Interfacial Tensions of Vegetable Oil/Water Systems: Effect of Oil Purification

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Methods were developed to determine the interfacial tension (IT) of vegetable oil/water systems as a function of time, and to remove interfacially active contaminants from commercial vegetable oils. Interfacial tensions between commercial vegetable oils and water decreased with time due to the presence of impurities. Interfacial tensions of purified oils against water were substantially higher than those reported in the literature, and remained unchanged with time, thereby indicating the absence of surface chemical impurities in the oil. The lowering of IT in the case of commercial oils was ascribed to the presence of mixtures of monoglycerides.

Interfacial tension (IT) is an important property of liquid/liquid systems. It serves as an index of the relative forces of intermolecular attraction and as a measure of the free energy per unit area of the interface, and also, provides information about the emulsifiability. Food emulsions are of particular interest to us. Vegetable oils (triglycerides) constitute the oil phase in such emulsions. In order to gain a fundamental understanding of food emulsions, it is important to have a knowledge of the IT between vegetable oil and water.

In order to understand the absorption behavior of a pure emulsifier and the competitive effects between emulsifiers at the vegetable oil/water interface, it is necessary to make sure that the system is free from surface active impurities. Vegetable oils consist of mixtures of triglycerides. However, small amounts of mono- and diglycerides, free fatty acids, and phospholipids may be present depending on the source and processing conditions. Refined oils are usually free from phospholipids, but may contain small quantities both of highly surface active monoglycerides and less surface active diglycerides.

One of the first studies of interfacial tension between vegetable oil (castor oil) and water was reported by Lord Rayleigh in 1890 (1). Despite the importance of such studies to food technology, there have been a limited number of investigations on this subject (2–8). Unfortunately, wide discrepancies exist between the results of different investigators and, in many cases, information on the characteristics such as source, processing conditions, impurities, degree of refining, etc., of the oils under investigation are missing. The discrepancies could be caused by the presence of impurities and/or differences in the methods of measurement. It should be pointed out that many investigators in the past have employed the du Nouy ring method because of its operational simplicity, although it suffers from the problems of ill-defined contact angle and rate of withdrawal of the ring (9).

Surface active impurities interfere with the adsorption of the molecules under investigation and can lead to erroneous results. Therefore, a method was developed to obtain vegetable oils free from surface active contaminants and also to measure the oil/water interfacial tensions as a function of time. Such oils can serve as reference oils for studying the adsorption characteristics of pure emulsifiers as well as to study the competitive effects between them.

MATERIALS AND METHODS

Soybean oil and corn oil were obtained from Kraft Food Ingredients Group, canola oil was obtained from CSP Foods, Canada, and olive oil (Bartolli, Product of Italy) from a local super market. Monopalmitin, monoolein, monolinolein, and dilinolein (all >99% pure) were obtained from Nu-Chek-Prep. Florisil (100–200 mesh) and silica gel (100–200 mesh) were procured from J.T. Baker Chemical Company and used as received. Water used in this study was of HPLC grade (American Burdick & Jackson) and had an IT of 51.0 dyn/cm against purified n-hexane. This value is in excellent agreement with that reported in the literature (10), thus indicating its high purity. Therefore, the water was used as received.

Microscope cover glasses (Corning) were employed as the Wilhelmy plate to sense the pull due to the IT. It is important that we either maintain zero contact angle between the plate and water (complete wetting of the plate) or have an accurate knowledge of the contact angle. It is relatively easy to fulfill the first condition by sandblasting the plate. Gaonkar and Neuman have examined the wettability of smooth and sandblasted Wilhelmy plates by an autoradiographic technique. They demonstrated that the smooth plates are not completely wetted by water while the sandblasted ones are (11). Hence, the Wilhelmy plate used in this investigation was sandblasted with #5 Al_2O_3 (S.S. White, Airbrasive Powder). The Wilhelmy plate and glassware were cleaned by soaking them in a mixture of sulfuric acid and Nochromix (Godax), washing them with copious amounts of distilled water, and finally rinsing them with HPLC water.

Purification of oils. As will be seen later, the IT of commercial vegetable oils with water was found to decrease with time, suggesting the presence of impurities in the oils. They were purified by percolating them through a column packed with Florisil. About 40 g of Florisil was needed per liter of vegetable oil to completely remove the higher levels of impurities. Silical gel and charcoal were less effective in removing the impurities.

Determination of IT. For the present study we used a method where the interfacial area remained constant during the time of the measurement. One such method is the Wilhelmy plate method. This method was selected because of its simpler experimental design, faster operational capability, more straightforward data manipulation, and ease of automation.

An interfacial tensiometer similar to the one described by Gaonkar and Neuman (12) was constructed to obtain data on the IT of vegetable oil/water systems. In the present set-up, however, acquisition and analysis of the data were done with an I.B.M. personal computer and μMac System (Analog Devices). Such automation led to an increase in the productivity of the experimenter and enabled us to perform overnight runs.

In the actual procedure, 100 ml water was taken in a Pyrex cell, thermostatted to 20°C, and the clean Wilhelmy plate was hung by means of a stirrup to a thin platinum wire, which in turn was hooked to the B arm of a calibrated Cahn electrobalance. The stirrup was adjusted so as to make the bottom edge of the plate parallel to the air/water interface by looking at its mirror image. Then the surface of the water was sucked and the cell was raised so that the distance between the bottom edge of plate and the cleaned air/water interface was about 1 mm. An electrical laboratory jack (Lab-line) and a precision motorized vertical translator (Oriel) were employed for the coarse and fine adjustments, respectively.

A computer program was written so that on giving a command to start a run the cell rises slowly until the bottom edge of the plate just touches the air/water interface, then rises another 5 mm. This brings the bottom edge of the plate to 5 mm below the air/water interface. Then, 100 ml oil (pre-equilibrated to 20°C) is added carefully to the cell. Soon after the complete addition of the oil, the cell lowers 5 mm so that the bottom edge of the plate is at the oil/water interface. Then the readings of pull and IT commenced as a function of time. Interfacial tensions were calculated using the equation IT=mg/P, where m is the mass of the water meniscus supported by the plate, g is the acceleration due to gravity (g=980.3 cm/sec^2), and P is the effective periphery of the plate that was obtained by calibrating the plate with purified n-hexane/water and n-heptane/water system for which the interfacial tensions are known precisely.

RESULTS AND DISCUSION

Curves A, B, C, and D in Figure 1 show that the IT of vegetable oils against water decreases significantly with time, thereby indicating the presence of interfacially active contaminants in the oils. Residual contamination in olive oil (curve A) and soybean oil (curve B) seems to be greater than that in canola oil (curve C) and corn oil (curve D). If we use commercial oils in the investigation of adsorption characteristics of pure emulsifiers, the impurities present in the oil may interact with the emulsifier molecules under investigation and lead to erroneous results. Therefore, the oils were purified as mentioned earlier. The results of the IT for purified oils are also depicted in Figure 1 (curves E, F, G, and H). It is noteworthy that the values of IT for purified oils are considerably higher (in the vicinity of 31 dyn/cm) than those reported in the literature (2,7,8) and that the IT remained unchanged with time. Further percolation of the purified oil through a column of Florisil does not seem to increase the IT substantially. The equilibrium values of IT for purified oils are 30.2 dyn/cm for corn oil (curve E), 30.7 dyn/cm for soybean oil (curve F), 31.0 dyn/cm for olive oil (curve G), and 31.5 dyn/cm for canola oil (curve H). However, the equilibrium value of IT for deacidified olive oil is reported to be 24.17 dyn/cm (8), which is much lower than the value we obtained. Although the distribution of fatty acid residues in vegetable oils are different, they tend to yield similar IT values. This observation is in agreement with that of Fisher *et al.* (8), but is in marked contrast with the findings of earlier workers (2,5,7,13). In the case of hydrocarbon oils, however, Jasper *et al.* (14) have shown that the structure of the hydrocarbon chains contributes a little to the hydrocarbon oil/water interfacial tensions (14).

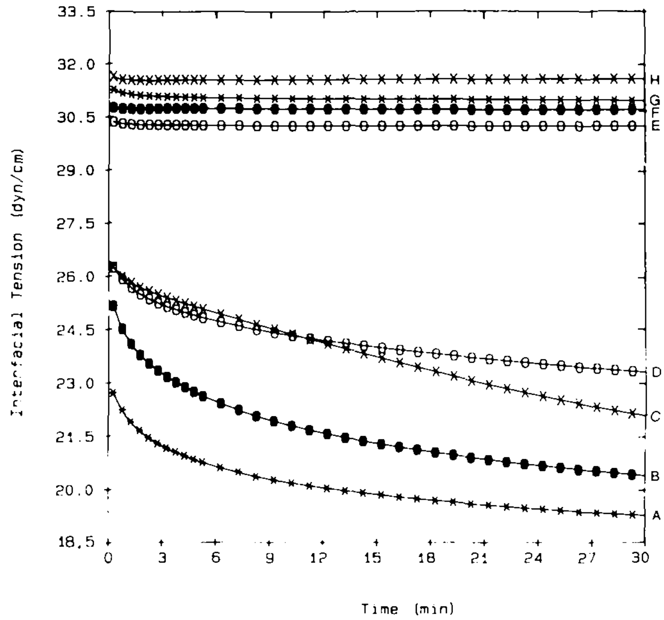

FIG. 1. Interfacial tensions of commercial (A) olive oil, (B) soybean oil, (C) canola oil, (D) corn oil, and purified (E) corn oil, (F) soybean oil, (G) olive oil, and (H) canola oil against water as a function of time at 20°C.

Effect of Contaminants. The role of probable contaminants on the IT of purified soybean oil/water system was investigated by reconstituting the commercial soybean oil. Chemical analyses confirmed the absence of phosphatides and presence of 0.1% free fatty acids in both commercial and purified soybean oils. Although as little as 0.2% solution of palmitic acid lowered the IT between n-hexane and water from 51.0 dyn/cm to 20.0 dyn/cm, it did not lower the IT of the purified soybean oil/water interface. Thus, fatty acids, although present, do not exhibit interfacial activity at the vegetable oil/water interface. The other contaminants in commercial oils were mono- and diglycerides at levels of <0.1% and 1.7%, respectively. Purified soybean oil, on the other hand, contained 0.9% diglycerides and no monoglycerides.

Three major fatty acid residues that are present in soybean oil as triglycerides are linoleic acid, oleic acid, and palmitic acid. Because the linoleic acid residue is predominant in soybean oil, the effect of small quantities of mono- and dilinoleate on the IT of the purified soybean oil/water systems was studied. The results are presented in Figure 2, which also suggests that in addition to linoleates some other fatty acid residues contribute to the IT lowering in commercial

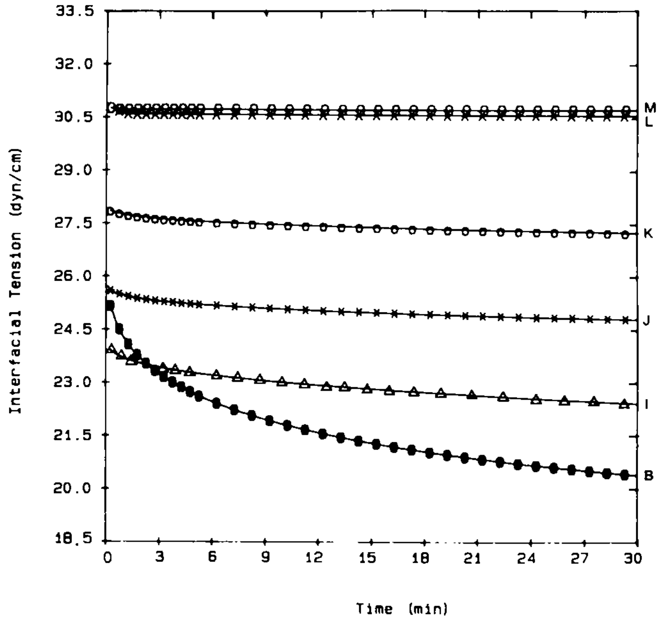

FIG. 2. Effects of monolinoleate (ML), dilinoleate (DL), and their mixtures on the interfacial tension of purified soybean oil against water as a function of time at 20°C; (B) commercial oil, (I) 0.1% ML + 0.1% DL, (J) 0.075% ML, (K) 0.375% ML + 0.375% DL, (L) 0.075% DL, and (M) 0% ML + 0% DL.

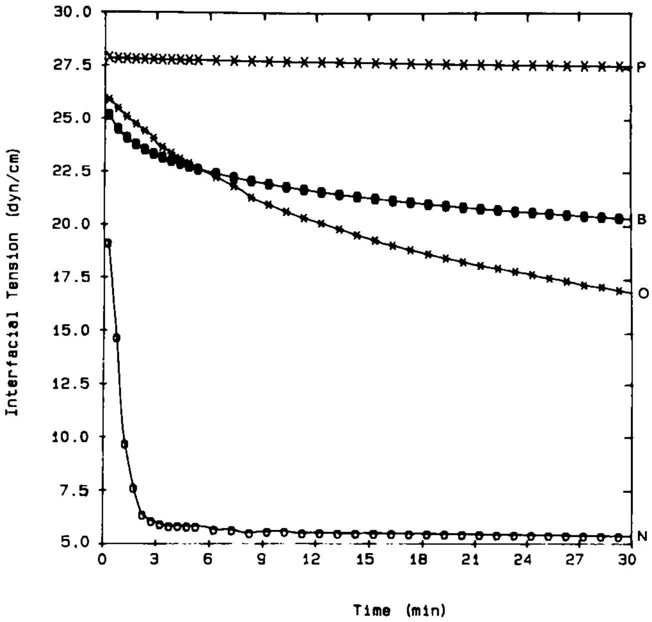

FIG. 3. Effects of mixtures of monopalmitate (MP), monooleate (MO), and monolinoleate (ML) on the interfacial tension of purified soybean oil against water as a function of time at 20°C; MP:MO:ML::3:5:12; Concentration of monoglycerides=(N) 0.075%, (O) 0.055%, and (P) 0.037%.

oils. Also, it shows that the IT decreases with an increase in the concentration of the monooleate, and that the dilinoleate by itself is virtually inactive (curve L).

Because the monoglycerides are the active species and other prominent fatty acid residues present in soybean oil are oleic acid and palmitic acid, it was thought worthwhile to add appropriate amounts of monolinoleate, monooleate, and monopalmitate to purified soybean oil. This was done to determine whether we could obtain behavior analogous to that of the commercial soybean oil. Figure 3 depicts the effects of the mixtures of these three monoglycerides on the IT versus time behavior of purified soybean oil/water interface. The ratio between monolinoleate, monooleate, and monopalmitate was held constant (3:5:12) while the total concentration of monoglycerides was changed. Interfacial behavior close to the commercial soybean oil was displayed by 0.055% mixed monoglycerides.

The results suggest that the lowering of the IT in commercial vegetable oil/water systems is due to the presence of a mixture of monoglycerides. This observation is in agreement with the results of the chemical analyses which were discussed earlier. Because the IT is very sensitive to trace contaminants, it can be an excellent tool to study the oxidative stability of vegetable oils. It should be emphasized that the purified oils are ideal for investigating the interfacial behavior of pure emulsifiers and to study the competitive effects. Also, if we employ purified oils in basic research it is not critical to know about the source, processing conditions etc., of the oils or to worry about batch-to-batch variations which exist in commercial oils.

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