

Studies of the Double Surfactant Layer Stabilization of Water-Based Magnetic Fluids

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A comparison of the ability of C_6 – C_{18} carboxylic acids to stabilize aqueous magnetite fluids is made. Micelle formation prevented complete dispersion of magnetite by stearic and myristic acids, but was overcome by introducing the acid in several portions. Improvements in fluid preparation are reported, achieved by perchloric acid treatment of surfactant-stabilized magnetite produced in basic solution, followed by redispersion of the particles in dilute base. The quantity of surfactant in the primary layer has been determined for C_{10} – C_{18} acids, and the particle surface area occupied per molecule of surfactant found to range between ca. 21 and 38 Å². For decanoic and myristic acids the groups pack efficiently and form a "condensed" film over the surface of the particles. Ammonium and monomethylammonium salts of the same acids were used in attempts to form the secondary layers. Ammonium salts produced dispersion in all cases except Sarkosyl-“O,” whereas $MeNH_3^+$ salts of oleic and myristic acids were successful. Quantitative data on the relative amounts of surfactant in each layer are presented and discussed.

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INTRODUCTION

The principle of the double surfactant layer for stabilizing magnetic particles in aqueous media has been established by Shimoiizaka *et al.* (1), and dilution-stable magnetite fluids prepared. Magnetite particles, commonly precipitated from aqueous iron (II) and iron (III) solutions (2), are initially coated with a surfactant such as oleic acid. Such particles, having a hydrophobic surfactant sheath, may be extracted directly into organic carrier liquids such as kerosene, but not into water (3). Shimoiizaka *et al.* in their work (1) first separated oleic acid coated particles, then dispersed them in aqueous solutions of anionic and nonionic surfactants such as sodium dodecylbenzene sulphonate, poly(oxyethylene)nonylphenyl ethers, and di(2-ethylhexyl)adipate. The colloidal particles had double surfactant layers, first a monolayer of oleic acid, then an outer layer of the physically absorbed second surfactant. These dispersions were found to be

very stable even in magnetic fields up to 1 T. Stable water-based fluids have been produced also using proteins and carbohydrates as stabilizers (4).

Khalafalla and Reimers (3) reported the preparation of water-based fluids using dodecanoic acid as the surfactant. Following their method our attempts to reproduce these and related fluids often produced semistable dispersions which quickly settled out in an applied magnetic field. This inconsistency led us to study the factors affecting the stabilization and to develop modified methods of producing water-based fluids. Also the method of Shimoiizaka *et al.* (1) produced an oleate-coated magnetite "cake," which contained excess oleic acid. This excess of acid, surplus to primary layer coverage, further complicates controlled studies directed toward the second layer.

EXPERIMENTAL

Iron (II) and (III) chlorides, oleic, myristic, and octanoic acids, ammonia, aqueous

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methylamine, and perchloric acid were obtained from BDH Chemicals, stearic acid from Koch-Light, and lauric and decanoic acids from Aldrich. Sarkosyl-"O" was a gift from Ciba-Geigy. The iron (II) chloride was stored under nitrogen to avoid oxidation, while iron (III) chloride was kept dry with silica gel desiccant. All chemicals were used as supplied. Ammonium and monomethylammonium salts were prepared by adding the fatty acids in small portions to aqueous ammonia and aqueous methylamine respectively, warming gently to facilitate solution.

Iron analyses were obtained by atomic absorption using a Perkin-Elmer 5000 spectrometer. Samples were dissolved in concentrated nitric acid prior to dilution with water to produce solutions containing 3–5 ppm total iron in solution. Commercial iron (III) standard solutions were used for calibration purposes.

*Preparation A: Aqueous Dispersions
Prepared Using a One-Stage
Surfactant Treatment*

Magnetite (1.0 g) was precipitated from a mixture of iron (III) chloride hexahydrate (2.35 g) and iron (II) chloride tetrahydrate (0.86 g) dissolved in deaerated distilled water (40 ml) and kept under an atmosphere of nitrogen. Aqueous ammonia (0.4 ml, 33%) in excess was added rapidly to the mixture at 60°C stirred efficiently with a mechanical paddle. The fatty acid (1.0 g) was immediately added and the suspension heated to 90°C for 30 min. The suspension/dispersion was cooled to ambient temperature then perchloric acid (2 M, 30 ml) added. Immediately a black gum-like solid formed which settled over a magnet, leaving a clear supernatant liquid with a thick surface scum of excess surfactant. The liquid was decanted and the black residue was washed several times with distilled water. Redispersion of the magnetite in water (20 ml) was achieved at 80°C by adding several drops of concentrated ammonia.

Preparation of Myristic Acid Fluids

The procedure described above was followed and five separate fluids were prepared using myristic acid as the surfactant. The same overall quantity of surfactant (1 g) was introduced but in a different number of portions over a 30-min period at 90°C. The number of additions and the quantity added on each occasion are given in Table III.

*Preparation B: Aqueous Dispersions
Prepared Using a Two-Stage
Surfactant Treatment*

Fe₃O₄ (5 g) was precipitated from aqueous solution (200 ml) by scaling up the proportions of reactants given in preparation A. The neat surfactant (5 g, see Table IV for surfactants used) was added slowly to the ammoniacal suspension over a period of 30 min, and stirred at 90°C for a further 30 min. After cooling the mixture to ambient temperature, the suspended magnetite was flocculated by addition of acetone (200 ml). After separation of the magnetite using a magnet and decanting the mixed solvent, the solid was washed with warm ethanol and acetone. A small portion of the solid was dried *in vacuo* for subsequent iron analysis. Each preparation was undertaken in an identical way, the only difference being the surfactant used.

The five bulk samples of the Fe₃O₄, prepared using the five surfactants named in Table IV, were each divided into two equal parts and were suspended separately in water (50 ml). Ten suspensions were prepared in this way, two for each of the surfactants. Solutions of ammonium and monomethylammonium salts of the same five surfactants were also prepared separately in water (50 ml) using 5 g surfactant and ammonium/monomethylammonium hydroxide, respectively. The final pH value was 8.

Each solution in turn was added via a burette to the Fe₃O₄ suspension (50 ml) containing the same adsorbed surfactant, at 80°C and with vigorous stirring until the first signs

TABLE II
Critical Micelle Concentrations for Various
Straight-Chain Surfactants

Surfactant	Surfactant in fluid prep (mol/dm ⁻³)	Critical micelle concentration (mol/dm ⁻³) ^a
Stearic acid (C ₁₈)	3.5×10^{-2}	4.4×10^{-4}
Myristic acid (C ₁₄)	4.4×10^{-2}	4.8×10^{-3}
Dodecanoic acid (C ₁₂)	5×10^{-2}	2.58×10^{-2}
Decanoic acid (C ₁₀)	6×10^{-2}	7.1×10^{-2}
Octanoic acid (C ₈)	7×10^{-2}	0.36

^a E. K. Fisher, "Colloid Dispersions," p. 47. Wiley, New York, 1950.

amount of surfactant available for particle stabilization will have been reduced. This explains why complete dispersion was not achieved using stearic and myristic acids. Both oleic acid and Sarkosyl-"O" gave complete dispersions of 1-g samples, despite having C₁₈ alkyl chains. Micelle formation for these materials is hampered by the geometry of the hydrocarbon chains which have a double bond. Even concentrated solutions of Sarkosyl-"O" showed no signs of turbidity.

Attempts were made to prevent micelle formation by adding the surfactant in portions. Five separate fluid preparations were performed using myristic acid as the surfactant, the same overall quantity of surfactant being used, but in portions (Preparation A), the number of which differed for each preparation (see Table III). The greater the number of separate additions, the lower was the concentration of free surfactant present at any one time. This is reflected in the amount of Fe₃O₄ incorporated. With 10 separate additions of 0.1 g surfactant, almost all the magnetic material was dispersed.

The Double Surfactant Layer

The principle of the double surfactant layer has already been established (1), and oleate coated particles have been dispersed in water containing a second surfactant. It appears that

surfactant in excess of that required for primary layer coverage, while superfluous for dispersion in organic solvents, is essential for the stabilization of particles in aqueous media. This was illustrated using Sarkosyl-"O." When the secondary layer surfactant is removed from particles, they disperse in nonaqueous but not aqueous solvents.

The bilayer phenomenon enables the formation of aqueous dispersions, using low-molecular-mass, straight-chain fatty acids, e.g., octanoic acid (see Table I), to be explained, and the failure to form fluids in organic solvents to be understood. In aqueous media the particles are stabilized by a double sheath of surfactant providing steric repulsion far greater than that provided by single sheaths which may interpenetrate to some extent. Stabilization in aqueous systems is further enhanced by anionic groups at the periphery of the double sheath, which increase electrostatic repulsions between particles.

The significance of the acid treatment prior to redispersion (Preparation A) is also understood by this model. Quenching with perchloric acid converts excess surfactant into the un-ionized form, causing it to separate from aqueous solution with the coated magnetite. This ensures the formation of a bilayer surfactant sheath prior to redispersion. The fluid reforms when surface carboxylic groups are converted to their ionic form by addition of base.

Octanoic acid, decanoic acid, and Sarkosyl-"O" have greater solubility in aqueous am-

TABLE III
The Effect of Stagewise Myristic Acid Addition on the
Dispersion of Fe₃O₄

Expt	Number of additions	Quantity of addition (g)	Total reaction time	Weight %Fe ₃ O ₄
1	1	1	30 min	2.8
2	2	0.5	30 min	3.2
3	3	0.33	30 min	3.8
4	6	0.17	30 min	4.5
5	10	0.1	30 min	4.7

TABLE IV

The Quantity of Surfactant Material Required for the Stabilization of Magnetic Particles in Aqueous Media

Surfactant	%Fe ₃ O ₄	Primary layer			Secondary layer		
		Wt surfactant per g Fe ₃ O ₄ (g)	No. molecules on each particle $\times 10^2$	Surface area per molecule	NH ₄ ⁺ surfactant per g Fe ₃ O ₄ (g)	No. molecules on each particle $\times 10^2$	MeNH ₃ ⁺ surfactant per g Fe ₃ O ₄ (g)
Sarkosyl-"O"	81.3	0.23	4.1	37 Å ²	—	—	—
Oleic acid	84.8	0.18	4.0	38 Å ²	0.36	8.4	0.37
Myristic acid	80.6	0.24	6.6	23 Å ²	0.27	7.4	0.27
Decanoic acid	83.2	0.20	7.3	21 Å ²	0.31	11	—
Octanoic acid	88.5	0.13	5.7	27 Å ²	0.95	42	—

monia than the other acids studied, and consequently micelle formation occurs at higher concentrations. Sarkosyl-"O" differs from oleic acid in that it has an additional amide group which increases its overall polarity and hence water solubility. Hence, these surfactants have a greater tendency to remain in solution, rather than associate together in micelles, resulting in the natural formation of double surfactant layers.

Surfactant Coverage of Particles

A series of Fe₃O₄ suspensions was prepared under identical conditions (Preparation B), using one of a series of surfactants (see Table IV); then excess surfactant was removed by washing with a polar solvent prior to drying and analysis. Using a value of 70 Å for the mean diameter of the particles, the surface area occupied by each surfactant given in Table IV was calculated.

The numbers of surfactants attached to the particle surface vary between 4.0 and 7.3×10^2 per particle (Table IV), differences being apparent between acids with saturated and unsaturated hydrocarbon chains. Saturated chains pack much more efficiently than unsaturated chains, and occupy a much lower surface area. Interestingly, the surface area occupied by each myristate and decanoate group (23 and 21 Å², respectively) bears a close similarity to the areas occupied by straight-chain

fatty acids as monomolecular films on water (20–22 Å² molecule⁻¹ irrespective of the chain length) (7). In the films the packing of the molecules approaches that of the crystalline state, and for crystalline stearic acid this cross-sectional area is ca. 18.5 Å² at normal temperatures. The area of 20–22 Å² represents the limit to compression of the "condensed" film and occurs when the molecules become tightly packed together. Thus myristate and decanoate groups are tightly packed at the surface of the magnetite, and cover the surface efficiently. For octanoate groups (27 Å² molecule⁻¹) the film is more "expanded," and for Sarkosyl-"O" and oleate groups, having unsaturation in their hydrocarbon chains, an even more "expanded" coating is indicated. These two surfactants occupy >1.5 times the

TABLE V

Percentage of Total Surfactant in Each Surfactant Layer

Surfactant	% of whole ^a	
	Primary layer	Secondary layer
Oleic acid	33	67
Myristic acid	47	53
Decanoic acid	39	61
Octanoic acid	12	88

^a Assumes the concentration of free secondary layer surfactant in solution in equilibrium with secondary layer adsorbed surfactant is negligible. Estimated error limits $\pm 3\%$.

surface area occupied by decanoic and myristic acids.

A notable feature of the data in Table V is that the secondary layer contains the greater proportion of overall surfactant. This is predicted on the basis of the spherical surface area and on packing considerations. Anomalous behavior is observed with octanoic acid (see also Table IV), for which the greater affinity of the surfactant for water, and the correspondingly larger solvation energy, make it less favorable for adsorption to occur at the particle with accompanying loss of hydration. A feature of the calculations is the assumption that all surfactant added subsequently to the primary layer enters the secondary layer. This is undoubtedly not the case for octanoic acid which, when converted to the ammonium salt in basic solution, has a higher solubility in water.

The data in Table V indicate a decrease in the proportion of surfactant in the secondary layer in going from oleic to myristic (C_{14}) acid, but an increase in going to decanoic (C_{10}) acid. A balance occurs between the screening of the alkyl chains from the aqueous environment, and the need to maintain a sufficiently thick absorption layer of surfactant to sterically stabilize the particles. Salts of the lower molecular mass fatty acids are increasingly water soluble and are hence more likely to remain in solution. For octanoic acid, this will lead to an overestimate of the amount of surfactant in the secondary layer, and hence underestimate the proportion in the primary layer.

Insight into the process of formation of the double surfactant layer may be gleaned from the use of ammonium and monomethylammonium salts to disperse magnetite particles having a single surfactant layer. A basic difference between the salts relates to their behavior toward heating at temperatures $>80^{\circ}\text{C}$. Ammonium salts decompose to the free acid, whereas this does not occur for MeNH_3^+ salts. Complete dispersion was achieved using both salt forms of oleic and myristic acids, indicat-

ing that the hydrophobic bilayer interactions are favored, despite the surfactants being in their ionized form. Conversely, with salts of decanoic and octanoic acid prior conversion to the more hydrophobic parent acid appears to be a prerequisite for interaction with the primary layer. No fluid was obtained with the MeNH_3^+ salts.

For Sarkosyl-"O" bilayer interactions were unfavorable under all conditions used, and may be attributed to the additional amide function which is present in Sarkosyl-"O" but not in oleic acid. In contrast, if excess Sarkosyl-"O" is added to an ammoniacal suspension of Fe_3O_4 , an instant water-based fluid results. Thus we may deduce that, under these conditions, interaction between surfactant molecules occurs in the bulk solution prior to adsorption. Small clusters, micelle-size or smaller, may be adsorbed as discrete units. The magnetite from which all Sarkosyl-"O" surfactant has been removed, except that forming the primary surfactant layer, may on remixing with water absorb water by hydrogen bonding to the free amide groups. Thus, bonded water within the primary layer may restrict interaction of this layer with the hydrocarbon chains of the surfactant added at a later stage and weaken their interaction.

SUMMARY

Improvements in the stabilization of aqueous magnetite dispersions by fatty acids are reported, and differences between the effectiveness of the acids discussed. The secondary layer is applied at a subsequent stage to particles receiving a primary coverage of surfactant. Distribution of the acids between the two layers is given for C_{10} – C_{18} acids, and the particle surface-area occupied by each acid group in the primary layer calculated. Decanoic and myristic acids form "condensed" films on the surface of the particles, whereas oleic acid and Sarkosyl-"O" form "expanded"

films. Differences are recorded between the use of ammonium (NH_4^+) and methylammonium (CH_3NH_3^+) salts of the fatty acids for applying the secondary layer.

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