



Effect of Triton X-100 on the stability of aqueous dispersions of copper phthalocyanine pigment nanoparticles

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ABSTRACT

The effect of Triton X-100 on the colloidal dispersion stability of CuPc-U (unsulfonated and hydrophobic) and CuPc-S (surface sulfonated and hydrophilic) particles in aqueous solutions (water and NaNO₃) was investigated at 25 °C. Its adsorption density was determined from surfactant concentrations analyzed by an HPLC method with a UV detector. The experimental dispersion stability ratios of the particles were determined from dynamic light scattering (DLS) data, with the Rayleigh-Debye-Gans (RDG) light scattering theory.

The adsorption densities of Triton X-100 on both the CuPc-U and CuPc-S increase with increasing concentration of surfactant up to the critical micelle concentration (cmc), and then reach a plateau. The maximum adsorption density Γ_m is higher for the CuPc-U ($d_h = 160$ nm) than that for the CuPc-S ($d_h = 90$ nm). The hydrophobic chains are inferred to be adsorbed onto the surfaces, and the hydrophilic ethylene oxide chains are in a coil conformation. The W_{app} -values for the CuPc-U dispersions are affected mainly by the surfactant fractional surface coverage θ . Adding NaNO₃ has no significant effect on the dispersion stability. The stabilization mechanism for the CuPc-U is inferred to be primarily steric, as expected. The stability ratios for the CuPc-S in solutions with NaNO₃ are higher than those for CuPc-U, and decrease with increasing concentration of NaNO₃, indicating that the stabilization is affected by the screening of electrostatic repulsive forces. The zeta potential is not a good predictor of the electrostatic stabilization, pointing to the need for new and improved theories.

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1. Introduction

Aqueous dispersions of copper phthalocyanine (CuPc) pigment nanoparticles are commonly used in inkjet printing, and in paint and varnish industries, because of favorable color strength, brightness of shade, fastness properties, and relatively low cost [1,2]. For many of these applications, it is essential to have good dispersion stability for weeks and months. The question is how to achieve stabilization for weeks or months, as needed for their applications in ink-jet printers. In this article it is shown that the available ideas and theories may be inadequate to researchers seeking to achieve these goals. Further experimentation and theories are needed.

The dispersion stability of solid nonspherical hydrophobic CuPc nanoparticles is quite poor, unless the particles are stabilized by electrostatic, steric, or other mechanisms [3,4]. The advantage of electrostatic stabilization is that it can be achieved via the chemical attachment of charged groups. Stabilization with this mechanism has certain disadvantages, with the stability being sensitive to pH or electrolyte concentrations. Steric stabilization may be used

for obtaining stable dispersions in aqueous solutions at high electrolyte concentrations or in non-aqueous media. It is quite challenging to find combinations of surfactants and electrolytes which ensure substantial stability over long times (see below). Moreover, the available experimental methods and theoretical results have been developed for spherical shapes. Shape effects can be important.

The stability of CuPc particles stabilized by chemically attached sulfonate groups on the surface in water at various concentrations of NaNO₃ was reported recently [5]. The particles effective non-retarded Hamaker constant, which is a measure of the van der Waals attractive interactions between the particles, was determined from the London dispersion coefficient, which was computed with a time-dependent density functional theory method [6]. A semi-empirical correction to the standard formula for the Hamaker constant was developed. The estimated Hamaker constant allowed predictions of the classical Derjaguin–Landau–Verwey–Overbeek (DLVO) theory [7] for the Fuchs–Smoluchowski dispersion stability ratio (W) of non-spherical CuPc-S particles in water and in aqueous NaNO₃ solutions. Predictions were obtained with the particles shape assumed to be spherical or cubical. The W -values, or apparent W_{app} values for the spheres of the same hydrodynamic

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diameter as the actual particles were also determined from dynamic light scattering (DLS) data and the Rayleigh-Debye-Gans (RDG) scattering theory [5]. Large discrepancies were found between the two sets of W -values, indicating that either significant particle shape effects were important, or that there were additional short-range repulsive forces not predicted by the macroscopic DLVO theory. Electrostatic repulsive forces played a substantial role in the dispersion stability, as revealed qualitatively by the effect of the ionic strength, and since the particles were quite unstable (see Section 3.3) in the absence of the sulfonate groups.

CuPc particles without attached sulfonate groups can be stabilized by a steric mechanism, achieved by physical adsorption of nonionic surfactants. Using the commercial nonionic surfactant Triton X-100 to control dispersion stability, the evaluation of the adsorbed density and dispersion stability are the objects of this article. The adsorption density on hydrophobic CuPc particles was reported previously, where total organic carbon analysis was used for determining surfactant concentrations, and adsorption data were fitted to the Freundlich adsorption model [8]. No dispersion stability data were reported. Romero-Cano and coworkers investigated the adsorption and desorption of Triton X-100 on polystyrene latex particles with various surface functional groups, such as sulfate, carboxyl, or amidine, in anionic or cationic buffers using UV spectroscopy for analysis [9–11]. They evaluated the particle colloidal stability by measuring the turbidity as a function of time for different electrolyte concentrations [12,13]. Other dispersants, polyvinyl acetate and disodium-methylene-bis-naphthalenesulphonate were also used to stabilize hydrophobic CuPc particles in aqueous solutions. After the particles were separated by filtration, the optical density of the dispersions containing the remaining smaller particles was used as an indirect measure of the colloidal stability [14].

Although many studies of dispersion stability for colloidal particles have been reported, finding practical conditions for effective long-term stabilization remains a challenging task. Despite much work reported and much progress [5,12,14], no theories are available for quantitatively describing or predicting the precise surface chemical interactions of such particles with the solutes and their influence on colloidal stabilization. Moreover, the CuPc particles considered have flat surfaces, which make dispersion stability predictions more difficult than with spherical particles. The effect of premicellar and post-cmc (critical micelle concentration) concentrations of Triton X-100 on the dispersion stability of CuPc particles in water and in aqueous NaNO_3 solutions was determined. Two types of CuPc particles were examined: (a) CuPc-U particles, which are unsulfonated and initially hydrophobic; and (b) CuPc-S particles, which have chemically attached surface sulfonate groups. The adsorption and desorption amounts of Triton X-100 were determined using analysis of the supernatant aqueous solution with an HPLC method. From these results, the possible conformations of Triton X-100 molecules on the two types of CuPc surfaces are proposed. The relative stability ratios for various surfactant and salt concentrations, reported in Section 3.3, allowed inferences of possible stabilization mechanisms.

2. Experimental

2.1. Materials and some key properties

CuPc-U particles were obtained from BASF as dry solid powder. Its chemical formula is $\text{C}_{32}\text{H}_{16}\text{CuN}_8$. Particles were crystalline, in the β -CuPc polymorphic form, according to the manufacturer. The particle density ρ_p was found to be 1.62 g/cm^3 [15]. The primary particle size in the powder was not available, because hydrophobic particles without added stabilizer tend to agglomerate. The

initial average hydrodynamic particle diameter d_h in aqueous dispersions at high surfactant concentration after sonication was taken to be the primary particle size, with a value of $160 \pm 3 \text{ nm}$ (see Section 3.3). CuPc-S particles were obtained from Cabot Corp. (MA, USA) as a 10 wt.% stable dispersion in water, and were used as received. All CuPc particle dispersions were blue. According to the manufacturer specifications, these particles were crystalline, also in the β -CuPc polymorphic form. This was confirmed experimentally [5]. The experimentally determined density was 1.56 g/cm^3 . The initial average hydrodynamic diameter of the particles was $90 \pm 2 \text{ nm}$. A Thermo Evolution 600 UV-Visible spectrophotometer was used to obtain the visible spectrum of CuPc-S. The spectrum shows absorption peaks at 617 and 707 nm (see Supplementary Material). Throughout the UV region, the absorbances are high. Further information of particles size, shape, morphology, and specific surface area are given in Section 3.1.

Triton X-100, which is a mixture of 4-*t*-octylphenoxyethoxyethanols with an average molecular weight of 625 dalton (g/mol), was purchased from Sigma-Aldrich (MO, USA) and was used without further purification. Its chemical formula is $(\text{CH}_3)_3\text{C}-\text{CH}_2-\text{C}-(\text{CH}_3)_2-\text{C}_6\text{H}_4-\text{O}-(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$, with an average number n of ethylene oxide (EO) groups of 9.5. According to the supplier data and Ref. [16], the cmc at 25°C in water is $0.23 \pm 0.01 \text{ mM}$. Since one study showed evidence that NaNO_3 (up to 500 mM) did not change the cmc materially by more than 3% [17], the value of 0.23 mM was also used for the cmc in 50 and 100 mM NaNO_3 solutions at 25°C .

HPLC-grade acetonitrile, ammonium acetate, and sodium nitrate were purchased from Sigma-Aldrich (MO, USA). Distilled water was from a Millipore four-stage cartridge system.

2.2. X-ray photoelectron spectroscopy (XPS), high resolution transmission electron microscopy (HRTEM) imaging, and BET measurements

XPS spectra were acquired with a Kratos Axis Ultra electro spectrometer using a monochromatic Al $K\alpha$ source operated at 75 W, using a hybrid lens system with a magnetic lens, and a charge neutralizer. The CuPc-U particles were used as received. The CuPc-S particles were obtained by air-drying the 10% dispersion. Samples were deposited on a stainless steel sample holder. The binding energy scale was referenced to the C 1s peak of CuPc, set at 284.8 eV. Processing of the spectra was done with CasaXPS software. XPS was used to confirm the particle composition, identify any surface impurities, and confirm the presence of chemically attached sulfonate groups on the CuPc-S particles. For CuPc-U, the results indicated the expected structure with some oxygen containing impurities. For CuPc-S, the results indicated the expected structure with sulfonate groups at the surface.

HRTEM images of CuPc-S particles and CuPc-U particles stabilized with Triton X-100 were obtained with a JEOL 3100 TEM microscope. A LaB6 emission source was used with an accelerating voltage of 300 kV. A 10 μL drop of a 0.1 wt.% CuPc-S dispersion or a 200 ppm CuPc-U dispersion with 0.32 mM Triton X-100 was deposited on a lacey carbon-laid copper grid. The particles were allowed to dry.

Nitrogen adsorption measurements for obtaining the BET specific surface areas of CuPc-U and CuPc-S particles were performed at 77 K on a Micromeritics ASAP 2000 volumetric adsorption analyzer. CuPc-U powder was used as received. CuPc-S powder was obtained from air-drying a 10 wt.% aqueous dispersion. Before the adsorption analysis, each sample 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 p/p_0 from 0.03 to 0.3.

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