The Influence of Food Emulsifiers on Fat and Sugar Dispersions in Oils. I. Adsorption, Sedimentation

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The adsorption isotherms of several emulsifiers to fat and sugar crystals dispersed in oils have been determined. Further, the influence of the emulsifiers on the interactions between the crystals has been estimated in sedimentation experiments, where an increased sediment volume due to adsorption corresponds to an increased adhesion between the crystals and *vice versa*. Most of the emulsifiers examined adsorb weakly to fat crystals and form tight monolayers, resulting in increased adhesion between the crystals at high concentrations. On the other hand, loosely packed layers are formed at low concentrations, and a decreased adhesion is observed. Unsaturated monoglycerides and phospholipids cause a decrease in adhesion for all concentrations examined.

The emulsifiers adsorb more strongly to sugar crystals than to fat crystals and form tightly packed monolayers with hydrocarbon chains directed to the oil. The crystals are then stabilized sterically—the adhesion between them is weaker and the sediments are more compact. At low concentrations, the opposite behavior often occurs. Monoglycerides interact in a specific way with sugar and cause increased adhesion between the crystals for all concentrations examined. Phospholipids reduce the adhesion between sugar crystals, resulting in much denser sediments. Saturated monoglycerides in amounts over the solubility limit tend to precipitate as a network between fat or sugar crystals, which causes bulky sediments and results in better stability against oiling out.

KEY WORDS: Adsorption, emulsifiers, fat, food, isotherms, sedimentation, sugar, triglycerides.

Several food systems consist of a dispersion of particles (fat crystals, sugar crystals, proteins) in a continuous oil phase. An example of such a system is chocolate, which is a dispersion of fat, sugar and cacao in a liquid oil (1,2). Margarine, on the other hand, is an emulsion where water droplets are captured in a network of fat crystals in the oil (3). Most oil-continuous food dispersions contain emulsifiers, which are of natural origin or added as stabilizers, regulators of rheological properties and/or regulators of crystallization of fats. The emulsifiers function mainly due to their ability to adsorb to different surfaces like oil/water, water/air or particle surfaces.

The adsorption of food emulsifiers to oil/water, water/air or oil/air interfaces has been studied by surface tension measurements (4). The adsorption isotherms for the food emulsifiers to different crystals dispersed in oils rarely appear in the literature. Strong adsorption of phospholipids to different particles dispersed in several solvents has been observed—*e.g.*, to silica particles dispersed in alcohols (5,6); to silica and alumina particles dispersed in hexane and water (7); to silica and carbon particles dispersed in benzene, chloroform, ethanol and amyl alcohol (8); and to silica particles in benzene (9). Lucassen-Reynders (10) has presented the adsorption isotherm for monoolein to tristearin crystals in paraffin oil. van Boekel (11) has assumed that there is no adsorption of emulsifiers from the oil to nonpolar fat crystals. In most of the prior studies, both the oil and the crystals differ greatly from those appearing in real food systems. Therefore, the practicality of these results is questionable.

The lack of basic investigations in this area limits our understanding of emulsifier behavior in food systems. Thus, the purpose of this study was to survey how different emulsifiers adsorb to various crystals dispersed in vegetable oils. We calculated the adsorbed amount, the strength of the adsorption and how it depends on the character of the emulsifier, crystal and oil. Finally, we propose a model for the adsorbed layers and their influence on crystal-crystal interactions. The latter topic was studied by simple but informative sedimentation experiments. The experiments were interpreted in terms of the often cited relationship of high sediment density (small sediment volume) and weak adhesion between particles (12–20). Hence, a decrease in sediment volume with increasing emulsifier concentration indicates a weaker attraction and/or a stronger repulsion between the particles due to the presence of adsorbed layers. The opposite effect, an increase in sediment volume, indicates a stronger adhesion of crystals caused by the adsorbed emulsifier.

EXPERIMENTAL PROCEDURES

Aside from a few pure compounds, most chosen materials were commercial samples.

Emulsifiers. The trade names of the emulsifiers, their manufacturers and some of their physical properties (21–23) are listed in Table 1. The lengths of the hydrocarbon chains and the structures of the polar head groups of the emulsifiers are shown in Table 2. All emulsifiers were used without further purification.

Crystals. Fat crystals were represented by pure tristearin obtained from Fluka (Buchs, Switzerland) (purity > 99%, density 1.0577 g/mL, mole mass 892 g/mole). They were recrystallized from acetone of analytical grade in portions, passed through filter paper and dried in a vacuum dryer to remove residual solvent. DTA (differential thermal analysis) and melting point microscopy showed that only pure β-crystals were present in the samples. The specific surface of each recrystallized portion was between 2.5 and 7 m^2/g by BET adsorption measurements with nitrogen gas. The crystals were stored in a freezer and were stable over the time of the experiments (BET measurements after approximately one year storage gave the same results). Microscopic studies in oils showed needle-like crystals, which were weakly flocculated (any shear on the samples destroyed the flocs). No changes in crystal appearance in the oils could be observed after long periods of storage (months). The crystals were (as expected) oil-insoluble.

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TABLE 1

Characterization of Emulsifiers

Emulsifier	Trade name	Purity (%)	Density (g/mL)	Mole mass (g/mole)	Iodine value	HLB[a]
Phosphatidylcholine from SBO[b]	Epikuron 200	⩾98	Not specified	~773	~100	~8[c]
A mixture of phospholipids[b]	Metarin P	~80	Not specified	~760	80	~7[c]
Monolein[d]		>99	0.942	366	50	3.4[e]
Unsaturated MG[d,f]	Dimodan LS	⩾90	Not specified	~363	105	5.2[e]
Saturated MG[d]	Dimodan PV	⩾90	Not specified	~365	⩽2	3.8[e]
Polyglycerol EFA[d]	Triodan R90	⩾90	Not specified	~505	85	7.7[e]
Lactic acid EMG[d]	Lactodan P22	Not specified	Not specified	~550	⩽2	~7[c]
Sorbitan EFA[d]	Famodan MS	Not specified	Not specified	~595	⩽2	4.7[e]
Diacetyl tartaric acid EMG[d]	Panodan ATD	Not specified	Not specified	~579	30	~8[c]
Propylene glycol EFA[d]	Promodan SP	⩾95	Not specified	331	⩽2	3.4[e]

[a] HLB, hydrophilic lypophilic balance.

[b] From Lucas Meyer (Hamburg, Germany).

[c] Estimated from solution properties.

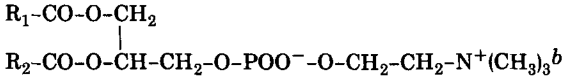
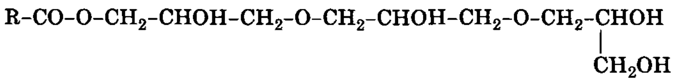
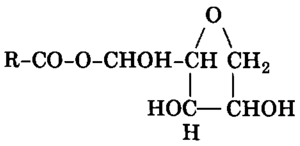
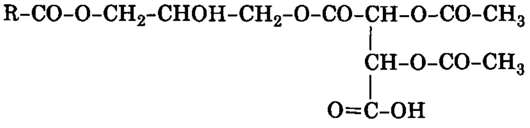
[d] From Grinsted (Brabrand, Denmark).

[e] Reference 22.

[f] MG, monoglycerides; EMG, esters of MG; EFA, esters of fatty acids; SBO, soybean oil.

TABLE 2

Characterization of Polar Groups and Hydrocarbon Chainlengths of the Emulsifiers

Emulsifier	Chainlengths	Polar head groups
Phosphatidylcholine from SBO[a]	Mostly C18	 $\begin{array}{l} R_1\text{-CO-O-CH}_2 \\ \qquad\qquad\;\, | \\ R_2\text{-CO-O-CH-CH}_2\text{-O-POO}^-\text{-O-CH}_2\text{-CH}_2\text{-N}^+(\text{CH}_3)_3 \end{array}$[b]
A mixture of phospholipids	C16/C18	~21% PC, ~21% PE, ~18% PI[c]
Monoolein	C18	$\text{R-CO-O-CH}_2\text{-CHOH-CH}_2\text{OH}$
Unsaturated MG	Mostly C18	$\text{R-CO-O-CH}_2\text{-CHOH-CH}_2\text{OH}$
Saturated MG	Mostly C18	$\text{R-CO-O-CH}_2\text{-CHOH-CH}_2\text{OH}$
Polyglycerol EFA	Mostly C18	 $\begin{array}{r} \text{R-CO-O-CH}_2\text{-CHOH-CH}_2\text{-O-CH}_2\text{-CHOH-CH}_2\text{-O-CH}_2\text{-CHOH} \\ | \quad\;\; \\ \text{CH}_2\text{OH} \end{array}$
Lactic acid EMG	C16/C18	$\text{R-CO-O-CH}_2\text{-CHOH-CH}_2\text{-O-CO-CHOH-CH}_3$
Sorbitan EFA	C16/C18	
Diacetyl tartaric acid EMG	C16/C18	 $\begin{array}{l} \text{R-CO-O-CH}_2\text{-CHOH-CH}_2\text{-O-CO-CH-O-CO-CH}_3 \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \text{CH-O-CO-CH}_3 \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\qquad\qquad\quad \text{O=C-OH} \end{array}$
Propylene glycol EFA	C16/C18	$\text{R-CO-O-CH}_2\text{-CHOH-CH}_3$

[a] As in footnote f, Table 1.

[b] R, R_1, R_2, hydrocarbon chains.

[c] PC, phosphatidylcholine; PE, phosphatidylethanolamine; PI, phosphatidylinositol.

Sugar crystals (saccharose, purity ≈ 100%, density 1.5805 g/mL, mole mass 342 g/mole) were obtained from Swedish Sugar Company (Arlöv, Sweden). They were specially ground and sieved to obtain the largest possible specific surface (1.15 m^2/g; measured by BET adsorption with nitrogen and argon). The sugar crystals were stored in a dessicator to insure a stable specific surface area. The crystals were irregular and formed a few flocs in the oil. These flocs were stronger than the fat crystal flocs. Saccharose is insoluble in oil and the crystal appearance did not change over long periods.

Other materials and chemicals. Most of the experiments were performed in soybean oil, which was supplied by Karlshamns AB (Karlshamn, Sweden). The oil was refined and its lecithin content was below 1 ppm, monoglycerides were below 0.03% and diglycerides were below 0.7%, according to the supplier. The oil is a natural mixture of triglycerides with a majority of C18 (>85%) and C16 (≈10%) hydrocarbon chains. Soybean oil is highly unsaturated with an iodine value of about 132 (≈2.5 double bonds per hydrocarbon chain on average). Its density is 0.921 g/mL, and the molar mass is approximately 868 g/mole.

The high-performance thin-layer chromatography (HPTLC) plates (silica 60) were purchased from Merck (Darmstadt, Germany). Merck also supplied the solvents (dodecane, decanol, chloroform, hexane, acetone, diethyl ether, ethanol, acetic acid, phosphoric acid, *etc.*), as well as the developing agents for TLC:PMA (thin-layer chromatography:phosphomolybdic acid) and anhydrous cupric sulfate. All chemicals were of analytical grade.

Direct adsorption measurements. Saccharose crystals (2 g) were carefully mixed with 3 g of the oil solution to give a 40% (w/w) dispersion. With tristearin, 0.75 g of the crystals were mixed with the oil solutions to give a 15% (w/w) dispersion. Concentrations were chosen as high as possible to maximize surface area in each sample, thereby increasing the accuracy of the analysis. The upper limits for these concentrations were determined by mixability and presence of a clear upper phase after centrifugation. Both saccharose and tristearin were added as crystals with known specific surfaces. Recrystallization in the oil was not performed so as to avoid incorporation of the emulsifiers in the crystals, which often occurs in such systems (24–26). Oil solutions were prepared by weighing. The emulsifier concentrations were kept in the region of about 1–15 mmol/L.

The dispersions were allowed to stand about 24 h at room temperature (∼22°C) to reach equilibrium before they were centrifuged (Labofuge from Heraeus Christ, Osterode, Germany) for about 1 h at about 4200 rpm. The samples gave 1.5–2 mL of upper phase, which was carefully transferred to a small test tube for analysis by HPTLC to obtain the equilibrium concentrations in the dispersions. The adsorbed amounts on the crystals were then calculated as the difference between the initial and the equilibrium concentrations. The surface excess Γ [$\mu mol/m^2$] was estimated by dividing the adsorbed amount by total crystal surface allowed. A control test showed that centrifugation of the samples did not affect the adsorbed amounts. In this test the adsorbed amount was estimated by the analysis of the oil phase before and after centrifugation of the sample. The number of layers on the surface was calculated by dividing the maximum adsorption, estimated from the isotherms, by the maximum adsorption for a tightly packed monolayer, Γ_m, which was estimated by assuming an area of about 35 $Å^2$/hydrocarbon chain for the adsorbed emulsifier molecules (27). Generally, the standard deviation for adsorption points is 5–30%. Saccharose data deviate by 5–20%, and tristearin by 10–30%.

Adsorption of components from soybean oil to the fat or sugar crystals was controlled by mixing crystals in the oil without any emulsifier. The upper phase obtained after centrifugation of such samples was analyzed by HPTLC and compared with a sample of a pure oil. The control showed no selective adsorption to the fat crystals. For sugar crystals a small and unclear difference in the pattern of the pure oil was observed. In any case, this difference does not significantly influence adsorption results.

HPTLC. We followed previously published procedures (28–31) for this method. The silica gel plates (10 × 20 cm) were pre-washed and dried in a fume hood prior to contact with chloroform. Samples were applied with a microapplicator (Camag, Muttenz, Switzerland) to give exact volumes in the range of 0.5–2 μL (±0.01 μL). Twelve spots/plate gave good resolution. Sample spots (called P) were alternated with the standard spots (S) in the following way: S1, P, S2, P, S1, P, S2, P. . ., where S1 has a lower concentration than P, and S2 higher one. Many possible errors (for example, errors caused by nonuniformity of plates in their development or charging) were avoided by comparison of each P spot with the two neighboring S-spots. Each sample was analyzed by at least six spots. Some samples were analyzed in duplicate or triplicate to check reproducibility, which was reasonably good (standard deviation was less than ±5%).

Spotted plates were developed in hexane/diethyl ether/acetic acid (70:30:1, vol/vol/vol) and dried in a fume hood. Spots were detected by dipping the plate into the developing reagent with an automatic dipping device (Camag). Unsaturated emulsifiers were visualized with 5% PMA in ethanol. After dipping, the plates were heated to 120°C for about 6 min. Blue-colored spots appeared on a yellow background. For saturated emulsifiers, solutions of anhydrous cupric sulfate (100 g) in phosphoric acid (80 mL) and distilled water (to give 1 L) were used as a dipping reagent. The dipped plates were heated to 160°C for 10 min, and dark spots appeared on the light background.

Charged plates were scanned automatically at least three times with a TLC Scanner (Shimadzu, Japan), which measures the spots' absorption of a UV-VIS light beam. Wavelengths for maximum absorption were ≈630 nm for the PMA-dipped plates and ≈380 nm for the cupric sulfate-dipped plates. The lower limit for the analysis was estimated to be about 0.01–0.02% of emulsifier in the oil, or to approximately 0.1–0.2 μg of emulsifier in the spot. The developed plates underwent less than 1% change after about 1 h, the time necessary for three scans.

Sedimentation experiments. For the experiments with soybean oil, 0.5 g of saccharose crystals were mixed with 4.5 g of the oil or the oil solution to give a 10% (w/w) dispersion. For tristearin, 0.05 g of the crystals were mixed with 4.95 g of the oil or oil solution. For experiments with the organic solvents, the amounts of crystals and liquid phases are specified in the figure legends.

Four solutions of each emulsifier in the oil were prepared with the following concentrations in mmol/L: 1, Between 2 and 3, between 5 and 7 and between 10 and 15 (the same concentration region as in the adsorption measurements). The concentrations were recalculated to the equilibrium concentrations with the help of the adsorption isotherms.

The sedimentation experiments were performed in a series of five samples. Each series included one type of crystal (fat or sugar) and one type of emulsifier with increasing concentration from 0 to ≈15 mmol/L. Five to eight series were prepared simultaneously to compare the sediment volumes (particularly those of zero samples) and to estimate the reproducibility, which was found to be reasonably good (SD < 10%).

The results are presented in relative units:

$$\Delta V[\%] = 100\% \times (V - V_0)/V_0$$

where V is the sediment volume of the sample and V_0 is the sediment volume of a corresponding zero-sample without emulsifier.

Water content. The water content of the samples was estimated to be <0.1% in the adsorption experiments and <0.2% in the sedimentation experiments. Because real food systems are never free of water, we have chosen to work with samples with some amount of water.

Validity of the adsorption and sedimentation results. The results for tristearin crystals are qualitatively of general validity for other types and polymorphic forms of triglyceride crystals because all solid triglycerides have similar crystal surfaces of nonpolar hydrocarbon character (32). The results for saccharose are generally valid for similar OH-rich, nonionic surfaces. The differences between different triglyceride oils are expected to be small, because differences in chemical nature of these oils are small.

RESULTS

Nature of solvents. Figures 1 and 2 show a comparison between the adsorption of monoolein to sugar and fat crystals from three different oils—dodecane, decanol and soybean oil—and the corresponding sedimentation results. This comparison shows that adsorption and sediment volumes differ greatly in thease oils.

Monoolein adsorbs strongly to sugar in dodecane (Fig. 1) and forms more than one monolayer (monolayer adsorption occurs at about 5 μmol/m² surface). The adsorption causes a decrease in the sediment volume of the dispersion. Adsorption from soybean oil is much weaker, and a loosely packed monolayer is formed. The adsorption increases the sediment volume. In decanol, the detected adsorption and decrease in sediment volumes are smaller than errors in the Experimental Procedures.

A similar pattern is observed for fat crystals (Fig. 2). Adsorption is strongest in dodecane and weakest in soybean oil. The adsorption isotherm in soybean oil is similar to that in paraffin oil as presented by Lucassen-Reynders (10). No adsorption can be observed from decanol. Generally, the adsorption to fat is weaker than that to sugar, and the adsorbed amounts are smaller (loosely packed layers). The corresponding sedimentation results show that the adsorption of monoolein to fat crystals does not change the sediment in decanol, while in dodecane and soybean oil a small decrease in the sediment volumes is observed. Furthermore, strong adsorption of phosphatidylcholine (PC) is observed, in a quantity much larger than needed for formation of a monolayer on sugar in soybean oil (Fig. 3). This result can be compared to a weak monolayer adsorption of PC to silica gel particles in alcohols (5,6). The latter systems were suggested as a model for chocolate products.

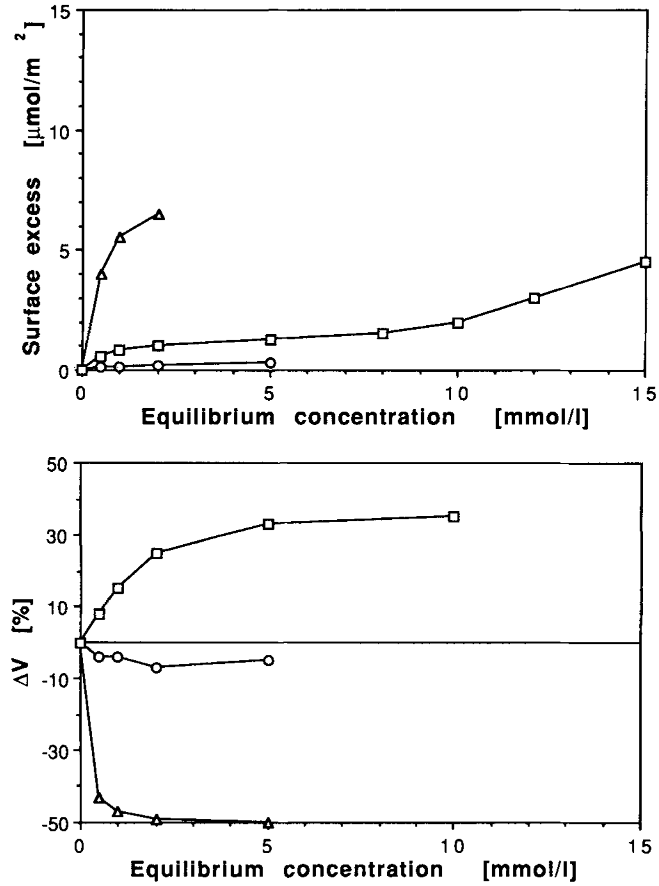


FIG. 1. A comparison of adsorption on, and sedimentation of, saccharose crystals in different solvents at room temperature (~22°C). The adsorbed amount (Γ) and the relative change in sediment volume of the crystals (ΔV) are given as a function of equilibrium concentration of emulsifiers in the solvents. Monoolein in dodecane (△), soybean oil (□) and decanol (○). For sedimentation, the crystal volume is 1.25 mL, while the total sample volume is 6.1 mL. The sediment volumes in the zero-samples are 5.1 mL in dodecane, 3.6 mL in soybean oil and 3.2 mol in decanol, respectively.

Our results show that both adsorption and sedimentation depend strongly on the specific nature of oil phases. Hence, if one wants to understand food systems based on oils, the experimental media should be triglyceride oils. Simple organic solvents, such as hydrocarbons or alcohols, do not represent the real systems because the interactions in the systems are specific for the solvent. Thus, all further experiments were performed in a refined vegetable oil (from soya) to assure the applicability of the results.

Sugar crystals in soybean oil. The adsorption isotherms for 10 common food emulsifiers to sugar crystals dispersed in soybean oils are presented in Figures 3, 4 and 5, together with the sedimentation results for the corresponding systems. The results are summarized in Table 3.

Phospholipids (lecithins) adsorb strongly in large amounts (Fig. 3) and form multilayers or aggregates on the surface. The formation of lecithin aggregates in oils

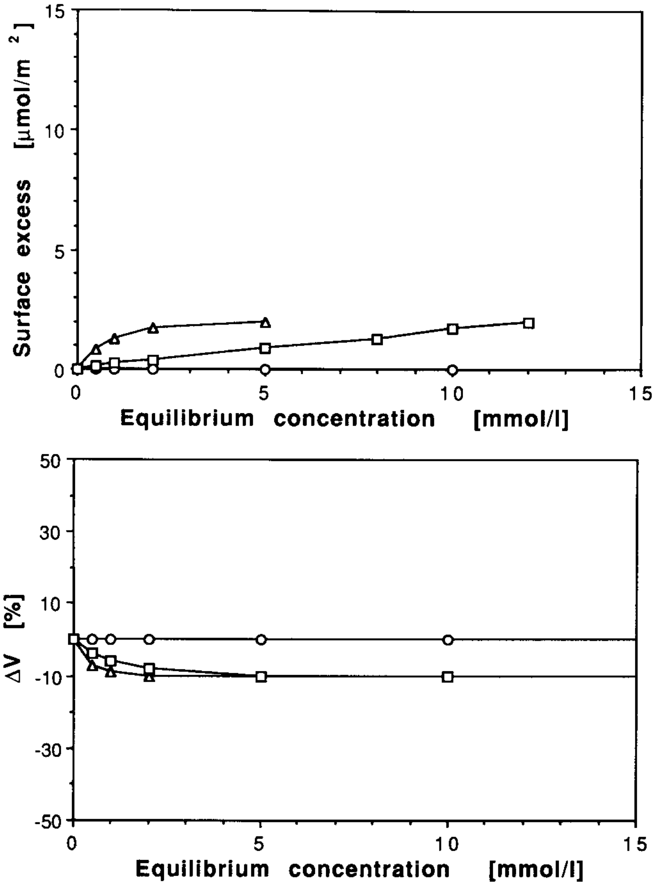


FIG. 2. A comparison of adsorption on, and sedimentation of, tristearin crystals in different solvents at room temperature (~22°C). The adsorbed amount (Γ) and the relative change in sediment volume of the crystals (ΔV) are given as a function of equilibrium concentration of emulsifiers in the solvents. Monoolein in dodecane (Δ), soybean oil (□) and decanol (○). For sedimentation, the crystal volume is 0.2 mL, while the total sample volume is 5.0 mL. The sediment volumes in the zero-samples are 4.3 mL in dodecane, 4.0 mL in soybean oil and 3.8 mol in decanol, respectively.

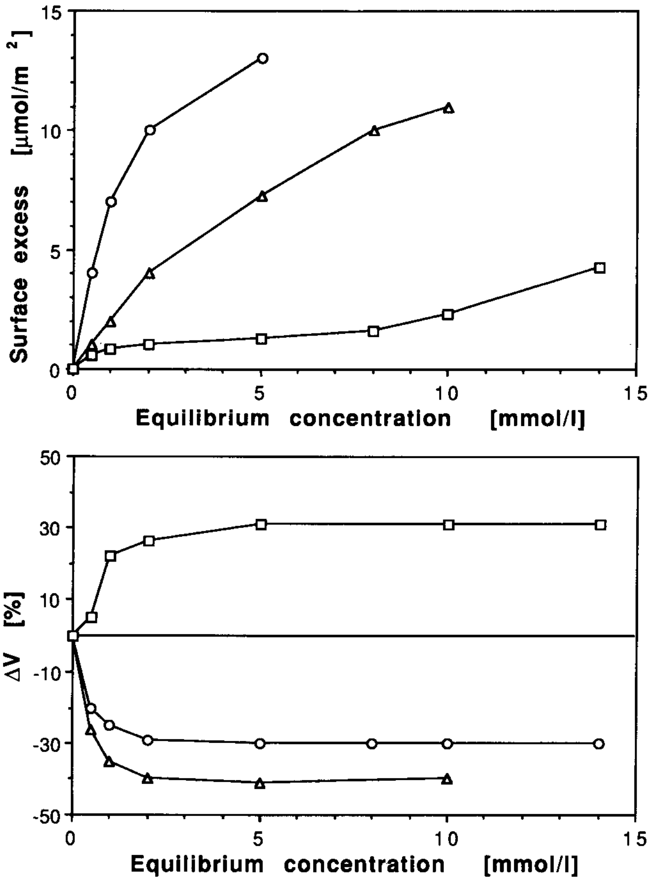


FIG. 3. Adsorption isotherms for, and the sedimentation of, saccharose crystals dispersed in soybean oil at room temperature (~22°C). The adsorbed amount (Γ) and the relative change in sediment volume (ΔV) are plotted as a function of the equilibrium concentration of emulsifiers. For sedimentation, the crystal volume is 0.3 mL, the total sample volume is 5.5 mL and the volume of the zero-samples is 3.0 mL. Phosphatidylcholine (PC) from soybean oil (○), a commercial mixture of soybean phospholipids (Δ) and a pure monoglyceride monoolein (□).

has been reported previously (33–35), as well as formation of lecithin aggregates (hemimicelles) on surfaces (8,36). The presence of lecithins decreases sediment volumes of sugar by about 30%. A technical grade lecithin, containing different phospholipids, seems to be slightly more effective than a pure phosphatidylcholine.

Monoglycerides adsorb weakly or moderately, depending on their degree of saturation (Fig. 4). Saturated monoglyceride adsorbs strongly, resulting in about a monolayer on the surface, up to the concentration where it precipitates (~3 mmol/L). Weakly adsorbing unsaturated monoglycerides result in loosely packed monolayers at low concentrations. These layers become tighter at higher concentrations. Monoglycerides display the opposite effect on the sedimentation of sugar as compared to lecithins. They increase the sediment volumes by about 30%. Saturated monoglycerides, which are less oil-soluble, increase sediment volumes up to 200% (not shown in Fig. 4), probably due to precipitation of some monoglyceride between the sugar particles.

Lactic acid and diacethyl tartaric acid esters of monoglycerides adsorb relatively weakly, while polyglyerol and sorbitan esters of fatty acids adsorb much more strongly (Fig. 5). All of them (except sorbitan esters, which precipitate at concentrations > 5 mmol/L) form tightly packed monolayers on the surface. Propylene glycol esters of fatty acids, which have a smaller and less polar head group than the other emulsifiers (Table 2), show no detectable adsorption.

Lactic acid esters increase the sediment volume of sugar in the oil, while propylene glycol esters have no significant effect. The remaining emulsifiers decrease the volume occupied by sugar when present in large concentrations. Polyglycerol and sorbitan esters display the opposite effect at low concentrations.

Fat crystals in soybean oil. The adsorption isotherms of the emulsifiers on fat crystals dispersed in oils are presented in Figures 6, 7 and 8, together with the sedimentation results. The results are summarized in Table 4.

Lecithins adsorb moderately and form at least double layers (Fig. 6). Monoglycerides adsorb weakly. Adsorption increases with degree of saturation of monoglycerides (Fig. 7). The monoglycerides usually form loosely packed layers on the surface. With lecithins and unsaturated

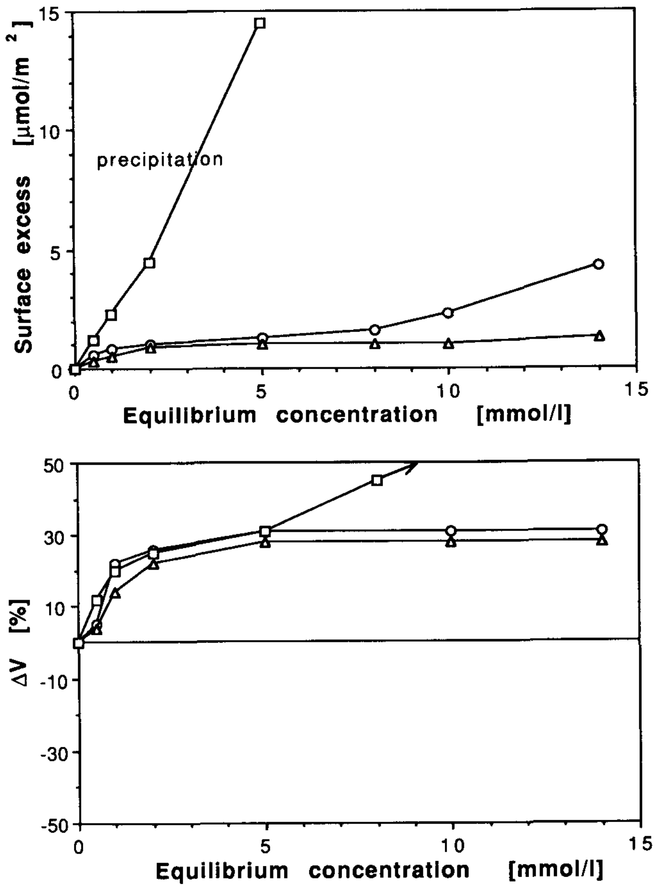


FIG. 4. Adsorption isotherms for, and the sedimentation of, saccharose crystals dispersed in soybean oil at room temperature (∼22°C). The adsorbed amount (Γ) and the relative change in sediment volume (ΔV) are plotted as a function of the equilibrium concentration of emulsifiers. For sedimentation, the crystal volume is 0.3 mL, the total sample volume is 5.5 mL and the volume of the zero-samples is 3.0 mL. Three different monoglycerides were used: A pure monoolein with iodine value 50 (○), distilled unsaturated monoglycerides with iodine value ≈105 (△) and a distilled saturated monoglyceride with iodine value ⩽2 (□).

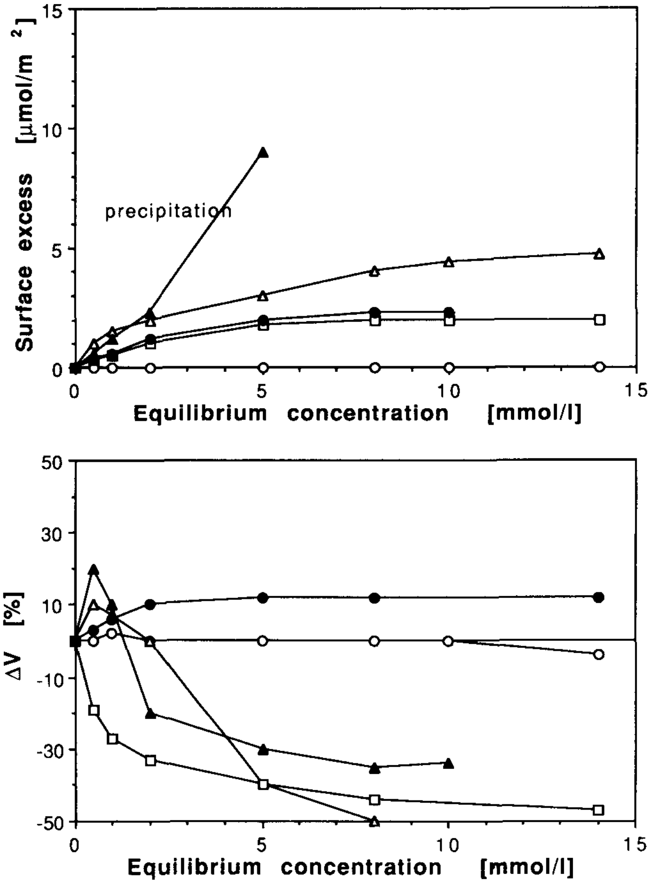


FIG. 5. Adsorption isotherms for, and the sedimentation of, saccharose crystals dispersed in soybean oil at room temperature (∼22°C). The adsorbed amount (Γ) and the relative change in sediment volume (ΔV) are plotted as a function of the equilibrium concentration of emulsifiers. For sedimentation, the crystal volume is 0.3 mL, the total sample volume is 5.5 mL and the volume of the zero-samples is 3.0 mL. Lactic acid (●) and diacetyl tartaric acid (□) esters of monoglycerides and polyglycerol esters (△), sorbitan esters (▲) and propylene glycol esters (○) of fatty acids.

TABLE 3

Adsorption and Sedimentation Data for Sugar Crystals

Emulsifier	Slope of adsorption isotherms	Slope of sedimentation curves	Maximum adsorption	Surface per molecule at maximum adsorption	Number of monolayers at maximum adsorption[a]	Change in sedimentation volume at maximum adsorption
	(μmole/m²) (mmol/L)	% (mmol/L)	(μmole/m²)	(Å²)		(%)
PC from SBO[b]	8.0	40	15.0	11	⩾6	−30
A mixture of phospholipids	3.0	52	10.0	16	⩾4	−40
Monoolein	1.2	10	5.0	33	∼1	+30
Unsaturated MG	0.6	8	1.2	140	⩽1	+25
Saturated MG	2.4	24	(precipitation)		⩾1	+200
Polyglycerol EFA	2.0	20	4.5	37	∼1	−70
Lactic acid EMG	0.8	6	2.5	66	<1	+10
Sorbitan EFA	1.4	40	(precipitation)		⩾1	−30
Diacetyl tartaric acid EMG	0.6	38	2.0	83	<1	−45
Propylene glycol EFA	0.0	0	0	—	—	0

[a] Surface area per hydrocarbon chain is assumed to be around 35 Å² (70 Å² for phospholipids with two chains per emulsifier molecule).

[b] PC, phosphatidylcholine; SBO, soybean oil; MG, monoglycerides; EMG, esters of monoglycerides; EFA, esters of fatty acids.

TABLE 4

Adsorption and Sedimentation Data for Fat Crystals

Emulsifier	Slope of adsorption isotherms	Slope of sedimentation curves	Maximum adsorption	Surface per molecule at maximum adsorption	Number of monolayers at maximum adsorption[a]	Change in sedimentation volume at maximum adsorption
	(μmole/m^2) (mmol/L)	% (mmol/L)	(μmole/m^2)	(Å^2)		(%)
PC from SBO[b]	1.0	24	4.0	41	~2	−15
A mixture of phospholipids	1.2	34	5.0	33	~2	−25
Monoolein	0.2	8	3.0	55	≤1	−10
Unsaturated MG	0.05	0	1.0	166	<1	−5
Saturated MG	0.6	30		(precipitation)	≫1	+350
Polyglycerol EFA	0.4	14	2.0	83	~1	+15
Lactic acid EMG	0.6	30	2.0	83	~1	+15
Sorbitan EFA	1.0	20		(precipitation)	≫1	+25
Diacetyl tartaric acid EMG	0.2	20	2.0	83	~1	+20
Propylene glycol EFA	0.0	0	0	—	—	0

[a] Surface area per hydrocarbon chain is assumed to be around 35 Å^2 (70 Å^2 for phospholipids with two chains per emulsifier molecule).
[b] As in Table 3.

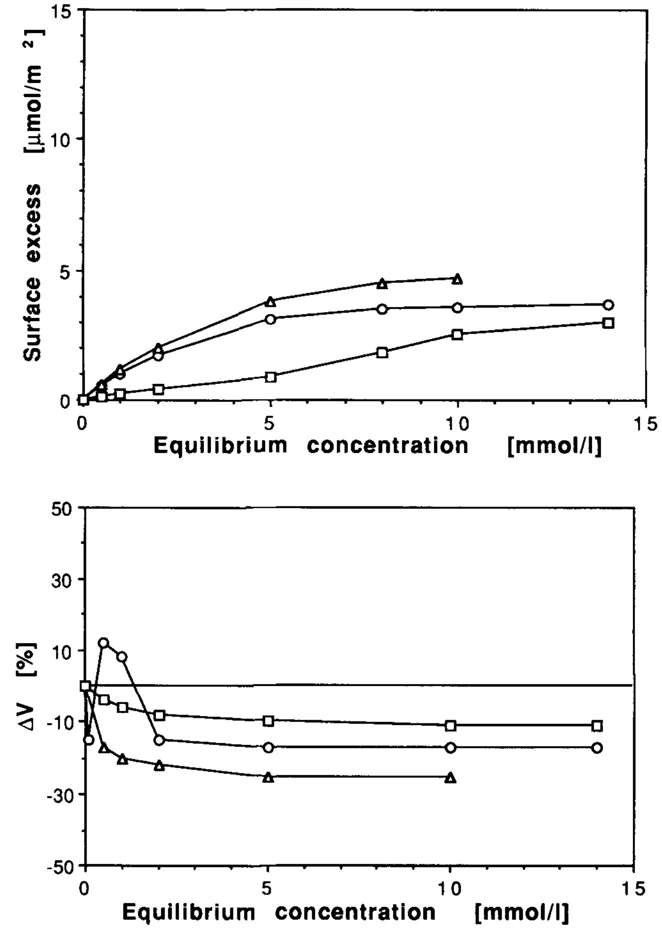


FIG. 6. Adsorption isotherms for, and the sedimentation of, tristearin crystals dispersed in soybean oil at room temperature (~22°C). The adsorbed amount (Γ) and the relative change in sediment volume (ΔV) are plotted as a function of the equilibrium concentration of the emulsifiers. For the sedimentation experiments, the crystal volume is 0.1 mL, the total sample volume is 5.5 mL and the volume of the zero-sample is 1.0 mL. Phosphatidylcholine (PC) from soybean oil (○), a commercial mixture of soybean phospholipids (△), a commercial mixture of soybean phospholipids (△) and a pure monoglyceride monoolein (□).

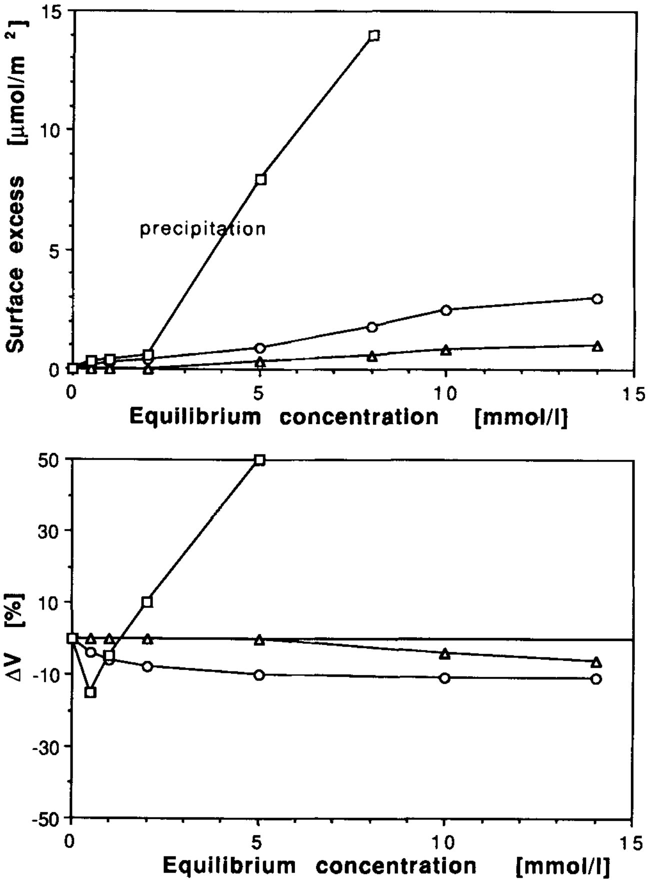


FIG. 7. Adsorption isotherms for, and the sedimentation of, tristearin crystals dispersed in soybean oil at room temperature (~22°C). The adsorbed amount (Γ) and the relative change in sediment volume (ΔV) are plotted as a function of the equilibrium concentration of the emulsifiers. For the sedimentation experiments, the crystal volume is 0.1 mL, the total sample volume is 5.5 mL and the volume of the zero-sample is 1.0 mL. Three different monoglycerides were used: A pure monoolein with iodine value 50 (○), distilled unsaturated monoglycerides with iodine value ≈105 (△) and a distilled saturated monoglyceride with iodine value ≤2 (□).

monoglycerides present in sufficient concentrations, a moderate decrease in fat sediment volumes is observed. A commercial mixture of phospholipids is most effective in this sense, and the most unsaturated monoglyceride shows the lowest efficiency. The saturated monoglycerides, which initially decrease the sediment volumes, display the opposite effect at higher concentrations, giving an increase in volume by about 300% (not shown in Fig. 7). This might indicate the formation of bridges between the crystals.

Diacetyl tartaric acid esters of monoglycerides also adsorb weakly, while lactic acid esters of monoglycerides and polyglycerol esters of fatty acids adsorb slightly stronger, and sorbitan esters of fatty acids are the strongest (Fig. 8). All of them form tightly packed monolayers on the surface. No detectable adsorption is observed with the propylene glycol esters. Most of these esters of fatty acids and esters of monoglycerides give a moderate increase in the sediment volume of fat crystals when present in sufficient amounts, whereas they show the opposite effect at low concentrations. The exceptions are polyglycerol esters of fatty acids, which increase the sediment volumes for all examined concentrations, and the propylene glycol esters, which do not influence sedimentation.

Generally speaking, adsorption to fat is weaker than to sugar crystals. The sequence of the strongest to weakest adsorbing emulsifiers is also different for fat and sugar crystals, which indicates that the adsorption mechanisms are of a different nature. Adsorption of different emulsifiers influences the sediment volumes of fats and sugars differently. The same emulsifiers also can adsorb in different manners at different concentrations.

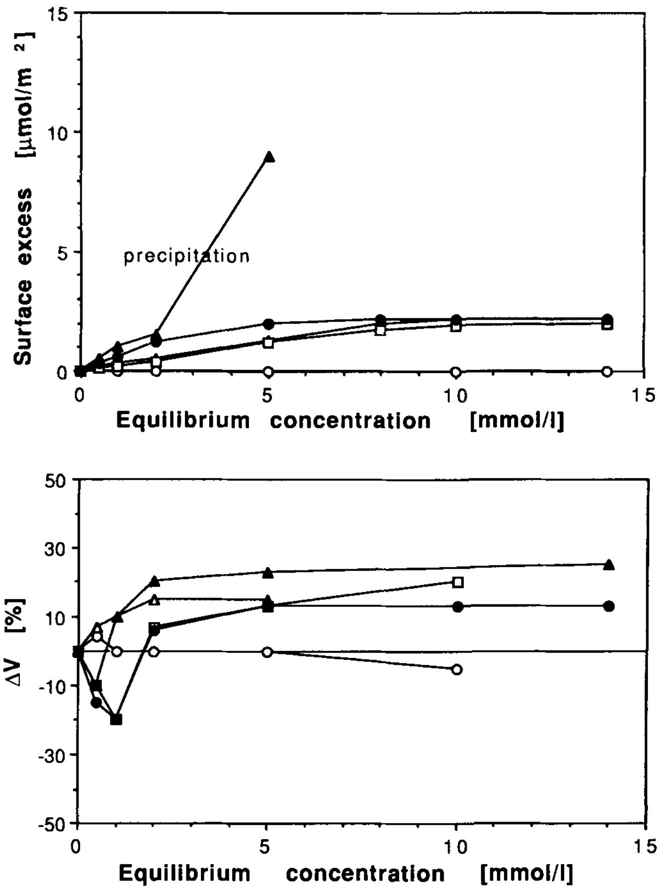


FIG. 8. Adsorption isotherms for, and the sedimentation of, tristearin crystals dispersed in soybean oil at room temperature (∼22°C). The adsorbed amount (Γ) and the relative change in sediment volume (ΔV) are plotted as a function of the equilibrium concentration of the emulsifiers. For the sedimentation experiments, the crystal volume is 0.1 mL, the total sample volume is 5.5 mL and the volume of the zero-sample is 1.0 mL. Lactic acid (●) and diacetyl tartaric acid (□) esters of monoglycerides (EMG) and polyglycerol esters (△), sorbitan esters (▲) and propylene glycol esters (○) of fatty acids (EFA).

DISCUSSION

Sedimentation as a fingerprint for adsorption and interactions. The adsorbed layers change the chemical nature of the particle surfaces and, consequently, the forces between the particles. The forces between particles influence sedimentation of the dispersions (12–20), as schematically illustrated in Figure 9. As adhesion (attraction) between the particles increases, they stick more easily to each other, with a formation of larger flocs and looser, more bulky sediments as a consequence. Increased repulsion has the opposite effect: Particles do not stick to each other, they can pass each other more easily when settling, and they form denser, more compact sediments.

A correlation between adsorption and sedimentation at low surface coverages is clear from the comparison between the slopes of the adsorption isotherms and the sedimentation curves presented in Tables 3 and 4 and in Figure 10a. A relationship exists but is clouded by the spread of the points, caused by uncertainty in experimental

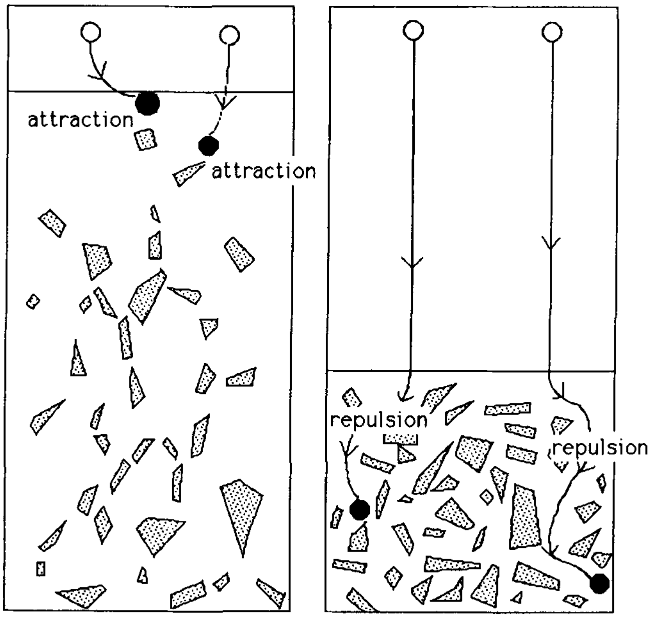


FIG. 9. The influence of interparticle forces on particle trajectories and on sediment volumes. Predominating attraction between particles results in large sediment volumes and loosely packed particles, while predominating repulsion results in small sediment volumes and tightly packed particles. ○, A particle before sedimentation; and ●, a particle after sedimentation.

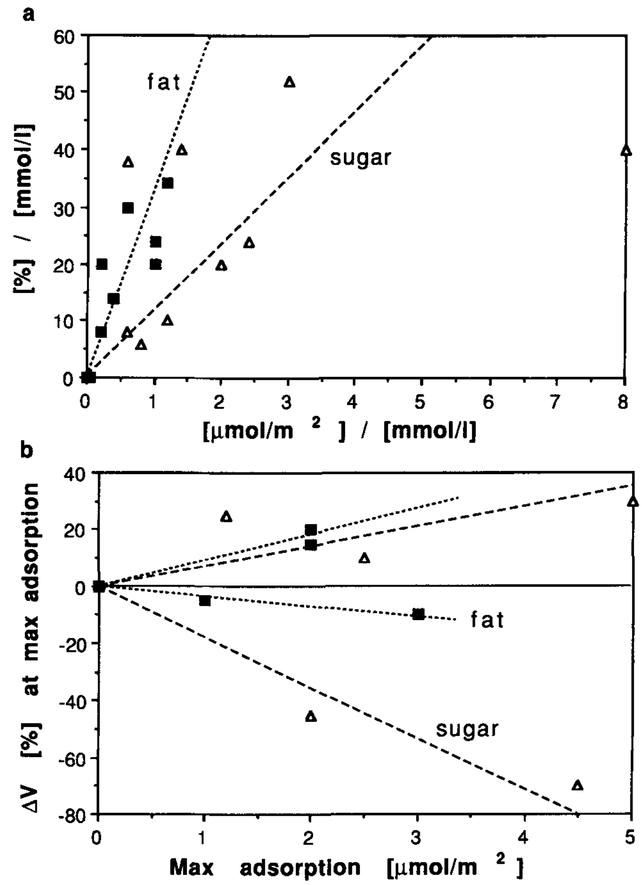


FIG. 10. A comparison of adsorption and sedimentation results. a) The slopes of the sedimentation curves (Y-axis) as a function of the slopes of the adsorption isotherms (X-axis), for sugar crystals (△) and for fat crystals (■). b) The maximum changes in relative sediment volumes, ΔV (Y-axis) as a function of the maximum adsorbed amount (X-axis), for sugar crystals (△) and for fat crystals (■). Only the emulsifiers adsorbing in monolayers are considered.

methods, as well as by differences in the nature of the adsorbed molecules and of the interparticle forces.

A correlation between adsorption and sedimentation also exists at high surface coverages for the emulsifiers adsorbing in monolayers. This relationship is presented in Figure 10b, where the relative change in sediment volume, ΔV, at maximum adsorption measured is presented as a function of the maximum adsorbed amount. The emulsifiers adsorbing in multilayers or as aggregates (phospholipids) and the precipitating emulsifiers (satured monoglycerides and sorbitan esters of fatty acids) are excluded from this comparison. Figure 10b shows that as the adsorbed layers become tighter, they cause bigger changes in interactions and sediments. The relationship is different for sugar and fat (separate curves occur). It is also different for the emulsifiers adsorbing with hydrocarbon chains directed to the oil (giving steric stabilization, weaker interactions and lower sediments) and for emulsifiers adsorbing with polar head groups directed to the oil (giving additional polar interaction and higher sediments). In general, the strongest changes in interactions (the steepest curve) are given by the steric stabilization of polar sugar surfaces by the emulsifier chains. The weakest changes in interactions result from steric stabilization of nonpolar fat surfaces by the emulsifier chains. The increase in interaction due to the additional polar interaction of head groups is intermediate and about the same for fat and sugar.

Adsorption model—Henry's isotherm. To interpret the adsorption data, a theoretical model has to be applied. The most common model for adsorption from solution to solid surfaces is the Langmuir model (31,32). However, the assumptions in this model are not always met in our adsorption experiments (see Tables 3 and 4). Some of the emulsifiers adsorb in multilayers or as aggregates. In some other cases inflection points are present on the isotherms (S- or LS-shaped isotherms), which indicate a reorganization of the adsorbed molecules on the surface, or a presence of different sites, which means that the Langmuir model not applicable either.

An alternative way to estimate the equilibrium constants and free energies of adsorption is *via* Henry's isotherm for the low concentration region (37,38):

$$\theta = k_c \times C \qquad [1]$$

where $\theta = \Gamma/\Gamma_m$ and represents a degree of surface coverage, Γ is the adsorbed amount (μmole/m^2) and Γ_m the monolayer adsorption (μmole/m^2), C is the equilibrium concentration (mmol/L) and k_c the equilibrium constant for the adsorption (L/mmol). Eq. [1] can be rewritten as:

$$\Gamma/C = \Gamma_m \times k_c \qquad [2]$$

where Γ/C is the initial slope of the adsorption isotherms with units (μmol/m$_2$)/(mmol/L). The slopes Γ/C, estimated directly from the adsorption isotherms, are presented in Tables 3 and 4.

Γ_m values can be estimated from the assumed value for the cross-sectional area of 35 Å^2/hydrocarbon chain. This is slightly larger than the cross-sectional area per hydrocarbon chain in lamellar structures, which is fairly constant, close to 30 Å^2, regardless of the type of the head group. It is strongly influenced by the degree of unsaturation of the hydrocarbon chain (27). By using this approximation one assumes that the molecules adsorb standing, with the hydrocarbon chains in optimal position for tight packing, and there is no influence of the head groups or the surface chemistry on the packing density.

A better way would be to estimate Γ_m directly from the experimental adsorption data, which is done in Table 5 for all possible cases. For the two phospholipids, which adsorb in multilayers or as aggregates, the adsorption data are not precise enough to determine the monolayer adsorption. For saturated monoglycerides and sorbitan esters of fatty acids, one cannot be sure that monolayers are formed before precipitation. Thus, these four emulsifiers are excluded from further theoretical considerations.

The equilibrium constants, k_c (L/mmol), calculated from Eq. [2], can be converted to dimensionless mole-based equilibrium constants, k_a, by the following equation:

$$k_a = 10^6 \times k_c \times \varrho_{oil}/M_{oil} \qquad [3]$$

where ϱ_{oil} is the density of the oil (g/mL), and M_{oil} is the molar mass of the oil (g/mol). The equilibrium constant, k_a, is presented in Table 6 together with the free energy

TABLE 5

Monolayer Adsorption Obtained from Adsorption Isotherms. Surface Area per Adsorbed Molecule, a_m, is Calculated from the Monolayer Adsorption

Emulsifier	Monolayer adsorption Γ_m (μmol/m^2)		Surface area per adsorbed molecule a_m (Å^2/molecule)	
	Saccharose	Tristearin	Saccharose	Tristearin
Phosphatidylcholine from SBO[a]	b	b	—	—
A mixture of phospholipids	b	b	—	—
Monoolein	1.5	1.00	111	166
Unsaturated MG	1.0	0.75	166	221
Saturated MG	b	b	—	—
Polyglycerol EFA	4.5	2.00	37	83
Lactic acid EMG	2.5	2.00	66	83
Sorbitan EFA	b	b	—	—
Diacetyl tartaric acid EMG	2.0	2.00	83	83
Propylene glycol EFA	0.0	0.0	—	—

[a] Abbreviations as in footnote b in Table 3.

[b] Data are not precise enough to determine monolayer adsorption.

TABLE 6

A List of Equilibrium Constants for Adsorption, k_a (estimated from Henry's model), and Free Energies for Adsorption, $-\Delta G_a$

Emulsifier	Equilibrium constant, k_a		Adsorption free energy, $-\Delta G_a$ (kJ/mole)	
	Saccharose	Tristearin	Saccharose	Tristearin
Phosphatidylcholine from SBO[a]	—	—	—	—
A mixture of phospholipids	—	—	—	—
Monoolein	850	210	16.6	13.1
Unsaturated MG	640	70	15.9	10.4
Saturated MG	—	—	—	—
Polyglycerol EFA	470	210	15.1	13.1
Lactic acid EMG	340	320	14.3	14.2
Sorbitan EFA	—	—	—	—
Diacetyl tartaric acid EMG	320	110	14.2	11.5
Propylene glycol EFA	1	1	0.0	0.0

[a] As in Table 5.

of adsorption, ΔG_a, calculated from (37,38):

$$\Delta G_a = -RT \ln (k_a) \qquad [4]$$

Driving forces to adsorption. Solubility of emulsifiers in the oil. The driving force for adsorption consists of three distinct parts—the surface-oil interaction (which diminishes due to the adsorption), the emulsifier-oil interaction and the surface-emulsifier interaction.

In the case of sugar, interaction between its polar surface and nonpolar oil is unfavorable and weak, with no polar contributions. The emulsifier-oil interaction depends on the emulsifier and is reflected in its oil solubility (presented in Table 7). The surface-emulsifier interaction also depends on the kind of emulsifier, which interacts with the surface by van der Waals forces and by polar head group interactions (for example, by formation of hydrogen bonds).

Interaction between the nonpolar fat crystal surface and nonpolar oil is expected to be favorable. Hence, the main driving force for adsorption is an unfavorable interaction between the emulsifer and the oil which, again, is reflected

TABLE 7

Solubility of Emulsifiers in Soybean Oil, Estimated Visually (macroscopically and in microscope), and Solubility Parameters, Estimated from the Group Contributions to Molar Volumes and to Molar Attraction Constants[a]

Emulsifer or solvent	Solubility, S_{SBO} (mmole/L)	Solubility parameters, δ_t (mJ/mole)
Phosphatidylcholine from SBO[b]	20	19.1
A mixture of phospholipids	30	19.1
Monoolein	25	20.9
Unsaturated MG	30	21.0
Saturated MG	3	20.9
Polyglycerol EFA	30	23.4
Lactic acid EMG	20	22.8
Sorbitan EFA	5	23.0
Diacetyl tartaric acid EMG	30	22.1
Propylene glycol EFA	50	19.9
SBO		18.3

[a] See Table 8.

[b] Abbreviations as in Table 3.

in its oil solubility. The emulsifiers interact with a nonpolar crystal surface mainly by van der Waals forces.

A relationship between the adsorption equilibrium constants, k_a, and the solubilities of the emulsifiers (which represent the emulsifier-oil interactions) is presented in Figure 11a for sugar and fat crystals. The correlation coefficients for the straight lines are 0.66 for sugar and 0.85 for fat, respectively. These correlation coefficients suggest the existence of a correlation for the fat crystals, but a much less pronounced correlation for sugar crystals. This suggests that adsorption to fat is mainly due to the unfavorable emulsifier-oil interaction. Further, the interaction between the sugar surface and the emulsifier molecules is dominated by polar interactions, which strongly depend on the character of the polar group of the emulsifier.

Solubility parameters. The interactions between different molecules can be expressed by the solubility parameters or other related cohesion parameters (39). The solubility parameters of Hildebrand, δ, are defined in the following way:

$$\delta = (\Delta U/V)^{1/2} \qquad [5]$$

where $\Delta U = \Delta H - RT$ is the molar internal energy of vaporization (J/mol), ΔH is the enthalpy of vaporization (J/mol), R is the gas constant (J/mol × K), T is the temperature (K), and V is the molar volume of the substance (m^3/mol). Generally speaking, the solubility parameters of polar liquids are high and those of nonpolar liquids are low.

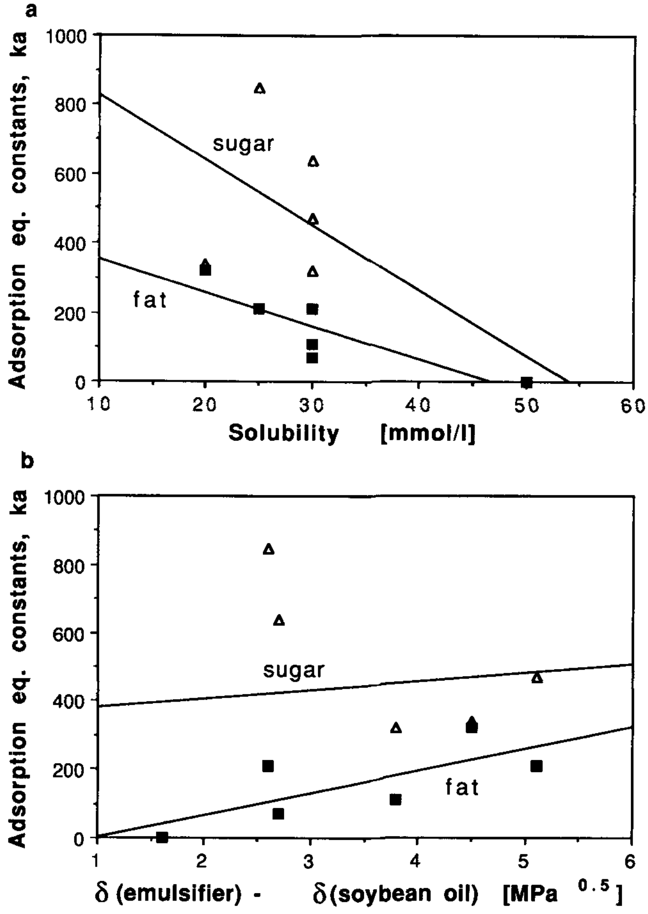


FIG. 11. The equilibrium constants for adsorption (k_a) to sugar crystals (△) and to fat crystals (■) in soybean oil, as a function of the solubility of the emulsifiers: a) Measured in mmol/L; b) expressed as a difference in solubility parameters for the emulsifiers and for the oil.

Solubility parameters can be used to describe the solubility of different molecules in liquids. If the δ-parameters for the solute and the solvent are nearly equal, mutual solubility is good. As the difference between the parameters ($\Delta\delta$) increases, solubility decreases. For $\Delta\delta \approx$ 4–5 $MPa^{1/2}$, the solute precipitates. Solubility and other cohesion parameters also can be used to describe adsorption, which depends on the relative interaction between the solute, the solvent and the surface. Some models have been suggested in the literature (39–41).

Solubility parameters are experimental parameters, but a simplified estimation can be done by the approximate group contribution method (39). The contributions of different groups to the molar volume (^zV) and the molar attraction constants are presented in Table 8. The solubility parameters of the emulsifiers and solvents are then calculated from:

$$\delta = (\textstyle\sum {}^zF + 276.3)/\sum {}^zV \ [MPa^{1/2}] \qquad [7]$$

where the summation is over all groups in each molecule. The calculated solubility parameters are presented in Table 7.

The relationship between the equilibrium constants for adsorption, k_a, and the solubility of the emulsifiers in the oil (expressed by $\Delta\delta$) is presented in Figure 11b. The correlation coefficients for the lines are 0.11 for sugar and 0.73 for fat, respectively. Despite a large scattering of points (mainly due to uncertainty in determining the solubility parameters), a correlation seems to exist between adsorption to fat and solubility of the emulsifiers, while no such relationship exists for sugar. This is consistent with the results presented in Figure 11a. For more quantitative and precise predictions of the adsorption of unsymmetrical species (emulsifiers) in multicomponent

TABLE 8

Group Contributions to Molar Volumes (^zV) and Molar Attraction Constants (^zF)

Structural group, z	^zV (cm^3/mol)	^zF ($J^{1/2}cm^{2/3}$/mol)
$-CH_3$	33.5	303.4
$-CH_2-$	16.1	269.0
CH-	−1.0	175.9
C	−19.2	65.5
$=CH_2$	28.5	258.8
=CH-	13.5	248.5
=C	−5.5	172.8
-OH	10.0	673.8
-O-	3.8	235.2
-CO-	10.8	538.0
-COOH	27.0	564.8
-COO-	18.0	668.1
$-NH_2$	19.2	463.5
-NH-	4.5	368.2
-N	−9.0	125.0
$=PO_4^-$	28.0	1020.0
5-Membered ring		42.9

systems, the experimental evaluation of a set of different interaction parameters is necessary (39).

Structure of adsorbed layers to sugar crystals. From the experimental results we suggest the following sequence for the adsorption. When the emulsifier molecules adsorb from low concentrations, they may lay on the surface if more polar bonds per molecule can be formed in this position. This increases the adhesion between the crystals due to bridging by hydrogen bonds. Most of the emulsifiers examined (monoglycerides, their esters and esters of fatty acids) show increased adhesion at low concentrations. However, some molecules cannot be expected to orient along the surface due to steric hindrance (such as with a bulky head group of diacetyl tartaric acid esters of monoglycerides). These molecules are likely to adsorb perpendicular to the surface, with the hydrocarbon parts sticking out into the oil, resulting in a weak steric stabilization.

When the concentrations are increased, the adsorbed layers will increase their packing densities. The molecules laying down will "stand up" to provide space for the new molecules. The upright molecules also can interact with each other and contribute to the adsorption energy in this way. At higher concentrations, tightly packed monolayers with the hydrocarbon chains directed towards the oil are formed, and steric stabilization of sugar crystals occurs.

There are some exceptions from the adsorption pattern described above. Monoglycerides and their lactic acid esters seem to have a specific geometry of the polar head groups that favor adsorption of molecules laying down at both low and high concentrations. This leads to increased adhesion between the crystals, due to the possibility of bridging by hydrogen bonds.

Phospholipids adsorb perpendicular to the surface, with the hydrocarbon chains directed towards the oil phase at all concentrations. A strong decrease in the adhesion is observed at low concentrations. When the concentration increases, condensed layers and multilayers (or large aggregates) are formed on the surfaces. The outermost layer is always directed with the hydrocarbon chains towards the oil, and a strong steric stabilization occurs.

Structure of adsorbed layers to fat crystals. Monoglycerides, their esters and esters of fatty acids are expected to adsorb with the hydrocarbon chains directed to the crystals, due to their chemical similarity to the surface. This is in agreement with the results presented by Darling and Campbell (42,43), who show (from contact measurements) that food emulsifiers (monoglycerides, lecithins) render fat crystals more polar. At low concentrations, loosely packed layers are formed by these emulsifiers, causing a weak steric stabilization of the fat crystals. This has sometimes been described for food products, when, for instance, sorbitan esters of fatty acids are added to margarine to stabilize the β'-form of the fat crystals). The strength of the crystal network thereby decreases (due to a weak stabilization effect of the sorbitan esters), resulting in oiling out (44).

For some emulsifiers, whose head group is large and highly polar, a destabilization can occur, due to an increased polar interaction between the crystals even at low emulsifier concentration (for instance, with the polyglycerol esters of fatty acids). Generally, when emulsifier concentrations increase, tight layers are formed, and adhesion between the crystals increases. The increased adhesion may be interpreted as an increased polarity of the surface.

The unsaturated monoglycerides behave somewhat differently. They adsorb weakly to the fat crystals in the whole concentration region investigated, and only weak steric stabilization is observed. Generally, adsorption is reduced with increasing degree of unsaturation. This is not in agreement with the observations by Campbell (43), that more unsaturated monoglycerides give lower contact angles at the oil/water interface (more polar surfaces) than more saturated ones. In any case, this may be a result of a stronger affinity of the unsaturated monoglycerides to the oil/water interface and not to the oil/crystal interface, because the systems examined by Campbell are in equilibrium with the water phase, which is not the situation in our investigations.

Pure phosphatidylcholine stabilizes fat crystals weakly at low concentrations. At slightly higher concentrations, a small region with destabilization occurs, which changes to strong stabilization at intermediate and high concentrations. Hence, adsorption is complicated and difficult to understand, at least at low concentrations. At high concentrations, double layers (or aggregates) on the fat surface are formed, with the hydrocarbon chains directed towards the oil in the outermost layer.

The commercial mixture of phospholipids stabilizes fat particles for all of the concentrations examined. This mixture, which is soluble in the oil, probably adsorbs as mixed layers at low concentrations and forms at least one double layer (or aggregate) on the surface at high concentrations.

The precipitating emulsifiers. Two of the emulsifiers investigated precipitate at higher concentrations. However, their precipitation has quite different consequences. When the saturated monoglycerides precipitate, a large increase in the sediment volume is observed. The magnitude of the increase suggests the formation of a tight network together with the sugar and fat crystals. The sorbitan esters of fatty acids seem to precipitate as a separate phase and do not noticeably influence the sugar or the fat crystal networks.

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REFERENCES

1. Minifie, B.W., *Chocolate, Cocoa and Confectionary; Science and Technology,* AVI Publishing Company, Inc., Westport, 1982.
2. Moran, D.P.J., *Rev. Int. Choc. 24*:478 (1969).
3. Mulder, H., and P. Walstra, *The Milk Fat Globule,* Centre for Agricultural Publishing and Documentation, Wageningen, The Netherlands, 1974.
4. Friberg, S. (ed.), *Food Emulsions,* Marcel Dekker, New York, 1976.
5. Hey, M.J., A.C. Mackie and J.R. Mitchell, *J. Colloid Interface Sci. 114*:286 (1986).
6. Mackie, A.C., M.J. Hey and J.R. Mitchell, in *Food Colloids,* edited by R.D. Bee, P. Richmond and J. Mingins, Royal Society of Chemistry, Special Publication No. 75, London, 1989, p. 172.
7. Tamamushi, B., in *Adsorp in Solution,* edited by R.H. Ottewill, C.H. Rochester and A.L. Smith, Academic Press, London, 1983, p. 79.

8. Benko, E.M., A.L. Kamyshnyi, E.S. Chukhrai and O.M. Poltorak, *Coll. J. of the USSR 41*:165 (1979).
9. Benko, E.M., A.L. Kamyshnyi, E.S. Chukhrai and O.M. Poltorak, *Ibid. 41*:648 (1979).
10. Lucassen-Reynders, E.H., Ph.D. Thesis, Agricultural University, Wageningen, The Netherlands, 1962.
11. van Boekel, M.A.J.S., Ph.D. Thesis, Agricultural University, Wageningen, The Netherlands, 1980.
12. Welzen, J.T.M.A., H.N. Stein, J.M. Stevels and C.A. Siskens, *J. Colloid Int. Sci. 81*:455 (1981).
13. Vargha-Butler, E.I., E. Moy and A.W. Neuman, *Colloid Surf. 24*:315 (1987).
14. Patzkó, Á., and F. Szántó, *Ibid. 25*:173 (1987).
15. Chander, S., and R. Hogg, in *Flocculation in Biotechnology and Separation Systems,* edited by Y.A. Attia, Elsevier Science Publishers B.V., Amsterdam, 1987, p. 279.
16. Belugina, G.V., V.V. Konstantinova, O. Mirza-Abdullaeva, S.Kh. Zakieva and P.A. Rebinder, *Coll. J. of the USSR 32*:142 (1970).
17. Grodski, A.S., I.A. Titova and Yu.G. Frolov, *Ibid. 46*:779 (1984).
18. Buscall, R., *Colloid Surf. 43*:33 (1990).
19. Zrinyi, M., M. Kabai-Faix and F. Horkay, *Progr. Colloid Pol. Sci. 77*:165 (1988).
20. Tiller, F.M., and Z. Khatib, *J. Colloid Int. Sci. 100*:55 (1984).
21. Griffin, W.C., in *Kirk Othomer Encyclopedia of Chemical Technology 8,* 1979, p. 910.
22. Becher, P., *Emulsions, Theory and Practice,* 2nd edn., Reinhold Publishing Corp., New York, 1966.
23. McGowan, J.C., *Tenside Surf. Det. 27*:229 (1990).
24. Schlichter, J., N. Garti and S. Sarig, *J. Am. Oil Chem. Soc. 63*:788 (1986).
25. Garti, N., J. Schlichter, I. Mayer and S. Sarig, *Tenside Surf. Det. 24*:42 (1987).
26. Garti, N., *Crystallization and Polymorphism of Fats and Fatty Acids,* Marcel Dekker Inc., New York & Basel, 1988, p. 267.
27. Söderberg, I., Ph.D. Thesis, Lund University, Lund, Sweden, 1990, p. 39.
28. Sherma, J., and S. Bennett, *J. of Liq. Chrom. 6*:1193 (1983).
29. Touchstone, J.C., S.S. Levin, M.F. Dobbins and P.C. Beers, Ibid. 6:179 (1983).
30. Privett, O.S., M.L. Blank and W.O. Lundberg, *J. Am. Oil Chem. Soc. 38*:312 (1961).
31. Stahl, E. (ed.), *Thin-Layer Chromatography, A Laboratory Handbook,* Springer-Verlag, Academic Press Inc., Publishers, Berlin, 1965.
32. Hernqvist, L., Ph.D. Thesis, Lund University, Lund, Sweden, 1984.
33. Jones, P., E. Wyn-Jones and G.J.T. Tiddy, *J. Chem. Soc., Faraday Trans. 1.83*:2735 (1987).
34. Kumar, V.V., and P. Raghunathan, *Chem. Phys. Lipids 41*:159 (1986).
35. Elworthy, P.H., and D.S. McIntosh, *Kolloid Z, Z. Pol. 195*:27 (1964).
36. Yeski, M.A., and J.H. Harwell, *J. Phys. Chem. 9*:2346 (1988).
37. Atkins, P.W., *Physical Chemistry,* Oxford University Press, Oxford, 1982.
38. Stenius, P., *Yt-och Kolloidkemins Grunder,* Institute for Surface Chemistry, Stockholm, Sweden, 1986.
39. Barton, A.F. (ed.), *Handbook of Solubility Parameters and Other Cohesion Parameters,* CRS Press Inc., Florida, 1983.
40. Kronberg, B., *J. Colloid Int. Sci. 96*:55 (1983).
41. Kronberg, B., and P. Stenius, *Ibid. 102*:410 (1984).
42. Darling, D.F., *J. Dairy Research 49*:695 (1982).
43. Campbell, I.J., in *Food Colloids,* edited by R.D. Bee, P. Richmond and J. Mingins, Royal Society of Chemistry, Special Publication No. 75, London, 1989, p. 272.
44. Madsen, J., *Fett Wissenschaft Technologie 89*:165 (1987).

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