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Application Report

Ageing of cooking oils

Application report: AR203e
Industry section: Food technology
Author: CR
Date: 09/1995

Method:

Drop Volume Tensiometer – DVT10

Keywords: Dynamic interfacial tension, drop volume tensiometry, defoamer, soybean based cooking oil

The effects of ageing on the properties of soybean based cooking oils

An Example of the Application of Dynamic Tensiometry to Problems that Cannot Be Solved by Static Tensiometry

Background

One of the large challenges in food science technology is the development of cooking oils with extended usable lifetimes. Extended lifetime oils decrease: (1) the necessity for hot-oil cooker downtime, (2) the overall quantity of oil used per item cooked, and (3) the amount of used oil that subsequently needs disposal. The advantages are economic as well as environmental.

After cooking oil has been used for a period of time, a stable froth (or foam) begins to develop on the surface of the oil during the cooking process. Soon thereafter, controlling this surface layer becomes a problem. The esthetics of cooked food, which has passed through a layer of foam during removal from the cooker, also becomes a consideration. It then becomes time to shut down the cooker and change the oil. However, if foaming can be prevented, then the oil would be useable over a longer period.

The "foam" is primarily stabilized bubbles of steam which result from the vaporization of water that is either contained within the food being cooked or, in the case of frozen foods, attached to the food in the form of ice. The foam is stabilized by interfacially active (surfactant like) molecules in the oil. This implies that as the oil ages, in terms of use, the amount of interfacially active materials present increases. This is, in fact, the case. During the cooking process, interfacially active materials are often extracted from the foods being cooked. Many fish proteins and potato starches, for example, are highly interfacially active. Also, at cooking temperatures, which are typically 175° to 200°C (350° to 400°F), interfacially active molecules may be formed due to oxidation, hydrolysis, and/or polymerization reactions involving the oil itself.

In order to counteract the ability of such interfacially active materials to stabilize the bubbles of steam, and thus to counteract foam formation, molecules known as "defoamers" or "anti-foamers" can be added to cooking oils. Such molecules are interfacially active in their own right. However, they provide little stabilization for the oil/steam interface. By adsorbing to developing oil/steam interfaces (bubbles) they can displace stabilizing molecules and thus prevent foam formation. However, the focus of this note is not to provide a detailed discussion of foam stability and defoamers. Such discussions are provided elsewhere.[i,ii,iii]

The primary purpose of this note is to introduce a scientific technique which can be used to quantify increases in the foam stabilization ability of a cooking oil as a function of the oil's used lifetime. The technique provides cooking oil manufacturers with the ability to research the effects of defoamers and other additives on the usable lifetime of their oils in a straightforward, quantitative manner.

However, if cooking oils are not your interest, don't throw this note away quite yet. There is also an underlying and much more universal message in these pages. It is that dynamic tensiometry (tensiometry on interfaces which are not at thermodynamic equilibrium) can, in certain situations, be used to solve problems that are impossible to solve by static (equilibrium) tensiometry. We at KRÜSS believe that it is important for everyone involved in surface science to understand this concept so that they may make informed chooses concerning their instrument needs, and design experiments which provide them with the maximum amount of useful data. The cooking oil system discussed here is an excellent example of a system for which dynamic tensiometry techniques can achieve understanding which static tensiometry techniques cannot provide.

The dynamic technique employed in this work was drop volume interfacial tensiometry. The principle of drop volume interfacial tensiometry is that the interfacial tension (the energy per unit area necessary to expand the region of contact) between two immiscible liquids can be determined from a balance of the forces which act on a drop of one of the liquids suspended in a continuous phase of the other liquid. Much of the credit for the development of this concept is attributed to Tate[iv] who more than a century ago introduced the equation:

$$\gamma = \frac{V_D \, \Delta\rho \, g}{\pi \, d}$$

where γ = the interfacial tension between the liquids, V_D = the volume of the drop, $\Delta\rho$ = the difference in density between the drop liquid and the continuous liquid, g = gravity, d = the diameter of the tip on which the drop is suspended, and π has its standard mathematical meaning.

Since it is a balance of the forces acting on a drop in the upward and downward directions, this form of Tate's equation only applies to a drop on a thin walled capillary tip which is precisely at the volume required for spontaneous detachment. See figure 1, which is a schematic representation of a drop formed on a syringe tip in a drop volume experiment.

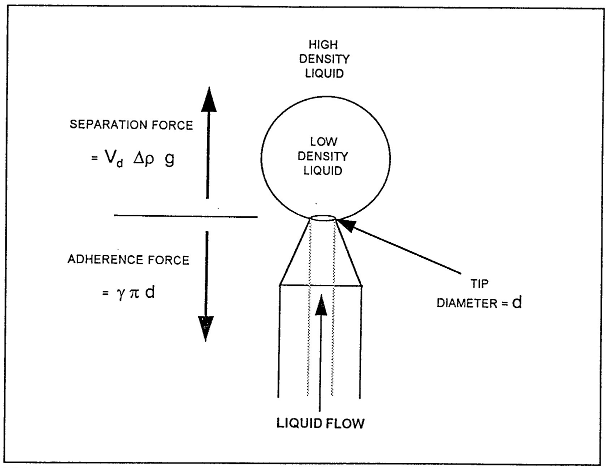

Figure 1

Assume that the drop in figure 1 is formed on a proper capillary and has the precise volume at which Tate's law applies. If the drop had any more volume, the separation force would overcome the adherence force and the drop would detach from the tip and rise through the continuous phase. If the drop had less volume, the adherence force would be greater than the separation force and the drop would not spontaneously detach.

Please note that this description has focused on the lower density liquid being the drop phase and a higher density liquid being the continuous phase. The KRÜSS Drop Volume Tensiometer, DVT-10, can be operated either in this configuration or in the opposite configuration, wherein the higher density liquid is the drop phase. This "opposite" configuration is analogous in terms of the Tate's law equation except that the tip is pointed downward into the less dense, continuous phase. The adherence force then acts in the upward direction and the separation force acts in the downward direction.

An examination of Tate's equation shows that, for a given experiment, all values other than the volume of the drop and the interfacial tension are constants. Therefore, by pumping liquid at a fixed flow rate through the tip and detecting the volume of each drop at its point of detachment, the interfacial tension between virtually any pair of immiscible liquids can be measured. The KRÜSS Drop Volume Tensiometer DVT-10 operates on this principle. The system employs a precision syringe pump and a specially designed tip which precisely controls droplet formation and eliminates the need for Tate's law correction factors. Drops are grown at various rates on the tip and their detachment from the tip is detected by an infrared LED/photodiode device. Resultant values of interfacial tension are calculated by the DVT-10 (one for each drop produced). Collection of this data using a personal computer with DVT-10 software facilitates data analysis.

The precision tip is very much the key to the whole system. Historically, drop volume tensiometry has been hampered by the need to use empirical correction factors in combination with the Tate's law equation. These correction factors account for, among other things, the possibility of incomplete droplet detachment from the tip during experimentation. The most pleasing, and therefore widely used, sets of these empirical correction factors were developed by Harkins and Brown[v] and Lando and Oakley[vi]. The bulk of the current scientific literature on drop volume tensiometry relies heavily on these somewhat ambiguous correction factors. All of this makes the tip design on the KRÜSS DVT-10 drop volume tensiometer, which is technology that was originally developed by Kevin Hool at Dow Chemical, a radical breakthrough in tensiometry. Those interested in the historical aspects of drop volume tensiometry are encouraged to study the design of the DVT-10 tip in the KRÜSS DVT-10 brochure and the literature cited above. Table 1 of the DVT-10 brochure provides data which has been developed on pure liquids in support of the DVT-10 system.

What makes drop volume tensiometry a dynamic (non-equilibrium) technique is simply that the rate of droplet formation can be varied. For pure liquids that are truly immiscible, interfacial tension will be independent of the rate at which droplets are formed, because the interface between the two liquids will always be at equilibrium. For non-pure liquids, particularly ones which contain a substantial concentration of interfacially active materials, interfacial tension will generally decrease with decreasing rate of droplet formation. The reason for this is that the interface does <u>not</u> reach equilibrium within the time frame of the experiment. Figure 2 displays this concept in schematic format.

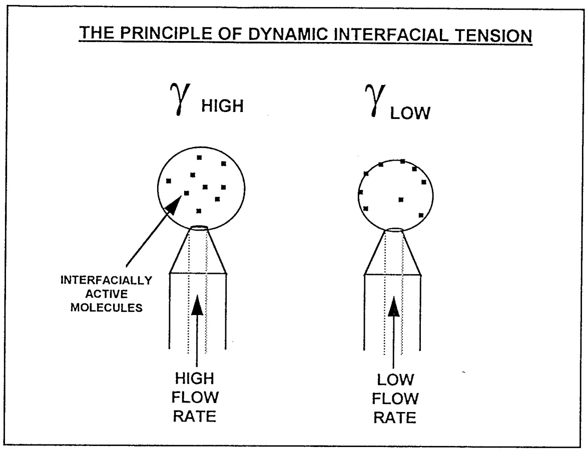

Figure 2

Consider the solid squares in this figure to be interfacially active molecules. If a drop volume experiment is performed at a "high" rate of droplet formation, then the rate of expansion of the liquid/liquid interface competes favorably with the rate at which the interfacially active material diffuses to and adsorbs at that interface. The interfacial tension will therefore be higher, when the droplet is ready for detachment from the tip, than it would be the case of an experiment performed at a "low" flow rate. At a "low" flow rate, the interfacially active material simply has more time to adsorb at the interface. The establishment of an equilibrium "layer" of interfacially active material at the liquid/liquid interface is thus accomplished to various degrees depending on the rate at which the drops are formed. The DVT-10 software allows dynamic interfacial tension data to be plotted as a function of liquid flow rate or as a function of drop age, so that the kinetics of this situation are clearly displayed.

This rather crude molecular level discussion leads to the following concept (which will turn out to become an integral part of our investigation of foam formation in cooking oils): <u>Different interfacially active materials can be expected to diffuse to and adsorb at a developing liquid/liquid interface at different rates.</u> For a simple system consisting of two liquids with a single type of interfacially active material contained in either of the liquids, the rate of adsorption of the interfacially active material to the interface will be governed by two factors: (1) the frequency of random (Brownian motion driven) collisions between the molecules of the material and the interface, and (2) the efficiency of such collisions in leading to adsorption. For this three component system it is possible, based on drop volume experimentation, to determine an "adsorption/diffusion coefficient" which characterizes the rate of adsorption of the interfacially active material at the liquid/liquid interface.[vii,viii] It has been suggested that adsorption/diffusion coefficients represent the mathematical product of an interfacially active material's Brownian diffusion coefficient and the material's efficiency of adsorption at the liquid/liquid interface.[ix] The mathematics involved in determining the adsorption/diffusion coefficient for an interfacially active material from drop volume experimentation are complex enough to be beyond the slope of this text. They have also not yet been applied to systems containing more than one interfacially active material.

However, it is evident that in systems containing multiple interfacially active materials there will be competition between the various materials for available space at interfaces. Further, the competition can be kinetic as well as thermodynamic. For example, imagine that there are two hypothetical materials (#1 and #2) competing for adsorption on a newly developed interface. Assume that material #1 will strongly bind to the interface such that the free energy of the entire system will be lower if it fills the available interfacial sites, even if it has to displace adsorbed material #2 to do so. However, also assume that material #1 diffuses slowly in solution relative to material #2. (It is a larger molecule and its Brownian diffusion coefficient is much lower.) What will happen to a fresh liquid/liquid interface developed in the presence of these materials? It will quickly adsorb material #2, and, therefore, over some finite interval of time it will exhibit characteristics of an interface containing material #2. After a substantial period of time (perhaps at thermodynamic equilibrium) the interface will be saturated with material #1 and have certain corresponding characteristics. How will a product which contains both material #1 and material #2 perform in applications which depend on interfacial properties? It depends, of course, on the time scale of the application relative to the time scale for the establishment of thermodynamic interfacial equilibrium.

Would static tensiometric measurements on such a product be expected to provide any insight into the products performance, if the product is used in the time frame over which the interface is dominated by material #2? No, static measurements will instead be very effective in characterizing an interface which is saturated by material #1 and, therefore, has little to do with the product's application. It will be shown that the cooking oil which is the subject of this note is an example of this type of system, albeit an even more complex one.

Experimental & Discussion

A soybean based cooking oil, containing defoaming additives that shall remain proprietary, was studied. Actual cooking tests suggested that, despite the defoaming additive, this soybean oil had a useable lifetime of only approximately 8 to 10 days under rigorous cooking conditions. Our initial theory was that the amount of interfacially active materials developed over this period of use became substantial enough to dominate the defoamer. In other words, the defoamer began to become the loser in the ongoing thermodynamic competition for adsorption sites at steam/oil interfaces. At periods of use less than about 8 days, the quantity of interfacially active material produced was not substantial enough to dominate the situation, but near this time the equilibrium shifted.

In investigating this initial theory, our first efforts focused on static surface tension measurements by Wilhelmy plate techniques. (For those who are unfamiliar which such techniques, KRÜSS would be happy to supply literature on the subject.) The idea was that if the interfacially active materials which develop during cooking actually competed, thermodynamically, with the defoamer additive for the steam/oil interface, then a similar competition would exist for the air/oil interface. In other words, static surface tension measurements on a series of oils, each having been previously used in actual cooking for a certain period, would reflect the development of the interfacially active materials by revealing that static surface tension was dependent on the period of use. A result that would not have been surprising might be that the static surface tension of the oil increases with period of use. This would have indicated that the interfacially active materials being developed were taking up adsorption sites at the air/oil surface thus displacing the defoamer. It then might have been possible to use static surface tensiometry as a research tool in the investigation of the effects of various defoaming additives on the oil properties. Static surface tensiometry could have acted as a guide to improved cooking oil formulation.

This, however, was not found to be the case. The following oil samples were tested by static surface tensiometry: unused oil, 4-day oil, 5-day oil, 8-day oil, 11-day oil, and 18-day oil. The results in figure 3 show no change in static surface tension with increased period of oil use

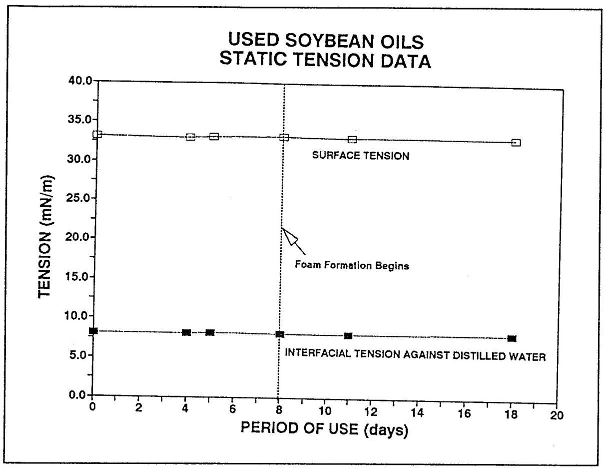

Figure 3

Especially considering that an unused oil was included in this testing, these results indicate that interfacially active materials developed during the cooking process do not at all compete with the defoamer additive for adsorption at the cooking oil/air surface, at least not in a thermodynamic sense. It is possible that the composition of the air/oil surface did change in a static (thermodynamic) sense, and yet this change went undetected by the surface tension measurements. This would be the case if the developed interfacially active materials replaced the defoamer at the surface and yet left the surface tension constant. For completeness of understanding this must be considered. It could explain why the oil foams during cooking for periods of use greater than 8 to 10 days. However, in reality, it is a trivial explanation. For this to actually occur, the developed interfacially active materials would need to fill adsorption sites at the air/oil interface in precisely the same manner as the defoamer (in order to keep the surface tension constant). This is extremely unlikely, since the defoamer and the interfacially active material can be expected to have radically different chemical structures.

Static surface tensiometry has thus lead to the conclusion that the nature of the air/oil interface is unchanged by the development of interfacially active materials during cooking oil use. The defoamer dominates the interface even after 18 days of oil use. This is, apparently, completely contradictory to the direct observation that the steam/oil interface is readily stabilized by some component of the cooking oil, after 8 to 10 days of oil use. Foaming does become a problem after this period of use. Two possible explanations for this contradiction exist.

The first is that the static air/oil surface is not a good experimental model for the steam/oil interface. If this is the case, then since steam is water in the gaseous state, the next logical room temperature experimental model would be the water/oil interface. Figure 3 also shows results of static interfacial tension studies between the series of oil samples discussed previously and water. These results were obtained using Du Nouy ring tensiometry. (KRÜSS will also provide those interested with a detailed explanation of Du Nouy ring based tensiometry, but as was the case for Wilhelmy plate tensiometry, such an explanation is beyond the scope of this text.) The results show that, in a static sense, the water/oil interface model is no better than the air/oil surface model was for investigating foam formation in this set of cooking oils. These static interfacial tension results are also not useful in predicting stabilized foam formation.

The second, and correct, explanation for static surface (and interfacial) tension results contradicting observations is quite simply that there is no contradiction. The key to investigating the behavior of this system is that it represents a kinetic rather than a thermodynamic problem. The added defoamer does, over the entire age range of oils studied, perform as it was intended, but only in a thermodynamic (static) sense. Regardless of the prior period of use of the oil, if an interface is established between air and the oil, or water and the oil, and allowed a period of equilibration the defoamer dominates the interface. The molecular architecture of the equilibrated interface, and therefore the tension at that interface, is independent of the quantity of interfacially active material that may have been developed during the oil's use. However, if a dynamic interface is established involving the oil, the nature of that interface is quite different.

Figure 4 shows the results of drop volume interfacial tension studies performed for the same set of oils against pure distilled water.

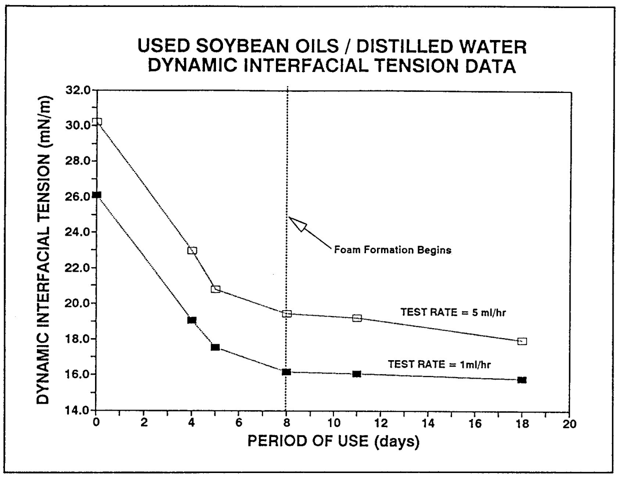

Figure 4

There are two sets of data in figure 4. One is for the tests performed at a flow rate of 1 ml/hr and the other is for tests performed at a flow rate of 5 ml/hr. These two flow rates correspond to formation times of approximately 50 seconds per drop and 10 seconds per drop, respectively, for these systems. Both data sets reveal the same trend. As the period of oil use increases, the dynamic interfacial tension decreases. It is known from static interfacial work (figure 3) that at equilibrium, the interfacial tension between each of the oils and water is the same (approximately 8.1 mN/m) with the defoamer dominating the interface. All of the dynamic interfacial tensions obtained are, of course, greater than 8.1 mN/m since the interfaces are not at equilibrium. The differences between the oils which are reflected in this dynamic data must be due to the development of interfacially active materials during the oil's use. The longer the interval of use, the lower the dynamic interfacial tension is at any given rate of droplet formation. Also, note that as drop formation rate is increased from 1 ml/hr to 5 ml/hr, the interfacial tension for each sample oil increases. This is the result expected from giving the active materials in the oil less time to diffuse to and adsorb at the interface.

The data indicate that the competitive situation, between the defoamer additive in this soybean oil and the interfacially active materials which are generated during the oil's use, is exactly the same as that of the hypothetical system (for interfacially active materials #1 and #2) which was described in the Background section. Static (thermodynamic equilibrium) tensiometry reports that the defoamer dominates for well-aged interfaces. Dynamic (non-equilibrium) tensiometry shows that the concentration of developed interfacially active materials has a direct impact on the nature of the oil/water interface. This can only mean that at least some of the interfacially active materials which develop during the cooking process diffuse to the oil/water interface faster than the defoamer can.

A further aspect of the drop volume data, which rather strongly suggests that the dynamic oil/water interface is a good model for the oil/steam interface in a cooking process, is that each of the curves in figure 4 generally approaches a steady value of interfacial tension which is relatively independent of further increases in period of use. This occurs after about an eight day use period, which is (probably not coincidently) the same period after which foam formation begins to become a problem for the oil. This phenomena could possibly be due to a critical concentration of interfacially active material being reached after approximately eight days, which in turn allows for some critical level of interfacial saturation to be met.

Conclusions

This application note has served three purposes. It has explained drop volume interfacial tensiometry and how it functions as a dynamic technique for evaluating the adsorption of materials to liquid/liquid interfaces. It has shown an example of a surface/interfacial chemistry problem that cannot be solved by using static tensiometry, but can be solved using dynamic tensiometry. And, it has used a cooking oil problem to sustain the discussion. In the process, it has come very close to developing a full understanding of foaming in the particular cooking oil studied.

Two issues remain regarding the cooking oil, however, which require a few words of conclusion. These issues are: (1) In hindsight, at least, does it make intuitive sense that the foaming problem in the cooking oil is a kinetic rather than a thermodynamic interfacial problem? and (2) Does the interfacial tension data that has been produced suggest a means of formulating a cooking oil with a longer usable lifetime?

Fortunately, the answer to both questions is yes. Anyone who has watched a hot oil cooker in operation has undoubtedly observed that the bubbles formed during cooking pass through the oil to the surface quite rapidly. Therefore, it seems reasonable that there is little time for the adsorption of interfacially active materials to the developing steam/oil interfaces. Further, once the bubbles reach the surface and become part of the "froth", they are no longer exposed to the bulk of the oil. The steam/oil interface is simply a thin film between each of the bubbles. It seems logical that, in this situation, exchange of the interfacially active material at the steam/oil interfaces would be slowed dramatically. In other words, it is more "difficult" for the defoamer molecules to even get to the stream/oil interface to displace the other interfacially active materials, and thereby cause bubble collapse once the bubbles have separated from the bulk of the oil. This undoubtedly causes substantial increases in the stable lifetime of the foam. Obviously, at the point when bubbles are being formed much more rapidly than they are collapsing, foaming becomes a problem.

This non-equilibrium explanation is further supported by the observation that, in general, if the hot oil cooker is turned off and the oil is allowed to sit, the foam will eventually completely collapse. The molecular explanation for this, based on the data presented here, would be that the defoamer eventually acts to displace the other interfacially active materials from the interfaces and provides for the collapse of the foam. However, in reality this is probably only one of the factors controlling collapse of the foam. Other factors surely include film drainage and condensation of the steam once the temperature of the oil begins to decrease. The findings reported here suggest that the useable lifetime of the soybean oil under study would be improved by changing defoamers. A defoamer should be sought which, not only thermodynamically, but also kinetically dominates the interfacially materials produced during cooking in terms of adsorption to steam/oil interfaces. Finding or synthesizing such a defoamer may not be an easy task. However, we would suggest that dynamic interfacial tension experimentation could be of assistance in this quest.

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