Interactions Between Fat Crystal Networks and Sodium Caseinate at the Sunflower Oil–Water Interface

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ABSTRACT: A Couette-type torsion wire surface shear viscometer was used to measure the apparent interfacial shear viscosity of pH 7 (I = 0.05 M) buffered solutions of sodium caseinate in contact with sunflower oil. The sunflower oil contained 1% fat crystals in either the β or β′ polymorphic form, or was crystal free. In all cases, the fat crystals increased the interfacial shear viscosity synergistically, with the β′ crystals causing the biggest increase. Substituting the protein for a small-molecule surfactant (Tween-40) showed that this was not simply due to the protein lowering the interfacial tension. Sedimentation studies of the different fat crystal slurries suggested that the extent of the interfacial shear viscosity increase was related to the strength of crystal-crystal interactions in the oil phase. It seems likely that when protein is present at the interface, it fixes the adsorbed layer of fat crystals to the cross-linked protein film at the interface. When this film was sheared, the strength of the crystal-crystal interactions in the oil phase became important. However, when Tween-40 was in the aqueous phase instead of the protein, the crystal-crystal interactions were not relevant, presumably because the Tween-40 interfacial film simply flowed around the adsorbed crystals
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KEY WORDS: Fat crystal polymorphism, interfacial rheology, interfacial viscosity, protein, sodium caseinate, sunflower oil, surface viscosity, triglyceride crystals, tristearin crystals, Tween-40.

In food emulsions, the presence of triglyceride crystals in the oil phase, or at the oil–water interface, can have a dramatic effect on droplet coalescence. Depending on the nature of the continuous phase, triglyceride crystals can either decrease (oil-in-water) or increase (water-in-oil) coalescence stability through Pickering stabilization (1). The situation is more complex in mixed emulsions and aerated emulsions, especially when proteins are present. In food systems, there is a large difference in the behavior of aerated emulsions such as cake batters and bread mixes, depending on the polymorphic form of the fat crystals. When the fat is in the β′-form, the incorporated air bubbles tend to be much smaller than when the crystals are in the β-form. This results in a finer product with a larger air volume (2,3). This has been attributed to the much smaller size of β′-crystals in food systems, which allows them to arrange themselves around the surface of bubbles more easily than the larger β-crystals (4).

In aerated emulsions, proteins are thought to adsorb to the surfaces of any fat crystals adsorbed to the air–water interface (5). It is likely that proteins would also adsorb to fat crystals at an oil–water interface. Such interactions between proteins and fat crystals in the interfacial region would be expected to have an effect on the mechanical properties of the interfacial film, and hence on coalescence stability. Interfacial viscosity of a protein film is a sensitive probe of composition, structure and interactions at the interface, as well as any associated interactions extending into either bulk phase (6).

While interfacial dilational viscosity is more important with small-molecule surfactant films (7,8), with protein films the case is not so clear-cut (9). For protein films at oil–water interfaces a number of workers have suggested that shear rheological properties appear to influence the rate of droplet coalescence (9–13). Martinez-Mendoza and Sherman (14) found that under shear conditions, both the interfacial elasticity and interfacial viscosity could be directly related to drop coalescence rates in corn oil-in-water emulsions prepared with different water-soluble meat protein/monoglyceride/diglyceride ratios. Dickinson *et al.* (9) found that lysozyme, κ-casein and β-casein also showed a positive correlation between interfacial shear viscosity and coalescence stability with a hydrocarbon oil phase.

In the case of sodium caseinate and a purified triglyceride oil (olive oil) Kiosseoglou (15) found that the film was purely viscous. It seems that some surface-active lipids are required for any interfacial elasticity to develop in this system. Due to the similarities between triglyceride oils, we can expect that sodium caseinate films at a purified sunflower oil interface will also be purely viscous. Hence interfacial shear viscosity is the parameter chosen in this study.

At the planar oil–water interface, we have previously shown that the presence of tristearin crystals in an *n*-tetradecane oil phase causes a synergistic increase in the interfacial shear viscosity when proteins are present in the aqueous phase (16,17). In an effort to move to progressively more applied systems, we have also demonstrated that similar results are obtained with a purified sunflower oil phase (16,18). The increase in interfacial shear viscosity when crystals and proteins were both present at

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the interface was not a result of the proteins lowering the interfacial tension, and hence changing the adsorption behavior of the crystals. Experiments where a small-molecule surfactant, Tween-40, was substituted for the protein as the surfactant in the aqueous phase at matched interfacial tensions showed that this was only a minor factor (16).

In these studies, the tristearin crystals were always present in the thermodynamically stable β-polymorphic form, whereas in food systems, the fat crystals are usually complex mixtures which are crystallized in the β′-form. However, to the knowledge of the authors, only the β-form of tristearin has been crystallized from any solvent (19). α-Tripalmitin has been found to transform rapidly to the β-form in both triolein (20) and butterfat (21), confirming that triglyceride oils act as solvents for tripalmitin and cause a transformation to the thermodynamically stable β-form. Since tripalmitin and tristearin exhibit similar polymorphic behavior, it seems likely that tristearin would also transform to the β-form regardless of the history of the crystals. In order to study the effect of different crystal polymorphs, an alternative source of fat crystals was sought. 1,3-Dipalmitoylstearin (PS_tP) is unusual in that it has been isolated in both the β and β′-forms from solvent (22–24) and hence may be stable (or metastable) in both forms when suspended in the oil phase. This has subsequently been confirmed for both pure PS_tP and a hydrogenated palm-oil mid-fraction (HPMF) which contains approximately 80% PS_tP (25).

The present work aims to investigate the relative increase in interfacial shear viscosity due to fat crystals in the oil phase in both β and β′-polymorphic forms, using the sodium caseinate/sunflower oil system. In addition to the interfacial shear viscosity, the sediment density of the oil slurry and the effect of crystal mass were investigated.

MATERIALS

Tristearin (glycerol trioctadecanoate) was purchased from Sigma Chemical Company (Poole, United Kingdom), product number T-1521 (lot 11H8353). Tristearin was recrystallized once from toluene and then once from diethyl ether. Analysis for non-triacylglycerols was by silica HPLC/laser light scattering using 12-OH octadecanol as internal standard. Species are separated on the basis of polarity. Polar species present were: oxidized triglycerides and/or free sterols (400 mgkg^{-1}); monoglycerides, diglycerides, and sterol esters not detected (below 200 mg kg^{-1}). Tristearin was stored in a sealed bottle at –18°C.

HPMF was provided by Unilever Research Colworth Laboratory (Bedford, United Kingdom). It was recrystallized once from toluene/ acetone and then once from diethyl ether before use. Polar species present were: oxidized triglycerides and/or free sterols (400 mg kg^{-1}); diglycerides (400 mg kg^{-1}); monoglycerides and sterol esters not detected (below 200 mg kg^{-1}). HPMF was stored in a sealed bottle at –18°C.

Sunflower oil was mixed with hexane and passed through a silica column, and the hexane was removed *in vacuo* prior to use. The remaining levels of polar species prior to use were: oxidized triglycerides (epoxides + peroxides) plus free sterols (1.0% w/w); diglycerides (180 mg kg^{-1}); monoglycerides not detected; nonpolar sterol esters (0.5 % w/w).

Sodium caseinate powder (spray bland) was from De Melkindustrie (Veghel, The Netherlands). Typical analyses provided by the manufacturer show 5.2% moisture, 94.5% protein (N*6.38) on a moisture free basis, 0.8% fat, 0.2% carbohydrates, 0.05% calcium, and 1.4% sodium.

Tween-40 (polyoxyethylene[20]sorbitan monopalmitate) was from ICI Specialty Chemicals (Everberg, Belgium).

AnalaR grade buffer salts, potassium dihydrogen orthophosphate and disodium hydrogen orthophosphate were obtained from BDH Chemicals (Poole, United Kingdom). Before use they were dried at 130°C for 2 h and stored over silica gel.

Water used throughout the study was deionized by reverse osmosis (Elgastat UHP, United Kingdom) and had a minimal resistivity of 18 MΩ m.

All glassware was cleaned as described previously (17).

METHODS

Interfacial shear viscometer. A Couette-type torsion wire interfacial shear viscometer was used as described previously (16). The torsion wire had a torsion constant of 1.86×10^{-7} N m rad^{-1}, the water-jacketed dish was held at 20 ± 0.2°C and was rotated at a speed of 1.25×10^{-3} rads^{-1}. Interfacial shear viscosities were calculated using the formula:

$$\eta_s = \frac{\tau}{4\pi\omega}\left(\frac{1}{R_1^2} - \frac{1}{R_2^2}\right) \quad [1]$$

where η_s = interfacial shear viscosity (N m^{-1} s), R_1 = radius of the disc (m), R_2 = radius of the dish (0.0675 m), ω = relative angular velocity (rad s^{-1}) and τ = torque due to film (N m). For each experiment presented, results are the average values of two independent runs. The average range between duplicate results is 3 mN m^{-1} s.

Interfacial tension measurements were performed as described previously (16).

The polymorphic form of the fat crystals was determined using powder X-Ray diffraction crystallography. The instrument was a Philips (Cambridge, United Kingdom) PW1720 X-ray generator with a vertical goniometer. CuK_α radiation (λ = 1.5418 Å, 35 kV, 35 mA) was used with an NiK_β filter, or CoK_α radiation (λ = 1.7902 Å, 30 kV, 30 mA) was used with an FeK_β filter. The samples were scanned from d-spacings of 3.6 to 5.0 Å.

Oil slurry preparation. Where fat crystals were formed directly in the oil phase, tristearin (0.6 g) or HPMF (0.6 g) was weighed into a 100 mL conical flask, and 60 mL of sunflower oil was added. The slurry was heated on a steam bath for 15 min, during which time the fat crystals dissolved. The oil solution was then placed in a water bath controlled to 20°C and left to recrystallize overnight. The slurry was swirled in the

morning and left at 20°C for several hours until required. Crystal-free oil phases were treated in the same manner.

For experiments using specific fat (HPMF) crystal polymorphs, a different procedure was followed. The fat was crystallized from *n*-hexane (99%, Lancaster, Morecombe, United Kingdom). Different speeds of crystallization altered the polymorphic form of HPMF produced. HPMF is stable in the β′-form, and as expected, slow crystallization from *n*-hexane at room temperature produced β′-HPMF (XRD: d = 3.78, 4.02, 4.20, 4.33). Rapid crystallization (using an ice/water slurry and swirling the conical flask) produced β-HPMF (XRD: d = 3.73, 3.86, 4.58). β-HPMF was found to be unstable if left in the *n*-hexane for even a few minutes, so the crystals were isolated by filtration immediately. Both β-HPMF and β′-HPMF crystals were stable in sunflower oil for several days.

Oil slurries of these *n*-hexane crystallized fats were formed by mixing the particular fat crystals required with the sunflower oil. The sunflower oil had previously been heated on a steam bath and allowed to cool to 20°C before mixing with the crystals. Any clumps of crystals were broken up as much as possible with a stirring rod.

Aqueous phase preparation. In all cases, the aqueous phase was a phosphate buffer solution (pH 7.0, I = 0.05 M). Solutions were made up using a two-step procedure as described previously (16). For sodium caseinate solutions the final concentration was 1.0×10^{-3} % (wt/vol). In order to mimic the interfacial tension profile of the sodium caseinate solution against the purified sunflower oil, a Tween-40 concentration of 1.3×10^{-4} % (wt/vol) was chosen. When solutions were not in use, they were held in a water bath controlled at 20 ± 0.5°C. All solutions were made up fresh on the day that an experiment was started, and were degassed in an ultrasonic bath for 30 min before use.

Oil slurry sediment densities. All slurries were prepared as for the interfacial shear viscosity experiments and left in a waterbath at 20°C for 24 h to ensure complete crystallization. As close as possible to the same time, all slurries were transferred to measuring cylinders, and the position of the descending phase boundary was monitored over time. The experiment was left for 300 h, by which time a final sediment density was recorded.

RESULTS AND DISCUSSION

There were two sources of β-crystals (hexane-crystallized HPMF and sunflower oil-crystallized tristearin) and two sources of β′-crystals (hexane-crystallized HPMF and sunflower oil crystallized HPMF). All four crystal types showed different morphologies (Fig. 1), despite the fact that both were fully saturated triglycerides. The interfacial tension of the 1×10^{-3} % wt/vol) sodium caseinate solution after 24 h was 14.2 mN m^{-1}, compared to 14.3 mN m^{-1} for the Tween-40 solution at a concentration of 1.3×10^{-4} % wt/vol). In fact, the interfacial tension profiles of the two solutions are well matched over the entire time scale of the experiments, as can be seen in an earlier publication (16).

To test the effect of polymorphic form on the interfacial shear viscosity, a fat mixture which was principally 1,3-dipalmitoylstearin (PS_tP) was used. PS_tP is thermodynamically stable in the β′-form, and can be crystallized from *n*-hexane to give either the β′-form or the β-form, depending on the crystallization conditions employed (23,26). The β-PStP could be formed by rapid crystallization from *n*-hexane, but it had to be isolated immediately to avoid conversion to the β′-form. Most importantly, β-PS_tP was stable against transformation to the β′-form in purified sunflower oil for several days. The fat mixture was an HPMF which was approximately 80% PS_tP, and displayed identical polymorphic behavior.

Figure 2 shows the increase in interfacial shear viscosity of the four different fat crystal slurries, over the sum of the protein at the interface without crystals, and the crystals in at the interface without protein, but with the same interfacial tension as exhibited by the protein. Both the polymorphic form and the method of crystallization affects the extent by which fat crystals increase the interfacial shear viscosity. The largest increases were found for the two β′ slurries. However, even these results were quite different from each other. A possible explanation for the differing extents of the increase were found in the sediment densities of the various oil slurries.

The bulk viscosity of suspensions is closely related to inter-particle interactions. The behavior of a concentrated flocculated dispersion in shear flow correlates strongly with the sedimentation rate (27–29). According to Tambe and Sharma (30), in solids-stabilized emulsions there must be some level of particle interactions between the solids in the continuous phase and at the interface. This may be related to changes in the interfacial rheology of the system due to the particles at the interface (31). Since interfacial shear viscosity is affected by interactions extending into the bulk phases, it seems feasible that the weak attractive forces between the fat crystals could be affecting the interfacial shear viscosity.

To determine the sediment density of the fat crystal slurries, a sample of each slurry was mixed and poured into a measuring cylinder, and the position of the descending phase boundary was monitored until they had all stopped moving. These final sediment densities are recorded in Table 1. There is an inverse relationship between sediment density and the adhesive forces between the crystals (32). If there are strong attractive forces between the crystals in a suspension they stick to each other easily, form large flocs and consequently a loosely packed, bulky sediment. At the other extreme, if there are repulsive forces between the crystals, they can pass each other easily as they are settling, forming more compact sediments. Fat crystals in an oil would be expected to have very small (or zero) electrostatic surface charges (33), so differences would be more likely to be due to the degree of attractive forces between them. It would appear from the sedimentation experiments conducted on the crystal slurries used in the present study that the type of fat, crystallization medium, and polymorphic form all affected the adhesive forces between the crystals. Of these four samples, crystals in the β′-form had bulkier sediments. It seems that crystals in the β′-

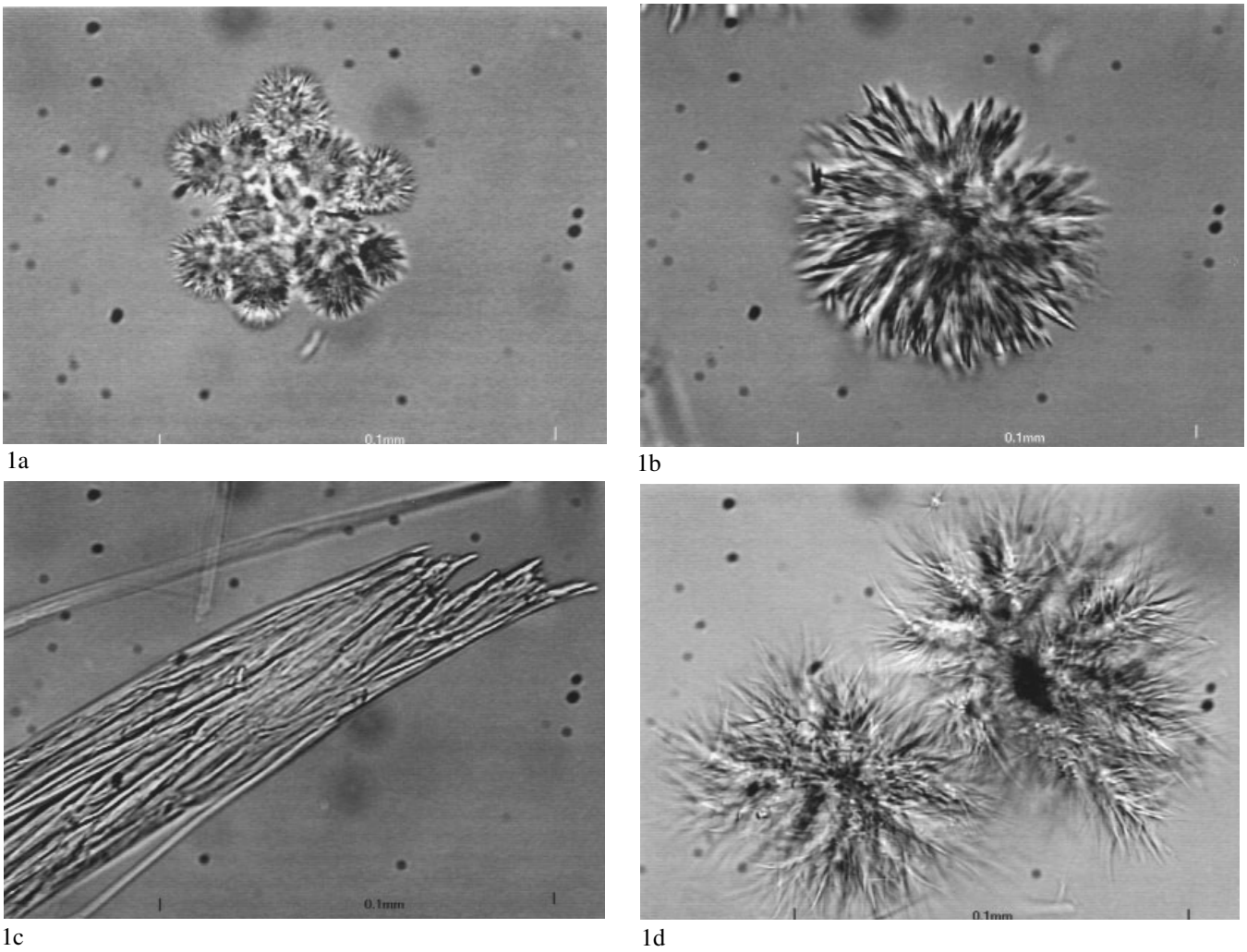

FIG. 1. Images of fat crystals. (a) b-tristearin crystallized in sunflower oil; (b) β-HPMF crystallized from n-hexane, isolated, then suspended in sunflower oil; (c) β′-HPMF crystallized from *n*-hexane, isolated, then suspended in sunflower oil; (d) β′-HPMF crystallized in sunflower oil.

form may have stronger adhesive forces between them, compared to crystals in the b-form, although with only four samples this proposal is speculative. The external surfaces of the crystals should almost entirely consist of methyl end-groups regardless of the polymorphic form of the fat, so the differences between the types of sediment densities are unlikely to be due to crystal surface effects. However, settling phenomena can also be affected by particle size, shape and distribution, state of aggregation, density, and the structure of the sediment (34). It should be noted that the fat crystals obtained under these conditions are much larger than those generally found in food emulsions. Smaller crystals were formed by rapidly cooling the slurries, but this caused the oil slurry to be so viscous that it could not be poured over the aqueous phase.

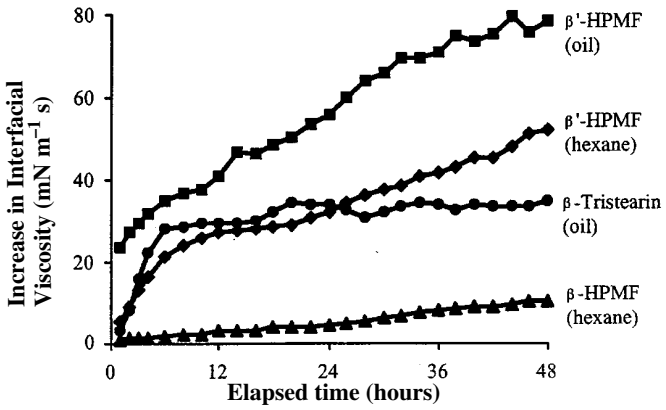

FIG. 2. Synergistic increase in interfacial shear viscosity due to 1.0×10^{-3} % sodium caseinate and 1% fat crystals in purified sunflower oil ("with crystals" minus "no crystals").

The strength of the adhesive forces between the fat crystals may account for the observation that β′-crystals are superior to b-crystals in stabilizing food emulsions and foams (3,5,35). It is often suggested that this is simply due to the crystal size and shape (morphology). Crystals in the β′'-form are usually much smaller than those in the β-form, and it is thought that they can follow the contours of the droplet surface more easily, forming an effective steric barrier between droplets. However, the crystallization conditions employed here have resulted in the β-crystals forming the smaller crys-

TABLE 1
Equilibrium Sediment Density of the Different Sunflower Oil Slurries

Crystal type	Crystallization medium	Polymorphic form	Final sediment density (g l^{-1})	Strength of adhesive forces
HPMF	Sunflower oil	β′	20	Strong
HPMF	*n*-Hexane	β′	25	↔
Tristearin	Sunflower oil	β	38	↔
HPMF	*n*-Hexane	β	125	Weak

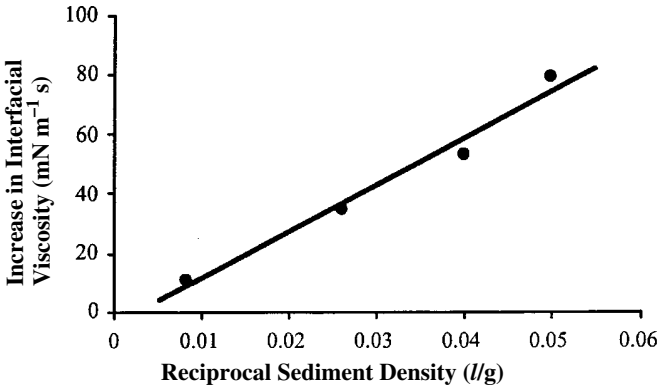

FIG. 3. Synergistic increase in interfacial shear viscosity (48 h) due to 1.0×10^{-3} % sodium caseinate and various fat crystals in sunflower oil versus the reciprocal of the sediment density for sunflower oil crystal slurries.

tal aggregates. Despite this, they still increased the interfacial shear viscosity the least, and they produced slurries with a higher sediment density (smaller adhesive forces between the crystals). According to Tiller and Khatib (34), for large particles such as the ones used in the present study, inter-particle forces should be small compared to gravitational forces, and aggregate formation should not be an important factor. They claim that the porosity of the sediment is then determined by the shape of the particles. Results from this study, however, do not support this.

A plot of the increase in interfacial shear viscosity *versus* the reciprocal of the sediment density is shown in Figure 3. When the mass of crystals is held constant, there is a clear trend suggesting that the interfacial shear viscosity increase is inversely proportional to the sediment density. As the sediment density is itself inversely proportional to the adhesive forces between the crystals, it follows that the interfacial shear viscosity increase is directly proportional to the adhesive forces between the crystals. As different crystal types vary in their levels of adhesion, even when the oil phase is constant, this may explain the large differences in interfacial shear viscosity increase between the different systems shown in Figure 2.

These attractive forces between the fat crystals would have also been present in the experiments where Tween-40 was the surfactant in the aqueous phase. However, the large increase in interfacial shear viscosity was not observed for these systems. This was probably because the fluid at the interface could flow around the adsorbed crystals when there were small-molecule surfactants present. On the other hand, when there is protein at the interface a strong film is built up by cross-linking of peptide residues on both sides of the interface. Interactions between the side-chains of the protein are strong enough to give some resistance to shearing forces, and they may also have effectively held the bottom layer of crystals in a fixed position relative to the protein film at the interface. Once this bottom layer of crystals was "anchored" to the interface, the effect of the adhesive forces between the fat crystals may have become important. The shearing force would have then experienced resistance not only from the protein film, but also from the network of fat crystals at the interface and adjacent crystals in the oil phase, due to the adhesive forces between them. Although this crystal network would also be present when Tween-40 was the surfactant, if the film flowed around the layer of adsorbed crystals, then the strength of the crystal network would not affect the interfacial shear viscosity.

The sediment density is not the only property of the oil slurry which appears to affect the increase in interfacial shear viscosity. The previous relationship between sediment density and the increase in interfacial shear viscosity assumed a constant mass (0.6 g) of crystals in the slurry. The mass of crystals present is also expected to affect the viscosity increase. This was tested by holding the sediment density approximately constant and varying the mass of crystals present. One of the systems (oil-crystallized HPMF) was tested at three different crystal loadings (the total volume of oil was held constant); the results are displayed graphically in Figure 4.

These preliminary results suggested that if the crystal mass were less than 0.2 g (e.g., 0.33% crystals in the oil phase) there would have been no increase in interfacial shear viscosity. This corresponds to a crystal loading at the interface of

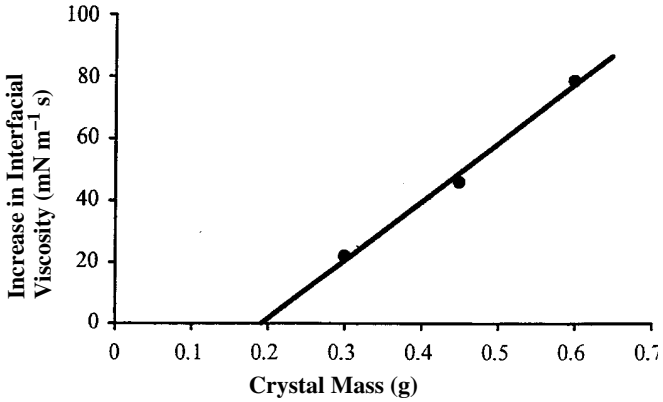

FIG. 4. Synergistic increase in interfacial shear viscosity (48 hours) versus crystal mass for HPMF–sunflower oil slurries.

0.014 kg m^{-2}. It may be that this is the minimum crystal concentration at the interface for which a crystal network will form.

The precise nature of the relationship between crystal mass, sediment density and interfacial shear viscosity increase is uncertain. However, it can be said generally that as the crystal mass decreases, so does the interfacial shear viscosity. In addition, as the sediment density increases, the interfacial shear viscosity decreases. If we assume that the interfacial shear viscosity varies with crystal mass linearly, then the total sediment volume (per 60 mL oil phase) combines the effects of crystal mass and sediment density, since they are both related to the sediment volume (V_{sed}) by the equation $V_{sed} = m/\rho_{sed}$.

Although there is now more scatter in the data, a trend between the sediment volume and the increase in interfacial shear viscosity can be seen (Fig. 5). In the absence of more suitable data, this trend could possibly be used to predict the approximate increase in interfacial shear viscosity to be expected by a particular crystal slurry over that from the sunflower oil phase alone.

While the cause of this measured increase appears to be related to interactions between fat crystals in the bulk oil phase, once some crystals are anchored to the interface by the protein, it can still be considered to be an increase in interfacial viscosity. In contrast to interfacial tension, interfacial viscosity takes into account interactions extending into both bulk phases as they affect the viscosity measured at the interface (36). Such interactions would be expected to affect film drainage between droplets in an emulsion, as predicted by interfacial shear viscosity measurements. They would also be expected to affect the bulk viscosity, but this has limited importance unless some other method of stabilization occurs as well. If the effect was purely a bulk phenomenon, then the interfacial shear viscosity increase would have been observed with or without proteins at the interface, and this was not the case. When Tween-40 replaced the protein in the aqueous phase, there was only a very small interfacial shear viscosity increase due to the fat crystals in the oil phase, so the bulk viscosity of the oil phase is not the reason for the increase in interfacial shear viscosity independent of the type of surfactant. The synergism clearly requires some interaction between the proteins and fat crystals in the interfacial region.

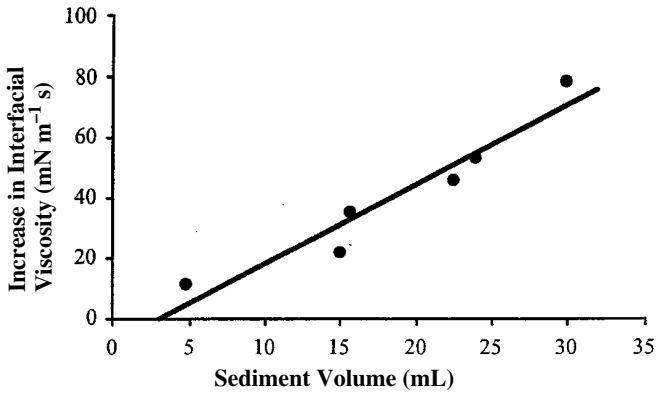

FIG. 5. Synergistic increase in interfacial shear viscosity (48 h) versus sediment volume for HPMF–sunflower oil slurries. Variation in sediment density and crystal mass.

In summary, when fat crystals and proteins were both present at an oil–water interface, a synergistic increase in the interfacial shear viscosity was observed. The magnitude of the synergism was dependent on both the polymorphic form of the crystals and the method of crystallization. The total interfacial shear viscosity is thought to be due to two factors:

(a) The protein molecules forming a film at the interface, as measured in the "no crystals" experiments.
(b) When there is protein in the aqueous phase, in the absence of other surface-active species, adhesive forces between the fat crystals in the bulk oil phase contribute to the total interfacial shear viscosity observed. It is proposed that once a protein film "anchors" the adsorbed layer of fat crystals to fixed positions on it, these fat crystals and the protein film rotate together. The magnitude of the synergistic increase in interfacial shear viscosity is then related to the strength of the crystal-crystal interactions and the mass of crystals present.

Fat crystals in the β′ polymorphic form may produce crystal networks in the oil phase which are stronger than those of β-crystals. Of the four oil slurries tested, the two β′ slurries displayed stronger crystal-crystal interactions and increased the interfacial shear viscosities the most.

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