Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Colloid and Interface Science 292 (2005) 46–53

JOURNAL OF
Colloid and
Interface Science

www.elsevier.com/locate/jcis

A rheological investigation of the self-assembly and adsorption behavior of a surfactant salt

Genhai G. Liang [a], Brian S. Hawkett [a,*], Roger I. Tanner [b]

[a] *Key Centre for Polymer Colloids, School of Chemistry, F11, University of Sydney, Sydney, NSW 2006, Australia*
[b] *School of Aerospace, Mechanical & Mechatronic Engineering, J07, University of Sydney, Sydney, NSW 2006, Australia*

Received 11 February 2005; accepted 21 May 2005

Abstract

The properties of a surfactant salt obtained by neutralizing oleic acid with an ethoxylated stearylamine were determined in blends of water and propylene glycol. The adsorption of this surfactant salt onto the surface of a commercial TiO_2 dispersed in blends of water and propylene glycol was studied using a rheometer. At low propylene glycol content the dispersions exhibited Newtonian behavior, but became shear-thinning fluids with high viscosity at propylene glycol contents above a critical concentration. The observed behavior is consistent with a model involving a surfactant bilayer below the critical point, moving to a monolayer above the critical point. The high viscosity above the critical point is generated by reversible flocculation via hydrophobic forces. The viscosity of the dispersion flocculated by the hydrophobic forces was found to be much higher than that caused by flocculation via van der Waals forces in the absence of surfactant. Changing both the total concentration of the surfactant in the dispersion and the dispersion temperature resulted in a reversible transition between the bilayer and the monolayer. Although the surfactant was always above its critical micelle concentration (CMC) the amount on the particle surface varied appreciably with both propylene glycol and surfactant concentration.

Keywords: Reversible flocculation; Hydrophobic force; Bilayer; Monolayer; Titanium dioxide; Surfactant salt; Dispersion; Viscosity; Cloud point; CMC

1. Introduction

Reversible flocculation has been used extensively in industry as a mechanism to control the viscosity and sedimentation behavior of pigment dispersions. Such dispersions can often be readily redispersed by minor stirring, if the product undergoes settling during long-term storage, to recreate a product with properties that are the same as those of the freshly made product [1]. It is also possible to generate reversibly flocculated pigment dispersions where the wet settling volume is greater than or equal to the dispersion volume, in which case the dispersions do not undergo sedimentation at all. This is a particularly important property for pigment dispersions for use as inks and for those used for the tinting of paints. Ethylene oxide adducts of long chain fatty amines used, in combination with anionic surfactants, have been found particularly useful as surfactant combinations for preparation of stable pigment dispersions [2]. In unpublished work, a combination of oleic acid and an ethylene oxide adduct of stearylamine with 10 mol of ethylene oxide added was found particularly useful in generating high yield strength dispersions of inorganic pigments that maintained uniform composition on a scale of years. The formulations also showed no evidence of loss of tint strength, also over a period of years, indicating that any flocculation that occurs is quite reversible and readily overcome by the normal conditions of use.

Tadros [3] has described a number of types of flocculation, which included bridging flocculation [4–9], where high-molecular-weight polymers are used to form links between particles; depletion flocculation [10–15], where osmotic effects due to dissolved polymers are used to floc-

---

[*] Corresponding author. Fax: +61 2 9351 8651.
E-mail address: b.hawkett@chem.usyd.edu.au (B.S. Hawkett).

0021-9797/$ – see front matter © 2005 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcis.2005.05.077

culate particles; electrostatically stabilized dispersions can be destabilized by the addition of electrolyte to compress the double layer [16–22]; sterically stabilized dispersions can be flocculated by adjusting the solvency of the continuous phase to theta conditions, thus preventing the stabilizing polymer chains from "seeing" each other [23]. More recently flocculation by hydrophobic forces has been reported [24,25]. By this mechanism particles can be flocculated by the addition of organic chemicals with relatively small molecular weights such as various organic carboxylic acids and amine-based surfactants. The particles of the dispersions become coated with the surfactant so that the hydrophobic portions of the small molecules present to the continuous phase, and the particles flocculate via so called hydrophobic forces between the now hydrophobic surfaces of the particles. Interactions via hydrophobic forces are found to be much stronger than interactions via van der Waals forces [18, 22,24,26–29].

In the present work we examine the properties of a surfactant salt obtained by neutralizing oleic acid with a stearylamine ethoxylate containing 10 mol of ethylene oxide, in various blends of water and propylene glycol. We use rheological tools to investigate the self-assembly and adsorption behavior of this surfactant combination in the context of its use to stabilize TiO_2 dispersions and propose a model to explain the observed behavior.

2. Experimental

2.1. Materials

Rutile, titanium dioxide, coated with alumina and zirconia, was manufactured by Huntsman Corporation Australia Pty Ltd and supplied by HCA Colours Australia under the commercial name of Tioxide TR92. This product had an average particle diameter of 0.24 µm and an isoelectric point of 7.3 [30].

The propylene glycol used was an industrial product supplied by Swift & Company.

Teric 18M10 (stearylamine with 10 mol of ethylene oxide added) was supplied by Huntsman Corporation Australia Pty Ltd.

Oleic acid was a commercial product supplied by Dragon Chemical Co. Pty Ltd.

Methanol, ethanol, *n*-propanol, and *n*-butanol were laboratory reagent grade.

All chemicals were used without further purification.

2.2. Preparation of samples

Dispersions of the TiO_2 in propylene glycol–water were prepared in the following manner: TiO_2 (157.9 g) was added into a mixture of propylene glycol (154.7 g) and water (104.4 g) in a 1-L pot and dispersed at 1000 rpm for about 15 min using a high-speed disperser (Dispermat AE 3C); surfactant salt (46.1 g) was then added dropwise. After about 20 min, TiO_2 (526.9 g) was slowly poured into the mill, while stirring was maintained at 1500 rpm. Once addition was complete, mill speed was maintained at 1500 rpm until no aggregates could be detected on a Hegman gauge (about 1.5 h).

Aliquots of 5.5 g of the above grind base were let down in 22.5-ml clear glass bottles by adding 16 ml of various blends of propylene glycol and water to form 5.0 vol% TiO_2 dispersions. The dispersions thus formed were thoroughly mixed using a mechanical mixer (Ratex, Vortex Mixer) for about 2 min followed by an ultrasonic bath (Cole-Parmer, Model 8891) for 1 h. By this procedure, all samples contained the same amount of TiO_2 (5.0 vol%) and surfactant salt (1.4 vol%), but with continuous phases with various ratios of propylene glycol to water.

Dispersions of the TiO_2 in mixtures of water and other alcohols (methanol, ethanol, *n*-propanol, and *n*-butanol) were prepared in a similar way except that propylene glycol was replaced in the grind base by an equal volume of water while the various alcohols were added in the let down stage only. This approach enabled all of the dispersions containing these alcohols to be prepared from the same grind base, thus eliminating the impact of grind base variation on the rheological results.

2.3. Measurements

The viscosities of the samples were measured at 25 °C using a stress-controlled rheometer (Reologica of Stress-Tech) with a 25-mm-diameter concentric cylinder rotor in the sample cup.

Sedimented dispersions were prepared by pouring samples of dispersion into 10-ml measuring cylinders (8.4 mm in diameter), which were kept in the laboratory for 6 months without further disturbance. After this time the initially uniform samples were separated into a clear layer and a sedimented layer. Samples were prepared for optical microscopy by taking a drop of settled sample from near the interface of the sediment and the clear layer, so that a very dilute dispersion of the sample was prepared, thus the state of flocculation of the sedimented pigment could be readily observed by optical microscopy.

The amount of the surfactant on the particle surface was calculated by difference after the amount of surfactant in the continuous phase was determined gravimetrically from the clear layer generated by centrifugation of the sample. Samples of supernatant were dried to constant weight in a 60 °C oven. This method was checked against standard surfactant solutions to ensure reliable data. As the amount of surface area exposed in the dispersion process depends on the degree of dispersion the calculation of the area occupied by each surfactant molecule is not absolute. We have obtained what we believe to be a realistic estimate of the surface area available for adsorption of surfactant by assuming that the