Double Emulsions of Water-in-Oil-in-Water Stabilized by α-Form Fat Microcrystals. Part 1: Selection of Emulsifiers and Fat Microcrystalline Particles

N. Garti*, A. Aserin, I. Tiunova, and H. Binyamin

Casali Institute of Applied Chemistry, The Hebrew University of Jerusalem, 91904 Jerusalem, Israel

ABSTRACT: Double emulsions are commonly stabilized by monomeric and/or polymeric emulsifiers. Pickering stabilization by solid particles such as colloidal microcrystalline cellulose has been mentioned only once as a possible technique to stabilize the external interface of the water-in-oil-in-water emulsion. No further work was carried out exploring this option. The present study shows that solid microcrystalline fat particles of α-form are capable of adsorbing at the water-oil interface and, together with other hydrophobic emulsifiers, can stabilize water-in-oil (W/O) emulsions. The crystals must be submicron in size in order to effectively adsorb and arrange at the interface. Large crystals do not fit and were found to flocculate as free crystals in the continuous oil phase. The α-form crystals can be obtained by flash-cooling saturated triglycerides in vegetable oils in the presence of emulsifiers, such as polyglycerol polyricinoleate (PGPR), that stabilize the dispersion and serve as α-tending crystal structure modifiers. It was assumed that PGPR also serves as a cross-linker or bridge between the crystalline fat particles and the water, and facilitates the anchoring of the fat particles in the oil phase in one direction while dangling itself in the water phase. The double emulsion droplets prepared with these W/O emulsions are relatively large in size (6–18 μm), but stable to coalescence. The marker (NaCl) does not seem to release with time, suggesting that the fat particles form microcapsules on the water interface, totally sealing the water from releasing its addenda. The systems seem to have a significant potential for food emulsions.

Paper no. J8794 in *JAOCS 76*, 383–389 (March 1999).

KEY WORDS: Crystallization, double emulsions, flash-cooling dispersions, α-, β′-, β-form polymorphs, microcrystalline fat, Pickering stabilization, polyglycerol polyricinoleate, release of active matter, solid particles' stabilization, tristearin.

Double emulsions, prepared with monomeric or food-grade macromolecules (proteins, gums), consist of very large droplets (5–25 μm) and are thermodynamically unstable (1–3). Efforts have been made to add hydrophilic proteins, such as bovine serum albumin (BSA), casein and gelatin, to the external continuous phase (4,5) in order to improve stability of the double emulsion and to slow down the release rates of active matter or markers from the inner water phase to the continuous water phase during storage. The results are encouraging, but not sufficiently good (4,5). The droplets are relatively large and the release rates are controlled only to some extent. In our recent work we added blends of BSA and monomeric emulsifiers (hydrophobic Span 80 in the inner phase and hydrophilic Tween 80 in the outer phase) (5). These blends tend to form protein–emulsifier complexes adsorbing as thick films at the interfaces. The films are "release carriers" at the inner interface and "stability improvers" at the outer interface. The monomer–polymer associative structure at the oil membrane phase helps to control the release of water-soluble matter. In a proposed reverse micellar transport mechanism, the release is governed by the amount of reverse monomeric micelles present in the oil phase. The number of the reverse micelles is reduced by the polymeric protein and its solubilization capacity.

Tailor-made graft copolymers are capable of controlling both the release and the stability of the double emulsions (6–8). However, these synthetic silicon-based copolymeric amphiphiles are not allowed in food applications.

Oza and Frank (9–11) are the only scientists who have considered the use of colloidal microcrystalline cellulose (CMCC) as "mechanical stabilizers" for double emulsions. They demonstrated that the addition of CMCC to both the inner water-in-oil (W/O) emulsion and the outer water-in-oil-in-water (W/O/W) emulsion helped to slow down the release of electrolytes to the outer phase.

Recently, the stabilization mechanism of W/O margarine emulsions was reconsidered and elucidated (12–14). It was demonstrated that α- and β′-form fat crystals are more hydrophilic than the β-crystals, and tend to adsorb more strongly onto the oil-water interface. The role of the emulsifiers was claimed to be that of "bridging species between the fat crystals and the oil phase" (see Fig. 1).

In view of these recent findings we decided to reconsider the Pickering mechanism stabilization by fat crystals for stabilizing W/O emulsions, as part of the final preparation of double W/O/W emulsions to reevaluate the stability and the release rates.

---

*To whom correspondence should be addressed.
E-mail: garti@vms.huji.ac.il

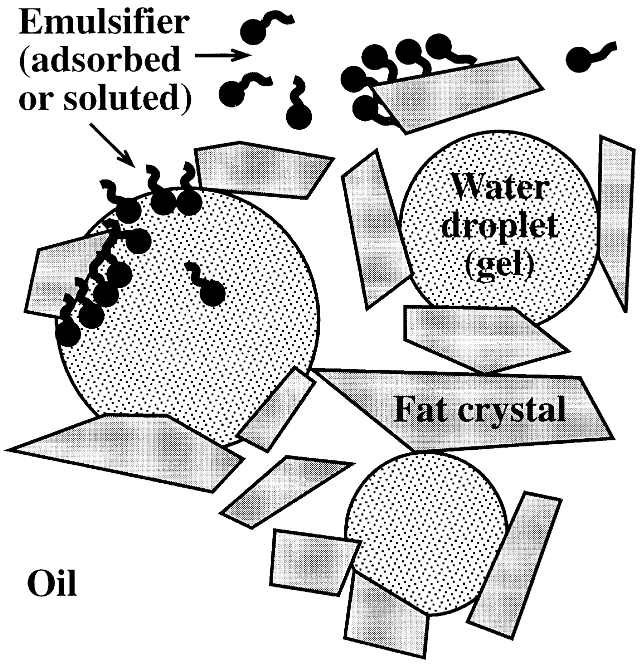

FIG. 1. A schematic picture of colloidal margarine structure demonstrating the role of emulsifiers and fat crystals in stabilizing water-in-oil (W/O) emulsion of margarine by colloidal fat crystals.

EXPERIMENTAL PROCEDURES

Materials. Three types of hydrogenated fats were used: fully hydrogenated tristearin (TS) with iodine value (IV) <1 (Akodur S) from Karlshamns (Karlshamns, Sweden); fully hydrogenated palmstearin (Cessapowder, IV < 1) from Karlshamns, and hydrogenated palm oil (IV < 1) from Adumim Chemicals (Mishor Adumim, Israel.

The soybean oil was deodorized and winterized by Etz-Hazayit (Petach Tikva, Israel.

The emulsifiers were: commercial grade lecithin (Sternwet P, deoiled, microfine powder soybean lecithin) from Stern-Chemi (Hamburg, Germany); glycerol monooleate (GMO) from ICI (Middlesbrough, Cleveland, United Kingdom); sorbitan monooleate (Span 80) from Sigma Chemicals (St. Louis, MO); ethoxylated sorbitan monooleate (Tween 80) from ICI, and polyglycerol polyricinoleate (PGPR, S-100) from Croda Chemicals Ltd. (Goole, North Humberside, England).

The internal marker in the inner water phase was 0.1 M wt% NaCl. All emulsions contained 0.005 wt% sodium azide (NaN_3) as preservative.

Analytical methods. Size distributions of fat crystals were measured by Zetamaster (Malvern, United Kingdom) and Galai (Migdal Haemek, Israel).

Droplet size distributions of the W/O emulsion were measured by a laser detecting instrument (Galai) and by microscopic observations (light microscope, Nikkon model F; Tokyo, Japan). Droplet size distributions of the W/O/W double emulsions were measured by a Coulter counter (Coulter Electronics, Luton, Beds., United Kingdom).

Viscosity measurements were carried out on a Brookfield (Stoughton, MA) viscometer. Fat crystals and W/O emulsions were tested by X-ray diffractions (Philips PW 1820 diffractometer with CuKα radiation; Eindhoven, Holland) and by a differential scanning calorimeter (DSC) (TA 4000 thermal analysis system, Mettler; Greifensee, Zurich, Switzerland, equipped with a TC 11 TA processor and a DSC 30 low-temperature cell) to establish the nature of the polymorphic form of the fat crystals prior to being added to the water-oil emulsion, after the formation of the emulsion and after storage. The DSC measurements were carried out as follows: samples (5–15 mg) were weighed, using a Mettler M3 microbalance, in standard 40 μL aluminum pans and immediately sealed by a press. All DSC measurements were performed with an empty pan as a reference. The calorimeter recorded the heat flow rate of the sample as a function of temperature.

Flash-crystallization of fat microcrystals. Three flash-cooling procedures have been employed to obtain microcrystalline fat particles: (i) fast-cooling of molten (hot) tristearin in oil solution from 80°C to room temperature, (ii) direct flash-cooling of hot emulsifier-TS-oil solution in liquid nitrogen, and (iii) fast-cooling of the test tube, containing molten tristearin in oil with the emulsifiers, to liquid nitrogen temperature. All the semisolid TS-in-oil dispersions were gently brought to room temperature for analysis and use in the W/O emulsions. No significant differences in the size of the microcrystals or in their polymorphic structures were detected when using procedure ii or iii. When procedure i was employed, large crystals were obtained consisting of mixtures of α- and β′-forms. Therefore, in most reported experiments procedure iii was employed to guarantee formation of uniform, small crystals of the α-form.

Preparation of W/O emulsions. In most W/O emulsions, the water inner phase was kept constant at 25 wt%. The emulsifiers and the fat concentrations are expressed in wt% from the oil phase. The water phase was added dropwise to the freshly prepared microcrystalline fat particles while stirring. The emulsions were further homogenized using Ultra-Turrax T-25 homogenizer (Janke & Kunkel, Germany) at 8,000 to 24,000 rpm for 15 min.

In some of the emulsions (for controlled release tests) 0.1 M sodium chloride was added to the aqueous inner phase prior to being added to the oil phase.

Preparation of W/O/W emulsions. Double emulsions were prepared from freshly made W/O emulsions, added dropwise to an aqueous emulsifier solution (Tween 80 or mixtures of Tween 80 + Span 80). All double emulsions contained 20 wt% W/O emulsions and various external emulsifier concentrations, expressed as wt% of the total double emulsion.

Stability evaluation. Stability evaluation of the W/O emulsions was done by both light microscope and laser detector (Galai). Size distributions were presented both by number and by volume.

Stability of W/O/W emulsions was determined by light microscope, coalescence rates, and Coulter counter size distributions.

Release profiles. Release profiles were obtained from the direct measurements of the NaCl concentration by electrical conductivity in the external phase with time. The electrical conductivity measurements were performed at 25 ± 0.5°C using a conductivity meter, type CDM-83 (Radiometer, Copenhagen, Denmark).

RESULTS

W/O emulsions stabilized by commercial food-grade emulsifiers. Two sets of W/O emulsions were prepared. The first was based on 25 wt% water-in-soybean oil and 2–6 wt% of a blend (1:1, w/w) of GMO and deoiled lecithin. These emulsions are similar to margarine-type emulsions, except that the emulsions are cooled to room temperature (from 60°C) without using Votator-type cooling (fast cooling while shearing the crystallizing fat). These emulsions were extremely unstable and coalescence occurred within minutes.

The second set of preparations was based on our previous experience (14) with PGPR at 0.2–2.0 wt%, and 25 wt% water in soybean oil. These emulsions were easy to prepare (even in the absence of votation). The average droplet size of the W/O emulsions was 0.5–1 μm, and stable emulsions with no coalescence for periods of several hours were obtained. The second set of preparations was therefore used in most W/O emulsions in which fat particles were not present (control). It should be noted that these W/O emulsions were susceptible to creaming. Best stability of the W/O and W/O/W emulsions was obtained with 1 wt% PGPR (see Fig. 2 for W/O emulsion and Fig. 3 for a typical photomicrograph of W/O/W emulsion).

W/O emulsions stabilized by micronized fat crystals. Attempts were made to micronize β-form fat crystals (by grinding in a ball-mill) and to use them as such in W/O emulsions. All experiments with any size of micronized fat crystals (0.5–2 μm) failed. All the emulsions were unstable to coalescence, and the fat crystals were, in most cases, found in a flocculated form in the continuous oil phase.

Crystallization of microcrystalline fat particles by flash-cooling. TS at 0.5–4.0 wt% was added to 1 wt% PGPR soybean oil solution, and the system was heated to 80°C to obtain a totally clear solution. The test-tube procedure iii (see Experimental Procedures section) of the clear, heated solution was flash-cooled in liquid nitrogen, and an opaque oil dispersion, in which TS crystals were dispersed, was obtained. The dispersion was submitted to structural analysis. Table 1 summarizes the results from this set of experiments.

The average particle size was 285 to 1858 nm. The particle sizes increased with an increase in TS concentration in the oil. When the PGPR concentration was kept at 0.5 or 1.0 wt%, and the PGPR/TS ratio was kept constant, the particle size did not change significantly (particles of 301 and 285 nm were obtained for 1 wt% TS and 1 wt% PGPR, or 0.5 wt% TS and 0.5 wt% PGPR). However, as the PGPR/TS ratio decreased the size of the particles increased significantly (to 837 or 956 nm).

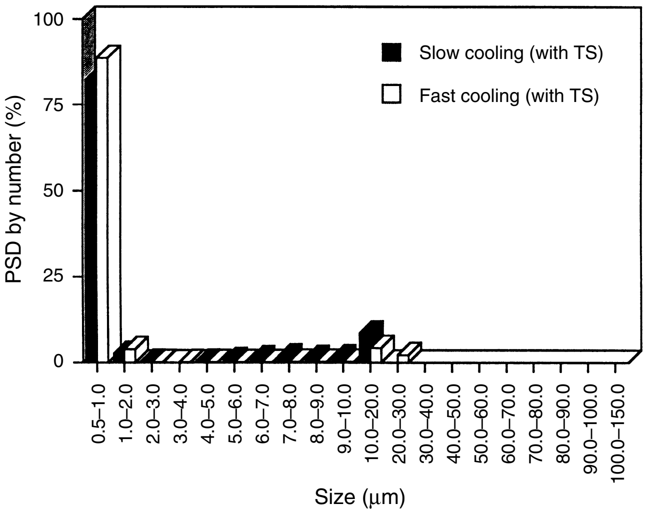

FIG. 2. Particle size distribution by number (PSD) of 25 wt% W/O emulsions prepared with soybean oil and a blend of a molten 0.2 wt% PGPR and 2.0 wt% tristearin by slow (■) and fast (□) cooling processes (see Experimental Procedures section). PGPR, polyglycerol polyricinoleate; TS, tristearin. For other abbreviation see Figure 1.

It was concluded that in order to obtain crystal sizes below 300 nm with a narrow distribution, it is essential to use low levels of TS and high levels of PGPR and to keep the PGPR/TS ratio high. The PGPR, as expected, is a crystal structure modifier and also inhibits the growth of the fat crystals in the oil phase.

Polymorphic structure of fat microcrystals. Fat crystals are known to form several polymorphic structures as a function of crystallization conditions (15–18). α-Form crystals are the least thermodynamically stable, with the lowest melting points, irregular shapes, and small size. α-Form crystals tend to transform into the more stable β′ and β forms when sufficient mobility is provided (temperature fluctuations, melting temperatures, solvent mediation). β-Form, being the most stable form, grows (develops) into a more ordered crystal lat-

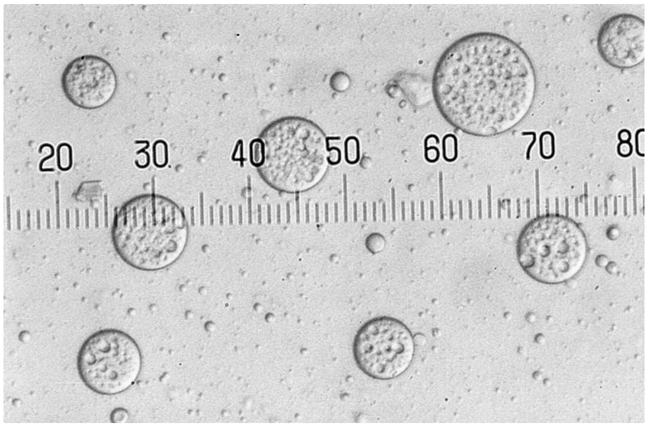

FIG. 3. Typical photomicrograph of water-in-oil-in-water (W/O/W) emulsion prepared with 25 wt% water in soybean oil in the presence of 1.0 wt% PGPR in the inner phase and 2.0 wt% Tween 80 in the outer phase (10 units Bar is 25 μm). For abbreviation see Figure 2.

TABLE 1
Particle-Size Distributions of Fat–Tristearin Crystals Obtained by a Flash-Cooling Procedure in Soybean Oil (procedure iii, Experimental Procedures section)[a]

			Particle size distribution of fat crystals		
TS (wt%)	PGPR (wt%)	PGPR/TS (wt/wt)	Average (nm)	Percent (<500 nm)	Percent (<1000 nm)
0.5	0.5	1.0	285	92	100
0.5	1.0	2.0	302	97	100
0.5	2.0	4.0	380	100	100
1.0	0.5	0.5	837	0	90
1.0	1.0	1.0	301	79	98
1.0	2.0	2.0	440	100	100
2.0	1.0	0.5	956	0	23
4.0	1.0	0.25	1858	0	0

[a] TS, tristearin; PGPR, polyglycerol polyricinoleate.

tice, i.e., large-size crystals with high melting points. The β-crystals have the lowest free energy and therefore are obtained under slow and controlled growth conditions. Flash-cooling mostly yields the α-form in small, ill-defined crystals. Our experimental results confirm these assumptions. TS is partially soluble in unsaturated triglycerides (vegetable oils), and will crystallize in soybean oil only upon flash-cooling to very low temperatures.

The dispersed fat particles were examined microscopically, by DSC and X-ray diffraction. The pattern of the filtered particles, although not very explicit, indicates the existence of α-form crystals. The DSC thermograms are somewhat difficult to interpret because of the complexity of the participating ingredients. Nevertheless, the endothermic peak of the α-form can be easily recognized and, upon heating, one can also detect the exothermic peak of its transformation to the β′-form (see Fig. 4).

W/O emulsions with PGPR and TS. Judging from the internal composition of soybean oil, it is evident that considerable amounts of the oil components are triacyl-long-chain saturated fatty acids, such as tripalmitin, TS, palmstearin (PPP, SSS, PSP, SPP), etc. These components tend to precipitate during the cooling process, even in the absence of external TS. Therefore, it was clearly observed that W/O emulsions, prepared with 0.2 wt% PGPR (with no TS added), when flash-cooled and brought to room temperature, were more stable than emulsions prepared in a slow-cooling process. The emulsions (Fig. 5) showed two droplet/particle populations. It seems that the particles in the range of 0.5 to 3.0 μm were W/O emulsion droplets, while the particles in the range of 10–60 μm were of aggregated fat crystals floating in the soybean oil. When the oil is flash-cooled the aggregated fat particles do not grow efficiently in the oil, but rather adsorb onto the oil-water interface. Therefore, no large particles were detected in these emulsions.

When W/O emulsions with similar internal compositions were prepared in the presence of 2.0 wt% dispersed microcrystalline TS, they were composed of smaller droplets with narrower size distribution than those prepared in the absence of TS. The fast cooling of the emulsions helped to eliminate the wide particle population distribution. The emulsions were very uniform and almost monodispersed.

The droplet size distribution of the emulsion showed only little change with time. After 6 wk a small portion of the fat

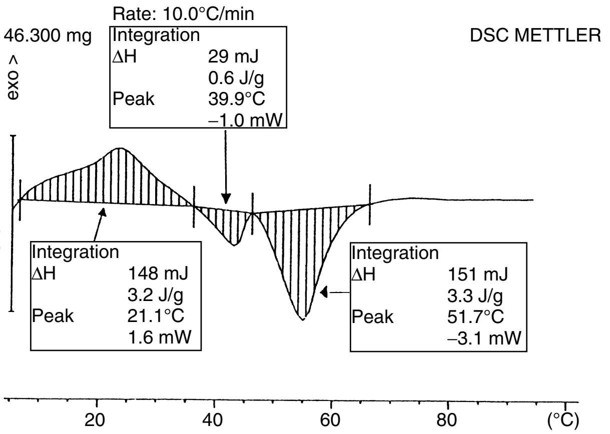

FIG. 4. Typical differential scanning calorimeter thermogram of TS-in-oil dispersion prepared by flash-cooling of the 2 wt% TS-in-soybean oil (samples heated at 10°C/min). The peak at 39.9°C is of α-form and the peak at 51.7°C is of β′. The β-form will melt at 60–70°C (not seen since β-form crystals are not formed). For abbreviation see Figure 2.

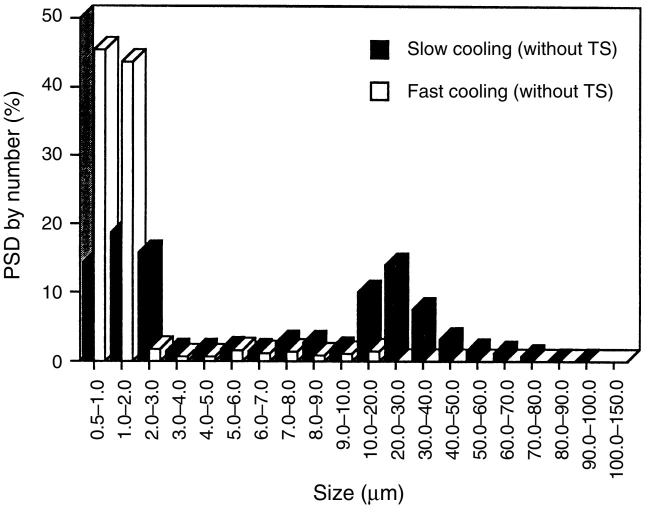

FIG. 5. PSD of W/O emulsions prepared with 1.0 wt% PGPR and slow-cooling (■) and 1.0 wt% PGPR and fast cooling (□). For abbreviations see Figures 1 and 2.

crystals migrated from the interface to the continuous oil phase, and flocculated or grew into larger particles. The uncovered droplets coalesced slowly to larger droplets (see Fig. 6). It should be stressed that the coalescence is very minor in comparison to W/O emulsions prepared only with TS or PGPR. The best emulsions were obtained with 1 wt% PGPR and 1 wt% TS (see Fig. 7).

Attempts to increase the amounts of TS in the oil phase to 4–8 wt% have failed, since the TS crystals dispersed in the oil phase impart very high viscosity to the system.

W/O emulsions with other triglycerides. The TS was replaced by two other saturated fats with lower melting points and a lower tendency to transform from the α-form to the β-form.

Hydrogenated palm oil emulsions (mostly tripalmitin) showed a minimal percentage of free unadsorbed particles in the continuous phase, expressed only in minor amounts of "second population" of particles in the range of 10–60 µm, and are emulsions with excellent stability (see Fig. 8).

Double emulsions. The composition of the two sets of double emulsions prepared with the W/O Pickering stabilized emulsions are illustrated in Table 2. Droplet size averages and the conductivity of the systems (reflecting the release) are also presented immediately after preparation (t = 0) and with 10 d of storage.

Figures 9A and B are photomicrographs of a typical double emulsion stabilized with a combination of fat crystals and emulsifiers, 24 h after preparation (A) and after 3 wk storage (B).

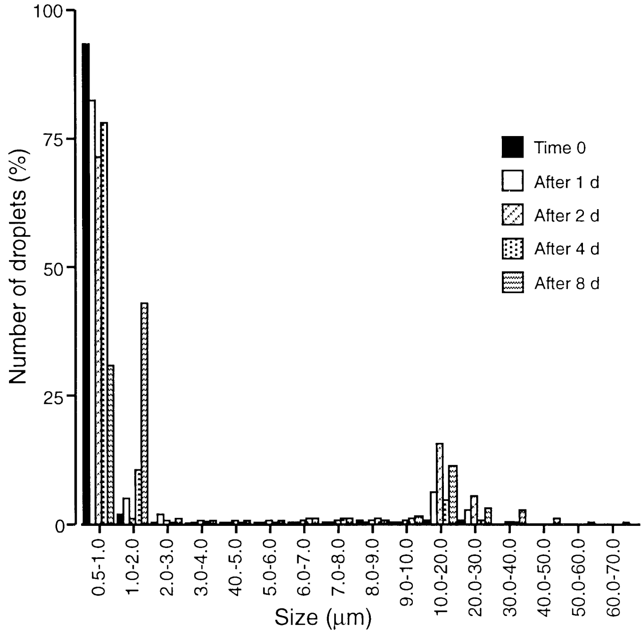

FIG. 6. Droplet size distribution of W/O emulsion particles prepared with 0.2 wt% PGPR and 1.0 wt% TS at time = 0 and within 8 d of aging at room temperature. Two different populations of particles are detected. The first is W/O droplets (0.5-2.0 µm) and the second is solid fat particles (10.0 to 40.0 µm). For abbreviations see Figures 1 and 2.

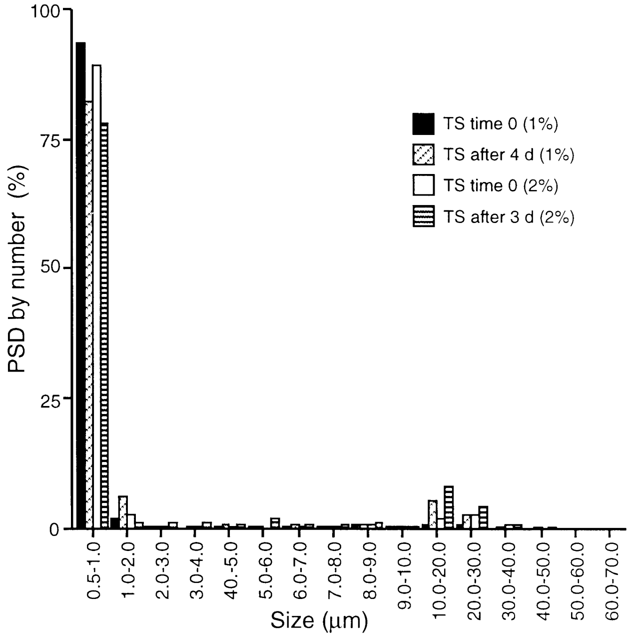

FIG. 7. Particle size distribution of W/O emulsions stabilized with 1–2 wt% TS and 1.0 wt% PGPR and aged over 0–4 d. For abbreviations see Figures 1 and 2.

Those results support the following generalizations: (i) The internal composition of the W/O emulsion has only a minor effect on droplet size, release pattern, and stability of the double emulsions. Emulsions prepared with 1 or 0.5 wt% TS have similar stability patterns, provided the PGPR/TS rate is kept at a minimum of 1.0. (ii) Tween 80 is a suitable emulsifier for the external phase. Levels of 0.5 to 2.0 wt% are suf-

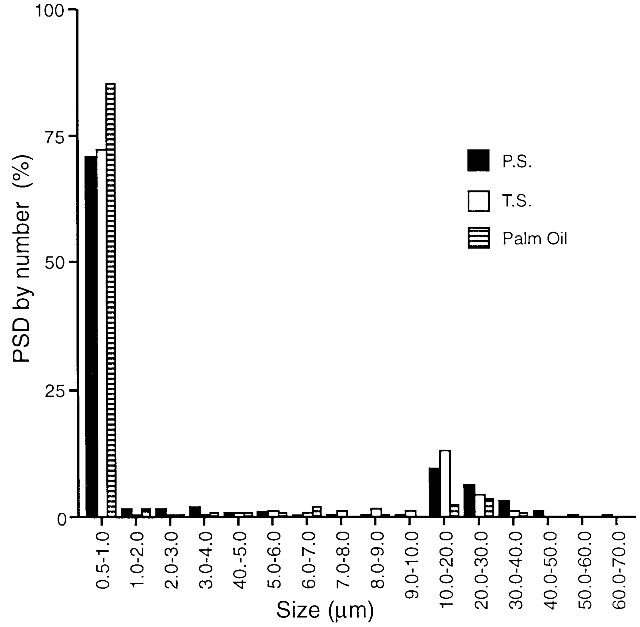

FIG. 8. Droplet size distribution of water dispersed in oil (W/O) of emulsions stabilized with 1.0 wt% PGPR and 0.2 wt% microcrystalline solid fat particles of (i) palmstearin (PS), (ii) tristearin (TS), and (iii) hydrogenated palm oil. For other abbreviations see Figures 1 and 2.

TABLE 2
W/O/W Double Emulsions (with 20 wt% W/O emulsions, prepared) with (A) 25 wt% Water, 1% PGPR, 0.5 wt% TS, and 73.5 wt% Soybean Oil, and (B) 25 wt% Water, 1% PGPR, 1% TS, and 73.0 wt% Soybean Oil[a]

	Tw-80 (wt%)	Sp-80 (wt%)	Size (W/O/W) $t = 0$ (µm)	Size (W/O/W) $t = 14$ d (µm)	Conductivity $t = 0$ $(\text{mS})^{-1}$	Conductivity $t = 10$ d $(\text{mS})^{-1}$
Set A	0.5	—	8	20	0.4	1.0
(1% PGPR,	1.0	—	7	22	0.8	1.4
0.5 % TS)	2.0	—	6.5	25	1.2	1.4
$\varphi_1^{w/o} = 0.25$[b]	3.0	2.0	14	14	1.0	1.1
$\varphi_2^{w/o} = 0.2$[c]	6.0	4.0	18	18	1.8	2.2
Set B	0.5	—	11	11	1.1	0.8
(1% PGPR,	1.0	—	10	9	1.0	1.1
1 % TS)	2.0	—	13	10	0.7	1.2
$\varphi_1^{w/o} = 0.25$	3.0	2.0	12			
$\varphi_2^{w/o} = 0.2$	6.0	4.0	13			

[a] The external phase contained various compositions of Tween 80 (Tw-80) and Span 80 (Sp-80). W/O/W, water-in-oil-in-water; W/O, water-in-oil. For other abbreviations see Table 1.

[b] $\varphi_1^{w/o} = 0.25$, weight fraction of oil phase or water-in-oil emulsion consisting of 25 wt% oil.

[c] $\varphi_2^{w/o} = 0.2$, weight fraction of W/O emulsion in the double W/O/W emulsion.

ficient concentrations to obtain double emulsions with an average droplet size of 6–10 µm. Higher concentrations of external emulsifiers will cause a destabilization effect and faster release of the NaCl. This phenomenon is consistent with previous findings by Matsumoto (19) and our group (20–22), clearly showing that increased levels of external emulsifiers will increase the release rates. The exchange of emulsifiers between the external and internal interfaces is well-documented and in most cases is destructive to both interfaces. (iii) The use of blends of Span 80 and Tween 80 did not prove to be more beneficial to emulsion stability than the use of Tween 80 alone. (iv) Relatively stable double emulsions can be formed at a proper emulsifier–TS blend, and only a minor change in droplet size was observed over 14 d of aging. (v) The release of NaCl was totally blocked by the fat particles, and the emulsions behaved, to some extent, like microcapsules, almost sealed to the release of the NaCl.

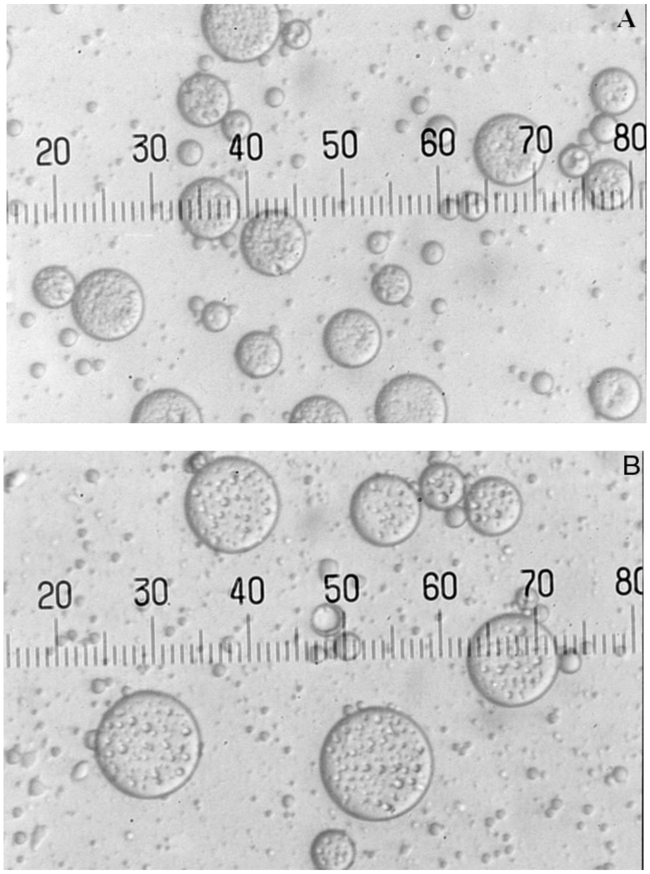

FIG. 9. Photomicrographs of double emulsions (W/O/W) stabilized with fat crystals and PGPR at the inner interface and Tween 80 at the outer interface: (A) After 24 h, and (B) after 3 wk. For abbreviations see Figures 2 and 3.

REFERENCES

1. Garti, N., and A. Aserin, Double Emulsions Stabilized by Macromolecular Surfactants, in *Surfactants in Solutions*, edited by A.K. Chattopadhyay and K.L. Mittal, Marcel Dekker, New York, 1996, pp. 297–332.
2. Garti, N., and A. Aserin, Pharmaceutical Emulsions, Double Emulsions, and Microemulsions, in *Microencapsulation: Methods and Industrial Application,* edited by S. Benita, Marcel Dekker, New York, 1996, pp. 411–534.
3. Garti, N., and A. Aserin, Double Emulsions Stabilized by Macromolecular Surfactants, *Adv. Colloid Interface Sci. 65*:37–69 (1996).
4. Omotosho, J.A., T.K. Law, T.L. Whateley, and A.T. Florence, The Stabilization of W/O/W Emulsions by Interfacial Interaction Between Albumin and Nonionic Surfactants, *Colloids Surf. 20*:133–144 (1986).
5. Garti, N., A. Aserin, and Y. Cohen, Mechanistic Considerations on the Release of Electrolytes from Multiple Emulsions Stabilized by BSA and Nonionic Surfactants, *J. Controlled Release 29*:41–51 (1994).
6. Sela, Y., S. Magdassi, and N. Garti, Release of Markers from the Inner Water Phase of W/O/W Emulsions Stabilized by Silicone Based Polymeric Surfactants, *Ibid. 33*:1–12 (1995).
7. Sela, Y., S. Magdassi, and N. Garti, Polymeric Surfactants Based on Polysiloxanes-*graft*-poly(oxyethylene) for Stabilization of Multiple Emulsions, *Colloids Surf. A: Physicochem. Eng. Aspects 83*:143–150 (1994).
8. Sela, Y., S. Magdassi, and N. Garti, Newly Designed Polysilox-

ane-*graft*-poly(oxyethylene) Copolymeric Surfactants: Preparation, Surface Activity and Emulsification Properties, *Colloid Polym. Sci. 272*:684–691 (1994).

9. Oza, K.P., and S.G. Frank, Microcrystalline Cellulose Stabilized Emulsions, *J. Dispersion Sci. Technol. 7*:543–561 (1986).
10. Oza, K.P., and S.G. Frank, Multiple Emulsions Stabilized by Microcrystalline Cellulose, *Ibid. 10*:163–185 (1989).
11. Oza, K.P., and S.G. Frank, Drug Release from Emulsions Stabilized by Colloidal Microcrystalline Cellulose, *Ibid. 10*:187–210 (1989).
12. Johansson, D., Colloids in Fats. The Fat Crystal as a Functional Particle, Ph.D. Thesis, Lund University, 1994.
13. Johansson, D., B. Bergenståhl, and E. Lundgren, Water-In-Triglyceride Oil Emulsions. Effect of Fat Crystals on Stability, *J. Am. Oil Chem. Soc. 72*:939–950 (1995).
14. Johansson, D., and B. Bergenståhl, Sintering of Fat Crystal Networks in Oil During Post-Crystallization Processes, *Ibid. 72*:911–920 (1995).
15. Goubran, R., and N. Garti, Stability of W/O Emulsions Using High MW Emulsifiers, *J. Dispersion Sci. Technol. 9*:131–148 (1988).
16. Johansson, D., The Influence of Temperature on Interactions and Structures in Semisolid Fats, *J. Am. Oil Chem. Soc. 72*:1091–1099 (1995).
17. Garti, N., and K. Sato, *Crystallization and Polymorphism of Fats and Fatty Acids, Surfactant Science Series*, Marcel Dekker, Inc., New York, 1988, Vol. 31.
18. Hernqvist, L., Polymorphism of Fats, Ph.D. Thesis, Lund University, Sweden, 1984.
19. Matsumoto, S., W/O/W-type Multiple Emulsions, in *Nonionic Surfactants*, edited by M.J. Schick, Marcel Dekker, New York, 1987, Vol. 23, pp. 549–600.
20. Magdassi, S., M. Frenkel, N. Garti, and R. Kasan, Multiple Emulsions II—HLB Shift Caused by Emulsifier Migration to External Interface, *J. Colloid Interface Sci. 97*:374–379 (1984).
21. Magdassi, S., and N. Garti, Release of Electrolytes in Multiple Emulsions: Coalescence and Breakdown or Diffusion Through Oil Phase?, *Colloids Surf. 12*:367–373 (1984).
22. Magdassi, S., M. Frenkel, and N. Garti, On the Factors Affecting the Yield of Preparation and Stability of Multiple Emulsions, *J. Dispersion Sci. Technol. 5*:49–59 (1984).

[Received February 17, 1998; accepted November 5, 1998]