0835	53.219	0.9969
nonane + water	−0.0822	53.621	0.9953
decane + water	−0.0803	53.874	0.9942
undecane + water	−0.0813	54.211	0.9956
dodecane + water	−0.0757	54.333	0.9930

Table 3. Comparison between Interfacial Tension Values Calculated in This Work and Those Reported by Goebel and Lukenheimen[4] at 22 °C

	γ (1) (this work)	γ (2) (lit.)	$\Delta\gamma = \gamma(1) - \gamma(2)$
system	mN·m^{-1}	mN·m^{-1}	mN·m^{-1}
hexane + water	50.55	51.4	−0.85
heptane + water	51.02	51.9	−0.88
octane + water	51.38	52.5	−1.12
nonane + water	51.81	52.4	−0.59
decane + water	52.11	53.2	−1.09
undecane + water	52.42	53.1	−0.68
dodecane + water	52.67	53.7	−1.03

Figure 5. Interfacial tension calculated from the correlation proposed in this work (2) as a function of interfacial tension experimental values (1): ●, hexane; ○, heptane; ▲, octane; ■, nonane; □, decane; △, undecane; ◆, dodecane.

these values do not match perfectly, the tendencies of interfacial tension values with the number of carbon atoms are the same up to octane ($n = 5$). Beyond this point Goebel and Lunkenheimer's results present an oscillation, while the results of this work keep the tendency of the increment of interfacial tension with the number of carbon atoms. Theses differences could be caused by the lack of similarities in purity and quality of the chemicals used in both research works.

Aveyard and Haydon[5] reported interfacial tension values for alkane + water systems ($n = 5, 6, 7, 8, 10, 12, 14,$ and 16) in a reduced range of temperature of 20 °C and 37.5 °C. In the case of pentane and decane, the interfacial tension was only reported at 20 °C. Their results are similar to those reported in this work.

All the experimental data were correlated with an equation that has the form

$$\gamma/(\text{mN·m}^{-1}) = A(t) n^{B(t)} \tag{3}$$

where n is the number of carbon atoms. The coefficients $A(t)$ and $B(t)$ are a function of the temperature and can be calculated using the following equations:

$$A/(\text{mN·m}^{-1}) = -(7.4 \times 10^{-8}) t/(°\text{C})^6 + (1.5 \times 10^{-5}) t/(°\text{C})^5 - (1.2561 \times 10^{-3}) t/(°\text{C})^4 + (5.1645 \times 10^{-2}) t/(°\text{C})^3 - 1.1131 t/(°\text{C})^2 + 11.7029 t/(°\text{C}) \tag{4}$$

$$B = -(2.9 \times 10^{-11}) t/(°\text{C})^7 + (5.9 \times 10^{-9}) t/(°\text{C})^6 - (4.5570 \times 10^{-7}) t/(°\text{C})^5 + (1.7209 \times 10^{-5}) t/(°\text{C})^4 - 0.0003 t/(°\text{C})^3 + 0.0025 t/(°\text{C})^2 \tag{5}$$

Correlations 3−5 can be used to predict interfacial tension (γ) as a function of temperature (t) and the number of carbon atoms (n) with a deviation of less than 0.05% from experimental values (Figure 5). This correlation is simple to use because the only alkane property required to calculate surface tension is the number of carbon atoms.

Literature Cited

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(3) López de Ramos, A. Capillary Enhanced Diffusion of CO_2 in Porous Media. Doctor of Philosophy Dissertation, The University of Tulsa, 1993.

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