Lecithins in Oil-Continuous Emulsions. Fat Crystal Wetting and Interfacial Tension

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ABSTRACT: Lecithin is a powerful emulsifier widely used in foods, feeds and pharmaceuticals. Several analytical methods have been proposed to characterize lecithins, but they are often inadequate to determine the industrial functionality. The purpose of this study was to find a relationship between the interfacial properties of lecithins (adsorption to oil/water and fat crystal/oil/water interfaces), phospholipid composition and functionality. Results show that all lecithins adsorb to fat crystals at the triglyceride oil/water interface, making their surface more polar (observed as an increase in the contact angle measured through the oil at the interface: fat crystal/oil/water). This adsorption process is quick (less than five minutes) for relatively polar lecithins, such as soybean phosphatidylcholine (PC), and results in highly polar surfaces (contact angle ≈180°). Less polar lecithins give slow adsorption (some hours) and less polar crystals (contact angle ≤90°). The adsorption of different lecithins to the oil/water interface, observed as a decrease in interfacial tension, follows the adsorption pattern to the fat crystals. We found a relation between high-fat crystal polarity and poor lecithin functionality in margarine (margarines spatters during frying), and also between high-fat crystal polarity and a high polar to nonpolar phospholipids [Σ(PI + PA + LPC)/ΣPE; PI, phosphatidylinositol; PA, phosphatidic acid; LPC, lysoPC; PE, phosphatidylethanolamine] ratio in lecithin. The correlations might be *via* aggregation properties of lecithin in the oil. We found also that monoolein shifted the adsorption kinetics of lecithin (soybean PC) to fat crystals and the hydrophilicity of adsorbed layers probably due to formation of mixed aggregates between monoolein and soybean PC.

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KEY WORDS: Adsorption, advancing and receding contact angles, association, fat crystals, food, interfacial tension, lecithins, oil/water interface, phospholipids, vegetable oils, wetting.

Lecithin is widely used in the food, feed and pharmaceutical industries, due to its surface activity, high nutritional value and high consumer acceptance (1,2). The food and feed industries mostly use soybean lecithin, which is a complex mixture of mainly phosphatidylcholine (PC), phosphatidylethanolamine (PE), phosphatidylinositol (PI) and phosphatidic acid (PA), and may contain relatively large amounts of triglycerides. A negative consequence of its natural origin is a great variation in composition and quality of technical lecithin. Several analytical methods have been proposed to characterize the lecithins (1,3), but they are often inadequate to determine the physical properties and industrial functionality.

Technical lecithin is often dissolved in oil prior to use, as its molecular solubility in water is very limited [~10^{-14} M for PC (Ref. 4)] due to aggregation phenomena. Lecithin self-association in water has been extensively studied. Micelles are not formed by phospholipids with two fatty acid chains for geometrical reasons. The hydrophilic soybean phospholipids (PC, PI, PA) form lamellar structures and the more hydrophobic soybean PE forms a reversed hexagonal phase. Mixtures of phospholipids are expected to have the association properties which are a function of ingredient properties. It has been found that PI is more decisive for the aggregation of phospholipid mixtures than PC, and the PI/PE ratio is probably more important for the functionality of technical lecithins than the PC/PE ratio (5).

Aggregation of lecithin in triglyceride oils, which is expected to influence functionality, has not been studied. Aggregation in reversed hexagonal or lamellar phases is considered to be the reason that pure phospholipids are poorer viscosity depressers in chocolate systems than are technical lecithins (6), likely forming reversed micelles. Different behavior of PE and PC in displacing the sodium caseinate from the oil/water interface (7,8) has been also explained from the phase behavior of the phospholipids—reversed hexagonal phase by PE and bilayers (lamellar phase) by PC.

It is known that lecithin functions due to adsorption at interfaces. It adsorbs to the oil/water interface and lowers interfacial tension. It also adsorbs to fat and sugar crystals dispersed in vegetable oils (9). The adsorption increases the hydrophilicity of fat crystals, and facilitates their wetting by water in emulsion systems (described by the contact angle) which is important for the stability of emulsions: stabilization is achieved if the crystals are preferentially wetted by the continuous phase, and vice versa (10–17).

Interfacial tension and contact angle are industrially relevant characteristics of lecithins. In our previous work, the interfacial tension and wetting of fat crystals in the presence of a broad selection of emulsifiers were determined. Some lecithins were included, but no consideration was given to aspects such as wetting kinetics or concentration dependence.

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Therefore, the purpose of this study was to determine interfacial tension and wetting of fat crystals in systems containing various lecithins with an emphasis on kinetics. Further, we correlated wetting properties, phospholipid composition and the industrial functionality of lecithins in margarine spattering tests. Differences observed were assigned to aggregation in oils as the central parameter.

MATERIALS AND METHODS

Emulsifiers. We have examined five different lecithins—a pure PC from soybean oil (soybean PC, Epikuron 200; Lucas Meyer, Hamburg, Germany) and four technical lecithins: Bolec ZTD (Unimills, Hamburg, Germany), Topcithin (two batches; Lucas Meyer), Sterncithin (two batches; Stern Chemie, Hamburg, Germany) and Metarin P (Lucas Meyer). The emulsifiers are specified in Table 1. We have also studied the behavior of a mixture of pure soybean PC together with pure monoolein. Monoolein was supplied by Grindsted A/S (Brabrand, Denmark). Its purity was ~99%, the molar mass 366 g/mol, hydrophile–lipophile balance value 3.4 (17), and iodine value 50. The emulsifiers were added to the oil phase in all the systems studied. Two concentrations were examined for most lecithins—a low level (0.1%) and a high level (1%). The emulsifier concentrations calculated from the pure active compound are also summarized in Table 1.

Fat crystals. Fully hydrogenated palm oil (palm stearin) from Karlshamns AB (Karlshamn, Sweden) was used as a standard crystal surface in the wetting experiments. The palm stearin had an average molar mass of 756 g/mol and an iodine value of 2.6. The palm stearin was stable in the polymorphic form β′, which has a melting point of 57–59°C. The α-form of rapidly cooled palm stearin has a melting point of about 46°C. The composition of the hydrocarbon chains in the palm stearin was: 53% C16:0 (palmitic acid), 42% C18:0 (stearic acid), 2% C18:1 (oleic acid), 3% others; and the composition of triglycerides was: 3% POO/MPP, 23% PPP, 37% PPSt, 26% PStSt, 11% StStSt, where M stands for C14:0 (myristic acid), P for C16:0, St for C18:0 and O for C18:1.

The palm stearin crystals (β′ as confirmed by X-ray diffraction at Karlshamns) were recrystallized from analytical grade acetone and were weighed in oil to give 1% w/w. Crystal-specific surface (4.55 m^2/g) was determined at Chalmers Technical University (Gothenberg, Sweden) by BET (Brunauer, Emmett and Teller) adsorption measurements with nitrogen gas.

Technical grade tristearin (purity 65%) from Fluka (Buchs, Switzerland) was used as a base fat filling the plug in the contact angle equipment (Fig. 1).

Oils. A refined soybean oil from Karlshamns AB was used as the oil phase. The interfacial tension between this oil and distilled water was slightly higher than 30 mN/m. This high value indicates that the oil was very pure with respect to surface active components (monoglycerides <0.05%, diglycerides <0.7%, free fatty acids <0.03%, lecithins <1 ppm). The oil had an iodine value of about 130 (~2.5 double bonds per hydrocarbon chain), a melting point of –20°C, density of 0.921 g/mL at 20°C and 0.918 g/mL at 25°C. The composition of fatty acids was: 10.6% C16:0, 3.6% C18:0 , 18.2% C18:1, 56.7% C18:2 (linoleic acid), 9.5% C18:3 (linolenic

TABLE 1
Characterization of Lecithin Systems Studied

	Epikuron 200[a]	Bolec ZTD[b]	Topcithin 1[a]	Topcithin 2[a]	Sterncithin 1[c]	Sterncithin 2[c]	Metarin P[a]
Purity (+) in %	≥98	~47.8	~46.1	~38.6	~46.4	~43.5	~71.3
Molar mass (g/mol)	~773	~802	~808	~817	~810	~811	~776
HLB[d]	~8[e]	7–8[f]	~7[f]	~7[f]	2–4[f]	2–4[g]	4–5[g]
Phospholipid content in %[h]							
PC	≥98	15.4	16.0	14.7	17.2	16.0	24.5
PE	—	12.9	13.6	9.7	13.9	13.1	22.2
PA	—	8.5	5.4	4.2	4.2	4.0	8.5
PI	—	9.8	10.3	8.5	10.7	9.2	15.6
LPC	—	1.2	0.8	1.5	0.4	1.2	0.5
Pure phospholipid concentration in %/mM							
at tot. conc. 0.1%	0.1%/1.2 mM	0.05/0.54	0.05/0.53	0.04/0.44	0.05/0.53	0.05/0.50	0.07/0.85
at tot. conc. 1%	1%/11.6 mM	0.5/5.4	0.5/5.3	0.4/4.4	0.5/5.3	0.5/5.0	0.7/8.5

[a] From Lucas Meyer (Hamburg, Germany). Epikuron 200 stands for pure phosphatidylcholine (PC) from soybean oil, the rest are technical lecithins.

[b] From Unimills (Hamburg, Germany).

[c] From Stern Chemie (Hamburg, Germany).

[d] HLB, hydrophilic–lipophilic balance.

[e] Griffin, W.C., in *Kirk Othomer Encyclopedia of Chemical Technology 8,* 1979.

[f] From solution and adsorption properties.

[g] *Lecithin—Properties and Applications,* Lucas Meyer, Hamburg, 1973.

[h] PE, phosphatidylethanolamine; PA, phosphatidic acid; PI, phosphatidylinositol; LPC, lysoPC; tot. conc., total concentration.

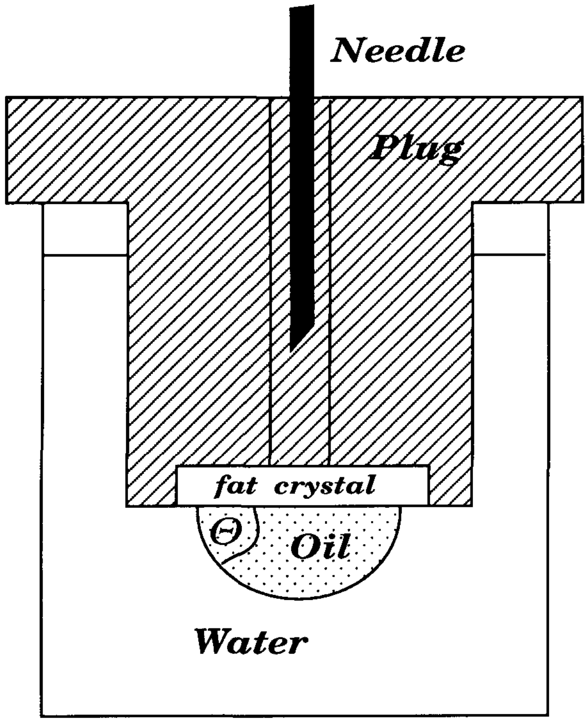

FIG. 1. Contact angle apparatus for measurement at the three-phase boundary: fat crystal/oil phase/water phase.

acid), 0.3% C20:0 (arachidic acid), 0.4% C22:0 (behenic acid) and 0.7% other, and the composition of triglycerides in the oil was: 23.7% LeLeLe, 1.5% LeLeLn, 31.2% OLeLe, 11.6% OOLe, 2.6% OOO, 13% PLeLe, 1.3% PLeLn, 2.6% PLeP, 7.7% POLe, 3.0% POO, 0.7% POP, 0.5% POSt, and 0.5% StOO, where Le stands for C18:2 and Ln for C18:3. The oil was not further purified prior to use.

Interfacial tension. Pendant drop method. The interfacial tension between oil and water phases was measured by a pendant drop method (18). An oil droplet was pressed upward from a bent needle into the water phase. Droplet shape was recorded by a CCD video camera and analyzed with an image processing program (Professor Fihn Knut Hanssen, Oslo University, Oslo, Norway). The reproducibility of this method is good (≤5%). It is especially suitable for recording the time dependence of the interfacial tension for systems with a slow equilibrium adsorption where other methods, like the Wilhelmy plate or Du Noüys ring, fail.

Contact angles. The contact angle at the three-phase contact—water phase/fat crystal surface/oil phase—was measured through the oil phase in the system presented in Figure 1. The plug, made of PTFE (Poly Tetra Fluor Ethylene), was first described by van Boekel (11) and further developed by Campbell (12) and Darling (13). The plug was filled with fat and dipped in a glass vessel containing water at room temperature. The oil droplet was pressed through the plug onto the fat crystal surface. Contact angle was observed with a goniometer from Ramé-Hart Inc. (Mountain Lake, NJ). The advancing contact angle, determined by pressing an oil droplet (~100 μL) onto the water-covered fat crystal surface, was monitored for periods of 2–4 h.

The preparation of fat crystal surfaces for contact angle measurements. A base fat (tristearin of technical grade) was melted at about 80°C. The hollow in the plug (Fig. 1) was filled with the melted base fat, which was allowed to crystallize in air at room temperature. The fat to be examined was then melted at about 80°C, and the plug was dipped into it. The plug was cooled in the refrigerator in order to obtain the α form of palm stearin by rapid supercooling. To obtain the β′ form of palm stearin, the samples were conditioned for 90 min (1.5 h) at 40°C. The presence of the β′ form was confirmed by DTA (differential thermal analysis) and X-ray diffraction analysis performed at Karlshamns.

RESULTS

Interfacial tension. Time dependence. The time dependence of interfacial tension between oil and water in the presence of lecithin is shown in Figure 2A on a long-time scale and in Figure 2B on a short-time scale. A low concentration of lecithins (0.1%) gave a slow reduction over a period of 2–3 h (Fig. 2A), and a higher concentration (1%) gave a faster equilibrium (5–10 min). There were clear differences between technical products: The slowest time dependence was shown by the most hydrophobic Sterncithin and Metarin, the most rapid by the hydrophilic soybean PC. Topcithin gave an intermediate dependence.

Interfacial tension. The influence of fat crystals in the oil. In Figure 3, interfacial tensions are compared for systems of distilled water/oil; distilled water/0.1% soybean PC in oil; distilled water/0.1% soybean PC in oil + 1% fat crystals (palm stearin β′) in oil. The interfacial tension between oil and water was ~30 mN/m and showed no time dependence. The addition of 0.1% soybean PC lowered the tension to ~5 mN/m with a subsequent decrease to ~1 mN/m after about 10 min. In the presence of 1% fat crystals, the interfacial tension at equilibrium increased to ~10 mN/m. Soybean PC adsorbs to fat crystals [~1.5 μmol/m^2 at concentration of 0.1% ≈ 1.2 mM (Ref. 9)], which decreases its concentration in the oil (by roughly 10%) and at the oil/water interface resulting in a higher interfacial tension. The time dependence, a continuous decrease from the pure oil value (~30 mN/m) to 10 mN/m after 20 min, is interpreted as being due to a slow desorption of soybean PC from the fat crystal/oil interface and adsorption to the oil/water interface.

Contact angles. Time dependence for different lecithins. The time dependence of the advancing contact angle for the fat crystals of palm stearin β′ at the interface between distilled water and lecithin solutions in soybean oil is presented in Figure 4A for low concentration of lecithins (0.1% ≈ 1.2 mM), and in Figure 4B for high concentration of lecithins (1% ≈ 12 mM). The lecithins examined are specified in Table 1.

Results show that 0.1% of technical lecithin did not significantly change the wetting of fat crystals, with the exception of soybean PC, which led to an increase in the contact angle

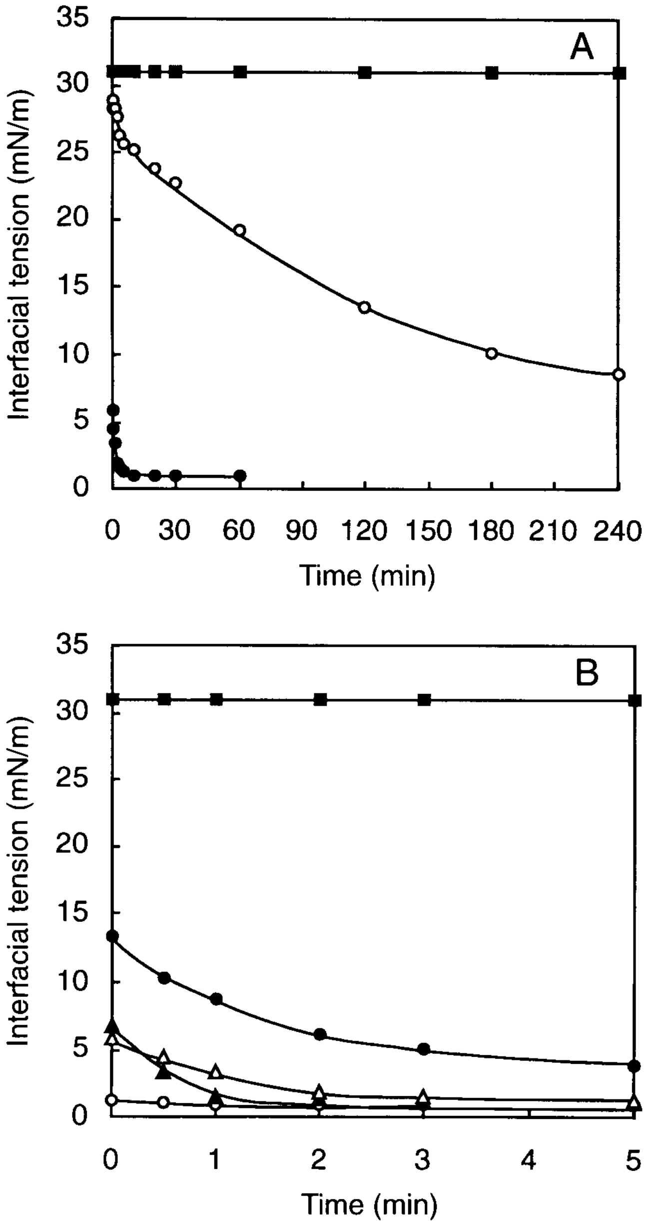

FIG. 2. Interfacial tension between distilled water and lecithin solutions in soybean oil as a function of time. Interfacial tensions were determined with a pendant drop method. Lecithins examined are specified in Table 1. A. Long-time dependence (~4 h) for pure soybean oil (■), 0.1% (○) and 1% (●) Metarin P in soybean oil. B. Short-time dependence (~5 min) for pure soybean oil (■) and 1% solutions of Sterncithin 1 (●), Topcithin 1 (▲), Metarin P (△) and soya phosphatidylcholine (○) in soybean oil (lower graph).

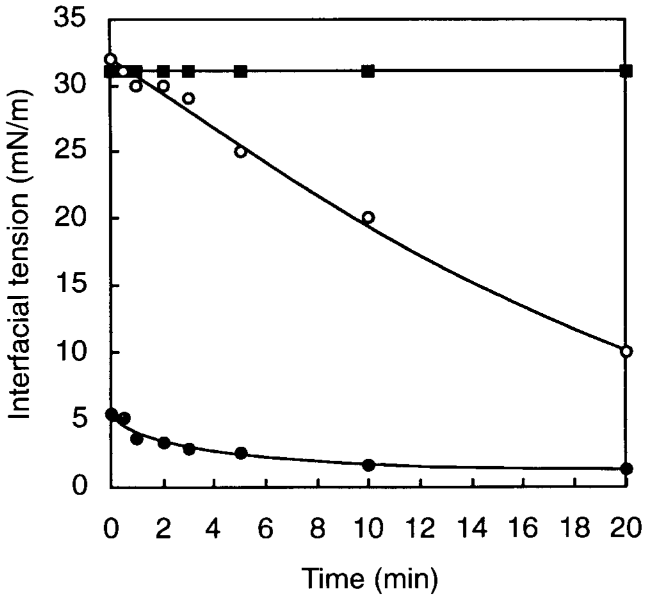

FIG. 3. Time dependence (~30 min) for interfacial tension between distilled water and soybean oil (■), oil solution of 0.1% soya phosphatidylcholine (PC) (●) and oil solution of 0.1% soya PC with 1% fat crystals of palm stearin β′ (○).

over 10–15 min. Crystals became polar at equilibrium (contact angles ~120°). At a concentration level of 1%, all lecithins gave a time-dependent increase in crystal hydrophilicity. The equilibrium was reached rapidly in the case of a hydrophilic lecithin (~5 min for soybean PC), slower for less hydrophilic lecithins (~30 min for Bolec), and slowest for hydrophobic lecithins (≥2 h for Topcithin and ≥3 h for Sterncithin). The equilibrium contact angle values (summarized in Table 2) were also dependent on the type of lecithin, and were high for hydrophilic lecithins and relatively low for hydrophobic lecithins.

Contact angles. Mixtures of lecithins and monoglycerides. The time dependence of the advancing contact angle for soybean PC (0.1, 0.2 and 1%), and for a mixture of 0.2% soybean PC and 0.8% monoolein, is presented in Figure 5. When the concentration of soybean PC was increased, the contact angles increased and the equilibrium was reached more rapidly. For a mixture of soybean PC and monoolein, the initial polarity of the crystals (contact angle ~35°) was much lower than for 0.2% soybean PC (contact angle ~150°), but of the same order of magnitude as for 0.8% monoolein (contact angle ~40°). The contact angle increased slowly and approached a level slightly above the values for the surface in the presence of 0.1% soybean PC (~110°) after 2 h. This increase with time is expected to continue until the contact angles approach the levels for the surface in the presence of 0.2% pure soybean PC (~150°).

The isotherm of the advancing contact angles for a mixture of soybean PC and monoolein (weight ratio 1:4) at the fat crystal surface palm stearin β′ was determined and compared to the isotherms for the pure compounds soybean PC and monoolein (Fig. 6). The isotherm for the mixture is plotted in three different ways: as a function of the entire concentration of both emulsifiers, as a function of soybean PC in the mixture, and as a function of monoolein in the mixture. The results show that the isotherm for the mixture, plotted as a function of soybean PC, is slightly below the isotherm for the pure soybean PC. This indicates that almost pure soybean PC was adsorbed to the fat crystal surface at equilibrium, at least at relatively high concentrations (monoolein + soybean PC

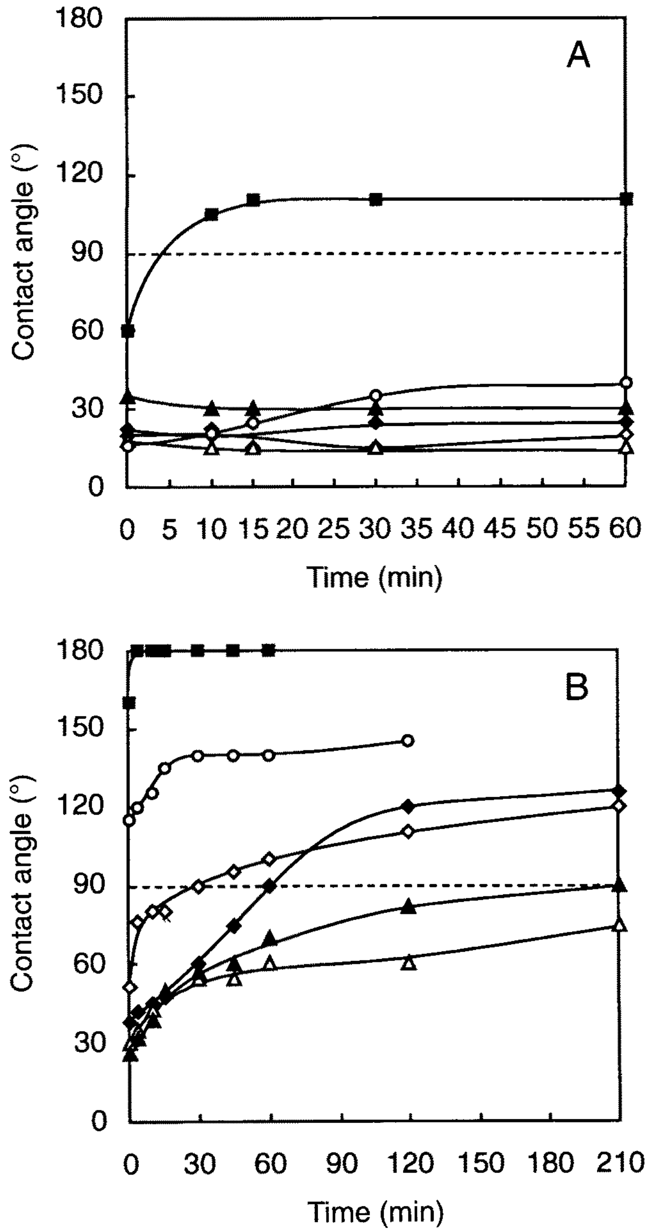

FIG. 4. Time dependence for the advancing contact angle at the three-phase boundary: distilled water—a solution of lecithin in soybean oil–fat crystal surface (palm stearin β′). The following lecithins have been studied: soya phosphatidylcholine (PC) (■), Bolec (○), Topcithin 1 (◇), Topcithin 2 (◆), Sterncithin 1 (△) and Sterncithin 2 (▲). The lecithins are specified in Table 1. A. Low concentration of lecithins: 0.1% ≈ 1.2 mM. B. High concentration of lecithins: 1% ≈ 12 mM.

≥10 mM). At low concentrations (monoolein + soybean PC ≤2 mM), the contact angle isotherm for the mixture seems to follow the isotherm for pure monoolein.

DISCUSSION

Phospholipid ratios. There is a qualitative correlation between the contact angle at equilibrium and the ratio of anionic-to-hydrophobic phospholipids [Σ(PA + PI)/ΣPE] and the ratio of hydrophilic-to-hydrophobic phospholipids [Σ(PA + PI + LPC)/ΣPE] (LPC, lysoPC) presented in Figure 7, but not the ratio of PC to PE (ΣPC/ΣPE) as indicated in Table 2 by correlation coefficients. Thus, the PI, the PA and the LPC were more decisive for the properties of the phospholipid mixtures than was the PC. This result agrees with the behavior of phospholipid mixtures in water (5), where the ratio PI/PE is much more indicative than PE/PC in making the phospholipid mixtures more hydrophilic (observed as the formation of lamellar liquid crystalline phases instead of reversed hexagonal phases). The differences in the fat crystal wetting observed in the presence of different lecithins seem to be related to aggregation.

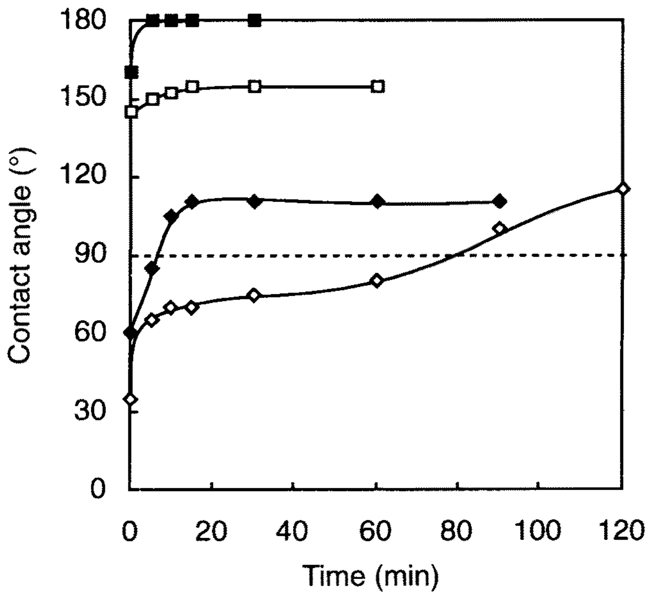

FIG. 5. Time dependence of the advancing contact angle at the three-phase boundary: distilled water—solutions of soya phosphatidylcholine (PC) and monoolein in soybean oil–fat crystal surface (palm stearin β′). The following concentrations of soya PC have been studied: 1% (■), 0.2% (□), 0.1% (◆), and compared to the mixture of 0.2% soya PC and 0.8% monoolein (◇).

Consequences to industrial functionality. A correlation was observed between the advancing contact angle for lecithins adsorbed to the fat crystals (palm stearin β′) at the oil/water interface and the lecithin functionality determined in an industrial spattering test at Van den Berghs Foods in Sweden (Table 2 and Fig. 7). Hydrophilic fat crystals (high contact angle) corresponded to poor lecithin functionality (the margarine spatters extensively during frying). This correlation is unlikely to be due to any direct effect of the crystals on the margarine droplets because the crystals clearly melt below the temperature for frying. A more probable explanation is that both fat crystal polarity and the emulsion droplet instability in margarine depend on the lecithin type and on its solution properties in oil (formation of aggregates). Thus, hydrophilic lecithin tends to form aggregates permitting rapid adsorption from solution resulting in polar layers and unstable emulsion droplets. This is supported by the correlation be-

TABLE 2
Advancing Contact Angles Between Three Phases (refined soybean oil/fat crystals of palmstearin β′/distilled water) and Industrial Functionality (spattering tests at Van Den Bergh Foods, Helsingborg, Sweden) for Lecithins[a]

Lecithin	Functionality[b]	Advancing contact angle at equilibrium	$\frac{\Sigma PC}{\Sigma PE}$	$\frac{\Sigma(PA + PI)}{\Sigma PE}$	$\frac{\Sigma(PA + PI + LPC)}{\Sigma PE}$
Soya PC	—	180°	—	—	—
Bolec	Very bad	145°	1.19	1.42	1.51
Topcithin 1	Bad	120°	1.18	1.15	1.21
Topcithin 2	Bad	125°	1.15	1.31	1.46
Sterncithin 1	Good	75°	1.24	1.07	1.10
Sterncithin 2	Acceptable	90°	1.22	1.00	1.10
Metarin P	—	65°	1.10	1.09	1.11
Correlation coefficients for relation between contact angle and phospholipid ratio:					
Without soya PC			0.029	0.848	0.889
Without soya PC and Metarin P			−0.780	0.897	0.901

[a] Ratios of phospholipids are also specified, as well as correlation coefficients for relations between contact angle and the ratio. Abbreviations and company sources as in Table 1.
[b] Good functionality indicates no spattering of margarine during frying.

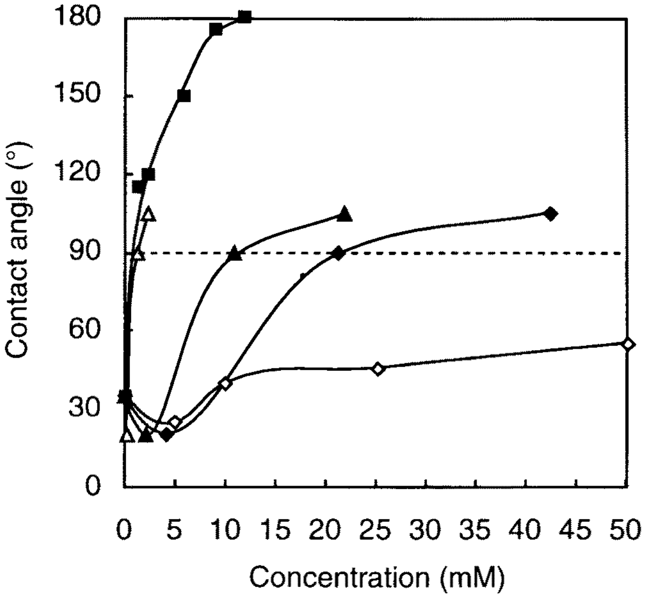

FIG. 6. Advancing contact angle at the three-phase boundary: distilled water–soybean oil (SBO) and solutions of different emulsifiers in soybean oil–fat crystal surface (palm stearin β′) as a function of the emulsifier concentration in the oil (contact angle isotherm). The following emulsifiers in soybean oil were investigated: soya phosphatidylcholine (PC) (■), monoolein (◇) and a mixture of soya PC and monoolein in a weight ratio 1:4. For the mixture, the advancing contact angle is plotted as a function of: a sum of concentrations of soya PC and monoolein (◆), concentration of monoolein in the mixture (▲), and concentration of soya PC in the mixture (△).

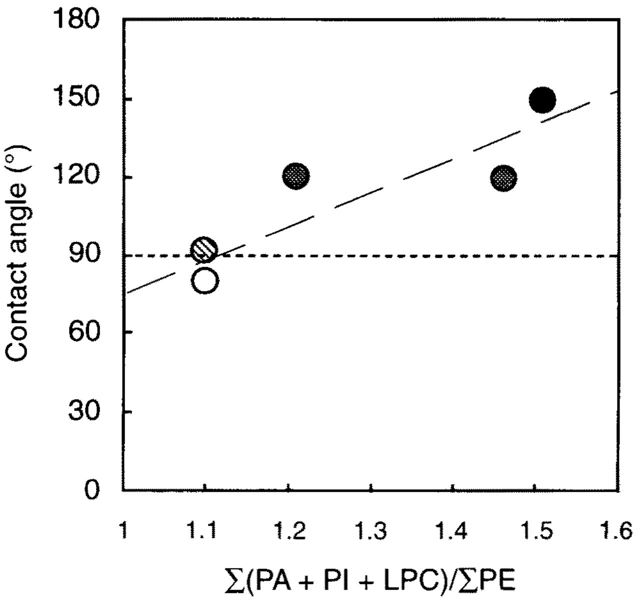

FIG. 7. Equilibrium values of the advancing contact angle at three-phase boundary: distilled water–solutions of lecithins in soybean oil (1%)–fat crystal surface (palm stearin β′), as a function of the phospholipid ratio Σ(PA + PI + LPC)/ΣPE = Σhydrophilic/Σhydrophobic. The functionality of the lecithins (determined in a spattering test at Van Den Bergh Foods, Helsingborg, Sweden, see Table 5) is indicated as follows: open circle, good; diagonal lined circle, acceptable; shaded circle, bad; closed circle, very bad. PA, phosphatidic acid; PI, phosphatidylinositol; LPC, lysophosphatidylcholine; PE, phosphatidylethanolamine.

tween high contact angles for fat crystals and a high ratio of hydrophilic-to-hydrophobic phospholipids [Σ(PI + PA + LPC)/ΣPE] in lecithin. Finally, our results show that some aspects of the industrial functionality of lecithins can be characterized by simple contact angle measurement.

Adsorption and aggregation. The time dependence for interfacial tension and contact angle in systems containing lecithins depends on the slow adsorption kinetics at oil/water and to the fat crystals/oil/water interfaces. The slow adsorption kinetics are probably due to the formation of lecithin aggregates in the oil. These aggregates influence both lecithin solubility and diffusion in oil. A rearrangement of the adsorbed layers with time can also take place. Differences between the lecithins are significant and reflect the different adsorption, aggregation and rearrangement phenomena. There appears to be a qualitative agreement between contact angle and interfacial tension.

Results for the mixture of monoolein and soybean PC (Fig. 5) indicate that monoolein probably adsorbs initially to the fat crystals. Soybean PC adsorbs more slowly but displaces the monoolein from the surface. Further, the adsorption of the mixture is slower than that for each component. This kinetic shift is probably due to changes in aggregation properties of soybean PC or to formation of mixed aggregates between soybean PC and monoolein.

The contact angle isotherms for a mixture of soybean PC and monoolein (Fig. 6) indicate that layers of almost pure soybean PC are adsorbed to the fat crystal surface at intermediate and high concentrations. At low concentrations, monoolein primarily adsorbs to the surface. This shift in the composition of adsorbed layers at equilibrium could be a result of aggregate formation by the soybean PC and monoolein. These aggregates show a concentration dependence.

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