Wetting of Fat Crystals by Triglyceride Oil and Water. 1. The Effect of Additives

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ABSTRACT: Wetting of fat crystals has been extensively examined in this work by contact angle (θ) measurements of fat crystal, oil, and water in three-phase contact. Contact angle was measured in oil. The crystals were nonpolar and wetted by oil for a contact angle equal to 0°, and polar and wetted by water for an angle equal to 180°. Fat crystals are expected to contribute to the stability of margarine emulsions if they are preferentially wetted by the oil phase ($0° < \theta < 90°$), but result in instability if they are preferentially wetted by the water phase ($90° < \theta < 180°$). In the absence of oil and water additives, fat crystals in α and β′ polymorphs were introduced to the oil/water interface from the oil side (contact angle $\theta \sim 30°$). β Polymorphs were completely wetted by oil ($\theta \approx 0°$). The contact angle for β′ crystals decreased with increasing temperature and was slightly lower in butter oil than in soybean oil. Emulsifiers in the oil phase (lecithins, monoglycerides and their esters, ethoxylated emulsifiers) and surface-active proteins in the water phase (milk proteins) made the crystals more polar (higher θ). Nonsurface-active proteins, sugar, and citric acid had no significant effect, although concentrations of salt lowered θ. Contact angle increased with temperature for emulsifiers of limited solubility in the oil, e.g., saturated monoglyceride.
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KEY WORDS: Advancing and receding contact angles, emulsifiers, emulsions, fat crystals, food, interfacial tension, oil/water interface, triglycerides, vegetable oils, wetting.

Margarine, butter, and most low-fat spreads consist of water-in-oil (W/O) emulsions. One critical component is a semisolid fat phase that consists of colloidal fat crystals in vegetable oil. The fat crystals interact and form a three-dimensional network, giving a hard, gel-like character to these foods (1–5). Interactions between the crystals are influenced by the adsorption of food emulsifiers (6,7) that are usually added to margarines and spreads as emulsion stabilizers and controllers of fat crystallization (8,9). The interactions become even stronger with traces of water in the oil (10).

Fat crystals in spreads influence emulsion stability. In general, colloidal particles influence the stability of emulsions when attached to emulsion droplets. This phenomenon was first described by Pickering for oil-in-water (O/W) emulsions (11). In a margarine-like system, containing paraffin oil and water, stable W/O emulsions were found with tristearin crystals attached to water droplets from the oil side, provided that oil-soluble emulsifiers like monoolein or Aerosol OT (sodium dioctyl sulfosuccinate) were present in the oil (12). In a similar margarine-like system, stable W/O emulsions were formed upon addition of relatively polar monoglyceride crystals (13). Triglyceride and fatty acid crystals, which are less polar, produced less-stable emulsions. In dairy applications, a relationship was found between the stability of O/W butterfat emulsions and fat crystal position at the oil/water interface (14). Due to addition of emulsifiers, the crystals became polar and pierced the oil droplets, giving unstable and rapidly churning emulsions. A similar result was found in O/W emulsions stabilized by surfactants (15). The emulsions without fat crystals were stable but became less stable with crystals introduced in the paraffin oil droplets when the crystals appeared at the interface. This instability was promoted bv creaming and shear.

Particle wetting by oil and water (position at oil/water interface) can be macroscopically characterized by contact angle measurements in a three-phase system (as presented later in Figure 1) for fat crystal/oil/water systems. This method, introduced by Boekel (15) and further developed by Darling (14) and Campbell (13), makes it possible to measure wetting of fat crystals crystallized against air, water, or oil. Wetting of fat crystals in margarine-type emulsions is influenced by addition of food emulsifiers to the oil and/or by addition of proteins to the water. For example, Darling (14) measured contact angles through oil on the high-melting fraction fat crystals of butterfat at the soybean oil/water interface. He examined the influence of low concentrations of emulsifiers in the oil and of sodium caseinate in the water phase and found that monoglycerides did not influence the contact angles, whereas more polar emulsifiers (lecithins, sorbitan esters) and sodium caseinate made the crystals more polar. In the absence of the additives, the crystals were rather nonpolar and became attached to the oil/water interface from the oil side. Campbell (13) determined contact angles through water for systems that contained hardened palm oil/soybean oil/water. He added emulsifiers, such as monoglycerides, sorbitan esters, and a technical lecithin, to the oil and sodium caseinate to the water phase. He found that, in the absence of

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emulsifiers or proteins, the fat crystals were nonpolar and loosely attached to the oil/water interface. Wetting of the crystals was unaffected by addition of low concentrations (≤1%) of emulsifiers. The crystals became more polar at high concentrations. In most cases, the crystals became more polar with simultaneous addition of low concentrations of emulsifiers to the oil, and of sodium caseinate to the water. Campbell (13) and Lucassen-Reynders and Reynders (16) stated that contact angles in systems of fat crystals/oil/water were not influenced by increasing concentrations of emulsifiers in the oil until the interfacial tension between the oil and water approached low constant values [interpreted as critical micelle concentration (CMC)], where the contact angles rapidly changed and the crystals became more polar.

Some important parameters were not evaluated in the previous wetting studies, and relatively few emulsifiers and additives to the water phase were examined. This study aims to increase the understanding of wetting of fat crystals by investigating a comprehensive selection of emulsifiers and considering the influence of factors, such as polymorphism, temperature and oil type.

EXPERIMENTAL PROCEDURES

Emulsifiers. The following nonionic emulsifiers were studied: monoolein (purity ~99%, M = 366 g/mol), saturated monoglycerides (Dimodan PV, purity ≥ 90%, mole mass M ≈ 365 g/mol), and their lactic acid esters (Lactodan P22, purity not specified, M ≈ 560 g/mol) from Grindsted (Brabrand, Denmark); polyoxyethylene (20) sorbitan monostearate (ethoxylated sorbitan monostearate, Tween 60, purity 100%, M = 1 295 g/mol) from ICI Surfactants (Everberg, Belgium); penta ethyleneglycol mono-*n*-dodecylether (ethoxylated alkyl ether, Nikkol BL5SY, purity 100%, M = 406 g/mol) from Nikko Chemicals (Tokyo, Japan); polyoxyethylene (12) castor oil (Bredol 691, purity not specified, M ≈ 1 458 g/mol) and polyoxyethylene (20) castor oil (Bredol 697, purity not specified, M ≈ 1 810 g/mol) from Akzo Nobel (Stenungsund, Sweden). We also examined pure phosphatidylcholine (PC) from soybean oil (soybean PC, Epikuron 200, purity ≥ 98%, M ≈ 773 g/mol) from Lucas Meyer (Hamburg, Germany) and three technical lecithins: Metarin P with phospholipid content of ~71.3% and average mole mass 776 g/mol (Lucas Meyer), Topcithin with phospholipid content of ~ 46.1% and average mole mass of 808 g/mol (Lucas Meyer), and Sterncithin with phospholipid content of ~46.4% and average mole mass of 810 g/mol from Stern Chemie (Hamburg, Germany). The first four nonionic emulsifiers mentioned and all lecithins were of food quality. Ethoxylated castor oils were emulsifiers for feed products, and ethoxylated alkyl ether was a speciality chemical for research purposes. The phospholipid composition of the technical lecithins was as follows: 24.5% PC, 22.2% phosphatidylethanolamine (PE), 8.5% phosphatidic acid (PA), 15.6% phosphatidylinositol (PI), and 0.5% lysoPC (LPC) for Metarin P; 16.0% PC, 13.6% PE, 5.4% PA, 10.3% PI, and 0.8% LPC for Topcithin; 17.2% PC, 13.9% PE, 4.2% PA, 10.7% PI, and 0.4% LPC for Sterncithin. Emulsifiers were dissolved in the oil phase in all systems studied. Two concentrations were examined for most of the emulsifiers—a low concentration (0.2% for the nonionic emulsifiers and 0.1% for the lecithins) and a high concentration (2% for the nonionic emulsifiers and 1% for the lecithins). The concentrations of the emulsifiers (in % and in mM), calculated as the total amount added and as the amount of pure active compound, are summarized in Table 1.

Oils. Refined soybean oil from Karlshamns AB (Karlshamn, Sweden) was used as the main oil phase. Interfacial tension between this oil and distilled water was slightly above

TABLE 1
Specification of Emulsifier Concentrations in the Oil

	Low concentration				High concentration			
	Total		Pure compound		Total		Pure compound	
Emulsifier[a]	(%)	(mM)	(%)	(mM)	(%)	(mM)	(%)	(mM)
Soya PC	0.1	1.2	0.1	1.2	1	11.9	1	11.6
Topcithin	0.1	1.1	0.05	0.53	1	11.4	0.5	5.3
Sterncithin	0.1	1.1	0.05	0.53	1	11.4	0.5	5.3
Metarin P	0.1	1.2	0.07	0.85	1	11.9	0.7	8.5
Monoolein	0.2	5.0	0.20	4.98	2	50.3	2.0	49.8
Saturated monoglycerides	0.2	5.0	0.18	4.54	2	50.4	1.8	45.4
Lactic acid esters of monoglycerides	0.2	3.4	—	—	2	33.5	—	—
Ethoxylated alkyl ether	0.2	4.5	0.2	4.5	2	45.3	2	45.3
Ethoxylated sorbitan monostearate	0.2	1.4	0.2	1.42	2	14.2	2	14.2
Ethoxylated (12) castor oil	0.2	1.3	—	—	2	12.6	—	—
Ethoxylated (20) castor oil	0.2	1.0	—	—	2	10.2	—	—

[a] PC, phosphatidylcholine; from Lucas Meyer (Hamburg, Germany). Topcithin and Metarin P also from Lucas Meyer. Sterncithin from Stern Chemie (Hamburg, Germany).

30 mN/m. This high value indicates high purity with respect to surface-active components. The oil was not further purified. The oil had an iodine value of about 130 (~2.5 double bonds per hydrocarbon chain on average), a melting point of −20°C, and a density of 0.921 and 0.918 g/mL at 20 and 25°C, respectively. A few experiments were performed in butter oil, separated from milk by Swedish Dairies Association (SMR, Lund, Sweden). The melting point of this oil was not well specified (between room temperature and 40°C). Measurements with this oil as a liquid were performed at 40°C. Further analytical information about this oil was not obtained from the supplier.

Fat crystals. Contact angles at two crystal surfaces were studied—a pure tristearin from Fluka (Buchs, Switzerland) and a fully hydrogenated palm stearin from Karlshamns AB. Tristearin was of high purity (>99%), density 1.0577 g/L and mole mass of 892 g/mol, and had a low iodine value (<1). Tristearin is stable in the polymorphic form β, which has a melting point of 72°C. The α form (appearing in rapidly cooled fat) has a melting point of 53°C (17). Palm stearin had a mole mass of 756 g/mol on average and an iodine value of 2.6. Its density was not specified. It is stable in the polymorphic form β', which has a melting point of 57–59°C. The α-form appears in rapidly cooled palm stearin and has a melting point of about 46°C. The composition of fatty acids in palm stearin was as follows: 53% 16:0 (palmitic acid, P), 42% 18:0 (stearic acid, St), 2% 18:1 (oleic acid, O), 3% others. The composition of triglycerides is: 3% POO/MPP, 23% PPP, 37% PPSt, 26% PStSt, and 11% StStSt, where M stands for 14:0 (myristic acid). These data were obtained from the supplier.

Palm stearin crystals were used as an oil additive in some measurements of interfacial tension between oil and distilled water. Crystals (1%) were weighed into soybean oil and dispersed with a vibro-mixer to obtain a uniform dispersion. The β' crystals were obtained by recrystallization from acetone, which was confirmed by X-ray and differential scanning calorimetry analysis at Karlshamns AB. The specific surface of these crystals was 4.55 m^2/g, determined by BET adsorption measurements with nitrogen gas. Tristearin of technical grade (purity 65%) from Fluka was used as a base fat to fill the plug in the contact angle equipment (Fig. 1).

Other chemicals. Doubly distilled water was used as the water phase in most experiments. In some experiments, the following substances were added to water: sodium chloride, citric acid, gelatin, and bovine serum albumin (BSA) from Merck (Darmstadt, Germany), sucrose from The Swedish Sugar Company (Arlöv, Sweden), and spray-dried skim milk from Semper (Stockholm, Sweden). These substances were not further purified. Two types of milk also were used as the water phases in contact angle measurements—a sour buttermilk from production of butter with fermented cream, and a sweet buttermilk from production of butter from a sweet concentrated (fat content 75%) cream. Both types of milk were supplied by Swedish Dairies Association (SMR). Acetone for recrystallization of solid fat (palm stearin) was of analytical grade and supplied by Merck.

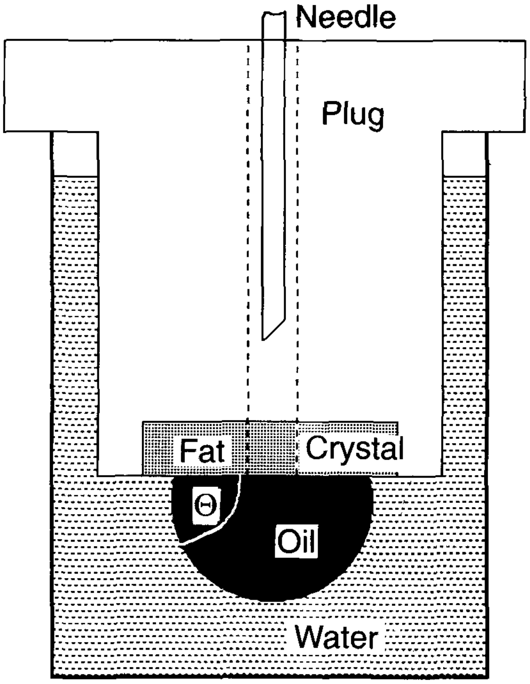

FIG. 1. Contact angle apparatus for measurements at three-phase boundary: fat crystal/oil phase/water phase.

Interfacial tension. Interfacial tension between oil and water was measured by a pendant drop method (18), where the tension is obtained from the shape of a droplet. The oil droplet was pressed upward from a bent needle into water. The droplet shape was recorded by a CCD video camera (Sango Electric Co., Tokyo, Japan) and analyzed on a personal computer with an image-processing program (Micro GOP 300; CONTEXTVISION AB, Linköping, Sweden), by an algorithm of Finn Knut Hanssen (University of Oslo, Norway). The reproducibility of this method is ≤5%. It is particularly suitable for recording the time-dependence of interfacial tension for systems with slow equilibrium adsorption, where other methods, such as Wilhelmy plate or Du Noüys ring, fail.

Contact angles. The contact angle at water/fat crystal/oil contact was measured through the oil phase with equipment presented in Figure 1. The plug, made of poly(tetrafluoroethylene), was filled with fat and dipped in a glass vessel filled with water at room temperature. The oil droplet was pressed through the plug onto the fat crystal surface. For measurements with milk, the reverse system was used. In this case, the milk droplet was placed onto the fat surface, crystallized on the bottom of a measuring cell of glass, and oil was added to the vessel around the milk droplet. Contact angles were read from a microscope goniometer in a conventional apparatus from Ramé-Hart Inc. (Mountain Lake, NJ). Each measurement required a new plug. Most measurements were done in duplicate, some in triplicate. The standard deviation (derived for systems without any additives to oil or water) was ±5°. Advancing contact angles were determined by pressing an oil droplet (~100 μL) on the water-covered fat crystal. The receding contact angles were determined afterward by sucking back ~50 μL of the oil phase.

The contact angle may be used to characterize the fat crystal position at the oil/water interface. For contact angles (measured through the oil) close to 0°, the crystals are nonpolar and located in the oil phase. For contact angles close to 180°, the crystals are polar and located in the water phase. For contact angles between 0 and 90°, the crystals should be attached to the oil/water interface from the oil side and are expected to stabilize W/O emulsions and to destabilize O/W emulsions. For contact angles between 90 and 180, the crystals should be attached to the oil/water interface from the water side and are expected to stabilize O/W emulsions. Advancing contact angles should correspond to fat crystals approaching the oil/water interface from the water side in emulsion when, for example, shear forces press them into it. Receding contact angles correspond to fat crystals approaching the oil/water interface from the oil side.

Preparation of fat crystal surfaces for contact angle measurements. A base fat (tristearin of technical grade) was melted at 80°C. A niche in the plug (Fig. 1) was filled with the melted base fat and allowed to crystallize in air at room temperature. The pure fat (tristearin or palm stearin) was melted at 80°C, and the plug was dipped into it. The plug was placed in a refrigerator to obtain a thin layer of the top fat in α form through quick super cooling. A total top-layer thickness of 1.5–2 mm was developed by dipping 3–4 times. The presence of the α form was confirmed by differential thermal analysis (DTA) and X-ray diffraction analysis, performed at Karlshamns AB on the material scraped from the top layer. To obtain tristearin β and palm stearin β′, samples were tempered for 150 min (2.5 h) at 55°C and 90 min (1.5 h) at 40°C, respectively. Again, the β and β′ form were confirmed with DTA and X-ray diffraction analysis.

RESULTS AND DISCUSSION

Interfacial tension: equilibrium values. Equilibrium interfacial tension between distilled water and refined soybean oil, or solution of different emulsifiers in soybean oil, are presented in Figure 2. The soybean oil was pure with respect to surface-active components, as indicated by the high oil/water interfacial tension (above 30 mN/m). Addition of low concentrations of emulsifiers to the oil lowered the interfacial tension. Monoolein, lactic acid ester of monoglycerides, and ethoxylated alkyl ether reduced the equilibrium interfacial tensions to about 20 mN/m. Soybean PC, ethoxylated castor oils, and ethoxylated sorbitan monostearate produced the lowest interfacial tensions (≤1 mN/m). The saturated monoglyceride (Dimodan PV) adsorbed more extensively to the interface than unsaturated (monoolein) at low concentrations. However, this difference was not observed at high concentrations when the saturated monoglyceride crystallized in the oil. The highest interfacial tension (7–8 mN/m) at high concentration level (2%) was obtained with lactic acid ester of monoglycerides. Among the lecithins examined, Metarin P was more hydrophobic than soybean PC. Metarin P also produced a higher interfacial tension than soybean PC (~9 and ~1 mN/m, respectively, at the concentration level of 0.1% ≈ 1.2 mM). No measurements for 0.1% Sterncithin or Topcithin in the oil were performed. At high concentrations (1% ≈ 12 mM), the interfacial tensions were low (~1 mN/m), and differences between products were small.

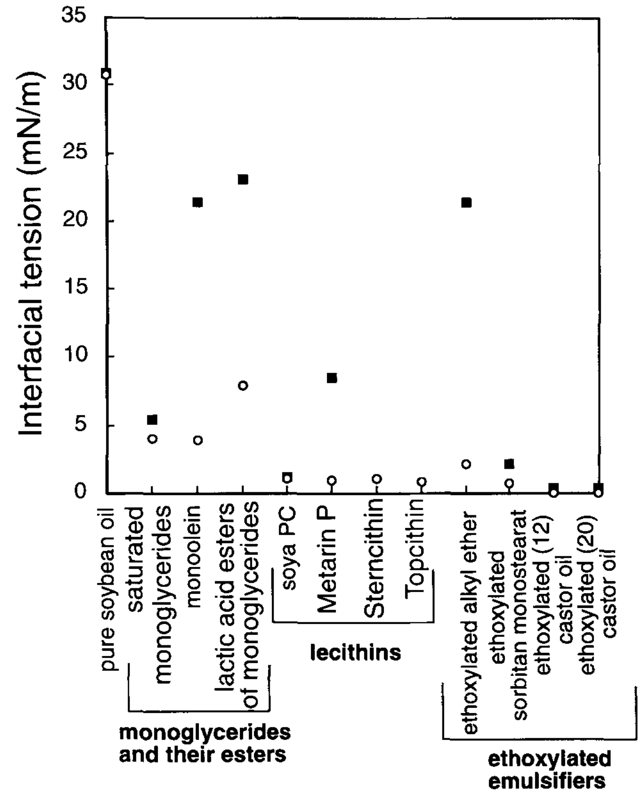

FIG. 2. Equilibrium values for interfacial tensions between distilled water and soybean oil or solutions of different emulsifiers in soybean oil. Two concentrations of each emulsifier were examined: low (0.1–0.2%) (■), and high (1–2%) (□). The concentrations of emulsifiers and company sources are specified in Table 1. PC, phosphatidylcholine.

The influence of fat crystals in the oil. Equilibrium interfacial tensions between distilled water and oil, or oil solutions of soya PC and monoolein, were compared with interfacial tensions for the same systems with 1% fat crystals (palm stearin β′). The differences between samples with and without crystals were observed only at low emulsifier concentrations (Fig. 3). For 0.1% soybean PC, addition of 1% fat crystals to the oil caused an increase in interfacial tension from 1 to 10 mN/m. The increased interfacial tension is due to strong adsorption of soybean PC to the fat crystals [~1.5 μmol/m^2 at concentration of 0.1% ≈ 1.2 mM (6)], which lowers its concentration in the oil. For 0.2% monoolein (~5 mM), only a small increase in interfacial tension, from 21 to 24 mN/m, was observed when the fat crystals were added. Monoolein at this concentration adsorbs weakly to the fat crystals [~1 μmol/m^2, (6)], lowering the concentration of free monoolein in the oil and at the oil/water interface, resulting in a slight increase in interfacial tension.

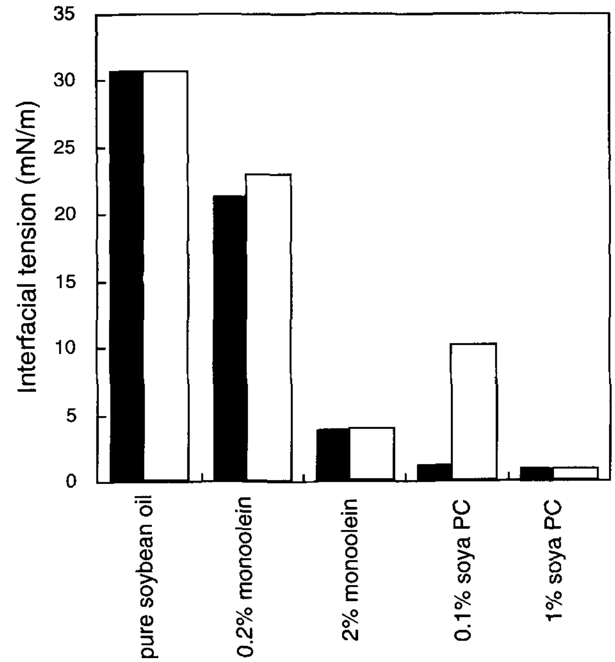

FIG. 3. Equilibrium values for interfacial tensions between distilled water and soybean oil or solutions of different emulsifiers in soybean oil. Values for oil solutions (■) are compared to values for 1% fat crystal dispersions (palm stearin β′) in oil solutions (□). Concentration of emulsifiers are specified in Table 1. Abbreviation as in Figure 2.

Contact angles: no additives to oil and water. Equilibrium contact angles at the fat crystal/oil/water contact are presented in Table 2. The results show the interval for 5–6 repeated measurements. Equilibrium was rapidly reached in these systems (less than a few minutes). Results show that the fat crystals of tristearin β were completely wetted by oil (advancing and receding contact angles ≈ 0°) and had no tendency to adsorb at the oil/water interface. β′ Crystals of palm stearin produced higher contact angles (30–40°), which is in good agreement with the published value of ~30° for the hardened palm oil/soybean oil/water system (13), but lower than the published value of ~60° for the butterfat/soybean oil/water system (14). α Crystals of both tristearin and palm stearin produced intermediate contact angles, between those for β and β′ crystals. The differences observed between α and β′ crystals were rather small and may not be significant. Thus, tight packing of triglyceride molecules in β polymorph might be the reason for completely nonpolar surfaces, whereas a looser packing in α and β′ crystals produced slightly polar surfaces. There were no differences between wetting by refined soybean oil and chromatographically purified soybean oil (contains only triglycerides). At elevated temperature (40°C), the α crystals of palm stearin produced slightly lower contact angles than at room temperature, probably due to increased mobility of hydrocarbon chains on the surface (screening of the polar islands). Butter oil contains more saturated hydrocarbon chains than soybean oil, making it more similar to fat crystals, thus enhancing wetting (produced lower contact angles on palm stearin α and β′ surfaces).

Generally, in the systems without additives in oil or water, fat crystals should not spontaneously migrate from the oil into the water phase (receding contact angles <90°). Even if the crystals were forced into the water phase by shear forces, they should spontaneously return to the oil phase (advancing contact angles <90°).

The influence of emulsifiers. Equilibrium values for advancing and receding contact angles for fat crystals of palm stearin β′ at the distilled water/soybean oil interface, or oil solution of emulsifiers, are presented in Figure 4A for low concentrations of emulsifiers (0.1–0.2%) and in Figure 4B for high concentrations of emulsifiers (1–2%). Emulsifier concentrations (in % and mM) are specified in Table 1. At high concentrations (1–2%, Fig. 4B), the emulsifiers increased the contact angle as in earlier studies (13,14). The advancing contact angle was higher than 90° for most of the emulsifiers examined. In that case, fat crystals may migrate into the water phase in the presence of shear and destabilize W/O emulsions.

TABLE 2
Contact Angles Between Three Phases (oil/fat crystal/distilled water) for Different Systems Without Emulsifiers in the Oil

Crystal type	Polymorphic form	Temperature (°C)	Oil	Advancing contact angle θ_a (°)	Receding contact angles θ_r (°)
Tristearin	α	22	SBO[a]	19–31	8–15
	β	22	SBO	0	0
	α	22	CPLSBO[a]	25–33	16
	β	22	CPLSBO	0	0
Palm stearin	α	22	SBO	27–35	9–16
	β′	22	SBO	25–39	6–19
	α	22	CPLSBO	20–25	5–12
	β′	22	CPLSBO	36–38	17–18
Palm stearin	α(+β′)[b]	40	SBO	16–20	10
	α(+β′)[b]	40	Butter oil	8	2
	β′	40	Butter oil	15	5

[a] SBO stands for soybean oil, CPLSBO for chromatographically purified soybean oil (contains only triglycerides).

[b] At 40°C, fat crystal surface is under transformation from α to β′ polymorphic form, and a mixture of both forms most likely occurs.

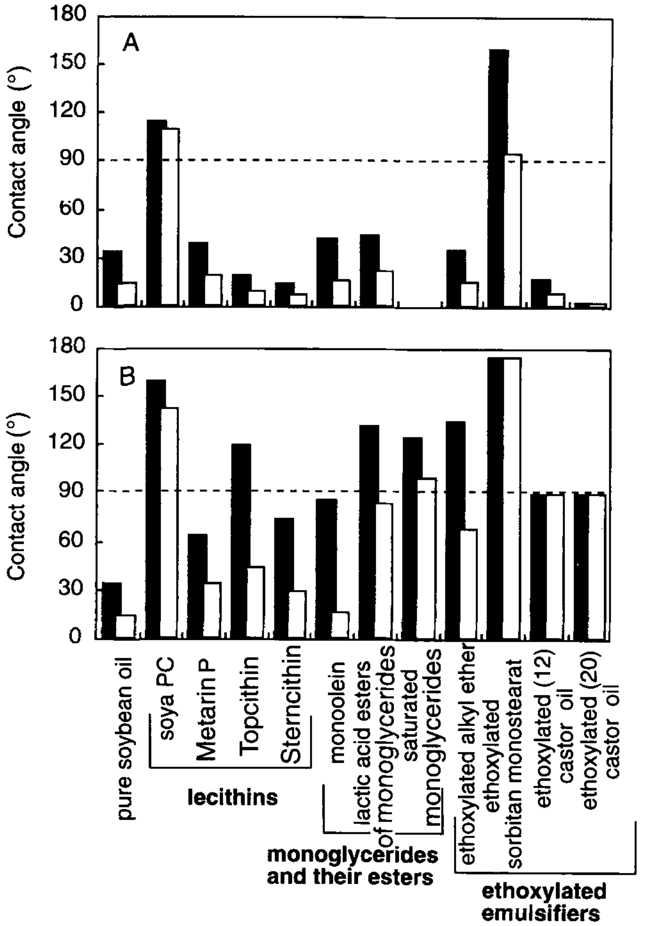

FIG. 4. Equilibrium values for contact angles at three-phase boundary: distilled water/soybean oil or solutions of different emulsifiers in soybean oil/fat crystal surface (palm stearin β′). Advancing contact angles (■) are compared to receding contact angles (□). A, Low concentration of emulsifiers (0.1–0.2%); B, high concentration of emulsifiers (1–2%). Abbreviation as in Figure 2. Company sources as Table 1.

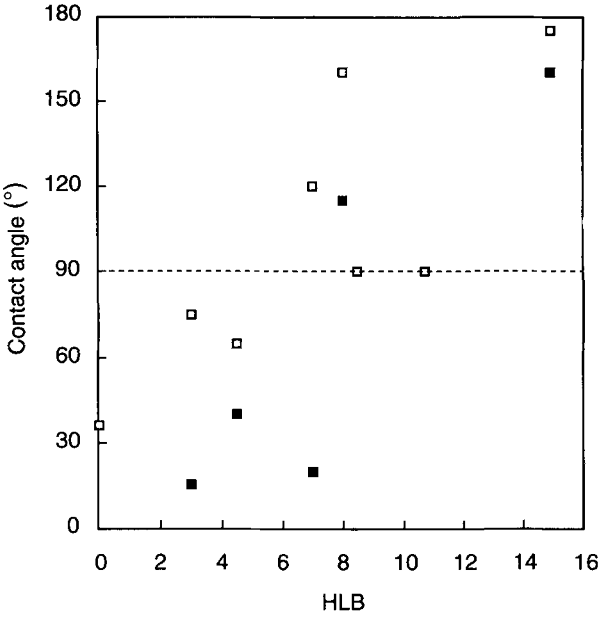

FIG. 5. Equilibrium values for advancing contact angles at three-phase boundary: distilled water/soybean oil or solutions of different emulsifiers in soybean oil/fat crystal surface (palm stearin β′), plotted as a function of hydrophilic lipophilic balance (HLB) values for emulsifiers. Emulsifiers were present in the oil at concentration levels of ~1 mM (■) and ~11–14 mM (□). The HLB values for the emulsifiers were: 3.4 for monoolein, 3.8 for saturated monoglycerides, ~7 for lactic acid ester of monoglyceride, 8.5 for ethoxylated (12) castor oil, 10.7 for ethoxylated (20) castor oil, 14.9 for ethoxylated sorbitan monostearate, and ~8 for pure soya PC, according to Reference 20; 5 for ethoxylated alkyl ether, according to Reference 23; ~4.5 for Metarin P according to Reference 24. HLB values for Sterncithin and for Topcithin have been estimated from solution properties at ~3 and ~7, respectively.

The receding contact angle was also higher than 90° for the systems containing hydrophilic lecithin (soybean PC), saturated monoglycerides, lactic acid ester of monoglycerides, ethoxylated castor oils, and ethoxylated sorbitan monostearate. Only hydrophobic lecithins (Metarin P and Sterncithin) and unsaturated monoglycerides, such as monoolein, gave crystals that were preferably wetted by oil (θ_{adv}, θ_{rec} <90°). They are expected to stabilize W/O emulsions. At low concentrations (0.1–0.2%), most emulsifiers influence the contact angle and the crystal polarity only to a minor degree, which is also in agreement with earlier studies (13,14). Then, the crystals remain attached to the oil/water interface from the oil side and should contribute to the stability of W/O systems. Low concentrations of polar emulsifiers, such as hydrophilic lecithin soybean PC or ethoxylated Tween 60, make the crystals polar and result in their migration into water (destabilization of W/O systems).

Hydrophilic lypophilic balance (HLB) of emulsifiers. The HLB describes a hypothetical balance between the hydrophobic and the hydrophilic parts of the emulsifier molecule (19–22). A large HLB value (≥10) implies that the emulsifier is hydrophilic, and a small HLB value (≤7) that the emulsifier is hydrophobic. The HLB values for the emulsifiers studied were found in the literature (19,23,24) or estimated from the solution properties where references were not available. The influence of emulsifier hydrophilicity on contact angles at the fat crystal/oil/water interface is presented in Figure 5. Generally, hydrophilic emulsifiers with high HLB values adsorbed strongly to fat crystals at the oil/water interface and resulted in high contact angles. This relation is only qualitative. The scattering of points is partly due, to uncertainty in the HLB values and partly to other parameters also influencing contact angle.

The influence of fat crystal type on emulsifier adsorption. Advancing contact angles for palm stearin β′ and for tristearin β at low emulsifier concentration (0.1–0.2%) in the oil are presented in Figure 6. Emulsifier concentrations are specified in Table 1. The contact angles for palm stearin β′ were higher than for tristearin β with most emulsifiers. A likely reason for this is stronger adsorption of the emulsifiers to the palm stearin β′ surface, which was slightly more polar (higher contact angle) as compared to the tristearin β surface. Ethoxylated sorbitan monostearate and hydrophobic lecithin Metarin P resulted in about the same contact angles for both types of polymorphs.

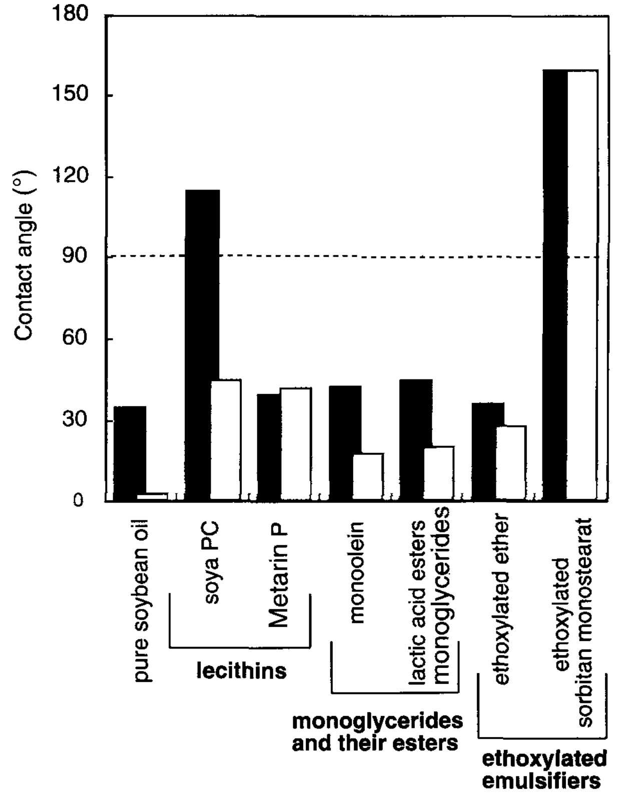

FIG. 6. Equilibrium values for advancing contact angles at three-phase boundary: distilled water/soybean oil or solutions of different emulsifiers in soybean oil/fat crystal surface of palm stearin β′ (■) and tristearin β′ (□), respectively. The emulsifiers were present in the oil at concentration level of 0.1–0.2% (Table 1). Abbreviation as in Figure 2.

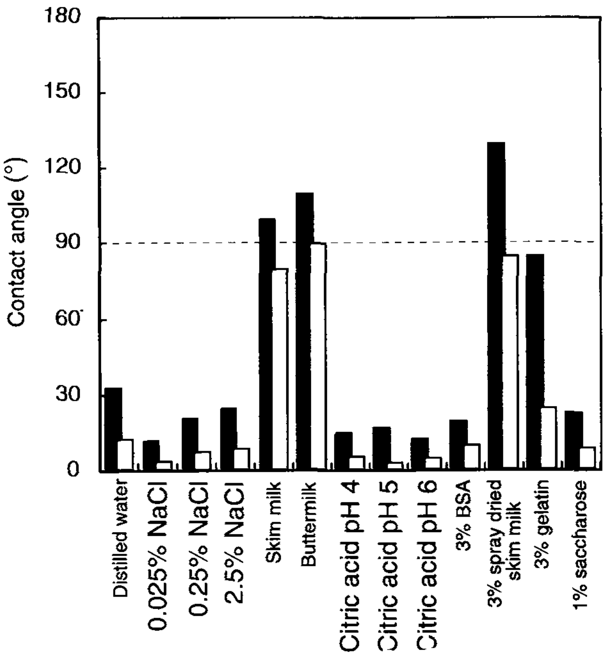

FIG. 7. Equilibrium values for advancing and receding contact angles at three-phase boundary: distilled water or water solutions of salt, citric acid, sucrose, proteins/refined soybean oil/fat crystal surface (palm stearin β′). Advancing contact angles (■) are compared to receding contact angles (□). BSA, bovine serum albumin.

Additives to the water phase. Additives to water influenced the contact angles, as presented in Figure 7, for palm stearin β′ crystals at the soybean oil/water interface. A slight lowering of contact angle was observed with sodium chloride, citric acid, and sucrose. Salt is known to increase adsorption of surface-active oil impurities at the oil/water interface (25), which may be the reason for the restrictions in fat crystal/water interaction. BSA (a small protein adsorbing weakly to interfaces) at 3% concentration did not influence the contact angles significantly. Gelatin (3%) appeared to adsorb onto fat crystals forced into water and increased the advancing contact angle to ~90°. Receding contact angle was nearly unaffected by gelatin. Milk proteins (from skim milk, spray-dried skim milk, and buttermilk) adsorbed to the crystals at the oil/water interface and increased both advancing and receding contact angles to 85 and 120°, respectively. This is in agreement with earlier studies for similar systems (13,14). Thus, there is a relationship between the surface activity of a protein in water (ability to reduce interfacial tension) and its adsorption to fat crystals at the oil/water interface. Highly surface-active proteins make the fat crystals polar and may destabilize W/O emulsions in this way.

The influence of temperature. Advancing and receding contact angles for palm stearin β′ at the interface of distilled water/1% saturated monoglyceride in soybean oil were determined as a function of temperature in the 10–50°C interval (Fig. 8). Both the advancing and the receding contact angles were ~90° at 10°C and increased to ~150° at 50°C. The increasing crystal polarity with temperature is likely due to the increased solubility and surface activity of the emulsifier. In this case, high temperature may promote migration of fat crystals into water droplets, and a destabilization of W/O emulsions may occur. During measurements, a warm (~70°C) oil solution of monoglyceride was injected onto the fat crystal surface immersed in water at the desired temperature. The contact angle was determined after 5-min equilibration when the oil droplet (~100 μL) reached the temperature of the water. This method of measurement is relevant to the industrial production for margarines, where fat crystals are precipitated upon cooling of a warm oil phase containing emulsifiers.

Contact angle isotherms. Adsorption of emulsifiers to different interfaces. Isotherms of advancing contact angles are presented in Figure 9A for soybean PC, monoolein, and saturated monoglycerides. The results show that all emulsifiers adsorbed to fat crystals at the oil/water interface and increased contact angles. Hydrophilic lecithin soybean PC adsorbed the strongest and gave the highest contact angle at low concentrations (0.1% ≈ 1 mM). Soybean PC also adsorbed strongly to the fat crystal/oil interface (6). Hydrophobic monoolein gave a high contact angle (>90°) only at concentrations as high as 4% (≈100 mM). Monoolein also adsorbed weakly to the fat crystal/oil interface (6). Saturated monoglycerides produced intermediate contact angle (Fig. 9A) and adsorption (6) isotherms. Thus, adsorption of emulsifiers onto fat crystals in the oil and at the oil/water interface are qualita-

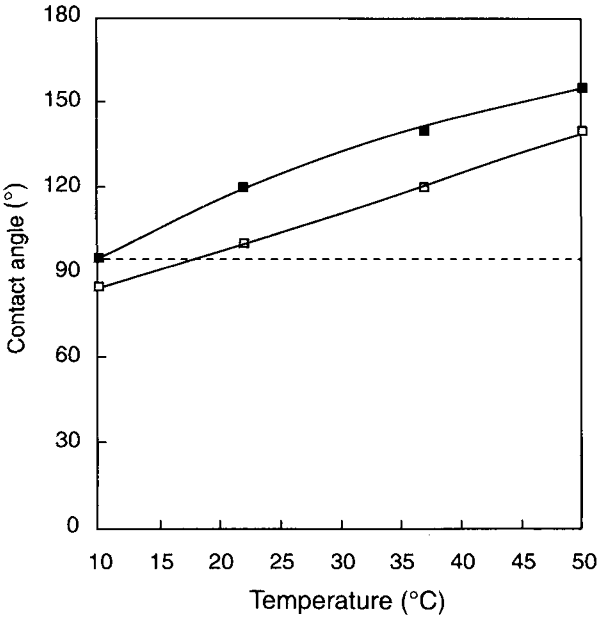

FIG. 8. Equilibrium values for advancing and receding contact angles at three-phase boundary: distilled water/a solution of 1% saturated monoglyceride in soybean oil/fat crystal surface (palm stearin, β′), as a function of temperature.

tively related, and both depend on the balance between emulsifier/fat surface and emulsifier/oil interactions. For monoolein, the contact angle isotherm showed a hysteresis between the advancing and receding angles (Fig. 9B). Advancing contact angles were about 30–60° higher than receding contact angles. Monoolein concentrations of about 6–8% (150–200 mM) were required to shift the receding contact angles above 90° compared to about 4% for the advancing contact angles.

Contact angles are compared to interfacial tension in Figure 10. At first glance, the graph gives the impression that there is a correlation between high contact angle (strong adsorption to fat crystal/oil/water interface) and low interfacial tension (strong adsorption to oil/water interface). Closer analysis reveals a low correlation coefficient of 0.291 for this relationship. Adsorption onto the fat crystal/oil/water interface (contact angle) is dependent upon the fat crystal/emulsifier interaction, while adsorption at the oil/water interface (interfacial tension) does not include this interaction.

Wetting and displacement of fat crystals from the oil/water interface. Solid particles in Pickering emulsions must adsorb to the oil/water interface of droplets to stabilize emulsions. The stabilizing action should be strong if the amount of energy required to displace the particles from the interface is high. This displacement energy may be calculated for the droplets stabilized by spherical monodisperse particles (23,26). In this case, the energy of displacement to the oil phase (E_{oil}) is equal to the interfacial tension between oil and water (γ_{OW}) multiplied by the crystal area immersed in the water phase having to pass through the interface during displacement, and integrated from contact angle θ to contact angle θ = 0°:

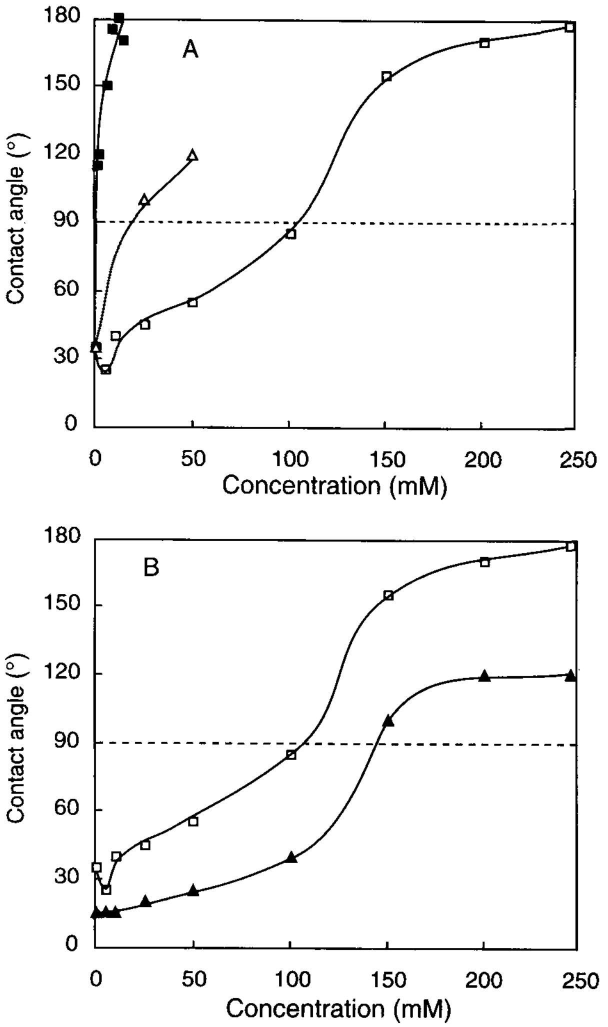

FIG. 9. Equilibrium values for contact angles at three-phase boundary: distilled water/soybean oil and solutions of emulsifiers in soybean oil/fat crystal surface (palm stearin β′), as a function of the emulsifier concentration in the oil (contact angle isotherm). A, Advancing contact angles for oil solutions of soya PC (■), monoolein (□), and saturated monoglyceride Dimodan PV (△); B, a hysteresis between advancing (□) and receding (▲) contact angles for monoolein. Abbreviation as in Figure 2.

$$\frac{E_{oil}}{\pi \cdot r^2} = \gamma_{ow} \cdot (1 - \cos\Theta)^2 \qquad [1]$$

The displacement energy, estimated for β′ crystals from Equation 1, is presented in Table 3 for emulsions stabilized by various emulsifiers. The order of magnitude for this energy is in the range 0.1–10 mJ/m^2. A crystal of diameter 1 µm has a displacement energy of 10^{-16}–10^{-14} J, corresponding to about 10^4–10^6 hydrogen bonds. This energy is strongly influenced by emulsifiers and increases, for example, one order of magnitude when a hydrophobic lecithin, such as Sterncithin, is used instead of a hydrophilic one, such as soybean PC. An extremely high displacement energy is achieved in the presence of lactic acid esters of monoglycerides as a result of the high interfacial tension in combination with high contact angle in this system.

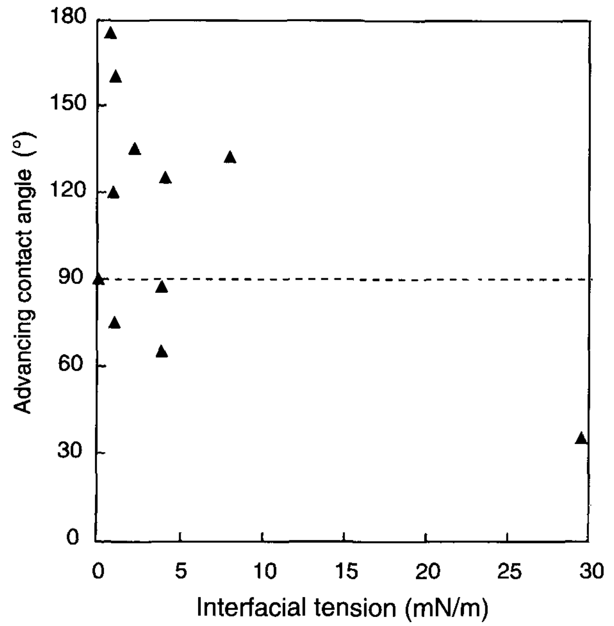

FIG. 10. Equilibrium values for advancing contact angles at three-phase boundary: distilled water/solutions of emulsifiers (1–2%) in soybean oil/fat crystal surface (palm stearin β′) as a function of equilibrium value for interfacial tension. The emulsifiers and their concentrations are specified in Table 1.

Emulsifiers, fat crystals and stability of W/O emulsions. Emulsifiers in margarine emulsions have many functions. Formation and stability of emulsions is possible due to the adsorption of emulsifiers at the oil/water interface lowering the interfacial tension (23). The type of emulsifier and its HLB also determines the type of emulsion formed (O/W or W/O). There is a competition between adsorption of emulsifiers at oil/water, fat crystal/oil/water and fat crystal/oil interfaces. This competition determines the wetting of fat crystals and the crystals' ability to influence the emulsification process and to stabilize the emulsions. Competitive adsorption also is important in stabilizing against "oiling out" and for consistency of products (6,7).

Some predictions concerning the influence of emulsifiers and fat crystals on the formation and stability of margarine-type emulsions are summarized in Table 4. These predictions are derived from data in Table 3 according to the specified criteria. The following aspects have been taken into account: the type of emulsion formed (O/W or W/O), the droplet size, the stabilization of W/O emulsion at rest and at shear, and the displacement of crystals from the oil/water interface. In the predictions, one assumes that macroscopic contact angle represents a fat crystal position at microscopic droplets. Furthermore, shear forces are assumed to be able to press fat crystals into water droplets, which is likely true for large margarine

TABLE 3
Experimental Properties of the Systems Studied[a]

Emulsifier	HLB[b]	Interfacial tension γ [mN/m]	Receding contact angle (θ_{rec} [°])	Advancing contact angle (θ_{adv} [°])	Displacement energy ($E/\pi r^2$ [mJ/m^2])
None	—	~30	12	32	0.69
Soya PC[b]	~8	1.03	143	160	3.87
Topcithin	~7	0.86	45	120	1.93
Sterncithin	2–4	1.03	30	75	0.56
Metarin P	4–5	0.94	36	65	0.31
Monoolein	3.4	3.85	17	87	3.45
Saturated monoglyceride	3.8	4.02	100	125	—
Lactic acid esters of monoglyceride	~7	7.96	85	132	22.15
Ethoxylated alkyl ether	5	2.14	69	135	6.23
Ethoxylated sorbitan monostearate	14.9	0.68	175	175	2.71
Ethoxylated (12) castor oil	8.5	~0	90	90	~0
Ethoxylated (20) castor oil	10.7	~0	90	90	~0

[a] The displacement energy for fat crystals to the oil was calculated as $E/\pi r^2 = \gamma_{OW} \times (1 - \cos \theta)^2$ (the advancing contact angles were used). Adsorption of emulsifiers to β fat crystals in [μmol/m²] originates from Reference 6. The equilibrium concentrations of the emulsifiers in the oil phase were assumed to be high (~1–2%). Company sources as in Table 1.

[b] HLB, hydrophilic-lypophilic balance; PC, phosphatidylcholine.

TABLE 4
Some Predictions Concerning W/O Emulsions Containing Distilled Water, Soybean Oil, and Fat Crystals (ß') on the Basis of the Data from Table 3[a]

Emulsifier	Emulsion type[b]	Droplet size[c]	Stabilization by crystals at rest[d]	Stabilization by crystals at shear[e]	Displacement of crystals to the oil[f]	Consistency changes due to adsorption[g]
Soya PC	O/W & W/O	Small	Destabilization	Destabilization	Difficult[h]	Much thinner
Topcithin	O/W & W/O	Small	Good	Poor	Relatively difficult[g]	
Sterncithin	W/O	Small	Good	Very good	Easy	
Metarin P	W/O	Small	Good	Very good	Easy	Very much thinner
Monoolein	W/O	Big	Poor	Very good	Difficult	Thinner
Saturated monoglyceride	W/O	Big	Questionable	Poor	—	Much thicker
Lactic acid esters of monoglyceride	W/O	Big	Very good	Poor	Very difficult	Thicker
Ethoxylated alkyl ether	W/O	Relatively small	Very good	Destabilization	Difficult	
Ethoxylated sorbitan monostearate	O/W	Small	Destabilization	Destabilization	Relatively difficult[h]	
Ethoxylated (12) castor oil	O/W & W/O	Small	Unknown	Unknown	Easy	
Ethoxylated (20) castor oil	O/W	Small	Unknown	Unknown	Easy	

[a] Equilibrium concentrations of emulsifiers in the oil phase were assumed to be high (~1–2%). Company sources as in Table 1.

[b] Formation of water-in-oil (W/O) emulsion is favored by low HLB, and oil-in-water (O/W) by high HLB for emulsifiers. Other abbreviations as in Table 3.

[c] Low interfacial tension gives small droplets and the converse.

[d] Stabilization of W/O emulsion at rest is favored by receding contact angles between 60–80°.

[e] Stabilization of W/O emulsions at shear is favored by advancing contact angles around 60–80°.

[f] The crystals are easily displaced from the oil/water interface to the oil phase when contact angles and interfacial tensions are low (close to 0°), and easily displaced to the water phase when contact angles are high (close to 180°) and interfacial tensions low.

[g] Data from Reference 6.

[h] Easy to remove crystals to the water phase due to their high polarity (high contact angles).

droplets. The table shows the complex functionality of the emulsifiers in food emulsions.

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