The Influence of Food Emulsifiers on Fat and Sugar Dispersions in Oils. II. Rheology, Colloidal Forces

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The influence of food emulsifiers on the viscoelastic properties (storage modulus and yield value) of fat and sugar dispersions in vegetable oils has been investigated. It was found that almost all of the emulsifiers tested influence the rheology of the dispersions. The magnitude and the direction of the rheological changes depend on both the type and the amount of emulsifier. In most cases the changes are relatively small, especially for fat crystals. Generally speaking, the largest changes are caused by lecithins and saturated monoglycerides. The magnitudes of colloidal forces and equilibrium distances between the particles have been estimated from the rheological network model of van den Tempel [*J. Colloid Sci. 16*:284 (1964)] and from the correlation of the yield value to the interaction energy by Gillespie [*J. Colloid Sci. 15*:219 (1960)] and Tadros [*Langmuir 6*:28 (1990) and *Chemistry and Industry 7*:210 (1985)]. The results indicate that van der Waals forces alone cannot be responsible for the interparticle interaction in fat or sugar dispersions. The formation of water bridges is discussed as a probable source of interaction in both cases. Furthermore, the validity of the network model for fat and sugar dispersions in oils is questionable.

KEY WORDS: Colloidal forces, emulsifiers, fat, food, network model, oils, rheology, sugar, triglycerides.

Several food emulsions (spreads, margarines, butter) consist of a network of solid fat particles in a continuous oil phase, with water droplets captured in it. Chocolate is an example of a fat-continuous food dispersion, where a continuous network is formed by solid fat, sugar, protein particles and ground cacao particles. All of these systems contain emulsifiers as stabilizers, rheology regulators or fat crystallization regulators. The emulsifiers are effective mainly because of their ability to adsorb to different interfaces. The adsorption of different food emulsifiers to fat or sugar crystals dispersed in oils has been presented in the first article of this series (1), which also describes the influence of the adsorbed layers on crystal-crystal interactions, qualitatively studied by sedimentation experiments.

Rheological characteristics are most important for oil-continuous foods. They govern properties such as consistency, mouth feel, spreadability and handling of the product during various production and transportation steps. The rheological properties depend on particle-particle interactions and particle microstructure and are directly influenced by the adsorption of different molecular species to the particles. The results from adsorption, sedimentation and rheological experiments are often compared with each other (2-5).

The viscosity of chocolate systems and its dependence on different food emulsifiers has been briefly presented in the literature (6-8), but to our knowledge there are no fundamental studies in the area.

The rheology of pure fat crystal dispersions is better understood, as fundamental studies and theories are available in the literature. For example, Nederveen (9) has investigated the dynamic mechanical properties of suspensions of fat particles in oil, Kamphius and Jongschaap (10) have described the rheology of suspensions of fat particles in oil and interpreted it in terms of a transient-network model; and deMan and Beers (11) have reviewed the structure and rheological properties of fat crystal networks. However, several important issues, such as sintering of fat crystals during aging [suggested by Walstra (12)] or the influence of different emulsifiers on the rheological characteristics are still open for investigation.

The aim of this study is to illustrate how emulsifiers affect the rheological properties of fat and sugar dispersions in oils. The rheological network model, suggested by van den Tempel (13), is used together with the yield value correlation to the interparticle interaction potential, as derived by Gillespie (14) and Tadros (15,16). van der Waals forces and water bridges are applied in the models. The results are correlated to previous adsorption and sedimentation results (1).

EXPERIMENTAL PROCEDURES

The materials have been described in detail previously (1). Thus, only a brief presentation is given below.

Emulsifiers. The following food emulsifiers have been used: Two different phospholipids (a pure phosphatidylcholine from soybean oil and a soybean lecithin of technical grade); three monoglycerides with different degrees of saturation [pure monoolein with an iodine value (IV) of about 50, distilled monoglycerides with two double bonds per hydrocarbon chain on average and IV $\approx$ 105, distilled saturated monoglycerides, IV $\leqslant$ 2]; two esters of monoglycerides (lactic acid and diacetyl tartaric acid esters); and three esters of fatty acids (polyglycerol, sorbitan and propylene glycol esters). The emulsifiers exemplify a range of different polarities and different degrees of saturation. The hydrocarbon chain lengths of the emulsifiers are mostly C16 and C18, which commonly occur in nature.

Crystals and oil. Fat crystals consist of pure tristearin, which has been recrystallized in acetone to give well-characterized β-crystals with an upper dimension of about 10–20 μm. The crystals are nonpolar, with the hydrocarbon chains at the surface. Ground and sieved sugar crystals consist of pure saccharose with an upper dimension of about 30 μm. Sugar crystals are polar and have mostly OH-groups on the surface. All the rheological experiments were performed with a technical-grade refined soybean oil.

Methods. The Bohlin VOR rheometer (Bohlin Rheology, Lund, Sweden) was used in our rheological studies. This rotational rheometer is of the Couette type with a rotating bottom plate or outer cylinder, where the stress in the sample is measured as a function of applied shear rate.

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Viscosity measurements. Viscosity measurements were performed with a pure soybean oil and with solutions of food emulsifiers in soybean oil. The measuring system was concentric cylinders with bob diameter of 25 mm and cup diameter of 27.5 mm (denote C25), the temperature was 20°C, and the torque bar was 3.9 g (~0.4mNm). The choice of torque bar determines the sensitivity of measured torque, which is further recalculated to give the shear stress in the sample. Shear rates were varied between 2 and 100 reciprocal seconds [1/s], giving shear stresses between 0.2 and 6.5 Pa. The emulsifier concentrations were varied from 0.1 to 2% (~1–50 mmol/L).

Oscillation. Storage (elastic) and loss modulus as a function of the frequency (in the region 0.1–10 Hz) were determined for the sugar and the fat dispersions. The concentrations were 50% w/w for sugar (≈36.5%, vol/vol) and 10% w/w for the fat crystals (≈8.7%, vol/vol). The measuring geometry was cone and plate, with plate diameters of 30 mm and a cone angle of 5° (denote CP 5/30). This geometry gives a constant shear rate through the whole sample volume. The temperature was 20°C, the torque bar 3.9 g and the amplitude 0.5%. The amplitude controls the angular deflection of the rotating bottom plate (amplitude of 100% gives a deflection of 20 mrad), *i.e.*, the strain in the sample. The strains applied on the samples were in the range $10–50 \times 10^{-5}$ for sugar dispersions and $30–50 \times 10^{-5}$ for fat dispersions. A linear elastic response of the dispersions was expected within these regions.

Strain sweep. The strain sweeps were performed in the oscillation mode for both sugar and fat dispersions at concentrations of 50% w/w (≈36.5%, vol/vol) and 25% w/w (≈22%, vol/vol). The influence of each emulsifier on the rheology of the dispersion was examined at two concentration levels—low (~0.05–0.1%) and high (~0.5–1%). The measuring system was CP 5/30 (a bottom plate with diameter of 30 mm and an upper plate with a cone angle of 5°), the torque bar was 3.9 g and the temperature was 20°C. The strain sweeps were extended over a deformation region 0.0001–0.2. A frequency of 1 Hz was chosen for sugar and 0.1 Hz for fat dispersions (the latter was chosen so as to disturb the more sensitive fat dispersions as little as possible).

The influence of the largest particles. One condition for acceptable measurements with geometry CP 5/30 is the absence of particles larger than one-tenth of the gap between the cone and the bottom plate, which is 150 μm. Since some particles are larger than 15 μm, especially in the case of sugar, it is necessary to control their influence on the results. The results from the CP 5/30 geometry were compared with results from other geometries that were less sensitive to the presence of large particles (for example, two parallel plates with 30 mm diameter, 30 PP, with a gap of 1 mm). The comparison showed no significant differences between the geometries for sugar or for fat dispersions. The conclusion is that the results are not influenced by the presence of the largest particles, because of their relatively low concentration in the samples.

Sample preparation. All dispersions were prepared by weighing the desired amount of crystals and the oil (or the oil solution of the emulsifiers). The samples were carefully mixed in test tubes and stored for 24 h at room temperature to each equilibrium. The crystals were characterized prior to mixing. No further recrystallization in the oil was made to avoid differences in the size of the crystals, in their polymorphy and morphology, and incorporation of emulsifiers in the crystals. All these parameters might influence the rheological behavior of the systems (17–24).

Water content. The water content of the samples was determined gravimetrically after drying in vacuum at pressure 10^{-2} torr. The water content was ≤0.2%, which is roughly the same as in the previous adsorption and sedimentation studies (1).

RESULTS

Viscosity measurements for the oil and oil solutions. The results are presented in Table 1. Pure refined soybean oil shows Newtonian flow with a viscosity of ~67 mPas. Most of the emulsifiers examined do not change the oil viscosity when present at concentrations up to ~2%.

Emulsifiers with limited solubility in the oil (saturated monoglycerides and sorbitan esters of fatty acids) increase the viscosity of the oil (by 20% and 10%, respectively) when their concentration exceeds the solubility limits. Phosphatidylcholine is difficult to disperse or dissolve, but as soon as the solution is macroscopically uniform, it remains stable. On addition of phosphatidylcholine, the oil viscosity increases by about 30% at low concentrations and by a factor of 10 at higher concentrations. The character of the solutions changes from Newtonian to shear thinning. This indicates the presence of lecithin aggregates [also reported in the literature (25–28)]. Phosphatidylcholine forms lamellar aggregates and vehicles in water (29), and structures with hydrocarbon chains directed outward (reversed micelles, reversed hexagonal phase or cubic phase) are expected in the oil.

A soybean lecithin of technical grade is oil-soluble. It affects the oil viscosity in a similar way as phosphatidylcholine, but to a lesser extent and only at higher concentrations, where the magnitude of the increase is about 100%. A shear-thinning character also is observed. The technical lecithin probably forms smaller aggregates in the oil than does pure phosphatidylcholine. Technical lecithins often form a reversed hexagonal phase in water (30), and are expected to form reversed micelles in oil.

Oscillation. Frequency sweep. The dependence of the storage and loss modulus on the frequency of oscillation was examined for both sugar (50% w/w) and fat (10% w/w) dispersions. The results for the sugar dispersion (Fig. 1a) show a constant storage and loss modulus, which is typical for solid-like materials. The storage modulus is about seven times larger than the loss modulus. The results for the fat dispersion (Fig. 1b) show weakly increasing G′ and G″ of the same order of magnitude, indicating that this dispersion is liquid-like. Consequently, for further experiments, higher concentrations of fat crystals were chosen to create solid-like properties.

Strain sweep. Sugar crystals. An example of results for a 50% w/w sugar dispersion in soybean oil is presented in Figure 2a. The open circles represent a dispersion without any emulsifier, while the other symbols (●,▲,△,■) represent dispersions with emulsifiers dissolved in the oil. Error bars are marked in the Figure.

The storage moduli, G′, in the linear region and its limit of linearity, γ_{lin}, are determined from the strain sweep curves. The yield stress, τ_y, is estimated by multiplying G′ with γ_{lin}. The results are summarized in Table 2.

TABLE 1

The Viscosity of Pure Soybean Oil Compared to Viscosities of Solutions of Different Emulsifiers. Shear Rate Region: 2-100 s^{-1}; Shear Stress Region: 0.2-6.5 Pa

Emulsifier	Concentration (%)	Concentration (mmol/L)	Viscosity range (Pa)	Comments
None			0.067	Constant, Newtonian
Phosphatidylcholine from SBO[a]	0.1	1	0.087-0.070	Decreasing, shear-thinning
	2.0	24	0.670-0.100	
A mixture of phospholipids	2.0	24	0.130-0.070	Decreasing, shear-thinning
Monoolein	2.0	50	0.067	Constant, Newtonian
Unsaturated MG	1.0	25	0.062-0.066	~ Constant, Newtonian
Saturated MG	0.1	2	0.064-0.067	~ Constant, Newtonian
	0.5	12	0.081-0.079	
Polyglycerol EFA	2.0	35	0.068-0.072	~ Constant, Newtonian
Lactic acid EMG	2.0	30	0.062-0.066	~ Constant, Newtonian
Sorbitan EFA	0.1	1	0.062-0.066	~ Constant, Newtonian
	2.0	30	0.071-0.073	
Diacetyl tartaric acid EMG	1.0	15	0.067	Constant, Newtonian
Propylene glycol EFA	2.0	55	0.060-0.064	~ Constant, Newtonian

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

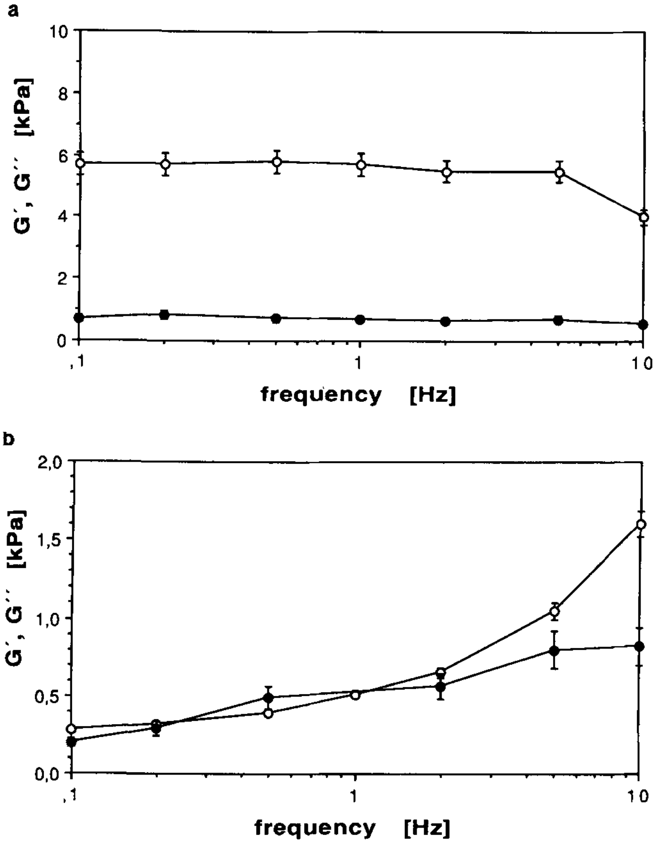

FIG. 1. Storage (elastic) modulus, G′ (○), and loss modulus, G″ (●), as a function of frequency of oscillation. Error bars are presented on the plots (in some cases they are smaller than the plot symbols). a, Sugar crystal dispersions, 50% w/w, in soybean oil; and b, fat crystal dispersions, 25% w/w, in soybean oil.

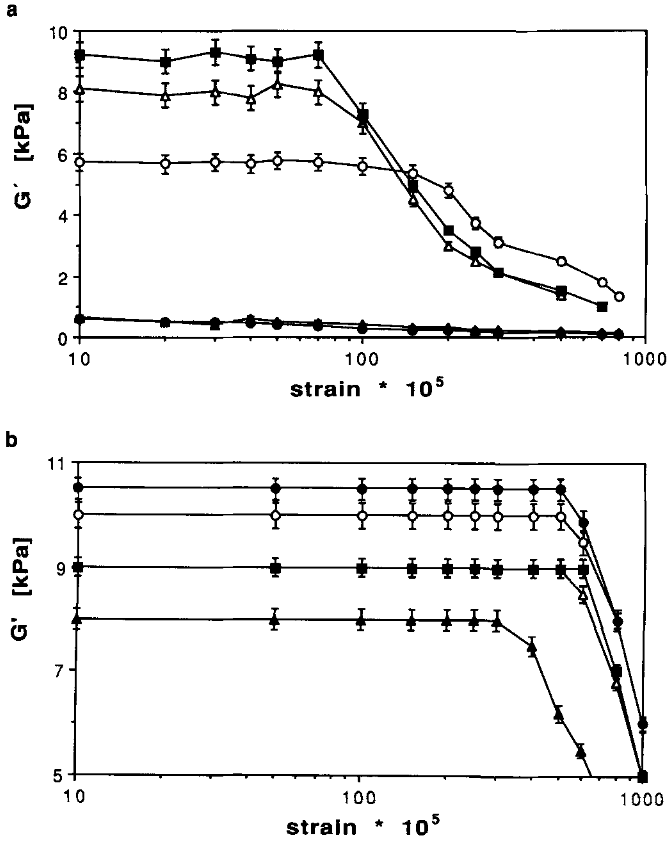

FIG. 2. An example of strain sweep measurements. Storage (elastic) modulus, G′, is plotted as a function of strain for the following dispersions in soybean oil: Without emulsifier (○), with 0.1% phosphatidylcholine from soybean oil (●), with 1% phosphatidylcholine from soybean oil (▲), with 0.05% monoolein (△) and with 0.5% monoolein (■). Error bars are presented on the plots (in some cases they are smaller than the plot symbols). a, Sugar crystal dispersions, 50% w/w; and b, fat crystal dispersions, 25% w/w.

TABLE 2

Rheological Parameters for Dispersions of Sugar Crystals (50% w/w ≈36.5% vol/vol) and Fat Crystals (25% w/w ≈22% vol/vol) in Soybean Oil. The Storage Modulus Corresponds to Small Deformations (strain ≈10^{-4})

Emulsifier	Concentration (mmol/L)	Storage modulus G′ (kPa)		Limit of linearity $\gamma \cdot 10^5$		Yield stress τ_y (Pa)	
		Sugar	Fat	Sugar	Fat	Sugar	Fat
None		5.70	10.0	75	500	4.3	50.0
Phosphatidylcholine from SBO[a]	0.5	0.55	10.5	25	500	0.1	52.5
	10.0	0.55	8.0	25	300	0.1	24.0
A mixture of phospholipids	1.0	1.30	9.0	20	300	0.3	27.0
	10.0	0.40	4.0	30	100	0.1	4.0
Monoolein	2.0	8.0	9.0	70	500	5.6	45.0
	12.0	9.2	9.0	70	500	6.4	45.0
Unsaturated MG	2.5	7.0	10.0	50	500	3.5	50.0
	12.0	7.2	9.0	70	300	5.0	27.0
Saturated MG	2.0	8.5	8.5	70	500	6.0	42.5
	8.0	11.0	11.0	70	600	7.7	66.0
Polyglycerol EFA	1.5	6.3	10.2	100	500	6.3	51.0
	11.0	0.3	11.0	100	500	0.3	55.0
Lactic acid EMG	2.0	9.5	8.6	50	400	4.8	34.4
	12.0	10.5	11.2	50	500	5.3	56.0
Sorbitan EFA	2.0	1.2	10.5	30	500	0.4	52.5
	12.0	0.3	11.2	100	500	0.3	56.5
Diacetyl tartaric acid EMG	1.5	2.5	8.5	100	500	2.5	42.5
	11.0	0.3	11.2	100	500	0.3	56.0
Propylene	2.5	3.0	10.0	40	500	1.2	50.0
Glycol EFA	13.0	5.2	10.0	40	500	2.1	50.0

[a] As in Table 1.

The storage modulus of the sugar dispersion is about 5.7 kPa and the yield stress is −4.3 Pa. Both parameters are strongly reduced (by a factor of 10 and 40, respectively) when pure phosphatidylcholine or technical lecithin are added. Hence, the effects on the elastic properties have to be due to adsorption of the emulsifiers to sugar particles and due to changes of the interactions in the particle network, and/or to changes of the particle network structure.

Similar decreases are observed on addition of diacetyl tartaric esters of monoglycerides and sorbitan or propylene glycol esters of fatty acids, but the magnitude of decrease is less pronounced than for lecithins. All monoglycerides examined and their lactic acid esters cause increases of the storage modulus and the yield value for the sugar dispersions. The magnitude of the increases is between 20% and 100%. The presence of polyglycerol esters of fatty acids also increases the storage modulus at low concentrations, but reduces it at higher concentrations.

Strain sweep. Fat crystals. An example of results for a 25% w/w dispersion in soybean oil is presented in Figure 2b. The open circles (○) represent a dispersion without any emulsifier, and the other symbols (●,▲,△,■) represent dispersions with emulsifiers dissolved in the oil. Error bars are marked in the Figure.

The storage moduli, G′, the limits of linearity, γ_{lin}, and the calculated yield values, τ_y, are presented in Table 2. The G′ of the fat dispersion is about 10 kPa and τ_y − 50 Pa. The addition of phospholipids decreases both the storage modulus and the yield value. Pure phosphatidylcholine causes a weak increase in both parameters when it is present in very small concentrations.

Monoglycerides reduce both the storage modulus and the yield value of fat dispersions. Saturated monoglycerides precipitate at higher concentrations, resulting in an increase of the rheological parameters due to the formation of an additional solid phase, probably as bridges between the fat particles in the network. Diacetyl tartaric acid esters and lactic acid esters of monoglycerides cause a slight decrease in G′ and τ_y when present at low concentrations. At higher concentrations, these emulsifiers operate conversely. A slight increase in G′ and τ_y is also attained with polyglycerol and sorbitan esters of fatty acids. Propylene glycol esters of fatty acids do not significantly influence the rheology of fat dispersions.

Generally speaking, emulsifiers influence the rheology of fat and sugar dispersions in oils. The direction and the magnitude of the changes vary with the type of emulsifier and with its concentration. The magnitude of the changes is less in fat dispersions than in sugar dispersions.

DISCUSSION

Network model. Rheological parameters are a reflection of particle interactions (both of hydrodynamic and surface force origin) and of particle structure. These parameters can be estimated with the rheological network model. This model has been proposed by van den Tempel

(13) and further developed and applied upon experimental data by several other authors (9–11,31–33). The newer versions of the model result in similar expressions for the dispersion elasticity as the initial version. Therefore, we have applied the initial version for simplicity.

The network model assumes that the attractive forces between the particles dominate particle-particle interactions. The particles flocculate and arrange themselves into a three-dimensional network of chains. Each chain consists of a linear array of particles attached to each other. The network model does not take into consideration a possible fractal nature of the dispersions. Mechanical (rheological) properties can be investigated if no appreciable breakdown occurs during measurement, *i.e.*, at low stress and with small strain values.

If the average force between the particles is F, and N is the number of chains crossing the unit area of the sample perpendicularly, the stress, S, transmitted during shear from one part of the sample to the other is given by (13):

$$S = F \times N \qquad [1]$$

Further, N is given by the following equation (assuming two contacts per particle and a three-dimensional network):

$$N = 2\phi/\pi d^2 \qquad [2]$$

where ϕ is the volume fraction of particles, and d is the average diameter of particles (assuming that they are spherical).

The geometry of the model is only approximate. The quantity N (number of particle chains crossing the unit area of the sample) gives only a rough description of the real system. In any case, errors in N are not large, certainly less than a factor of 10. Since the particles are nondeformable, the relative extension of the sample, ε, is:

$$\varepsilon = (H - H_0)/d \qquad [3]$$

where H_0 is the equilibrium distance between the particles and H the distance during the deformation. Assuming that each particle is in contact with two other particles, the shear strain is $\gamma = 2(H - H_0)/d$. The storage modulus of the dispersion at low strain is then:

$$G_0 = (1/3) \times (dS/d\varepsilon)_H \qquad [4]$$

This, together with Eqs. [1–3] gives:

$$G_0 = (2/3) \times (\phi/\pi d) \cdot (dF/dH)_H \qquad [5]$$

and

$$(dF/dH)_H = (3\ G_0 \cdot \pi d/2\phi) \qquad [6]$$

where $(dF/dH)_H$ is the slope of the force-distance curve at distance H, which is equal to the "elasticity" of the particle bonds. The calculated $(dF/dH)_H$ for the sugar and fat dispersions examined is presented in Table 3.

Yield stresses. A yield stress is the minimum stress required to break the structure in the sample (32) to cause

TABLE 3

Depth of the Energy Minimum, $-\Delta E$, "Elasticity" of the Forces, $-dF/dH$, and Equilibrium Distances Between Particles, H_0, Calculated from the Storage Moduli on the Assumption that van der Waals Forces Dominate in the Systems

Emulsifier	Concentration (%)	$-\Delta E$ (10^{-16} J)		$-\Delta E$ (10^3 kT)		$-dF/dH$ (N/m)		H_0 (Å)	
		Sugar	Fat	Sugar	Fat	Sugar	Fat	Sugar	Fat
None		4.41	1.22	108.0	30.1	0.243	0.171	48.1	18.3
Phosphatidylcholine from SBO[a]	0.05	0.14	1.28	3.5	31.6	0.023	0.180	93.8	18.0
	1.0	0.14	0.59	3.5	14.6	0.023	0.137	93.8	19.5
A mixture of phospholipids	0.1	0.27	0.66	6.7	16.3	0.055	0.154	73.4	18.8
	1.0	0.12	0.10	3.0	2.5	0.017	0.068	102.7	23.8
Monoolein	0.05	5.77	1.10	142.6	27.2	0.341	0.154	43.7	18.8
	0.5	6.64	1.10	164.1	27.2	0.392	0.154	41.9	18.8
Unsaturated MG	0.1	3.61	1.22	89.2	30.1	0.298	0.171	45.4	18.3
	0.5	5.20	0.66	128.5	16.3	0.307	0.154	45.0	18.8
Saturated MG	0.1	6.13	1.04	151.5	25.7	0.361	0.145	42.9	19.2
	0.5	7.94	1.61	196.2	39.8	0.469	0.188	39.9	17.8
Polyglycerol EFA	0.1	6.50	1.24	148.3	30.6	0.268	0.174	46.7	18.2
	0.5	0.31	1.34	7.7	33.1	0.013	0.188	111.6	17.8
Lactic acid EMG	0.1	4.90	0.84	121.1	20.8	0.405	0.147	41.6	19.1
	1.0	5.41	1.37	133.7	33.9	0.447	0.192	40.4	17.7
Sorbitan	0.1	0.37	1.28	9.1	31.6	0.051	0.180	75.1	18.0
	1.0	0.31	1.39	7.7	34.3	0.013	0.193	111.6	17.7
Diacetyl tartaric acid EMG	0.1	2.58	1.04	63.7	25.7	0.107	0.145	60.9	19.2
	1.0	0.31	1.37	7.7	33.9	0.013	0.192	111.6	17.7
Propylene glycol EFA	0.1	1.24	1.22	148.3	30.1	0.128	0.171	57.8	18.3
	0.5	2.14	1.22	52.9	30.1	0.222	0.171	49.4	18.3

[a] As in Table 1.

the sample to flow. The yield stress is usually determined from the flow curve. For more complicated polydisperse systems, different yield stresses (lower τ_l, Bingham τ_B and upper τ_u) can be defined, each corresponding to a break of a different fraction of the bonds (32).

Another method for estimation of the yield stress is analysis of the measurements of storage modulus. When the last is determined as a function of strain, it is usually linear up to a certain strain limit. Within this so-called linear viscoelastic region, the sample behaves as an elastic, solid-like body and does not flow under stress. When the limit (γ_{lin}) is exceeded, the interparticle bonds start to break, the material flows and the storage modulus diminishes. The yield stress, which corresponds to the break point, can be determined by multiplying the storage modulus in the linear region with the strain limit of linearity—$\tau_y = G' \times \gamma_{lin}$. The yield stress determined in this way usually corresponds to the lower or Bingham yield stress. Thus, in our case we can assume that: $\tau_y \leqslant \tau_B$.

A simple relationship between the Bingham yield stress, τ_B, and the energy of interaction, $\Delta E_{(H_0)}$, between the flocculated particles at equilibrium distance H_0, has been proposed by Gillespie (14) and Tadros (15,16):

$$\tau_B = \Delta E_{(H_0)}\, N' \qquad [7]$$

where N′ is the average number of particle-particle contacts per m^3. The model assumes that all particle contacts break simultaneously. By assuming a network model, N′ can be estimated (16) from:

$$N' = (\phi/V_p) \times n \qquad [8]$$

where V_p is the average volume of one particle ($= \pi d^3/6$) and n is the average number of contacts for a particle with other particles in the network. In our case n is assumed to be three.

Because $\tau_y \leqslant \tau_B$ and because not all particle bonds break simultaneously, one can estimate the minimum average energy of interaction between particles in the network from Eqs. [7] and [8]:

$$\Delta E_{(H_0)} = (\tau_y \times \pi d^3/18\phi) \qquad [9]$$

$\Delta E_{(H_0)}$ for sugar and fat dispersions examined is given in Table 3.

By applying the models of van den Tempel (13,17) and Gillespie (14) mentioned above, the forces and the energies of interactions can be estimated from the rheological data (storage moduli and yield values). These parameters can be used further for a discussion on the nature of interactions influencing structure formation in the systems examined.

van der Walls forces. van der Waals forces (also known as dispersion or London forces) are always present and arise from induced and permanent dipole-dipole interactions between molecules or particles (32,34). They are always attractive between identical particles or surfaces. They are theoretically well described and are often assumed to have a dominant role in oil-continuous systems (13). The attractive force, F, between two spheres with the diameter, d, at a distance $H \leqslant d$ is (13,32,34):

$$F = (A_H \times d/24\, H^2) \qquad [10]$$

where A_H is a Hamaker constant, which depends on the polarizabilities of the atoms in the particles and in the medium (units [J]). The energy of interaction, ΔE, is then given by:

$$\Delta E = -\int_{H_0}^{\infty} F \cdot dH = (A_H \times d/24\, H_0) \qquad [11]$$

The average force between particles of various shapes and orientations may be obtained by considering the attraction as intermediate between spheres and well-oriented cubes (13):

$$F = (A_H \times d^{1.5}/8\, H^{2.5}) \qquad [12]$$

$$\Delta E = -(A_{H_0} \times d^{1.5}/12\, H^{1.5}) \qquad [13]$$

$$(dF/dH)_{H_0} = -(5\, A_{H_0} \times d^{1.5}/16\, H^{3.5}) \qquad [14]$$

The Hamaker constants A_H, can be estimated from the difference in refractive indexes (32,34):

$$A_H = (3/4)\, kT\, ((\varepsilon_1 - \varepsilon_2)/(\varepsilon_1 + \varepsilon_2))^2 + (3\, h\gamma_e/16\sqrt{2}) \times [(n_1^2 - n_2^2)^2/(n_1^2 + n_2^2)^{3/2}] \qquad [15]$$

where A_H is a Hamaker constant for particles 1, interacting across a medium 2; ε is a dielectric permitivity; h is the Planck constant ($6.62 \cdot 10^{-34}$ J s); k is the Bolzmann constant $1{,}38 \cdot 10^{-23}$ J/k); T is the temperature in Kelvin; γ_e is the adsorption frequency, which can be assumed to be about $3.0 \cdot 10^{15}$ 1/s; and n is the refractive index.

The Hamaker constants are often of the order of magnitude of 10^{-19}–19^{-20} J, when the particles interact across vacuum or water (32,34). Hamaker constants can be estimated with relatively good accuracy. Another parameter that needs to be estimated is the mean particle diameter d. For a polydisperse system, d can be calculated from the specific surface area for particles, A_{sp} (m^2/g), and the particle density, ϱ (g/mL), by assuming that the particles are spherical:

$$d = (6/A_{sp}\, \varrho) \times 10^{-6}\ (m) \qquad [16]$$

The theoretical models for dispersion rheology are valid for monodisperse spherical particles. The particle polydispersity shifts the viscosity (and probably the elasticity) of the dispersions towards lower values, while irregularly shaped particles give the opposite effect—a shift to higher viscosities (32). Thus, as a first approximation we can assume that the parameters mentioned compensate for each other and do not influence the rheological results to any great extent.

The calculated van der Waals energy (−ΔE) and force (F) as a function of the interparticle distance (H) are presented in Figures 3a and 3b, respectively.

Liquid bridges. Oil-continuous food systems are never completely free of water. Water can accumulate at the particle surfaces and strongly change the interactions (34). Water bridges can be formed when water-covered particles are in close contact. Water bridges are a well-known source of adhesion between solid particles (powder) in air and are often referred to as capillary forces (34–36).

The adhesive forces due to the formation of liquid bridges between particles in air have been evaluated by

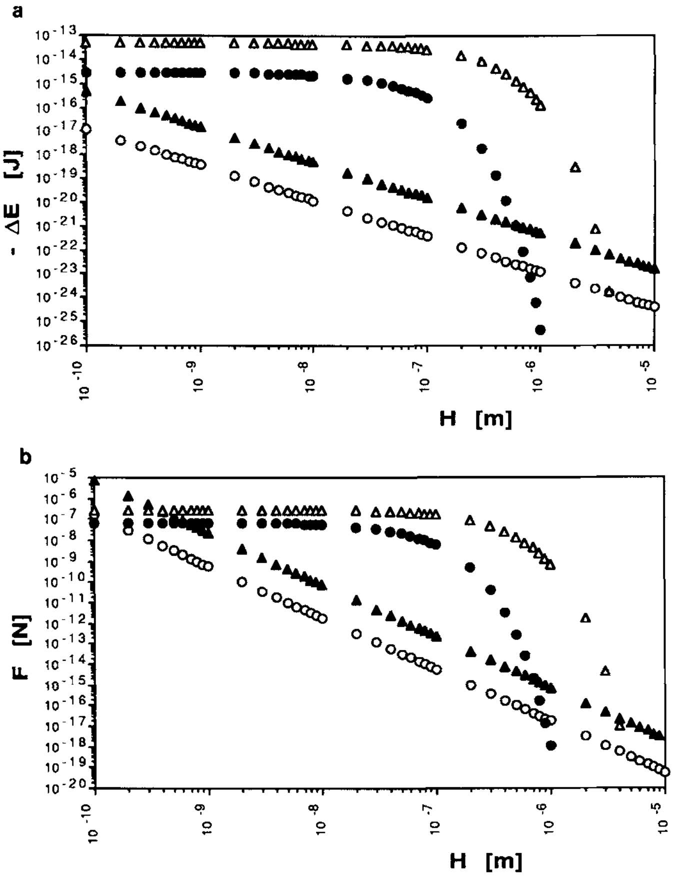

FIG. 3. Calculated energy of interactions (−ΔE) and calculated forces (F) as a function of the distance between crystals, H: van der Waals interaction in the fat dispersion (○) and van der Waals interaction in the sugar dispersion (▲), water bridges in the fat dispersion (●) and water bridges in the sugar dispersion (△). a, Energy of interaction, −ΔE; and b, interaction force, F.

Shubert (35,36). The reduced adhesive force is a function of the following parameters:

$$(F/\gamma d_1) = f[(V_L/V_1), (d_1/d_2), \theta, (H/d_1)] \qquad [17]$$

Where F is the adhesive force; γ is the surface tension between water and air (or water and oil); d_1, d_2 are the diameters of a bigger and a smaller particle, respectively, which are bridged together by a liquid bridge; V_L/V_1 is the ratio of a bridge volume, V_L, to the solid volume, V_1, of a particle of diameter d_1; θ is the contact angle at the interface particle-water-air (or particle-water-oil); and H is the distance between the particles.

Some of the parameters are difficult to estimate correctly. However, we have made an estimation of this interaction to roughly illustrate the influence of water bridges on the properties of oil-continuous dispersions. The contact angle, θ, is assumed to be 0°, *i.e.*, the crystals are well wetted by water where water bridges are formed. This is expected to be true in the case of a polar sugar, but is questionable in the case of a nonpolar fat unless emulsifiers are present. The ratio V_L/V_S is approximated from the ratio of the total water content to the total particle volume in the samples, *i.e.*, $\approx 5 \cdot 10^{-3}$. However, the reduced force $F/\gamma \cdot D$ is not very sensitive to this ratio.

The ratio d_1/d_2 is set at two. This is just an arbitrary number, which takes into consideration that particles are not monodisperse. The d_1 value is calculated in the same way as for the van der Waals interaction (Eq. [16]). The interfacial tension between water and refined sybean oil has been measured to be 25 mN/m. This value is reduced in the presence of emulsifiers.

Shubert (35,36) solved a number of differential equations numerically and presented the results in diagrams. To be able to compare these data with the van der Waals interaction, we have fitted the data to the following approximate expression for the force, the interaction energy and the derivative of the force.

$$F = 3.5315 \times d \times \gamma \times 10^{-8.62146H/d} \qquad [18]$$

$$\Delta E = -0.18 \times d^2 \times \gamma \times 10^{-8.6214H/d} \qquad [19]$$

$$(\delta F/\delta H)_{H_0} = -70.1 \times \gamma \times 10^{-8.6214H/d} \qquad [20]$$

Relationships between the calculated energy (−ΔE) in the water bridges, the force (F) and the interparticle distance (H) are presented in Figure 3.

Other forces. Solid bridges, formed by precipitated material between the particles, often is stated as the origin of the stiff adhesive interaction of powders in air (35,36). It also has been suggested for fat crystals in oils (11–13).

Structural forces (32,34) arise from the molecular nature of the solvent and are especially important for the solvents consisting of large and rigid molecules. They are short-distance interactions with a range of a few molecular diameters and oscillate with a wavelength equal to the solvent molecular diameter. With more flexible solvent molecules, the structural forces are reduced and the structures do not extend beyond a couple of molecular diameters. Furthermore, a trace of water can dramatically affect the structural forces in nonpolar liquids, especially if there is preferential adsorption of water onto the surfaces.

Unsaturated triglyceride molecules can be assumed to be highly flexible in the liquid state, with a molecular diameter, D, of the order of 1.5 nm. This diameter is estimated from of the oil density, ϱ (kg/L), its average mole mass M (g/mole) and the Avogadro number $N_A = 6.02252 \times 10^{23}$ (1/mole). The average molecule then has a volume equal to $(M \times 10^6)/(\varrho \times N_A)$. By comparing this volume with a volume of a sphere $(\pi \times D^3/6)$, the diameter can be calculated.

The samples examined are not completely free of water, which tends to adsorb to the surfaces, at least in the case of sugar crystals and in the presence of emulsifiers. Hence, the structural forces are probably of little importance for sugar dispersions, but their influence for fat dispersions can be expected to be more pronounced. Another probable source of interactions lies in the formation of hydrogen bonds. Hydrogen bonds are common between polar particles. Electrostatic interactions, which can be extremely long-range in nonpolar systems, are not expected in fat and sugar dispersions, because there is practically no origin for charges on the crystal surfaces.

Solvaton or hydration forces are caused by interactions between a polar solvent with a polar surface. This type of force is not expected in oil dispersions, due to the nonpolar character of the oil. But they can be present in the presence of water bridges. In any case, they are short-range, about 2 nm (37).

Sugar dispersions in oils. The Hamaker constant for sugar crystals in soybean oil is estimated from Eq. [15] to be about 10^{-21} J [the dielectric permitivities from the literature (38,39) are: $\varepsilon_{SBO} \approx 2.5$, $\varepsilon_{saccharose} = 3.32$; and the refractive indices: $n_{SBO} = 1.4735$, $n_{saccharose} = 1.5376$]. The Hamaker constant might change due to adsorption to the particle surface. Since the adsorbed layers of emulsifiers are mostly thin (about one monolayer), we can assume that the Hamaker constant for sugar does not change to any great extent due to adsorption. The mean diameter of sugar particles, d, calculated from Eq. [16], is about 3.3 μm.

To estimate the contributions of van der Waals potentials and water bridges to the interaction between the particles in the dispersions, the minimal interaction energy in the network (calculated from the yield value) is plotted against the derivative of the interaction force between the particles (calculated from the storage modulus). The experimental points are compared with the calculated forces in Figure 4.

The van der Waals forces and water bridges are not supposed to be additive because the presence of water bridges influences the Hamaker constant of the system and, therefore, the van der Waals forces. Analysis of the results shows that van der Waals forces cannot be responsible for the interactions in the sugar system, since they are too weak. Figure 4a shows that the energy of interaction ($-\Delta E$) for van der Waals forces is a couple of orders of magnitude lower than the energy of interaction for the experimental dispersions, which is also specified in Table 3. For example, when no emulsifiers are present, the energy of interaction between the sugar crystals in oil is 4.41×10^{-16} J. If van der Waals forces alone would be responsible for this interaction, the distance between the crystals should be as little as 10^{-10} m (1 Å), because only at these short distances can the energy of interaction be around 5×10^{-16} J (see Fig. 3a). Such a small distance between the particles is not realistic because it is much less than the size of oil molecules (estimated to about 1.5 nm).

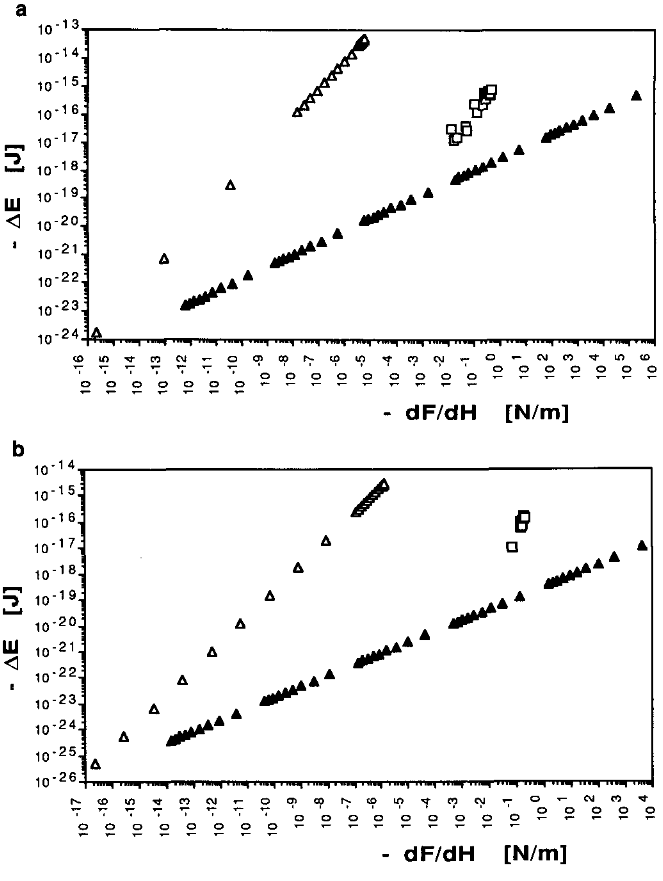

FIG. 4. The calculated energy of interaction, $-\Delta E$, as a function of the "elasticity" of interparticle forces, $-dF/dH$, for different interactions: van der Waals forces (▲) and water bridges (△). Each point corresponds to one distance between the particles, H. The experimental points also are plotted in the diagram (□). a, Sugar crystal dispersions; and b, fat crystal dispersion.

On the other hand, water bridges could be responsible for the interaction energy between sugar crystals in the oil, because they are much stronger than van der Waals forces (Fig. 4a). Water bridges have low "elasticity" (parameter $-dF/dH$ is low). This parameter is of the order of $\leqslant 10^{-5}$ N/m, while it is in the order of 10^{-2}–10^{-1} N/m for the experimental dispersions (see Fig. 4a and Table 3). This difference is much larger than, for example, errors in the geometry of the model. The high experimental values for $-dF/dH$ can be explained by van der Waals forces, where $-dF/dH$ reaches values as high as 10^6 N/m. Thus, if the network model is valid, the parameter $-dF/dH$ and the storage modulus (which was used for calculating $-dF/dH$) for the sugar dispersions may be primarily determined by van der Waals forces. Then, the equilibrium distances between the particles, H_0, can be estimated from Eq. [14]. The value of H_0 for the sugar dispersion with no emulsifier, presented in Table 3, is about 5 nm, which is a realistic value. The energy of interaction of J is about 3–4 orders of magnitude stronger than for hydrogen bonds. This strong interaction could be a result of water bridges or other types of colloidal interactions.

One possible explanation for the results is that a lot of contacts between sugar crystals in the network primarily form under the influence of van der Waals forces. The water then rearranges and forms bridges between the crystals. These bridges are mainly responsible for the strong adhesion in the system. On the other hand, van der Waals bonds are much stiffer and more elastic, and are responsible for the relatively high storage modulus of the system.

The adsorption of emulsifiers to sugar crystals changes the interaction energies, ΔE, the "elasticities" of the interactions, $-dF/dH$, and the distances between the particles, H_0 (Table 3). Generally speaking, as the energy of interaction increases, the elasticity also increases and the distance decreases. For example, the adsorption of multilayers of phospholipids increases the distance between the crystals by about 5 nm and decreases the energy about 15 times, while the adsorption of about one monolayer of sorbitan esters of fatty acids increases the distance by more than 6 nm, but decreases the energy only 10 times. Thus, the adsorption of different emulsifiers changes not only the magnitude of the interaction by changing the equilibrium distance, but also the character of the interaction (steric interaction or specific polar interactions may occur), and probably the particle network structure.

Fat crystals in oils. The Hamaker constant for fat crystals in soybean oil is estimated at about $2 \cdot 10^{-22}$ J

[Eq. [15]; $\varepsilon_{\text{tristearinh}} \approx 2.0$; $n_{\text{tristearin}} \approx 1.45$ (38,39)]. This is about 1.5–2 orders of magnitude lower than the values used previously (9,13). The Hamaker constants are again assumed to be independent of the adsorbed layers of emulsifiers. The mean particle diameter (from Eq. [16]) is 0.8 μm.

The plot of the calculated energy of interaction ($-\Delta E$) *vs.* the calculated force derivative ($-dF/dH$) is presented in Figure 4b for the fat crystal dispersions. The points correspond to van der Waals interaction (▲), water bridges (△) and experimental results (□). Again, van der Waals forces result in energies that are too low in relation to the experimental values—the points for van der Waals forces are located 2–3 orders of magnitude below the experimental points. The energy of interaction for fat dispersion in the oil without any emulsifier is 1.22×10^{-16} J (Table 3). Figure 3a shows that this order of magnitude for energy of van der Waals interaction can be found only for distances between particles of less than 10^{-10}m (1 Å). These short distances are not reasonable.

Water bridges could be responsible for energies in the order of 10^{-16} J, as can be seen in Figure 4b. However, the "elasticity" parameter $-dF/dH$ is too low in this case; it reaches values $\leqslant 10^{-5}$ N/m, while it is in the order of 10^{-2}–10^{-1} N/m for the examined fat dispersions (Table 3). van der Waals forces for the fat dispersions give interparticle bondings with "elasticities" ($-dF/dH$) of this order of magnitude (Fig. 4b) and could be responsible for the storage modulus of the dispersions. The equilibrium distances, H_0, between fat crystals can then be estimated from Eq. [14]. The calculated values are presented in Table 3 and are of the order of 20×10^{-10} m (2 nm), which is reasonable. At these distances, which are comparable to the diameter of an average triglyceride oil molecule (~1.5 nm), oscillating structural forces probably play a role. The energy of interaction of 1.22×10^{-16} J (Table 3) is about four times less than in the case of sugar dispersions, which seems reasonable.

When adsorption of emulsifiers to fat crystals causes an increase in yield value, G′ also increases and H_0 decreases (Table 3). However, the equilibrium distances between particles (around 18 Å) are almost unchanged by the adsorption. This shows that the model does not adequately describe the system and/or that adsorption changes the character of the interactions (the appearance of steric and polar forces), and is not explained by changes in van der Waals forces alone. Generally speaking, our results imply a great need of direct force measurements between the fat and sugar surfaces in the oil, with and without emulsifiers, and with and without traces of water in the system.

Rheological contra sedimentation results. Because both rheological and sedimentation properties are related to interparticle forces, they should also correlate with each other. Comparison of the sedimentation results [presented previously (1)] with the rheological parameters is illustrated in Figure 5a for sugar crystals and in Figure 5b for fat crystals. The relative changes in sediment volumes (ΔV), due to adsorption of the various emulsifiers, are plotted as a function of the resulting relative changes in storage moduli (G'/G'_0) and in the yield values (τ_y/τ_{y0}). An increase in the sediment volume corresponds to increases in the storage modulus and in the yield value—both are interpreted as an increased attraction/adhesion between the particles in the network. The opposite, a decrease in ΔV, corresponds to decreases in G'/G'_0 and τ_y/τ_{y0}—both are interpreted as a decrease in the attraction/adhesion in the dispersions. Figure 5 shows a satisfactory qualitative agreement between the rheological and sedimentation results, which supports our interpretations of the sedimentation experiments.

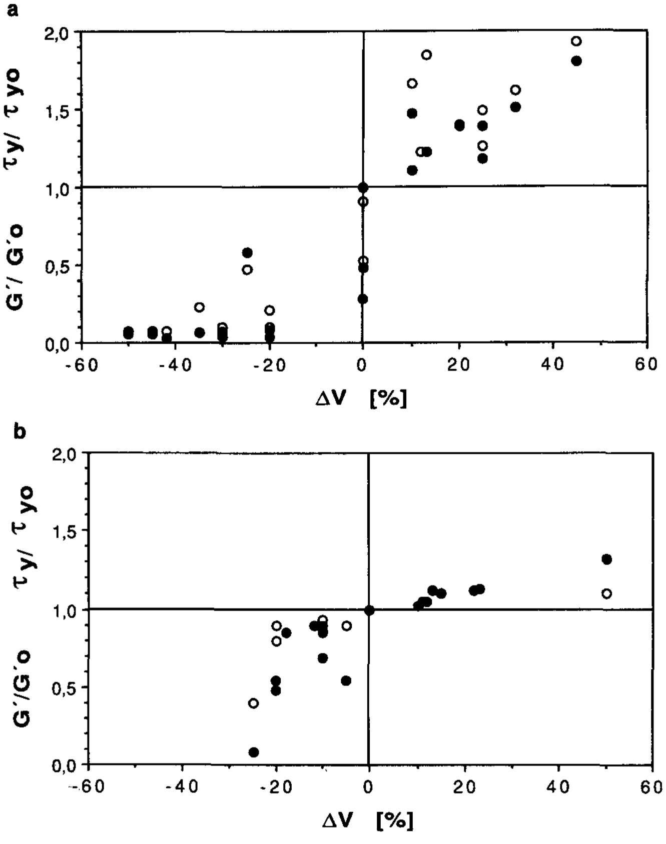

FIG. 5. A comparison of sedimentation results from reference 1 (relative change in sediment volume, ΔV) with the rheological results: Relative change of storage modulus G'/G'_0 (○) and yield value τ_y/τ_{y0} (●). a, Sugar crystal dispersions; and b, fat crystal dispersions.

Our research has shown that different classes of emulsifiers perform differently, as follows: Monoglycerides and their lactic acid esters increase storage moduli and yield values for sugar dispersions. The same properties decrease for fat dispersions, except at higher concentrations of saturated monoglycerides and lactic acid esters. Similar effects have been reported by Lucassen-Reynders and van den Tempel (40,41). Phospholipids strongly decrease the elastic properties of both fat and sugar dispersons. However, some pure phospholipids at low concentrations can have the opposite effect, at least in the case of fat dispersions. Esters of monoglycerides and fatty acids, when present at high enough concentrations, give an increase in storage modulus and yield value for fat crystal dispersions, and a decrease for sugar crystal dispersions. When present at low concentrations, most of them operate conversely.

Finally, rheology, as well as sedimentation stability of several food dispersions, can be regulated by choice of a proper emulsifier and concentration level. The network model probably does not correctly describe the structures in oil-continuous dispersions, and van der Waals forces alone cannot be responsible for the interactions in these systems.

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