Int J Thermophys (2010) 31:2416–2424
DOI 10.1007/s10765-010-0825-6

Influence of Drop Growth Rate and Size on the Interfacial Tension of Triton X-100 Solutions as a Function of Pressure and Temperature

A. Miquilena · V. Coll · A. Borges · J. Melendez · S. Zeppieri

Received: 1 July 2009 / Accepted: 13 September 2010 / Published online: 30 September 2010

Abstract The interfacial tension (IFT) between decane and aqueous solutions of Triton X-100 was determined by the pendant-drop technique, and the effects of the temperature, pressure, surfactant concentration, droplet growth rate, and size were studied. Three aqueous solutions of surfactant were used (0.48×10^{-4} mol · L^{-1}, 0.96×10^{-4} mol · L^{-1}, 1.43×10^{-4} mol · L^{-1}), and the experiments were performed at (2, 3, and 4) MPa and at (30, 40, and 50) °C. As expected, the alkane drop changed its shape, and the IFT of the system decreased as the surfactant adsorbed onto the interface, until the drop finally separates from the capillary, in a maximum time of 2120 s. According to the results, the influence of temperature on the IFT is inversely proportional to the surfactant concentration, because when the concentration increases, the temperature has little effect on it. It was also noticed that the effect of pressure on the IFT at lower surfactant concentrations is less significant than at higher concentrations. When the temperature decreases, the pressure reduces its effect on the IFT, as occurs with systems at 30 °C. The droplet growth rate does not significantly affect the IFT value, while its size does; therefore, when transient studies are carried out, it is required to control the drop size.

Keywords Alkane · Aqueous solution · Interfacial tension · Pendant drop · Triton

---

A. Miquilena · V. Coll · A. Borges · J. Melendez · S. Zeppieri (✉)
Departamento de Termodinámica y Fenómenos de Transferencia, Sartenejas, GFT_{USB}, Universidad Simón Bolívar, Caracas 1080, Venezuela
e-mail: zeppieri@usb.ve

A. Miquilena
e-mail: adrianamiquilena@gmail.com

1 Introduction

The interfacial tension (IFT) is the surface-free energy that exists between two immiscible liquid phases, such as oil and water. This property can be measured by several experimental methods; the most widely used are those based on the shapes of bubbles or droplets. One of these techniques is the pendant-drop method, which has been commonly used because of its simplicity and advantages, discussed elsewhere [1–4].

Nonionics include the most diverse type of surfactants with respect to properties, structure, and fractional composition, and their total world production has reached up to two million tons per year, occupying up to a quarter of the total surfactant production [4]. Triton X-100 (Octyl phenol ethoxylate, also known as TX-100) is a nonionic surfactant which has a hydrophilic polyethylene oxide group and a hydrocarbon lipophilic group, and its main use lies in industrial and domestic applications such as detergents and emulsifier agents. Several studies in air/TX-100 solutions have been carried out; however, the reduction of the tension at an interface by a surfactant in aqueous solution when a second liquid phase is present may be considerably more complex than that when a second phase is absent, i.e., when the interface is a surface [5].

Alkane/water and air/water systems have been previously investigated in several studies. In 1967 Harley [6] measured the IFT of benzene/water and decane/water by the pendant-drop method for a wide range of pressures and temperatures, and they concluded that temperature has a greater effect on the IFT than pressure.

Cai et al. [7] studied the effects of temperature, pressure, and salt content on the IFT of 10 n-alkane + water/brine and hydrocarbon mixtures + water/brine systems. It was found that the IFT is sensitive to temperature and salt concentration but weekly dependent on pressure. On the other hand, since the pendant drop is one of the most simple and used techniques to measure the IFT, and given the fact that it is a geometric method, it is important to take into account for the factors that might affect its accuracy, in order to achieve, by a combination of the more favorable conditions, the desired effect on the IFT. In 1995 Lin et al. [8] determined the IFT of n-tetradecane/water/diethilenglycol monohexyl ether and the surface tension of a bubble immersed in water, noticing that the bigger the bubble was, the more approximate the IFT value was that is reported in the literature at 25 °C($72\,\mathrm{mN \cdot m^{-1}}$). In both systems, bigger drops lead to higher values of IFT; however, these authors did not find any severe differences between the standard deviations for different droplet sizes. Jenning and Pallas [9] numerically examined the dependence of error in the IFT on the drop. These authors concluded that the largest possible stable drop for a given tip radius gives the most accurate determination of the IFT; however, this study was carried out for a water/air interface only. Later, Semmler et al. [10] studied the IFT for an aqueous solution of an anionic surfactant against hexane, concluding, through the development of an apparatus which yields the coordinates of a pendant drop with high accuracy, that exact measurements of the IFT of fluid interfaces and the determination of contact angles are of vital interest.

It is well known that the study of interfacial phenomena is essential in processes where there is a contact between two or more substances; and it becomes even more relevant when there are surfactants involved. Therefore, in this study, we present a series of experimental measurements of the IFT between decane and aqueous solutions of Triton X-100 using the rising-drop technique, which is a variation of the pendant-drop method, in order to study the effects of factors such as temperature, pressure, surfactant concentration, droplet growth rate, and size upon this property for diluted nonionic surfactant solutions.

2 Experimental

A diagram of the experimental apparatus is shown in Fig. 1. It allows surface and interfacial-tension measurements for two-phase systems, using the pendant- or rising-drop method.

The apparatus has a feed system consisting of two metallic cylinders (j and k) for each of the solutions. After the temperature is set, these cylinders are pressurized with compressed air in order to achieve the injection of the substances into the system. The imaging system consists of an arrangement of a light source, a stainless steel viewing cell, a computer, and a CCD DXC-151 SONY® camera with Nikkon 60 mm microlenses; and the whole setup is mounted on a vibration-free base. The experiments were carried out using distilled water, TX-100 (Scharlau Chemie®), and decane (Fisher®) without further purification. The temperature was measured with a precision of 0.8 °C and the pressure with a precision of 0.03 MPa. A minimum of four measurements were made for each condition. A more detailed description of this experimental setup and procedure is available in previous studies [11,12].

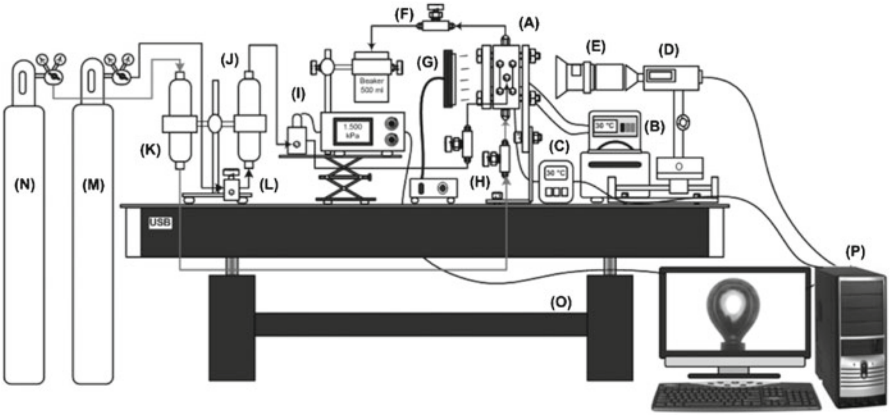

Fig. 1 Experimental setup: (a) high pressure cell, (b) thermostat, (c) digital thermometer, (d) CCD camera, (e) optical lenses, (f) relief valve of the cell, (g) lamp, (h) micrometric valve, (i) pressure transducer, (j, k) sample cylinders, (l) pressure regulator, (m, n) air cylinders, (o) anti-vibration table, and (p) computer

3 Results

The droplet phase was the aqueous TX-100 solution, and the continuous phase was the decane. Several drops were formed at the tip of the capillary at different growth rates and final sizes, and the effects of these factors and temperature and pressure were studied. It is important to mention that while studying pressure and temperature effects, the drops for every set of experimental conditions were formed at nearly constant volume so the effect of this factor on the IFT could be neglected. Another important observation is that when similar results were obtained for several conditions, only one representative plot will be shown, and the solid lines that might be present are only a guide for the eye.

3.1 Temperature Effect

Taking the 1.43×10^{-4} mol · L^{-1} solution as an example, at 3 MPa, it could be thought that the temperature should not be considered as a determining factor on the variation of IFT since even with differences of 10 °C, as shown in Fig. 2, the isotherms overlap. However, for all three concentrations of TX-100, by plotting the IFT versus time for the lowest and highest temperatures, the temperature effect upon the IFT appears clearer (see Figs. 3 and 4). In Figs. 3 and 4, the time dependence of the IFT for the surfactant solution of 9.56×10^{-5} mol · L^{-1} is shown for 30 °C and 50 °C, respectively, and it shows that the IFT decreases at lower temperatures, which was expected since ethylene oxide derivatives show an inverse temperature effect on solubility in water. This behavior was observed for the other concentrations. Our results also indicate that this effect is more pronounced when the concentration of TX-100 is low, from which it can be concluded that the concentration has a greater effect on the IFT than does the temperature.

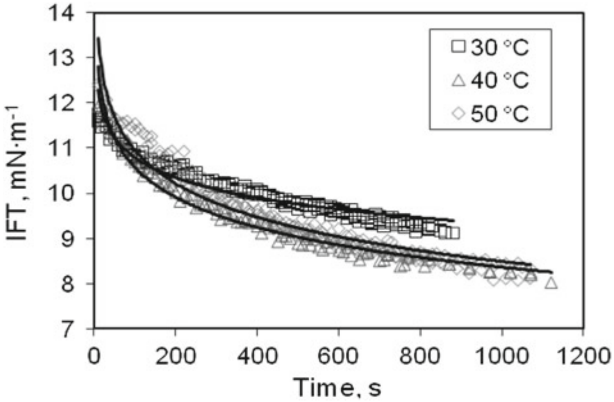

Fig. 2 IFT of decane/water-TX100 at 1.43×10^{-4} mol · L^{-1} and 3 MPa

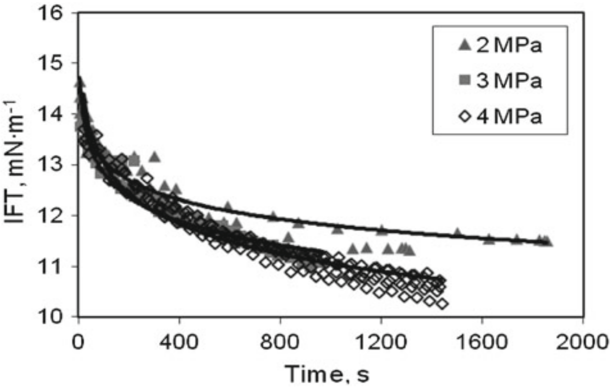

Fig. 3 IFT of decane/water-TX100 at 9.56 × 10^{-5} mol · L^{-1} and 30 °C

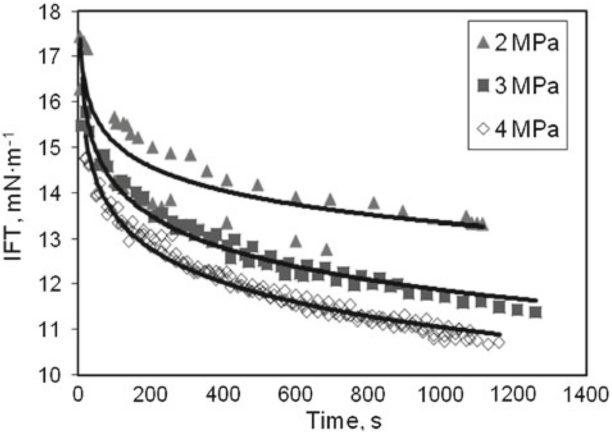

Fig. 4 IFT of decane/water-TX100 at 9.56 × 10^{-5} mol · L^{-1} and 50 °C

3.2 Pressure Effect

The curves in Fig. 5 indicate that the effect of pressure does not show a definite tendency at low temperatures, since these curves overlap at every concentration of TX-100. Even at other temperatures, the influence of the pressure on the IFT is not clearly defined, showing that the temperature has a greater effect on the IFT than does the pressure.

This behavior also agrees with Michaels and Hauser [3] who studied decane/water systems and concluded that the effect of pressure upon the IFT is relatively small, the maximum change being somewhat over 2 mN · m^{-1} over a pressure range of 70 MPa in their study.

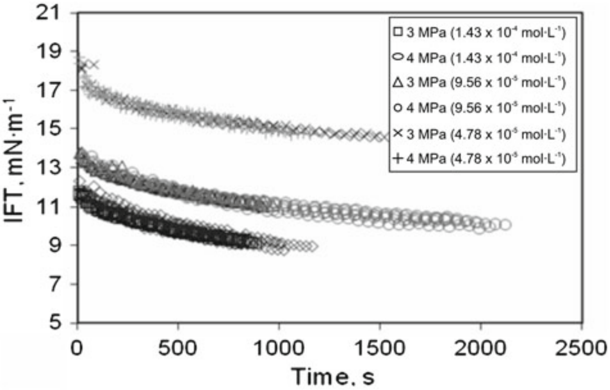

Fig. 5 IFT of decane/water-TX100 dependence on pressure and concentration at 30 °C

3.3 Surfactant Concentration Effect

Figure 6 shows that for both pressures the IFT decreases as the amount of molecules of TX-100 increases. This is due to the reduction of the instability of the immiscible phases, as a result of the hydrophilic–hydrophobic structure of the surfactant. This behavior was also observed in previous studies [4]. The solubility of TX-100 decreases as the temperature rises, which is demonstrated by the decrement of its tensoactive effect, shown in Fig. 6.

Previous studies of the IFT in decane/water systems have shown that this property increases as the pressure increases [7,13]. In this study with aqueous solutions of TX-100, this behavior can be validated at every temperature for the 4.78×10^{-5} mol · L^{-1} solutions (Fig. 7), however, it is not observed at 9.56×10^{-5} mol · L^{-1}. This indicates that at lower concentrations of the surfactant, the pressure upon the IFT is greater, in contrast to what occurs at 9.56×10^{-5} mol · L^{-1}, when the amount of TX-100

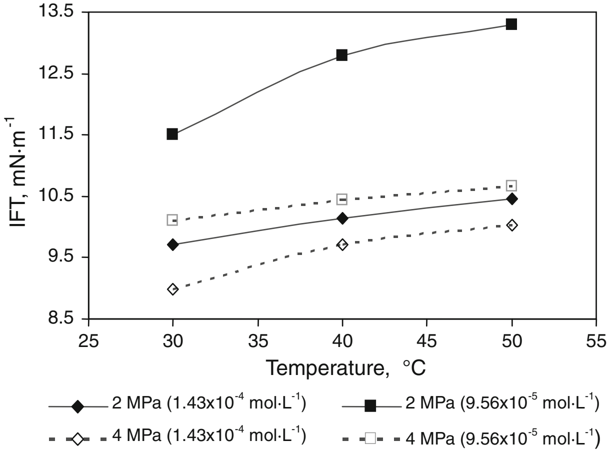

Fig. 6 IFT behavior with the temperature, pressure, and concentration of the solution

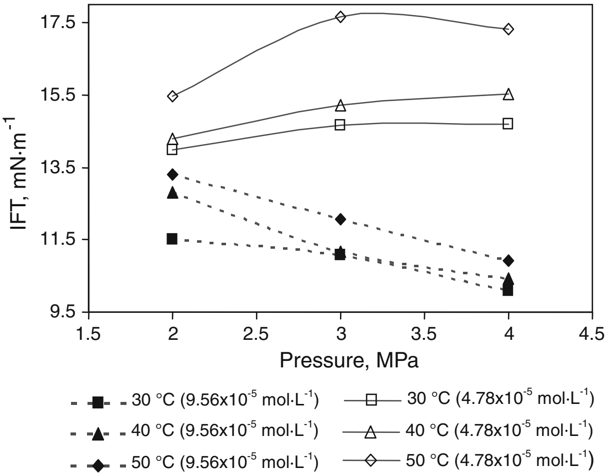

Fig. 7 IFT behavior with the pressure for different temperatures and solution concentrations

molecules on the interface has a dominant effect on the IFT, causing its reduction. Additionally, it can be observed that for both concentrations, if the same pressure is maintained while increasing the temperature, the IFT will increase.

3.4 Drop Growth Rate and Size

Decane droplets were formed at 0.08 cm · s^{-1} and 0.03 cm · s^{-1} with a constant initial volume. According to Fig. 8, the growth rate is not a decisive factor on the IFT value, since the two curves overlap; however, the initial drop volume has a major influence on the IFT (Fig. 9). This was verified by forming droplets with an average $Ro = 0.123$ cm and $Ro = 0.129$ cm and a constant growth rate, with Ro the radius of the maximum circumference that can be circumscribed within the droplet profile from its apex. As

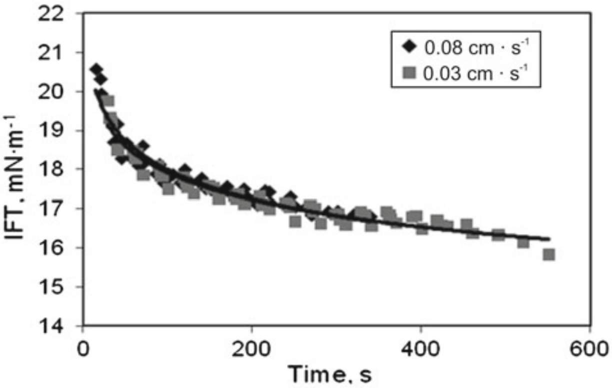

Fig. 8 IFT of decane/water-TX100 at 30 °C for two growth rates

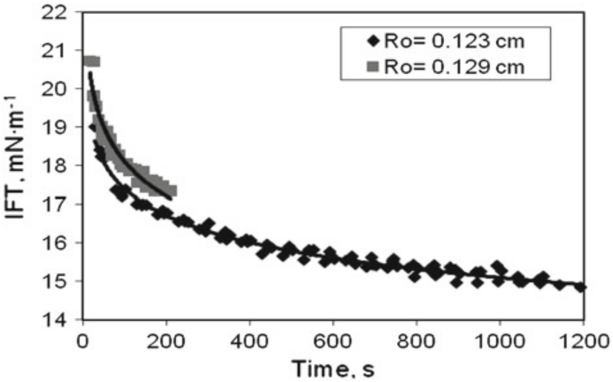

Fig. 9 IFT of decane/water-TX100 at 30 °C

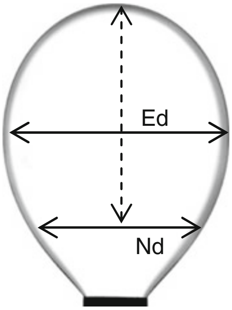

Fig. 10 Drop of decane rising from the capillary: (Nd) neck diameter and (Ed) equatorial diameter

mentioned previously, Lin et al. [8] carried out experiments for air/water and fluid–fluid interfaces and they found that the measured IFT is drop dependent; however, their data indicated that for drops without an equator, the IFT did not change as the volume changed. In our case, the drops had a defined equator, much higher than the neck diameter (see Fig. 10). Our results show that there is a clear influence of the drop size on the measurement of the IFT. Bigger drops are more suitable for measurements of IFT by the pendant-drop method, because with them there is higher accuracy in the image edge detection process. This observation agrees with Yang et al. [14] who also studied the influence of drop size on the IFT and adsorption of surfactants, and it shows that the high accuracy with which the drop coordinates must be determined not only depends on the numerical treatment of the information, but also on the original experimental data itself.

4 Conclusions

Pendant drops of solutions containing surfactants, although formed with a fixed initial volume, show a progressive change of shape due to ageing of the interface, until it finally detaches from the capillary due to the thinning of the neck.

When working with TX-100 solutions at 50 °C, the IFT was higher than at 40 °C and 30 °C for every concentration studied; however, the higher is the concentration, the smaller is the effect of the temperature upon the IFT. It is important to mention that of all the factors studied (not including concentration), it was the temperature that showed the greatest influence on the IFT, and it is advisable to combine both temperature and concentration effects to achieve the desired variation on the IFT, according to need. Previous studies [6,13–15] have found that there is a linear dependence between the pressure and IFT in fluid–fluid interfaces; however, it was not possible to observe this behavior in the studied range of values. Therefore, and considering the ranges of pressures studied by other authors, we conclude that in liquid–liquid systems this dependence can only be observed for very high pressures.

The measurement of the IFT by the pendant-drop method and its calculation by means of the geometrical parameter algorithm require that droplets have a defined neck and equatorial diameter in order to achieve accurate results. The size of the drop is very important when working with surfactants since these substances modify the shape of the drop or bubble: if the drop is too small, and the calculus algorithm involves its equatorial diameter, the results might be wrong due to the incorrect estimate of geometric parameters; on the other hand, if the drop is too big, there might be an early detachment of the drop from the capillary, before it reaches equilibrium. It is possible to make measurements by using drops outside of the optimum size range; however, these measurements will be subject to additional uncertainty.

References

1. L. Scharmm, *Surfactants: Fundamentals and Applications in the Petroleum Industry* (Cambridge University Press, Cambridge, 2000)
2. S.Y. Lin, H.F. Hwang, Langmuir **10**, 4703 (1994)
3. A.S Michaels, E.A. Hauser, J. Phys. Chem. **55**, 408 (1951)
4. V. Fainerman, D. Möbius, R. Miller, *Surfactants-Chemistry, Interfacial Properties and Application, Studies in Interface Science*, vol. 13 (Elsevier, Amsterdam, 2001)
5. M. Rosen, *Surfactants and Interfacial Phenomena* (Surfactant Research Institute, Brooklyn College, New York, 2004)
6. J. Harley, J. Colloid Interface Sci. **24**, 323 (1967)
7. B.Y. Cai, J.T. Yang, T.M. Guo, J. Chem. Eng. Data **41**, 493 (1996)
8. S.Y. Lin, L. Chen, J. Xyu, W. Wang, Langmuir **11**, 4159 (1995)
9. J.W. Jennings, N.R. Pallas, Langmuir **4**, 959 (1988)
10. A. Semmler, R. Ferstl, H. Kohler, Langmuir **12**, 4165 (1996)
11. S. Zeppieri, J. Rodríguez, A. López de Ramos, J. Chem. Eng. Data **46**, 1086 (2001)
12. A. López, *Capillary Enhanced Diffusion of CO_2 in Porous Media*, Ph.D. Dissertation, University of Tulsa, Tulsa, OK, 1993
13. K. Motomura, H. Iyota, M. Aratono, M. Yamanaka, R. Matuura, J. Colloid Interface Sci. **93**, 264 (1982)
14. M. Yang, H. Wei, S. Lin, Langmuir **23**, 12606 (2007)
15. T. Al-Sahhaf, A. Elkamel, A. Suttar, A. Khan, Chem. Eng. Commun. **192**, 667 (2005)