CHAPTER 5

CORRELATION BETWEEN SURFACE FREE ENERGY PARAMETERS OF SOLIDS AND SEPARATION EFFICIENCY IN MINERAL BENEFICIATION

5.1. INTRODUCTION

Knowledge of surface free energies (and its components) between two entities is important. They dictate not only the strength of the interaction, but also control the processes such as the stability of aqueous colloidal suspensions, the dynamics of molecular self-assembly, wetting, spreading, deinking and adhesion (1-4). Many of the mineral processing techniques, e.g. froth flotation, selective flocculation, filtration and thickening are also controlled by the interfacial energies of the solid and the liquid involved. Therefore, characterization of the surface properties, especially the surface free energy components is important for understanding the mechanisms of the various surface-based phenomena.

The standard approach used for determining the surface free energies of solids and the interfacial surface free energies between two interacting surfaces has been through wetting experiments. Specifically, the contact angle method has been widely used to characterize the surface properties of solids (5-10). The most commonly used measure of surface hydrophobicity is the water contact angle (11-15). The higher the contact angle value is, the more hydrophobic the solid surface becomes. The value of the water contact angles can also be used to determine the surface free energies. In principle, the higher the contact angle, the lower the surface free energy (γ_S) of a solid surface (16-19).

Besides direct contact angle measurements, microcalorimetric measurements give valuable information regarding the surface properties of powdered solids such as surface hydrophobicity-hydrophilicity and acidity-basicity characteristics. The interactions between various reagents and the solid surfaces in aqueous or non-aqueous media can also be studied by using a microcalorimeter. Microcalorimetric studies should also be useful in explaining the physico-chemical aspects of mineral separation techniques such as flotation and selective flocculation.

Flotation is one of the most widely used methods of separating particulate materials from one another in aqueous media. This technique uses the differences between the surface hydrophobicities of minerals involved. It is well recognized that in flotation the solid/liquid interface is the most important parameter. A hydrophilic mineral can only be floated after collector molecules adsorb at the surface. As a result, the surface free energy of the solid (γ_S) is reduced. Such a decrease in surface free energy is necessary for bubble-particle adhesion to occur. It is, therefore, crucially important to study the changes in the surface free energy of the solid taking place upon adsorption of hydrophobic reagent molecules.

Recent publications have revealed that the differences in surface hydrophobicities between various mineral particles are also very important for a successful separation by selective flocculation (20-24). In selective flocculation, certain mineral particles are aggregated selectively from an aqueous suspension of mineral mixture by the aid of a bonding agent (i.e. a flocculant) that attaches to these particles. In general, a flocculant is initially adsorbed on the particles then form larger aggregates or flocs which settle or sediment out of the suspending liquid. Flocculants can be natural products such as starch, guar gum and alginates or synthetic polymers such as polyacrylamides, polyacrylates and polyethylene oxides. The success of a selective flocculation process depends chiefly on the adsorption of the conditioning agent (i.e. surfactant) on mineral particles to be settled out from the suspension. As a result of surfactant adsorption, the surface free energy of solid (γ_S) is reduced.

5.1.1. Contact Angle

For powdered samples, the thin layer wicking technique can be used to determine the contact angles (25-26). In this technique, a powdered sample is deposited on a microscopic glass slide in the form of aqueous slurry on which a thin layer of the powdered mineral has been formed. After drying the sample, one end of the glass slide is immersed vertically in a liquid. The liquid will start to rise along the height of the slide through the capillaries formed between the particles deposited on the glass surface. The driving force for the penetration of the liquid into a dry layer of particles on the glass surface is the capillary pressure across the liquid-vapor interface. Therefore, the liquid enters the capillaries spontaneously if the contact angle is less than 90°. The velocity at which a liquid creeps up the slide is measured, and then converted to a contact angle using the Washburn equation [27, 28].

$$l^2 = \frac{\gamma_{LV} r^* t \cos\theta}{2\eta} \qquad [5.1]$$

where η is the liquid viscosity. The value of mean pore radius (r^*) in the Washburn equation can be determined using completely spreading liquids (apolar) such as heptane, octane, decane and dodecane. In this case, it is considered that $\cos\theta=1$. Once the value of r^* is known, it is possible to calculate the value of the contact angle for a given liquid, i.e., water, formamide etc, on the powdered solid surface using the Washburn equation (Eq. [5.1]). It has to be mentioned here that advancing contact angles are measured by a thin layer wicking technique.

Alternatively, capillary rise technique may be used to determine the contact angles for powdered mineral surfaces. One problem with this technique might be the uncertainty associated with determining r^*. There is no guarantee that the value of r^* determined with a completely wetting liquid is the same as that determined by a less than completely wetting liquid. Reproducibility and repeatability of test results also depend on the shape and size of the particles. It has been stated that monosized and spherical particles give more reproducible results [25]. However, particle bed disturbances and skewing may be observed when the particles are extremely fine and platy in shape leading to unrealistic values of contact angles.

5.1.2. Heat of Immersion and Adsorption Enthalpies

Groszek and Partyka (29) described a method of determining the percentages of the surface area of a solid surface that are hydrophobic and hydrophilic. In this technique, the heat of adsorption of butanol is measured from a butanol-in-heptane solution (2 g/l). The heat effect is mostly due to the adsorption of butanol on the hydrophilic sites (i.e., edge surface) of the sample, with the OH-groups in touch with the surface and the hydrocarbon tails pointing towards the aqueous phase. Thus, the heat effect is proportional to the hydrophilic surface area. By dividing this heat effect given in units of mJ with the heat of adsorption of butanol on silica (197.0 mJ/m^2) from n-heptane, one can determine the hydrophilic surface area.

Several investigators determined the contact angles of water on powdered mineral surfaces by measuring the heats evolved when they were immersed in water (30-32). In the present work, a more rigorous method of converting heat of immersion to contact angle was developed and it was tested on various powdered talc samples. It has to be noted here that the heat of immersion in water by itself can be used as a measure of hydrophobicity. As the results presented in Chapter 3 showed, the smaller the heat of immersion, the more hydrophobic a solid became.

5.1.3. Surface Free Energies

Fowkes [33] proposed that the work of adhesion (W_a) between a liquid on a solid surface is given by:

$$W_{\mathrm{a}} = W_{\mathrm{ad}}^{\mathrm{d}} + W_{\mathrm{ad}}^{\mathrm{nd}} \qquad [5.2]$$

where W_a^d represents the contributions from dispersion (nonpolar) interactions, and W_a^{nd} represents the same from non-dispersion interactions. The latter includes interactions due to chemical bonding, hydrogen bonding, and columbic interactions due to the charge separation at the interface. The dispersion forces are always present, and the dominant term in the case of saturated hydrocarbons and hydrophobic surfaces such as graphite and teflon etc. In the case of oxide minerals and aluminosilicate minerals such as quartz, anatase (TiO_2), mica, and clay, the surface can form strong hydrogen bonding with water molecules. Laskowski and Kitchener [34] suggested that all solids would be hydrophobic if W_{ad}^{nd}=0, i.e., if the surface is free of polar groups on which water molecules can be bonded.

In the last twenty years, significant advances have been made in the thermodynamic treatment of surface free energies, largely due to the pioneering work of Fowkes et al. [35-37] and van Oss, Chaudhury and Good [38-41]. According to these approaches the surface free energy of a phase *i* is given by:

$$\gamma_{\mathrm{i}} = \gamma_{\mathrm{i}}^{\mathrm{LW}} + \gamma_{\mathrm{i}}^{\mathrm{AB}} \qquad [5.3]$$

where $\gamma_{\mathrm{i}}^{\mathrm{LW}}$ and $\gamma_{\mathrm{i}}^{\mathrm{AB}}$ refer to the apolar and polar (acid-base) components of surface free energy, respectively. The former can be represented by the Lifshitz-van der Waals (or LW) interactions that include the dispersion (London), induction (Debye) and orientation (Keesom) components. The polar interactions are generally considered to be intermolecular interactions between Lewis acids (electron acceptor) and bases (electron donor) on the surface.

According to Van Oss-Chaudhury-Good's (OCG) approach the surface free energy change upon two interacting surfaces (e.g. solid and liquid) is given by:

$$\Delta G_{SL} = -2\sqrt{\gamma_S^{LW}\gamma_L^{LW}} - 2\sqrt{\gamma_S^{+}\gamma_L^{-}} - 2\sqrt{\gamma_S^{-}\gamma_L^{+}} \qquad [5.4]$$

The changes in free energy associated with the solid liquid interaction is given by the following relation [42]:

$$\Delta \mathrm{G}_{\mathrm{SL}} = \gamma_{\mathrm{SL}} - \gamma_{\mathrm{S}} - \gamma_{\mathrm{L}} \qquad [5.5]$$

Substituting Eq. [5.5] into Eq. [5.4], one obtains:

$$\gamma_{SL} = \gamma_S + \gamma_L - 2\left(\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + \sqrt{\gamma_S^{+}\gamma_L^{-}} + \sqrt{\gamma_S^{-}\gamma_L^{+}}\right) \qquad [5.6]$$

which allows one to determine the interfacial surface tension of two interacting surfaces (e.g. liquid and solid). As shown, there are four unknowns for the calculation of γ_{SL}; the surface free energy components of solid, i.e., γ_S, γ_S^{LW}, γ_S^+, and γ_S^-. The surface free energy components of liquid are generally available in literature. The surface free energy components of solid can be determined by using van Oss-Chaudry-Good's (OCG) equation that is derived as follows:

Work of adhesion or Gibbs free energy of interaction can be related to the interfacial energies through Young's equation [43],

$$\gamma_{\mathrm{L}}\cos\theta = \gamma_{\mathrm{S}} - \gamma_{\mathrm{SL}} \qquad [5.7]$$

where γ_L is the surface tension of water and γ_{SL} is the interfacial tension between the solid and liquid.

Combining Equations [5.5] and [5.7],

$$-\Delta\mathrm{G}_{\mathrm{SL}} = \gamma_{\mathrm{L}}(1+\cos\theta) = W_{ad} \qquad [5.8]$$

Substituting Eq. [5.8] into Eq. [5.6], one obtains:

$$(1+\cos\theta)\gamma_{\mathrm{L}} = 2\left(\sqrt{\gamma_{\mathrm{S}}^{\mathrm{LW}}\gamma_{\mathrm{L}}^{\mathrm{LW}}} + \sqrt{\gamma_{\mathrm{S}}^{+}\gamma_{\mathrm{L}}^{-}} + \sqrt{\gamma_{\mathrm{S}}^{-}\gamma_{\mathrm{L}}^{+}}\right) \qquad [5.9]$$

which is very useful information for characterizing a solid surface in terms of its surface free energy components, i.e., γ_S^{LW}, γ_S^+, and γ_S^-. To determine these values, it is necessary to determine contact angles of three different liquids of known properties (in terms of γ_L^+, γ_L^-, γ_L^{LW}) on the surface of the solid of interest. One can then set up three equations with three unknowns, which can be solved to obtain the values of γ_S^{LW}, γ_S^+, and γ_S^-. Table 5.2 gives a list of liquids that can be used for the contact angle measurements, along with the values of γ_L, γ_L^{LW}, γ_L^+, and γ_L^-.

If an apolar liquid is placed on the surface of a talc sample and its contact angle is measured, Eq. [5.9] can be reduced to:

$$(1+\cos\theta)\gamma_{\mathrm{L}} = 2\sqrt{\gamma_{\mathrm{S}}^{\mathrm{LW}}\gamma_{\mathrm{L}}^{\mathrm{LW}}}\ , \qquad [5.10]$$

because both γ_L^+ and γ_L^- are zero. Thus, Eq. [5.10] can be used to determine γ_S^{LW} from a single contact angle value, provided that the contact angle measurement is conducted with an apolar liquid of known γ_L and γ_L^{LW}. (In fact, $\gamma_L=\gamma_L^{LW}$, γ_L^+ and γ_L^- are zero.) As the value of γ_S^{LW} is already estimated from Eq. [5.10], Eq. [5.9] can now be used to determine the values of γ_S^+ and γ_S^- by solving two simultaneous equations.

Once the three surface tensions, i.e., γ_S^{LW}, γ_S^+, and γ_S^-, are known, the surface tension of the solid, γ_S, can be determined as follows:

$$\begin{aligned}\gamma_{\mathrm{S}} &= \gamma_{\mathrm{S}}^{\mathrm{LW}} + \gamma_S^{AB} \\ &= \gamma_S^{LW} + 2\sqrt{\gamma_{\mathrm{S}}^{+}\gamma_{\mathrm{S}}^{-}}\end{aligned} \qquad [5.11]$$

The surface free energy, γ_S, is a material specific parameter which, when known for two materials, can be used to estimate the wettability, work of adhesion and the changes in the Gibbs free energy upon interaction.

It was the primary objective of the present work to study the important role of the surface free energy properties of solids in separating mineral particles by mineral beneficiation processes. A surface treated anatase (TiO_2) under controlled conditions was chosen as a model of the solid with varying hydrophobicities. The contact angle values of surface treated anatase particles were determined using the thin layer wicking technique. In addition, the heat of immersion values in different liquids and percentages of hydrophobic and hydrophilic surfaces on anatase samples with varying hydrophobicities were determined using a flow microcalorimeter. The contact angle values were used to determine the surface free energy parameters of surface treated anatase samples using van Oss-Chaudhury-Good's thermodynamic approach. The results served as a guide in predicting the conditions under which flotation and selective flocculation was possible or favorable. Furthermore, the results of the model were tested on a crude east Georgia kaolin clay that contains anatase (TiO_2) as a main discoloring impurity using flotation and selective flocculation techniques. It is hoped that such information regarding the surface free energy properties of solid (e.g., anatase) will not only help to understand the surface hydrophobicity and surface free energies, but will also be useful for understanding the molecular origin of the adhesion between two interacting surfaces.

5.2. EXPERIMENTAL

5.2.1. Materials

The flotation and selective flocculation experiments were conducted using a run-of-mine east Georgia kaolin clay obtained from Thiele Kaolin Company located in Sandersville, GA. Upon arrival, the clay sample was homogenized and then split into representative lots of 500 grams each using a riffler. Divided samples were placed into bags and stored until required. The crude kaolin clay used in the test work assayed 3.0% TiO_2 and 1.0% Fe_2O_3 as the discoloring impurities by X-ray fluorescence (XRF) analysis.

The free moisture content of the clay sample was approximately 17.1%. Wet screen analysis results showed that there was almost 6.5-7.0% sand (+325 mesh fraction) in the sample. It has been reported by the producer (Thiele Kaolin Co.) that 90% of the crude clay was minus 2 μm in size. Because of the ultrafine particle size distribution and high impurity level, this clay is known to be very difficult to beneficiate using conventional beneficiation methods such as flotation and magnetic separation.

A pure –325 mesh (45 μm) anatase sample was acquired from Acros Chemicals for microcalorimetric and contact angle measurements. The surface area of the pure anatase was determined to be 8.45 m^2/g using a Quantachrome Surface Area analyzer (See Table 5.1).

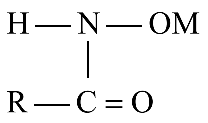
5.2.2. Reagents

5.2.2.1. For Flotation and Selective Flocculation

The conditioning reagents used in the flotation and selective flocculation tests were alkylhydroxamic acids, octylhydroxamic acid being the major component. The process of using alkylhydroxamic acids in the flotation for removing anatase from kaolin clay was patented by Yoon and Hilderbrand (44). These reagents have several advantages over the conventional fatty acid collectors. They do not require activators, are more selective, and give high recoveries. The hydroxamic acids can be prepared by reacting alkyl esters with hydroxylamine in organic solvents (44-45).

In the selective flocculation of kaolin clay, the objective is the removal of anatase and iron oxide particles from a mixture of mineral particles. To achieve this selectivity, the flocculant should only adsorb on anatase and iron oxide particles. In order to make the flocculant adsorb selectively, the particles of anatase are hydrophobized using different types of reagents. The most commonly used reagents are fatty acids (46-48) and hydroxamates. The use of hydroxamates in selective flocculation for removing anatase impurities from kaolin clay appears to be developed at the same time by Nagaraj (23) et al and Shi et al (24). Ravishankar et al (49) used a modified polyacrylamide containing up to 8.3% hydroxamate functional groups to selectively flocculate iron oxide from kaolin. In this latter work, an artificial mixture of kaolin and synthetic iron oxide was dispersed at a pulp density of 1%; the hydroxamate containing modified polyacrylamide was then added to flocculate and sediment the iron oxide particles.

In the present work, two types of commercial brand hydroxamates, Aero 6493 and 6973, were used. The reagents were obtained from Cytec Industries. The difference between the two lies in the types of organic solvents, in which alkylhydroxamic acids were formed. Aero 6493 has been formed in dodecanol, while Aero 6973 has been obtained using 2-methyl hexanol as solvents. Dodecanol is a well-known froth suppressor; therefore, the frothing property of Aero 6493 is not as good as Aero 6973. When a collector does not have sufficient frothing property, one can use a frother. It has to be noted that any hydroxamate reagent having the following formula may be suitably used in the flotation:



$$\begin{array}{ccccc} \mathrm{H} & — & \mathrm{N} & — & \mathrm{OM} \\ & & | & & \\ \mathrm{R} & — & \mathrm{C} & = & \mathrm{O} \end{array}$$

in which R is an alkyl, aryl or alkylaryl group having 4-28 carbon atoms, and preferably 6-24 carbon atoms, and M represents hydrogen, an alkali metal or alkaline earth metal.

For blunging, sodium silicate (SiO_2/Na_2O=3.2:1; 50% water) and sodium polyacrylate were used as dispersing agents in various combinations. The pH of the flotation pulp was adjusted with sodium carbonate. For selective flocculation tests, various anionic polymer flocculants from Nalco Chemicals, IL and Sharpe Flocculants, GA have been used. The names and properties of the polymers are given in Table 5.2.

5.2.2.2. For Contact Angle Measurements

The contact angle values of various liquids on as received anatase and on the treated anatase surfaces with varying amounts of Aero 6493 were obtained from the thin layer wicking measurements. In these measurements, 1-bromonaphthalene, water and formamide were utilized as the test liquids. The contact angle values were used to calculate the values of the surface free energy parameters (γ_S^{LW}, γ_S^+, and γ_S^-) on the anatase surface. An average of 3 to 5 measurements were obtained for each liquid and the values were averaged.

5.2.2.3. For Microcalorimetric Measurements

The solvents used for the heat of immersion measurements were HPLC grade n-heptane (>99.5% purity) and GC grade methylene iodide (>98% purity) from Aldrich Chemical Company and, ACS grade (99.9% purity) formamide from Fisher Scientific. They were dried overnight over 3 to 12 mesh Davidson 3-A molecular sieves before use. All experiments were conducted using conductivity water produced from a Barnstead Nanopure II water treatment unit.

For the heat of adsorption measurements, HPLC grade butanol (from Fluka) was used. Purity of butanol was greater than 99.5%. Solutions were prepared fresh daily before use in the experiments. All the glassware was oven-dried for at least 24 hours at 75 oC prior to use. The syringe, calorimeter cell, fittings and the teflon tubing lines of the microcalorimeter were cleaned using HPLC grade acetone (Fisher Scientific) after each run. All of the experiments were conducted at 20±2 ^{o}C. Table 5.3 gives the values of surface tension parameters and viscosities of liquids used in the contact angle and microcalorimetric measurements.

5.2.3. Procedure

5.2.3.1. Flotation

Flotation tests were conducted on the east Georgia clay sample using a standard Denver D-12 laboratory flotation machine. A 2.5-liter flotation cell was used at approximately 25-30% solids by weight. All tests were conducted using the Blacksburg tap water.

For each test, 350 ml of tap water was added to an Osterizer kitchen blender containing 450 g (bone dry) of the east Georgia clay sample to bring the solid content to 60%. The mixture was agitated for 10 minutes at the highest speed after adding 6 lb/t sodium silicate, 1 lb/t sodium polyacrylate and 3 lb/t sodium carbonate. The pH of the dispersed clay slip was in the range of 9.0-9.5. The blunged clay was conditioned for another 10 minutes after adding 1.0-4.0 lb/t of a collector at the same speed for blunging.

After conditioning, the clay slip was transferred to the flotation cell and diluted to 25-30% solids by adding tap water. The slurry was agitated for a few minutes at 1,500 rpm before introducing air into the cell to start flotation. The froth, which contained TiO_2 and Fe_2O_3 impurities, was collected until exhaustion. It took usually 35-60 minutes of flotation time. Both the froth products and the clay left in the flotation cell were filtered, dried, and weighed. Representative samples were analyzed using an XRF spectrophotometer.

5.2.3.2. Selective Flocculation

The selective flocculation process employed in the present work involved three steps, i.e., i) blunging, ii) collector addition, and iii) flocculant addition. The collector addition allows anatase particles to be hydrophobized, which in turn allows anionic flocculant molecules to adsorb selectively on anatase. The procedures involved for blunging and collector addition were the same as those employed for the flotation of east Georgia clay. The pH of the slurry in the selective flocculation experiments was 9.0-9.5, which was the same as that of the flotation experiments. After addition of a diluted solution (0.02 or 0.05% by weight) of the polymer flocculant in the amounts of 25-125 g/ton, the solids content was adjusted to 22.5% by adding tap water. The clay slurry was gently agitated for a few minutes, and then allowed to settle at a settling rate of 7.5 minutes per inch of slurry depth. All flocculation experiments were conducted in 1-liter graduated cylinders. The unsettled clay slip was siphoned-off, filtered, dried, weighed, and analyzed for TiO_2 and Fe_2O_3 using an XRF spectrophotometer. Figure 5.1 shows the schematic representation of procedure used for the batch selective flocculation experiments.

5.2.3.3. Surface Treatment of Anatase with Hydroxamates

The surface treatment was applied as a means of controlling the surface hydrophobicity of pure anatase, using Aero 6493 hydroxamate collector solutions of different concentrations. A 25 g of anatase sample was first dispersed in a laboratory shaker using 6 lb/t sodium silicate, 1 lb/t sodium polyacrylate and 5 lb/t sodium carbonate for 10 minutes at 35% solids to simulate the flotation and selective flocculation experiments. The pH of the slurry was 9.25. The slurry was then conditioned on a hot plate using a magnetic stirrer for mixing. Conditioning was performed for 30 minutes at 55 ^{o}C by adding 2-4 lb/t of Aero 6493 to the dispersed slurry. The treated samples were separated from the solution by filtration and dried at 110 ^{o}C for 24 hours. The surface treated anatase samples prepared using the above manner were used for the contact angle and microcalorimetric measurements. Table 5.1 gives the specific surface areas of anatase samples treated with varying amounts of Aero 6493, along with the surface area of untreated (as received) anasate. As shown, the surface area of the untreated anatase sample was 8.45 m^2/g, while it decreased to a value of 6.50 m^2/g on the surface treated anatase sample using 2 lb/t Aero 6493 and then leveled off. The results suggest that certain portion of pores on the anatase sample was initially occupied by the Aero 6493 molecules; as a result, the specific surface area decreased on the surface treated samples.

5.2.3.4. Contact Angle Measurements

To prepare thin layers coated on microscope glass slides (1 by 3") for wicking measurements, each of the surface treated anatase powder was dispersed in distilled water at 5% (w/v), and the suspension was agitated with a magnetic stirrer. The pH of the suspension was adjusted to 9.0 using NaOH. A small volume (4 ml) of suspension was withdrawn with a pipette and distributed on clean, horizontal glass microscope slides. Upon evaporating the water at room temperature, the samples were further dried in an oven at 110 ^{o}C to remove any residual pore water that might interfere with the measurements. Following this procedure, a uniform thin layer of anatase firmly adhering to the glass was obtained. The coated slides were then stored in a desiccator until required.

The coated glass slides were then immersed in the testing liquid in the vertical position to a depth of about 5 mm a cylindrical glass container with a gas-tight ground-glass stopper. Before the immersion, the coated slide was kept inside the container for at least one hour for the equilibration of powder with the vapor of the wicking liquid [25]. The slide was then immersed into the liquid, and the vertical movement of the liquid through the particle layer was observed. After the liquid reached to the required distance (e.g. between 1 and 3 cm), the experiment ended by removing the slide from the glass container. With low-energy liquids typically the wetting took from 3 to 10 minutes, whereas it took as long as 20 minutes with high-energy liquids. The tests were repeated at least three times in a given liquid.

The value of r^* in the Washburn equation was determined using completely spreading liquids (apolar) such as heptane, octane, decane and dodecane. In this case, it was considered that $\cos\theta=1$. For each surface, the $2\eta l^2/t$ vs. γ_L for alkanes yielded a straight line whose slope is the mean pore radius (r^*). Once the value of r^* was obtained, it was then possible to calculate the value of the contact angle for a given liquid on the anatase surface using the Washburn equation (Eq. [5.1]). In the present work, 1-bromonapthalene, water, and formamide were used as the wetting liquids for the contact angle measurements.

5.2.3.5. Microcalorimetric Measurements

Heats of immersion and adsorption measurements were conducted using a Model 3V flow microcalorimeter (FMC) from Microscal, United Kingdom. The FMC has a teflon cell fitted in a metal block that is insulated with mineral wool. A calorimeter cell, made of teflon, was placed in a metal block, which was insulated from the ambient by mineral wool. Two glass-encapsulated thermistors were placed inside the cell to monitor the changes in temperature of the sample, and two reference thermistors were placed in the metal block outside the cell. These thermistors have sensitivity capable of detecting temperature changes as low as 10^{-5} ^{o}C inside the cell. The calorimeter was calibrated by means of a calibration coil, which was placed in the sample bed. During the calibration, a known amount of electrical energy is passed through the coil in the sample bed while the solvent is being pumped through the bed. The entire unit was housed in a draft-proof enclosure to reduce the effect of temperature fluctuations in the ambient.

In each measurement, the anatase sample was dried overnight in an oven at 110 ^{o}C. A known amount (usually 0.07-0.15 gram) of the dried sample was placed in the calorimeter cell, and degassed for at least 30 minutes under vacuum (<5 mbar) at ambient temperature. The vacuum system consisted of a vacuum pump and a liquid nitrogen vapor trap. The solvent was then introduced to the calorimeter cell at a steady flow rate of 3.3 ml/h by means of a syringe micropump, and two Valco Instrument changeover valves for switching between the solvent and the solution. The heat effect was recorded by means of a strip chart recorder and a PC. After the thermal equilibrium was reached, which usually took 5 to 20 minutes, the solvent was switched over to the solvent containing adsorbate and the solution was introduced to the cell at a flow rate of 3.3 ml/h. The heat of interaction of adsorbate on the solid was also recorded using a strip chart recorder and a PC. The recorded experimental data was analyzed using the Microscal Calorimeter Digital Output-Processing System (CALDOS). This program enables the analysis of the calibration and experimental data and converts the raw downloaded data into the heat of immersion (h_i) and heat of adsorption (h_{ads}) values.

5.3. RESULTS AND DISCUSSION

5.3.1. Flotation and Selective Flocculation

In order to compare the performance of two different hydroxamate collectors (Aero 6493 and 6973), a series of batch flotation tests were conducted on the crude kaolin sample from east Georgia as a function of collector dosage. Figure 5.2 shows the results obtained with Aero 6493 at pH 9.2. As shown, as the collector addition increased from 1 lb/t to 4 lb/t, the higher TiO_2 rejections were obtained as evident from grade vs. recovery curves. At 4 lb/ton Aero 6493 dosage, TiO_2 content was reduced from 3.0% to 1.14% with a 73.2% clay recovery (or yield).

Figure 5.3 show the results obtained using Aero 6973 as the collector at pH 9.2. The trend was similar to those observed using Aero 6493 as the collector. The TiO_2 rejection increased with increasing collector addition. At 4 lb/t Aero 6973 dosage, a clay product could be obtained assaying as low as 1.05% TiO_2 with a yield of 75.4%. It has to be noted that the slurry pH of 9.0-9.5 is the optimum pH range for the removal of anatase impurities from kaolin as reported by other investigators (24, 44-45, 50-51). For this reason, the pH of the flotation pulp was kept in this range during the entire test work.

Figure 5.4 compares the results obtained with the east Georgia clay using 4 lb/t Aero 6493 and 6973 hydroxamate collectors. As shown, the results obtained using Aero 6973 are better than those obtained using Aero 6493 collector. This can be attributed to the relatively strong frothing property of Aero 6973 compared to that of Aero 6493. As mentioned earlier, the main ingredient of Aero 6493 collector is octylhydroxamic acid. It contains, however, considerable amounts of dodecanol. This long-chain alcohol was used as solvent for hydroxylamine and methyloctanoate, from which octylhydroxamic acid was formed. Hydroxamic acid (or hydroxamate) in its pure form has an excellent frothing property in addition to a collecting power for anatase and iron oxides. Although short-chain alcohols are used as frothers in flotation, long-chain alcohols whose hydrocarbon chains are longer than 8 are froth suppressors. Therefore, Aero 6493 acts as a collector with poor frothing property due to the presence of docecanol. It was expected that the frothing properties of the collector Aero 6493 would improve if a small amount of frother were added to the flotation pulp. In the present work, for better comparison no frother was used during flotation.

Because Aero 6973 contains a shorter chain alcohol (2-ethyl hexanol), it has a better frothing property than Aero 6493. Obviously, the frothing action of the Aero 6973 helped remove anatase and gave a better grade-recovery curve. The %TiO_2 was reduced to as low as 1.05 at 75.2% recovery when 4 lb/ton Aero 6973 was used.

In the present work, no bleaching tests were applied to the beneficiated clay samples. Instead, the variation of brightness as a function of TiO_2 content in the clay product was obtained from the plot given in Figure 5.5. The data given in this figure was the reproduction of the brightness measurement results from Shi et al (24), who conducted selective flocculation tests on the east Georgia clay. As a common procedure, the clay product obtained from flotation is bleached using 5.0-20.0 lb/t aluminum sulfate ($Al_2(SO_4)_3 \cdot x18H_2O$) and 5.0-10 lb/t of sodium hydrosulfite ($Na_2S_2O_4$) in a dilute sulfuric acid solution (pH 3-3.5). The brightness measurements on the bleached clay can then be done using standard techniques (TAPPI standard). As shown, in order to produce a clay product with +90% brightness it is necessary to reduce the TiO_2 content below 1.0% in the beneficiated clay. However, as the flotation results showed the minimum achievable TiO_2 content in the clay product is 1.05%. Obviously, flotation was not able to produce a clay product with GE brightness higher than 90%. Because of the ultrafine particle size, it is difficult to float anatase using conventional flotation process.

Due to the difficulties associated with the flotation technique in removing anatase impurities to the desired level from east Georgia kaolin clay, another method of upgrading kaolin, i.e., selective flocculation was tested. This method should be particularly useful for removing colored anatase impurities found in ultra-fine east Georgia clay, which did not respond well to flotation method.

A variety of commercial flocculants with different properties were employed in the selective flocculation experiments to find out the effect of molecular weight and degree of anionicity on the recoveries and TiO_2 contents in the clay product. The properties of the polymer flocculants are presented in Table 5.2. As shown in this table, the molecular weight of the polymer flocculants was in the range from 5-30 million, while the percent anionicity was in the range from 7-75%.

The results of selective flocculation tests obtained using various polymer flocculants are given in Table 5.4. All the polymer flocculants were tested at two different dosages, i.e., 62.5 and 125 g/t. As shown in Table 5.4, the best results were obtained with the medium molecular weight polymer flocculants (e.g., M.W. 10-15 million). The data given in this table also show that the polymer flocculants with 20-30% anionicity gave the best results. However, TiO_2 reduction was relatively poor when polymer flocculants with higher and lower anionicities and molecular weights were used in the selective flocculation. It is most likely that flocculants with high and low anionicities and molecular weights do not adsorb on the hydrophobic anatase particles. These findings are consistent with those reported by Shi et al (24) who conducted the selective flocculation tests on an east Georgia kaolin clay. These authors also found that the medium molecular weight and slightly anionic polymers gave the best results.

Also shown in this table are the results obtained using Nalco 9601 polymer flocculant at 25 and 45 g/t dosages. It has been experimentally observed that higher dosages of this polymer cause unrealistically higher values of slurry viscosity. At 62.5 and 125 g/t Nalco 9601 dosages, it was not possible to obtain a clear settling zone of flocculated particles because of the viscous medium. Therefore, it was decided to use this polymer at lower dosages. At 25 and 45 g/t polymer dosages, colored anatase impurities were successfully flocculated. Sharpefloc 9010 was also tested at lower dosages, i.e. 25 and 45 g/t; however, no improvement was obtained. It was concluded that Sharpefloc 9010 do not adsorb on the anatase particles at any given dosage.

The data given in Table 5.4 for various polymers was plotted as the TiO_2 content versus recovery and the results are shown in Figure 5.6. As the figure shows, Nalco 9806, Nalco 9823, and Sharpefloc 9131 polymer flocculants gave the best grade vs. yield values. It should be noted that these three polymers are classified as the medium molecular weight and slightly anionic flocculants. As it can also be seen in Table 5.4 and Figure 5.6, the lowest TiO_2 content in the clay product was obtained using Sharpefloc 9131 flocculant. At 125 g/t Sharpefloc 9131 addition, the %TiO_2 was reduced to 0.44% with a 64.5% clay recovery. Because of the lowest value of TiO_2 in the clay product was obtained using Sharpefloc 9131, it was selected as the flocculant polymer for the rest of the selective flocculation tests.

Table 5.5 shows the effect of hydroxamate concentration on grades and recoveries of the clay product in the selective flocculation of east Georgia kaolin. In these tests, Sharpefloc 9131 was used in the amount of 125 g/t for flocculating anatase impurities. Since Aero 6973 gave better results in the flotation tests, initially the clay slurry was conditioned with this reagent. However, problems occurred after addition of the polymer flocculant due to the excessive frothing properties of the reagent Aero 6973. A steady froth layer formed at the top of the dispersed clay zone. Therefore, it was decided to use only Aero 6493 for conditioning the clay in these series of experiments. It should be mentioned that relatively poor frothing property of Aero 6493 due to the presence of dodecanol was used advantageously in the selective flocculation tests.

As shown in Table 5.5, as the hydroxamate concentration is increased from 1 to 4 lb/t, the selectivity is increased dramatically as indicated by the significant reduction in TiO_2 content. For example, TiO_2 content decreased from 1.32% at 2 lb/t Aero 6493 to 0.44% at 4 lb/t Aero 6493 concentration. The results suggest that the selectivity of the flocculation process is strongly dependent on the amount of conditioning agent (hydroxamate) used and, hence, the degree of surface hydrophobicity of the mineral (e.g. anatase) particles to be flocculated.

The results reported here are in excellent agreement with those reported by Xu (20) who conducted the coagulation experiments with natural (untreated) and methylated silica samples. This author reported that the natural hydrophilic silica does not coagulate at any pH (pH from 2.8 to 9), while the coagulation occurred with the methylated silica over a wide pH range up to 10.7. He correlated the coagulation efficiencies of natural and methylated silica surfaces with zeta potentials, contact angle values and the contributions of polar (γ_S^p) and non-polar (γ_S^d) surface free energy components to the work of adhesion (W_{ad}). The author found that the strong hydrophobic attraction force is induced due to the increased hydrophobicity of the silica surface upon methylation as evidenced by contact angle measurements.

Xu (20) and Honaker (22) demonstrated the role of hydrophobic interactions in the coagulation of strongly hydrophobic colloidal particles. These studies showed that hydrophobic coal particles coagulated spontaneously around pH 7-9 due to the hydrophobic interaction. Honaker (22) also showed that the efficiency of the selective coagulation process is dependent on the surface hydrophobicity of coal, i.e., the coagulation efficiency increases with increasing surface hydrophobicity.

Also shown in Table 5.5 for comparison are grades and recoveries obtained in the absence of hydroxamate and polymer flocculant. In this test, the crude clay was dispersed at 60% solids with 6 lb/t sodium silicate, 1 lb/t sodium polyacrylate and 3 lb/t sodium carbonate using an Osterizer blender at the highest speed for 10 minutes. The pH of the dispersed slurry was 9.25. After dispersion, the clay slip was diluted to 22.5% solids and allowed to settle at 7.5 minutes per inch depth of slurry. As the Table 5.4 shows, there is no significant reduction in the TiO_2 content with the settling of the suspension in the absence of hydroxamate and a flocculant. Although 10.6% of the material was obtained as the settled product, the TiO_2 content in the dispersed clay (unsettled zone) was only reduced to 2.85%.

Table 5.5 also compares the grades and recoveries obtained using only polymer flocculant with those of using both conditioner (hydroxamate) and flocculant in the selective flocculation experiments. The same procedure was employed for dispersing the feed clay as described above. The crude kaolin was blunged at 60% solids with 6 lb/t sodium silicate, 1 lb/t sodium polyacrylate and 3 lb/t sodium carbonate for 10 minutes using an Osterizer blender at the highest speed. The pH of the dispersed slurry was 9.25. After blunging, the slurry was diluted to 22.5% solids and a polymer flocculant (Sharpefloc 9131) was added to promote flocculation of anatase impurities. The slurry was settled at 7.5 minutes per inch. In the absence of hydroxamate to condition the kaolin slurry, the TiO_2 content was reduced from 3.0% to only 2.71% despite loosing

26.8% of the feed material, after addition of 125 g/t Sharpefloc 9131. These results indicate that the flocculation is not selective when no hydroxamate was used as the conditioning agent.

The results given in Table 5.5 shows that it is possible to produce a clay product with 93-93.5% GE brightness when using 4 lb/t Aero 6493 as the conditioning reagent and 125 g/t Sharpefloc 9131 as the polymer flocculant. The brightness value was predicted by extrapolating the data given in Figure 5.5, i.e., TiO_2 content (0.44%) in the clay product vs. % brightness. Obviously, obtaining a clay product with 93-93.5% brightness with a reasonably high recovery (64.5%) is not only profitable for the clay producer, but also technically beneficial for the final user (e.g. paper manufacturers etc.). The results given in Table 5.5 suggest also that even at 2.5-3 lb/t hydroxamate dosages, a clay product with +90% brightness can be obtained using the selective flocculation method.

The dependence of grades (TiO_2) and recoveries on the polymer concentration for kaolin clay is presented in Figure 5.7. The results reveal that increasing the polymer concentration causes a significant reduction in the TiO_2 content, but with the expense of clay recovery. At 25 g/t of Sharpefloc 9131 concentration, the TiO_2 content was reduced from 3.0% to 0.75% with 75.5% recovery. At 125 g/t polymer concentration, a clay product containing 0.44% TiO_2 with 64.5% recovery could be produced. As shown, as the flocculant addition is increased from 25 g/t to 125 g/t, the selectivity of the process deteriorates and clay particles are also settled by entrapping within the anatase particles. Nevertheless, it is possible to produce a clay product with +90% GE brightness by adding a polymer flocculant in the range from 25-125 g/t. As the polymer dosage increases, the brightness of the clay product increases, accordingly. Figure 5.8 shows the selective flocculation tests conducted in the graduated cylinders as a function of polymer concentration. As shown, as the concentration of the polymer flocculant (Sharpefloc 9131) increases from 25 g/t (far left in Figure 5.8) to 125 g/t (far right in Figure 5.8), the volume of settled material also increases. The volume of the settled material was 15-16% at 25 g/t flocculant addition, where as it increased to 20-22% at 125 g/t flocculant addition.

Figure 5.9 compares the flotation and selective flocculation methods in terms of grade vs. recovery curves obtained using 4 lb/t Aero 6493 in the experiments. The results given in this figure clearly demonstrates the superiority of selective flocculation process over flotation for treating ultrafine east Georgia kaolin clay. It can be estimated from Figure 5.9 that the use of selective flocculation process gives clay yields at least 12% higher than the case of using flotation at the TiO_2 contents lower than 1.0%. The results also indicate that the selective flocculation process was able to produce high-brightness clay with GE brightness well over 90%, while the flotation method did not. Thus, the limitations associated with the flotation for removing very fine anatase impurities from kaolin clay could be overcome by employing selective flocculation process developed in the present work.

5.3.2. Contact Angles

The results given in the foregoing section reveal that the efficiency of anatase removal from kaolin clay using both flotation and selective flocculation techniques is strictly dependent on the amount of conditioning reagent (hydroxamate) used. The results showed that the reduction of TiO_2 from kaolin clay increased with increasing Aero 6493 concentrations. Therefore, a series of contact angle and microcalorimetric measurements were conducted on the pure anatase surfaces treated with varying amounts of Aero 6493 to determine the changes in the surface hydrophobicity and surface free energies of anatase powders and to explore the origin of the molecular interaction between two interacting surfaces.

The contact angles of anatase samples treated with varying amounts of Aero 6493 were determined using the thin layer wicking technique. Linear plots of l^2 *vs.* t were obtained from the thin layer wicking experiments for all the anatase powders studied. The plots of l^2 vs. t for various wicking liquids in the thin layer wicking measurements obtained using 4 lb/t Aero 6493 for the surface treatment are shown in Figure 5.10. The linear lines obtained for alkanes (e.g. heptane, octane, decane and dodecane) were used to estimate the value of mean pore radius (r^*) in the Washburn equation (Eq. [5.1]), while linear plots obtained for the other wetting liquids (e.g. 1-bromonaphthalene, water and formamide) were used to calculate the contact angles. A sample plot for determining r^* using alkanes in the thin layer wicking experiments is given in Figure 5.11 for anatase sample treated with 4 lb/t Aero 6493 hydroxamate. As shown, the plot of $2\eta l^2/t$ vs. γ_L yields a straight line whose slope is found to be r^* [25].

The values of r^* for anatase powders treated with varying amounts of Aero 6493 are given in Table 5.6. As shown, the value of r^* determined from thin layer wicking measurements increases with increasing reagent concentrations used for the surface treatment. For example, the value of r^* is 133.6 nm for the anatase powder treated with 2 lb/t Aero 6493, whereas it is 163.2 nm for the anatase surface treated with 4 lb/t Aero 6493.

The advancing contact angles of various liquids on the surface treated anatase samples obtained from the thin layer wicking measurements are presented in Table 5.7. The results given in this table show that as the concentration of hydroxamate used for the surface treatment increases from 2 lb/t to 4 lb/t, the values of advancing water contact angles on the anatase samples increase and, so does the surface hydrophobicity. The advancing water contact angle on the anatase surface treated with 2 lb/t Aero 6493 was 75.9^o. However, at 4 lb/t Aero 6493 concentration, the water contact angle of anatase was increased up to 87.5^o. A similar contact angle trend was obtained for the other test liquids, e.g., 1-bromonaphthalene and formamide.

The values of water contact angle reported here explain why the best results were obtained from both flotation and selective flocculation tests at 4 lb/t hydroxamate dosage. The surface of the anatase becomes very hydrophobic at 4 lb/t Aero 6493 addition. Therefore, it is easy to remove such a hydrophobic mineral surface from completely hydrophilic kaolin clay by using selective flocculation technique. It should also be easy to remove such a hydrophobic surface using flotation method; however, the flotation has limitations because of the ultrafine particle size distribution of anatase, i.e., 65-75% of the particles finer than 0.5 μm (50). It has been shown by many investigators that in a flotation system, the probability of attachment of colloidal size particles to the air bubbles is substantially lower compared to those of intermediate size range, i.e., 10-74 μm (52-

55). That is basically the main reason why flotation was not able to remove anatase from kaolin clay despite such a high water contact angle exhibited by this surface.

5.3.3. Microcalorimetry

Table 5.8 shows the results of the heats of immersion measurements conducted on as received anatase and on the anatase samples treated with varying amounts of Aero 6493 reagent using various liquids in the experiments. Also shown in this table are the values of heat of displacement enthalpies of water on the anatase surfaces from n-heptane.

It can be seen from Table 5.7 that the values of heat of immersion enthalpies for n-heptane, which is an apolar liquid, were in the range from 67.4-94.6 mJ/m^2. As shown, the highest value was obtained with the untreated anatase surface, and the heat of immersion enthalpies of treated samples gradually decreased as a function of increasing reagent dosage used for the surface treatment. It has to be noted that the value of immersion enthalpy reported here for the untreated anatase surface is in agreement with those reported by other investigators (20) for n-heptane. Fowkes (5) reported a heat of immersion enthalpy value of 97 mJ/m^2 for anatase in heptane, while Suda (56) reported a value of 100 mJ/m^2 on a commercial anatase pigment.

As shown in Table 5.8, the lowest value of the heat of immersion enthalpy in n-heptane was obtained for the anatase surface treated with 4 lb/t Aero 6493. Since the interaction between anatase surface and n-heptane is only due to the Lifshitz-van der Waals interactions, it can be expected that the apolar surface free energy component (γ_S^{LW}) is lower on the treated anatase surfaces compared to that on the untreated anatase surface. Based on the values of the immersion enthalpies in n-heptane, the lowest value of γ_S^{LW} would be on the anatase surface treated with 4 lb/t Aero 6493. However, as shown in Chapters 2 and 3, any reduction in the value of γ_S^{LW} was a direct consequence of a reduction in the value of the total surface free energy (γ_S) on the solid surface. Therefore, the lower the heat of immersion value in n-heptane, the lower the γ_S on a solid surface would be.

To verify the heat of immersion enthalpies obtained with n-heptane, the heat of immersion enthalpies of anatase samples in a high surface tension apolar liquid, methylene iodide, have been determined. The experimental results are given in Table 5.8. As shown, similar to n-heptane results, the values of immersion enthalpies of anatase samples in methylene iodide decreased with increasing reagent dosage used for the surface treatment. The values of immersion enthalpies in methylene iodide, however, were smaller for all anatase surfaces compared to those obtained with n-heptane. Again, the lowest value of immersion enthalpy in methylene iodide was obtained for the anatase surface treated with 4 lb/t Aero 6493. The results confirms that the Lifshitz-van der Waals component (γ_S^{LW}) and total surface free energy (γ_S) decreases on the anatase surface as the amount of Aero 6493 increases from 2 lb/t to 4 lb/t for the surface treatment.

As shown in Table 5.8, a similar trend can also be observed for the reagent dosage used in the surface treatment and the heat of immersion enthalpies obtained using formamide. The heat of immersion enthalpy was the highest with the untreated anatase sample (184.6 mJ/m^2), and the lowest with the anatase surface treated with 4 lb/t Aero 6493 (115.1 mJ/m^2). As formamide is known to be the most basic polar liquid, the results indicate that the surface basicity of anatase decreases with increasing reagent dosage employed for the surface treatment. It has to be pointed out that the values of immersion enthalpies obtained at 2 lb/t Aero 6493 and 4 lb/t for surface treatment are close to each other, even though there is a slight decrease in the measured value. Probably, small changes in the surface acidity/basicity properties are in effect beyond 2 lb/t Aero 6493 addition.

The heats of n-heptane displacement by water on treated anatase surfaces are shown in Figure 5.12. For plotting, the values were taken from Table 5.8. As shown in Figure 5.12, the heat of n-heptane displacement by water decreases with increasing hydroxamate concentration used for the surface treatment of anatase. Note that the heat effect measured as such represents the enthalpy change in displacement of n-heptane by water primarily from the polar sites of the anatase surfaces. Thus, the decrease in the value of the displacement enthalpy of water from heptane suggests that the number of polar surface sites decreased on the anatase surface with increasing reagent dosage. In other words, the surface hydrophobicity increased with increasing hydroxamate dosage used for the surface treatment. The heat of displacement enthalpies of water from n-heptane correlates well with the contact angle results.

Table 5.9 presents the values of the heats of adsorption (-ΔH_{ads}) of butanol from n-heptane on untreated and treated anatase samples with varying hydrophobicities. Also shown in this table is the heat of adsorption of butanol on silica (197 mJ/m^2), as reported by Malandrini, et al. (32). Knowing that silica is 100% hydrophilic, which is responsible for the high heat of adsorption, one can determine the percentage of hydrophilic surface by dividing the heat effect (-ΔH_{ads}) measured for each anatase surface with the heat of adsorption of butanol on silica (197 mJ/m^2) from n-heptane. Table 5.9 lists the values of percent hydrophilic surface and the total and specific hydrophilic surface area of anatase samples. Figure 5.13 shows the heat of butanol adsorption on anatase surfaces from n-heptane, plotted as a function of Aero 6493 concentration.

It can be seen from Table 5.9 and Figure 5.13 that the heat of butanol adsorption, and hence the percentage of hydrophilic surface on anatase, decreases with increasing hydroxamate reagent used for the surface treatment, suggesting an increase in the surface hydrophobicity. As shown, 75.4% of the surface is hydrophilic on the untreated surface, while 29.8% of the surface is hydrophilic on the anatase surface treated with 4 lb/t Aero 6493. These results suggest that with increased hydroxamate adsorption, the anatase surface changes from one bearing polar groups that can readily participate in hydrogen bonding with water molecules to a hydrocarbon surface (exposing its hydrocarbon tail to the water phase) that show little tendency to interact with water molecules. The results of heat of adsorption enthalpies of butanol from n-heptane on anatase samples are consistent with those obtained from contact angle measurements and heat of n-heptane displacement by water as reported earlier.

5.3.4. Surface Free Energy

It is well documented in literature that the solid/liquid interfacial tension is the most important parameter in flotation. Based on experimental results presented in this work, it can be predicted that it is also a crucially important parameter in selective flocculation. A hydrophilic mineral, e.g. anatase, can only be floated or flocculated after conditioning with hydrophobic reagent (e.g., surfactant) molecules adsorb at the surface. As a result of the surfactant adsorption, the surface free energy of the solid (γ_S) is reduced. Such a decrease is necessary for bubble-particle adhesion in flotation and particle aggregation in selective flocculation to occur. Therefore, it is necessary to determine the changes in the surface free energy of solid taking place upon adsorption of hydrophobic reagent molecules.

In the present work, the changes in the values of the Lifshitz-van der Waals (γ_S^{LW}), Lewis electron donor (γ_S^-) and electron acceptor (γ_S^+) components of the surface free energy on the anatase samples upon surface treatment with varying amounts of hydroxamate reagent have been calculated using Eq. [5.9]. In using Eq. [5.9], the contact angle values for different liquids were taken from Table 5.7. As discussed in previous chapters, the calculation requires a set of three contact angles for three different liquids, along with their surface tension components. The values of γ_L^{LW}, γ_L^+, and γ_L^- for liquids were taken from literature (See Table 5.3). For a given surface, the contact angles measured using three liquids -1-bromonaphthalene; water and formamide- were used for calculating the surface free energy components of anatase samples. The results are shown in Table 5.10. Also shown in this table are the values of γ_S^{AB} ($=2\sqrt{\gamma_S^+\gamma_S^-}$) and γ_S calculated using Eq. [5.11] from the values of the surface free energy components. To better visualize the correlation between the reagent dosage and the various surface free energy parameters, the results given in Table 5.10 are illustrated graphically in Figure 5.14.

Table 5.10 and Figure 5.14 show that the values of both the γ_S^{LW} and γ_S^{AB} components decrease as the amount of Aero 6493 increased for the surface treatment. As shown, the γ_S^{LW} for the anatase sample treated with 2 lb/t Aero 6493 was 21.4 mJ/m^2, while it decreased to 16.9 mJ/m^2 on the sample treated with 4 lb/t Aero 6493. Similarly, the value of γ_S^{AB} decreased from 3.8 mJ/m^2 on the anatase sample treated with 2 lb/t Aero 6493 to 2.9 mJ/m^2 on the sample treated with 4 lb/t Aero 6493.

Note that the γ_S^{LW} values reported here for the surface treated anatase samples appear to be substantially lower than those reported by Fowkes (5) for the untreated anatase surface. This author found a value of 92 mJ/m^2 for γ_S^{LW} (or γ_S^d) on the anatase surface by conducting adsorption and microcalorimetric measurements. Thus, the results presented in Table 5.9 and Figure 5.14 indicates that there is a substantial reduction in the value of γ_S^{LW} on anatase surface due to the surface treatment. Most likely, the polar (acid-base, γ_S^{AB}) component of the surface free energy of anatase decreases with increasing degree of hydrophobicity due to the substitution of surface polar groups by non-polar groups that carry low or no permanent dipole. Similarly, the observed reduction in the value of γ_S^{LW} with increased surface hydrophobicity may be due to the replacement of easily polarizable high surface energy groups by non-polarizable low surface energy groups.

It should also be noted here that a similar trend have been observed by the other investigators (16-17, 21). Chibowski and Hoylsz (17) found a drastic reduction in the polar component of quartz surface free energy from 115 mJ/m^2 (untreated surface) to 7.2 mJ/m^2 at only 0.25 of a monolayer of dodecylamine hydrochloride (DAH$^+$). The authors also showed that at one monolayer coverage, the flotation recovery was at maximum and the polar interaction at the quartz-water interface was non-existent. The London-van der Waals dispersion component (γ_S^{LW}) was also measured and it initially changed from 76 mJ/m^2 (untreated quartz) to 28.2 mJ/m^2 at 0.25 monolayer of DAH$^+$. Similar reductions in the values both of γ_S^{LW} and γ_S^{AB} were obtained by Yoon and Yordan (16), who treated the fused silica plates with varying amounts of trimethyl chlorosilane (TMCS) or dodecylamine hydrochloride (DAHCl).

Also shown in Table 5.10 and Figure 5.14 are the values of γ_S^- and γ_S^+. As shown, the values of γ_S^- component decrease as the amount of Aero 6493 increased from 2 lb/t to 4 lb/t for the surface treatment, while the value of γ_S^+ remains constant. The value of γ_S^-, however, is much higher than the value of γ_S^+ in the entire range of hydroxamate concentration studied. For example, at 2 lb/t Aero 6493 concentration, $\gamma_S^- = 18.1$ mJ/m^2 and $\gamma_S^+ = 0.2$ mJ/m^2, whereas at 4 lb/t reagent concentration γ_S^- is 10.8 mJ/m^2 and γ_S^+ is 0.2 mJ/m^2. The trend obtained here agrees well with those reported in literature for the surface treated mineral samples (19, 57-59). These findings suggest that the surface treated anatase surface is essentially more basic than acidic. The surface basicity of anatase should most likely be attributed to the basic oxygen molecule that is exposed as a result of adsorbed layer of water molecules on the surface of anatase (19, 57-58).

Table 5.10 and Figure 5.14 also gives the values of γ_S. As shown, the value of γ_S decreased as the amount of Aero 6493 increased from 2 lb/t to 4 lb/t for the surface treatment. For example, γ_S changes from 25.2 mJ/m^2 at 2 lb/t Aero 6493 to 19.8 mJ/m^2 at 4 lb/t Aero 6493 dosage. It has to be noted that the reduction in the value of γ_S is achieved due to the decreases in the values of both the γ_S^{LW} and γ_S^{AB} components. This finding suggests that the value of γ_S becomes smaller as the surface hydrophobicity of solid increases.

Furthermore, the results presented in this chapter and in Chapter 4 suggest that the value of heat of butanol adsorption on solid surfaces from n-heptane obtained from microcalorimetric measurements is dependent on the surface hydrophobicity (i.e., θ_{adv}). From this standpoint, a relationship was established between advancing water contact angles measured using the thin layer wicking technique and, the percentage of hydrophilic surface obtained from microcalorimetric measurements and the surface free energy parameters of anatase samples treated with varying amounts of hydroxamate reagent. The results are summarized in Figure 5.15, where the values of θ_{adv} were obtained from Table 5.6, the values of percent hydrophilicity of anatase surfaces were taken from Table 5.8, and the values of γ_S, γ_S^{LW}, γ_S^-, γ_S^+ and γ_S^{AB} were taken from Table 5.9.

According to Figure 5.15, the percentage of hydrophilic surface of anatase decreases as θ_{adv} increases. It should be noted that there is a very good correlation between the surface free energy parameters and the % hydrophilic surface on the anatase surfaces. Note also that an increase in the value of advancing water contact angle is achieved primarily due to an increase in the adsorption density of the hydroxamate molecules on anatase surface.

Figure 5.15 also suggest that an increase in the value of θ_{adv} with increasing hydrophobicity of anatase is achieved due to the reduction in the values of both γ_S^{LW} and γ_S^{AB}, hence, a decrease in the value of γ_S. The values of γ_S^{LW} and γ_S^{AB} on an initially hydrophilic surface decrease with increasing surfactant (hydroxamate) concentration and a hydrophobic solid is obtained. For example, the γ_S^{LW} was 21.4 mJ/m^2 at θ_{adv} =75.9^o and it decreased to a value of 16.9 mJ/m^2 at θ_{adv} =87.7^o. On the other hand, the decrease in the value of γ_S^{AB} is smaller compared to that of γ_S^{LW}. The trend obtained here is very similar with those reported by Pazhianur (19), who treated fumed silica plates and silica powders with varying amounts of OTS. He obtained a similar plot except that instead of % hydrophilicity of surface determined from microcalorimetric measurements in the present work, he used the values of hydrophobicity constant (K) that are obtained from direct force measurements for each methylated silica surface.

Pazhianur (19) showed that at θ_{adv} =109°, the acid-base surface free energy component (γ_S^{AB}) on methylated silica surface was non-existent. Thus, the existence of γ_S^{AB} (2.9 mJ/m^2) on surface treated anatase surface at θ_{adv}=87.5° obtained in the present work is in agreement with what has been published in literature. Despite the presence of γ_S^{AB} on the treated anatase surface at θ_{adv}=87.5°, it was successfully removed from kaolin clay using selective flocculation technique.

One of the most important aspect of knowing the surface free energy and its parameters on a solid surface is that it gives a possibility in estimating the interfacial surface free energy of two interacting surfaces and, hence, the Gibbs surface free energy change upon interaction in a liquid medium (aqueous or non-aqueous). Using the values of Lifshitz-van der Waals and Lewis acid-base components of surface free energy for anatase samples and water, the change in the Gibbs free energy can be calculated between two interacting anatase particles in water as a function of advancing water contact angle from Van Oss's approach shown below.

According to Van Oss et al. (41, 60-61), the free energy (ΔG_{131}) of interaction between two identical entities 1 (particles, biopolymer, molecules etc.) immersed in a polar liquid 3 can be calculated from:

$$\Delta G_{131} = -2\left[\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_3^{LW}}\right]^2 - 4\left[\sqrt{\gamma_1^+\gamma_1^-} + \sqrt{\gamma_3^+\gamma_3^-} - \sqrt{\gamma_1^+\gamma_3^-} + \sqrt{\gamma_1^-\gamma_3^+}\right] \qquad [5.12]$$

Thus, introducing into Eq. [5.12] the determined values of the Lifshitz-van der Waals component, electron-acceptor and electron-donor parameters of anatase samples treated with varying amounts of Aero 6493, the Gibbs free energy of interactions (ΔG_{131}) in the anatase-water-anatase system was calculated. The results are presented in Table

5.11. Also included in this table are the values of water contact angles for anatase samples obtained from thin layer wicking measurements. As shown, the calculated values of ΔG_{131} are negative for all the surface treated anatase powders studied. The negative value of ΔG_{131} obtained here is, therefore, an indication of a net attraction between anatase particles in water. Thus, a spontaneous aggregation of the anatase particles in water should be expected at any given hydroxamate concentration used here for the surface treatment.

As shown in Table 5.11, however, the negative value of ΔG_{131} increases with increasing reagent dosage used for the surface treatment. For example, the Gibbs free energy of interaction is –14.65 mJ/m^2 at 2 lb/t 6493 addition, whereas it becomes –33.09 mJ/m^2 at 4 lb/t Aero 6493. Comparing these two values, the Gibbs free energy of interaction becomes more than 2 times favorable when using 4 lb/t Aero 6493 compared to using 2 lb/t Aero 6493 in flotation. The efficiency of the flotation process for removing anatase from kaolin clay, therefore, increases with increasing hydroxamate dosage employed to condition initially hydrophilic anatase surface.

A more fundamental insight into the flotation process may be obtained by examining the relationship between θ_{adv} and, the Gibbs free energy of interaction (ΔG_{131}) and surface free energy components of anatase surfaces, i.e., γ_S^{LW}, γ_S^-, γ_S^+, γ_S^{AB} and γ_S. Therefore, θ_{adv} values have been plotted against $-\Delta G_{131}$ and surface free energy components of anatase samples, as shown in Figure 5.16. It is interesting to see that as the contact angle value increases, the value of $-\Delta G_{131}$ also increases in a linear fashion. On the other hand, the value of γ_S and its components (γ_S^{LW} and γ_S^{AB}) decreases with increasing θ_{adv} values. Since the value of $-\Delta G_{131}$ is a measure of interaction strength between two solid particles suspended in water, an increase in the magnitude of the $-\Delta G_{131}$ as a function of increasing θ_{adv} is indicative of increased aggregation efficiency of two interacting anatase particles. This means that the anatase particles become larger by adding hydroxamate as the conditioning reagent during conditioning stage. As a result, the probability of bubble-particle attachment significantly enhances and the separation efficiency of flotation increases.

Although the Gibbs free energy of interaction between two interacting anatase particles (ΔG_{131}) is sufficient to explain the efficiency of flotation process, the interpretation of selective flocculation results requires the knowledge of the Gibbs free energy of interaction between treated anatase 1, and polymer flocculant 2, immersed in water (ΔG_{132}). The ΔG_{132} can be calculated using (41):

$$\Delta G_{132} = 2\begin{bmatrix} \sqrt{\gamma_1^{LW}\gamma_3^{LW}} + \sqrt{\gamma_2^{LW}\gamma_3^{LW}} - \sqrt{\gamma_1^{LW}\gamma_2^{LW}} - \gamma_3^{LW} \\ \sqrt{\gamma_3^{+}}\left(\sqrt{\gamma_1^{-}} + \sqrt{\gamma_2^{-}} - \sqrt{\gamma_3^{-}}\right) + \sqrt{\gamma_3^{-}}\left(\sqrt{\gamma_1^{+}} + \sqrt{\gamma_2^{+}} - \sqrt{\gamma_3^{+}}\right) \\ -\sqrt{\gamma_1^{+}\gamma_2^{-}} - \sqrt{\gamma_1^{-}\gamma_2^{+}} \end{bmatrix} \qquad [5.13]$$

Eq. [5.13] suggests that it is necessary to determine the surface free energy components of treated anatase, 1 and polymer flocculant, 2. Eq. [5.13] suggests also that it is necessary to know the surface free energy parameters of water, 3. For the calculation of ΔG_{132}, the surface free energy components of anatase given in Table 5.10 can be used. The surface free energy components of water can be taken from the literature (Table 2.1). However, in the present work, the surface free energy parameters of polymer flocculant have not been determined. Therefore, it was not possible to obtain the values of ΔG_{132} as a function of hydroxamate dosage used for the surface treatment of anatase.

Since there is no data regarding the surface free energy components of polymer flocculant, it is difficult to predict whether the interaction between polymer and anatase surface is through hydrophobic or acid-base interactions. However, it can be suspected that as the surface of anatase becomes more hydrophobic by surface treatment, the hydrophobic moiety of polymer may adsorb on the surface treated anatase. Although the polymer is hydrophilic, some part of it might be hydrophobic. Therefore, it should adsorb on the treated anatase surface through hydrophobic interaction.

It is also possible that the interaction between the polymer flocculant and anatase surface is governed by acid-base interactions. As the results given in Table 5.10 show, the basic component of anatase surface (γ_S^-) decreases with increasing hydroxamate dosage, while the acidic component (γ_S^+) remains constant. On the other hand, the polymer adsorption and, hence, the separation efficiency of selective flocculation process increases with decreasing surface basicity of anatase. The results suggest that the polymer flocculant must be basic in order to adsorb onto the anatase surface that becomes less basic as a result of increasing hydroxamate dosage used for the surface treatment. In this case, acid-base interactions may play an essential role for the adsorption of polymer flocculant onto the surface of treated anatase. The origin of the molecular interaction between polymer and treated anatase surface must be validated by experimental studies using variety of techniques, i.e., FTIR, XPS, AFM, UV, microcalorimeter etc.

5.4. CONCLUSIONS

The following conclusions can be drawn based on the experimental results obtained in this work:

1. A series of flotation tests were conducted on east Gerogia kaolin clay showed that the hydroxamate flotation can reduce the TiO_2 content from 3.0% to less than 1.05% with 75% yield. However, such a reduction in TiO_2 content was not able to increase the brightness of clay product above 90%.

2. Similar to flotation, the selective flocculation process uses the differences between the hydrophobicity of minerals to aggregate selectively and separate hydrophobic particles from dispersed hydrophilic particles. In the present work, hydroxamate reagents were employed, which were also used in the flotation experiments, to increase the selectivity and make the anatase particles more hydrophobic. Various promoters (polymer flocculants) were utilized in the selective flocculation tests to selectively adsorb on the hydrophobic anatase particles and to flocculate them.

3. Experimental results showed that the solids, agitation speed, pH, the type and amount of dispersing reagents and the collector concentration during blunging and conditioning are vitally important for a successful selective flocculation process. The

type and amount of polymer flocculant added has also affected the overall efficiency of the process. The anionic polymer flocculants with medium molecular weight (M.W. ≈10-15 million) and with percent anionicity in the range from 20-30% gave the best results, while those of lower and higher molecular weight and/or anionic polymers did not flocculate the discoloring anatase (TiO_2) particles selectively from kaolin clay.

4. The selective flocculation process has been successfully applied toward the upgrading of ultrafine east Georgia clay. Selective flocculation tests conducted on a run-of-the-mine east Georgia clay containing 3.0% TiO_2 showed that %TiO_2 can be reduced to 0.44% with a recovery of 64.5%. This corresponds to 93.0-93.5% brightness in the bleached clay product. It is also possible to produce a clay product with +90% brightness with recoveries higher than 80% using the selective flocculation process developed in the present work. This process can also be used for treating many other problematic clays, i.e. hard clays, that can be found in Brazil, Australia etc.

5. It has been shown that the adsorption of surfactant molecules at the solid/liquid interface reduces both the London-van der Waals (γ_S^{LW}) and Lewis acid-base (γ_S^{AB}) components of the surface free energy (γ_S) of the solid investigated.

6. The separation efficiency of flotation and selective flocculation processes is strictly dependent on the surface hydrophobicity and the surface free energies of solid particles. As the surface of the mineral becomes more hydrophobic, the Gibbs free energy of interaction between two hydrophobic particles in aqueous medium increases. This initial interaction between particles due to the hydrophobic forces facilitates the bubble-particle interaction during flotation. A more detailed study is necessary to reveal adsorption mechanism of the polymer onto the anatase and the origin of the molecular interaction between the treated anatase surface.

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Table 5.1 Specific surface areas of anatase sample treated with varying amounts of Aero 6493

Amount of Aero 6493	Surface Area (m^2/g)
0	8.45
2 lb/t	6.50
3 lb/t	6.45
4 lb/t	6.38

Table 5.2. The properties of polymer flocculants used in the selective flocculation tests

Polymer Flocculant		Molecular weight	% Anionicity	Form
Nalco	7875	48 RSV (high) (≈30 million)	75	Liquid
"	8872	23 RSV (low) (<10 million)	7	Liquid
"	9806	33 RSV (medium) (>10 million)	29	Liquid
"	9601	Medium (>10 million)	25	Powder
"	9823	40 RSV (medium) (>10 million)	20	Liquid
"	9825	44 RSV (high) (>20 million)	40	Liquid
Sharpefloc	9010	low	very low (<20)	Powder
"	9131	medium	slightly (20-30)	Powder
"	9341	medium	slightly (20-30)	Powder
"	9541	high	highly	Powder
"	9770	high	highly	Powder

Table 5.3. Values of the surface tension components (in mJ /m^2) and of the viscosities (in poise) of the liquids used in the microcalorimetric and contact angle measurements

Liquid	γ_L	γ_L^{LW}	γ_L^{AB}	γ_L^{+}	γ_L^{-}	η
Heptane	20.3	20.3	0	0	0	0.00409
Octane	21.6	21.6	0	0	0	0.00542
Decane	23.8	23.8	0	0	0	0.00907
Dodecane	25.35	25.35	0	0	0	0.01493
1-Bromonaphthalene	44.4	44.4	0	0	0	0.0489
Methylene iodide	50.8	50.8	0	0	0	0.028
Formamide	58.0	39.0	19.0	2.28	39.6	0.0455
Water	72.8	21.8	51.0	25.5	25.5	0.010

Table 5.4. The results of selective flocculation testing conducted on east Georgia kaolin using various polymer flocculants at two different dosages

Polymer Flocculant		62.5 g/ton		125 g/ton	
		Clay Product % Yield	% TiO_2 in Clay Product	Clay Product % Yield	% TiO_2 in Clay Product
Nalco	7875	77.5	0.93	72.1	0.90
"	8872	61.4	0.80	53.9	0.55
"	9806	72.3	0.54	68.2	0.48
"	9601(*)	77.3	0.83	74.4	0.76
"	9823	72.3	0.55	71.3	0.49
"	9825	72.1	0.58	61.2	0.52
Sharpefloc	9010	90.1	2.83	89.7	2.75
"	9131	69.0	0.50	64.5	0.44
"	9341	68.4	0.64	61.4	0.61
"	9541	77.6	1.32	73.9	1.24
"	9770	74.9	1.19	71.3	1.15

(*) *Employed at 25 and 45 g/t dosages.*

Table 5.5. Effect of hydroxamate dosage on the selective flocculation of east Georgia kaolin clay

Hydroxamate (Aero 6493) (lb/t)	Polymer Flocculant (Sharpefloc 9131) (g/t)	Clay Product (% Yield)	% TiO_2 in Clay
0	0	89.4	2.85
0	125	73.2	2.71
1	125	69.2	2.23
2	125	68.5	1.32
3	125	67.7	0.79
4	125	64.5	0.44

Table 5.6. Average pore size (r^*) of TiO_2 samples treated with varying amounts of Aero 6493 determined by thin layer wicking (at 20±2 °C)

Reagent Dosage	r^* (nm)
2 lb/t	133.6
3 lb/t	151.0
4 lb/t	163.2

Table 5.7. The values of contact angles for various liquids on TiO_2 surface treated with varying amounts of Aero 6493 measured using thin layer wicking technique

Liquid	Advancing Contact Angle (θ_{adv})		
	2 lb/t Aero 6493	3 lb/t Aero 6493	4 lb/t Aero 6493
1-Bromonaphthalene	67.1±1.6	72.2±1.7	76.4±1.5
Formamide	71.8±1.4	76.4±1.8	81.4±1.7
Water	75.9±1.3	81.4±1.2	87.7±1.0

Table 5.8. The heat of immersion enthalpies of various liquids on TiO_2 surfaces treated with varying amounts of Aero 6493 (20±2 °C)

Solvent	$-\Delta H_i$, mJ/m^2			
	As received	2 lb/t Aero 6493	3 lb/t Aero 6493	4 lb/t Aero 6493
n-Heptane	94.6	77.5	72.1	67.4
Methylene Iodide	78.8	62.1	55.7	51.8
Water$^{(*)}$	200.8	152.2	138.3	125.5
Formamide	184.6	136.3	125.7	115.1

(*) Heat of displacement enthalpy of water on TiO_2 surface from n-heptane

Table 5.9. % Hydrophilic surface and specific hydrophilic surface area of TiO_2 treated with varying amounts of Aero 6493

Sample	$-\Delta H_{ad}$ of Butanol on Talc from n-Heptane (mJ/m^2)	% Hydrophilic Surface	Specific Surface (m^2/g)	
			Total $^{(2)}$	Hydrophilic Surface
As received	148.5	75.4	8.45	6.37
2 lb/t Aero 6493	103.8	52.7	6.50	3.43
3 lb/t Aero 6493	80.4	40.8	6.45	2.63
4 lb/t Aero 6493	58.7	29.8	6.38	1.92
Silica (Reference)	197 $^{(1)}$	100.0	--	--

$^{(1)}$ *from Malandrini et al (1997)*
$^{(2)}$ *from BET measurements.*

Table 5.10. Surface free energy and its components of TiO_2 treated with varying amounts of Aero 6493

Reagent Dosage	Surface Free Energy, mJ/m^2				
	γ_S^{LW}	γ_S^+	γ_S^-	γ_S^{AB}	γ_S
2 lb/t Aero 6493	21.4	0.2	18.1	3.8	25.2
3 lb/t Aero 6493	18.9	0.2	14.5	3.4	22.3
4 lb/t Aero 6493	16.9	0.2	10.8	2.9	19.8

Table 5.11. Values of water contact angles (θ_{adv}) and ΔG_{131} for anatase treated with varying amounts of Aero 6493

	Water Contact Angle (θ_{adv})	ΔG_{131} (mJ/m^2)
2 lb/t Aero 6493	76.4±1.5	-14.65
3 lb/t Aero 6493	81.4±1.7	-23.06
4 lb/t Aero 6493	87.7±1.0	-33.09

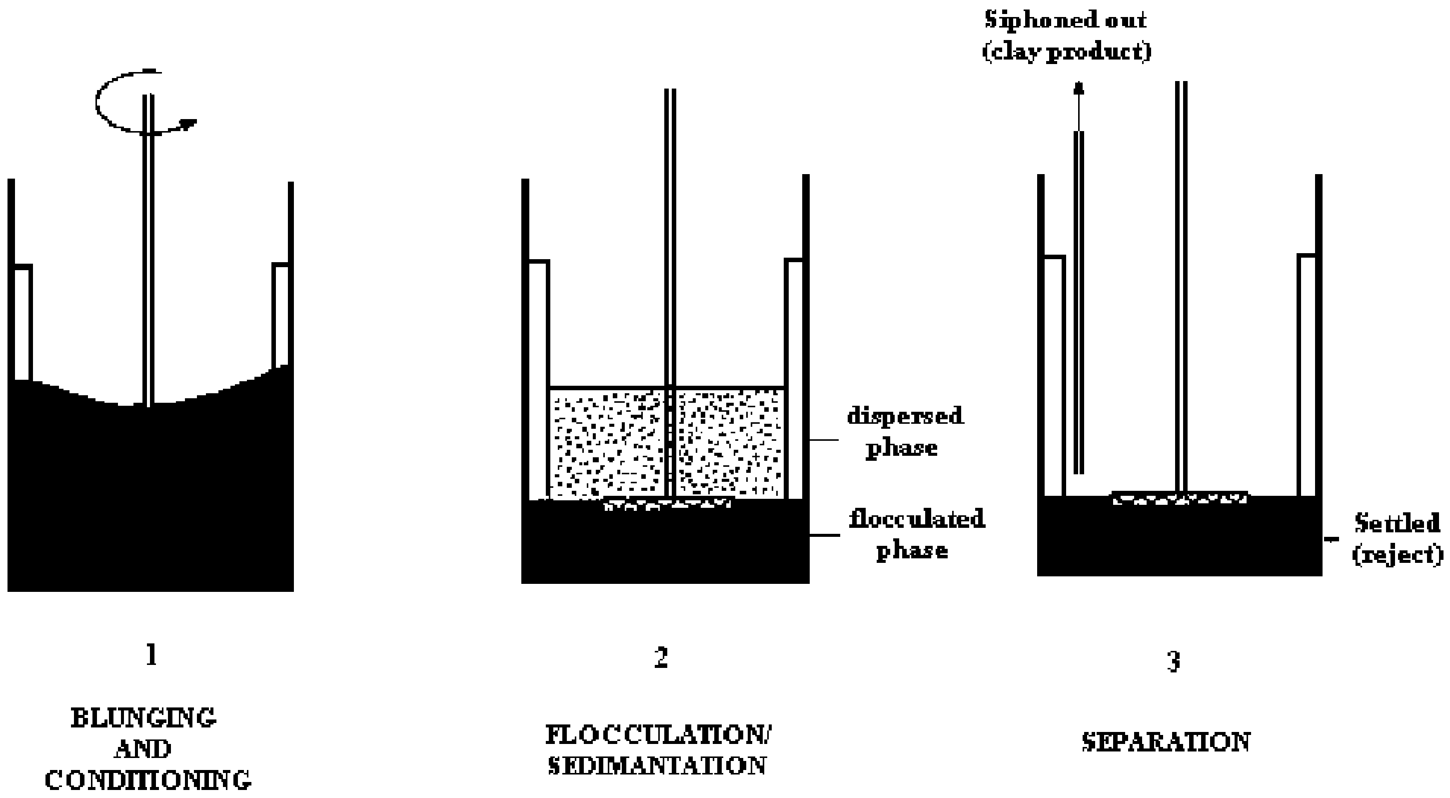

Figure 5.1. Schematic representation of the procedure employed for the batch selective flocculation experiments.

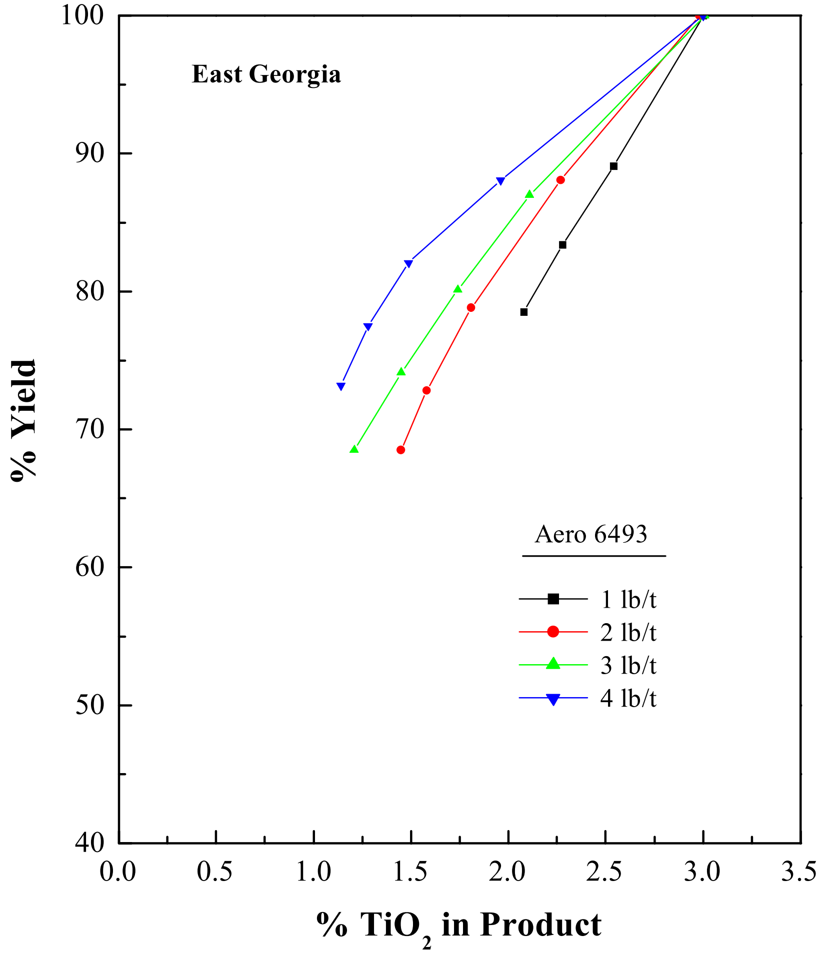

Figure 5.2. Grade vs. recovery curves for east Georgia clay obtained using Aero 6493 as collector at various dosages.

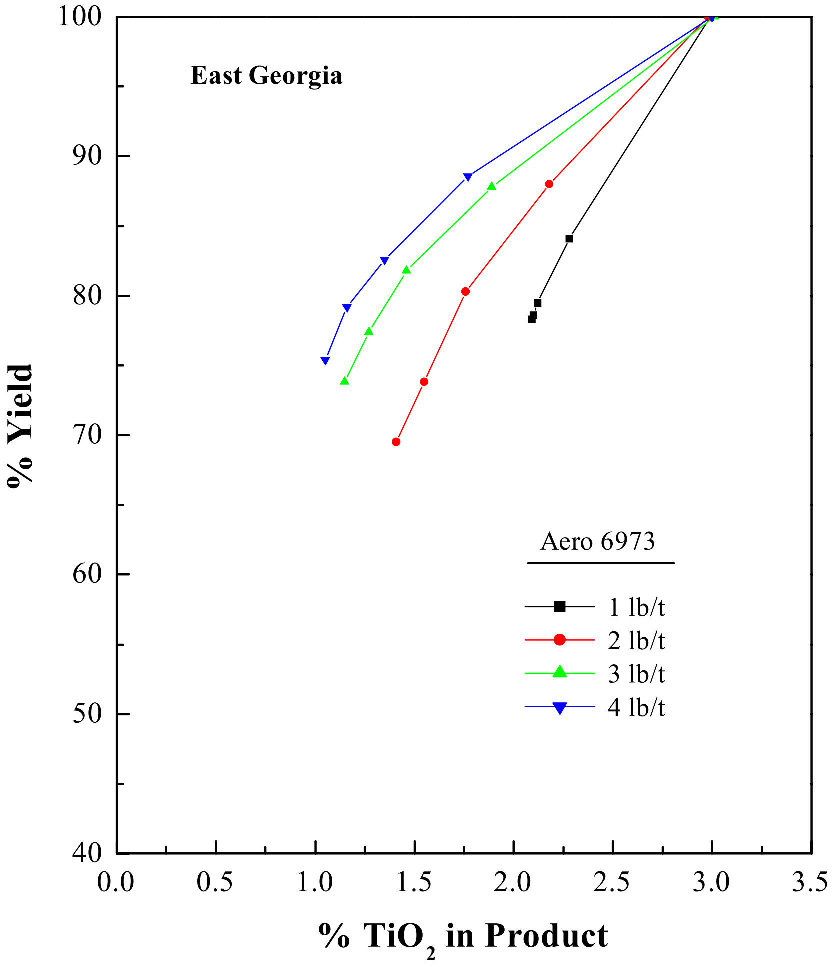

Figure 5.3. Grade vs. recovery curves for east Georgia clay obtained using Aero 6973 as collector at various dosages.

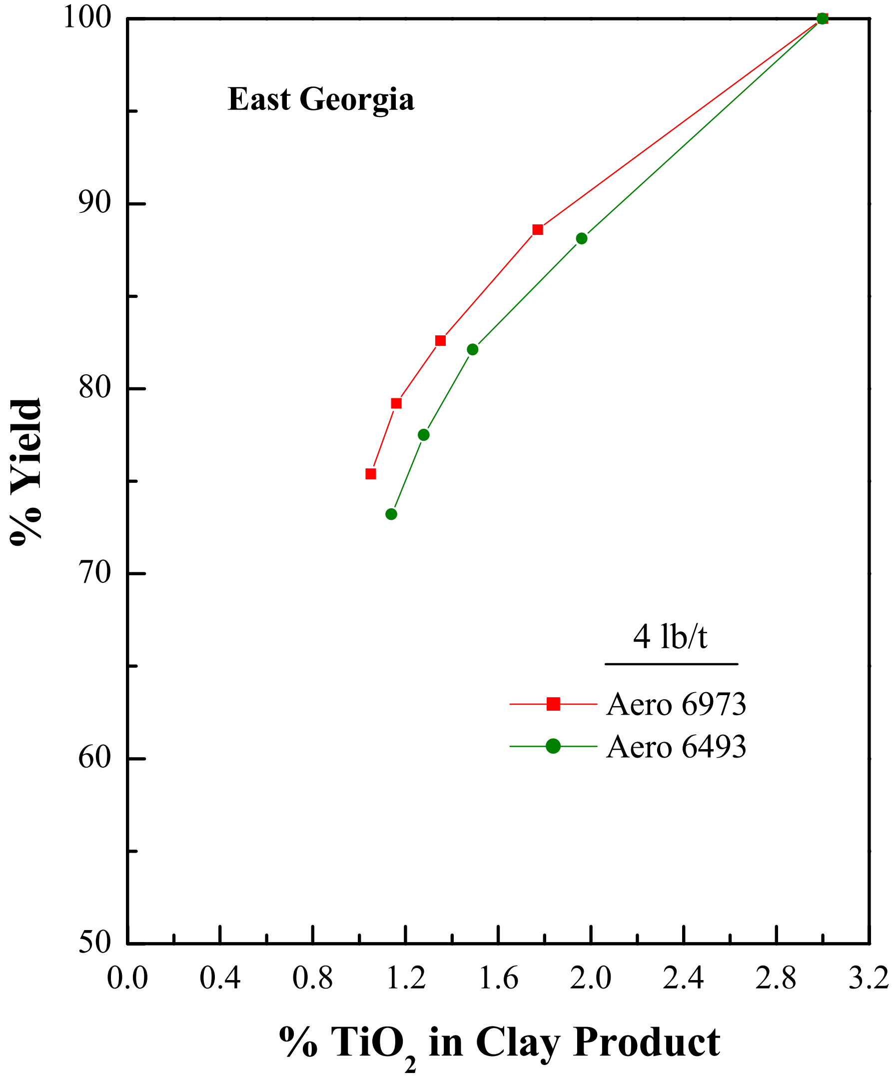

Figure 5.4. Grade vs. recovery curves for east Georgia clay obtained using Aero 6493 and Aero 6973 at 4 lb/t reagent dosage.

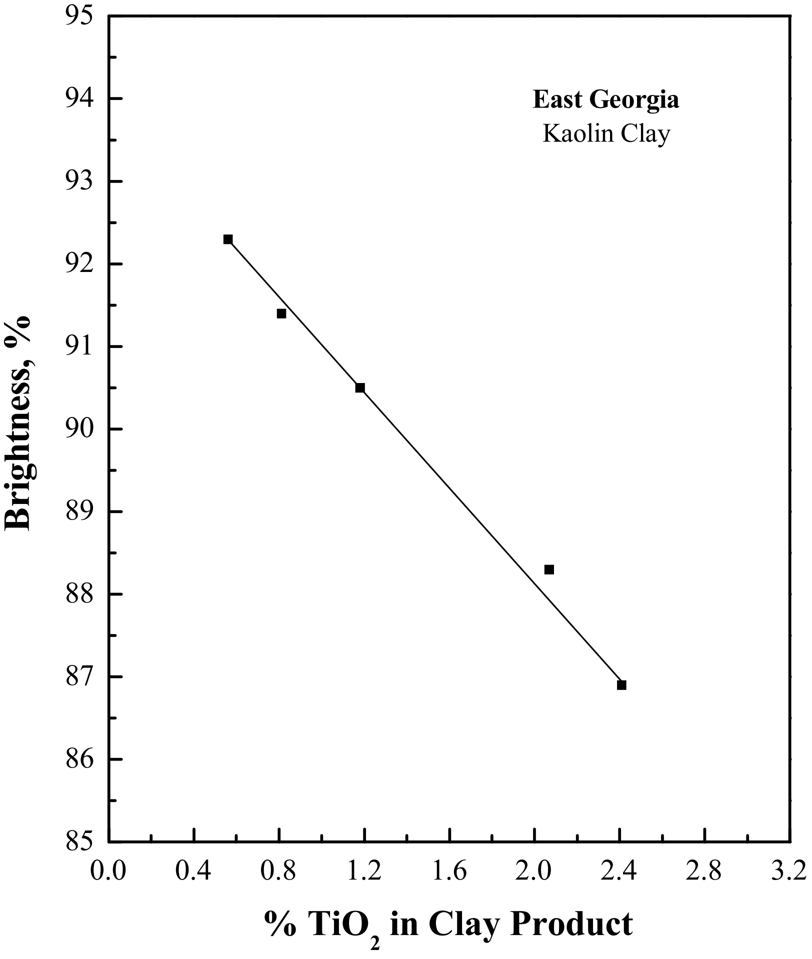

Figure 5.5. Relationship between TiO_2 content and brightness for the beneficiated east Georgia clay (Reproduced from the data given in Ref. 24).

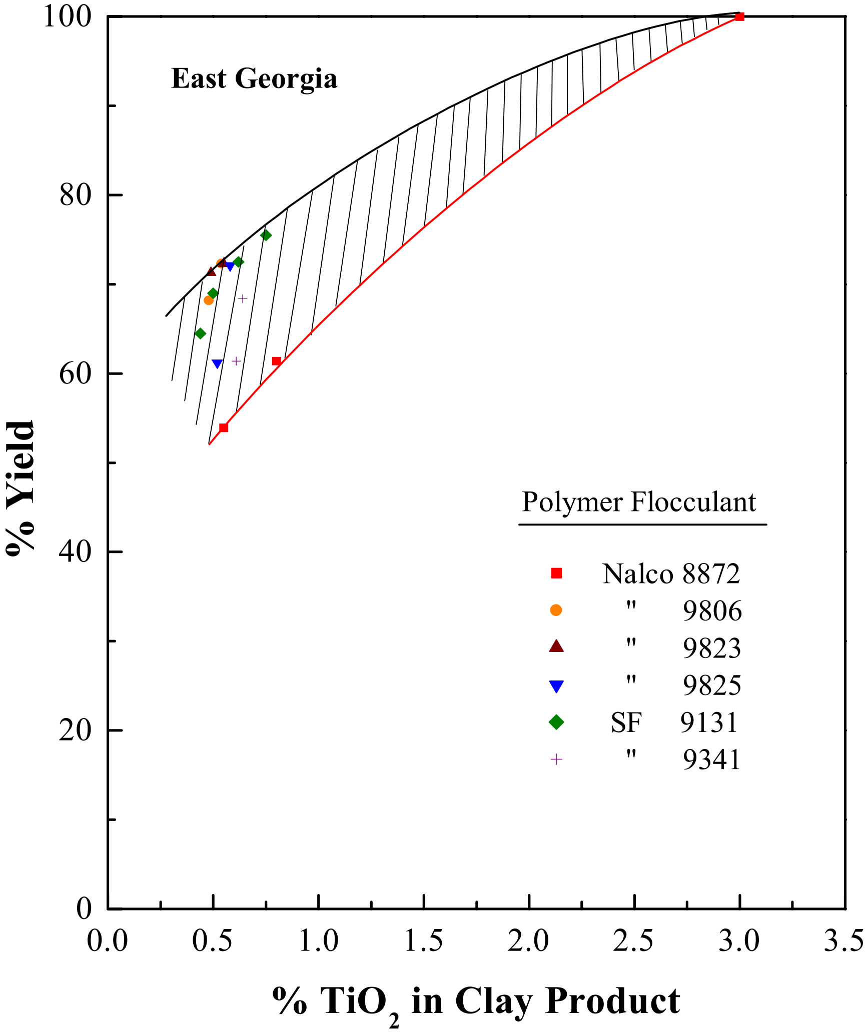

Figure 5.6. Grade vs. recovery curves for east Georgia clay obtained using various polymer flocculants in the selective flocculation.

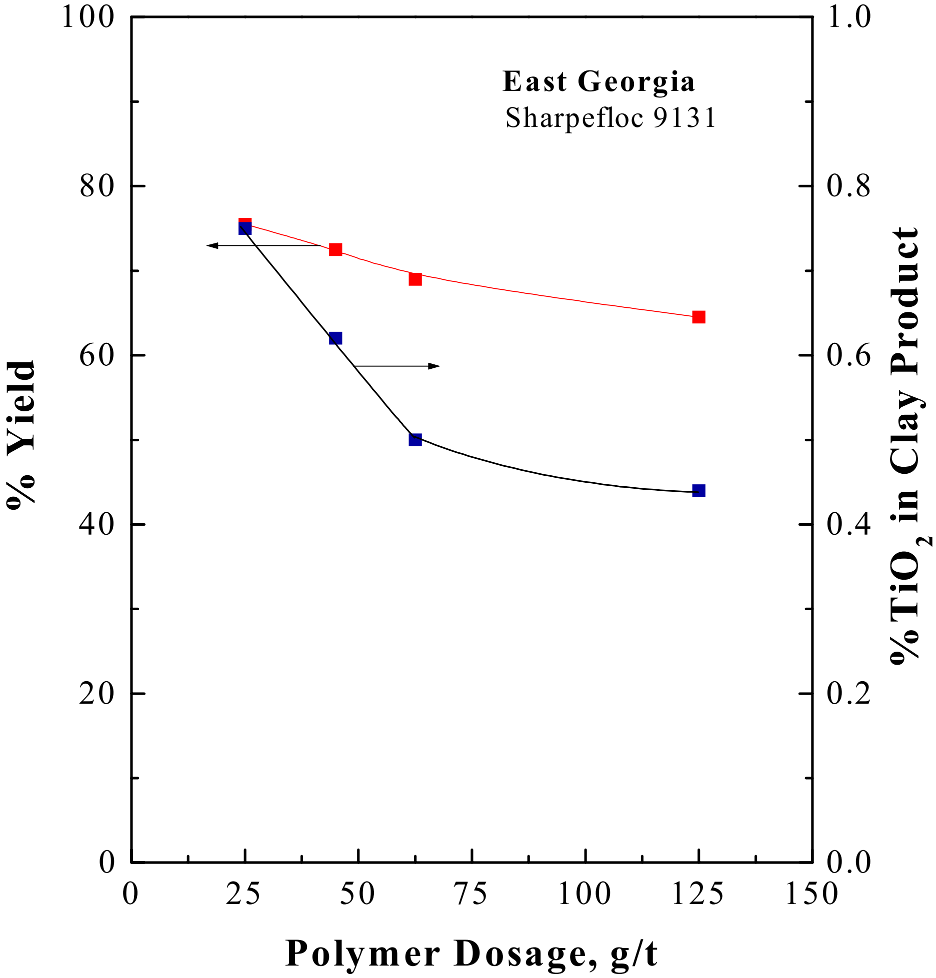

Figure 5.7. Effect of Sharpefloc 9131 polymer flocculant dosage on the yields and TiO_2 contents of clay product obtained from selective flocculation of east Georgia kaolin.

Figure 5.8. The selective flocculation of anatase from kaolin clay as a function of polymer flocculant (Sharpefloc 9131) dosage. From left to right: 25, 45, 62.5 and 125 g/t polymer addition.

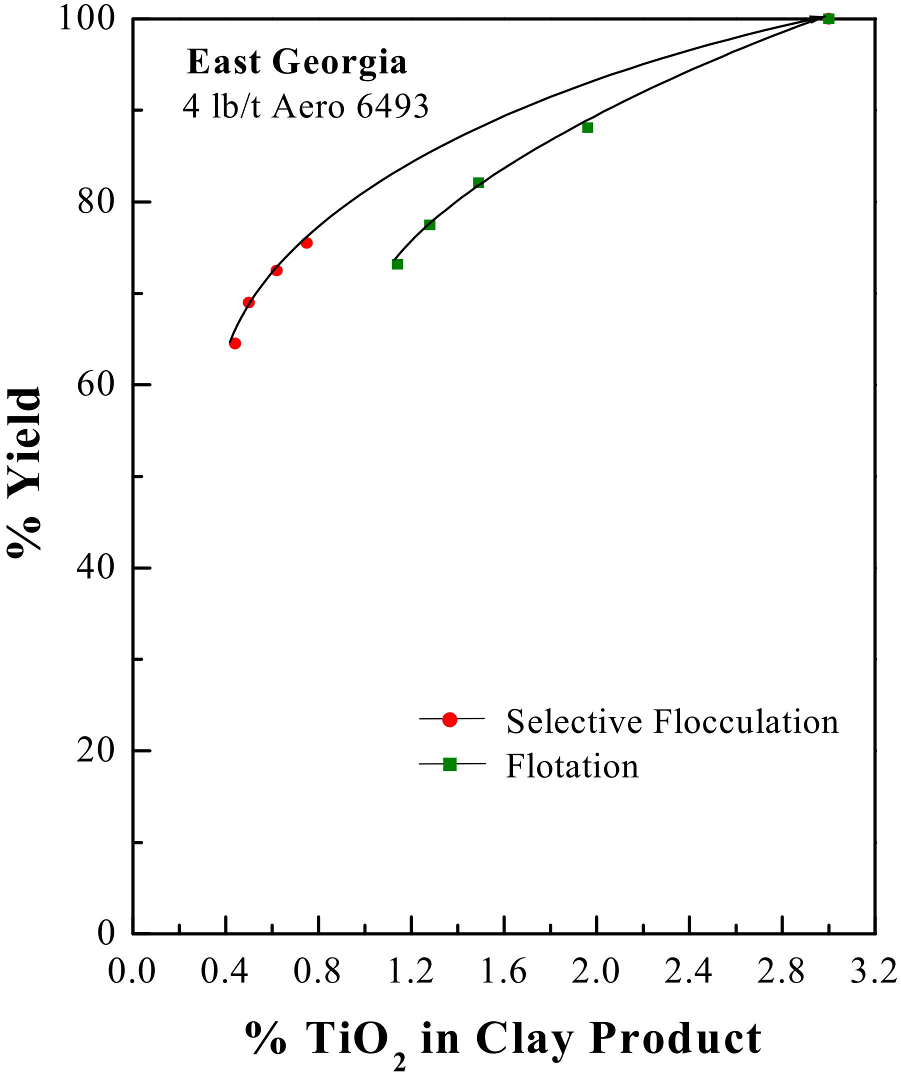

Figure 5.9. Comparison between flotation and selective flocculation methods on the TiO_2 contents and yields for clay product at 4 lb/t Aero 6493 dosage.

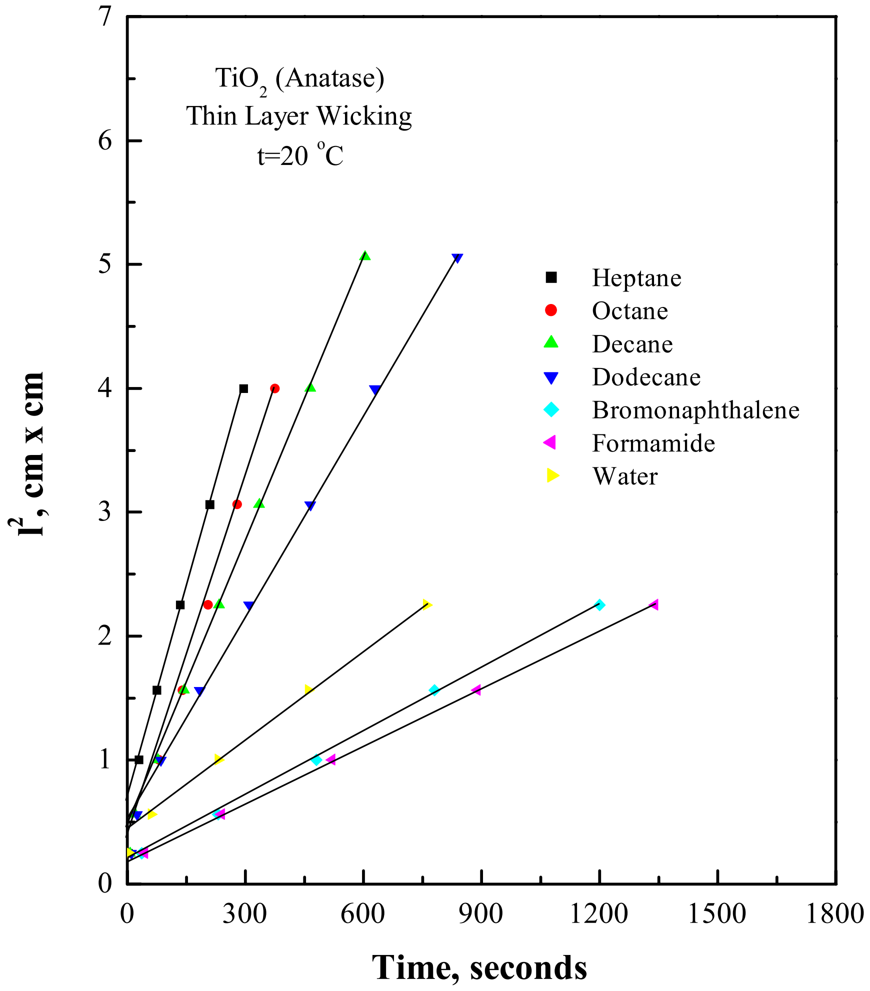

Figure 5.10. Wetting kinetics of anatase powder treated with 4 lb/t Aero 6493 using low-energy (alkanes) and high-energy liquids in the thin layer wicking experiments measured at 20 °C.

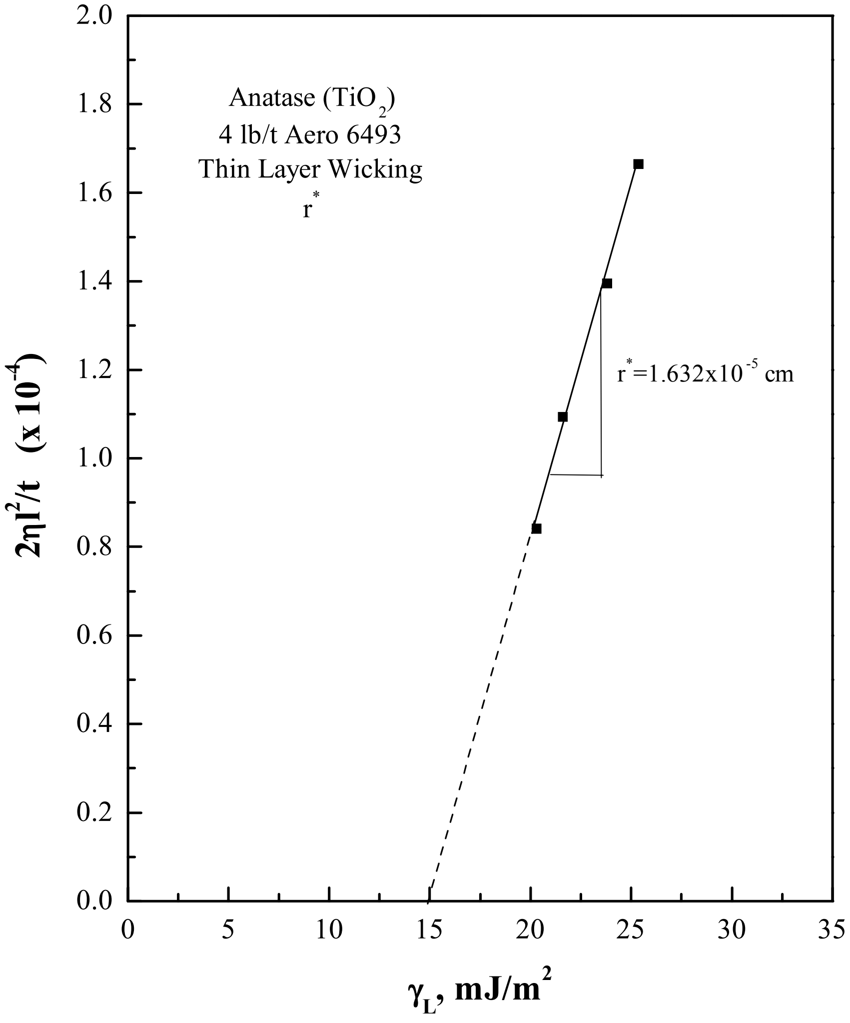

Figure 5.11. Plot of $2\eta l^2/t$ vs. γ_L obtained from thin layer wicking on anatase powder treated with 4 lb/t Aero 6493 using the low-energy liquids (alkanes).

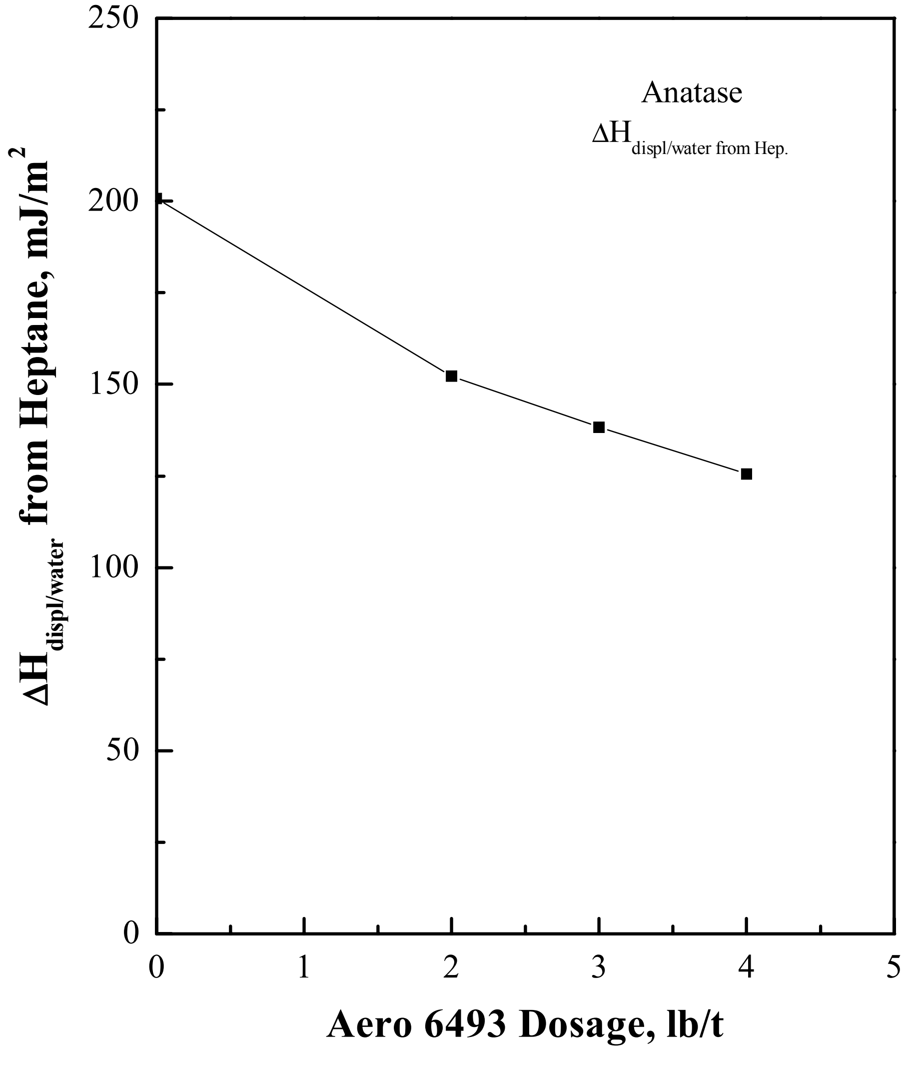

Figure 5.12. Heat of displacement enthalpies of water from n-heptane on anatase surfaces treated with varying concentrations of hydroxamate reagent.

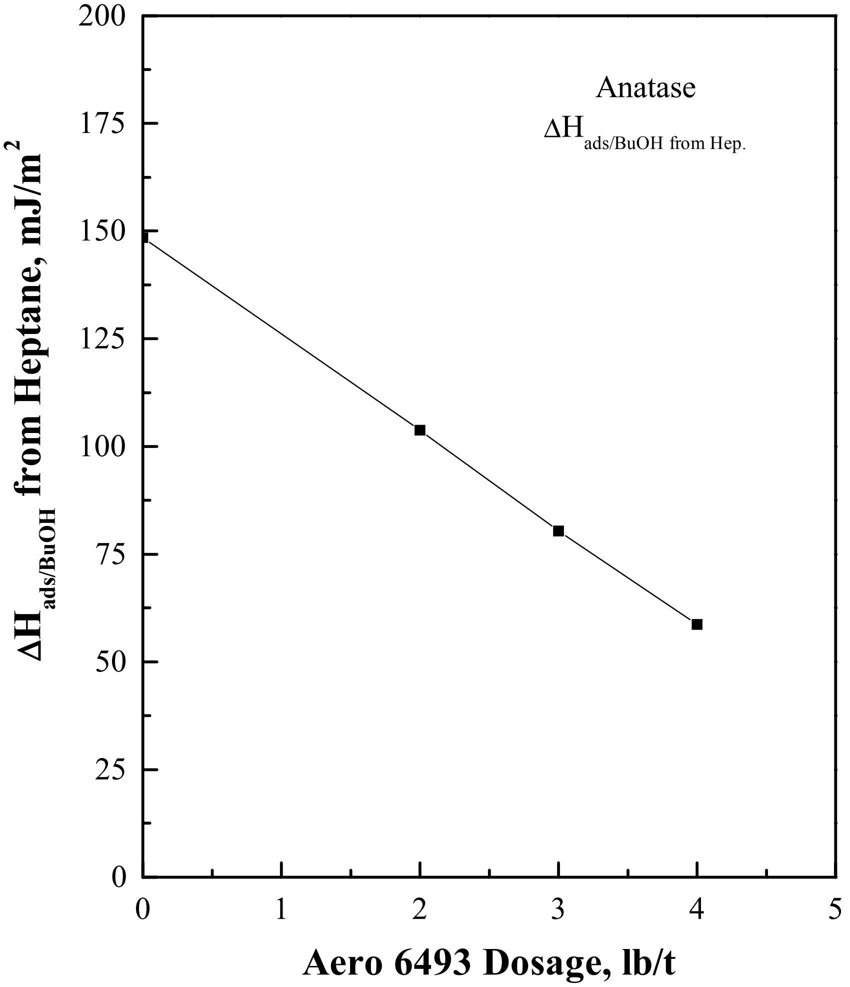

Figure 5.13. Heat of butanol adsorption from n-heptane on anatase surfaces treated with varying concentrations of hydroxamate reagent.

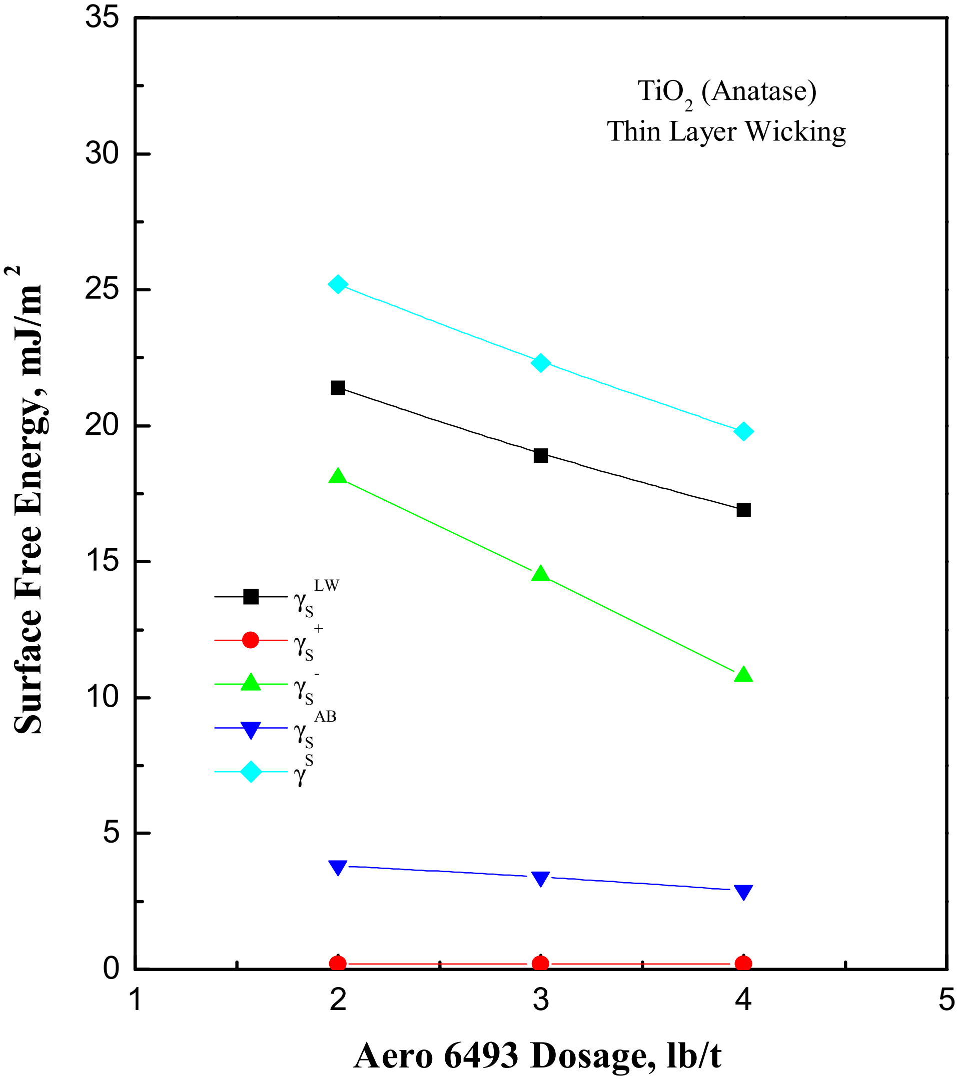

Figure 5.14. Effect of Aero 6493 concentration on the surface free energy and its components for anatase surface.

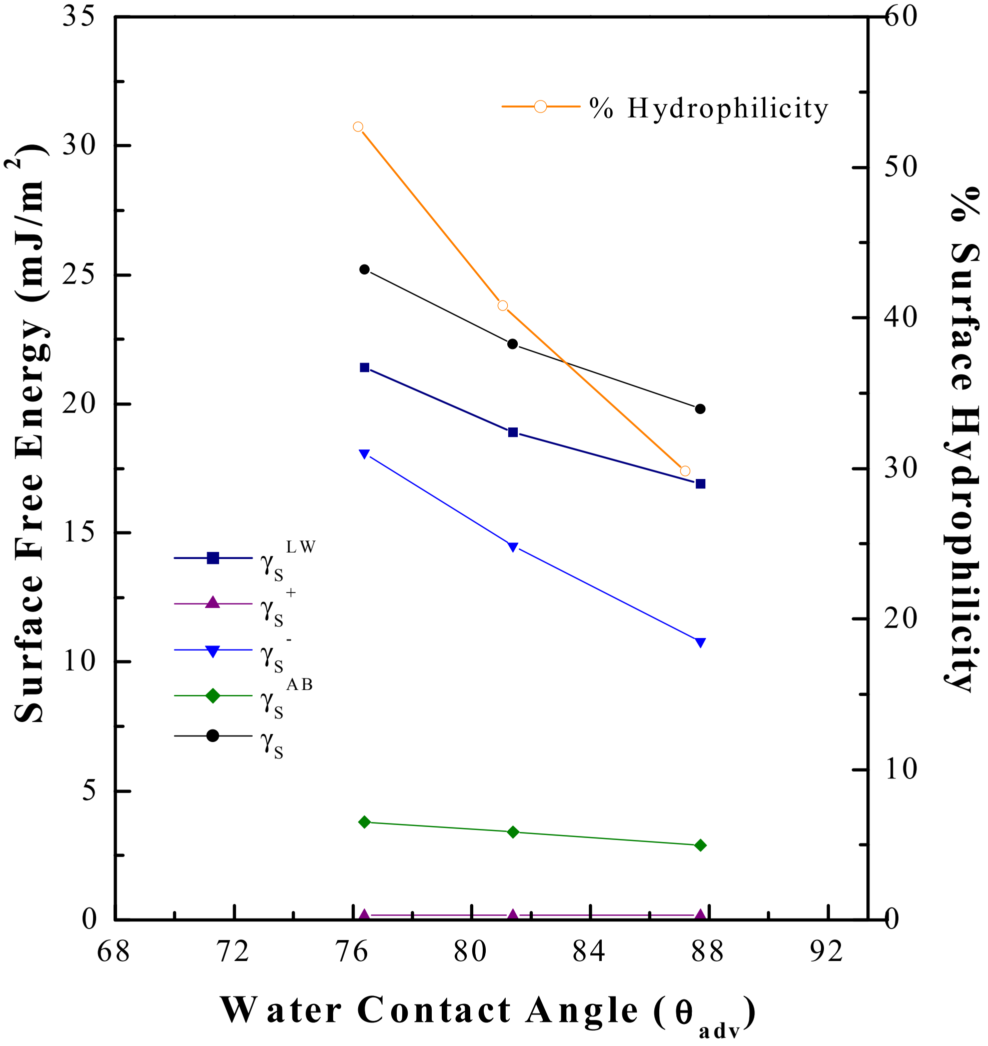

Figure 5.15. The surface free energy parameters, γ_S, γ_S^{LW}, γ_S^{AB}, γ_S^{+}, and γ_S^{-} and percentage of hydrophilic surfaces obtained for surface treated anatase powders of varying hydrophobicities. The surface free energy parameters and percentage of hydrophilic surface are plotted as a function of the advancing water contact angle. The hydrophilic surface percentage values are presented in Table 5.8 and the individual components of surface free energy are given in Table 5.9.

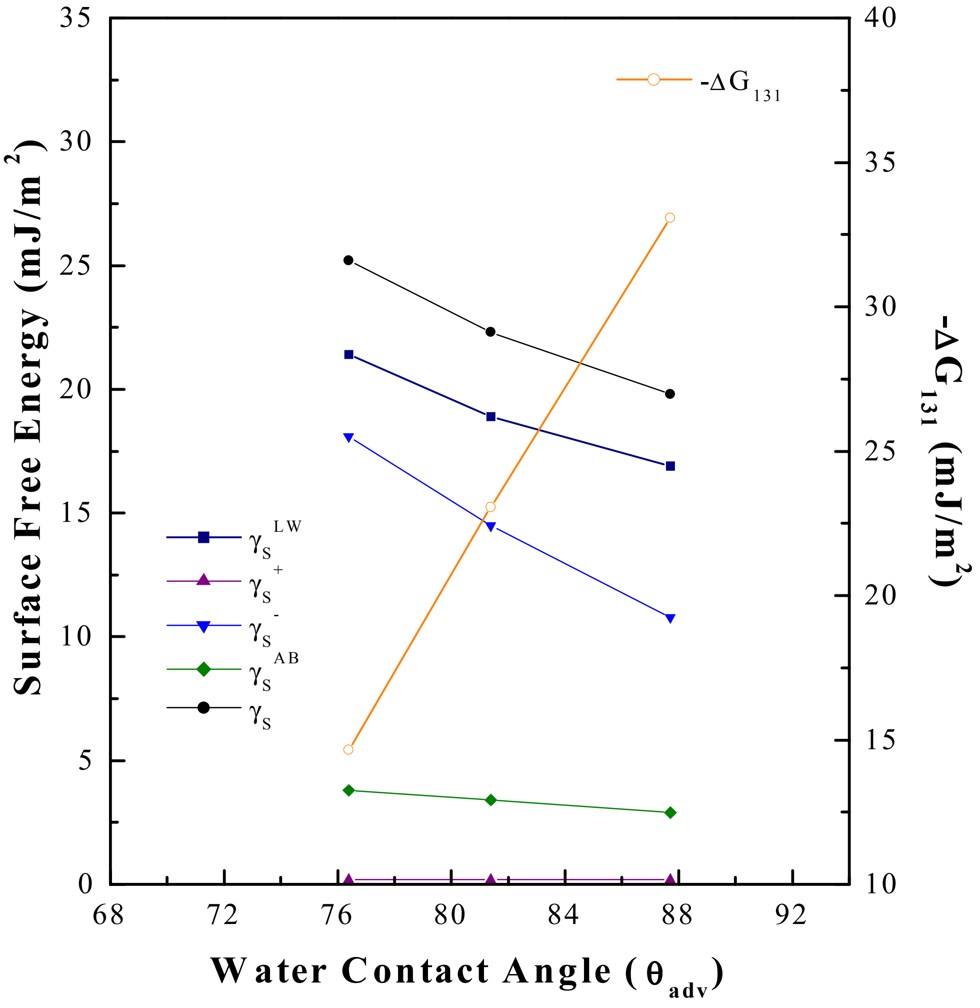

Figure 5.16. The surface free energy parameters, γ_S, γ_S^{LW}, γ_S^{AB}, γ_S^{+}, and γ_S^{-} and the Gibbs free energy of interaction ($-\Delta G_{131}$) obtained for surface treated anatase powders of varying hydrophobicities. The surface free energy parameters and the values of $-\Delta G_{131}$ are plotted as a function of the advancing water contact angle. The $-\Delta G_{131}$ values are presented in Table 5.10 and the individual components of surface free energy are given in Table 5.9.