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The temperature stability of single and mixed emulsions stabilized by nonionic surfactants

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Abstract

Reasonably monodisperse (vegetable) oil-in-water emulsions have been prepared with three different non-ionic surfactants, each of having the same hydrophobic tail group, but with poly(ethylene oxide) (PEO) head groups containing 18, 27 or 48 monomer units. A set of three emulsions, containing similar sized oil droplets (∼400 nm diameter), has been prepared using these three surfactants. In addition, an emulsion with 200 nm diameter droplets has been prepared using the smallest head group surfactant. The critical flocculation temperatures (CFT) of the dilute emulsions have been determined using standard turbidimetric techniques, whilst those of the more concentrated emulsions have been determined using a Turbiscan *MA2000* instrument. A systematic study of the effect of surfactant head-group size and concentration (beyond the CMC), droplet size and volume fraction, and added electrolyte ($MgSO_4$), 1,2-propandiol and urea concentrations on the CFT of the single emulsions has been carried out. In addition, the CFT values of binary mixtures of the emulsions have been determined, and the possible effects of oil exchange (Ostwald ripening) and surfactant exchange, between droplets, have been determined.

Keywords: Critical flocculation temperature; Nonionic surfactants; Weak flocculation; Depletion flocculation; Emulsions; Binary emulsions

1. Introduction

Oil-in-water (o/w) emulsions stabilised by nonionic surfactants are commonly used in the agrochemical, cosmetic, food, pharmaceutical and other industries, where maintenance of stability at elevated temperatures, for prolonged periods of time, is often a key issue [1]. Flocculation at a critical temperature on heating is often observed, particularly when the nonionic surfactant contains poly(ethylene oxide) (PEO) moieties. The primary objective of the research described in this paper was to investigate the critical flocculation temperature (CFT) behaviour of a set of reasonably monodisperse o/w emulsions, in which the droplets were sterically stabilized with nonionic surfactants.

The authors are only aware of one previous study, by March and Napper [2] in 1977, where the flocculation of o/w emulsions, stabilized with PEO-based, nonionic surfactants, has been systematically studied as a function of temperature. In that work, the following parameters were investigated: the dispersed phase type, the tail and head group sizes, and the tail group type. Upon heating, March and Napper found that a given emulsion flocculated at a temperature (i.e. the CFT) which was close to the corresponding theta (θ) temperature, under the relevant solution conditions, of the PEO head group of the nonionic surfactant. This condition prevailed provided the tail group was of sufficient size, and sufficiently soluble in the dispersed phase droplets, to effect "anchoring" of the PEO head groups at the o/w interface. March and Napper concluded that sterically stabilized oil droplets behaved, in this respect, in an equivalent manner to sterically stabilized poly(vinyl acetate) latex particles, carrying terminally attached PEO chains, which Napper [3] had studied previously. No dependence on PEO molecular weight was found in these earlier studies by the Napper group, but the PEO chain lengths used by them were, in general, much greater than in the present study. Since the 1970s a number of other studies have been reported concerning CFT values for particulate dispersions, where the constituent particles were stabilized with adsorbed nonionic surfactants. The CFT value was found to be dependent on the nonionic surfactant type and size [4], the particle size

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[5], the particle volume fraction [6], and (where present) the co-solvent type and concentration [7].

Cowell and Vincent [6] showed that the flocculation which occurred in particulate dispersions of the type described above, at temperatures just beyond the CFT value, is weak and reversible, and that the flocculated dispersion separates into two phases: a dilute, dispersed phase in co-existence with a concentrated, floc phase. They suggested a close analogy with a vapour to condensed (liquid or solid) phase change for simple molecular systems. The CFT of the dispersions studied depended strongly on the particle volume fraction (and hence the *osmotic* pressure of the dispersion), just as the temperature (on cooling, in this case), beyond which a molecular condensed phase forms, in equilibrium with the vapour, depends on the *total* pressure (or equivalently, the saturation vapour pressure of a vapour is temperature dependent).

In a recent paper [8], the current authors studied the CFT of aqueous dispersions of hydrophobised silica particles, in the presence of adsorbed non-ionic surfactants containing PEO chains of varying length. It was demonstrated that the weak flocculation and phase separation, observed above the CFT, was primarily associated with the van der Waals interactions between the particles (plus their adsorbed layer sheaths). This accounted adequately for the trends in CFT values with changes in particle size and concentration, and also the PEO chain length. The steric barrier merely acted in effect as a hard wall, with little or no interpenetration of the two adsorbed layer sheaths on two approaching particles. Thus, no direct correlation between the CFT of the dispersions and the θ-temperature of PEO was observed in this case.

In this paper we investigate whether similar considerations apply to emulsions containing droplets with adsorbed surfactants similar to those used in ref [8]. To this end, the CFT of well-defined emulsions has been examined as a function of the surfactant head-group size and concentration (beyond the critical micelle concentration (CMC)), the droplet size and volume fraction, and added electrolyte ($MgSO_4$), 1,2-propandiol and urea concentrations. In addition, the CFT values of binary mixtures of the emulsions have been determined, to investigate any possible effects of oil exchange (Ostwald ripening) or surfactant exchange between the droplets.

2. Experimental

2.1. Materials used

Water, with a resistivity of >18 MΩ cm^{-1}, was supplied from a *MilliQ* unit. The oil phase for all the emulsions was sunflower oil, supplied by Bayer Crop Science GmbH, and was used as received. At 20 °C this oil has a density of 916 kg m^{-3} and a refractive index of 1.475. Magnesium sulfate (Lancaster), urea (Merck, *pro-analysis*), and 1,2-propandiol (Riedel-de Haën, *extra pure*) were all used as received.

The three oligomeric, nonionic surfactants used in this work were: *Ts16*, *Ts29*, and *Ts54* (in the *Soprophor* series), kindly supplied by Rhodia; they each contained a tristyrylphenol tail group and (nominally) 16, 29, or 54 ethylene oxide (EO) units, respectively. NMR analysis showed that in fact each surfactant contained a mixture of bi and tristyrylphenol tail groups. Matrix assisted laser desorption/ionization mass spectrometry showed that *Ts16*, *Ts29*, and *Ts54* actually contained a number average of EO units of 18, 27, and 48, respectively. Gel permeation chromatography (GPC) measurements showed that *Ts16*, *Ts29*, and *Ts54* all had M_w/M_n values of 1.10 or less. The critical micelle concentration (CMC) was determined for each surfactant in water from surface tension–concentration plots, which were established using a *K100* Processor Tensiometer (Kruss).

2.2. Emulsion preparation

Aqueous surfactant solutions and vegetable oil were pre–emulsified for one minute using an *Ultraturrax T25* (Janke and Kunkel). The pre-emulsion was then passed four times through a *Microfluidizer M-110Y* with a *H-10-Z* 100 μm interaction chamber (Microfluidics) at a pressure of 105 MPa. After each pass the emulsion was cooled under running water until it reached room temperature. The prepared (stock) emulsions, having an oil phase volume fraction (ϕ) of 0.4, were stored at 4 °C. In all cases the actual emulsions used in experiments were prepared from these stock emulsions by a suitable dilution procedure and simple inversion in a glass vial. Binary droplet emulsions were mixed together by inversion from the stock emulsions in different proportions such that the total droplet volume fraction was constant. The mixed emulsions were allowed to equilibrate for 30 min, prior to any measurements being made.

2.3. Droplet characterization

The average hydrodynamic diameter of the emulsion droplets was measured, as a function of time, using photon correlation spectroscopy, and the droplet electrophoretic mobility was measured in 1×10^{-4} mol kg^{-1} KCl, and also as a function of $MgSO_4$ concentration. In both cases a Brookhaven *Zeta Plus* instrument was used.

2.4. CFT and CPT measurements

The CFT of the emulsions was determined using two different methods, depending on the droplet volume fraction, as outlined below.

For low droplet volume fractions, the turbidity (τ)/wavelength (λ) spectra of low volume fraction emulsions ($\phi = 9 \times 10^{-5}$), containing 0.05–0.5 mol kg^{-1} $MgSO_4$, were recorded as a function of temperature. The method of Long et al. [9] was then used to determine the CFT. At the CFT a sharp break is observed in a plot of n ($= d \log \tau / d \log \lambda$) versus temperature. The wavelength range used was 600 and 800 nm.

For high droplet volume fractions a Turbiscan *MA 2000* instrument was used. Six grams of emulsion were equilibrated in a sample cell, which was placed in a controlled temperature bath for 2 h. This instrument scans the intensity of the backscatted light (at 45° to the incident beam; wavelength 850 nm) from the emulsion, as a function of cell height. If no flocculation of the droplets was observed the temperature of the bath was