Chemical and Physical Aspects of Macroemulsions Stabilized by Interfacial Colloids

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Here we discuss macroemulsions stabilized by interfacial colloidal films, in terms of the basic processes of colloid nucleation, colloid flocculation, and assembly in interfacial films. By monitoring the droplet-diameter, we present the effect of a variety of surfactants, additives, and organic solvents, as well as the amount of the colloid, and that of the continuous and the dispersed liquid phases. A quantitative analysis explains the experimental results and enables us to estimate the film thickness and the floc size. A modified hydrophilic/ lyophilic balance scale accounts for the role of the surfactants. It is demonstrated that monitoring the droplet size on the submillimeter scale is a powerful tool in the investigation of colloid processes on the nanometer scale and colloid flocculation in the micrometer and submicrometer scales.

Introduction

Pickering was the first to show that solid particles could stabilize oil−water dispersions.[1] These so-called Pickering emulsions, or, in general, solid-particle-stabilized emulsions (SPSEs), have been investigated since then with a variety of solid powders.[2−4] The specific surface properties of the solid particle determine the type of emulsion it stabilizes. By treating the surface of the particle, such as by selective surface adsorption of certain materials, one can observe phase inversion in a Pickering emulsion.[5] The sizes of the emulsion droplets are determined by the amount and the size of the stabilizing particles (Pickering effect). Usually additional surfactant improves the stability of SPSE,[6,7] though its presence is not mandatory.[8,9]

The major general factors which govern the size distribution and the stability of the SPSEs have been summarized by Levine and Sanford.[10] They are as follows: (1) The size of the particle must be considerably smaller than the size of the droplet in the emulsion. (2) The particles should be in a state of incipient flocculation.[6,11] This means that the interactions between particles are an important factor in the emulsion stabilization. (3) The particle has to be partially wettable by both phases but more wettable by the continuous phase.[12] If the particles are completely wetted by either water or oil, they become dispersed in that phase and coalescence of the emulsion occurs.

MELLFs, standing for metal liquidlike films, are systems of highly concentrated metal (silver) colloidal films separating two immiscible liquid phases.[13,14] The films are characterized by a high specular reflectivity. They are fluid, in the sense that they can flow, and can be penetrated and ruptured, remaining virtually intact. The particulate structure is responsible for the latter characteristic, while the high concentration of metal particles is the reason for the high reflectivity.[15] MELLFs are special cases of interfacial colloids, i.e., colloids confined to the interface between two liquids or to the surface of a single liquid phase.

MELLFs can appear in an emulsion-like form, termed macroemulsion MELLFs, ME-MELLFs.[16] In this system, aqueous droplets, enveloped by the MELLF, are suspended in an organic medium. Very recently, we demonstrated that the elementary processes of the formation of a ME-MELLF are directly expressed in the macroscopic emulsion droplet size.[17] An explanation for the observed Pickering effect in MELLF

emulsion systems, i.e., the dependence of the droplet size on system parameters, has been suggested on the basis of the colloidal nucleation/growth rate ratio. An enhanced colloid nucleation rate, compared to growth, results in a size decrease of the MELLF emulsion droplets. Alternatively, changes in the packing of the interfacial colloids as flocs are suggested.[18]

The metal particles, in a ME-MELLF, differ from most of the fine particles which have been previously investigated as emulsion stabilizers. Unlike the preformed particles, ME-MELLFs involve a stage of formation of the colloid, its assembly into flocs, and its arrangement at the interface, concurrently with the stabilization of the emulsion. ME-MELLFs enable the use of powerful *in situ* spectroscopical techniques, UV−visible absorbance, and (surface-enhanced) Raman spectroscopy. These are of great help in the understanding of SPSEs, in general, and ME-MELLFs, in particular.

This paper is devoted to a general study of the dependence of silver macroemulsion MELLFs on the main chemical and physical factors that are involved in their formation and determine of the droplet size and system stability.

Experimental Section

A standard production of a macroemulsion MELLF has been described in detail previously.[14,15] It involves 10 mL of 0.05 N silver nitrate solution, with 0.1% anisic acid and 0.03% FC143, stirred together for 30 min with 30 mL of 1-chloro-butane. The reductant was 1 mL of 0.5% hydrazine sulfate. We use this standard sample unless specifically noted otherwise. The aqueous silver colloidal suspension (used as a reference system) was prepared by adding 10 mL of 2×10^{-3} N silver nitrate, dropwise, into 20 mL of 4×10^{-3} M NaBH$_4$. A yellow colloidal solution was obtained with a sharp silver plasmon absorption peaking at 384 nm. The water is of 18 MΩ·cm resistivity, obtained from a Barnsted E pure water purifier.

The surfactants we used were as follows: Those produced by 3M are FC143, ammonium perfluoroalkyl carboxylates, 100% active; FC98, potassium perfluoroalkyl sulfonates, 100% active; FC129, potassium fluoroalkyl carboxylates, 50%, in 2-butoxyethanol, CH$_3$(CH$_2$)$_3$OCH$_2$CH$_2$OH, 14%, ethanol, 4%, and water 32%; FC135, fluorinated alkyl quaternary ammonium iodides, 50% active, in isopropyl alcohol, 33%, and water, 17%, w/w; FC170, fluorinated alkyl poly(oxyethyleneethanol)s; and FC170-C, fluoroaliphatic oxyethylene adduct, 81%, lower poly-(oxyethylene glycol)s, 12%, 1,4-dioxane, <0.3%, and water,

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TABLE 1: Surfactant Ability To Form MELLF Macroemulsions and Emulsions[a,d]

| | FC A | | | FC C | | | FC N | | | HC A | | | mixture | |
solvents	FC143	FC98	FC129	0.05% FSC	0.025% FSC	FC135	FSN	FC170	FC170-c	DIO60	AP85W	MS	FC143 + FSN	FC143 + FSC
1-chlorobutane	+	+	−	−	−	−	+	+	+	−	−	+	+	−
2-chlorobutane	+	+	−	−	−	−	+	+	+	−	−	+	−	−
chlorobenzene	+	+	−	−	−	−	+	+	+	−	−	+	+	−
emulsion[b]	−	+	−	−	−	−	−	+	+	+	−			
emulsion[c]	−	−	o/w	−	−	−	−	w/o	w/o	w/o	w/o			

[a] Symbols: "+" denotes that an emulsion/macroemulsion forms. "−" denotes that an emulsion/macroemulsion does not form. [b] Emulsions of an aqueous ammoniacal solution of silver nitrate, anisic acid, and the surfactant, at the standard composition, and 1-chlorobutane. [c] Emulsions of water at pH ∼9 and 1-chlorobutane. [d] The surfactants are listed in the Experimental Section. FC stands for a fluorocarbon surfactant, HC for a hydrocarbon surfactant, A marks an anionic, C a cationic, and N a nonionic surfactant.
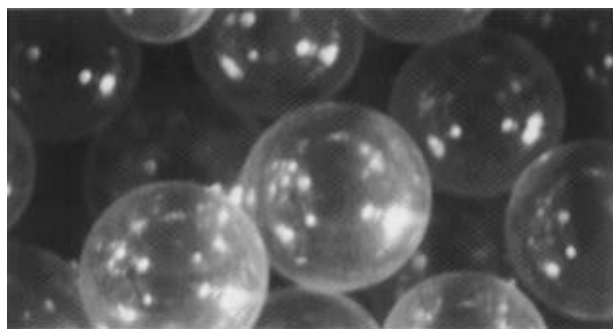

Figure 1. Silver macroemulsion MELLF. The ME-MELLF is the standard preparation, except for the reductant. We used 0.1 mL instead of the standard 1 mL. Magnification ∼20.

7% max. Those produced by Du Pont are FSC, zonyl FSC, $R_fCH_2CH_2SCH_2CH_2N^+(CH_3)_3CH_3SO_4$, 50% active solids, in water, 25%, and isopropyl alcohol, 25%, w/w; and FSN, zonyl FSN, $R_fCH_2CH_2O(CH_2CH_2O)_xH$, 40% active solids, in water, 30%, and isopropyl alcohol, 30%, w/w; $R_f = CF_3(CF_2)_{5-15}$. Those produced by Kempen are DIO60, merpasol DIO 60, diisooctylsulfosuccinate sodium salt, 60% active solids, in water, 32%, and an unspecified solvent, 8%; and AP85W, Merpisap AP85W, linear sodium dodecylbenzene sulfonates, 85% active solids. That produced by Merck was MS, myristic acid, $CH_3(CH_2)_{12}CO_2H$.

The droplet sizes and their distribution were measured using a video camera, Sony SSC-370ME, a Data Translation Fidelity 100, Model 3955, frame grabber, installed on a 486PC. The pictures were analyzed using the Particle Tool in the Global Lab Image analysis package (Data Translation). A HP 8542 diode array spectrophotometer, in the range 190−820 nm, with a resolution of 2 nm, served for the UV−visible measurements. The exposure time was 0.5 s for 1-cm path quartz cuvettes.

Results

(A) Effects of Surfactants. Surfactants are known to be of importance in MELLFs[13,14] and in SPSE.[6,7] We chose a variety of surfactants with a range of structures and properties (Table 1), denoted by FC, perfluorocarbon; HC, hydrocarbon; A, anionic; C, cationic; and N, nonionic. A photograph of a silver macroemulsion MELLF with large droplets is shown in Figure 1. The smaller droplets are similar but, of course, are more difficult to observe.

There are several pertinent points: (1) A suitable surfactant is mandatory for the production of stable macroemulsion silver MELLFs. (2) Surfactants with an anionic or nonionic headgroup promote the production of ME-MELLFs. Carboxylates and sulfonates work equally well. (3) Perfluoroalkylated chains are more efficient in producing ME-MELLFs. Equally long hydrocarbon chains (such as C7) do not produce ME-MELLFs. Only longer-chain surfactants, myristic acid, for example, work
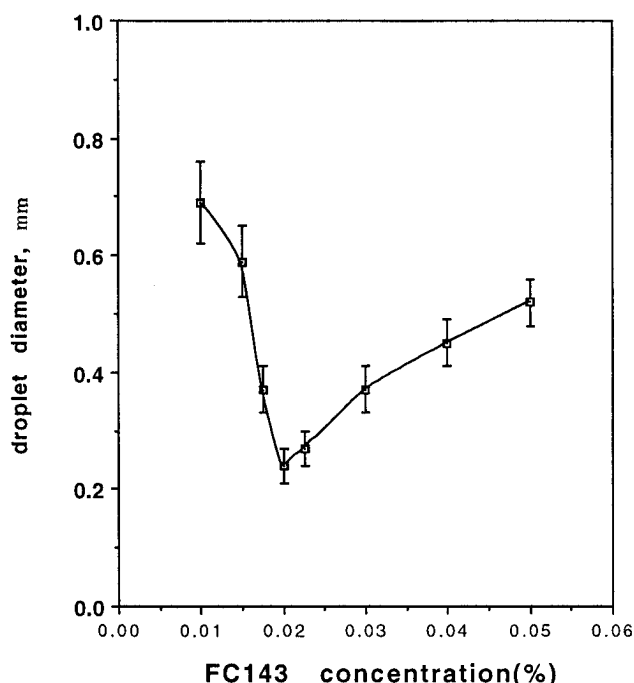

Figure 2. Dependence of the emulsion droplet size on the concentration of the surfactant FC143: 1 mL of 0.5% hydrazine was added into 10 mL of 0.05 M ammoniacal silver nitrate, in the presence of 0.1% anisic acid. The organic solvent was 30 mL of 1-chlorobutane.

well. (4) A mixture of two macroemulsion active surfactants is generally less effective. At least one of the surfactants in the mixture must promote emulsion formation by itself.

Let us consider a few mixtures of surfactants in more detail. FC143 (FC,A) and FSN (FC,N), as indicated in Table 1, each produce MELLF emulsions using the same concentration (0.03%). A mixture of the two surfactants, maintaining the same final apparent "surfactant" concentration by weight, strongly destabilized the droplets in 1-chlorobutane and chlorobenzene and altogether prevented the formation of silver emulsions in 2-chlorobutane. The mixture of FC143 and FSC (FC, C) did not produce ME-MELLFs, though there was quite enough FC143. Only at FSC concentrations below ∼17% of the total did its detrimental effect become negligible.

Using FC143, the emulsion droplet sizes were found to be inversely dependent on the surfactant concentration in the low concentration range, from 0.01% to 0.02%, as seen in Figure 2. An increase of the surfactant concentration, from 0.02% to 0.05%, results in large and unstable droplets. Thus, the optimal surfactant concentration for FC143, in terms of droplet size and stability, is between 0.02% and 0.03%.

Table 1 shows that there is no correlation between the formation of regular emulsions (of the silver nitrate solution and dichloromethane) and the formation of silver colloidal macroemulsions.
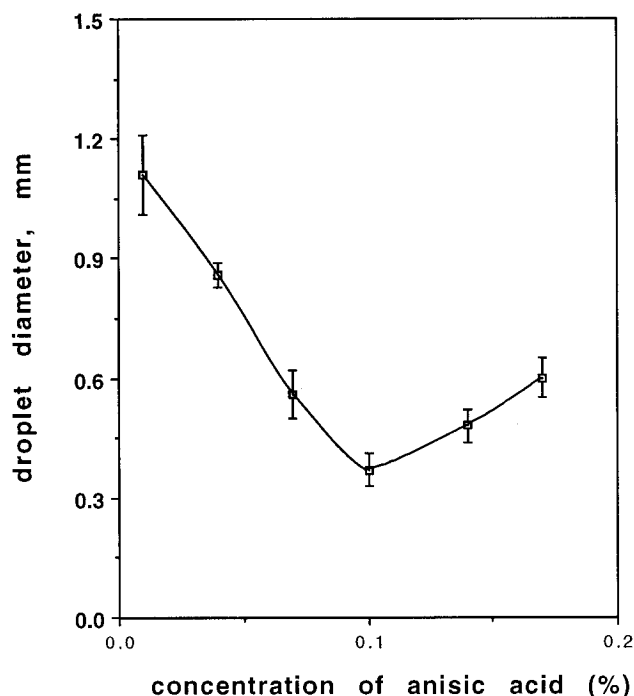
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Figure 3. Dependence of the emulsion droplet size on the concentration of anisic acid: 1 mL of 0.5% hydrazine was added into 10 mL of 0.05 M ammoniacal silver nitrate, in the presence of 0.03% FC143. The solvent was 30 mL of 1-chlorobutane.

TABLE 2: Methoxybenzoic Acid Isomer Solubilities and Their Effects on MELLF Macroemulsion Droplet Size

	anisic acid, 0.1% 4-methoxy	0.1% 2-methoxy	0.1% 2-methoxy	0.1% 3-methoxy
droplet size, μm	370 ± 40	1040 ± 100	650 ± 60	640 ± 60
solubility in 1-chlorobutane (pS)[a]	2.1	1.03		1.21
solubility in water (pS)[23]	2.74	1.54		2.40

[a] pS is −log(solubility of silver salt in M).

(B) Effects of Additives. In MELLF macroemulsions, silver particles are stabilized by the adsorption shell of organic additives (such as anisic acid) and surfactants. We find that a suitable concentration of anisic acid for a stable silver SPSE is between ~0.01% and 0.15% (Figure 3).

The upper limit could be partially related to the limited solubility of the anisic−silver salt (0.18%, as determined by UV spectroscopy). However, at a concentration of 0.17% anisic acid, the 1-chlorobutane phase showed a characteristic silver colloid absorption at 438 nm.[19] So one can attribute the size increase of the emulsion droplets at high concentrations of anisic acid also to the transfer of part of the silver particles to the bulk of the organic phase.

To explore the molecular effects we used 2- and 3-methoxy-benzoic acids. We found that 3-methoxybenzoic acid produced a ME-MELLF with droplets somewhat larger than those of the para isomer (Table 2). 2-Methoxybenzoic acid produced even larger droplets, and the system required about a day to settle as a ME-MELLF. In parallel, the dark and opaque organic suspension gradually became lighter. With anisic acid, this process usually took only a few minutes, indicating transfer of the colloid to the interface. A point to note is that when we used a 10-fold higher concentration of 2-methoxybenzoic acid, the droplet size decreased to 0.65 ± 0.06 mm.

In a separate set of experiments, we examined mixtures of anisic acid and 2-methoxybenzoic acid. We first prepared the

TABLE 3: Droplet Sizes in Macroemulsions Produced with Mixtures of *o*- and *p*-Methoxybenzoic Acid (Droplet Size in mm)

present during the reduction	added after ME-MELLF formation	
	ortho	para
ortho	1.65 ± 0.1	2.20 ± 0.1
para	0.71 ± 0.06	0.52 ± 0.05

TABLE 4: Solvent Dependence of ME-MELLF Droplet-Diameters

solvents	time of appearance of colloid color, min	droplet diameter, μm
	group A	
1-chloropropane	>30	
1-chlorobutane	3.5−4	370 ± 40
2-chlorobutane	2.5−3	410 ± 40
1-chloropentane		250 ± 30
1-chlorohexane		320 ± 40
1-chloroheptane		380 ± 40
1-chlorooctane		390 ± 40
	group B	
1-bromopropane	~4.5	350 ± 70
1-bromobutane	~3	330 ± 40
1-bromopentane		450 ± 80[a]
1-bromohexane		430 ± 40[a]
1-bromooctane		no ME-MELLF
	group C	
benzene		470 ± 110
chlorobenzene	~5	260 ± 40
heptane	1−1.5	
dichloromethane	~10	320 ± 30

[a] Regular emulsions, but not ME-MELLFs, see the text.

emulsion using 5 mL of the ammoniacal silver "soup" with either the ortho or the para isomer at the standard concentration of 0.1%. The silver ions were in excess of the reductant. Once the ME-MELLF was formed, we further added 10 mL of an aqueous solution soup containing either isomer. The droplet sizes are summarized in Table 3. Note the major influence of the additive in the reduction stage, when the elementary colloidal particles are formed. In the presence of anisic acid, the droplets are much smaller then when 2-methoxybenzoic acid is present. Note also that, in general, the droplets are larger when mixtures are used, regardless of the order of introduction, as compared to the case of a single material.

(C) Effects of the Organic Continuous Phase. The nature of the organic solvent has a very strong effect on the MELLF macroemulsions (Table 4). Table 4 also gives for selected solvents the characteristic times for the appearance of a strong colloidal coloration. In a series of singly chlorinated alkyl solvents (group A), the droplet size is at a minimum for 1-chloropentane.

The following experiments were carried out in order to probe the role of the organic phase in controlling the degree of flocculation of the colloid. An aqueous colloidal silver suspension was prepared as described in the Experimental Section. In each experiment, 10 mL of the hydrosol was mixed with 10 mL of the solvent, from groups A and B in Table 4. The aqueous phase was separated after 10 min of agitation, and its absorbance was measured. The results are summarized in Figure 4. All the spectroscopial variables exhibit sharp extrema at chloropentane, except for the peak area, which has a broad maximum. Figure 5 shows a monotonous decreasing dependence of the droplet size on the height/width ratio of the adsorption peaks, with the exception of 2-chlorobutane. Of the bromine-substituted solvents (group B), only 1-bromopropane and 1-bromobutane produced ME-MELLFs. Both fit well into
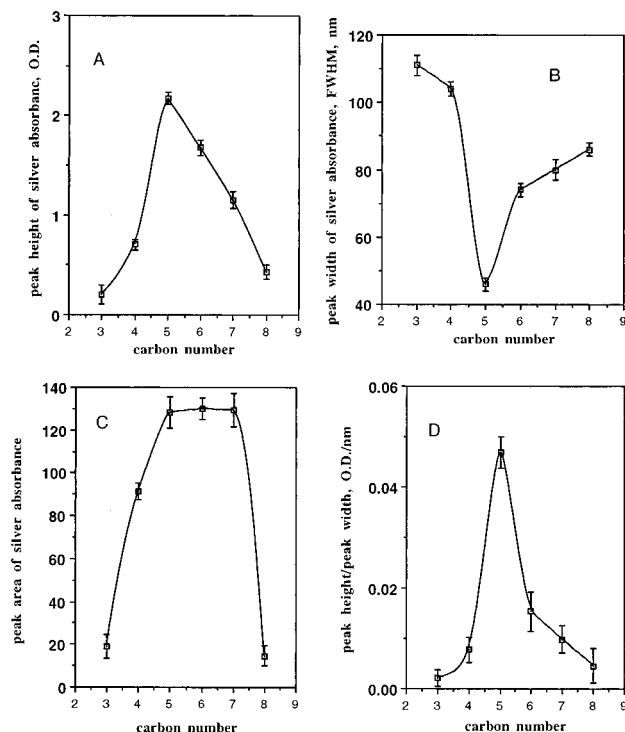
Figure 4. Colloid spectroscopical parameters of aqueous silver colloidal suspensions after 10 min of stirring with various chlorine-substituted solvents.
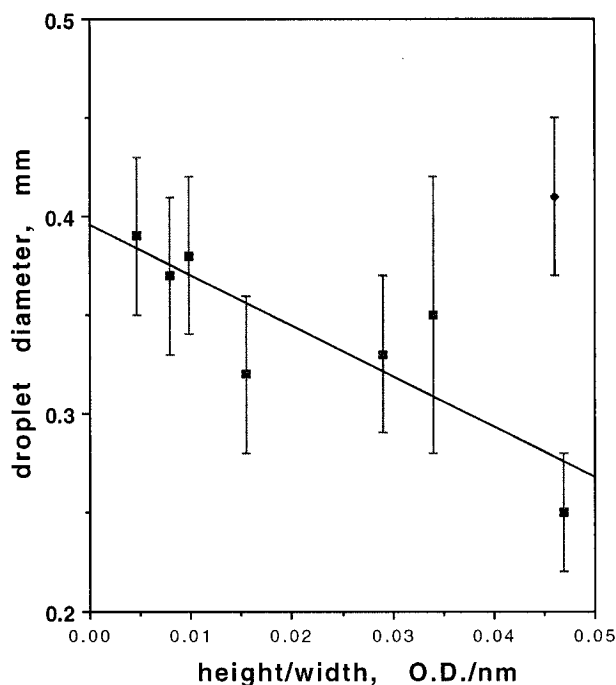

Figure 5. Dependence of the emulsion droplet size on the height/width ratio in the hydrosol spectrum, after stirring with various organic solvents.

Figure 5. In all these cases, no organosol was formed, as judged from the UV−visible absorbance.

The amount of the organic solvent plays a role in determining the final droplet size. As indicated in Figure 6, the size first decreases as the volume of the organic increases and then increases again. Here the volume of the organic phase was set at the beginning of each experiment. When the volume was changed to the final value only after the colloid itself had formed, i.e., 20 min after the beginning of the reaction, the behavior was different. There was hardly any change of
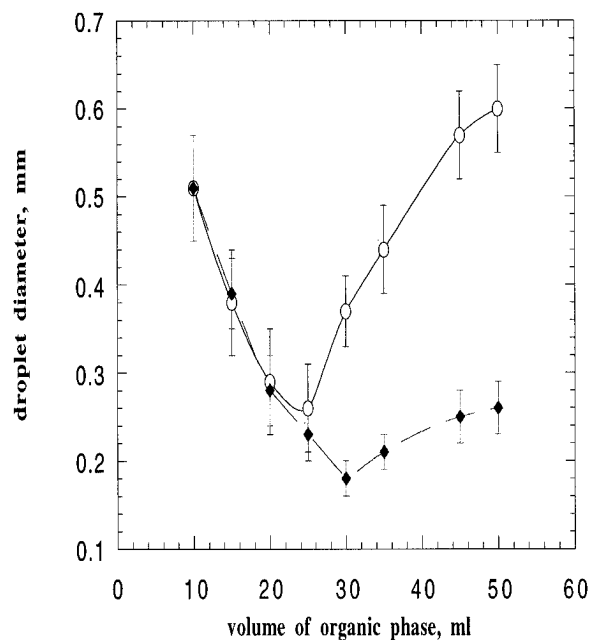

Figure 6. Dependence of the emulsion droplet size on the volume of organic solvent. Standard preparation. The organic solvent was added all at once before starting the preparation (○). Ten millliliters of the solvent was added in the beginning; additional volumes were added after 20 min of stirring (♦).

the droplet diameter as the volume was increased beyond ~25 mL.

We also looked at mixtures of organic solvents in order to probe densities near that of water, to alleviate gravitational effects. For instance, benzene and chlorobenzene, with densities of 0.8787 and 1.1058, respectively, are each a good solvent for MELLF macroemulsions. Their mixture was found to be an even better medium, with a droplet size as small as a few dozen micrometers.

The results for mixtures of 1-chlorobutane and 1-bromobutane are given in Table 5. As bromobutane was added and the mixture density approached that of the aqueous phase, the droplet size decreased, at first. The size rose again when the density of the mixture was still about 5% below that of the aqueous phase. The point when the average density of the emulsion droplets was equal to that of the solvent mixture is easily observed. It is indicated by the fact that the droplets just start to float and fill the whole volume of the organic phase. We will use this observation in the Discussion section to estimate the thickness of the MELLF film.

Other mixtures, as well, do not single out the density of water as a special case. In mixtures of dichloromethane and 1-chlorobutane, each separately produces macroemulsions, the droplet size hardly exhibited any noteworthy change as the density of the mixture was varied.

(D) Volume Ratio of the Two Liquid Phases. We produced MELLF macroemulsions using a wide range of volume ratios of the two liquid phases, between 18% and 73.3% water content. Note that 74.05% is the maximum volume fraction of a dispersed phase if hexagonal closest packing of undeformed uniform spheres is considered.[20] At a volume fraction of 74.3%, the system showed some instability. At a volume fraction of 75.3%, a more severe instability was observed. We have not observed any formation of macroemulsion MELLFs at 78.5% and beyond.

(E) Effects of the Amount of Reduced Silver. The amount of solid particles available as stabilizers in the water−oil interface is a major factor determining the size distribution of

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TABLE 5: ME-MELLF Droplet Sizes in Mixtures of 1-Chlorobutane and 1-Bromobutane[a]

vol of 1-chlorobutane, mL	30	28.5	27	25.5	24	22	20
vol of 1-bromobutane, mL	0	1.5	3	4.5	6	8	10
droplet diameter, μm	370 ± 40	250 ± 40	200 ± 20	100 ± 10	120 ± 10	190 ± 40	300 ± 40
density (calcd) g/cm^3		0.9058	0.9253	0.9447	0.9643	0.9902	1.016
density (exptl), g/cm^3	0.8864	0.9042	0.9226	0.9420	0.9611	0.9874	1.013

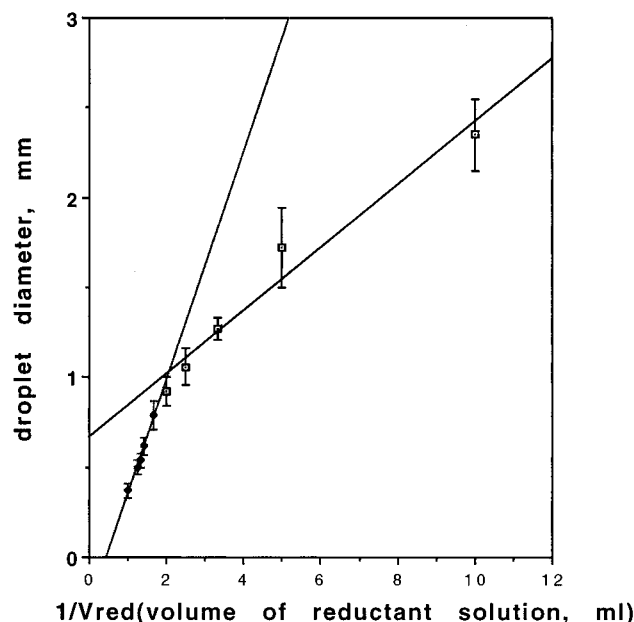[a] All sizes were measured for the standard preparation.

Figure 7. Dependence of the emulsion droplet size on the amount of reductant. Hydrazine was added into 10 mL of standard silver reaction solution (total aqueous phase volume was 11 mL). The organic phase was 30 mL of 1-chlorobutane.

Figure 8. Dependence of the macroemulsion droplet size on the total volume of the aqueous phase.

the emulsion droplets. We controlled the amount of reduced silver by varying the amount of reductant. One should be aware, however, that different initial concentrations mean different rates of particle nucleation as compared to their growth.[21] This indirectly affects the number and the size of the droplets, besides the direct effect.[17] The results are summarized in Figure 7. Here we show the dependence of the droplet size on the reciprocal of the volume of the reductant, at a fixed final total volume of the aqueous phase. Regular behavior is observed, with two linear regions.

(F) Aqueous Phase. In silver SPSE, the internal aqueous pH is about 10 and the silver ions are in their ammoniacal complex form. We find that the silver macroemulsion could be maintained even when the final internal aqueous pH was changed to as low as 2.3. As the pH was raised from 2.3 up to about 5, the emulsion droplets became distinctly smaller and more stable. At pH values above 5, the emulsion droplet size became independent of the internal aqueous pH.

We varied the volume of the aqueous phase from 10 to 20 mL, after the colloid production stage. The results are shown in Figure 8. The linear relationship is very clear.

Discussion

In order to focus the discussion, let us first reiterate the main features of the model of silver macroemulsion MELLFs.[14,15,25] According to this model, nanometer-size silver metal colloidal particles are stabilized by the adsorption of anionic molecules (such as anisic acid anion and surfactants). The adsorption layer makes the particles hydrophobic, causing them to flocculate. The micrometer-scale flocs congregate at the oil/water interface and form the emulsion. They are entrained at the interface, lowering the free energy,[10] being only partially wetted by both
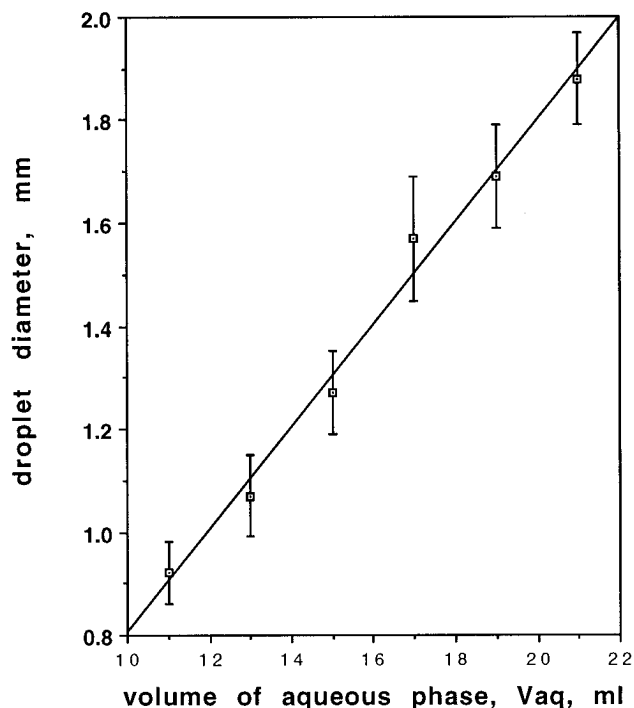
liquids (the three-phase contact angle is close to 90°). In the system investigated here, water disperses in the continuous organic phase. This means that the flocs are attracted to the organic solvent more than to water,[2,4,8,9,11,22–24] though not enough to be solubilized by it. At the interface, the boundaries between the separate flocs are dynamic and not well-defined. They form a continuous film, a dynamic network. This film is responsible for the inhibition of coalescence of the droplets and the stabilization of the emulsion.[9] Silver ME-MELLFs, as solid-particle-stabilized emulsions, SPSEs, concur with the three basic requirements of these systems[10] that we listed in the Introduction: particle size, incipient flocculation, and partial wettability.

In this report, we at times took the liberty of using the term "emulsion" liberally, even when the droplets are large and visible to the naked eye. We can produce systems with very small droplets, down to a few micrometers, but find it more convenient to study and visualize the larger sizes.

The formation of silver colloidal stabilized emulsions is a complex phenomenon. It can be divided into several stages: silver ion reduction into a colloid (nucleation and growth), particle flocculation, and film formation at the interface of the droplets. Later there is a relatively slower settling of the emulsion droplets. Finally, there is an even slower coalescence and breakdown. The first stage is generally absent from previous treatments of SPSEs.

The goal of this report is to provide a systematic study of a few of the important factors which control the overall processes and determine the size distribution and the stability of the system. It turns out that monitoring the size distribution is not only convenient but also provides an intimate picture of the underlying microscopic structures and molecular processes.

Surfactants. The stabilizers in silver MELLF macroemulsions are flocs of "dressed" silver particles. Surfactants and some organic additives are necessary for stabilizing the colloid itself, determining its surface properties (wetting and three-phase contact angle), associating the particles into weakly held flocs, driving them to the interface, and stabilizing the films there. Surfactant molecules and additives, which tend to associate with silver ions and silver surfaces, are the most efficient agents for the surface modification. Thus, many anionic (carboxylate, sulfate) or nonionic surfactants produce silver ME-MELLFs, while cationic surfactants, such as FC135 and FSC, fail to do so.

In general, the properties of the surfactant as given by its HLB, hydrophilic−lipophilic balance, determine the production and type of emulsion.[26,27] For instance, ammonium perfluorooctanoate (or the commercial FC143) has a HLB of ∼21. Such a HLB value is too high to promote the formation of O/W or W/O emulsions, though it is closer to values associated with O/W emulsions [8−18,27] and indeed, in the absence of the colloid, we found that FC143 does not form an emulsion in our experiments. Note that in the silver ME-MELLFs, a W/O emulsion forms. This is understandable, as the polar head of the surfactant is adsorbed on the silver and cannot direct itself toward the water subphase. Therefore, effectively, the contribution of the surfactant to the total HLB is determined by the perfluoro chain alone, with an HLB of $7(-0.87) + 7 = 0.9$. Here, -0.87 is the group HLB for CF_2.[27]

If we assume that the analysis and the classification of Davis and Rideal[27] holds also for SPSE, then to obtain a W/O system, one needs a HLB in the range 3.5−6. This means that the effect of the solid particle and its adsorbed layer, excluding that of the perfluoro chains, amounts to an effective HLB of ∼2.6−5.1. We denote this value by HLB_s. In the following analysis of various surfactants, we apply this HLB_s value instead of the contribution of the original headgroup.

FC98 has a sulfonate headgroup rather than the carboxylate of FC143 and a different counter cation. Both of these differences should not affect the value of the effective HLB when the surfactant is adsorbed on the silver colloids. Therefore, we would expect FC98 to stabilize ME-MELLFs, much as FC143 does. This is indeed the case. The droplet diameter is 0.40 ± 0.04 mm, very close to the value obtained with FC143.

FC129 has a major component (50%) similar to FC143. But it also has a considerable amount (14%) of a nonionic cosurfactant, 2-butoxyethanol, with an HLB of ∼7.3 and an effective HLB in a ME-MELLF of ∼8−10.5. This high value should have a destabilizing effect on the ME-MELLF. Assuming that the adsorption of these two components on the silver particles is in proportion to their concentrations, the average effective HLB is ∼4.5−7.0. Thus, it is conceivable that, from HLB considerations alone, FC129 will not produce ME-MELLFs, as indeed observed. Of course, the overlap between the range of the estimated HLBs for this system and the range of HLBs that forms W/O emulsions, 3−6, prevents an unequivocal prediction in this case.

Each additional CH_2 group in the carbon chain decreases the HLB by 0.48.[27] Thus, the hydrocarbon ammonium octanoate in a ME-MELLF should have an effective HLB value of ∼6.2−8.7, which might be just too high for a W/O emulsion. Therefore surfactants of short hydrocarbon chains per polar group (such as DIO60) usually do not produce ME-MELLFs. DIO60 has a calculated HLB of ∼15 (taking 6.8 for each ester group, 11 for the sulfonate, and -0.48 for each hydrocarbon group[27] and halving the total sum of these contributions to account for the double chain in the molecule). It forms a W/O

emulsion with the aqueous silver nitrate solution and 1-chlorobutane, as is expected. It does not form a silver ME-MELLF. The effective HLB of this molecule in a ME-MELLF is estimated to be in the range 10.8−12. This is just too high.

By using the HLB argument and the concept of HLB_s, we predict that myristic acid should have an HLB about equal to that of perfluorooctanoate. Therefore, it should produce stable ME-MELLFs, as we find. The droplet size was 0.88 ± 0.09 mm (at a nominal concentration of 0.002%). AP85W is quite similar to myristic acid, but its effective HLB is 2.0 units lower, estimated in the range 1.4−3.9. As expected, it is on the verge of producing a ME-MELLF, forming a single large aqueous globule enveloped by the MELLF.

Extending similar considerations to the nonionic surfactant FCN, its effective HLB in a ME-MELLF is in the range 2.1−6.3. Accordingly, a ME-MELLF should form, as it indeed does (Table 1). Similarly for the perfluoro nonionic FC170. It forms ME-MELLF droplets with a diameter of 0.50 ± 0.03 mm.

We are well aware of the limited applicability of the HLB scale in general, especially when ionic surfactants are involved and, more importantly, when it has to do with a complex system of a solid particle and adsorbed surfactants. Also, we are dealing here with relatively coarse emulsions, at times so coarse that they can hardly be called emulsions. Therefore one should consider the effective HLB analysis given above with caution. It is rather surprising that it works as well as it does.

Referring to Figure 2, we do a few simple calculations for a typical case (0.03%) to understand the quantitative implications of adsorption. One milliliter of 0.5% hydrazine sulfate added into 10 mL of 0.05 M silver nitrate forms $6.7 \times 10^{17}-5 \times 10^{16}$ silver particles of radius 1−2 nm,[14] with a total surface area of $4.6 \times 10^4-2.3 \times 10^4$ cm². By assuming that all the surfactant (4.2×10^{18} molecules) adsorbs on the particles, we find an area per surfactant molecule of 1.1−0.6 nm². Note that the surfactant molecular area in the liquid/air interface was found to be 0.24−0.51 nm².[28] Thus, this estimate might still allow for some of the area to be occupied by other additives, such as anisic anions, but a small increase in the concentration of the surfactant may nominally just fill the whole area and exclude other adsorbates. In addition, when the surfactant concentration becomes too high, it may aggregate at the surface, most probably modifying the surface properties of the silver particle and the contact angle. This will necessarily change the state of flocculation and the wetting that are so essential for the formation and stability of ME-MELLFs. The amount of surfactant determines the total surface area of the metal colloidal particles which it is capable of covering to produce an effective protective layer. Therefore, for a given initial amount of silver, the surfactant concentration should affect the size of the silver particles and of the flocs. This, in turn, is reflected in the emulsion droplet size (Figure 2).[17] These arguments and findings are in agreement with the discussion of the SPSEs of petroleum products.[29] Van der Waarden also discussed the concentration influence of interfacial active compounds on the droplet stability in W/O emulsions and claimed that it was closely related to the deflocculation ability of surface active materials.[23]

The point of our rough calculation was to show that beyond the optimal concentrations we used, one should indeed expect crowding of the surfactant at the surface, and therefore, significant changes in the nature of the suspension are expected. Thus, the value of the optimal concentration observed experimentally (Figure 2) makes sense in terms of the available area for adsorption on the silver particles.

Additives. The additives have a major influence on the production of the elementary silver colloidal particles, mainly

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through their influence on the nucleation stage.[17,18,30] Adsorption of the additives also helps in building up a protection layer for the silver particles against further aggregation, and they have a role in determining the hydrophilic/hydrophobic nature of the surface of the colloidal particles. This is one of the most significant factors controlling the macroemulsion. We believe that the last two functions are more affected by the surfactant than by the additive. However, the mere fact that planar MELLFs can form in the absence of a surfactant shows also that the additive participates in all the functions we mentioned above.

With regard to the anisic acid anions, at the standard concentration of 0.1%, if all of it is adsorbed on the silver cores, there is a surface area per molecule of 0.12−0.06 nm^2, for 1−2-nm particles. A lower concentration might not suffice for an efficient stabilization of the colloid, especially if only part of the molecules adsorb. This agrees with the finding that at a concentration below 0.01%, anisic acid does not produce ME-MELLFs or, for that matter, MELLFs in general. We have already shown that the upper limit of the concentration of anisic acid at which the ME-MELLF is still stable is related to a fractionation of the colloid between the interface of the two liquids and the bulk of the organic phase. At the higher concentrations, the exterior of the silver particles becomes increasingly hydrophobic due to the adsorption, and the particles lose the preference to the interface. The direct evidence for this is the appearance of a colloidal suspension in the organic phase and the destabilization of the macroemulsion, when a high concentration of anisic acid was utilized.

Compared to the surfactant, anisic acid is usually present in a much larger amount, about 10-fold molar wise in the standard preparation. Therefore, the situation is that the silver particle surface is covered also by adsorbed anisate, rather than being stabilized only by adsorbed surfactant molecules. We expect adsorption to be roughly in proportion to the concentration ratio in the solution. Raman spectroscopy and IR-ATR[13,14,16] reveal adsorbed anisic acid in the presence of the surfactant.

Unlike the case of the methoxy group in the para-position, the adsorption of 2-methoxybenzoic acid onto a silver surface must involve some steric hindrance. This should directly affect the adsorption and the formation of the surface layer. The particles become intrinsically less stable, which changes the flocculation and the affinity to the oil−water interface. In addition, a change in the additive is expected to affect the colloid nucleation. A weaker tendency of the 2-methoxybenzoate to associate with silver will result in a slower nucleation, as compared to the case of anisic acid itself. Thus, fewer particles will be produced and the emulsion will destabilize, with larger droplets being formed. This is borne out by the experiment (Table 2). We have previously reported on the inverse effect of alizarin yellow.[17] The perturbation by the methoxy group of 3-methoxybenzoic acid is expected to be smaller than for the ortho isomer. Therefore, the activity of *m*-methoxybenzoic acid should be intermediate between the two other isomers, as borne out by the experimental findings (Table 2).

Experiments with mixtures of 2- and 4-methoxybenzoic acids are summarized in Table 3. The droplets are larger than usual (for anisic acid), as we used a larger volume of water. We began with the standard amount of one of the isomers and added another 50% only after the nucleation and most of the growth had run their course. This is our usual method of separating the effects of nucleation and of flocculation.[17,18] It is clear from Table 3 that the additive has an important role in the nucleation. The para isomer, when present during this stage, gives considerably smaller droplets than when the ortho isomer is used. This

indicates a faster nucleation for 4-methoxybenzoic acid than for 2-methoxy. With the mixtures, the droplet sizes are larger than with one material only. It seems that the two isomers mutually perturb their adsorption on the silver particles, and in the mixed systems, flocculation is more pronounced.

The differences in behavior of 2-, 3-, and 4-methoxybezoic acids cannot be attributed to their pKa's, 3.9, 4.1, and 4.5, respectively,[31] because the internal aqueous phase is very basic (pH 10−11).[17] In a study of emulsion stability, Cockbain and McRoberts investigated the rate of coalescence of oil and water drops at the oil−water interface in the presence of stabilizers.[24] They found that the main factor determining stability is the resistance to wetting of the adsorbed film by the phases. Solubility can serve as a rough estimate for the wettability, just as it indicates whether an oil-in-water or water-in-oil emulsion will be obtained.[24] By using UV−visible absorption spectroscopy, we determined the solubilities in 1-chlorobutane (Table 2). Note that for the three isomers, the solubility in water is lower than in the organic phase, which explains the formation of a water-in-oil emulsion.[2,4,8,9,11,22−24] We compare here the solubility of the acid rather than of the anion, in spite of the ambient pH, 10−11. We believe this is more relevant to the interaction of the molecules with their surroundings, when the carboxylate group is "busy" as an anchor to the silver surface.

Anisic acid, in either phase, is the least soluble of the three isomers. Thus, it is expected to have a higher preference to accumulate at the water/oil interface and form thicker and more rigid protecting layers. The ortho isomer is least effective in stabilizing ME-MELLFs, also due to its higher solubility in both the organic and aqueous phases, as expressed in the fact that it forms an organosol. With a 10-fold higher concentration, considerably smaller macroemulsion droplets were formed (Table 2). Simply, more additive is available to partition between the bulk liquids and the surface.

The meta isomer has intermediate solubilities between those of the two other isomers. This agrees with its intermediate effectiveness as an additive in ME-MELLFs.

Along the same line of thought, we predicted that by using an organic solvent that has a very low tendency to solubilize the colloid, all the silver should congregate at the surface and an emulsion with very small droplets will form. We used carbon tetrachloride, which we know not to have any affinity to the silver colloid. With planar MELLFs, all the silver is pushed into the interface, producing a granular film rather than a liquid-like behavior.[14] We obtained a ME-MELLF with droplet size of 0.15 ± 0.01 mm. This seems to verify the analysis.

Organic Solvents. The organic solvents may have three main effects: (1) They may be involved in the reduction of silver ions to a colloid. (2) They may affect the efficiency and extent of the flocculation of the silver particles. (3) Their densities, relative to that of the aqueous phase, will influence the size and stability of the emulsion droplets.

We did not find any clear-cut correlation between ME-MELLF macroemulsion droplet sizes and the solvent dielectric constant, dipole moment, viscosity, or surface tension. The influence of density will be discussed in a later section. We, therefore, have no detailed explanation for the maximum suitability of 1-chloropentane, as compared to the other solvents.

Direct evidence for solvent involvement in the reduction kinetics is the distinct time differences between the various organic solvents as to the appearance of the brown, silver colloidal signature (Table 4). The time differences did not correlate with the solvent viscosity, as might be expected for colloid growth and flocculation.[26] For instance, both heptane

and 1-chloropropane, which have similar viscosity and surface tension, do not produce ME-MELLFs (with the procedure used here). Nevertheless, with heptane, the system turned brown within ~1−1.5 min of adding the reductant, while with 1-chloropropane, after 30 min only a faint pink coloration appeared. Also, 1-chloropropane is less viscous than chlorobutane, bromopropane, or bromobutane. Yet, the process in chloropropane is more than 10-fold slower than in these other liquids.

Another experiment that demonstrates the role of the solvent during the formation of the colloid was as follows. We initialized the silver reduction reaction in the aqueous solution. The organic solvent was added only 10 min later, when most of the nucleation had already occurred. For 1-chlorobutane, we found droplet diameters of 0.53 ± 0.05 mm, as compared to 0.37 mm obtained when the solvent was present throughout the process. The same experiment with 2-chlorobutane gave huge droplets of a diameter of 3.1 ± 0.15 mm.

One possible important role of the organic solvent is its flocculating power. The size and the number of flocs, produced from a given amount of colloid, should be a major factor determining the dispersion of the emulsion. An important condition for SPSE is that of incipient flocculation,[6,11] determined in general by the oil phase and by the nature of the particle.[23] The spectroscopic experiments with the hydrosols (Figures 4 and 5) were aimed at looking at this issue. We have seen a monotonous decreasing dependence of the droplet size on the height/width ratio of the adsorption peaks. Figure 4 showed a clear dependence on the solvent of all the spectroscopical characteristics, with an extremum for the best solvent.

In the UV−visible absorption spectrum, the area of the single peak of the silver plasmon reflects the total amount of silver particles in the aqueous phase.[30] The decrease of the area, caused by silver precipitation following flocculation, is a measure of the flocculating ability of the organic solvent. Also, it is well-known that the absorbance band of silver colloids usually broadens asymmetrically to the red, due to aggregation. Thus, the ratio of the band height to its width (H/W) should provide a semiquantitative measure of the aggregation of the silver colloid, as affected by each solvent. Lower values of this ratio indicate that more particles are in an aggregated state.

To date, excluding mixtures or when certain dye additives were present,[17,18] 1-chloropentane produces the smallest MELLF macroemulsion droplets. As shown in Figure 4, this solvent also causes the least flocculation to silver colloids. The weaker the flocculating power of the organic solvent is (or the stronger deflocculating it is, up to a limit), the smaller the silver flocs become and the larger the interfacial area they can stabilize is. Consequently, the droplet size will decrease. In chloropentane, not only was the total peak area conserved after 10 min of mixing, but also the size distribution of the particles became narrower as indicated by the higher H/W value compared to that of the initial aqueous H/W. This solvent acted here as a breaker of particle agglomeration. In comparison, for 1-chlorohexane and 1-chloroheptane, though they retained the same band areas within the experimental error, the H/W ratios are significantly smaller. The trend of the H/W ratio fits fairly well with the measured size of the emulsion droplets, in the various organic liquids.

We have seen that the volume of the organic phase has an effect on the droplet size of the emulsion, especially when it is added before the production of the system (Figure 6). On the one hand, addition of the organic liquid causes deflocculation of the colloid, resulting in a decrease of the size of the droplets. The effect should be apparent regardless of the stage in which

the volume of the organic phase is fixed at its final value. This is what is observed in Figure 6 for the smaller volumes. On the other hand, the organic solvent affects the formation of the colloid itself, for instance, by desorption of the adsorbed anisic acid and surfactant. An increase of the volume of the solvent would irreversibly decrease the nucleation rate of the silver particles. This irreversibly results in larger droplets as seen in the comparison in Figure 6. For the large volumes, the effect on the formation of the colloid seems to prevail.

Water/Oil Volume Fraction. We found that macroemulsions can form stable systems up to about 74% water content, which is the limit for close-packed spheres. This mere fact reconfirms that, indeed, the droplets are spherical and of uniform size. What is really important is the following point. The destabilization of the macroemulsion occurs over a very narrow range of volume fractions, of about 1%. This indicates that as soon as the droplets deform, even slightly, they coalesce. We did not explicitly address stability and destabilization mechanisms in this paper. Obviously this matter merits a serious investigation.

Amount of Reduced Silver. We analyze the results of Figure 7 as follows. Denote the film thickness by d_f, the silver volume fraction within the film by ϕ, the diameter of the droplets by D, and the total volume of the aqueous phase and the volume of the 0.5% hydrazine solution, respectively, as V_{aq}, and V_{red}. Using mass balance considerations, the following equation holds:

$$D = fd_f\phi V_{aq}/V_{red} \tag{1}$$

f is a numerical parameter given by

$$f = 6\rho M_{red}/(n_{red}C_{red}M_{Ag}) \tag{2}$$

C_{red} is the concentration of the hydrazine sulfate (g/mL), M_{red} is its molecular mass, M_{Ag} is the atomic mass of silver, ρ is the density of silver metal (g/cm^3) and n_{red} represents the stoichiometry of the chemical reaction (it is 4 for hydrazine and silver ions). Under the conditions of the experiment,

$$f = 3.80 \times 10^3 \tag{3}$$

If d_f and ϕ are assumed to be constant and V_{aq} is kept constant, the plot of D against $1/V_{red}$ should yield a straight line. The slope gives the product $fd_f\phi V_{aq}$. Figure 7 exhibits two straight lines intersecting at a reductant volume of 0.6 mL. V_{aq} in the experiments was 11 mL. In a previous study of planar MELLFs, the silver volume fraction was found in the range 6−20%, determined independently by SHG[32] and UV−visible spectroscopy.[33] By using these values, we obtain from Figure 7 $d_f = 2.5−0.8$ μm and $d_f = 0.7−0.2$ μm for the two linear sections. These results agree with the thickness determined from Moire patterns of planar MELLFs, 3−4 μm.[34] It is expected that the films in the macroemulsions will be stretched and, therefore, thinner. These results also agree with our estimates, 4.5−1.5 and 1.0−0.3 μm, based on mixtures of solvents and a flotation condition, as will be seen later. They also agree with the results we obtained by changing the volume of the aqueous phase, 2.2−0.7 μm, as shown below. Levine and Sanford showed, by minimizing the free energy as a function of particle size, that the optimal particle-size (which translates in our case into the floc size) is in the range of 0.4−1.0 μm.[10]

The appearance of a break point in the dependence of D on the amount of the reductant implies a transformation to a thicker film for the small emulsion droplets. It stands to reason that if there are more colloidal particles the degree of flocculation will increase, rendering the film thicker.

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Aqueous Phase. Compared with the continuous phase, the silver macroemulsions show much less dependence on the nature of the internal phase. In ref 7, the authors discussed *n*-decane/water emulsions stabilized by surfactants and solid particles (calcium carbonate, barium sulfate, silica, alumina, bentonite, and graphite). They showed that only when the pH was higher than the corresponding pK_a, of the surfactant, i.e., when the surfactant was in its dissociated state, were the emulsions stable. In our system, this argument applies both to the surfactant and anisic acid.

Equation 1 predicts that there should be a linear relation between the size of the droplets and the volume of the aqueous phase, other conditions being equal. From the slope of Figure 8, and for $\phi = 6-20\%$, d_f is 2.2−0.7 μm. This result is in agreement with what we found earlier when the amount of reductant was varied.

Mixtures of Organic Liquids: Density Considerations. The issue of density is important, as it may be the driving force for coalescence and may influence the size of the droplets and the stability of the emulsion. Mixtures enable us to study density effects, at a relatively constant chemical environment. For single liquids, we did not find any clear correlation between density and droplet size. However, in a mixture, clear trends evolve. Apparently, the minimum of droplet size is achieved close to, but not quite at, the points of equal densities of the organic phase and the aqueous solution. When densities are equal, the driving force for coalescence is minimal. We believe this is the main reason for the dependence on the relative densities. However, the fact that the smallest droplets and the most stable emulsions form slightly below the equal density point (3−6% lower) indicates that other (chemical and physical) factors are also important.

A useful situation is when the densities of the liquid phases are so close that the droplets simply float, as for a mixture of 1-chlorobutane (0.6 M fraction) and DCM. Let r indicate the internal radius of the aqueous phase in a droplet. R is the measured apparent radius of the emulsion droplet, and ρ_f the average film density. Its thickness h is $R - r$. In order to float, a balance between gravity and buoyancy should prevail, as given by

$$(r/R)^3 \rho_a - 3(r/R)\rho_f = -3\rho_f + \rho_o \qquad (4)$$

or to first order,

$$h/R = {}^1\!/_3 \, (\rho_o - \rho_a)/(\rho_f - \rho_a) \qquad (5)$$

ρ_a and ρ_o are the densities of the aqueous phase and the organic phase, respectively. ρ_o was measured as 1.051 g/mL. R in this sample was measured as 0.175 mm. By using eq 5 we find that h is 1.5−4.5 μm for a reasonable range of film density ρ_f (1.6−3). A similar calculation for the 1-chlorobutane and 1-bromobutane mixture with a density of 1.013 g/mL and a droplet radius of 0.15 mm gives the thickness of the film in the range 1−0.3 μm. These results agree fairly well with the experimental finding for planar films.[32] They are also in agreement with our previous analysis of the dependence of emulsion droplet size on the amount of reduced silver, from which the film thickness was evaluated as 0.2−2.5 μm. Note that the emulsion droplets, composed of the same aqueous phase in different mixtures, float at different densities, giving a different film thickness, i.e., a different floc diameter.

Summary

In this report we investigated some of the major factors controlling macroemulsions stabilized by interfacial colloids, as a special case of SPSEs. The main quantity we measured was the droplet size. It turns out that this variable manifests, in a transparent manner, the colloidal molecular processes, as well as the assembly of the colloids into an interfacial film. The experimental findings were explained on the basis of a detailed model of the system: nanometer-size silver colloids flocculate into micrometer-size flocs that assemble at the oil/water interface. The colloid interfacial film stabilizes a water/oil emulsion. Colloid nucleation, flocculation, and film formation are the basic processes that control the system.

We found that surfactants predominately affect the wetting properties of the colloid particles and their flocs. We suggested an effective HLB scale that can be used to predict the formation of ME-MELLFs. Instead of using the usual value for the headgroup, one uses a contribution of the silver particle, HLB_s = 2.6−5.1. This modified scale seemed to work surprising well. The dependence on the concentration of the surfactant was understood on the basis of surface coverage.

The organic, acidic additives were shown to be important for the nucleation of the colloid and its surface properties (wetting). Their influence follows their solubility in water and in the organic phase. Lower solubilities are associated with a higher effectiveness in the formation of stable ME-MELLFs with small droplet sizes. The small preference for the organic phase compared to water explains the formation of W/O rather than O/W emulsions. The effect of the concentration correlated with the adsorption of the additives on the colloid particles. At high concentrations, the surface became too hydrophobic and the film collapsed into an organosol.

The organic solvent affected both the nucleation and growth of the colloid, as well as its flocculation into an interfacial film. A correlation was found with the solvent flocculating power. The density of the organic solvent relative to that of water was found to be an important parameter, affecting droplet size and stability. The emulsions were most stable close to a density ratio of unity, but at a 3−6% lower value. A quantitative analysis of droplet floating conditions yielded an estimate of the floc size. An independent quantitative analysis of the dependence of the droplet size on the volume of the internal aqueous phase, and on the amount of silver, gave comparable estimates of the floc size. It seems that a structural transition occurs in the interfacial colloid film at high silver contents.

The emulsion droplets seem to be uniform and spherical. They quickly lose their stability when deformed, at about 74% loading.

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