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# Interfacial Tension and Density of Water + Branched Hydrocarbon Binary Systems in the Range 303–343 K

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Experimental results for the liquid–liquid interfacial tension of water + branched hydrocarbon binary systems were obtained using the pendant drop method. The branched hydrocarbons included in this study were 2-methylpentane and 3-methylpentane as structural isomers of C<sub>6</sub>H<sub>14</sub>; 2,3-dimethylpentane as isomer of C<sub>7</sub>H<sub>16</sub>; and 2,2,4-trimethylpentane and 2,3,4-trimethylpentane as isomers of C<sub>8</sub>H<sub>18</sub>. The temperatures at which the experiments were carried out were 303.15, 313.15, 323.15, 333.15, and 343.15 K. Density values of both saturated liquid phases were also experimentally determined. An experimental apparatus for achieving the liquid–liquid equilibrium with online sampling and density measurement was developed. Density values obtained for both saturated liquid phases follow the expected behavior with temperature: they decrease with increasing temperature, whereas the effect of the structural isomerism on density was mainly observed on the results for the hydrocarbon-rich liquid phase. Also, the interfacial tension values decrease with increasing temperature for a given water + hydrocarbon binary system and as the size of the hydrocarbon increases. Estimated values for the interfacial tension of the systems with the different branched isomers were obtained using a method developed in previous work.

## 1. Introduction

Interfacial tension is an important thermophysical property that has high relevance for both scientific and practical applications. It reflects the type of molecular interactions that take place during the liquid–liquid contact in systems conformed by molecules with marked difference in chemical nature and molecular interactions. These are some of the characteristics that make a given system to present liquid–liquid partial miscibility, which indicates high nonideality of the liquid phases of the system under study.

Interfacial tension governs the mass and heat transfer between two liquid phases and also the stability of emulsions, the mobility of a liquid through orifices, wetting, and miscibility.<sup>1</sup>

In the oil industry, interfacial tension is important because it plays a key role in different processes, such as liquid–liquid extraction and enhanced oil recovery.<sup>2</sup> It is also an important property to consider for the study of the liquid contact between liquefied petroleum gas (LPG) and the aqueous solvent used to remove acid gases during the sweetening of this type of hydrocarbon-rich stream.<sup>3</sup>

The physical manifestation of the interfacial tension, either liquid–liquid, solid–liquid, or liquid–gas, is one of the characteristics that has been widely studied to apply a large family of chemical products, known generically as surfactants. These compounds are found in many different applications, such as managing emulsion formation or rupture, enhancing the solubility of components (gases or liquids) in gas–liquid or liquid–liquid systems, modifying the formation of clusters of hydrates to influence the formation or rupture of foams, and so forth. Also, in the distribution of particles of immiscible metals in solid solutions, the effect of interfacial energy is crucial in the solidification processes of monotectic alloys.<sup>4</sup>

The systematic work carried out by our research group on the understanding of the influence of interfacial properties in different applications of industrial interest includes the evaluation and selection of solvents for the sweetening of liquid hydrocarbon streams,<sup>5</sup> the study of solvents to enhance the liquid extraction capacity and selectivity for aromatic components in a given hydrocarbon stream,<sup>6</sup> and the study of interfaces to establish the characterization of defoamers or foaming inhibitors in sweetening processes.<sup>7</sup> These efforts have taken us to develop some contributions, experimental,<sup>8</sup> correlation,<sup>9</sup> and prediction,<sup>10,11</sup> on the surface properties of systems of interest for the oil and natural gas production, transport, and processing industries.

The experimental results obtained in this work correspond to the interfacial tension of binary systems formed by water + a hydrocarbon, where the hydrocarbon is an isomer with the following structural molecular formulas: C<sub>6</sub>H<sub>14</sub> (hexane, 2-methylpentane, and 3-methylpentane), C<sub>7</sub>H<sub>16</sub> (heptane, 2,3-dimethylpentane), and C<sub>8</sub>H<sub>18</sub> (octane, 2,2,4-trimethylpentane, and 2,3,4-trimethylpentane). The temperatures at which this study was conducted were 303.15, 313.15, 323.15, 333.15, and 343.15 K. For these measurements, the pendant drop method was used. The experimental results were obtained with an average uncertainty of  $\pm 0.07$  mN m<sup>-1</sup>.

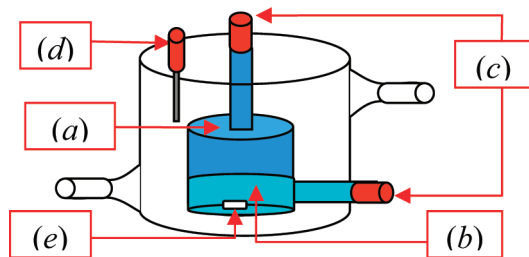
Also, as part of this study, density values of the saturated liquid phases formed by the partially miscible binary systems studied here were obtained using a vibrating tube densimeter. Density values were obtained for the saturated liquid (water-rich and hydrocarbon-rich) phases with an uncertainty of  $\pm 0.005$  kg m<sup>-3</sup> at 303, 313, and 323.15 K,  $\pm 0.010$  kg m<sup>-3</sup> at 333.15 K, and  $\pm 0.050$  kg m<sup>-3</sup> at 343.15 K.

## 2. Experimental Section

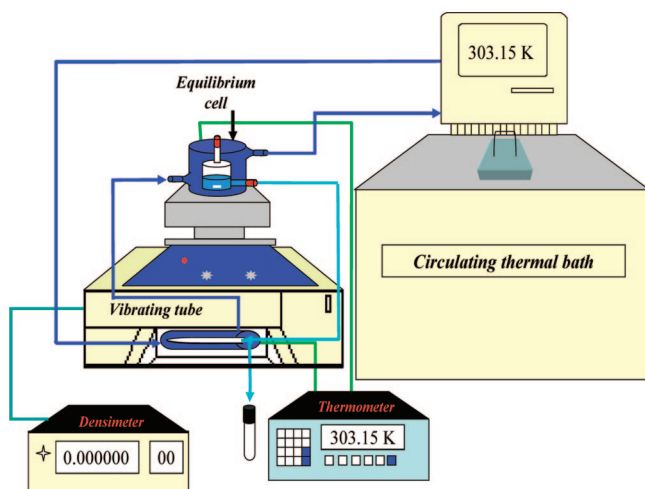
The materials used in this study were as follows: nitrogen (AGA Mexico, 99.5 mol %), hexane (Aldrich, lot 06723EQ, 99.1 mol %), 2-methylpentane (Aldrich, lot 07622HS, 99.7 mol %), 3-methylpentane (Aldrich, lot 01016KX, 99.9 mol %),

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**Figure 1.** Liquid–liquid equilibrium cell. (a) Water-saturated organic phase. (b) Hydrocarbon-saturated water phase. (c) Sampling ports for upper and lower liquid phases. (d) Thermowell for the platinum resistance sensor. (e) Magnetic bar.



**Figure 2.** Experimental device used to measure density values of liquid saturated phases.

heptane (Aldrich, lot 07046PY, 99.85 mol %), 2,3-dimethylpentane (Aldrich, lot 04721AI, 99.5 mol %), octane (Aldrich, lot 01638BE, 99.1 mol %), 2,2,4-trimethylpentane (Aldrich, lot 00840AC, 99.81 mol %), 2,3,4-trimethylpentane (Aldrich, lot 07029DY, 99.4 mol %), and water (bidistilled and deionized). The hydrocarbons were stored in bottles containing sodium to eliminate any traces of water. Both the hydrocarbons and water were degassed before their use for calibration or mixture preparation purposes, utilizing an ultrasound bath for a period of two hours. Nitrogen was passed through an activated molecular sieve column before being transferred into the densimeter for calibration purposes.

**2.1. Generation of Saturated Liquid Phases.** The experimental methods implemented to obtain density and interfacial tension values required the generation of saturated liquid phases shown by the binary water + hydrocarbon systems, under the studied conditions of temperature. For this, an experimental device was designed and constructed to achieve liquid–liquid equilibrium. This experimental device consisted of a liquid–liquid cell that was constructed in glass, with a glass jacket, a thermowell, and an equilibrium cell of a total volume of about 15 cm<sup>3</sup> where water (about 7 cm<sup>3</sup>) and hydrocarbon (about 8 cm<sup>3</sup>) were charged so that the liquid–liquid interface could be observed at the middle of this cell.

In Figure 1, a schematic diagram of this cell is presented. This cell is similar to that used in previous studies on liquid–liquid equilibrium from our laboratory.<sup>12–15</sup> The internal cell has three screw threaded tubes, two in the upper side and another at a lateral side near the bottom of the internal cell. One of the upper tubes allows the feeding of the substances under study at a given temperature, which is controlled with

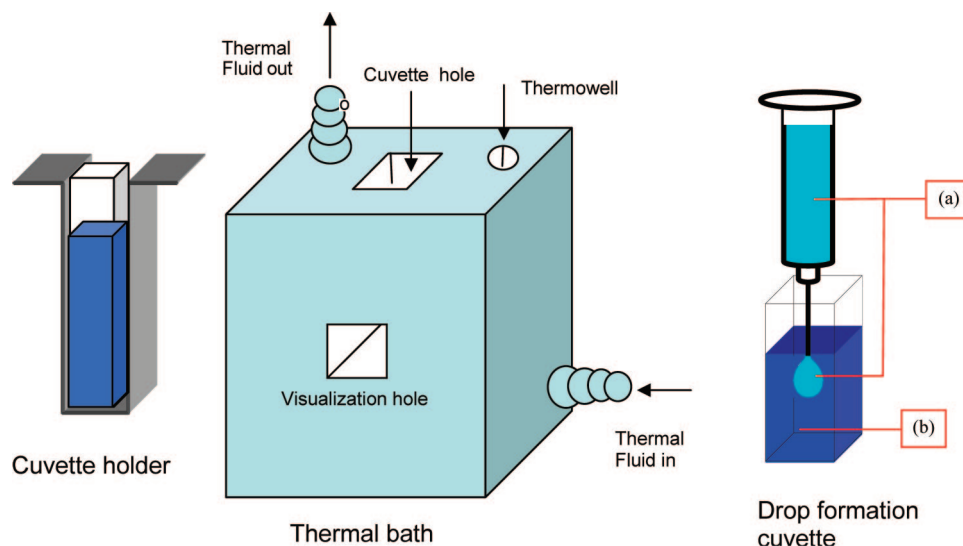
the aid of a Julabo F70 circulating bath using water as thermal fluid, which in turn filled completely the thermal jacket of the cell containing the system under study. This arrangement allows a control in temperature within  $\pm 0.003$  K, which was measured inside the thermal jacket using the third screw threaded tube with an F-250 Automatic Systems Laboratory digital thermometer together with a Pt-100 probe calibrated at the factory and traceable to the U.S. NIST with an accuracy of  $\pm 0.005$  K. Also, we placed inside the equilibrium cell a magnetic bar that allows the stirring of the sample with the aid of a Thermolyne Cimarec 2 heating and stirring plate.

The liquid–liquid separation process for each binary system was established after a stirring period of 48 h and a settling time of the two liquid phases of 12 h. It has to be mentioned that, to avoid the formation of emulsions during the saturation of the liquid phases, the stirring process was conducted without generating vortices through the liquid–liquid interface, which seems to promote the formation of both types of emulsions, water in hydrocarbon and hydrocarbon in water.

Using the two sampling ports identified as (c) in Figure 1, once the thermodynamic equilibrium of the system was reached at the pre-established working temperature, we carried out the online sampling and density study. Also, from these two sampling ports, samples from both liquid phases were drawn manually, and they were used for the interfacial tension measurements. Details of the steps followed for obtaining the experimental results reported in this work are given in the following sections.

The saturation pressure of each studied binary system at the different temperatures was determined from the pure components vapor pressure<sup>16</sup> taking into account that the mutual solubility is very low. Hence, the saturation or equilibrium pressure for the system 2-methylpentane + water, which is the most volatile, is 38.8, 58.0, 84.6, 120.4, and 167.8 kPa at 303.15, 313.15, 323.15, 333.15, and 343.15 K, respectively, whereas for the less volatile system formed by 2,3,4-trimethylpentane + water the saturation pressure is 8.8, 14.8, 23.9, 37.3, and 56.6 kPa at 303.15, 313.15, 323.15, 333.15, and 343.15 K, respectively.

**2.2. Density Measurement.** To obtain density values of both saturated liquid phases, an Anton Paar DMA 602 H vibrating tube densimeter was used. As mentioned above, samples from both saturated liquid phases in the equilibrium cell, shown in Figure 1, were transferred online to the densimeter to obtain the corresponding vibrating period of each sample at a given temperature. This process was carried out passing first the lighter (upper) liquid phase using a 1/16" Teflon tubing and vacuum as driving force for the transfer. The tubing was connected directly to one end of the vibrating tube cell of the densimeter, whereas the other end of the vibrating tube cell was connected to a vacuum line. Vacuum used in this step was regulated using a metering valve. For transferring the heavier (lower) liquid phase from the liquid–liquid equilibrium glass cell to the densimeter, a similar Teflon tubing was used, although for this case gravity was used as driving force for the transfer of the corresponding sample. The size of the samples used for the measurements of density was less than 1 cm<sup>3</sup>, enough to fill the "U" tube of the densimeter, whereas a 5 cm<sup>3</sup> total volume of both phases was stored in a vial, which in turn served as sample for the interfacial tension measurements. The lines connecting the liquid–liquid equilibrium cell and the densimeter were very short. Considering that temperature should be constant through the experiment, the lines used for transferring the



**Figure 3.** Schematic of the cuvette holder, the thermal bath, and the formation of a pendant drop. (a) Hydrocarbon-saturated water-rich liquid phase. (b) Water-saturated hydrocarbon-rich liquid phase.

**Table 1.** Experimental Density Values, Together with the Corresponding Experimental Uncertainty, of Water-Saturated Hydrocarbon-Rich Liquid Phases

hydrocarbon	$T$ [K]				
	$\rho$ [kg m <sup>-3</sup> ]				
	303.15	313.15	323.15	333.15	343.15
2-methylpentane	643.413 ± 0.005	634.024 ± 0.005	624.329 ± 0.005		
3-methylpentane	654.695 ± 0.005	646.069 ± 0.005	635.664 ± 0.005		
2,3-dimethylpentane	686.409 ± 0.005	677.540 ± 0.005	668.958 ± 0.005	660.03 ± 0.01	652.10 ± 0.05
2,2,4-trimethylpentane	710.948 ± 0.005	702.487 ± 0.005	696.745 ± 0.005	686.41 ± 0.01	679.14 ± 0.05
2,3,4-trimethylpentane	683.933 ± 0.005	675.167 ± 0.005	666.858 ± 0.005	659.48 ± 0.01	650.57 ± 0.05
hexane	650.113 ± 0.005	640.562 ± 0.005	631.237 ± 0.005		
heptane	675.284 ± 0.005	666.333 ± 0.005	657.738 ± 0.005	648.94 ± 0.01	640.96 ± 0.05
octane	694.318 ± 0.005	685.842 ± 0.005	677.748 ± 0.005	669.18 ± 0.01	662.09 ± 0.05

samples for both liquid phases were insulated, for which a coat of a buna polymer was used.

Both the liquid–liquid equilibrium cells and the densimeter were thermostatted using the same Julabo F70 thermal circulating bath; the temperature stability for the experimental determination of density was  $\pm 0.003$  K. A schematic diagram of the experimental device used in this work is shown in Figure 2. As can be seen in Figure 2, temperature was measured in both the liquid–liquid equilibrium cell and the “U” tube of the densimeter to know precisely and accurately the temperature at these two points of the experimental arrangement with the F-250 Automatic Systems Laboratory digital thermometer.

Density values were derived using the average period of vibration, which was in turn obtained from at least 20 stable measurements measured for each sample of the conjugated phases. The experimental method was reported in previous works from our laboratory.<sup>7,15,17–19</sup> In this work, we used for the calibration of the densimeter accurate density values for five different pure substances: nitrogen,<sup>20</sup> hexane,<sup>21</sup> heptane,<sup>21</sup> octane,<sup>21</sup> and water.<sup>22</sup>

As usual in density determinations using the vibrating tube technique, the working equation for the calibration process at a given temperature is:

$$\rho = a + b\tau^2 \quad (1)$$

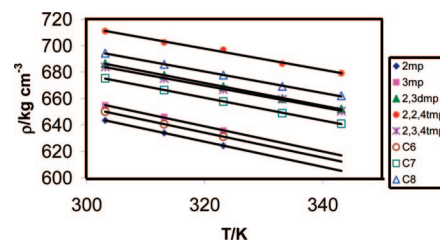
In eq 1,  $\rho$  is the density of the system under study and  $a$  and  $b$  are the calibration constants obtained from correlating known values of density for five reference substances to the square of the corresponding vibrating period  $\tau$ . The linearity obtained with

the above relationship allowed us to reproduce the experimental density values within an uncertainty of  $\pm 0.005$  kg m<sup>-3</sup> at the temperatures of 303.15, 313.15, and 323.15 K,  $\pm 0.01$  kg m<sup>-3</sup> at 333.15 K, and  $\pm 0.05$  kg m<sup>-3</sup> at 343.15 K.

Special care was taken for cleaning of the transfer lines of samples to the densimeter; hence, after each measurement they were evacuated using the normal vacuum service in the laboratory and then nitrogen gas was flown through the tubing until the repeatability of the measured vibration period of nitrogen was kept constant within  $\pm 10^{-5}$ . This process lead to the uncertainty values given above.

Taking advantage of the possibility of using the same circulating thermal bath for controlling the temperature of several equilibrium cells, we used a tandem of eight cells with the different water + hydrocarbon systems under study.

**2.3. Interfacial Tension Measurement.** Interfacial tension values for the binary (water + hydrocarbon) systems included



**Figure 4.** Experimental results of density, as a function of temperature, for water-saturated hydrocarbon-rich liquid phases. Lines indicate tendencies.



**Table 2. Experimental Density Values, Together with the Experimental Uncertainty, of the Hydrocarbon-Saturated Water-Rich Liquid Phases**

hydrocarbon <sup>a</sup> saturating the water-rich liquid phase	T [K]				
	$\rho$ [kg m <sup>-3</sup> ]				
	303.15	313.15	323.15	333.15	343.15
2mp	995.559 ± 0.005	992.076 ± 0.005	988.005 ± 0.005	983.14 ± 0.01	
3mp	995.588 ± 0.005	991.865 ± 0.005	988.017 ± 0.005	983.15 ± 0.01	
2,3dmp	995.569 ± 0.005	992.162 ± 0.005	988.013 ± 0.005	983.15 ± 0.01	976.67 ± 0.05
2,2,4tmp	995.552 ± 0.005	992.192 ± 0.005	988.005 ± 0.005	983.16 ± 0.01	976.66 ± 0.05
2,3,4tmp	995.520 ± 0.005	992.170 ± 0.005	988.010 ± 0.005	983.16 ± 0.01	976.66 ± 0.05
C <sub>6</sub>	995.508 ± 0.005	992.202 ± 0.005	988.017 ± 0.005	983.15 ± 0.01	
C <sub>7</sub>	995.513 ± 0.005	992.209 ± 0.005	988.018 ± 0.005	983.16 ± 0.01	976.64 ± 0.05
C <sub>8</sub>	995.509 ± 0.005	992.197 ± 0.005	988.001 ± 0.005	983.15 ± 0.01	976.64 ± 0.05

<sup>a</sup> 2mp = 2-methylpentane; 3mp = 3-methylpentane; 2,3dmp = 2,3-dimethylpentane; 2,2,4tmp = 2,2,4-trimethylpentane; 2,3,4tmp = 2,3,4-trimethylpentane; C<sub>6</sub> = hexane; C<sub>7</sub> = heptane; C<sub>8</sub> = octane.

**Table 3. Comparison of the Experimental Interfacial Tension Values,  $\sigma$ , from This Work, Together with Their Experimental Uncertainty, and Those from Literature, for Binary Water + Linear Hydrocarbon Systems**

hydrocarbon <sup>a</sup>	T [K]			
	$\sigma$ [mN m <sup>-1</sup> ]			
	303.15	313.15	323.15	333.15
C <sub>6</sub> (this work)	49.96 ± 0.05	48.92 ± 0.07	48.13 ± 0.08	
C <sub>6</sub> <sup>28</sup>	49.96	48.92	48.13	
C <sub>6</sub> <sup>29</sup>			48.04	
C <sub>7</sub> (this work)	50.30 ± 0.05	49.38 ± 0.07	48.55 ± 0.10	
C <sub>7</sub> <sup>27</sup>	50.30	49.38	48.55	
C <sub>8</sub> (this work)	50.74 ± 0.05	49.84 ± 0.07	48.95 ± 0.10	48.32 ± 0.10
C <sub>8</sub> <sup>28</sup>	50.74	49.84	48.95	48.32
C <sub>8</sub> <sup>29</sup>			48.33	

<sup>a</sup> C<sub>6</sub> = hexane; C<sub>7</sub> = heptane; C<sub>8</sub> = octane.

in this work were obtained with a First Ten Angstrom series 200 (FTA 200) commercial contact angle system. The technique used was that of the pendant drop. Details on the use of this technique for obtaining surface tension values were reported in previous works from our laboratory.<sup>7,15,23</sup> The special software of the device uses a version by Andreas et al.<sup>24</sup> of the Laplace–Young equation for surfaces to analyze the drop shape coordinates. The relationship between interfacial tension and other experimental parameters is given by eq 2:

$$\sigma = \frac{g\Delta\rho D^2}{H} \quad (2)$$

In eq 2,  $\sigma$  is the interfacial tension of a given water + hydrocarbon system,  $\Delta\rho$  is the difference in density of the two saturated liquid phases,  $D$  is the maximum horizontal diameter of the pendant drop, and  $1/H$  is a geometric factor of the pendant drop that is determined as part of the analysis of the shape and size of the pendant drop using the digitalized images taken by the apparatus. The meaning of this factor has been described by Andreas et al.<sup>24</sup> and Misak.<sup>25</sup>

The use of the commercial tensiometer was not straightforward; some additions and modifications had to be done to the experimental device to be able to measure the experimental interfacial tension results reported here.<sup>15</sup> Some characteristics of these additions are given below.

The cell used to contain the lighter phase was a quartz rectangular prism cuvette, similar to those used to carry out infrared spectrometric studies. The syringe used to form the drop was that supplied with the commercial apparatus. The flow used with the motorized drop maker and the syringe was 3  $\mu\text{L s}^{-1}$ , with which it took about 3 min to form a drop, which corresponds to the equilibration time to ensure that only gravitational forces were acting during the formation of the drop,

together with the interfacial tension of the system under study. Both the cell and the syringe were adapted to a thermal bath designed and constructed in this work to have good thermal equilibrium of the pendant drop system. The arrangement is shown schematically in Figure 3.

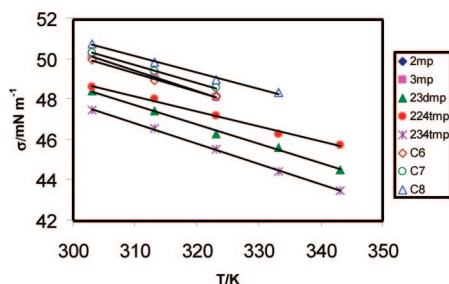
For the case of the determination of the interfacial tension using the pendant drop technique, the challenge was to form a well-defined drop with an interface separating the two liquid phases.<sup>15</sup> For this, the pendant drop was formed with the heavier liquid phase (water-rich liquid phase) inside the lighter liquid phase (hydrocarbon-rich liquid phase); this is also illustrated in Figure 3. In this figure, a compact thermal bath (a 12-cm-sided cube) fabricated in stainless steel is shown. It has two windows. The vertical window goes from the top up to the center of the bath and connects to the horizontal window in a way that these two internal channels are connected forming an inverted “T”. The horizontal window allows the visualization of the cuvette with the hydrocarbon-rich liquid-phase sample and the needle used for the formation of the pendant drop, as illustrated in Figure 3. The Julabo F 70 thermal bath allows a control in temperature of  $\pm 0.01$  K during the experiments. Also in Figure 3, the stainless steel sample holder is shown. This was used to support the quartz cuvette in which the hydrocarbon-rich liquid phase is charged, within which the pendant drop of the water-rich liquid phase is formed. This sample holder is introduced through the vertical window of the thermal bath. To measure the temperature, the thermowell of the thermal bath is used, in which the platinum resistance temperature probe is positioned. A digital thermometer from Systemtechnik, model AB, with a precision of  $\pm 0.001$  K was used. The readings from this thermometer were compared with those from the F-250 Automatic Systems Laboratory digital thermometer. The accuracy for the temperature measurements with the Systemtechnik thermometer, through narrow range comparisons with the reference thermometer, was  $\pm 0.02$  K.

Once the sample and cuvette were introduced into the thermal bath, this was positioned in front of the video system mounted on an optical platform of the FTA 200 tensiometer to allow the use of the computer-controlled dosing system that already holds the syringe with the water-rich liquid-phase sample. The experimental arrangement made possible to use the automated formation of the pendant drops once the working temperature of the system was constant. After thermal equilibrium was achieved, the pendant drop was formed and the final value for the interfacial tension reported by the analysis of the captured images and calculations that the tensiometer carried out was considered the correct interfacial tension value. This procedure was repeated for each binary system to establish the repeatability of the method. In fact, the reported interfacial tension results of this work correspond to an average value obtained with at

**Table 4. Experimental Interfacial Tension Values,  $\sigma$ , Together with the Experimental Uncertainty, for Binary Water + Branched Alkane Systems, at Several Different Temperatures**

hydrocarbon <sup>a</sup>	$T$ [K]				
	$\sigma$ [mN m <sup>-1</sup> ]				
	303.15	313.15	323.15	333.15	343.15
2mp	50.28 ± 0.05	49.11 ± 0.07	48.17 ± 0.08		
3mp	50.10 ± 0.05	49.09 ± 0.07	48.10 ± 0.10		
2,3dmp	48.40 ± 0.10	47.40 ± 0.06	46.55 ± 0.08	45.60 ± 0.10	44.50 ± 0.10
2,2,4tmp	48.62 ± 0.06	48.00 ± 0.10	47.16 ± 0.04	46.28 ± 0.07	45.73 ± 0.08
2,3,4tmp	47.45 ± 0.08	46.53 ± 0.05	45.50 ± 0.10	44.40 ± 0.10	43.46 ± 0.07

<sup>a</sup> 2mp = 2-methylpentane; 3mp = 3-methylpentane; 2,3dmp = 2,3-dimethylpentane; 2,2,4tmp = 2,2,4-trimethylpentane; 2,3,4tmp = 2,3,4-trimethylpentane.

**Figure 5.** Experimental results of the interfacial tension of water + branched C<sub>6</sub>–C<sub>8</sub> hydrocarbons, as a function of temperature. Lines represent linear regressions of the experimental results.**Table 5. Results of the Linear Regression Applied to the Experimental Interfacial Tension Results as a Function of Temperature:  $\sigma/\text{mN m}^{-1} = b + a(T/\text{K})$** 

hydrocarbon	$a$ [mN m <sup>-1</sup> K <sup>-1</sup> ]	$b$ [mN m <sup>-1</sup> ]	$r^2$	$\sigma$ [mN m <sup>-1</sup> ]
C <sub>6</sub>	-0.0915	77.6566	0.9938	0.06
C <sub>7</sub>	-0.0875	76.8106	0.9991	0.02
C <sub>8</sub>	-0.0815	75.3917	0.9936	0.08
2mp	-0.1055	82.2240	0.9961	0.09
3mp	-0.1000	80.4117	1.0000	0.01
2,3tmp	-0.0960	77.5124	0.9983	0.07
2,2,4tmp	-0.0750	71.3943	0.9944	0.10
2,3,4tmp	-0.0921	75.0501	0.9460	0.40

**Table 6. Results from the Correlation with Eq 3 of Experimental Interfacial Tension Values of Binary Systems Water + Linear Alkanes, as a Function of Temperature**

$a_1$ [mN m <sup>-1</sup> g mol <sup>-1</sup> ]	221.53
$a_2$ [mN m <sup>-1</sup> ]	0.4243
$a_3$ [mN m <sup>-1</sup> g mol <sup>-1</sup> ]	-158.78
$a_4$ [mN m <sup>-1</sup> ]	-0.5018
maximum absolute deviation [mN m <sup>-1</sup> ]	0.45
maximum relative error [%]	0.85
standard deviation [mN m <sup>-1</sup> ]	0.13

least 50 measurements reported by the calculation procedure implemented internally in the commercial FTA tensiometer, which correspond to 10 values for each of five different fresh drops for a given binary system, at a given constant temperature. For accepting a given experimental value of interfacial tension obtained with a fresh drop formed for a system under study, the dispersion of the 10 values reported by the apparatus should be equal or lesser than the average experimental uncertainty determined by using a complete error analysis, which was established to be  $\pm 0.07$  mN m<sup>-1</sup>.

### 3. Results and Discussion

**3.1. Density.** In this section, experimental values of density for both saturated liquid phases (hydrocarbon-rich and water-rich) are presented. We separated in the following two subsections the description of the corresponding density values.

**Table 7. Comparison of Estimated and Experimental Interfacial Tension Results for Water + Branched Hydrocarbon Systems as a Function of Temperature**

$T$ [K]	$\sigma_{\text{expt}}$ [mN m <sup>-1</sup> ]	$\sigma_{\text{pred}}$ [mN m <sup>-1</sup> ]	$\sigma_{\text{expt}} - \sigma_{\text{pred}}$ [mN m <sup>-1</sup> ]	relative error [%]
2mp IST = 0.9564				
303.15	50.28	47.80	2.48	4.93
313.15	49.11	46.96	2.15	4.39
323.15	48.17	46.07	2.10	4.36
3mp IST = 0.9868				
303.15	50.10	49.32	0.78	1.55
313.15	49.09	48.45	0.64	1.31
323.15	48.10	47.53	0.57	1.18
2,3dmp IST = 0.9803				
303.15	48.40	49.36	-0.96	-1.98
313.15	47.40	48.51	-1.11	-2.34
323.15	46.55	47.62	-1.07	-2.29
333.15	45.60	46.68	-1.08	-2.37
343.15	44.50	45.70	-1.20	-2.70
2,2,4tmp IST = 0.8959				
303.15	48.62	49.72	-1.10	-2.27
313.15	48.00	48.89	-0.89	-1.86
323.15	47.16	48.01	-0.85	-1.81
333.15	46.28	47.09	-0.81	-1.76
343.15	45.73	46.13	-0.40	-0.87
2,3,4tmp IST = 0.9944				
303.15	47.45	50.44	-2.99	-6.29
313.15	45.63	49.59	-3.96	-8.69
323.15	45.50	48.71	-3.21	-7.05
333.15	44.40	47.77	-3.37	-7.59
343.15	43.46	46.79	-3.33	-7.66

<sup>a</sup> 2mp = 2-methylpentane; 3mp = 3-methylpentane; 2,3dmp = 2,3-dimethylpentane; 2,2,4tmp = 2,2,4-trimethylpentane; 2,3,4tmp = 2,3,4-trimethylpentane.

#### 3.1.1. Water-Saturated Hydrocarbon-Rich Liquid Phases.

Samples of the water-saturated hydrocarbon-rich liquid phases correspond to those from the upper liquid phase formed when contacting water and a given hydrocarbon in the described equilibrium cell. In Table 1, experimental density values for systems for which the hydrocarbon-rich liquid phase contained one of the linear hydrocarbons (hexane, heptane, and octane) are also included. These three hydrocarbons, individually in water, were studied by other authors and are used here for comparison between the reported interfacial tension values and those obtained in this work. However, experimental density values for any of the saturated liquid phases for water with the linear hydrocarbons studied here were not found in the open literature.

Experimental density values for the branched hydrocarbon-rich liquid phases obtained in this work are also presented in Table 1. The different hydrocarbons studied individually with water are those included in the first column of Table 1. These

include structural isomers with six, seven, and eight carbon atoms and are the following: 2-methylpentane, 3-methylpentane, 2,3-dimethylpentane, 2,2,4-trimethylpentane, and 2,3,4-trimethylpentane. The density values are reported at 303.15, 313.15, 323.15, 333.15, and 343.15 K.

As can be observed in Table 1, the experimental density values are reported together with their corresponding experimental uncertainties. Overall, density values decrease as temperature increases, independently of the system. Also, it can be observed that the density values for systems of hydrocarbons with the same number of carbon atoms in its structure show that the isomerism gives rise to different packing of the molecules in the liquid phase, hence different density values (e.g., the saturated phase rich in 2-methylpentane presents lower density than that for the linear hydrocarbon and for 3-methylpentane, whereas the saturated phase rich in 3-methylpentane has larger values of density than any of the other two mentioned  $C_6$  isomers). This indicates that 3-methylpentane presents larger packing of its molecules in a given volume. Similar behavior is also observed for the three studied isomers with eight carbon atoms: the lowest density values are for the saturated phase with 2,3,4-trimethylpentane, whereas the saturated phase rich in 2,2,4-trimethylpentane has larger density values than any of the other two studied isomers. For three of the hydrocarbon-rich liquid phases (i.e., 2-methylpentane, 3-methylpentane, and hexane) density values are not included at 333.15 and 343.15 K, because at these temperatures the mentioned systems started to bubble, and hence the repeatability of the measured vibrating periods did not allow us to obtain density values within the experimental uncertainty given above.

The graphical representation of the experimental density results is included in Figure 4. It can be observed that the density values for a given system follow a linear behavior with temperature. Density for the hydrocarbon-rich liquid phases where the hydrocarbon is an isomer with six carbon atoms shows the lowest values.

### 3.1.2. Hydrocarbon-Saturated Water-Rich Liquid Phases.

Table 2 includes the experimental density results for the hydrocarbon-saturated water-rich liquid phases as a function of temperature. The values reported in this table include the corresponding experimental uncertainty for each density result. Because of what was mentioned above regarding the behavior of some systems at high temperature, we did not measure the density at 343.15 K for systems where the hydrocarbon contains six carbon atoms in its molecule. It is important to note that the results given in Table 2 show a small variation with temperature for any given system, and the density values of the water-rich phases, at constant temperature, are almost the same independently of the hydrocarbon isomer. This behavior finds its explanation on the very limited solubility of the different hydrocarbons in water. For example, at 298.15 K and 101.325 kPa the solubility is  $1.97 \times 10^{-6}$  for hexane;  $4.02 \times 10^{-7}$  for heptane;  $7.35 \times 10^{-8}$  for octane;  $2.993 \times 10^{-6}$  for 2-methylpentane;  $2.67 \times 10^{-6}$  for 3-methylpentane;  $9.48 \times 10^{-7}$  for 2,3-dimethylpentane;  $3.86 \times 10^{-7}$  for 2,2,4-trimethylpentane; and  $2.09 \times 10^{-7}$  for 2,3,4-trimethylpentane, where the solubility is expressed in mole fraction.<sup>26,27</sup>

**3.2. Interfacial Tension.** Experimental results for the eight binary systems studied are included in the following section together with a discussion about the relationship between interfacial tension and literature results for the solubility of the studied hydrocarbons in water. The interfacial tension for systems composed of water + linear alkane was correlated with a four-parameter equation, and values obtained from the

correlation were used to obtain estimated values for the interfacial tension of water + branched alkane systems. These results are given in section 3.2.2.

**3.2.1. Experimental Results.** We selected to test the experimental method with three different water + hydrocarbon binary systems for which there have been reported interfacial tension values as a function of temperature. Table 3 shows the comparison for the water + hydrocarbon binary systems, where the hydrocarbons are hexane ( $C_6$ ), heptane ( $C_7$ ), and octane ( $C_8$ ). It can be observed that there exists excellent agreement between the interfacial tension values obtained in this work and those from Zeppieri et al.<sup>28</sup> in the range 303.15–333.15 K. For the systems with hexane and octane, Cai et al.<sup>29</sup> reported values of the interfacial tension at 323.15 K; comparison of their values with those obtained in this work gave the differences  $-0.09$  and  $-0.62$  mN  $m^{-1}$ , respectively. These differences can be explained by the fact that the values reported by Cai et al.<sup>29</sup> were obtained at high pressure (3690 and 4040 kPa for hexane and octane, respectively), whereas those from Zeppieri et al.<sup>28</sup> and from this work were obtained at saturation pressure, whose range of values was illustrated in section 2.1. This comparison shows that both experimental devices and methods developed in this work are adequate to determine experimentally the density and the interfacial tension of partially miscible systems in a relatively large temperature range.

Experimental results of the interfacial tension for water + branched hydrocarbon binary systems are included in Table 4 together with their corresponding uncertainty obtained by applying an error analysis to the process of measurement. The experimental uncertainty found in this work has an average value of  $\pm 0.07$  mN  $m^{-1}$ , which agrees with the value reported by Drelich et al.<sup>30</sup> ( $\pm 0.10$  mN  $m^{-1}$ ) also for the pendant drop method.

It is observed from Table 4 that for a given system the interfacial tension decreases as temperature increases. An average decrease of  $0.10$  mN  $m^{-1}$   $K^{-1}$  is observed along the temperature interval of this work for all the studied binary systems. This behavior is observed in Figure 5 where the graphical representation of the interfacial tension values is presented as a function of temperature for all the binary systems included in this work. From Figure 5, it can be observed that the lowest values of interfacial tension correspond to the system containing 2,3,4-trimethylpentane as the hydrocarbon isomer with eight carbon atoms in its molecule, whereas the highest values are those for the system with 2-methylpentane, in the temperature range studied.

Several interesting features may be observed when considering the interfacial tension values for the systems with a given number of carbon atoms in the molecule of the hydrocarbon. In the case of the three systems with isomers containing six carbon atoms, the systems with branched isomers show interfacial tension values higher than those corresponding to the system with linear hexane. For the systems where the hydrocarbons contain seven carbon atoms in its molecule, the interfacial tension values for the systems containing 2,3-dimethylpentane were lower than those for the system with heptane in about  $2$  mN  $m^{-1}$  along the temperature interval for which these values were obtained. For systems with  $C_8$  isomers, the two branched isomers present values of interfacial tension that are lower than those corresponding to the system with linear octane. The values corresponding to the system with 2,2,4-trimethylpentane are higher than those obtained for the systems with 2,3,4-trimethylpentane; these differences are  $1.17$  mN  $m^{-1}$  at 303.15 K and  $2.27$  mN  $m^{-1}$  at 343.15 K.



The different behavior of the interfacial tension values shown by the systems included in this study can be considered as macroscopic evidence of the effect of the structural isomerism of the hydrocarbons and they should also prove useful to avoid the development of models that estimate thermophysical properties as a function of only the number of carbon atoms in the hydrocarbon. Some models have considered such differences through the use of specific parameters for each isomer.<sup>10</sup> Also, we observe from a limited amount of data that the interfacial tension values are directly related to the solubility of the hydrocarbon in water. For example, solubility data included in section 3.1.2 shows that hexane is more soluble in water than its isomers 2-methylpentane and 3-methylpentane, and hence the interfacial tension of the system water + hexane is lower than that for water + 2-methylpentane and water + 3-methylpentane. Heptane is less soluble in water than its isomer 2,3-dimethylpentane, and hence its interfacial tension is higher than that for the isomer. Equally, the solubility of octane in water is smaller than that of its two isomers 2,2,4-trimethylpentane and 2,3,4-trimethylpentane, and therefore its interfacial tension is higher than that for its two isomers in water. For the normal alkanes, their solubility in water changes as hexane > heptane > octane and their interfacial tension changes as hexane < heptane < octane, which clearly follows the discussed tendency.

**3.2.2. Correlation and Prediction.** The experimental results of interfacial tension were correlated with a linear regression for each binary system, as a function of temperature. Table 5 includes the parameters regressed using the least-squares method, together with the correlation coefficient and the standard deviation. Figure 5 shows a comparison between experimental and calculated interfacial tension results for the different studied systems.

To develop a prediction scheme for the interfacial tension of water + branched hydrocarbon systems, we performed the correlation of interfacial tension experimental results for binary systems of the type water + linear alkane. Zeppieri et al.<sup>28</sup> correlated their experimental interfacial tension results for each of the seven different water + linear alkane systems in the range 283.2–333.2 K with linear functions and also correlated all their experimental points with a 12 adjustable parameter equation that included a temperature functionality. We used in this work a four-parameter equation reported in a previous work by Romero-Martínez and Trejo<sup>9</sup> to correlate our interfacial tension results for the three studied systems water + linear alkane together with all the experimental results of Zeppieri et al.<sup>28</sup> as a function of temperature. The four adjustable parameter equation used to represent the experimental interfacial tension values is:

$$\sigma = (a_1 + a_2M)\tau^{1.26} + (a_3 + a_4M)\tau^{1.76} \quad (3)$$

where  $\sigma$  is the interfacial tension,  $a_1$ – $a_4$  are adjustable parameters,  $M$  is molar mass of each alkane, and  $\tau$  is a reversed reduced temperature scale ( $\tau = 1 - T/T_c$ ), where  $T_c$  is the critical liquid–vapor temperature of water (647.36 K).

The correlation was carried out using a least-squares minimization technique, and the results are included in Table 6, together with the standard deviation of the fit.

We applied in this work the prediction scheme reported by Romero-Martínez et al.<sup>10</sup> which makes use of an isomerism parameter to predict the surface tension behavior of structural isomers from data of the corresponding linear homologues compounds. Thus, we derived interfacial tension values for the water + branched hydrocarbon systems from the following equation:

$$\sigma_{\text{iso}}(T) = \sigma_{\text{nor}}(T) \cdot IST \quad (4)$$

where  $\sigma_{\text{iso}}$  corresponds to the predicted interfacial tension for a binary system water + isomer of a hydrocarbon at a given temperature,  $\sigma_{\text{nor}}$  is the interfacial tension value of the water + normal linear hydrocarbon at a given temperature, and  $IST$  is the isomerism parameter.

The correlation work carried out with eq 3 allows us to obtain interfacial tension values for a given water + linear hydrocarbon at a given temperature, and these values are used to estimate the corresponding interfacial tension for a given water + isomer of hydrocarbon system. We used this method to estimate interfacial tension values to compare with those obtained experimentally in this work for binary systems formed by water + branched hydrocarbon (i.e., 2-methylpentane, 3-methylpentane, 2,2-dimethylpentane, 2,2,4-trimethylpentane, and 2,3,4-trimethylpentane). Table 7 includes a comparison between estimated and experimental interfacial tension results for the five studied binary systems composed of water + branched hydrocarbon as a function of temperature. The table also includes the isomerism parameter<sup>10</sup> used in the calculations with eq 4. The comparison shows that the estimation scheme used here to extend the application of the isomerism parameter to obtain interfacial tension values for systems formed by water + branched hydrocarbon works well since it gives not only qualitative results but also quantitative agreement for several systems.

## 4. Conclusions

We present an experimental device suitable for achieving the liquid–liquid equilibrium of systems with a very limited mutual miscibility, which allows online sampling of both liquid phases. We report in this work high precision experimental values for the density of both saturated liquid phases (hydrocarbon-saturated water-rich and water-saturated hydrocarbon-rich) for binary systems formed by water + a structural isomer of hydrocarbons with six, seven, and eight carbon atoms in the range 303.15–343.15 K and at saturation pressure. We also report experimental interfacial tension values of high precision and accuracy for the same system as above in the range 303.15–343.15 K at saturation pressure. The temperature has a clear effect on the rate of change of the two properties reported in this work.

It has been shown that there is a clear relationship between interfacial tension of water + hydrocarbon systems and the solubility of hydrocarbons in water.

Experimental interfacial tension results for water + linear alkane were correlated with a four-parameter equation, and these values were used in a prediction scheme to obtain values of the interfacial tension for water + branched alkane systems, using an isomerism parameter, and the results compare well with the corresponding experimental results.

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## Nomenclature

$a, b$  = calibration constants for density measurements, at constant temperature

$D$  = maximum horizontal diameter of a pendant drop  
 $H$  = geometric factor of a pendant drop; it takes into account the shape and size of the drop  
 $T$  = temperature

#### Greek Symbols

$\rho$  = density  
 $\sigma$  = interfacial tension  
 $\tau$  = period of vibration

#### Literature Cited

- (1) Freitas, A. A.; Quina, F. H.; Carroll, F. A. *J. Phys. Chem. B* **1997**, *101*, 7488–7493.
- (2) Bahramian, A.; Danesh, A. *Fluid Phase Equilib.* **2004**, *221*, 197–205.
- (3) Nielsen, R. B.; Rogers, J.; Bullin, J. A.; DUEwall, K. J. *Hydrocarbon Process.* **1997**, 49–59.
- (4) Hoyer, W.; Kaban, I.; Merkwitz, M. *J. Optoelectron. Adv. Mater.* **2003**, *5*, 1069–1073.
- (5) Romero-Martínez, A. Ph.D. Thesis, Universidad Nacional Autónoma de México, 2004.
- (6) Mondragón-Garduño, M.; Romero-Martínez, A.; Trejo, A. *Fluid Phase Equilib.* **1991**, *64*, 291–303.
- (7) Águila-Hernández, J.; Trejo, A.; García-Flores, B. E. *Colloids Surf., A* **2007**, *308*, 33–46.
- (8) Águila-Hernández, J.; Hernández, I.; Trejo, A. *Int. J. Thermophys.* **1995**, *16*, 45–52.
- (9) Romero-Martínez, A.; Trejo, A. *Int. J. Thermophys.* **1998**, *19*, 1605–1614.
- (10) Romero-Martínez, A.; Trejo, A.; Murrieta-Guevara, F. *Fluid Phase Equilib.* **2000**, *171*, 1–10.
- (11) Ramírez-Verduzco, L. F.; Romero-Martínez, A.; Trejo, A. *Fluid Phase Equilib.* **2006**, *246*, 119–130.
- (12) García-Flores, B. E.; Galicia-Aguilar, G.; Eustaquio-Rincón, R.; Trejo, A. *Fluid Phase Equilib.* **2001**, *185*, 275–293.
- (13) Eliosa-Jiménez, G.; Trejo, A. *Rev. IMIQ*, **1997**, 3–4, 13–18.
- (14) García-Flores, B. E.; Gramajo de Doz, M.; Trejo, A. *Fluid Phase Equilib.* **2005**, *230*, 121–130.
- (15) García-Flores, B. E.; Trejo, A.; Águila-Hernández, J. *Fluid Phase Equilib.* **2007**, *255*, 147–159.
- (16) Dreisbach, R. R. *Physical Properties of Chemical Compounds*; Advances in Chemistry Series 22; American Chemical Society: Washington, DC, 1959.
- (17) Murrieta-Guevara, F.; Trejo, A. *J. Chem. Eng. Data* **1984**, *20*, 204–206.
- (18) Águila-Hernández, J.; Gómez-Quintana, R.; Murrieta-Guevara, F.; Romero-Martínez, A.; Trejo, A. *J. Chem. Eng. Data* **2001**, *46*, 861–867.
- (19) Rebolledo-Libreros, M. E.; Trejo, A. *J. Chem. Eng. Data* **2006**, *51*, 702–707.
- (20) Kaye, G. W. C.; Laby, T. H. *Tables of Physical and Chemical Constants*, 15th ed.; Longman: London, 1993.
- (21) Orwoll, R. A.; Flory, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 6814–6822.
- (22) Kell, G. S. *J. Chem. Eng. Data* **1975**, *20*, 97–105.
- (23) Águila-Hernández, J.; Trejo, A.; Gracia-Fadrique, J. *Fluid Phase Equilib.* **2001**, *185*, 165–175.
- (24) Andreas, J. M.; Hauser, E. A.; Tucker, W. B. *J. Phys. Chem.* **1938**, *42*, 1001–1019.
- (25) Misak, M. D. *J. Colloid Interface Sci.* **1968**, *27*, 141–142.
- (26) Reza, J.; Trejo, A.; Vera-Avila, L. E. *Int. J. Environ. Anal. Chem.* **1999**, *73*, 295–281.
- (27) Huibers, P. D. T.; Katritzky, A. R. *J. Chem. Inf. Comput. Sci.* **1998**, *38*, 283–292.
- (28) Zeppieri, S.; Rodríguez, J.; López de Ramos, A. L. *J. Chem. Eng. Data* **2001**, *46*, 1086–1088.
- (29) Cai, B.-Y.; Yang, J.-T.; Guo, T.-M. *J. Chem. Eng. Data* **1996**, *41*, 493–496.
- (30) Drellich, J.; Fang, Ch.; White, C. L. Measurement of interfacial tension in fluid-fluid systems. In *Encyclopedia of Surface and Colloid Science*; Hubbard, A. T., Ed.; Marcel Dekker: New York, 2002.

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