

Title: In situ structural modification and drying of pigment particles

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Time Span: Two years

Number of Graduate Students: 2

Pigments are widely-used commercial additives to impart color to inks, plastics, coatings and cosmetics. Being insoluble in the dispersing medium, compatibilization of pigments is essential to form stable pigment dispersions. This is achieved through the use of surfactants. The pigment particles display a multi-level hierarchical structure composed of primary particles on the nanoscale, a size too small to effectively scatter light, that are clustered into aggregates of about 10 to 100 nm in size.[1] Our recent work demonstrated that the size and density of these aggregates depends partly on the primary particle size and the surface interaction between particles in the carrier medium moderated by the surfactant.[2] For organic pigments the primary particles are solid clusters of elemental single crystals whose size depends on the quality of the surfactant/solvent/pigment interface. For these colloidal systems, we mapped out the thermodynamics of reversible aggregation using a new theory proposed by Vogtt.[3] We discovered that the affinity of the surfactant for the pigment crystallite surface increased as its solubility decreased with temperature (LCST behavior) by demonstrating a change in primary particle and aggregate size with temperature using USAXS / SAXS / WAXS as shown in Figure 1. The pigment particles collapsed and precipitated at the phase separation temperature of the surfactant also shown in Figure 1 (supporting document).

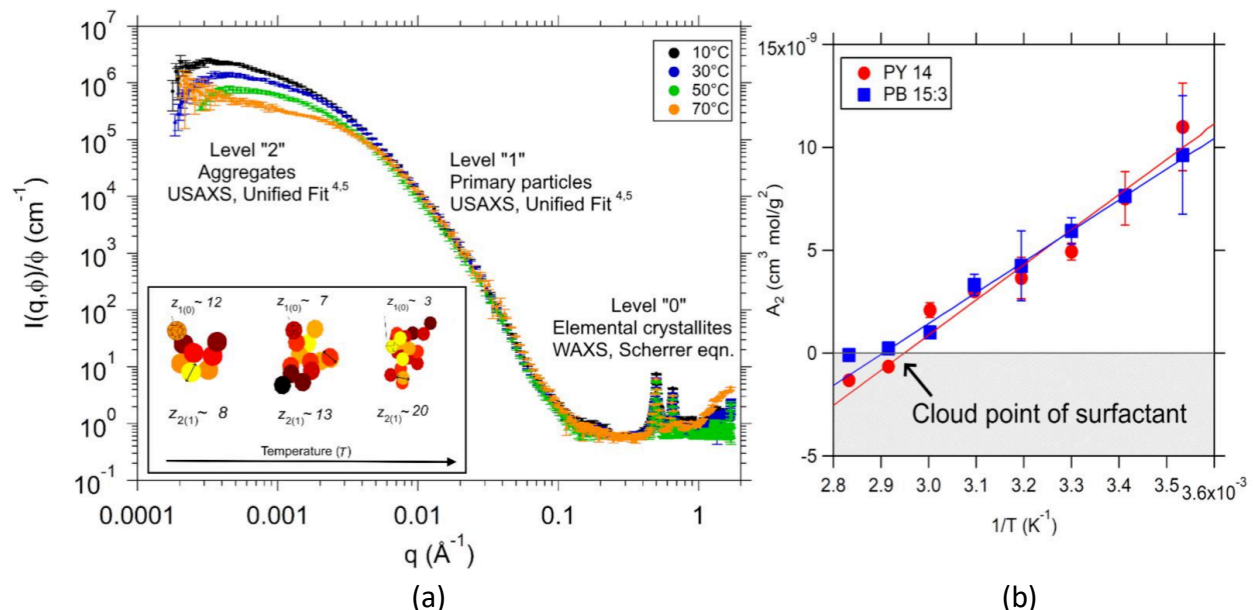


Figure 1. (a) Structural changes in pigment dispersions with temperature from combined USAXS/SAXS/WAXS. [1]; (inset) simulated pigment aggregates made of primary particles based on the scattering results indicating an increase in the number of primary particles per aggregate ($z_{2(1)}$) and a concomitant reduction in the number of elemental crystallites per primary particle ($z_{1(0)}$) with increasing temperature; (b) change in the second virial coefficient (A_2) from structural screening in semi-dilute pigment dispersions indicating that the pigment particles precipitate out at the cloud point of the surfactant. [1]

The thermal dependence of pigment interactions mediated by the surfactant effects the particle size and could potentially impact the optical properties of the ink. Commercial non-ionic surfactants such as Triton X-100 are micelles that comprise of a hydrophobic head that binds with the pigment crystals and a hydrophilic tail that binds with water. For the first part of our investigation, we intend to modify the surfactant's chemical structure through the reactive hydroxyl group on the micelle's tail. We wish to UV-cure the aqueous pigment dispersions prepared with this modified surfactant in situ using a photo-initiator while subjecting the dispersions to different temperatures, effectively locking the particle size by forming a cross-linked surfactant cage.

For the second part of our investigation, we wish to observe the structural changes during the drying process of these tailored inks in situ. Inks would be mixed with a rheology modifier that enhances their viscosity to prevent flow during vertical mounting on the beam. We have observed that thick ink plaques dried under ambient conditions display large 3D particles whereas dried thin films (~100 microns) exhibit a dual-hierarchical network [4] composed of clusters of aggregates that form a micron size network in the range of optimal light scattering. The structural changes during drying arising due to changes in the particle interaction [5] and the emergence of new mesoscale structures that impact the optical properties of ink are commercially relevant and can be potentially simulated resulting in a predictive tool with variables such as the surfactant type, drying rate, drying temperature.

Purpose and Importance of the Research:

The technical importance of the proposed research is to develop a more complete understanding of the kinetics and chemical/physical interactions at play during the drying process under ambient conditions for aqueous pigment dispersions. Additionally, suitable conditions to control pigment size in aqueous colloidal dispersions that depend on the phase behavior of the surfactant can be derived from ultra-small-angle X-ray scattering (USAXS/SAXS/WAXS) measurements detailed below. While the structure-property relationships of pigments have been studied in the literature [1-3] control over particle size has not been demonstrated thus far. Although, structural changes during drying in fillers such as colloidal silica suspensions have been investigated [4,5] systems that display reversible aggregation [6,7] such as pigment dispersions has not been attempted.

Quantifying particle interactions in aqueous inks: Binary interactions between colloidal particles is determined through the second virial coefficient in the expansion of osmotic pressure. In ideal dispersions, osmotic pressure is proportional to solute concentration. [8-10]. However, many colloidal dispersions are not ideal and the virial approach to osmotic pressure (a power series expansion in concentration) is used to determine second virial coefficient, A_2 . A_2 is affected by specific surface area, temperature and choice of surfactant. The random distribution of colloidal particles (modeled by the Unified Fit [11] under dilute conditions) results in uniform small-angle scattering from large-scale structures for samples above the overlap concentration. This phenomenon is called structural screening and results in a decrease in the reduced (volume fraction normalized) scattering intensity, $I(q)/\phi$, in the low- q regime for a given sample concentration due to overlapping structures as shown in Figure 2.[3,10,12] Since screening is proportional to concentration, $I(q)/\phi$; is reduced proportionally for higher solute

concentrations. The second virial coefficient, A_2 , determines the rate of change of structural screening with concentration and describes the quality of the dispersions. Therefore, A_2 can be determined from a concentration series of colloidal dispersions.

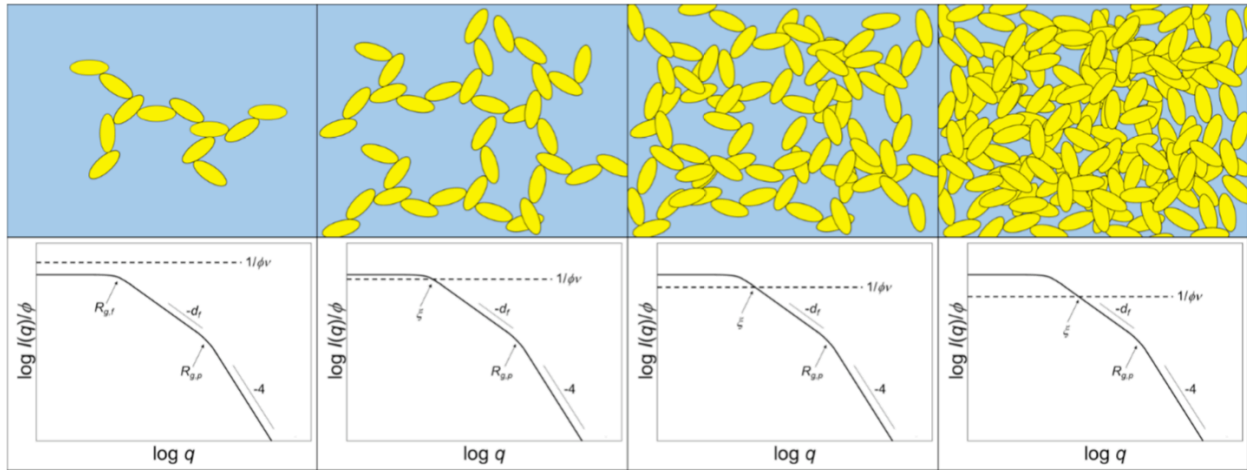


Figure 2. Cartoon depiction of dispersed particle aggregates and the corresponding one-dimensional USAXS data. [1] In the dilute condition, structural features can be observed at all length scales (leftmost figure). As the concentration increases (going from left to right), pigment aggregates begin to overlap and the larger features become obscured owing to structural screening for the reduced scattering intensity, $I(q)/\phi$, larger than $1/\phi\nu$ in the bottom graphs. ν quantifies the extent of screening and is proportional to the second virial coefficient, A_2 . Instead of the aggregate size, the largest observable structural feature is now the emergent mesh size, ξ . The mesh size quantifies the mean distance between structural features at concentrations above the overlap concentration in the top sketches.

Description of Experiments

The first part of the proposed experiment will require USAXS / SAXS / WAXS measurements on colloidal dispersions of pigment-based inks. Each sample will include pigment, water and surfactant (commercial and chemically modified). Dispersions will be prepared at the highest concentration of interest and lower concentrations will be prepared from aliquots of the concentrated solution.

For the second part of the proposed study, varying amount of rheology modifiers and suitable binders would be mixed with the inks to ensure good adhesion to the substrate and prevent flow during vertical mounting of the samples. Pigment/surfactant combinations will be deposited on Mylar (PET) substrates. The drying experiment will be conducted under ambient conditions and USAXS / SAXS patterns will be recorded for an hour per sample.

References

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