The adsorption of non-ionic surfactants on carbon black particles in hydrocarbon media

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ABSTRACT

Demand for improved fuel efficiency, decreased pollution emissions, and prolonged engine lifespan have given rise to the need for improved fuel and engine oil properties. In particular, the dispersion of carbon deposits is an important consideration. To this end, the adsorption of eight non-ionic, potential fuel-additive surfactants on carbon black particles from iso-octane solutions has been examined and compared. The surfactants all contain poly(iso-butylene) (PIB) tails of varying lengths and head groups based on phenol or amine-substituted phenols of various kinds. For the amine-substituted phenol surfactants, changes in the surfactant structure (number and type of amine groups in the head group and the PIB tail length) were observed to have no significant effect on the heat of adsorption, determined calorimetrically. However, changes were observed in the maximum adsorbed amount for the surfactants with different head group structures and PIB tail lengths. These are explained in terms of changes in the varying extents of solvent rejection of the different surfactants. In hydrocarbon media containing these surfactants, the only surfactants that showed anything other than marginal improvement in the stability to aggregation of dispersions of carbon black were those containing primary or secondary amine groups. Those surfactants with only tertiary amine groups showed no significant improvement in dispersion stability compared to dispersions of the bare particles. In the case of the primary and secondary amine groups, this is explained in terms of proton exchange between the head groups of the surfactant molecules and acid groups on the surface.

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1. Introduction

Carbon black is an inexpensive, versatile and strongly adsorbent material that is widely used in air and liquid separation and purification [1], as a filler and coloring agent in a range of products, and as an ink for printing. In fact, carbon black is a family of materials that are the product of incomplete combustion and are composed of parallel stacked layers of polyaromatic planes, similar to, but of a more turbostatic structure, than graphitic carbon [2]. Its physical and chemical properties can vary considerably, depending upon the combustion material, method and environment of manufacture. Particle size, porosity, degree of oxidation and even the oxidized group functionality (acidic or basic in nature) can be modified either during the combustion process or by post-manufacture chemical treatments [3]. This gives rise to surface properties that are process dependent and that can considerably alter the adsorbent properties of carbon black. Because it is the product of incomplete combustion,

carbon black is considered a good model substrate for examining the clean-up and prevention of carbonaceous deposits from combustion processes such as coal power plants, heavy-goods diesel engines and light-duty automotive engines [4]. These combustion deposits arise from the oxidation and incomplete combustion of impurities such as sulfurous, olefin and less volatile compounds present in fuels. The deposits are typically considered to be highly porous and to contain acidic oxidized groups [5,6] and have been shown to reduce engine efficiency, lead to engine run on, difficulty in starting and increased pollution emission [7].

With increased fossil fuel prices and environmental awareness, improved fuel efficiency and reduced environmental impact of combustion engine emissions are becoming increasingly important to consumers and legislative bodies. To this end, packages of hydrocarbon-soluble additives are commonly incorporated in hydrocarbon fuels and lubricants to improve engine combustion and running properties. These additives must function effectively under engine operating conditions and temperatures, and they must be inexpensive and also undergo efficient combustion along with the fuel. Due to environmental concerns and changes in fuel composition, new additives are required to replace older yet efficient molecules that contain pollution-causing elements such as

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sulfur, phosphorus or metal ion compounds. Surfactants form a key group of additives that reduce and prevent formation of carbonaceous deposits on engine components.

Effective fuel and lubricant surfactants are believed to act in two ways on carbonaceous deposits: (i) as dispersing agents, that is, the surfactants adsorb onto the deposit and disperse the particles in the hydrocarbon media; and (ii) as anti-deposition agents, that is, the surfactants form a protective, adsorbed film on the engine components, preventing formation of carbonaceous deposits. These features are typically modeled in the laboratory by characterizing the adsorption characteristics and subsequent stability of the particulate suspensions. The adsorption of surfactants in apolar hydrocarbon media is believed to occur via polar interactions between the surfactant head group and polar surface sites [8,9]. Previous studies and commercially developed products have focused on the adsorption interactions between a variety of surfactant head group structures (such as succinimide esters [10–12], azacarboxylates [13] and poly(ethylene glycols) [14]) and model carbonaceous deposits, in particular, carbon blacks.

The most widely studied and reported surfactant structures for automotive use are the poly(iso-butylene) succinimide ester surfactants (PIBSA). These studies have examined the adsorption and dispersion stability characteristics of these surfactants on carbon black particles in a variety of liquid hydrocarbon media. It has been previously shown that the adsorption interactions are influenced by the surfactant and substrate polarity [10,15]. Both increasing the PIBSA polyamine head group size and increasing the number of amine groups increased the surfactant adsorbed amount and enthalpy of adsorption [16]. A number of studies have also indicated these surfactants show adsorbed amounts that exceed monolayer coverage at high surfactant concentrations. This has been interpreted as multilayer or hemi-micelle aggregate surfactant structures on the surface. SANS and AFM studies have shown the formation of such hemi-micelles for PIBSA adsorption [16,17].

The stability of particulate dispersions, such as carbon black, in hydrocarbon media is dependent upon the interparticle forces of repulsion being greater than those of attraction. These repulsive forces may be electrostatic and/or steric. For dispersions of carbon black particles in liquid hydrocarbons, in the past their stability has generally been attributed to the steric forces provided by the adsorbed surfactants [18]. However, more recent research has indicated that steric forces on their own are insufficient to impart colloidal stability; therefore, electrostatic forces also must be present [19,20]. Electrostatic forces for PIBSA adsorption on carbon blacks are believed to result from proton transfer between the acidic (ionogenic) carbon black surface sites and the amine moieties of the surfactant in solution [21,22]. Increasing the PIBSA concentration has been shown to decrease the Debye length of the counter-ion atmosphere in hydrocarbon media [23], which is similar to increasing the salt concentration in aqueous media.

In this paper the adsorption isotherms for eight, amine-modified poly(iso-butylene) (PIB) surfactants on commercial carbon black particles, as a model for an engine valve deposit, are presented. The efficacy of the various surfactants is compared in terms of the maximum adsorbed amount, the enthalpy of adsorption and the corresponding stability of the carbon black dispersions.

This paper is a sequel to our previous, recent publication [24] on the adsorption of similar surfactants onto macroscopic stainless steel surfaces, using ellipsometry.

2. Materials and methods

Monarch 1000 carbon black was purchased from Cabot Carbon Limited. Prior to use, it was cleaned for three days in iso-octane by continuous Soxhlet extraction. The carbon black slurry was then dried overnight under vacuum to remove the solvent, and the resulting dry cake was sieved through a 250 μm and then a 75 μm mesh to produce a fine black powder.

The eight non-ionic surfactants used in this study are listed in Table 1. Their synthesis was carried out by us using a method described in a previous publication [24].

PLC grade iso-octane solvent was purchased from Rathburn Chemicals Limited, UK, and AR-grade sodium hydroxide, sodium hydrogen carbonate and dodecane were purchased from Sigma–Aldrich and used as received.

The carbon black surface area and porosity was determined by N_2 BET adsorption using a Quantachrome Autosorb Gas Sorption System 2.1 and by mercury porosimetry using a Quantachrome Porosimeter. Experiments were performed on 0.15 g of carbon black degassed overnight at 100 °C prior to analysis.

The carbon black surface-oxidized functional group concentration was determined by Boehm back-titration [3]. First, the surface concentration of protonic (e.g., carboxylic) acidic groups was determined by adding 10 ml of 6 mM $NaHCO_3$ to 0.3 g of carbon black. The suspension samples were then sonicated for 5 min and tumbled for 24 h to ensure equilibrium. After 24 h, the supernatant was removed by centrifugation and filtered through a 0.2 μm filter to remove any remaining carbon black particles. The concentration of unreacted base was determined by titrating the supernatant with a 2 mM HCl solution. The concentration of total surface acid groups was then determined in a similar manner, but now using a much stronger base, 10 mM NaOH.

Solution adsorbed amounts were determined using 0.3 g of carbon black powder to which 7 g of an iso-octane solution, containing increasing surfactant concentrations (0–6 μmol g^{-1} or 0–4 wt.%) was added. The samples were sonicated for 5 min to break up weakly aggregated particles and then tumbled for 24 h to ensure adsorption equilibrium had been reached. The samples were then centrifuged, and the surfactant supernatant concentrations were determined using a Hewlett-Packard Agilent 8453E UV–visible spectrometer at 280 nm. Desorption isotherms were conducted by replacing the removed supernatant with pure solvent and re-dispersing the particles by sonicating the system for 5 min, then tumbling for 24 h. This procedure was repeated five times. Calibration curves of surfactant absorbance versus concentration at 280 nm were constructed for each surfactant, and samples were diluted appropriately if the Beer–Lambert region of the calibration curve was exceeded. Error bars were generated for individual data points based on the standard error of each measurement.

Enthalpies of adsorption were measured using a Microscal Limited (London) flow microcalorimeter. Iso-octane was flowed at 6 ml h^{-1} through a packed bed of 0.045 g carbon black until a stable baseline had been reached, normally after approximately 1 h. The microcalorimeter was calibrated before each experiment using a built-in, wire-loop electric resistor heater. The instrument was then allowed to return to equilibrium, maintaining the 6 ml h^{-1} solvent flow rate. After a stable baseline had been achieved, 14 ml of a solution of 5.25 μmol g^{-1} of surfactant in iso-octane was introduced at 6 ml h^{-1}. Pure solvent was then pumped through at the same flow rate for an additional 2 h, to monitor the heat of desorption. The molar enthalpies of adsorption (ΔH_{ads}^m) were then calculated by multiplying the measured heat of adsorption by the total carbon black surface area, and dividing by the maximum adsorbed amount (Γ_{max}), for each surfactant.

The stability of the carbon black dispersions was assessed by measuring the light transmission at a wavelength of 600 nm. Dispersions of 4×10^{-2} % w/w carbon black in dodecane, with 5.25 μmol g^{-1} of added surfactant, were sonicated for 5 min and tumbled for 24 h prior to these measurements.