Hexadecylamine Adsorption at the Iron Oxide–Oil Interface

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ABSTRACT: The adsorption behavior of a model additive, hexadecylamine, onto an iron surface from hexadecane oil has been characterized using polarized neutron reflectometry, sum-frequency generation spectroscopy, solution depletion isotherm, and X-ray photoelectron spectroscopy (XPS). The amine showed a strong affinity for the metal surface, forming a dense monolayer at relatively low concentrations; a layer thickness of 16 (±3) Å at low concentrations, increasing to 20 (±3) Å at greater amine concentrations, was determined from the neutron data. These thicknesses suggest that the molecules in the layer are tilted. Adsorption was also indicated by sum-frequency generation spectroscopy and XPS, the latter indicating that the most dominant amine–surface interaction was via electron donation from the nitrogen lone pair to the positively charged iron ions. Sum-frequency generation spectroscopy was used to determine the alkyl chain conformation order and orientation on the surface.

INTRODUCTION

Amines and their derivatives are frequently added to engine oils for anticorrosive or lubricating purposes. However, the nature of their interactions with the surfaces that they protect remains unclear, particularly when used in conjunction with other additive species, such as fatty acids or zinc dialkylphosphates (ZDDPs). For example, it remains open to debate whether they directly bind to the surface or are used rather to improve the binding of other additives.1,2 Such questions remain unresolved because of the inability of traditional methods to study these additives in situ and to construct a molecular-level model of the additive interaction with the surface.

In this work, we combine a number of surface-specific and surface-sensitive techniques to address the detailed adsorption behavior and surface molecular structure of a model additive, 1-hexadecylamine adsorbed from hexadecane onto an iron surface. Zhu et al. demonstrated that 1-hexadecylamine in a tetradecane system between two mica surfaces shows similar performance to a commercial automatic transmission fluid in terms of the “hard-wall thickness” and rheological effects under shear.3 The amine molecules were reported to form monolayers at concentrations as low as 0.1 wt% in the oil, with film thicknesses of around 18 Å, separated by a small layer of oil and excess amine, as measured using a surface force balance.

Neutron reflectometry (NR) is a well-established technique for the study of the air/liquid and solid/liquid interfaces.4–8 In this approach, the generated reflectivity profile, obtained by reflecting a neutron beam at grazing angles close to the critical angle, has features that depend upon structural parameters of the adsorbed species, such as layer composition, thickness, and roughness. Here, in a modification of the standard approach, polarized neutron reflectometry (PNR) has been used;9 neutrons polarized either parallel (+) or antiparallel (−) (“up”- or “down”-spin) to an external magnetic field interact differently with magnetic materials, such as iron (magnetic moment, $\mu = 2.2 \, \mu_B$). For magnetic materials that are magnetized in the plane of the surface using an external field, the neutron refractive index, $n$, is dependent upon the neutron spin polarization. The measured reflectivity, $R^\parallel$, is spin-dependent, and the refractive index must be written as a combination of the nuclear ($n_{\text{nuclear}}$) and magnetic ($n_{\text{magnetic}}$) contributions

$$n_L = n_{\text{nuclear}} \pm n_{\text{magnetic}} = 1 - \left( \frac{N \mu^2}{2\pi} \right) (b \pm C\mu)$$

where $N$ is the number density, $C$ is a constant ($0.265 \times 10^{-12} \, \mu_B \, \text{cm}^{-1}$), $b$ is the scattering length, and $\mu$ is the moment per atom.

When two separate reflectivity profiles are acquired for the same sample using up- and down-spin neutrons successively, two independent data sets are obtained from the same sample. This additional information is important when extracting the structural model of the interface by data fitting, because the number of possible models that can be fitted to both sets of data is significantly reduced. The scattering power of each layer at the interface is quantified in the scattering length density.
interfacial molecules, is obtained by spatially and temporally overlapping a fixed visible and tunable infrared (IR) laser beam to generate an output laser beam with frequency equal to the sum of the two incident beams. The high energy of the laser beams gives rise to nonlinear optical effects, in particular the second-order susceptibility, $\chi^{(2)}$, which will only have a non-zero value in a non-centrosymmetric environment. Hence, importantly for surface studies, there is no signal from the bulk material, and only the interface, where the symmetry is broken and $\chi^{(2)}$ has a non-zero value, is specifically investigated.12

The SFG technique can be used to extract several interfacial parameters, including the tilt angle of various moieties within the molecule (most frequently methyl or methylene groups) to the surface normal, molecular conformation, and polar orientation. These may be determined by variation of the polarization combinations of the incident and reflected beams.13 The non-resonant contribution present for metal surfaces can be used to unambiguously identify the absolute orientation of a molecule on a surface.

Depletion isotherms are used to quantitatively determine the adsorbed amount of a species as a function of the solution concentration. In this technique, solutions of different initial adsorbate concentrations are added to a high-surface-area powdered substrate and allowed to equilibrate. Adsorption leads to a reduction of the adsorbate concentration in the solution, which may then be measured, in this case, using Fourier transform infrared (FTIR) spectroscopy. In many cases, the data can be best interpreted in terms of the Langmuir isotherm, where adsorption increases rapidly until monolayer coverage is attained.14

X-ray photoelectron spectroscopy (XPS) was used to characterize the nature of the iron surface to determine the metal surface composition and oxidation state of the iron. The interfacial amine was also probed using this technique.

### EXPERIMENTAL SECTION

**Materials.** The iron oxide substrates used for PNR and SFG experiments were sputtered to a thickness of 200 Å onto a polished silicon substrate, (111) orientation, (n) type, with a diameter of 55 mm and thickness of 5 mm, at the Helmholtz Zentrum, Berlin, Germany, using reactive magnetron sputtering.15 The iron oxide powder was purchased from Sigma-Aldrich (≥99% purity, 69.7% Fe, determined by titration), and Brunauer–Emmett–Teller (BET) surface area (determined by N2 adsorption fitted to the BET isotherm equation) was 4.15 m$^2$ g$^{-1}$. Hexadecylamine [98.1%, determined by gas chromatography (GC)] and dodecane (97.1%, determined by GC) were also purchased from Sigma-Aldrich. Deuterated hexadecane [99.2%, determined by proton nuclear magnetic resonance ($^1$H NMR)] was purchased from Cambridge Isotopes Laboratories, Inc., and deuterated hexadecylamine (99.2%, determined by GC) was purchased from QMX Laboratories. They were used without further purification.

**Solution Depletion Isotherm.** A solution depletion isotherm was measured by tumbling samples of 10 mL of hexadecyl-d$_{17}$amine in dodecane (over the concentration range of 0.0–3.5 x 10$^{-3}$ mol dm$^{-3}$) with iron oxide powder (0.5 g). Samples were allowed to equilibrate over 24 h, before centrifuging to separate the solid from the supernatant, before analysis of the final concentration by integration of peaks in the C–D stretching region of the IR spectra compared to a set of calibration standards.

**PNR.** The PNR experiments were conducted on the PolRef instrument at ISIS, Rutherford Appleton Laboratory, U.K. The sample setup is depicted in Figure 1. Briefly, a pulsed neutron beam from the spallation target is directed toward the sample at grazing angles and collimated by slits. Polarized neutrons were used to provide extra contrasts; polarization was achieved by the use of a transmission
RESULTS AND DISCUSSION

Solution Depletion Isotherm. An isotherm of hexadecyl-$d_{34}$-amine measured using the depletion method is given in Figure 4. The data exhibit a rapid rise in adsorption at low concentrations before reaching a plateau of approximately $3 \times 10^{-6}$ mol m$^{-2}$ at higher concentrations. This adsorption profile is in good agreement with a Langmuir adsorption model. BET measurements of the powder give a specific surface area of 4.15 m$^2$ g$^{-1}$. Hence, the adsorption at the plateau in the isotherm corresponds to each amine molecule occupying 55 Å$^2$ on the substrate surface. This is reasonable given that the amine headgroup surface area is expected to be about 20 Å$^2$, allowing for space to accommodate slightly bulkier alkyl chains.

The most common cleavage plane of the iron oxide ($\alpha$-Fe$_2$O$_3$) surface is the hexagonal (0001) plane, with a unit cell size of 5 Å (as reported by Shaikhutdinov et al.) between the uppermost iron atoms on the surface. Considering the size of the amine molecule, an adsorption model in which each of these Fe$^{3+}$ sites is occupied seems plausible given the extent of crowding this would entail; if each site were occupied, the area per molecule would be 21.7 Å$^2$, assuming a perfect homogeneous surface across the entire powder sample. A more disperse model (e.g., with alternate sites occupied) therefore seems more probable.

Adsorption at the solid/solution interface is an exchange process and can be described by a number of models, particularly those of Everett. However, where the adsorbate adsorbs strongly this adsorption may be approximated by the Langmuir model.

PNR. Figure 2a presents the neutron reflection data from the substrate under deuterated hexadecane compared to the data from the surface when exposed to 1.25 × 10$^{-3}$ mol dm$^{-3}$ hexadecylamine in deuterated hexadecane. The figure shows data obtained with both up- and down-spin neutron polarizations, clearly demonstrating the pronounced difference in reflectivity obtained for each, most markedly in the down-spin profiles. The iron-sputtered substrate was initially measured under air and then under the deuterated solvent to identify and characterize the metal and oxide layers present. The up-spin data exhibit a series of fringes, the spacing of which are inversely related to the thicknesses of the surface layers. The gradients of the reflectivity curves are determined by roughnesses at each interface. From a careful fitting of these data using the Polly software, these parameters were determined and are shown in Table 2. The up- and down-spin data were fitted simultaneously. The iron layer thickness of 202 Å corresponded to that estimated by XRR data provided by the Helmholtz Zentrum, Berlin, Germany, where the substrates were sputtered.

The magnetic behavior of the iron and iron oxide layers is also contained in the reflectivity data and can be estimated by fitting. Here, the magnetic moment, $\mu$, of the oxide layer ($\mu = 2.0 \mu_B$) was intermediate between Fe$_2$O$_3$ (non-magnetic, $\mu = 0.0 \mu_B$) and Fe$_3$O$_4$ (magnetic, $\mu = 4.1 \mu_B$), suggesting that the layer consists of a mixture of the two oxides. Examples of mixtures of such oxides have been reported for the sputtered iron layers in the literature.

The addition of increasing concentrations of hexadecylamine in hexadecane-$d_{34}$ led to changes in the reflectivity profiles generated, indicating that the amine molecules were interacting with the iron surface and adsorbing. The greatest changes were seen in the down-spin data, as expected. In Figure 3, the
simulated SLD profile is depicted schematically along the vertical z axis passing through the interface. For the down-spin simulation, there is only one major contrast, related to the adsorbed layer, whereas the presence of a larger contrast (between the iron and silicon) for the up-spin simulation causes the up-spin neutrons to be less sensitive to changes in the adsorbed layer.

Table 2. Fitted Layer Parameters and Fitted ρ Values for the Increasing Amine Concentrations with Their Corresponding Adsorbed Amounts

| Layer                  | Thickness (Å) | Roughness (Å) | [amine]_{Initial} (mol dm^{-3}) | ρ_{Initial} (×10^{-6}, Å^{-2}) | Coverage (%) | Adsorbed Amount (×10^{-6}, mol m^{-2}) |
|------------------------|---------------|---------------|---------------------------------|-------------------------------|--------------|----------------------------------------|
| Si                     | 12            | 1.03 × 10^{-4} | 5.00                            | 25.7                          | 2.26         |
| SiO2                   | 10            | 9.4           | 4.18 × 10^{-4}                  | 4.02                          | 39.4         | 4.05                                   |
| Fe                     | 202           | 15.6          | 1.25 × 10^{-3}                  | 3.82                          | 42.1         | 4.41                                   |
| Fe2O3                  | 30            | 10            | 4.25 × 10^{-3}                  | 3.16                          | 51.4         | 5.46                                   |
| amine layer, low concs (1 and 4 × 10^{-4} mol dm^{-3}) | 16 (+3)       | 4.9           |                                |                               |              |
| amine layer, high concs (1 and 4 × 10^{-3} mol dm^{-3}) | 20 (+3)       | 5.0           |                                |                               |              |
Examples of the down-spin data are shown in Figure 2b where reflectivity profiles obtained with down-spin neutrons for the two highest concentrations, $1.25 \times 10^{-3}$ and $4.25 \times 10^{-3}$ mol dm$^{-3}$ amine, are compared to that for the substrate under the deuterated solvent only. Models fitted to the experimental data for each concentration gave a layer thickness for the adsorbed amine of 16 (±3) Å at the two lower concentrations ($1.03 \times 10^{-4}$ and $4.18 \times 10^{-4}$ mol dm$^{-3}$) and 20 (±3) Å as the concentration was increased to $1.25 \times 10^{-3}$ and $4.25 \times 10^{-3}$ mol dm$^{-3}$ (the error in the layer thickness was estimated from the minimum and maximum thicknesses over a range of SLDs that could be fitted to the data). The variation in layer thickness with concentration (from 16 to 20 Å) is of the order of the experimental uncertainty, and hence any changes on layer thickness are rather modest. The extended hexadecylamine chain length is expected to be 21.5 Å, suggesting that the measured layer thickness is reasonable. The difference is proposed to arise from one or more of several possibilities; the amine molecules may sit tilted on the surface or may extend into the porous oxide surface, or conformation disorder in the chains may exist, producing a slightly thinner layer than the fully extended chain. At higher concentrations, the increased adsorption appears to have led to some reorientation of the alkyl chains.

The scattering length densities of the amine layer were also fitted and found to decrease with an increasing amine concentration. It is expected that the ratio of amine to solvent in the adsorbed layer will increase with more amine adsorption, and the SLD should therefore tend from that of hexadecane-$d_{34}$, 6.717 × 10$^{-6}$ Å$^{-2}$, toward that of hexadecylamine, −0.260 × 10$^{-6}$ Å$^{-2}$, as observed. The fitted values are shown in Table 2, also expressed as percent coverage of the two components (deduced from the amine/solvent ratio needed to attain the fitted scattering length density), along with the corresponding adsorbed amounts (calculated assuming the layer thickness of 16 Å and molecular volumes of 5.127 × 10$^{-28}$ and 4.867 × 10$^{-28}$ m$^3$ for the amine and solvent, respectively; these were calculated from molecular weights of 241.46 and 259.97 g mol$^{-1}$ and bulk densities of 0.782 and 0.887 g mL$^{-1}$ for the amine and solvent, respectively).

The concentration dependence of the reflectivity indicates that the amine shows a relatively high affinity for the iron surface even at low concentrations, reaching a coverage of around 50% (in terms of the amine/solvent ratio calculated from the fitted SLD) at saturation. The adsorbed amounts determined by PNR have been plotted alongside the depletion isotherm in Figure 4. While the curve shapes are very similar, with the half-maximum concentrations being the same for both sets of data, the PNR data show a plateau value significantly higher than that of the depletion isotherm, giving an area per amine molecule of around 30 Å$^2$, a value somewhat lower than that given by the solution isotherms outlined above. This difference in behavior may potentially arise from a number of effects. These include the surface roughness of the iron oxide layer in the neutron reflection experiments, because the adsorbed amounts are calculated assuming a completely flat surface. However, as reported above, the surface roughness is significant (approximately 10 Å), and hence the actual surface area is larger than the geometric area of the wafer. Simple calculations based on the experimentally determined roughness indicate that this effect can account for the difference in adsorption between the isotherm and neutron reflection approaches. Another potential contributing factor may be

![Figure 4. Comparison of the PNR (○) and depletion isotherm (●) data. Values calculated from the PNR data have assumed a completely flat surface. The calculated Langmuir isotherms are also shown (lines).](image)

**Figure 5.** (a) SFG spectra taken over the C–H stretching region (2800–3000 cm$^{-1}$) for hexadecylamine adsorbed onto iron from hexadecane-$d_{34}$ with the two polarization combinations PPP (top) and SSP (bottom) combinations. (b) PPP SFG spectrum of hexadecyl-$d_{13}$-amine in hexadecane. The amine concentration in both cases is $4.25 \times 10$ mol dm$^{-3}$.
cm$^{-1}$. It is immediately apparent that the methyl Fermi resonance is disproportionately strong in the spectra for both polarization combinations. Because the Fermi resonance draws intensity from the fundamental, its intensity should be no greater than equivalent to the fundamental band with which it is associated. In this case, the same effect has previously been reported by Zhang et al. for a mild steel surface on which octadecane thiol has been self-assembled. In their paper, the increased intensity of the Fermi resonance is attributed to the presence of iron oxide. Because our surface is predominately composed of an oxide layer, as will be demonstrated by the XPS data discussed subsequently, this strengthening of the Fermi resonance band may also be attributed to the iron oxide film. Because interpretation of the SFG spectra relies heavily on the relative intensities of the methyl and methylene bands, the PPP spectrum of deuterated hexadecylamine in the CD stretching region was also recorded (Figure 5b). This spectrum is markedly different from that observed in the CH region, being free from any distortion in band intensities arising from the Fermi resonance. This region is dominated by the methyl stretching bands at 2070, 2123, and 2217 cm$^{-1}$, corresponding to $r^1$, $r^2_{ff}$, and $r^1$, respectively, with only two small shoulders apparent at 2098 and 2197 cm$^{-1}$, corresponding to the d$^1$ and d$^2$ bands, respectively.

From both qualitative inspection of the spectra and comparison of the modeled spectral intensities, it is clear that the methylene symmetric stretching peaks (d$^1$, at 2846/2098 cm$^{-1}$) in the PPP spectra are of almost negligible intensity compared to the peaks that correspond to the terminal methyl group stretches (at 2871/2070, 2935/2123, and 2964/2117 cm$^{-1}$). This occurs when the alkyl chain conformational order is predominately all trans and the methylene modes become locally centrosymmetric and, hence, SFG-inactive, and it is therefore concluded that, although a small number of gauche defects are present, the adsorbed layer shows a high degree of conformational order.

This conclusion concerning the conformational order in the alkyl chains is supported by the work of Miranda et al. who report the SFG spectra of dioctadecyl dimethyl ammonium chloride (DOAC) from solvents of varying polarity onto quartz. For polar solvents, a high level of disorder was observed, but when a nonpolar solvent of comparable molecular length to DOAC was used, hexadecane, the monolayer formed was well-ordered. The authors attribute this increased ordering to interdigitation of the solvent molecule with the adsorbate to form a tightly packed layer. The fitted SLD values observed in our neutron data also indicate that a significant proportion of solvent is present in the monolayer; it seems probable therefore that a similar process of interdigitation occurs here.

SFG spectra recorded in the CH region for the deuterated amine in hexadecane failed to produce any significant spectra for hexadecane. This is most likely due to a combination of the reduced IR intensity on the metal surface because of absorption by the bulk oil and the presumed near all-trans conformational order of the interdigitated hexadecane, which would result in a centrosymmetric and, therefore, SFG-inactive hexadecane layer.

The polar orientation of the molecules on the surface has been inferred from a comparison of the spectra presented here to spectra reported in the literature of ODT on mild steel, in which the adsorbed monolayer has a known orientation; the signals attributed to methyl group stretches all appear as peaks with a modeled phase of 43° in close agreement with the 45° previously reported, suggesting that the terminal methyl groups are pointing away from the surface, and hence, the adsorbed layer sits with the amine headgroup oriented toward the iron surface, a result that is supported by the XPS data that show evidence of a nitrogen adsorption peak.

The tilt angle of the terminal methyl group to the surface normal was calculated by comparison of the ratio of symmetric and antisymmetric peak intensities in the PPP spectra to the theoretically simulated value derived from the method proposed by Zhang et al., found according to

$$I_{p,IR} = I_{p,vis}$$

where $L$ and $K$ are the nonlinear and linear Fresnel factors, respectively, $\chi^{(2)}$ is the second-order susceptibility, and $E_{p,s}$ is the surface electric field for the p- or s-polarized light. Because $\chi^{(2)}$ can be directly related to the tilt angle, $\theta$, this permits the plotting of a curve of the ratio of intensities for the two peaks as a function of $\theta$, from which the experimentally derived ratio may be used to determine the methyl tilt angle relative to the surface normal.

This approach gave a value for the methyl group inclination of 32°. However, this tilt angle should be treated as an estimate only given that the monolayer contains at least some gauche defects.

From simple geometric calculations using the layer thickness value of 20 (±3) Å at saturation determined by PNR and a chain length of 21.5 Å, a tilt angle of 22° to the surface normal is predicted.

**XPS.** The Fe 2p spectrum from the iron-sputtered silicon wafer is shown in Figure 6a; the broad peak at around 710 eV may be resolved into two peaks at 711.8 and 709.9 eV, which is consistent with the presence of the two types of iron oxide, Fe$_3$O$_4$ and Fe$_7$O$_8$. Many examples of peaks around this region exist for both oxides, and therefore, it is unsurprising that they merge in this instance. This suggestion of a mixture of oxides at the surface is consistent with the fitting of the magnetic moment seen for the PNR data. A small shoulder at 706.9 eV is attributed to the presence of unoxidized iron.

No change in the Fe 2p region was observed for the sample treated with amine in dodecane; this is unsurprising, because the proportion of iron affected by any reaction with the amine would be very small in comparison to the entire depth of iron analyzed (on the order of around 100 Å).

Figure 6b, the N 1s spectrum for the sample treated with hexadecylamine/hexadecane, shows a broad peak that is not evident in the untreated substrate; this may be resolved into three components, at 401.1, 399.7, and 397.2 eV (with a ratio of intensities roughly 1:6:3), which may be assigned by reference to expected peaks in various environments. The peak at 397.2 eV is presumed to result from amine that has not reacted with the surface but remains on the sample, "free amine", because the lower binding energy indicates a higher electron density than the species that give rise to the remaining peaks. We were not able to completely remove any excess solution prior to measurement, and therefore, this “free” amine is taken to represent amine that was dried onto the surface during the XPS measurements rather than amine adsorbed in the "wet" system. The peak at 399.7 eV corresponds well to
what might be expected for a nitrogen atom donating electron density to the iron surface via its lone pair (Willenbruch et al. report a value of 399.8 eV for ammonia on an iron surface) and, hence, is assumed to arise from the chemisorbed amine. The smallest peak, at 401.1 eV, has a rather high energy that indicates a more positively charged amine. This may arise from the interaction with negatively charged surface oxygen atoms; Weng et al. report a value of 401.5 eV for an "oxidized N" within a CNO\(^-\) group. Small water impurities present in the solvent may account for this protonation of the amine group. The low peak intensity relative to the other peaks indicates that this species would be present in far lower concentrations.

\section{CONCLUSION}

Experimental methods to characterize an iron/iron oxide surface and the adsorption behavior of an alkyl amine from oil thereupon have been presented in this work. All techniques used demonstrate the binding of the hexadecylamine species to the iron oxide surface. The XPS data indicate chemisorbed amine, where the nitrogen is donating electron density to the surface iron(III) ions. The strong affinity of the amine for the surface is also observed in adsorption isotherms using solution depletion and PNR methods, in both of which the adsorbed amount is seen to increase steeply with the concentration, resulting in a high plateau coverage. The SFG spectra demonstrate that the methylene groups are in an all-trans configuration with the polar headgroup directed toward the surface.

Several parameters that characterize the adsorbed layer were identified; from the PNR data fitting, a modest increase in layer thickness from 16 to 20 (±3) Å was observed as the amine concentration was increased, slightly above the experimental precision. The molecular tilt angle was also calculated both using this PNR value and also from consideration of the SFG peak intensity ratios. However, the latter was considered unreliable because of the unexpected enhancement of the Fermi peak intensity; therefore, the tilt angle of the methyl group is considered most likely to fall into the 30°–50° range, relative to the surface normal. A depiction of the model for hexadecylamine adsorption to the iron oxide surface is shown in Figure 7. The molecules are considered to sit fully extended on the surface in a well-ordered layer, whereby the amine nitrogens donate electron density to the iron cations that sit on top of the iron oxide (0001) plane. From the XPS nitrogen spectra, it seems possible that a small proportion of semi-positive amine molecules that interact electrostatically with the surface oxygen atoms may also be found in the adsorbed layer.

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\subsection{Notes}
The authors declare no competing financial interest.

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