

Determination of Monolayer Density by Potentiometric Titration

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Potentiometric titration of acidic groups originating from the functionalization of nanosized maghemite particles by a diacidic bolaamphiphile (DBSC-10) is described. The titrations are achieved in the solvent dimethylformamide (DMF), using 0.01 N potassium hydroxide (KOH) in water as titrant. A reproducible packing density of $3.4 \mu\text{mol}$ of DBSC-10/ m^2 of maghemite is found. This value falls between the approximated values estimated from molecular dimensions for vertically and horizontally oriented surfactant molecules, indicating that DBSC-10 adopts a tilted-vertical orientation with the maghemite surface. Titration does not affect the stability of the monolayer at higher pHs, as confirmed by infrared measurements on titrated particles. New strong peaks do appear at 1603 cm^{-1} ($\nu(\text{COO}^- \text{ asymmetrical stretch})$) and 1348 cm^{-1} ($\nu(\text{COO}^- \text{ symmetrical stretch})$), indicating the formation of ionic complexes between the free carboxylic moieties of the monolayer and K^+ ions from titrant.

Introduction

There are available a wide range range of techniques to study surface phenomena. These include imaging techniques (AFM, STEM, etc.) where morphology of the surface is revealed and spectrometric techniques (MS, XPS, FT-IR, Raman, etc.) where atomic and molecular information is obtained. It is possible using these techniques to determine molecular orientation and surface coverage (inferred from a thickness determination) of self-assembled monolayers (SAMs).¹

Recently, a series of publications has reported measurements of packing densities (moles adsorbed per unit area) of several aromatic and polyaromatic compounds adsorbed at Pt(111) electrodes, by means of Auger spectroscopy.^{2–5} Characterization of adsorption on planar substrates has so far concentrated on the molecular orientation of hematite ($\alpha\text{-Fe}_2\text{O}_3$)–stearate alternating Langmuir–Blodgett films, using grazing-angle infrared.^{6,7}

The study of SAMs, particularly to determine a monolayer packing density, using these techniques, however, is limited when the morphology of the substrate is not a flat surface. This is the case here in the characterization of self-assembly on nanosized particles. One solution is to develop indirect analysis techniques based on a difference method; i.e., analyze for nonadsorbed species in solution and calculate by difference the amount of adsorbed species per area of particles. The results lack the rigor of direct analysis and are suspect as to the correct representation of the adsorption mechanism. In search of a direct technique, a potentiometric titration method is suggested.

Potentiometric titration of weak acids, as a direct and quantitative analysis technique, is well documented in the pharmaceutical field.⁸ Carboxylic acids are compounds which are typically difficult to titrate in water, since well-characterized and sharp inflection points are seldom found in aqueous systems. Potentiometric titrations of dicarboxylic acids in alcohol (1-propanol)⁹ and carboxylic acids in dimethylformamide (DMF)¹⁰ have recently been reported. In the latter work, it was found that potassium hydroxide (KOH) could be successfully substituted for the traditionally used and fairly toxic titrant tetrabutylammonium hydroxide (TBAH), while achieving comparable

inflection point determinations. They also note hydrolysis of the DMF upon addition of titrant (i.e. water). Since hydrolysis is a slower process than the neutralization of acids in solution, fast titrant additions are necessary to ensure no effect of hydrolysis on the titration curves.

In this work, potentiometric titration is based on the neutralization of surface carboxylic groups originating from the functionalization of nanosized maghemite particles (average particle size 30 nm).¹¹ The titrant used is a solution of potassium hydroxide (KOH) in water, and the titration medium (solvent) is dimethylformamide (DMF). Solution potential as a function of volume of titrant added is obtained, from which the packing density (moles of bolaamphiphile per unit area of maghemite) can be inferred.

Materials and Methods

Materials. Nanosized maghemite particles, or $\gamma\text{-Fe}_2\text{O}_3$ (99+%), were received from Alfa Aesar (Ward Hill, MA). The solvent *N,N*-dimethylformamide 99.9+% HPLC grade was received from Sigma-Aldrich (Milwaukee, WI). The titrant 0.01 N potassium hydroxide in water was prepared from a 0.1 N KOH stock solution received from Sigma-Aldrich. All the chemicals used for the DBSC-10 bolaamphiphile synthesis were obtained from Sigma-Aldrich.

Synthesis of *N,N'*-Di-*p*-benzoic Acid Decane Diacid Diamide (DBSC-10). Although the preparation of DBSC-10 type bolaamphiphiles is known from the literature,¹³ a slightly different synthesis route was used in this work. Dodecanedioyl dichloride (2.34 mL, 0.0094 mol) is added dropwise to a solution of 6.4 g (0.047 mol) of *p*-aminobenzoic acid and 7.3 mL (0.1 mol) of triethylamine in 100 mL of *N,N*-dimethylformamide. After being stirred for 2 h, the solution is heated to 50 °C for an additional 12 h. The residue is filtered out and washed with water. The remaining white solid is suspended in hydrochloric acid (0.1 M) at 60 °C and stirred for 15 min. After filtration and drying, the crude product (4.19 g; about 95% yield) is obtained and used without further purification: ¹H NMR (DMSO) δ 1.3 (CH_2), 1.6 ($\beta\text{-CH}_2$), 2.3 ($\alpha\text{-CH}_2$), 7.7/7.9 (aromatic ring), 10.1 (amide), 12.7 (acid); IR (diluted in KBr powder) $\nu(\text{NH}) = 3317 \text{ cm}^{-1}$, $\nu(\text{C=O, amide + acid}) = 1678 \text{ cm}^{-1}$. Titrations of DBSC-10 are performed in 20 mL of DMF.

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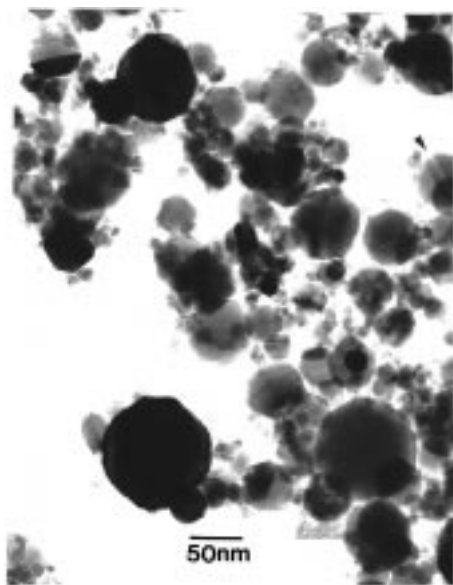


Figure 1. Maghemite sample by transmission electron microscopy (TEM), with indicated nanodiffraction patterns.

Monolayer Preparation. Monolayers are formed on maghemite particles by molecular self-assembly. Typically, solutions of 28 mg of DBSC-10 in 20 mL of DMF (3 mmol) are prepared. Different amounts of maghemite particles (25, 50, 75, and 100 mg) are added and the suspensions shaken overnight at room temperature. The coated particles were centrifuged, washed three times with DMF, and suspended in 20 mL of DMF for titration.

Titration Apparatus. All titration experiments are done at room temperature using a TitraLab titration laboratory (Radiometer Analytical, Copenhagen, Denmark) composed of a TIM90 titration manager, a ABU91 autoburet high-precision buret station, and a SAM90 sample station. The samples are stirred using an overhead stirrer part of the SAM90. Titrations are performed using a combined pH electrode (Radiometer pHC2401). Nitrogen is bubbled throughout the titration to prevent CO₂ contamination.

Titration Procedure. Titrations are run in the continuous inflection point IP mode, without predose and with a minimum/maximum speed fixed at 2%/min of a 10 mL buret. A smoothing parameter of 8 is used in the calculation of inflection points. Note that titrations of bare maghemite are performed on oven dried (350 °C) particles to yield surfactant-free surfaces.

Infrared Measurement. The DRIFT spectrum is recorded on a Bruker IFS-66 FT spectrometer with an ellipsoidal mirror, diffuse reflectance accessory (Spectra-Tech, Inc.). The spectrometer is equipped with a liquid-N₂-cooled MCT midinfrared (MIR) detector. The spectrum is measured at 4 cm⁻¹ resolution, and 100 scans are coadded. The MIR Kubelka–Munk spectrum is obtained by ratioing the resulting spectrum against a background of KBr (IR grade, Aldrich). The sample is diluted by grinding with a mortar and pestle to approximately 20 vol % in KBr.

TEM. To image the maghemite particles, a dilute sample was prepared by dispersing particles onto a carbon supported TEM grid, using deionized water. TEM investigation was performed with a JEOL 2000 FX at an accelerating voltage of 100 kV.

Results and Discussion

Maghemite Particles. Figure 1 is a micrograph of a maghemite sample obtained by transmission electron microscopy (TEM). The particles have an average diameter of 30 nm and

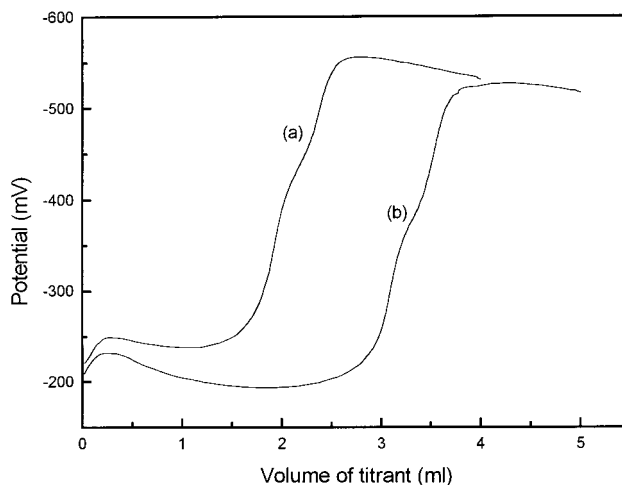
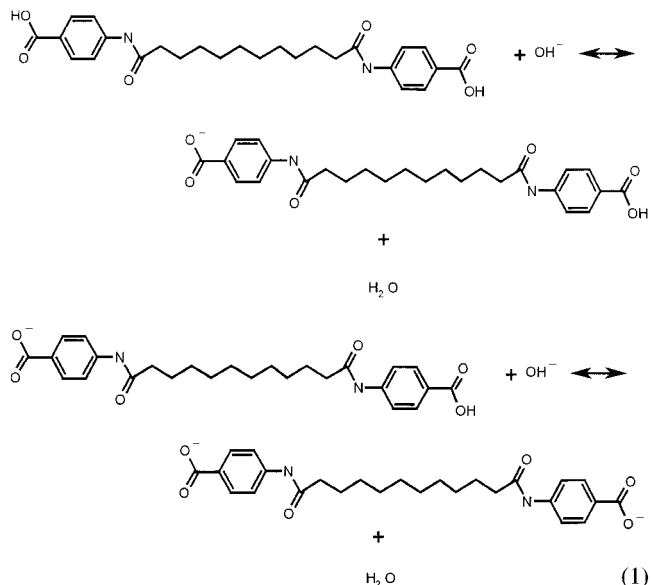


Figure 2. Titration curves from the neutralization of (a) 4.4 mg and (b) 8 mg of DBSC-10.

a surface area of 50 m²/g. Nanodiffraction patterns can be distinguished on some of the particles indicating the presence of a crystal structure typical of maghemite and similar to that of magnetite. As can also be seen in the figure, the particles show no observable porosity down to the 2 nm resolution limit of TEM.

DBSC-10 Titration. When KOH is added to a solution of DBSC-10, the following reaction takes place, based on the neutralization of a weak diacid:



Assuming the reaction between DBSC-10 and OH⁻ is complete, the equivalence point is then characterized by:

$$2C_{\text{DBSC-10}}V_{\text{Sample}} = C_{\text{Base}}V_{\text{Base total}} \quad (2)$$

where $C_{\text{DBSC-10}}$ and C_{Base} are the concentrations of surfactant and base, respectively, and V_{Sample} and $V_{\text{Base total}}$ are the volumes of sample and total base added, respectively.

Figure 2 shows the titration curves obtained from the neutralization of (a) 4.4 mg and (b) 8 mg of DBSC-10. The shape of these curves up to the equivalence point compares with the results obtained for benzoic acid in DMF by Nickel and Weber.¹⁰ It is characterized by the presence of two potential minima and one potential maximum, not seen in the titration of weak acids in water systems. The presence of two inflection

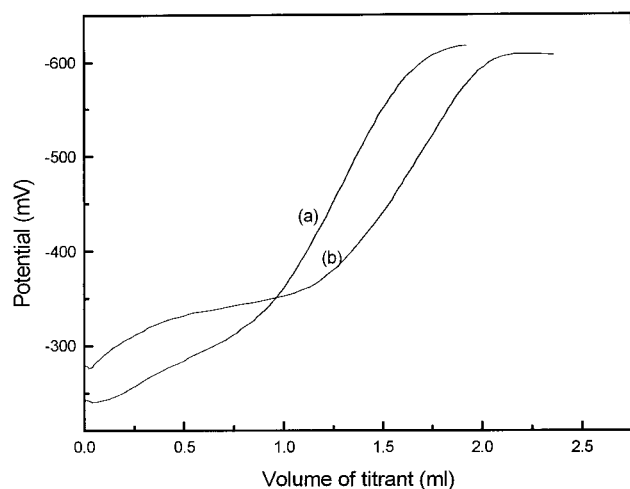


Figure 3. Titration curves of 50 mg of (a) bare maghemite and (b) DBSC-10 coated particles.

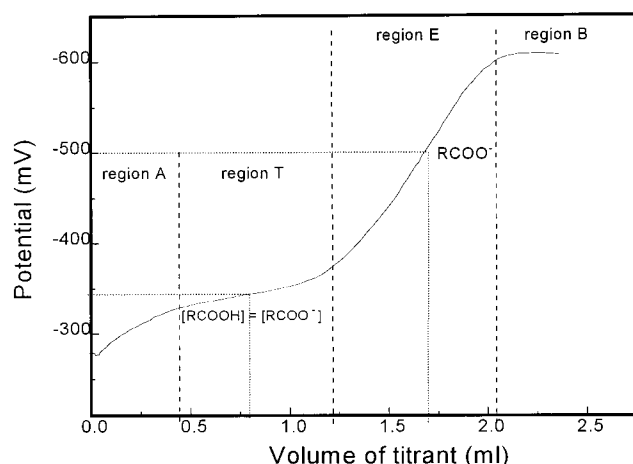


Figure 4. Titration of 50 mg of DBSC-10 coated particles by KOH.

points around the equivalence point is typical of the titration of a diprotic acid, i.e., successive titration of two ionizable protons. Their proximity indicates that the long hydrocarbon chain of DBSC-10 is almost sufficient to approximate the titration of two separate weak acids. Furthermore, the plateau or region of constant potential on curves a and b corresponds to the point where both the acid and the ionized species predominate, i.e., the buffer zone. The error between the experimental and theoretical (prepared) concentrations of DBSC-10 is $\pm 5\%$.

Titration of DBSC-10 Coated Particles. Figure 3 shows the titration curves of 50 mg of (a) bare maghemite and (b) DBSC-10 coated particles. The shape of curve a is indicative of the background response of the bare particle system. The unresolved inflection point around a potential of -450 mV can be attributed to the titration of some hydroxy species adsorbing on the bare surface of maghemite. The shape of curve b does indicate the titration of a weak acid, as seen from the presence of both a potential plateau around -350 mV and a single sharp inflection point (titration of a monoacid) at -500 mV.¹²

Curve b can be further divided in four different regions as seen in Figure 4: region A of the acid species, where the potential increases rapidly with the addition of base; region T, where the titration takes place and the potential increases slowly with the addition of base; region E of the equivalence point, where the jump in potential is observed; region B, dominated by the ionized species and where the potential increases very slowly with increasing addition of base.

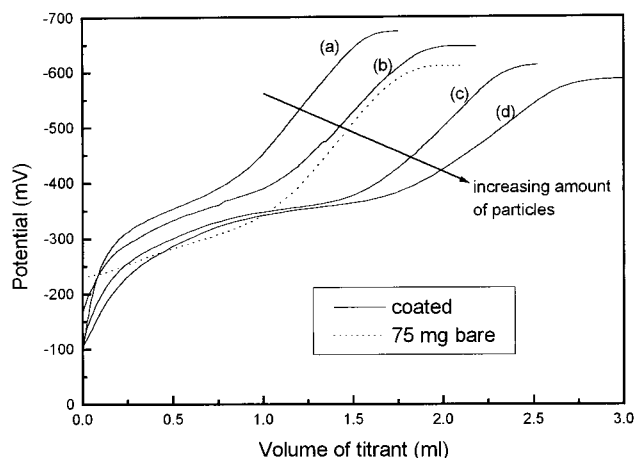


Figure 5. Titration of DBSC-10 coated particles: (a) 25 mg, (b) 50 mg, (c) 75 mg, (d) 100 mg, and 75 mg of bare maghemite.

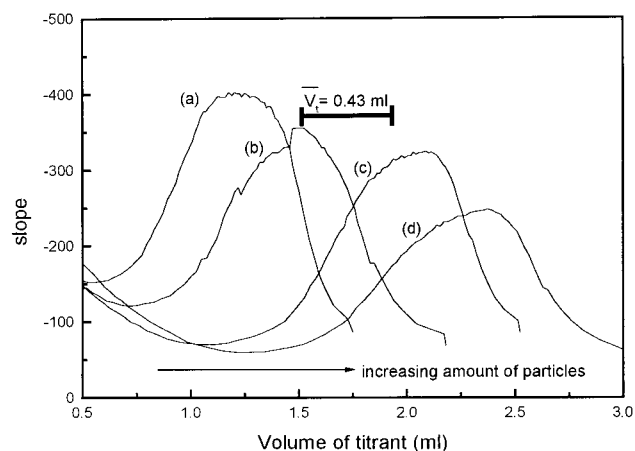


Figure 6. Inflection points of DBSC-10 coated particles: (a) 25 mg; (b) 50 mg; (c) 75 mg; (d) 100 mg.

Figure 5 presents curves corresponding to the titration of increasing amounts of DBSC-10 coated particles: (a) 25 mg, (b) 50 mg, (c) 75 mg, and (d) 100 mg. The dashed line of 75 mg of bare maghemite is also presented and provides a background for comparison. Increasing the amount of titrated particles results in a right shift of the curves, as seen in (a)–(d). As expected from the titration of more acid, the associated T regions of each successive curves become longer. The slight decrease in potentials of all four B regions is due to the dilution effect of increasing the volume of titrant necessary for the titration of more acid. All four associated inflection points (equivalence points) are observed around a potential of -500 mV.

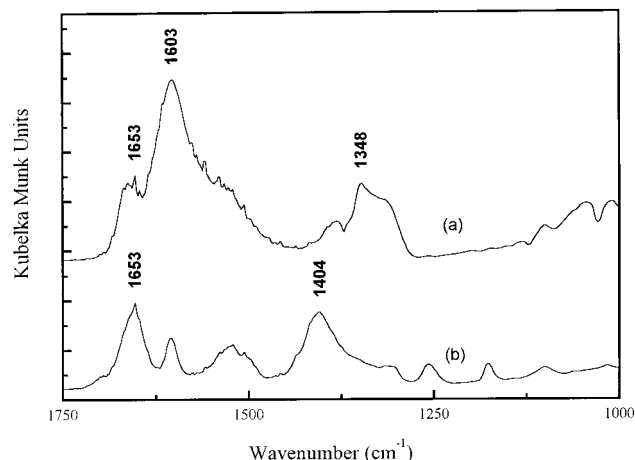
The volume of titrant added does not double from curve a to b, indicating the presence of a systematic background effect occurring during the titration. One such effect could be the adsorption of hydroxy species onto glassware and titration components (electrode, titrant dispenser, stirrer, etc.). For this reason, only the difference between the inflection points of the curves will be considered.

The corresponding inflection points of curves a–d from Figure 5 are shown in Figure 6. The difference in volume of titrant added per 25 mg increment of coated particles is seen to be approximately 0.43 mL. Table 1 shows this value to be reproducible within 28% of the replicate titrations mean.

This average volume corresponds to $4.3 \mu\text{mol}$ of DBSC-10 and to a density of $3.4 \mu\text{mol}/\text{m}^2$ of maghemite. This value is lower than the calculated density, obtained using

TABLE 1: Reproducibility of the Volume Difference between 25 mg Increments of Coated Particles

no. of replicates	mean diff of inflection points	sample std dev	90% confidence interval
5	0.43	0.13	0.43 ± 0.12

**Figure 7.** DRIFTS of DBSC-10 coated particles (a) after and (b) before titration with KOH.

the surface area of maghemite, and based on a cross-sectional area of vertically oriented DBSC-10 molecules of 30 nm^2 .¹³ For 50 mg of particles, we have a total surface area

$$0.05 \text{ g} \cdot 50 \text{ m}^2/\text{g} = 2.5 \text{ m}^2 \quad (3)$$

which yields

$$2.5 \text{ m}^2 / (30 \times 10^{-20} \text{ m}^2/\text{molecule}) = 8.33 \times 10^{18} \text{ molecules} \quad (4)$$

and with introduction of Avogadro's number, the density is

$$8.33 \times 10^{18} \text{ molecules} / (6.02 \times 10^{23} \text{ molecules/mol}) = 13.8 \mu\text{mol of DBSC-10}$$

or

$$13.8 \mu\text{mol of DBSC-10} / 2.5 \text{ m}^2 = 5.5 \mu\text{mol of DBSC-10/m}^2 \text{ of particle}$$

The observed packing density obtained by potentiometry is however greater than the reported calculated value based on molecular models of horizontally oriented biphenylcarboxylic acids ($1.7 \mu\text{mol/m}^2$).³ This indicates the formation of tilted vertical orientations of adsorbed DBSC-10.

DRIFTS spectra of DBSC-10 coated particles after (a) and before (b) titration with KOH are shown in Figure 7. The presence of surfactant on (a) is confirmed. The IR region scanned reveals the asymmetrical and symmetrical carboxylate vibrational peaks. It is interesting to note the presence of new

strong peaks in (a) at 1603 and 1348 cm^{-1} , assigned as the $\nu(\text{COO}^- \text{ asym stretch})$ and $\nu(\text{COO}^- \text{ sym stretch})$ of the free carboxylic moieties forming complexes with the K^+ ions. A difference between the asymmetrical and symmetrical wavelengths of 255 cm^{-1} , although on the high side, is consistent with these ionic species.¹⁴

Conclusions

Potentiometric titration, using the KOH/DMF system introduced by Nickel and Weber, has proven a successful and novel technique in the determination of the packing density of a self-assembled monolayer of a weak acid DBSC-10 onto maghemite particles. A reproducible packing density of $3.4 \mu\text{mol}$ of DBSC-10/ m^2 of maghemite was determined. This value is between the calculated value of $5.5 \mu\text{mol}$ of DBSC-10/ m^2 of maghemite obtained for vertically oriented DBSC-10 and the reported value for horizontally oriented biphenyl dicarboxylic acids, $1.7 \mu\text{mol}/\text{m}^2$. Infrared measurement confirmed the surfactant is not removed after titration. New strong peaks at 1603 and 1348 cm^{-1} , associated with the asymmetrical and symmetrical vibrations of a carboxylate group, confirm the formation of ionic complexes between the free carboxylic moieties of the coated maghemite and K^+ ions from the titrant.

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