

Evidence for the Existence of an Effective Interfacial Tension between Miscible Fluids: Isobutyric Acid–Water and 1-Butanol–Water in a Spinning-Drop Tensiometer

John A. Pojman,^{*,†} Colin Whitmore,[†] Maria Liria Turco Liveri,[‡] Renato Lombardo,^{*,‡} Jolanta Marszalek,[†] Rosie Parker,[†] and Brian Zoltowski[†]

Department of Chemistry and Biochemistry, University of Southern Mississippi, Hattiesburg, Mississippi 39406, and Dipartimento di Chimica Fisica “F. Accascina”, Università degli studi di Palermo, 90128, Palermo, Italy

Received August 2, 2005. In Final Form: January 18, 2006

We report definitive evidence for an effective interfacial tension between two types of miscible fluids using spinning-drop tensiometry (SDT). Isobutyric acid (IBA) and water have an upper critical solution temperature (UCST) of 26.3 °C. We created a drop of the IBA-rich phase in the water-rich phase below the UCST and then increased the temperature above it. Long after the fluids have reached thermal equilibrium, the drop persists. By plotting the inverse of the drop radius cubed (r^{-3}) vs the rotation rate squared (ω^2), we confirmed that an interfacial tension exists and estimated its value. The transition between the miscible fluids remained sharp instead of becoming more diffuse, and the drop volume decreased with time. We observed droplet breakup via the Rayleigh–Tomotika instability above the UCST when the rotation rate was decreased by 80%, again demonstrating the existence of an effective interfacial tension. When pure IBA was injected into water above the UCST, drops formed inside the main drop even as the main drop decreased in volume with time. We also studied 1-butanol in water below the solubility limit. Effective interfacial tension values measured over time were practically constant, while the interface between the two phases remains sharp as the volume of the drop declines. The effective interfacial tension was found to be insensitive to changes in temperature and always larger than the equilibrium interfacial tension. Although these results may not apply to all miscible fluids, they clearly show that an effective interfacial tension can exist and be measured by SDT for some systems.

Introduction

The interfacial tension between immiscible fluids is an equilibrium thermodynamic property that results from the differences in intermolecular interactions between the two different types of molecules. When two miscible fluids are brought in contact, a large concentration (and density) gradient can exist, which relaxes through diffusion as the system approaches the uniform, equilibrium state. Because the molecules are different, there are necessarily differences in intermolecular interactions. In the 19th century, there were reports of phenomena in which an *effective interfacial tension* (EIT) was invoked. (These are discussed by Joseph and Renardy.¹) Korteweg proposed in 1901 that stress caused by a density gradient could act like an interfacial tension.

We report here conclusive evidence for an interfacial tension between miscible fluids through two phenomena observed in a spinning-drop tensiometer. We considered two systems: The first system is partially miscible below a temperature but miscible above it. The second system was partially miscible, but we studied it below the solubility limit. We started with a two-phase system, isobutyric acid (IBA) and water, below its upper critical solution temperature (UCST). We then raised the temperature above the UCST and allowed the system to reach thermal equilibrium. The drop of the IBA-rich solution and the surrounding water-rich solution were miscible, but relaxation to chemical equilibrium required about 1 h. We studied the evolution of this quantity and

the drop volume as a function of time. We observed that, when the rotation rate was decreased rapidly by 80%, IBA drops break up through a Rayleigh–Tomotika instability.

The second system, 1-butanol in water, exhibited a sharp transition between the fluids that persisted even as the drop dissolved. The EIT was greater than the equilibrium values.

Background. For most systems, an infinitely narrow interface, consisting of a discontinuous jump in concentration, was an accurate description. However, for polymer systems and systems near their critical point, an infinitely narrow transition zone does not apply. van der Waals² was the first to propose an alternate definition of an immiscible interface. He assumed that the interface consisted of a continuous region in which there was a transition in concentration from one fluid to the other. Figure 1 depicts such a transition zone, with increasing concentration from right to left. The interface is then also defined by the width, δ , of the transition zone.

A thermodynamically stable interface can only exist between two immiscible fluids. Nonetheless, we use the term “miscible interface” to designate the transition zone between two miscible fluids, which will necessarily relax with time. Stresses at a miscible interface were first explored by Korteweg.³ He demonstrated that in the presence of a compositional gradient, stresses would result that would be analogous to stresses in immiscible fluids. Joseph and Renardy provided a superb review of the topic up to 1992.¹ Joseph has considered other problems.^{4,5} Lowengrub and Truskinovsky gave a thorough derivation of the Korteweg stress.⁶

* To whom correspondence should be addressed. E-mail: john@pojman.com (J.A.P.); r.lombardo@unipa.it (R.L.).

[†] University of Southern Mississippi.

[‡] Università di Palermo.

(1) Joseph, D. D.; Renardy, Y. Y. *Fundamentals of Two-Fluid Dynamics. Part II. Lubricated Transport, Drops and Miscible Fluids*; Springer: New York, 1992.

(2) van der Waals, J. D. *J. Stat. Phys.* **1979**, *20*, 197–244.

(3) Korteweg, D. J. *Arch. Néerlandaises Sci. Exactes Naturelles* **1901**, *6*, 1–24.

(4) Liao, T. Y.; Joseph, D. D. *J. Fluid Mech.* **1997**, *342*, 37–51.

(5) Joseph, D. D.; Huang, A.; Hu, H. *Physica D* **1996**, *97*, 104–125.

(6) Lowengrub, J.; Truskinovsky, L. *Proc. R. Soc. London A* **1997**.

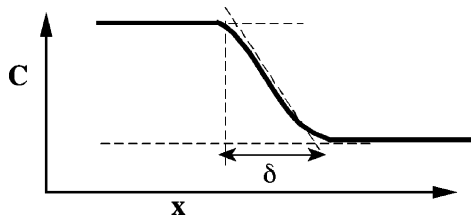


Figure 1. Schematic of a diffuse interface.

Volpert et al. performed two-dimensional simulations of miscible fluids with a Korteweg term and showed that elliptical “drops” became circular and that a stream would start to pinch via a Rayleigh–Tomotika-like instability.⁷ (A Rayleigh–Tomotika instability appears when a stream of fluid breaks into smaller drops because of the interfacial tension.^{8,9}) Bessonov et al. considered a miscible interface in a system in which the square gradient parameter was temperature dependent.¹⁰ They showed that a linear temperature gradient parallel to the interface could cause convection. Bessonov et al. also modeled a miscible interface with variations in the width of the transition zone and with gradients in concentration parallel to the transition zone.¹¹ Chen and Meiburg have performed numerical simulations of miscible displacement that included Korteweg stress.^{12–15}

The Korteweg term for miscible systems far from equilibrium can be compared to Cahn and Hilliard’s treatment of immiscible fluids at equilibrium. Using the Landau–Ginzburg free energy functional, they were able to show that the free energy of a nonuniform immiscible system includes a term proportional to the square of the concentration gradient.¹⁶ This is precisely the same situation Korteweg considered for miscible systems far from equilibrium.

For a system far from equilibrium, the free energy functional can be written as

$$F = \int_{\Omega} f_0(\xi) d\xi + \sigma A \quad (1)$$

where $f_0(\xi)$ is the free energy density, Ω is the total volume, ξ is a spatial coordinate, A is the area of the interface, and

$$\sigma = k \int_{\Omega} |\nabla c|^2 dx \quad (2)$$

is the effective interfacial tension (EIT), while x is the spatial coordinate normal to the transition zone.

This function can be simplified if we assume a linear concentration gradient. The resulting equation for the EIT is

$$\sigma = k \frac{\Delta c^2}{\delta} \quad (3)$$

Here the EIT is written in terms of the Korteweg term, k , henceforth referred to as the square gradient parameter (with units of N), the change in composition Δc , expressed as a mole fraction, and the width of the transition zone, δ .

Zeldovich showed that an interfacial tension should exist between miscible fluids brought into contact and that it should have the form given in eq 3.¹⁷ Davis proposed that when two miscible fluids are placed in contact they will immediately begin to mix diffusively across the concentration front and the composition inhomogeneities can give rise to pressure anisotropies and to a tension between the fluids.¹⁸ Rousar and Nauman, following the work of Rowlinson and Widom,¹⁹ proposed that an interfacial tension can be found without assuming that the system is at equilibrium.²⁰

Joseph and Renardy provide an excellent review of the history of this topic. Joseph and Renardy have impressive pictures of behavior in miscible fluids that appears to follow behavior attributed to interfacial tension.¹ They also present experiments with drops of water rising in glycerin. Joseph and his colleagues also considered many problems with Korteweg stress.^{4,5,21,22}

There have been several reports of phenomena in which the authors invoke an interfacial tension with miscible systems. Garik et al. injected water into a CuSO_4 solution or glycerin into water. They proposed that the pattern formation they observed was not viscous fingering but an interfacial-tension-induced instability.²³ Ma et al. performed molecular dynamics simulations of initially miscible fluids showing that the effective interfacial tension relaxes according to a $1/t^{1/2}$ rule.²⁴ Mungall reported that miscible molten silicates form a meniscus, indicating an interfacial tension.²⁵ He proposed a theoretical model in terms of the gradient stresses. Castellanos and González proposed that the wavelength selection in the electrohydrodynamic instability between miscible fluids of different conductivities can be explained by a transient interfacial tension.²⁶ Petitjeans and Maxworthy estimated the EIT from the wavelength selection of the displacement of water into glycerin in a capillary tube and determined a value of 0.43 mN m^{-1} .²⁷

Measuring the Effective Interfacial Tension. There have been several reports of attempts to measure an interfacial tension between miscible fluids. Smith et al. measured the interfacial tension between miscible silicone oils using the Wilhelmy plate method and found it to be 1 mN m^{-1} when extrapolated to $t = 0$.²⁸ However, this technique is not suited to making measurements of very low interfacial tensions.

Two techniques are useful for measuring very low interfacial tensions. One is spinning-drop tensiometry (SDT), and the other is light scattering.²⁹ In the second case, by the small-angle light scattering from the capillary waves at the interface between two fluids, it is possible to measure interfacial tensions as small as 0.001 mN m^{-1} . Chatenay et al. compared light scattering and SDT for the measurement of small interfacial tensions.³⁰

(17) Zeldovich, Y. B. *Zh. Fiz. Khim. (in Russian)* **1949**, *23*, 931–935.

(18) Davis, H. T. In *Numerical Simulation in Oil Recovery, Volumes in Mathematics and its Applications*; Wheeler, M., Ed.; Springer-Verlag: Berlin, 1988; Vol. 11, pp 105–110.

(19) Rowlinson, J. S.; Widom, B. *Molecular Theory of Capillarity*; Clarendon Press: Oxford, 1982.

(20) Rousar, I.; Nauman, E. B. *Chem. Eng. Comm.* **1994**, *129*, 19–28.

(21) Joseph, D. D. *Eur. J. Mech., B/Fluids* **1990**, *9*, 565–596.

(22) Galdi, G. P.; Joseph, D. D.; Preziosi, L.; Rionero, S. *Eur. J. Mech., B/Fluids* **1991**, *10*, 253–267.

(23) Garik, P.; Hetrick, J.; Orr, B.; Barkey, D.; Ben-Jacob, E. *Phys. Rev. Lett.* **1991**, *66*, 1606–1609.

(24) Ma, W. J.; Keblinski, P.; Maritan, A.; Koplik, J.; Banavar, J. R. *Phys. Rev. Lett.* **1993**, *71*, 3465–3468.

(25) Mungall, J. E. *Phys. Rev. Lett.* **1994**, *73*, 288–291.

(26) Castellanos, A.; González, A. *Phys. Fluids A* **1992**, *4*, 1307–1309.

(27) Petitjeans, P.; Maxworthy, T. *J. Fluid Mech.* **1996**, *326*, 37–56.

(28) Smith, P. G.; Van De Ven, T. G. M.; Mason, S. G. *J. Colloid Interface Sci.* **1981**, *80*, 302–303.

(29) Langevin, D. *Light Scattering by Liquid Surfaces and Complementary Techniques*; Dekker: New York, 1992.

(30) Chatenay, D.; Langevin, D.; Meunier, J. *Dispersion Sci. Technol.* **1982**, *3*, 245–260.

(7) Volpert, V. A.; Pojman, J. A.; Texier-Picard, R. *C. R. R. Mecanique* **2002**, *330*, 353–358.

(8) Tomotika, S. *Proc. R. Soc. (London)* **1935**, *A150*, 322–337.

(9) Tomotika, S. *Proc. R. Soc. (London)* **1936**, *153*, 302–318.

(10) Bessonov, N.; Pojman, J. A.; Volpert, V. J. *Eng. Math.* **2004**, *49*, 321–338.

(11) Bessonov, N.; Volpert, V. A.; Pojman, J. A.; Zoltowski, B. D. *Microgravity Sci. Technol.* **2005**, *XVII*, 8–12.

(12) Chen, C.-Y.; Meiburg, E. *J. Fluid Mech.* **1996**, *326*, 57–90.

(13) Chen, C.-Y.; Wang, L.; Meiburg, E. *Phys. Fluids* **2001**, *13*, 2447–2456.

(14) Meiburg, E.; Chen, C.-Y.; Wang, L.-L. *Trans. Aero. Astro. Soc. R.O.C.* **2001**, *33*, 7.

(15) Chen, C.-Y.; Meiburg, E. *Phys. Fluids* **2003**, *14*, 2052–2058.

(16) Cahn, J. W.; Hilliard, J. E. *J. Chem. Phys.* **1958**, *28*, 258–267.

Fluids with Critical Solution Temperature

IBA and water exhibit a UCST at 26.3 °C, which means that above the UCST the materials are miscible in all proportions but below it they form two phases.^{31–35} By rapidly raising the temperature above the UCST, thermal equilibrium is achieved quickly but chemical equilibrium takes hours. Thus, two miscible fluids are created with a sharp, well-defined transition zone between them.

May and Maher were the first to report the measurement of an interfacial tension between miscible fluids using light scattering.³⁶ They started with the two phases 0.2 K below the UCST and then rapidly raised the system's temperature above its UCST. The interfacial tension was initially 0.0017 mN m⁻¹ and then relaxed over 2 h to 0.0002 mN m⁻¹. Vlad and Maher studied the cyclohexane–methanol system by the same technique and claimed that gravity slowed the expected rate of diffusion.³⁷ Cicuta et al. contended that fluctuations measured by May and Maher and Vlad and Maher were not related to an interfacial tension but rather were instead nonequilibrium fluctuations associated with a diffuse gradient.³⁸ Cicuta et al. reported interfacial tensions for the aniline–cyclohexane system above its UCST using light scattering.³⁸

SDT has also been used to study fluids with critical behavior. Heinrich and Wolf studied the interfacial tension of coexisting phases of methylcyclohexane–polystyrene and cyclohexane–polystyrene within 0.5 K of the UCST and performed temperature-jump experiments.³⁹ They also studied methylcyclohexane–polystyrene in a spinning-drop tensiometer with temperature jumps but below the UCST.⁴⁰

Petitjeans was the first to study miscible fluids with SDT. SDT with miscible systems can be difficult to interpret because of the difficulty in separating interfacial effects from viscous relaxation of the drop. For example, Petitjeans reported an interfacial tension for a water drop in glycerin, but it did not relax with time.⁴¹

Theory of SDT

Vonnegut Method. In 1942, Vonnegut developed the spinning-drop method for measuring interfacial tension.⁴² A capillary is filled with the more dense phase, and a drop of the less dense phase is injected. The capillary is rotated at a high rotation rate (> 6000 rpm). The drop reaches an equilibrium shape, reflecting the balance between the interfacial energy and the rotational energy.

If the drop length is at least four times longer than the drop radius, the interfacial tension can be determined from the drop radius as long as the difference in densities between the two fluids are known, using eq 4.⁴³ To avoid complications from buoyancy, the drop rotation rate must be greater than a critical value.^{44–46}

$$\sigma = \frac{\Delta\rho\omega^2 r^3}{4} \quad (4)$$

Extended Vonnegut Method. Princen⁴⁷ and co-workers prove a numerical solution that permits the calculation of the interfacial tension (IT) in the case of a drop that does not meet the geometrical requirements for the Vonnegut method to be applied. The interfacial tension can be found using eq 5, where *c* is a correction factor to be read from a table based on measurements of the drop's half length and half-height.

$$\sigma = \frac{\Delta\rho\omega^2}{4c} \quad (5)$$

Experimental Section

Chemicals. IBA (Aldrich, 99%) and 1-butanol (Fisher Chemicals, 99.9%) were used without further purification. All solutions were prepared using deionized water.

Interfacial Tension Measurements. All the interfacial tension measurements have been conducted with a Krüss SITE100 spinning-drop tensiometer equipped with a digital camera. Krüss software DSII was used for calibration and to operate the instrument (e.g., setting rotation speed). Experiments were recorded using a digital monochrome camera connected to the PC using DIVX compression. When a drop was long enough to meet the Vonnegut condition, the radius was measured, but when the drop was too short, both radius and length were measured and the extended Vonnegut method was used.

When needed, a brightness/contrast filter was applied. Calibration for image distortion in both horizontal and vertical directions was performed at each temperature.

In the case of the IBA–water system, IBA and water were allowed to equilibrate at room temperature. The capillary was filled with the resulting aqueous phase, and while it was rotating, the temperature was lowered and a drop of the IBA-rich phase was formed. For the studies with pure IBA, a drop of IBA was injected into the capillary.

The SDT was thermostated with a VWR 1166 circulator that flowed oil around the capillary. A temperature probe in the instrument provided the temperature to within 0.1 °C. The oil also served to lubricate the bearings.

For the 1-butanol–water system, a drop (≈10 μL) of pre-thermostated 1-butanol was injected in the thermostated capillary filled with deionized water. The measurements have been conducted in a temperature range between 9 and 60 °C. The density of 1-butanol in this range was taken from the literature.⁴⁸

IBA–Water System Characterization. Density measurements of the IBA-rich phase and the water-rich phase were made with a Paar DMA 4500 densitometer. Equal volumes of water and IBA were stirred and equilibrated at the desired temperature for ~16 h. A sample of the water-rich phase was injected into the densitometer at the same temperature at which the phase had been equilibrated. The density was measured. The temperature of the densitometer was then increased. Ten minutes after the sample came to the desired temperature, the density was measured again. This was repeated for a range of increasing temperatures to approximately 35 °C. Because the temperature was always at or above the initial temperature at which the phases were equilibrated, no phase separation occurred.

The densitometer was then cleaned, and the acidic phase was injected. Densities were recorded for the same temperature range. This procedure was repeated for samples that were equilibrated ~16 h at temperatures between 15 and 24 °C.

Data for the construction of the phase diagram were obtained through cloud point determination. For the acidic branch of the diagram, 25 mL of IBA was pipetted into a 50 mL jacketed beaker. Temperature was controlled by a 1166D VWR circulator that flowed

(31) Greer, S. C. *Phys. Rev. A* **1976**, *14*, 1770–1780.

(32) Bouanz, M.; Beysens, D. *Chem. Phys. Lett.* **1994**, *231*, 105–110.

(33) Chu, B.; Schoenes, F. J.; Kao, W. P. *J. Am. Chem. Soc.* **1968**, *90*, 3042–3048.

(34) Chu, B.; Schoenes, F. J.; Fisher, M. E. *Phys. Rev. E* **1969**, *185*, 219–226.

(35) Rowley, R. L.; Horne, F. H. *J. Chem. Phys.* **1979**, *71*, 3841–3851.

(36) May, S. E.; Maher, J. V. *Phys. Rev. Lett.* **1991**, *67*, 2013–2015.

(37) Vlad, D. H.; Maher, J. V. *Phys. Rev. E* **1999**, *59*, 476–478.

(38) Cicuta, P.; Vailati, A.; Giglio, M. *Appl. Optics* **2001**, *40*, 4140–4146.

(39) Heinrich, M.; Wolf, B. A. *Polymer* **1992**, *33*, 1926–1931.

(40) Heinrich, M.; Wolf, B. A. *Macromolecules* **1993**, *26*, 6106–6110.

(41) Petitjeans, P. C. R. *Acad. Sci. Paris* **1996**, *322*, 673–679.

(42) Vonnegut, B. *Rev. Sci. Instrum.* **1942**, *13*, 6–9.

(43) Slattery, J. C. C.; Jing-Den J. *Colloid Interface Sci.* **1978**, *64*, 371–373.

(44) Manning, C. D.; Scriven, L. E. *Rev. Sci. Instrum.* **1977**, *48*, 1699–1705.

(45) Currie, P. K.; Van Nieuwkoop, J. J. *Colloid Interface Sci.* **1982**, *87*, 301–316.

(46) Hu, H. H.; Joseph, D. D. *J. Colloid Interface Sci.* **1994**, *162*, 331–339.

(47) Princen, H. M.; Zia, I. Y. Z.; Mason, S. G. *J. Colloid Interface Sci.* **1967**, *23*, 99–107.

(48) Technical Leaflet M 20984 e: *n*-Butanol. <http://www.basf.de> (accessed June 2005).

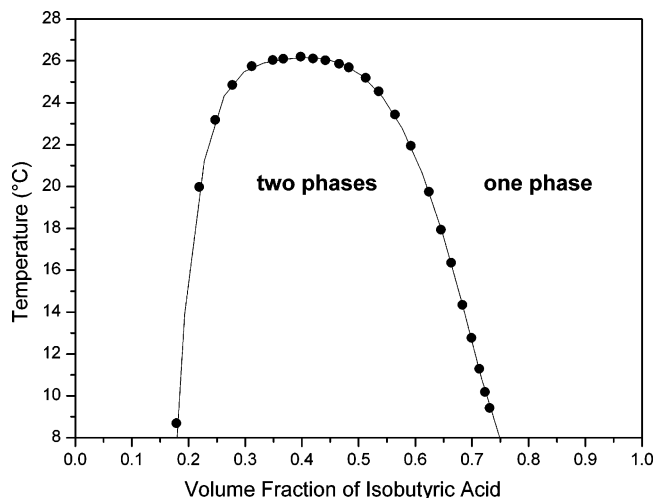


Figure 2. Phase diagram for the IBA–water system.

water through the beaker's jacket. The temperature of the acid was measured by a VWR platinum-resistance thermometer with an accuracy of 0.01 K. A small amount of water was added through a buret, and the resulting solution was stirred magnetically. The cloud point for the initial concentration was determined by slowly lowering the temperature until the solution became cloudy. The temperature was then increased slightly, and the solution was allowed to become clear. The temperature was then decreased at an even slower rate until the first cloudiness appeared. The temperature at which this occurred was recorded. More water was added from the buret, and the procedure was repeated.

The aqueous branch of the phase diagram was found in an analogous manner: IBA was added to water with stirring, the temperature was lowered, raised, and then lowered again to accurately determine the cloud point, then more IBA was added, and the new cloud point was determined. All the data obtained from each branch were plotted as cloud point temperature versus the volume fraction of IBA.

Results and Discussion

IBA–Water System. IBA and water are partially miscible below 26.3 °C but miscible in all proportions above the UCST, as shown in the phase diagram in Figure 2. The phase diagram is consistent with ones already reported.^{31,34}

We describe a typical experiment: A saturated solution of IBA in water was injected in the SDT capillary, and the temperature was lowered to 20 °C while the tensiometer was rotating. After the IBA droplets separated from the solution and coalesced into one large drop, the temperature was raised to 30 °C. (We determined that thermal equilibrium was reached within 100 s from the time the bath reached the final temperature by observing the relaxation of 1-butanol–water drops. We performed temperature jumps for equilibrated 1-butanol in water and observed the amount of time required for the system to reach its new equilibrium.) We chose to use initial temperatures so far from the UCST to increase the concentration difference between the drop and the matrix. Also, decreasing the temperature from room temperature allowed a drop to form spontaneously, and so no drop had to be injected.

Figure 4 shows a drop at different times. As the temperature is increased at 1.5 min, the drop lengthens because the interfacial tension decreases. After 5 min when the temperature reached 32 °C, the drop stretched significantly. The transition zone between the phases remains sharp even as the drop dissolves into the matrix.

To demonstrate that an effective interfacial tension exists, we show an IBA-rich drop above the UCST at high rotation (7000

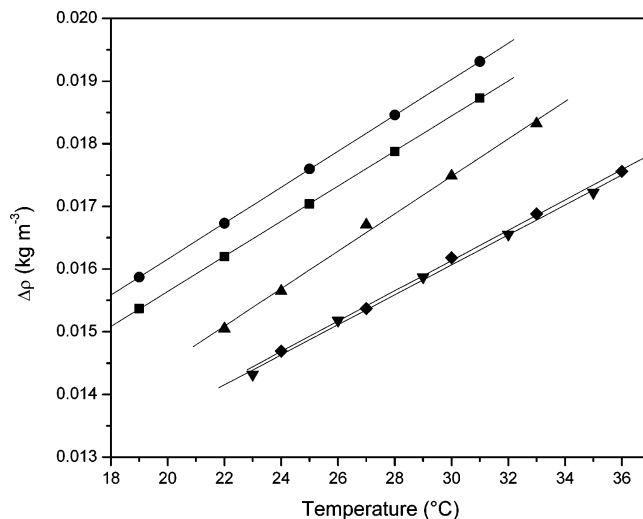


Figure 3. Density differences between the IBA-rich phase and the water-rich phase as a function of temperature. Initial temperatures for the equilibrated phases, from top to bottom: 15, 19, 21, 23, and 25 °C.

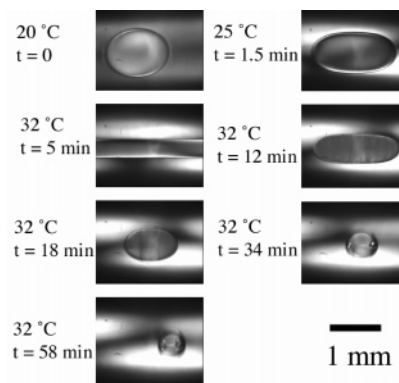


Figure 4. Time evolution of a drop of IBA-rich phase in a water-rich phase, before and after the jump in temperature. $\omega = 8000$ rpm.

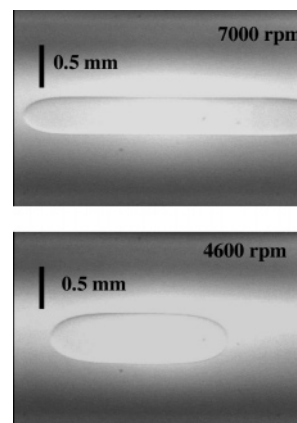


Figure 5. Images of an IBA-rich drop at different rotation rates after temperature jump from $T = 15$ to 30 °C. The elapsed time is 29 min.

rpm) and then after the rotation rate was reduced to 4600 rpm (Figure 5). Notice that the drop contracts, which is definitive evidence for an effective interfacial tension. Further confirmation is seen Figure 6 in which we plot r^{-3} vs ω^2 for a single drop above the UCST. The excellent linear fit indicates that an EIT does exist and that the Vonnegut formula can be used to measure it.

Figure 5 demonstrates that an EIT exists, but determining its value is complicated. In principle, if the drop is long enough,

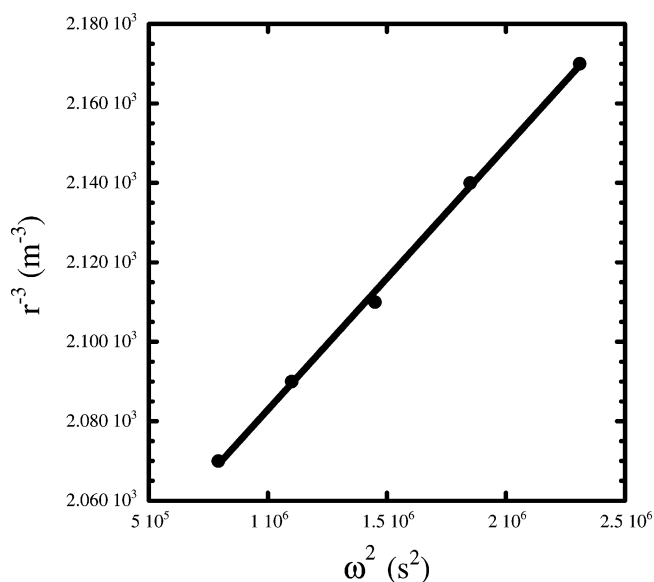


Figure 6. A plot of r^{-3} vs ω^2 for an IBA-rich drop after a temperature jump from 20 to 28.5 °C. The rotation rate was increased from 8500 to 14 500 rpm.

Table 1. EIT Values^a Obtained for 20–30 °C Jump with ω Varied from 8500 to 14 500 rpm

temperature (°C)	EIT (mN m ⁻¹) ^b (from the slope)
30.8	0.035
30.0	0.014
30.1	0.026
30.0	0.052

^a $\Delta\rho = 0.019 \text{ kg m}^{-3}$ was used. ^b Values obtained by the slope of the line of the plot of r^{-3} vs ω^2 .

effective interfacial tension values could be obtained measuring the radius of the droplet using eq 4 or, rearranging eq 4, from the slope of the line obtained plotting r^{-3} vs ω^2 . Moreover, when the drop is too short, the extended Vonnegut method could be applied by using eq 2. Both these methods require the density difference existing between the drop and the matrix to be known. However, due to the time required for the temperature jump, it is not possible to know this value with precision because at this time we do not know the effect of diffusion on the drop composition.

The results obtained by measuring the radius of a drop a few seconds after the final temperature has been achieved are shown in Table 1, while a typical plot of r^{-3} vs ω^2 is shown in Figure 6. In all cases, the length/radius ratios of the drops were large enough to permit the use of Vonnegut's method.

The linear correlations obtained in all the cases from the plot of r^{-3} vs ω^2 demonstrate that there is no gravitational effect and that the method is suitable for the system under study. The EIT values obtained have good consistency within each trial but poor agreement between the different trials. It is reasonable to assume that such a discrepancy is due to the temperature jump. In fact, if mass transport is occurring at an appreciable rate compared to the time required for the drop to come to thermal equilibrium, the EIT calculated is path dependent. The results in Table 1 are consistent with the values for the interfacial tension below the UCST. Howland et al. reported values of 0.05 mN m⁻¹ at 24.3 °C and 0.01 mN m⁻¹ at 25.8 °C.⁴⁹

(49) Howland, R. G.; Wong, N.-C.; Knobler, C. M. *J. Chem. Phys.* **1980**, *73*, 522–531.

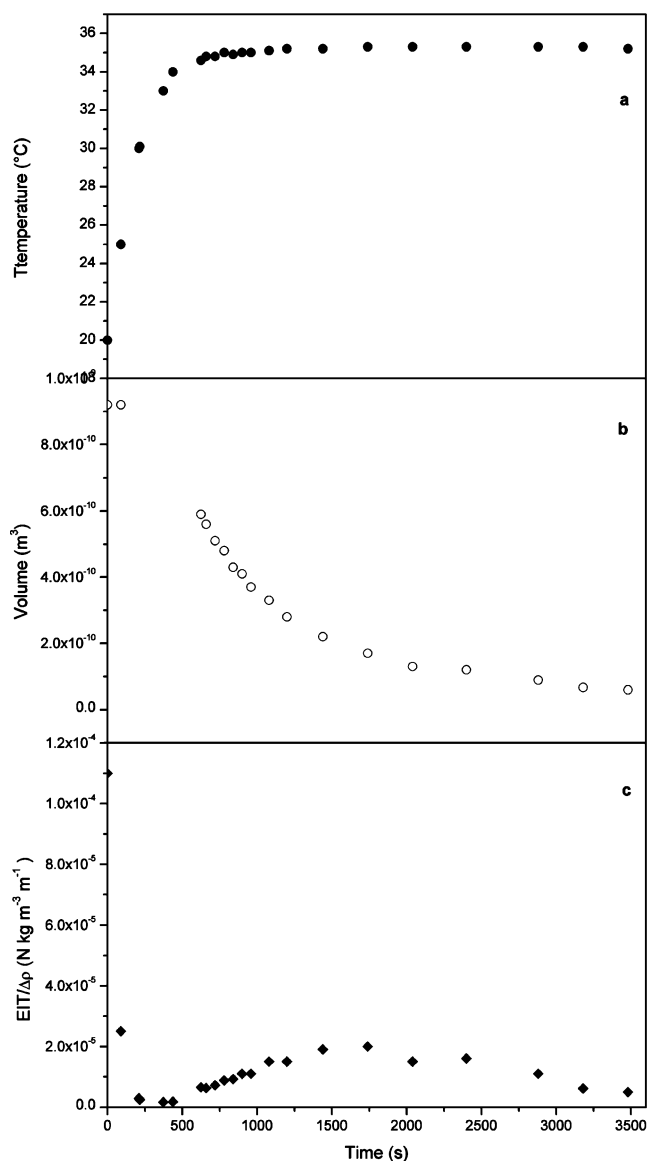


Figure 7. Temporal evolution of a drop of IBA-rich phase in a water-rich phase for a temperature jump from 20 to 28.5 °C with $\omega = 8000$ rpm. Time is referenced to the moment in which the final temperature has been set in the circulator. (a) Temperature, (b) volume, and (c) $\text{EIT}/\Delta\rho$.

Figure 4 illustrates that the transition zone between the drop and the matrix remains very sharp although the system is above the UCST and miscible. The drop shrinks with time until it completely dissolves in the matrix.

When the drop length is less than four times the drop radius, the extended Vonnegut method had to be applied. Moreover, it was also possible to determine the volume of the drop by calculating the radius of the equivalent sphere. Figure 4 shows the time evolution of the drop of IBA-rich phase in the water-rich phase during the temperature jump and after that final temperature has been achieved. Notice that after 30 min drops form inside the main drop. We discuss this below.

In Figure 7, we present the temporal evolution of the temperature, drop volume, and $\text{EIT}/\Delta\rho$. The graphs show that mass transport is occurring at a rate that could affect the measurement of effective interfacial tensions. The fact that diffusion does occur is most clearly demonstrated in the plot of volume vs time; the volume of the drop decreased by half within 15 min. A smaller drop volume does not imply that either its or the matrix's composition is changing significantly. If the drop

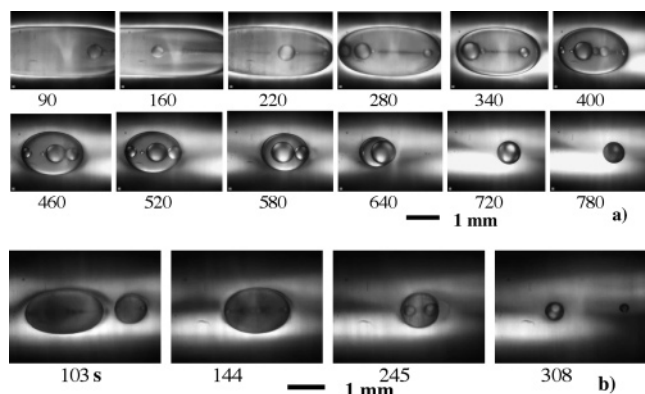


Figure 8. (a) Pure IBA in pure water below the critical temperature. Rotation: 8000 rpm. Times are in seconds. (b) Pure IBA injected into pure water. Initial and final temperatures: 27.5 °C. Rotation rate: 10 000 rpm. Times are in seconds.

maintains a constant composition while losing volume to the matrix, the percentage of acid added to the comparatively immense matrix would not significantly affect the matrix's composition.

Figure 7a and b shows what happens in the system while the drop loses volume. As expected, the value of $EIT/\Delta\rho$ decreases rapidly as the temperature in the SDT capillary rises. However, the $EIT/\Delta\rho$ reaches its minimum value at 6.2 min, well before the temperature approaches its maximum around 9 min. Between 7 and 30 min, the values for $EIT/\Delta\rho$ monotonically increase. A possible explanation for this increase is that $\Delta\rho$ decreases as IBA diffuses out of the drop. If this explanation is correct, $EIT/\Delta\rho$ might be expected to grow until the drop disappears. However, this does not occur. After 30 min, the $EIT/\Delta\rho$ reaches a maximum and starts to decrease. As the compositions of the two phases become more similar, the effective interfacial tension between them will decrease. Perhaps after 30 min, the composition of each phase is such that the interfacial tension will begin to decrease at a higher rate than $\Delta\rho$. Unfortunately, because we have no method to determine the composition of the drop during the experiment, we cannot resolve this issue.

Pure IBA in Water. We also studied pure IBA injected into water at 20.8 °C. In Figure 8, we can see that drops form inside the main drop of IBA. These very small drops coalesce and form a large drop. Eventually, even this drop dissolves into the matrix. Pure IBA was later injected into pure water at 27.5 °C to observe if being above the critical temperature would have an effect on the inner drop formation, which it did not. As can be seen, an inner drop is again formed. This inner drop is larger, and its formation can be seen more clearly than the inner drops that form between acidic and aqueous phases.

We can rule out the possibility that the drop is dissolved gas coming out of solution because it does not appear as a gas bubble, which is always very dark, and it ultimately disappears. We can also rule out the possibility that there is an intermediate composition with a lower density than pure IBA on the basis of the data provided by Melzer et al.⁵⁰ We can offer no explanation at this time.

Droplet Breakup. Quirion and Pageau⁵¹ demonstrated for immiscible systems that, upon a large decrease in rotation rate, a Rayleigh–Tomotika instability could be observed.^{8,9} Quirion and Pageau were able to measure the interfacial tension from the rate of the drop breakup. Figure 9 shows how the miscible drop

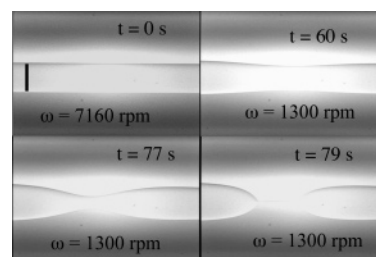


Figure 9. Image of droplet breakup after the rotation rate was decreased from 7160 to 1300 rpm. Scale bar corresponds to 4.7×10^{-4} m. The initial temperature was 15 °C. The temperature was jumped to 30 °C. Five minutes after the temperature jump, the rotation rate was rapidly decreased ($t = 0$ s).

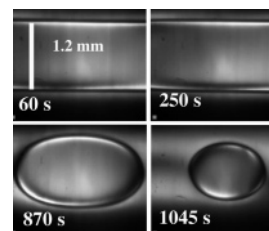


Figure 10. Images of a drop of 1-butanol with pure water as the dense phase. $T = 12$ °C; $\omega = 11$ 000 rpm. $t = 0$ when the rotation was started, which was immediately after the injection of the drop.

breaks apart upon the rapid decrease in rotation rate from 7160 to 1300 rpm for a drop of IBA-rich phase in water-rich phase at 30 °C; the phases were formed at 15 °C. This result provides evidence that an effective interfacial tension does exist between the unequilibrated phases of IBA and water.

Unfortunately, the diameter of the drop is too large, and the ratio of the drop's length to its diameter is too low. In fact, a drop as thick as the one depicted in Figure 9 must be considerably longer than the length of the SDT in order to prevent interference from end-pinching.⁵¹ Therefore, while this result undoubtedly shows that an EIT exists, the Rayleigh–Tomotika method could not be applied to measure the EIT in the current system.

Diffusion of Drops. The diffusion of the drop is unusual. For a miscible polymer–monomer system, dodecyl acrylate and poly-(dodecyl acrylate), Antrim et al.⁵² found that the transition zone between the monomer and polymer expands as would be expected for Fickian diffusion. Cicutta et al. found that the aniline–cyclohexane system followed Fickian diffusion.³⁸ However, for the IBA–water system, the transition zone remains sharp and the drop volume decreases with time. Future work will focus on understanding this process.

1-Butanol in Water. We also investigated 1-butanol in water. This system is partially miscible,⁵³ but the volume of 1-butanol that we used was always below the solubility limit, which was confirmed by the complete dissolution of the 1-butanol drop in the water phase. The dissolution process is slow enough to permit the observation of a droplet of 1-butanol in the water matrix and hence the determination of the EIT between the two fluids. Droplets were immediately formed on starting the rotation and could be observed for about 30 min.

Due to the fact that the system is already at thermal equilibrium, it is reasonable to assume that the densities of the drop and the matrix are the same as those of the pure components at that temperature. Therefore, it is possible to calculate the initial EIT values in the system by means of eq 4 or from the slope of the

(50) Melzer, W.-M.; Baldauf, W.; Knapp, H. *Chem. Eng. Process* **1989**, *26*, 71–79.

(51) Quirion, F.; Pageau, J. *J. Polym. Sci., Part B: Polym. Phys.* **1995**, *33*, 1867–1875.

(52) Antrim, D.; Bunton, P.; Lewis, L. L.; Zoltowski, B. D.; Pojman, J. A. *J. Phys. Chem. Part B* **2005**, *109*, 11842–11849.

(53) Donahue, D. J.; Bartell, F. E. *J. Phys. Chem.* **1952**, *56*, 480–484.

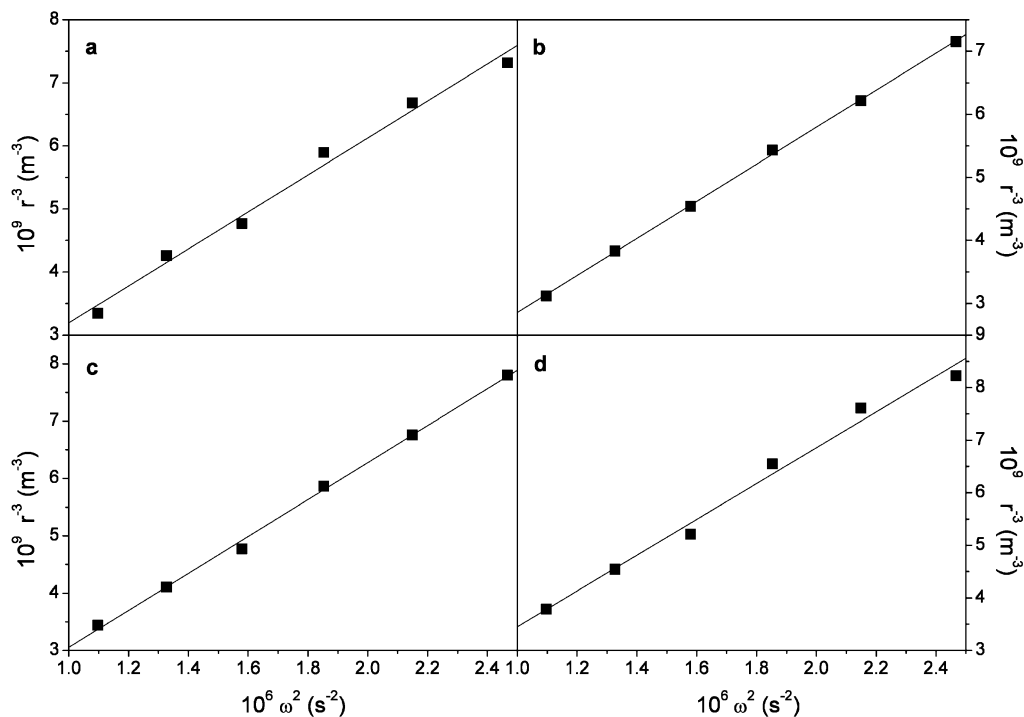


Figure 11. Plots of r^{-3} vs ω^2 for the 1-butanol–water system at different temperatures. (a) 9, (b) 18, (c) 40, (d) 60 °C.

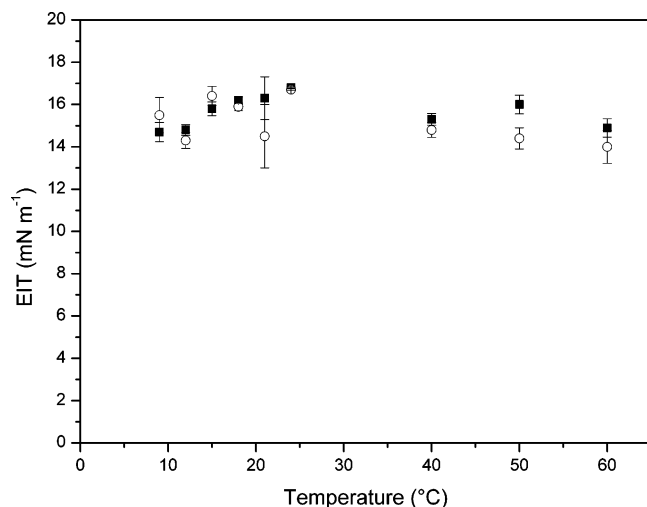


Figure 12. EIT for 1-butanol–water as a function of temperature. The EIT was determined by using eq 4 (●) and from plots of r^{-3} vs ω^2 (○).

line obtained by plotting r^{-3} vs ω^2 . The data obtained at different temperatures are listed in Table 1. Typical images of 1-butanol drops are shown in Figure 10 and typical plots of r^{-3} vs ω^2 are shown in Figure 11.

The good linear correlations obtained in the plot of r^{-3} vs ω^2 (see for example the typical plots in Figure 11) confirm that no significant gravitational effect is present. Moreover, the EIT values obtained by the slope of the lines are in very good agreement with those obtained from the averages of individual runs.

Figure 12 shows that, in the temperature range considered, EIT values remain virtually constant and are larger than the corresponding IT value for the equilibrated 1-butanol–water system (1.8 mN m^{-1}).⁵⁴ This can be explained considering that in this case the two phases differ more than those in the case of

the equilibrated system. Qualitatively, the same effect has been previously observed for a nonequilibrated 1-butanol–water system.⁵⁵ In that case, the values measured using a drop volume tensiometer were significantly smaller (between 2 and 2.5 mN m^{-1}) than those that we obtained. While the experimental procedure they used is not detailed enough for us to give a justification for this large difference in the results from the two methodologies, one possible explanation could be the fact that dynamic interfacial tension values measured with the drop volume method are quite dependent on the capillary flow rates (with larger IT measured at higher capillary flow rate).⁵⁶ Moreover, the drop volume is calculated by the time elapsed between subsequent drops that are formed and detached from the capillary.⁵⁷ It is possible, therefore, that the water matrix has in this case a higher 1-butanol content and consequently a lower interfacial tension. As for the fact that the measured values seems to be not dependent on temperature in the interval considered, it has to be pointed out that this is analogous to the behavior for the IT of the equilibrated system on varying the temperature in the same interval.⁵⁸

Time evolution of the EIT for different rotational rates and temperature values (calculated using both the Vonnegut and the extended Vonnegut methods, depending on the drop shape) are shown in Figure 13. The figure clearly shows that values of EIT obtained with the two different methods are in fair agreement, but when the drop became very small and nearly spherical, the errors introduced lead to unreliable EIT measurements and incoherent results.

Furthermore, it can be noticed that the EIT values remain almost constant for a long period of time. Considering eq 3, a constant value for the EIT implies that the concentration gradient

(55) Mollet, C.; Touhami, Y.; Hornoff, V. *Canadian J. Chem. Eng.* **1996**, *74*, 316–319.

(56) Drelich, J.; Fang, C.; White, C. L. In *Encyclopedia of Surface and Colloid Science*; Hubbard, A. T., Ed.; Marcel Dekker: New York, 2002; pp 3152–3166.

(57) Campanelli, J. R.; Wang, X. *J. Colloid Interface Sci.* **1997**, *190*, 491–496.

(58) Yeh, M. C.; Lin, P. C.; Chen, L. J. *J. Phys. Chem. B* **2004**, *108*, 9955–9961.

(54) Adamson, A. W. *Physical Chemistry of Surfaces*, 4th ed.; Wiley: New York, 1982.

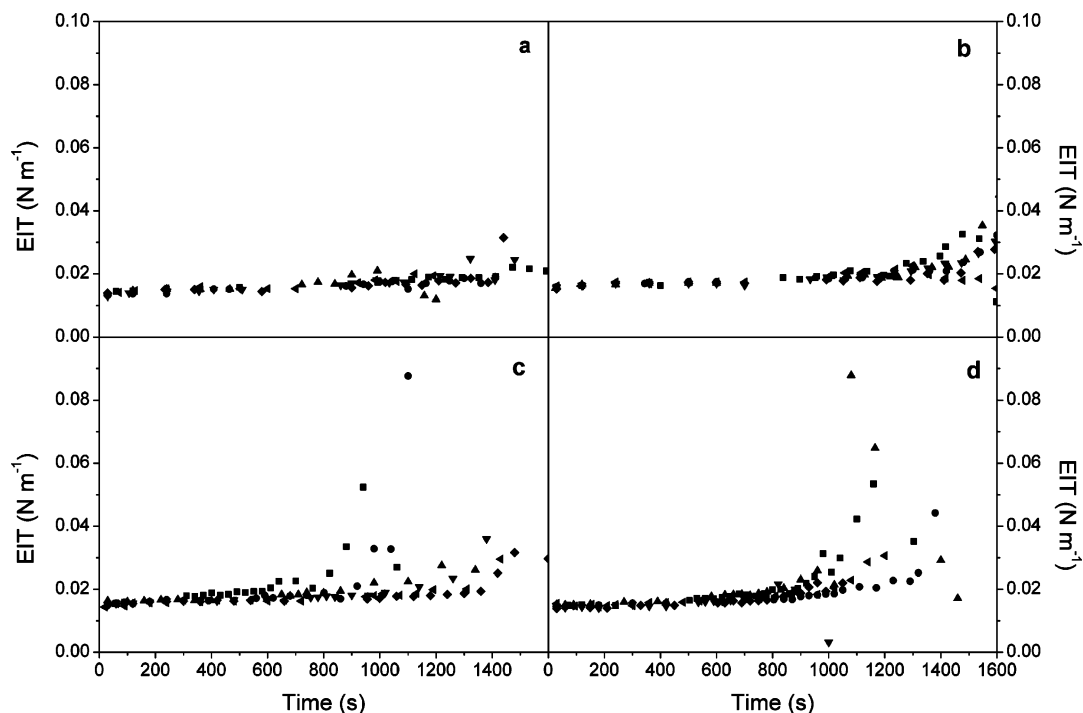


Figure 13. Plots of the EIT vs time for the 1-butanol–water system at different temperatures ((a) 9, (b) 18, (c) 40, (d) 60 °C) and rotation rates (■ = 10 000, ● = 11 000, ▲ = 12 000, ▼ = 13 000, ◆ = 14 000, sideways triangle = 15 000 rpm).

remains constant during the time interval. This can be explained considering that the drop shrinks because the 1-butanol flows out into the water matrix while no significant amount of water flows in. In this case, the drop composition would remain the same. An alternative explanation is that the density of the drop does not differ very much from that of the pure 1-butanol.⁵⁹ In any case, the composition of the matrix only changes slightly because the amount of 1-butanol is very small compared to the water volume.

In all the cases examined, the drop interface remains quite sharp for the complete duration of the experiment and does not broaden as would be expected in the case of Fickian diffusion. It is reasonable to assume that the 1-butanol flows out of the drop at a rate that is higher than that at which water flows in.

Rotational jumps lead to a change in the drop shape, but no drop breakup was observed. This is most likely a result of the large value of the EIT. The critical wavelength of the Rayleigh–Tomotika instability increases with interfacial tension.^{8,9} If the wavelength exceeds the length of the drop, then the drop will retract but not break up.

How General Are These Results? The two systems we selected are ideal for the observation of an EIT because the concentration gradients between the two fluids remain sharp with time. One possibility for this is that the high acceleration level in the tensiometer affects the diffusion, a phenomenon that is called “barodiffusion”.^{60,61} Careful experiments have demonstrated that diffusion, especially for a system near a critical solution point, can be affected by gravitational acceleration.^{62–67}

(59) Hao, L.; Leaist, D. G. *J. Chem. Eng. Data* **1996**, *41*, 210–213.

(60) Landau, L. D.; Lifshitz, E. M. *Fluid Mechanics*; Pergamon: Oxford, 1987.

(61) Jamshidi-Ghaleh, K.; Tavassoly, M. T.; Mansour, N. *J. Phys. D: Appl. Phys.* **2004**, *37*, 1993–1997.

(62) Cicuta, P.; Vailati, A.; Giglio, M. *Phys. Rev. E* **2000**, *62*, 4920–4926.

(63) Giglio, M.; Vendramini, A. *Phys. Rev. Lett.* **1975**, *35*, 168–170.

(64) Righetti, P. G.; Bossi, A.; Giglio, M.; Vailati, A.; Lyubimova, T.; Briskman, V. A. *Electrophoresis* **1994**, *15*, 1005–1013.

(65) Vailati, A.; Giglio, M. *Phys. Rev. Lett.* **1996**, *77*, 1484–1487.

(66) Vailati, A.; Giglio, M. *Phys. Rev. E* **1998**, *58*, 4361–4371.

(67) Brogioli, D.; Vailati, A.; Giglio, M. *Phys. Rev. E* **2000**, *61*, R1–R4.

We are currently studying both the IBA–water and 1-butanol–water systems by laser line deflection⁵² to determine how the diffusion under 1 g compares to what is seen in the tensiometer.

We can report that other alcohols (e.g., ethanol, propanol) with higher solubilities than 1-butanol could not be studied in the tensiometer because the drops dissolved too rapidly.

Another miscible system, honey and water, has been studied recently under weightlessness on the International Space Station to determine if the aspherical blobs of water injected into honey would become spherical or whether streams of honey would breakup via the Rayleigh–Tomotika instability.⁶⁸ Neither phenomena were observed, and so the authors concluded that either no Korteweg stresses were present or, more likely for the high viscosity of the system and relatively rapid diffusion, no macroscopic fluid motion could occur.

Conclusions

We present definitive evidence for the existence of an effective interfacial tension between miscible fluids using SDT. We studied IBA and water. Below the UCST of 26 °C, two phases can exist. We created a drop of IBA-rich phase in the water-rich phase and then jumped the temperature above the UCST. We were able to verify the existence of an interfacial tension by measuring the drop radius as a function of rotation rate. A plot of r^{-3} vs ω^2 was linear, demonstrating that the drop responds exactly as predicted by Vonnegut for immiscible fluids. The value of the EIT was on the order of 0.01 mN m⁻¹.

If pure IBA was injected into water, over time, small drops formed inside the main drop. This occurred if the system was initially above or below the UCST. We are unable to explain this phenomenon.

The drops above the UCST exhibited the Rayleigh–Tomotika instability when the rotation rate was rapidly decreased. This breakup is also evidence for the existence of an interfacial tension between the miscible fluids.

(68) Pojman, J. A.; Bessonov, N.; Volpert, V. *Microgravity Sci. Technol.*, submitted for publication.

We presented definitive evidence for the existence of an effective interfacial tension between 1-butanol and water using SDT when the amount of 1-butanol used is below the solubility limit. We were able to evaluate the EIT values, which turned out to be larger than the equilibrium interface tension between the saturated phases. The transition between the fluids remained remarkably sharp with time. The aqueous phase consumed the drop, whose volume monotonically decreased with time. The EIT values were not a function of temperature in the range between 9 and 60 °C.

The transition between the fluids for both systems remained remarkably sharp with time. The aqueous phase consumed the drops, whose volumes monotonically decreased with time.

Acknowledgment. Support for this project was provided by NASA's Microgravity Materials Science Program (NAG8-1466). We also thank Robert Lochhead and François Quirion for helpful discussions. We also thank Gloria Viner for her assistance. We offer special thanks for the staff at Krüss USA for assisting us.

LA052111N