Computational and Experimental Study of Colloidal Stability of CuPc Aqueous Dispersions

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Abstract

Dispersions of copper phthalocyanine (CuPc) pigments are commonly used in digital printing. Their colloidal stability is essential for fulfilling desirable shelf life and achieving good printing performance. In order to understand the role of electrostatic and van der Waals forces in their stability, a combined computational and experimental study has been performed to investigate the stability of the CuPc aqueous dispersions.

The Hamaker constant was calculated with a novel combination of an ab initio and an empirical methodology (J. Chem. Theory Comput., ***2010****, 6 (2), pp 491–498) to address the van der Waals attractions between the pigment particles. The calculated Hamaker constant was then employed in the DLVO (Derjaguin-Landau-Verwey-Overbeek) equation for dispersion stability simulation. The predictions allow comparisons with experimental colloidal stability study of CuPc aqueous dispersions (Langmuir,* ***2010****, 26 (10), pp 6995–7006)). The effect of a nonionic surfactant on the dispersion stability of CuPc particles was taken into consideration. The experimental dispersion stability ratio (W) was determined from dynamic light scattering (DLS) data and based on the Rayleigh-Debye-Gans (RDG) scattering theory. The adsorption isotherms show that the adsorption density increases with increasing equilibrium concentration of surfactant up to the cmc, and then reaches a plateau. Desorption tests were conducted to determine the reversibility or irreversibility of adsorption. Preliminary results suggest that a portion of the surfactant adsorbs irreversibly. The comparisons reveal that electrostatic forces play a significant role in the dispersion stabilization.*

Introduction

The dispersion stability of pigment particles plays an important role in the printing quality of different inks. The degree of dispersion stability not only affects the optical properties, but also influences the performance and the maintenance of the print head. In order to maintain the desirable dispersion stability for a considerably long time (months), there must be some strong repulsive interactions among the particles. Such repulsive interactions must be adequate to counteract and exceed the attractive interactions. There are several "mechanisms,": (i) electrostatic, "double-layer," interactions (DLVO); (ii) steric interactions; (iii) "hydration forces;" and perhaps others. For the past 60 years the Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory has been used as a basis for explaining or interpreting, at least in part, the stability of colloidal dispersions of charged particles in water [1]. In the context of this theory, the van der Waals attractive "long-range" forces cause particles to agglomerate, and the electrostatic double layer generates long-range repulsive forces which tend to keep particles from agglomerating.

A goal of our work is to propose a new empirical equation to calculate the Hamaker constants of materials based on the time-dependent density functional theory (TDDFT). The second goal is to test the applicability of the DLVO theory combined with the Fuchs-Smoluchowski theory in predicting the stability of copper phthalocyanine (CuPc) pigment dispersions. Furthermore, the effect of Triton X-100 surfactants on the colloidal dispersion stability has been investigated.

Computational and Experimental Methods

Hamaker Constants Calculation

We have benchmarked a computational approach based on time-dependent density functional theory (TDDFT) for predictions of the London dispersion coefficients (C_{11}) [2]. The validated TDDFT scheme is then employed to calculate the dispersion coefficients for copper phthalocyanine (CuPc), and for mono-sulphonated CuPc (CuPc-SO$_3$H). The molecular structures of CuPc and CuPc-SO3H are shown in Figure 1.

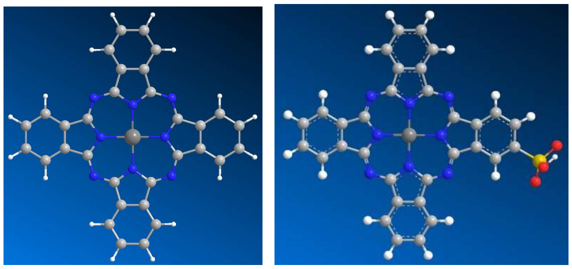

Figure 1*. Molecular structures of CuPc and CuPc-SO3H.*

A modified Hamaker equation has been used to calculate the non-retarded Hamaker constants from dispersion coefficient C_{12},

$$A_{12} = a\pi^2 C_{12}\rho_1\rho_2 \qquad (1)$$

where a=0.6815 is an empirical parameter developed in a previous paper[2] to account for the shortcomings of assumptions in the original Hamaker equation.

Materials

CuPc-U (unsulfonated and hydrophobic) particles were obtained from BASF as dry solid powder. CuPc-S (surface sulfonated and hydrophilic) particles were obtained from Cabot Corp. (MA, USA) as a 10 wt% stable dispersion in water, and were used as received. Water was first distilled and then passed through a Millipore four-stage cartridge system.

Triton X-100 was purchased from Sigma-Aldrich (MO, USA) and was used without further purification. HPLC-grade acetonitrile, ammonium acetate, and sodium nitrate were purchased from Sigma-Aldrich (MO, USA).

Measurements

The hydrodynamic diameter of CuPc particles was measured with a Brookhaven ZetaPALS Dynamic Light Scattering instrument, whereas XPS spectra were measured with a Kratos Axis Ultra electro spectrometer using a monochromatic Al Kα source operated at 75 W, using a hybrid lens system with a magnetic lens, and a charge neutralizer.

HRTEM images of CuPc-S particles and CuPc-U particles stabilized with Triton X-100 were obtained with a JEOL 3100 TEM microscope.

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.

The HPLC-MS consists of an HP 1100 manual injector with a 20 µl sample loop, an HP 1100 LC pump, and an LC-MSD HP 1100 quadrupole mass-selective detector equipped with atmospheric pressure electrospray ionization (ESI) interface. In the HPLC method, a UV detector was used for analysis. It consists of an HP 1100 autosampler with each injection volume set to 25 µl, an HP 1100 LC pump and an HP 1100 M diode array UV-visible detector.

The adsorbed densities at 25 ºC were determined by mixing ca. 0.1 g of CuPc-U or CuPc-S in 10 g of Triton X-100 aqueous solutions of various surfactant concentrations. The particles were dispersed using a Branson bath sonicator for 30 min. After adsorption, dispersions were centrifuged at 18K rpm for 30 min with a Beckman Coulter Microcentrifuge. The final steady state concentrations of Triton X-100 in the supernatants were analyzed with the HPLC-UV method for obtaining the overall amounts of surfactant on the particles surfaces.

For testing the adsorption reversibility or irreversibility, desorption experiments were done at 25 ºC by diluting CuPc dispersions with various amounts of DI water after the adsorption experiments had been completed. Dispersions with the final steady state or "equilibrium" concentration of Triton X-100 around the cmc were chosen for starting desorption experiments.

The stability of the dispersions was evaluated based on the time-dependent average hydrodynamic diameter d_h (t) as measured from the DLS data. See reference [3] for further details.

Results and Discussion

Hamaker Constants from TDDFT

Table 1 presents the benchmarking results of our new model (Eq 1) for the calculation of Hamaker constant.

As shown in Table 2, the new model gives much better accuracy than the original Hamaker Equation (a =1). The mean absolute percentage error of the new model is about 14 times smaller than the original Hamaker theory.

Table 1. Comparison of predicted A_{11} ($\times 10^{-20}$ J) values to the "best estimates" of Hough and White

Material	A_{11}	A_{11}	A_{11}
	best estimate [b]	a =1.0	a =0.6815
H_2O	3.70	5.38	3.66
Pentane	3.75	5.16	3.52
Decane	4.72	6.89	4.70
Hexadecane	5.23	7.67	5.23
Polystyrene	6.58	10.11	6.89
PMMA	7.11	11.32	7.71
MAPE [c]		48.08	3.48

[a] All dispersion coefficients are calculated with the SPZ functional and the HGH pseudopotentials using a grid spacing of 0.25 Å.

[b] Taken from Hough and White.[4]

[c] MAPE is the mean absolute percentage error for Hamaker constants.

The calculated Hamaker constants for CuPc are shown in Table 2.

Table 2. Calculated Values of A_{11} *and* A_{121} for CuPc using a = 0.6815 in Equation 1

particle	ρ_1(g/cm^3)	$A_{11}\times10^{-20}$(J) [a]	$A_{121}\times10^{-20}$(J)	Comment
α-CuPc	1.63	14.73	3.66	ideal density
β-CuPc	1.62	14.66	3.63	ideal density
β-CuPc	1.56	13.52	3.07	measured density

The calculated Hamaker constants for CuPc have been employed in our DLVO simulation.

TEM Images and Particle Shapes

The TEM images show discrete microcrystalline flat-edged particles, some of which probably aggregated during the sample preparation (Figure 2).

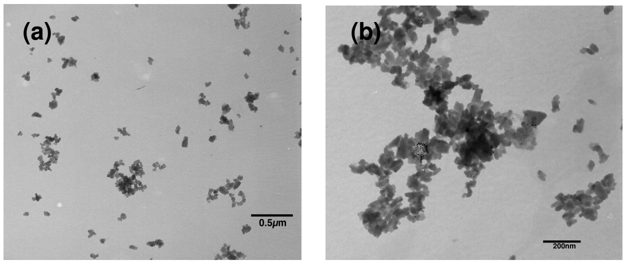

Figure 2. *TEM images of CuPc pigment particles dried from a 50 ppm dispersion in water, at magnification of (a) 28,500× and (b) 52,000×.*

Individual particles have globular and nonspherical morphology. Their shape resembles that of short right cylinders or parallelepipeds. For this reason, and for mathematical convenience, the particle shape was modeled below either as spheres or as parallel face-to-face cubes.

Dispersion Stability

In a previous paper [3], we have developed a method to estimate the stability ratio *W*. Table 3 presents comparisons of experimental *W*-Values with those predicted by the DLVO Theory.

Table 3. W-values calculated from the experiment and W-values predicted from the DLVO theory for two models.

c($NaNO_3$), mM	W_{exp}	DLVO Model for Spheres	DLVO Model for Cubes
0	1.4×10^{8}	5.2×10^{30}	3.1×10^{2}
1	$>3.2\times10^{6}$	1.4×10^{14}	1.9×10^{65}
10	$> 2.5\times10^{6}$	6.5×10^{5}	5.0×10^{106}
	$> 3.8\times10^{7}$	2.1×10^{2}	8.3×10^{61}
	7.9×10^{8}	7.8×10^{5}	1.5×10^{109}
100	$> 2.1\times10^{6}$	1^{a}	1^{a}
	2.6×10^{7}	1^{a}	1^{a}
500	1.0×10^{3}	1^{a}	1^{a}
	9.0×10^{3}	1^{a}	1^{a}

[a] When no positive potential maximum was predicted, fast coagulation limit (W=1) is assumed.

The initial stability ratios *W* were determined quantitatively from DLS data for the RDG scattering regime. As the $NaNO_3$ concentration increased from 1 to 500 mM, the W-values decreased from 3.2×10^{6} to 1.0×10^{3}. This indicates that the stability of CuPc dispersion depends on the electrolyte concentration and that electrostatic effects play an important role.

Two new models of the DLVO theory, for spheres and for parallel face-to-face cubes, at constant potential, have been reformulated in dimensionless form. The model for cubes, for the systems tested at 1 and 10 mM $NaNO_3$ concentrations, predicted higher stability than the model for spheres. At c =0 mM, the model for spheres overestimates the stability, while the model for cubes highly underestimates the stability. By contrast, at c=1 mM, both models overestimates the stability. At c=10 mM, the model for spheres underestimates the stability whereas the model for cubes overestimates the stability. This suggests some significant shape effects on the stability. At c=100 and 500 mM, both models underpredicted the stability substantially.

Shape and orientation effects and the effects of other short-range forces need to be investigated further, by molecular-scale theories or simulations. Especially at higher ionic strengths, some additional short-range force barrier may play a major role in the dispersion stability.

Effect of Triton X-100

The effect of a nonionic surfactant, Triton X-100, on the dispersion stability of the CuPc-U and CuPc-S particles in water and in $NaNO_3$ solutions was investigated at 25 ºC. The adsorption of Triton X-100 was determined with HPLC, and the adsorption isotherms are shown in Figure 3 [5].

The adsorption isotherms of Triton X-100 on the CuPc-U and CuPc-S indicate that the adsorption density increases with increasing concentration of surfactant and then reaches a plateau above the cmc. Desorption tests show that some surfactant molecules adsorb irreversibly, suggesting the presence of some strong and some weak adsorption sites on the CuPc particle surfaces. The maximum molar adsorption density is higher for the CuPc-U than that for the CuPc-S, implying that the surfactant does not adsorb on the sulfonate groups. The minimum areas per molecule for the CuPc-U and CuPc-S particles are estimated from BET specific surface areas to be about 0.65 nm^2 and 1.21 nm^2 respectively. The areas per molecule above the cmc indicate coil or “mushroom” conformations of the EO chains.

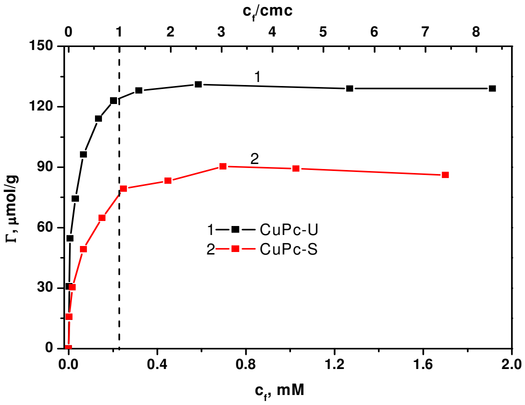

Figure 3. Adsorption isotherms of Triton X-100 on the CuPc-U and CuPc-S particles in water at 25 ºC. The lines are included to guide the eye.

CuPc-U particles are quite unstable and hydrophobic with no Triton X-100 added (Figure 4). At a surface coverage θ above 0.72, they become quite stable, apparently because of a steric mechanism. Adding $NaNO_3$ has no significant contribution to the dispersion stability.

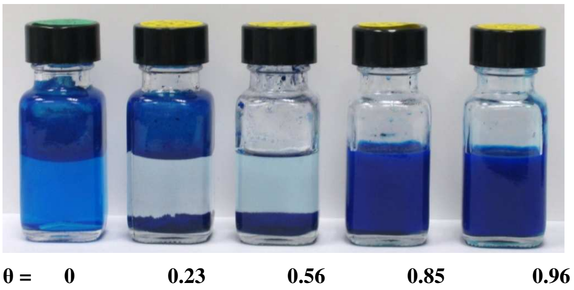

Figure 4. *Photographs of 1 wt% CuPc-U dispersions with various surfactant fractional surface coverage θ.*

Our results indicate that current theories and intuition may be inadequate to predict what conditions are needed for effective colloidal stabilization of CuPc particles in water. The problem becomes more challenging for nonspherical, flat-edged, and elongated particles, such as the ones studied here. The methods used here for determining surface adsorption densities and irreversibility may be used to screen other surfactants or dispersants.

The zeta potential of particles is affected by chemisorbed or attached ionic groups, but also by dissolved electrolyte, as is well known, but also by adsorbed surfactant [6]. The inferred change on the particles is affected also by preferential adsorption of negative ions, OH^- in water or NO_3^- in aqueous $NaNO_3$ as in this study. The zeta potential is found not to be a good predictor of the electrostatic stabilization. Still, experiments such as those discussed here need to be done to determine the relative stability ratios, the adsorbed surface densities of the surfactant, and its effect on colloidal stabilization because the interaction of the particle surface with the solutes and solvent are complex.

Conclusion

We have employed computational and experimental methods to investigate the stability of the CuPC pigment dispersion. A generic TDDFT method for the calculation of Hamaker constants have been developed. The calculated Hamaker constants have been employed in the DLVO equation to simulate the dispersion stability of CuPu aqueous suspension. Our study shows that electrostatic effects play a major role in the stability of CuPc-based dispersions. The calculated particle charge z per CuPc particle based on the zeta potential data and the area of the particles (assumed to be cubical) suggests that there is preferential adsorption of NO^{3-} ions on the uncharged CuPc surface, and the surface charge increases with increasing electrolyte concentration. Furthermore, two new models of the DLVO theory, for spheres and for parallel face-to-face cubes, were reformulated in dimensionless form, and the DLVO results have been compared to experiments. The comparison shows that, in water, the DLVO model for spheres overestimated the stability, while the model for cubes underestimated the stability.

The effect of Triton X-100 on the colloidal dispersion stability of CuPc-U and CuPc-S particles in aqueous solutions has been investigated at 25 ºC. 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 stability ratios for the CuPc-S in solutions with $NaNO_3$ are higher than those for CuPc-U, and decrease with increasing concentration of $NaNO_3$, indicating that the stabilization is affected by the screening of electrostatic repulsive forces. Our results show that the zeta potential is not a good indicator of the electrostatic stabilization, pointing to the need for new and improved theory.

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Author Biography

Yan Zhao received his BS in Materials Chemistry from Fudan University (1993) and his PhD in Physical Chemistry from University of Minnesota (2005). He has done three years postdoctoral research in Professor Truhlar's group. Since 2009, he has worked as a research scientist in HP Labs, and his research focused on the developments and applications of multiscale molecular modeling methods for printing materials.

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Dr. Eric Hanson is the Director of the Printing and Content Delivery Lab of Hewlett Packard Laboratories, in Palo Alto, California, where he has managed research investigating advanced digital printing since 1984. He is currently the Immediate Past President of IS&T, the Society for Imaging Science and Technology. He received a Ph.D. in physics in 1976 from the University of California at Berkeley and has been awarded 18 US patents.

Jiannan Dong received his B.S. in Biochemical Engineering from Zhejiang University in 2003, and his M.S. in Biochemical Engineering from Zhejiang University in 2006. Currently he is a Ph.D. candidate in Chemical Engineering at Purdue University. His research focuses on experimental investigation and simulation modeling of colloidal dispersion stability of pigment nanoparticles.

Professor Elias Franses received his B.S. in chemical engineering in Athens Greece in 1974, and his Ph. D. in chemical engineering in 1979 at the University of Minnesota. He has been at Purdue since 1979, with a one-year stint at NSF in 1990-1991 as a program manager. He specializes in molecular probing and modeling of Interfacial and Dispersion Stability Phenomena, and thermodynamic, dynamic, and spectroscopic properties. His current interests involve stability of water continuous and oil continuous dispersions.

Prof. Corti is currently Professor and Director of Undergraduate Studies in the School of Chemical Engineering at Purdue University. His research interests are in the areas of molecular thermodynamics, nucleation phenomenon, complex fluids and molecular simulation. He received a B.S. in Chemical Engineering from the University of Pennsylvania in 1991 and a Ph.D. in Chemical Engineering, from Princeton University in 1997. After completing a postdoctoral position within the Department of Chemistry and Biochemistry at UCLA, he joined the faculty of the School of Chemical Engineering at Purdue University.