

TEMPLATING OF NANOPARTICULATE IRON OXIDES AND OXYHYDROXIDES IN NON-IONIC SURFACTANT MEDIA

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The primary aim of this work was to develop a novel, generic method for templating low dispersity, nanoparticulate seed crystals for subsequent growth into iron(III) oxide or oxyhydroxide pigments with increased brightness. However, due to the increase in band gap observed with decreasing particle size, it is anticipated that the so-produced nanoparticulate iron oxides will also have a high potential as mediators in photoelectrochemical redox reactions. Examination of the Pourbaix diagram for iron shows that iron(III) species are unstable to hydrolysis at the pH used (1-3), so the iron(III) aqua species needed for commercial pigment formation are usually generated *in situ* by aerobic oxidation of iron(II) sulphate, itself generated from scrap iron and sulphuric acid. Thus, constraining the growth of iron oxide particles at low pH within the aqueous region of the lamellar phase of a lyotropic surfactant system was examined.

Matijevicⁱ reported the formation of akaganéite, β -FeOOH, in the presence of ethylene glycol and intimated that the alcoholic head groups exert a concentration dependant influence on particle morphology. Furthermore, Ward suggested that the glycolitic nature of a non-ionic surfactant may be responsible for the observed constraint of iron oxide particle size to the sub-micrometer range.ⁱⁱ Ward, however, carried out reactions in an isotropic micellar region of the surfactant system thus we decided to use similar surfactants, but employ a true, ordered lamellar phase, where the smallest dimension of the iron oxide particles should be constrained to about 3-5 nm. Initially, the pure non-ionic surfactant C₁₂EO₅ (Nikko Chemical Company, Japan) was investigated, but due to its high cost a commercial substitute averaging \sim C₁₂EO₅, Neodol (1-5E) (Shell Chemicals), was examined more fully. The region of the phase diagram of Neodol (1-5E) encompassing the extensive lamellar range was characterised using ²H-nmr spectroscopy and polarising microscopy, the size of the interlamellar aqueous domain estimated from SAXS measurements (3.3-5.5nm) and the effects of pH, anions (Cl⁻, NO₃⁻, SO₄²⁻ and PO₄³⁻) and cations (Na⁺, Ca²⁺, Mg²⁺ and Cr³⁺) on the lamellar phase boundaries determined. Thus a safe region for templating (<65°C, 0.035 mole ratio Neodol:water and <55°C, 0.1 mole ratio Neodol:water) was defined.

The iron oxyhydroxides were characterised using XRD, TEM, DTA, PCS, FTIR and UV-VIS spectroscopy. The β -FeOOH, from FeCl₃/HCl, formed cigar-shaped acicular particles at pH 2 in free solution and at pH 1 in the lamellar phase. Reactions were much faster in the presence of the surfactant. The particle sizes from free solution ranged between 300 – 500

nm in length and 30 to 60 nm in width, whilst those grown in the Neodol (1-5E) / water systems ranged from 25 to 40 nm in length and 4 to 7 nm in width and showed narrower size distribution, using PCS. At pH 2 in the presence of surfactant, a mixture of β -FeOOH and rhombohedral Fe₂O₃ (hematite) was formed as the hydrolysis reaction was too fast. α -FeOOH (goethite) particles produced from Fe(NO₃)₃/HNO₃ in aqueous and Neodol (1-5E) surfactant media appeared as aggregates of rods. Those produced in aqueous solution were not uniform in shape with sizes ranging from 100 to 200 nm, whilst those formed from the ordered surfactant phase were elongated in shape with sizes from 50 to 100 nm. PCS also showed a smaller size distribution of the α -FeOOH particles from templated synthesis compared to aqueous solution.

The effect of the ethylene oxide species, the surfactant head group, on the hydrolysis of Fe^{III} ions and the consequent production of β -FeOOH particles was examined using, a series of, ethylene oxide containing molecules (glymes). The glymes induced faster precipitation and greater control of particle sizes for β -FeOOH particles; they also showed evidence of possible chelating effects influencing the hydrolysis mechanistic processes.

Initial studies on pigment growth showed that self-seeding competes with growth from templated seeds, increasing the dispersity of pigment particles.

ⁱ Matijević E., Cimas S., Formation of Uniform Colloidal Iron(III) Oxides in Ethylene Glycol-Water Solutions, *Colloid Polymer Sci.*, 1987, 265, 155-163.

ⁱⁱ O'Sullivan E., Ward J. I., Budd T., Obvious and Nonobvious Influences of Surfactants on Formation of Nanosized Particles, *Langmuir*, 1994, 10, 2985-2995.