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Adsorption of Myrj 45 on copper phthalocyanine pigment nanoparticles and effect on their dispersion stability in aqueous solution

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ABSTRACT

The composition of a commercial nonionic surfactant, Myrj 45, was analyzed with mass spectrometry (MS). Six classes of components, which are polyglycols, monoesters (monostearates and monopalmitates), and diesters (distearates, dipalmitates, and mixed diesters which are the diesters with stearoyl residues at one end and palmitoyl residues at the other) were detected. Each class of components shows a wide distribution of homologues. The monoesters are the dominant components in Myrj 45. The adsorption isotherm of each class of components was obtained using HPLC with a MS detector. The adsorption densities increase with increasing concentrations of each class of components up to a plateau. The monoesters adsorb the most at the same total surfactant concentration. The diesters and polyglycols also adsorb, but to a minor extent. The overall adsorption densities of Myrj 45 by taking into account the contributions from these six classes of components, are much lower than those of Triton X-100 at the same total molar concentration. The effect of Myrj 45 on the dispersion stability of the CuPc particles in pure water was studied and compared to that of Triton X-100. Upon adsorption of Myrj 45, the CuPc particles become quite hydrophilic, dispersible, and colloidally stable. Freezing/thawing and heating/cooling cycles tests suggest that the dispersions of CuPc particles with adsorbed Myrj 45 are not as stable as those with adsorbed Triton X-100. Particle aggregation primarily occurred during the freezing/thawing process. The experimental Fuchs–Smoluchowski dispersion stability ratios W_{exp} of CuPc particles in surfactant solutions were determined from dynamic light scattering (DLS) data, for the Rayleigh–Debye–Gans (RDG) light scattering regime. The W_{exp}-values with Myrj 45 are found to be about one order of magnitude smaller than those with Triton X-100. The zeta potentials are substantial, in the range of −16 to −46 mV, while the resulting surface charge densities and the total particle charges are quite low. Hence, electrostatic interactions are unlikely to contribute to the dispersion stabilization mechanism, which appears to be primarily steric.

1. Introduction

Aqueous dispersions of crystalline non-spherical copper phthalocyanine (CuPc) pigment nanoparticles are commonly used in inkjet printing, and in paint and varnish industries, because of their favorable color strength, brightness of shade, fastness properties, and relatively low cost [1,2]. Since the particles are highly hydrophobic, it is important for many of these applications to induce hydrophilicity and dispersibility in aqueous solutions, leading to good dispersion stability. It is also desirable to retain some hydrophobicity for possible paper deinking and recycling applications via froth flotation.

Dispersibility and good dispersion stability of CuPc particles can be achieved by electrostatic, steric, or other mechanisms [3,4]. Electrostatic stabilization can be obtained via the chemical or physical attachment of charged groups. For example, when CuPc particles are stabilized by chemically attached sulfonate groups on the surface they can become quite stable in aqueous solutions [5]. Adsorption of ionic surfactants or polymers can also induce stabilization. Steric stabilization can be obtained, in principle, by physical adsorption of nonionic molecules such as nonionic surfactants or polymers. Compared to electrostatic stabilization, steric stabilization has several distinct advantages [6]. It is insensitive to pH or electrolytes concentrations, and it can be effective in both aqueous and non-aqueous dispersion media. In a recent article by the authors, the nonionic surfactant Triton X-100 was used to produce stable aqueous CuPc dispersions [7]. The adsorption density was measured and was found to correlate strongly with the Fuchs-Smoluchowski dispersion stability ratio, which was determined semi-quantitatively from dynamic light scattering measurements of the average time-dependent particle size. Other dispersants such as polyvinyl acetate and

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disodium-methylene-bis-naphthalenesulphonate have been used [8], whereby the optical density of the filtered CuPc dispersions containing the remaining smaller particles was used as an indirect measure of the colloidal stability.

The goal of this article is to understand how to balance dispersion stability and hydrophilicity with deinking potential, which requires some residual hydrophobicity to allow for flotation by using nonionic surfactants. Triton X-100, which has only one class of homologues components (n = 3–18 [7]), is a good candidate for fundamental studies, but may be too costly for potential practical applications. Myrj 45, which contains many classes of components with many homologues per class, is more practically relevant, but requires a more tedious and detailed characterization of its components. This article focuses on the effect of Myrj 45 on CuPc particle dispersibility and dispersion stability, and includes certain results with Triton X-100 for comparison. The following aspects are covered: (a) detailed characterization of Myrj 45 by mass spectroscopy; (b) a strategy for a detailed characterization of adsorption of the different classes of components by using a 6-pseudo-component model; and (c) characterization of CuPc particles with adsorbed surfactant via the particles' hydrophilicity (qualitatively) and the dispersion stability (semi-quantitatively). One key question this study answers is which components are mostly adsorbed and thus primarily responsible for the stability of the dispersion.

Another issue that is considered in some detail is the effect of thermal cycles on the dispersion stability of surfactant-layer-covered particles. It is often expected that at temperatures above the cloud point, nonionic surfactants may become much less soluble and less efficient dispersion stabilizers [9,10]. It is also believed that dispersions which are primarily stabilized by steric interactions remain generally stable after a freeze–thaw cycle [10]. By contrast, electrostatically stabilized dispersions become unstable after certain freeze–thaw cycles [11].

A third issue that is addressed is that many sterically stabilized particles also have a significant zeta potential. What then arises is the question of what extent do electrostatic interactions play a role in the overall stability of the dispersion. For water solutions at low ionic strength, it is shown here that even substantial values (10–50 mV) of zeta potential correspond to such low values of surface charge density σ, and overall particle charge z, that the electrostatic interactions may play a minor, if any, role.

2. Experimental

2.1. Materials

The CuPc particles, which have a chemical formula $C_{32}H_{16}CuN_8$, were obtained from BASF (NJ, USA) in the form of a dry solid powder. The particles are in the β-CuPc crystalline polymorphic form with polydisperse sizes and shapes. Their density ρ_p was previously reported to be 1.62 g/cm^3 [12]. The primary particle size was not provided by the manufacturer. In the dry state such hydrophobic particles were probably in an agglomerated form. After the particles were dispersed, dynamic light scattering measurements were used to determine the initial average hydrodynamic particle diameter d_h to be about 160 ± 3 nm in Triton X-100 solutions [7] and 200 ± 6 nm in Myrj 45 solutions (see Section 3.3.2). The BET specific surface area was found to be 51 ± 1 m^2/g, corresponding to an average diameter of an equivalent sphere of 73 nm. Hence, the DLS-based d_h may not correspond to the primary particle size but to aggregates which may not be completely broken into the "primary" particles by the sonication procedure used.

Myrj 45 was purchased from Sciencelab.com Inc. (TX, USA). It is thought to be produced by esterifying polydisperse-molecular-weight polyoxyethylene glycol with commercial stearic acid, which may also contain some palmitic acid as an impurity [13]. Since the reaction conditions are also favorable for diester formation, Myrj 45 is expected to be a mixture of polyoxyethylene monoesters, polyoxyethylene diesters, and remaining reactants, free polyoxyethylene glycols, stearic acid, and palmitic acid. It may also contain other impurities from the original reactant materials. Using an iodine solubilization method, Sulthana et al. reported that the cmc of Myrj 45 (assumed to be 100% monostearate for simplicity) at 35 °C was 0.286 mM (or 0.018 wt%). This estimate may be quite inaccurate because of the surfactant mixture complexity. The cloud point at which a significant drop in solubility is observed for a 0.1 wt% solution was found to be 67.7 °C [14]. The overall solubility at 25 °C is difficult to define and measure accurately, as there are components less soluble than others, and since several less soluble or insoluble components may be solubilized by other more soluble micelle-forming components. The concentration range used here for adsorption and dispersibility studies of 1 wt% CuPc dispersions is from 75 to 1508 μmol/L (or 0.005 wt%–0.1 wt%). For thermal cycles tests, two concentrations, 3619 and 4524 μmol/L (or 0.24 and 0.3 wt%) were used with 3 wt% CuPc dispersions. The average molecular weight is estimated in Section 3.2.

Triton X-100 is a mixture of 4-t-octylphenoxyethoxyethanols homologues with a chemical formula $(CH_3)_3$–C–CH_2–C–$(CH_3)_2$–C_6H_4–O–$(CH_2CH_2O)_n$H. The average number n of ethylene oxide (EO) groups is 9.5, and the average molecular weight is 625 da (g/mol). It was obtained from Sigma–Aldrich (MO, USA) and was used as received. The value of n was found by mass spectrometry (MS) to range from 3 to 18 [7]. The concentrations used for the adsorption and dispersibility studies with 1 wt% CuPc dispersions ranged from 160 to 3200 μmol/L (or 0.01 to 0.2 wt%). For thermal cycles tests for 3 wt% CuPc dispersions, two concentrations, 3840 and 4800 μmol/L (or 0.24 and 0.3 wt%), were used.

The HPLC-grade acetonitrile and ammonium acetate reagents for the HPLC–MS studies were purchased from Sigma–Aldrich (MO, USA). The water used was obtained from a Millipore four-stage cartridge system, which uses distilled water as input.

2.2. High resolution transmission electron microscopy (HRTEM) imaging and BET measurements

The purpose of HRTEM imaging is to determine particle dimensions and morphology. Images of CuPc particles stabilized with Myrj 45 were obtained with a JEOL 3100 TEM microscope (at the HP Labs, Palo Alto, CA). A LaB6 emission source was used with an accelerating voltage of 300 kV. A 10 μL drop of 200 ppm CuPc dispersion with 200 ppm Myrj 45 was deposited on a lacey carbon-laid copper grid. The particles were allowed to dry completely by evaporation at ambient conditions. A TEM image of CuPc particles stabilized with Triton X-100 has already been published [7]. The results for the particles with Myrj 45 are similar. The CuPc particles are single crystalline with flat edges. Their shapes are polyhedral, and look like elongated cylinders.

Nitrogen adsorption measurements for obtaining the BET specific surface areas of CuPc particles were performed at 77 K on a Micromeritics ASAP 2000 volumetric adsorption analyzer. Before the adsorption analysis, the CuPc powder was degassed overnight at 298 K under vacuum in the port of the adsorption analyzer. The BET specific area was calculated from adsorption data in the relative pressure range from $0.03p_0$ to $0.3p_0$, where p_0 is the saturated vapor pressure of nitrogen at 77 K.

2.3. HPLC–MS analytical chromatography method

The HPLC–MS apparatus consisted of an HP 1100 manual injector with a sample loop, an HP 1100 LC pump, and an LC–MSD