Microfluidic Approach for Rapid Interfacial Tension Measurement

J. H. Xu,* S. W. Li, W. J. Lan, and G. S. Luo*

The State Key Laboratory of Chemical Engineering, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

Received May 18, 2008. Revised Manuscript Received July 2, 2008

A novel microfluidic approach to measure interfacial tension of immiscible fluids rapidly is reported. This method rests upon quantitative force balance analysis of drop formation dynamics in a coaxial microfluidic device. The values of interfacial tension for several two liquids without/with surfactants are measured. These measurements compare well with those measured by the commercial interfacial tensiometry. The viscosity of water phase fluid can also be accurately measured in the same microfluidic device. Several model systems with interfacial tension from 1.0 to 10.0 mN/m and water phase viscosity from 1.0 to 10.0 mPa*s are tested in this work.

I. Introduction

Interfacial tension (IFT, ) is an important physical property of two immiscible liquids, since it controls their performance in many scientific and industrial applications, including foods, pharmaceuticals, cosmetics, paints, analysis, oil recovery, multiphase reaction, extraction, etc. Consequently, rapid and accurate measurements of are both practically and scientifically important.

The interfacial tension values can be measured by different methods that have been reviewed in detail by several authors. The classical methods usually involve the determination of the shape of drops/bubbles or the profile of menisci under a given force equilibrium, such as sessile drop and pendant-drop methods. In these methods, the interfacial tension is determined by the distortion of drop shape by interfacial tension and gravity, and measurement of the geometry of a drop allows the determination of interfacial tension. Measurements of the capillary and hydrostatic pressures of drops and bubbles forced out of a capillary can also yield interfacial tension. Furthermore, the interfacial tension can be measured directly by a force sensor using the microbalance method. Commercial systems use a plate, ring, sphere, cone, or cylinder that is made of platinum—iridium alloy or platinum. The plates or rings have standard dimensions, and thus no calibration is required. Extremely low interfacial tensions can be measured by the spinning drop (and spinning rod) method, from the balance of centrifugal and interfacial forces in a rapidly rotating field. By using this method, quite low values down to \(10^{-6}\) mN/m can be measured.

Besides the above-mentioned conventional techniques, there is growing interest in interfacial tension measurement of small samples. The measurement of interfacial tension on very small drops/bubbles and in finely dispersed systems is called microtensiometry. Two methods currently known for microtensiometry can be measured by the spinning drop (and spinning rod) method, from the balance of centrifugal and interfacial forces in a rapidly rotating field. By using this method, quite low values down to \(10^{-6}\) mN/m can be measured.

Recently, a novel microfluidic approach for rapid interfacial tension measurement by using the droplet deformation method was developed by Hudson and co-workers. In this method, drop deformation occurs in an extensional gradient flow field generated by a microchannel constriction. By calculating the rate of change of the droplet deformation, interfacial tension can be rapidly gained. These approaches have the advantages of being accurate, requiring small amounts of sample, and good repeatability.

In the past decade, the application of micromachining techniques has grown rapidly in various fields. And new applications are appearing in biotechnology and chemical reactions, such as microanalysis, on-chip separation, and chemical microreaction. Monodisperse droplets in microfluidic devices have been generated via a number of methods, including geometry-dominated breakup, hydrodynamic flow focusing, and cross-flowing rupture in T-junction microchannels, and coflowing rupturing in coaxial microchannels. The generation of a droplet is found to be mainly dominated by the viscous shear force and interfacial force, whereas the buoyancy

* Corresponding authors. E-mail: xujianhong@tsinghua.edu.cn (J.H.X.); gsluo@tsinghua.edu.cn (G.S.L.). Tel.: +86-10-62783870. Fax: +86-10-62783870.

(17) Xu, J. H.; Luo, G. S.; Li, S. W.; Chen, C. G. Lab Chip 2006, 6, 131.
(19) Xu, J. H.; Li, S. W.; Tan, J.; Luo, G. S. Lab Chip 2006, 22, 7943.
phases by using the coaxial geometry. Correlating the scaling law of droplet size with experimental characteristics show the possibility for rapid measurement of viscosity of continuous aqueous phase. Furthermore, we model oil/water systems with or without surfactants and discuss microfluidic devices. There are two typical flow regimes, namely, the dripping and jetting regimes. The droplet formation is affected by the flow rates of the continuous and the dispersed phases, fluid viscosity, and interfacial tension. The theoretical analysis of the droplet formation mechanism in a coflowing environment can also be found in previous work.\(^{21-25}\) In the dripping regime, the dynamics of breakup is dominated by the force balance between the viscous force and the interfacial tension force.\(^{21,23,25}\) So the force balance equation can be expressed as

\[
F_D = F_a
\]

where \(F_D\) means the viscous drag force on the forming droplet caused by continuous phase flow and \(F_a\) means the interfacial tension force between the oil and aqueous phases.

II.C. Viscous Drag Force. According to previous work, the values of viscous force can be approximately represented by the following equation at low values of Reynolds number \(Re\):\(^{15,17,21,23}\)

\[
F_D = 3\pi \eta c \left( u_c - u_d \right) d d c \mu c
\]

where \(u_c - u_d\) is the relative local velocity of the continuous phase flow \((u_c)\) with respect to the velocity of the drop \((u_d)\), \(d c\) means the droplet diameter, and \(\mu c\) is the viscosity of the continuous phase liquid. When we use the average velocity of the continuous and dispersed phase flow \(u_c\) and \(u_d\) to replace the local velocity, eq 2 can be approximately replaced by

\[
F_D = k_D (u_c - u_d) d d c
\]

where \(k_D\) is a constant for the fixed geometry. The values of \(u_c\) and \(u_d\) can be calculated by

\[
\begin{align*}
\bar{u}_d &= \frac{4Q_d}{\pi d_d^2} \\
\bar{u}_c &= \frac{4Q_c}{\pi (D_{in}^2 - d_d^2)}
\end{align*}
\]

where \(Q_d\) and \(Q_c\) are the dispersed and continuous phase flow rate, respectively, and \(D_{in}\) is the inner diameter of the glass capillary tube.

II.D. Interfacial Tension Force. From previous work, the interfacial tension force can be calculated by\(^{15,17,21}\)

\[
F_a = \pi d_b \sigma
\]

d\(\sigma\) is the interfacial tension and \(d_b\) is diameter of the dispersed phase channel. Herein we used the outer and inner diameters of the microneedle as the diameter of dispersed phase channel when the dispersed phase did not wet and wetted the needle, respectively. The interfacial tension force calculated using eq 6 is based on the assumption that the Laplace pressure of the drop is at its maximum value when the diameter of the drop curvature is equal to the needle or the nozzle diameter, whereas in this case, there was a departure of the interface from the rim of the needle during

---

the detachment process. So the interfacial tension force is expected to be greatly reduced, and the use of eq 6 is not accurate. Then, Husny and Cooper-White\(^\text{20}\) modified the interfacial tension force equation based on the equilibrium droplet diameter instead of the dispersed phase channel width. The final magnitude of the interfacial tension force can therefore be described by

\[
F_\sigma = \frac{\pi d_a^2 \sigma}{d_d}
\]

From eqs 1, 3, and 7

\[
k_D(\bar{u}_c - \bar{u}_d)d\mu_c = \frac{\pi d_a^2 \sigma}{d_d}
\]

Then, we can get the model to estimate the droplet diameter as

\[
\frac{d_d^2}{d_a^2} = \frac{\pi \sigma}{k_D(\bar{u}_c - \bar{u}_d)\mu_c} = \frac{k \sigma}{\mu_c(\bar{u}_c - \bar{u}_d)}
\]

where \(k\) is a parameter. The value of \(k\) depends on the wetting conditions at the needle, degree of confinement, surfactant distributions, and Marangoni effects. In this case, surfactant distributions and Marangoni effects are unimportant in the experiments, since the surfactant concentration far exceeds the critical micelle concentration. Moreover, the effects of the wetting conditions and degree of confinement can be avoided by using a fixed microfluidic device. So it is a constant for the fixed geometry, which can be gained by using a standard system known for the values of \(\mu_c\) and \(\sigma\). \(C_{\text{ac}} = \sigma/(\mu_c(\bar{u}_c - \bar{u}_d))\) is the capillary number for the continuous phase fluid. From eq 9, the scaling law of the relative droplet size can be approximated by a power law, \(d_d/d_a \sim C_{\text{ac}}^{-1/2}\), which is consistent with that of the previous work.\(^\text{21}\) Then, the interfacial tension \(\sigma\) can be measured when we know the values of \(k\) and \(\mu_c\). On the other hand, the continuous phase viscosity \(\mu_c\) can be measured when we know the values of \(k\) and \(\sigma\).

### III. Materials and Methods

#### III.A. Materials

Several oil/water systems were used as the models systems to measure the interfacial tension. 1-Butanol, \(n\)-hexane, and \(n\)-octanol was used as the oil phase. Deionized water was used as the water phase. Span 80 used as the oil-soluble surfactant was added into the oil phase. Tween 20 used as the water-soluble surfactant was added into the water phase. The surfactants’ concentrations all kept at 2.0 wt% in this work, which is much higher than the critical micelle concentration. For the measurement of continuous phase viscosity, different concentrations of glycerol (15, 30, 45, and 60 wt%) aqueous solutions were used as the continuous phase fluid.

#### III.B. Methods

The schematic diagram for the experimental setup is shown in Figure 2. In this work, we used the oil phase as the dispersed phase fluid and the water phase as the continuous phase fluid. Two microsyringe pumps and three gastight microsyringes were used to pump the two phases into the microfluidic device, respectively. Droplet formation experiments were carried out with a microscope at the magnification of \(100\times\). A high-speed CCD video camera was connected to the microscope, and the images were recorded with a frequency of 200 images/s with the typical image size of \(1280 \times 1024\) pixels. The diameter of droplets was measured from the microscope images. After changing any of the flow parameter, we allowed at least 30 s of equilibration time. The average droplet size \((d_m)\) and the polydispersity index (CV) were determined by measuring the sizes of at least 50 drops from recorded pictures using homemade images analysis software. CV is defined by the following equation, \(CV = \delta d_m \times 100\%\), where \(\delta\) is the standard deviation, and \(d_m\) is the average droplet diameter.

#### III.C. Accuracy and Precision of Results

To compare our measurements with the classical ones, we used the commercial

![Figure 2. Schematic diagram of the experimental setup.](image)

![Figure 3. Micrographs of the oil–water interface at the intersection channel during droplet formation processes.](image)

<table>
<thead>
<tr>
<th>Table 1. Comparison of Formed Droplet Sizes and Distributions for Different Systems</th>
</tr>
</thead>
<tbody>
<tr>
<td>system no.</td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>4</td>
</tr>
<tr>
<td>5</td>
</tr>
</tbody>
</table>

\(^a\) The values of \(\sigma\) and \(\mu_c\) were measured by the commercial interfacial tensiometry and the spinning digital viscometer, respectively.
interfacial tensiometry (OCAH200, DataPhysics Instruments GmbH) and the spinning digital viscometer (NDJ-5S, Shanghai Jingtian Electronics Instrument Co., Ltd.) to measure the interfacial tension and viscosity of the different systems in our experiments. The results measured by the microfluidic device are reported as the MV ± SD, where MV is the mean value and SD is the standard deviation. The accuracy is defined as the relative deviation of the measured MV from the values measured by the commercial interfacial tensiometry or viscometer. Precision is defined as the SD normalized by the MV.

IV. Results and Discussion

IV.A. Formation of Monodisperse Droplets. Monodisperse droplets were formed when the two-phase flow is in the dripping regime. Figure 3 gives four pictures of the typical droplet formation process in the microchannel device for two different systems, respectively. Table 1 shows the values of physical properties, average droplet size (\(d_{\text{av}}\)), and CV under different experimental conditions. The dispersed and continuous phase flow rates were 5 and 800 \(\mu\)L/min, respectively. In this regime, monodisperse droplets could be successfully formed for the systems without or with surfactants in different phases. And the droplet size was highly uniform, and the CV values were less than 2%. So the droplet formation processes are well repeatable. The droplet size decreased with the increase of the continuous phase flow rate and the continuous viscosity, whereas it increased measured by the microfluidic device are reported as the MV ± SD, where MV is the mean value and SD is the standard deviation. The accuracy is defined as the relative deviation of the measured MV from the values measured by the commercial interfacial tensiometry or viscometer. Precision is defined as the SD normalized by the MV.

Figure 4. Micrographs of the droplet formation process in the jetting regime. The dispersed and continuous phases are 1-butanol and deionized water, respectively, and the dispersed and continuous phase flow rates are 100 and 2000 \(\mu\)L/min, respectively.

Figure 5. Flow patterns with different two-phase flow rates. There are three flow regimes as dripping, jetting, and the transition region when the oil phase and water phase flow rates are in the range of 100–6000 and 5–200 \(\mu\)L/min, respectively. Systems 1, 3, and 6 in Table 1 are used as the working systems here.

Figure 6. Effect of continuous phase flow rate on the relative droplet size.

Figure 7. Determination of the value of \(k\). The slope is equal to the parameter \(k\).

interfacial tensiometry (OCAH200, DataPhysics Instruments GmbH) and the spinning digital viscometer (NDJ-5S, Shanghai Jingtian Electronics Instrument Co., Ltd.) to measure the interfacial tension and viscosity of the different systems in our experiments. The results measured by the microfluidic device are reported as the MV ± SD, where MV is the mean value and SD is the standard deviation. The accuracy is defined as the relative deviation of the measured MV from the values measured by the commercial interfacial tensiometry or viscometer. Precision is defined as the SD normalized by the MV.

IV. Results and Discussion

IV.A. Formation of Monodisperse Droplets. Monodisperse droplets were formed when the two-phase flow is in the dripping regime. Figure 3 gives four pictures of the typical droplet formation process in the microchannel device for two different systems, respectively. Table 1 shows the values of physical properties, average droplet size (\(d_{\text{av}}\)), and CV under different experimental conditions. The dispersed and continuous phase flow rates were 5 and 800 \(\mu\)L/min, respectively. In this regime, monodisperse droplets could be successfully formed for the systems without or with surfactants in different phases. And the droplet size was highly uniform, and the CV values were less than 2%. So the droplet formation processes are well repeatable. The droplet size decreased with the increase of the continuous phase flow rate and the continuous viscosity, whereas it increased measured by the microfluidic device are reported as the MV ± SD, where MV is the mean value and SD is the standard deviation. The accuracy is defined as the relative deviation of the measured MV from the values measured by the commercial interfacial tensiometry or viscometer. Precision is defined as the SD normalized by the MV.

IV. Results and Discussion

IV.A. Formation of Monodisperse Droplets. Monodisperse droplets were formed when the two-phase flow is in the dripping regime. Figure 3 gives four pictures of the typical droplet formation process in the microchannel device for two different systems, respectively. Table 1 shows the values of physical properties, average droplet size (\(d_{\text{av}}\)), and CV under different experimental conditions. The dispersed and continuous phase flow rates were 5 and 800 \(\mu\)L/min, respectively. In this regime, monodisperse droplets could be successfully formed for the systems without or with surfactants in different phases. And the droplet size was highly uniform, and the CV values were less than 2%. So the droplet formation processes are well repeatable. The droplet size decreased with the increase of the continuous phase flow rate and the continuous viscosity, whereas it increased measured by the microfluidic device are reported as the MV ± SD, where MV is the mean value and SD is the standard deviation. The accuracy is defined as the relative deviation of the measured MV from the values measured by the commercial interfacial tensiometry or viscometer. Precision is defined as the SD normalized by the MV.

IV. Results and Discussion

IV.A. Formation of Monodisperse Droplets. Monodisperse droplets were formed when the two-phase flow is in the dripping regime. Figure 3 gives four pictures of the typical droplet formation process in the microchannel device for two different systems, respectively. Table 1 shows the values of physical properties, average droplet size (\(d_{\text{av}}\)), and CV under different experimental conditions. The dispersed and continuous phase flow rates were 5 and 800 \(\mu\)L/min, respectively. In this regime, monodisperse droplets could be successfully formed for the systems without or with surfactants in different phases. And the droplet size was highly uniform, and the CV values were less than 2%. So the droplet formation processes are well repeatable. The droplet size decreased with the increase of the continuous phase flow rate and the continuous viscosity, whereas it increased measured by the microfluidic device are reported as the MV ± SD, where MV is the mean value and SD is the standard deviation. The accuracy is defined as the relative deviation of the measured MV from the values measured by the commercial interfacial tensiometry or viscometer. Precision is defined as the SD normalized by the MV.

IV. Results and Discussion

IV.A. Formation of Monodisperse Droplets. Monodisperse droplets were formed when the two-phase flow is in the dripping regime. Figure 3 gives four pictures of the typical droplet formation process in the microchannel device for two different systems, respectively. Table 1 shows the values of physical properties, average droplet size (\(d_{\text{av}}\)), and CV under different experimental conditions. The dispersed and continuous phase flow rates were 5 and 800 \(\mu\)L/min, respectively. In this regime, monodisperse droplets could be successfully formed for the systems without or with surfactants in different phases. And the droplet size was highly uniform, and the CV values were less than 2%. So the droplet formation processes are well repeatable. The droplet size decreased with the increase of the continuous phase flow rate and the continuous viscosity, whereas it increased measured by the microfluidic device are reported as the MV ± SD, where MV is the mean value and SD is the standard deviation. The accuracy is defined as the relative deviation of the measured MV from the values measured by the commercial interfacial tensiometry or viscometer. Precision is defined as the SD normalized by the MV.

IV. Results and Discussion

IV.A. Formation of Monodisperse Droplets. Monodisperse droplets were formed when the two-phase flow is in the dripping regime. Figure 3 gives four pictures of the typical droplet formation process in the microchannel device for two different systems, respectively. Table 1 shows the values of physical properties, average droplet size (\(d_{\text{av}}\)), and CV under different experimental conditions. The dispersed and continuous phase flow rates were 5 and 800 \(\mu\)L/min, respectively. In this regime, monodisperse droplets could be successfully formed for the systems without or with surfactants in different phases. And the droplet size was highly uniform, and the CV values were less than 2%. So the droplet formation processes are well repeatable. The droplet size decreased with the increase of the continuous phase flow rate and the continuous viscosity, whereas it increased measured by the microfluidic device are reported as the MV ± SD, where MV is the mean value and SD is the standard deviation. The accuracy is defined as the relative deviation of the measured MV from the values measured by the commercial interfacial tensiometry or viscometer. Precision is defined as the SD normalized by the MV.

IV. Results and Discussion

IV.A. Formation of Monodisperse Droplets. Monodisperse droplets were formed when the two-phase flow is in the dripping regime. Figure 3 gives four pictures of the typical droplet formation process in the microchannel device for two different systems, respectively. Table 1 shows the values of physical properties, average droplet size (\(d_{\text{av}}\)), and CV under different experimental conditions. The dispersed and continuous phase flow rates were 5 and 800 \(\mu\)L/min, respectively. In this regime, monodisperse droplets could be successfully formed for the systems without or with surfactants in different phases. And the droplet size was highly uniform, and the CV values were less than 2%. So the droplet formation processes are well repeatable. The droplet size decreased with the increase of the continuous phase flow rate and the continuous viscosity, whereas it increased measured by the microfluidic device are reported as the MV ± SD, where MV is the mean value and SD is the standard deviation. The accuracy is defined as the relative deviation of the measured MV from the values measured by the commercial interfacial tensiometry or viscometer. Precision is defined as the SD normalized by the MV.

IV. Results and Discussion

IV.A. Formation of Monodisperse Droplets. Monodisperse droplets were formed when the two-phase flow is in the dripping regime. Figure 3 gives four pictures of the typical droplet formation process in the microchannel device for two different systems, respectively. Table 1 shows the values of physical properties, average droplet size (\(d_{\text{av}}\)), and CV under different experimental conditions. The dispersed and continuous phase flow rates were 5 and 800 \(\mu\)L/min, respectively. In this regime, monodisperse droplets could be successfully formed for the systems without or with surfactants in different phases. And the droplet size was highly uniform, and the CV values were less than 2%. So the droplet formation processes are well repeatable. The droplet size decreased with the increase of the continuous phase flow rate and the continuous viscosity, whereas it increased measured by the microfluidic device are reported as the MV ± SD, where MV is the mean value and SD is the standard deviation. The accuracy is defined as the relative deviation of the measured MV from the values measured by the commercial interfacial tensiometry or viscometer. Precision is defined as the SD normalized by the MV.

IV. Results and Discussion

IV.A. Formation of Monodisperse Droplets. Monodisperse droplets were formed when the two-phase flow is in the dripping regime. Figure 3 gives four pictures of the typical droplet formation process in the microchannel device for two different systems, respectively. Table 1 shows the values of physical properties, average droplet size (\(d_{\text{av}}\)), and CV under different experimental conditions. The dispersed and continuous phase flow rates were 5 and 800 \(\mu\)L/min, respectively. In this regime, monodisperse droplets could be successfully formed for the systems without or with surfactants in different phases. And the droplet size was highly uniform, and the CV values were less than 2%. So the droplet formation processes are well repeatable. The droplet size decreased with the increase of the continuous phase flow rate and the continuous viscosity, whereas it increased measured by the microfluidic device are reported as the MV ± SD, where MV is the mean value and SD is the standard deviation. The accuracy is defined as the relative deviation of the measured MV from the values measured by the commercial interfacial tensiometry or viscometer. Precision is defined as the SD normalized by the MV.
a linear function of the interfacial tension, which is consistent with eq 9.

When we increased the flow rates, the two-phase flow was changed to the jetting regime, which can be seen in Figure 4. In this regime, the scaling of droplet size is much different to that in the dripping regime, and eq 9 is no longer valid. Furthermore, a satellite droplet with diameter of several micrometers is formed in the jetting regime (Figure 4). The mechanism and scaling of the droplet formation is rather complicated in this regime. So we should conduct the experiments of the measurement of interfacial tension and viscosity in the dripping regime.

IV.B. Two-Phase Flow Regimes. Before the measurement, the determination of the two-phase flow regimes is very important because it will show at which flow rates the droplet formation is in the dripping regime and eq 9 can be used. So we studied the influence of two-phase flow rate on the two-phase flow regimes, as shown in Figure 5. It can be seen that at low dispersed phase flow rate of 5 μL/min, the two-phase flow is in the dripping regime for the continuous phase flow rate from 100 to 3000 μL/min. And eq 9 is valid in this regime. So in the following sections, we demonstrate the measurement of interfacial tension and water phase viscosity for the different systems with the dispersed phase flow rate at the fixed value of 5 μL/min and the continuous phase flow rate in the range of 100−2000 μL/min and discuss the precision and accuracy of measurements.

IV.C. Determination of the Value of k. First, we used a standard system of 1-butanol/deionized water to determine the value of k for the used microfluidic device. The physical properties of the system can be seen in Table 1. Figure 6 shows the effect of continuous phase flow rate on the relative droplet size at the fixed dispersed flow rate of 5 μL/min. Then, \((d/d_n)^2\) was fit to a linear function of \(\sigma/\mu (u_c - u_j)\), to yield k according to eq 9, as shown in Figure 7. The value of \(k = 0.148\) for the used microfluidic device.

IV.D. Measurement of the Interfacial Tension \(\sigma\). The interfacial tensions of four oil/water systems without or with surfactants in different phases were used to test the measurement of interfacial tension in this case. Figure 8 shows the effect of continuous phase flow rate on the relative droplet size at the fixed dispersed flow rate of 5 μL/min. Then, \((d/d_n)^2\) was fit to a linear function of \(k/\mu (u_c - u_j)\), to yield \(\sigma\) according to eq 9, as shown in Figure 9. Table 2 shows the comparison of the values of interfacial tension measured by our coaxial microfluidic device and that by the commercial interfacial tensiometry. In each case, the measured results are in good agreement with those measured by the commercial interfacial tensiometry, and the relative deviation is less than 1%. It can be seen from eq 9 that the accuracy and precision of the measurement mainly depends on the accuracy and precision of the values of droplet size, continuous phase viscosity, and the two-phase velocities. The accuracy of droplet size mainly depends on the pixel resolution. In this case, the typical image size is 1280 × 1024 pixels, and the CV of the droplet size is less than 2%, which can be seen in Table 1. The accuracy and precision of viscosity depends on the measurement accuracy of the commercial spinning digital viscometer, and the relative deviation of the measurement is less than 1%. The accuracy and precision of velocity data depends on the accuracy of the two-phase flow rates by the microsyringe pumps. We have calibrated the flow rate of the pumps before the experiments, and the relative deviation is less than 2%. So the measurements by the present method have accuracy and precision of approximately several percent (1−3%), as shown in Table 2.

IV.E. Measurement of the Water Phase Viscosity. Water phases with four different concentrations of glycerol (15, 30, 45, and 60 wt %) were used to test the measurement of continuous phase viscosity in this case, where 1-butanol was used as the dispersed phase. The interfacial tensions of these systems were measured by the pendant-droplet interfacial tensiometry, as shown in Table 3. Figure 10 shows the effect of continuous phase flow rate on the relative droplet size at the fixed dispersed flow rate of 5 μL/min. Then, \(k\sigma (u_c - u_j)\) was fit to a linear function of \((d/d_n)^2\), to yield \(\mu_c\) according to eq 9, as shown in Figure 11. Table 3 shows the comparison of the values of water phase viscosity measured by our coaxial microfluidic device and that by the commercial viscometer. The results show that the viscosity of continuous phase fluid can also be accurately measured by using the droplet formation method in the microfluidic device, and the relative deviation is less than 2%.

| Table 2. Comparison of the Values of Interfacial Tension \(\sigma\) for the Different Systems |
|---|---|---|
| system no. | water phase | oil phase | \(\sigma\) ref (mN·m\(^{-1}\))\(^{a}\) | \(\sigma\) measured (mN·m\(^{-1}\)) |
| T1 | deionized water | 2.0 wt % Span80/hexane | 2.81 ± 0.02 | 2.80 ± 0.03 |
| T2 | deionized water | 2.0 wt % Span80/hexane | 4.33 ± 0.03 | 4.30 ± 0.04 |
| T3 | deionized water | n-octanol | 8.56 ± 0.03 | 8.60 ± 0.05 |
| T4 | 2.0 wt % Tween20/hexane | n-octanol | 1.78 ± 0.02 | 1.77 ± 0.03 |

\(^{a}\) The values of \(\sigma\) were measured by the commercial pendant-droplet interfacial tensiometry.

| Table 3. Comparison of the Values of Water Phase Viscosity for the Different Systems |
|---|---|---|---|
| system no. | water phase | oil phase | \(\mu_c\) ref (mPa·s)\(^{a}\) | \(\mu_c\) measured (mPa·s) |
| V1 | 15 wt % glycerol/water | 1-butanol | 1.67 ± 0.02 | 1.42 ± 0.01 |
| V2 | 30 wt % glycerol/water | 1-butanol | 1.63 ± 0.02 | 2.17 ± 0.02 |
| V3 | 45 wt % glycerol/water | 1-butanol | 1.61 ± 0.02 | 3.87 ± 0.02 |
| V4 | 60 wt % glycerol/water | 1-butanol | 1.57 ± 0.01 | 8.46 ± 0.03 |

\(^{a}\) The values of \(\sigma\) and \(\mu_c\) were measured by the commercial interfacial tensiometry and the spinning digital viscometer.
V. Conclusions

In this work, we first developed a novel microfluidic approach to measure the liquid–liquid interfacial tension based on the force balance analysis of the forming droplet during the droplet formation process in a coaxial microfluidic device. We described in detail the design of microfluidic device, fundamentals of the measurement, the operation of the microfluidic device, and measurement of interfacial tension for different systems and discuss the precision and accuracy of measurements. We also measured the viscosity of continuous aqueous phase in the same microdevice. Several model systems with interfacial tension from 1.0 to 10.0 mN/m and water phase viscosity from 1.0 to 10.0 mPa·s are tested in this work. The measured results are in good agreement with those measured by the commercial interfacial tensiometry and the spinning digital viscometer. And the measurements by the present method have accuracy and precision of approximately several percent. Our work has verified the feasibility and accuracy for the measurement of interfacial tension and viscosity by using the droplet formation method in microfluidic devices. This microfluidics approach has the advantages of being accurate, requiring small amounts of sample, and good repeatability. Furthermore, the coaxial microfluidic device we used here, in which the effect of the wetting properties of microchannels on droplet formation can be avoided, is more suitable for the measurement of physical properties of two liquids containing surfactants.

Acknowledgment. We gratefully acknowledge the support of the National Natural Science Foundation of China (20525622) and National Basic Research Program of China (2007CB714302) on this work.

LA801526N