The adsorption of 4-n-nonylphenol, carvacrol and ethanol onto iron oxide from non-aqueous hydrocarbon solvents

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ABSTRACT: The adsorption of 4-n-nonylphenol (4NP), carvacrol and ethanol onto the surface of iron oxide from non-aqueous solutions is presented. It is found that adsorption of 4NP from alkanes is strong and proceeds to monolayer formation where the molecules are essentially ‘upright’. However at high relative concentrations, ethanol successfully out-competes 4NP for the iron oxide surface. Estimates of the enthalpy and entropy of binding of 4NP were found to be exothermic and entropically disfavored. Sum frequency generation vibrational spectroscopy data indicate some evidence of binding through a phenolate anion, despite the non-polar, non-aqueous solvent. Carvacrol is also found to adsorb as a monolayer where the molecules are lying ‘flat’. The adsorption of ethanol onto iron oxide from dodecane was investigated through the use of quantitative NMR, used as a convenient analytical technique for measuring adsorption isotherms. It was concluded that ethanol does not form adsorbed monolayers on the surface. Instead it partitions onto the surface as a surface enhanced local phase separation related to its poor solubility in alkane solvents.

Introduction

The competitive adsorption of oil additives can be important in their commercial exploitation¹. The efficacy of these additives often depends on their interaction with solid surfaces. Hence, a fundamental study of their adsorption at the solid/oil interface is of relevance to a wide variety of industrial applications. Here we focus on the surface adsorption behavior of alkyl substituted phenols as chemical structural moieties present in various types of fuel and lubricant additives,² with a particular emphasis on the phenolic OH functionality.

In general, there are a wide range of oils used commercially³, often multicomponent blends. This work focuses on linear and branched alkanes as solvents. In addition, with the increased emphasis on biofuels⁴, we are keen to see the effect on the adsorption with added ethanol (typically present at 5–10 % by volume).

In this work we aim to capture the key elements of commercial systems and so have considered an iron oxide substrate. In many commercial cases the relevant surface will be steel. However, recent XPS and related work have indicated that the surface of some steels have a significant proportion of iron oxide present at the surface^{5–7}, even for stainless steels where chromium oxide is traditionally thought to be the passivating surface⁸. We expect the surface of the

iron oxide to be a combination of oxide and hydroxide chemical groups⁹.

While 4NP, illustrated in Figure 1a), is not used in fuel or lubricant formulations, alkyl phenols are representative of the types of chemical functionalities present in important classes of additives. These are namely detergent-like deposit control additives and anti-oxidants that combine a phenol head group with a hydrophobic tail¹⁰. We expect the OH of the phenol to be the dominant group binding to the iron oxide. We also briefly address the hindered phenol carvacrol, illustrated in Figure 1b).

Figure 1. a) 4-n-nonylphenol, b) carvacrol

Solution depletion adsorption isotherms are a powerful technique for extracting qualitative and quantitative information about an interfacial system. However, they rely on a robust and quantitative analytical technique for measuring solution concentration.

Techniques such as UV/Vis spectroscopy can be successfully employed to measure aromatic compounds in simple alkane solutions. However, for this work, as we intended to investigate the competitive adsorption of ethanol with 4NP, UV/Vis was not appropriate for quantifying ethanol as it has no significant UV/Vis absorption.

Quantitative ^1H NMR (qNMR) has been employed as an analytical technique since the 1960s^{11,12}, with recent advances allowing for the measurement of sub-mM concentrations¹³. NMR has been used in this work as a novel quantitative technique for the purpose of measuring adsorption isotherms via the solution depletion method.

Sum frequency generation vibrational spectroscopy (SFG) is a surface-specific technique where a vibrational infrared (IR) spectrum is obtained *in-situ* from molecules in solution at an interface¹⁴⁻¹⁶. The spectrum is collected by spatially and temporally overlapping a visible laser beam, with fixed frequency, and an IR laser beam, with tunable frequency, onto the interface of interest to generate a reflected laser beam with frequency equal to the sum of the two incident beams. This configuration gives rise to a non-linear optical phenomenon whereby there is no signal from centrosymmetric environments¹⁷. Hence, no signal is generated from a bulk isotropic material. However, at an interface the center of symmetry is broken and an SFG signal is obtained.

4NP has been identified as a toxic water pollutant, originating from biodegradation products of cleaning agents, pesticides and food packaging¹⁸. As such, its adsorption onto iron oxide^{19,20}, carbons²¹, bioadsorbents²², clays²³, magnetic particles²⁴, and soils²⁵ from aqueous solutions has been previously investigated in an attempt to develop effective removal processes. However, as far as the authors know, this work is the first study to focus on 4NP adsorption from non-aqueous solutions. This study complements and extends previous work on the adsorption of 4NP and other phenols from aqueous systems²⁶⁻²⁸.

Experimental Section

Materials and instruments

Iron (III) oxide powder ($< 5\ \mu\text{m}$, $\geq 99\%$), chromium (III) oxide powder ($< 100\ \text{nm}$, 99%), ethanol ($\geq 99.8\%$) and carvacrol (99%) were obtained from Sigma Aldrich. 4-n-nonylphenol (99.6%) was obtained from Alfa Aesar, while n-dodecane (99.7%) was obtained from VWR Laboratories. Deuterated n-dodecane (D26, 98.3% isotopic enrichment) was obtained from Cambridge Isotope Laboratories. All samples were used without further purification.

The centrifuge used was from Yingtai Instruments, model TG20. The UV-Ozone cleaner used was from Bioforce Nanosciences. UV/Vis measurements were performed using a PerkinElmer Lambda 25 spectrometer. The specific surface areas of the powdered solids were determined by adsorption of nitrogen using BET²⁹ analysis ($5.12\ \text{m}^2\ \text{g}^{-1}$) at the Department of Materials, University of Cambridge. All items and equipment were either at the Department of Chemistry or BP Institute, University of Cambridge.

Solution depletion isotherms

The majority of the work presented here exploits the solution depletion method^{30,31} for the determination of the adsorbed amount. In brief, a solution of the additive in oil at a known initial

concentration was contacted with a high surface area powder of the substrate of interest and allowed to equilibrate. The solids were then separated from the supernatant and the solution concentration re-measured. The difference in concentration was taken as the amount adsorbed on the substrate.

In preparing the isotherms a ratio, by mass, of approximately 1:2 solid powder to solution was allowed to equilibrate. Kinetic studies indicate that equilibrium was established in approximately 20 hours¹⁹. The solids were separated by centrifugation and the supernatant concentrations were determined through UV/Vis spectroscopy and qNMR. The measured intensity was used to give the solution concentration by means of comparison to a calibration curve established from measurements on samples with known concentrations.

Sum frequency generation vibrational spectroscopy (SFG)

The SFG spectra of the samples were recorded in air at room temperature using an Ekspla Nd:YAG 50Hz Sum Frequency Generation (SFG) spectrometer³² (29 ps pulses at 50 Hz) with a co-propagating beam geometry. The IR and the visible beams were incident at angles of 53° and 60° to the surface normal respectively. The visible beam wavelength was fixed at 532.1 nm and the IR wavelength varied. Polarizations of PPP and SSP (SFG, Visible, IR) were used and data were collected over the ranges 2800–3200 and 1100–1700 cm^{-1} corresponding to C–H and C–O stretching regions respectively. The data were normalized to the IR laser power.

The iron samples for SFG were prepared via thermal evaporation of an iron target onto a silicon wafer. The substrates were cleaned for 40 minutes under UV-Ozone to remove organic impurities prior to immersing in a solution of 15 mM 4NP in d26-dodecane. A hemicylindrical CaF_2 prism was placed on top of a micron-thick layer of solution prior to measurement. For measurements taken between 1100–1700 cm^{-1} , a BaF_2 prism was used.

Substrates

In employing a range of different experimental methods it is necessary to use different iron oxide substrates. Powdered iron oxide and deposited iron layers are necessary for adsorption isotherms and SFG respectively. A number of characterization methods (e.g. XRD, XPS and elemental analysis) have been performed on these two types of substrate, as outlined in the Supporting Information. The data indicate that both substrates have external surfaces of iron oxide, as expected, and are essentially hematite (Fe_2O_3). Note that we have also not taken steps to eliminate water from these systems, in order to capture commercial behavior more closely.

Quantitative ^1H NMR

NMR spectra were recorded using a Bruker 500 MHz AVIII HD Smart Probe NMR spectrometer, with WET solvent suppression³³. For each sample 512 scans were completed with an acquisition time of 0.957 s. Wilmad NMR tubes (diameter 5 mm) were used. A deuterated locking agent was added to samples in order to correct for the drift of the magnetic field and to ensure field stability and homogeneity. Deuterated d6-acetone was used at 10 % by volume. Analysis of NMR spectra was carried out with Bruker TopSpin software. The solvent suppression was performed to prevent the

signal from the solvent protons dominating those of the additive, which are present at much lower concentration.

Figure 2. a) UV/Vis calibration plot of 4NP in dodecane and b) adsorption isotherm of 4NP adsorbed from dodecane on iron oxide. Data are shown as points. Solid lines show a straight line fit and a Langmuir fit in a) and b) respectively. Error bars in a) are comparable to the size of the data points. The mean of the normalised root-mean-square deviations (NRMSD) from the fitted Langmuir model is 0.05.

Although somewhat more expensive than UV spectroscopy, the attraction of q-NMR is evident here as the ethanol does not have suitable UV bands. More generally, many simple hydrocarbon solvents have features at low chemical shift, while the additive's polar head groups typically have features at high field. This approach does not require chemical groups to be UV active and the features are usually sharper and overlap less than UV bands, allowing for several species to be considered. However, the sensitivity is not as good for qNMR as UV/Vis where very low concentrations of strongly absorbing species can be measured.

Results and Discussion

Solution depletion isotherms

Figure 2a) presents the calibration curve for 4NP in dodecane obtained from the UV spectra of the phenol in the oil at various concentrations. The linear region of this curve at low concentration was used for concentration determination and more concentrated samples were diluted into this region.

Figure 2b) presents the adsorption isotherm of 4NP adsorbed from dodecane on iron oxide. The adsorption appears to rise initial-

ly with increasing phenol concentration before reaching a plateau with approximately monolayer coverage of $(3.66 \pm 0.06) \times 10^{-6}$ mol m $^{-2}$. This value has been estimated by initially fitting the data to a linear form of the Langmuir equation and then employing the Levenberg-Marquardt method of least squares³⁴. The corresponding area per molecule is approximately (45.4 ± 0.7) Å 2 molecule $^{-1}$.

Using simple geometric arguments, which are detailed in the Supporting Information, one can estimate the dimensions of 4NP to be approximately $(6.2 \times 3.4 \times 18.6)$ Å. Hence, if the molecule were flat on the surface, the area per molecule would be 115 Å 2 , somewhat larger than observed. If the molecule were upright then the area would be approximately 21 Å 2 . Although these must be considered estimates, one can conclude that the molecules are reasonably upright on the surface. An angle of inclination can be calculated, but we do not consider this appropriate with these simple estimates. In addition, we note that the model has assumed the 4NP alkyl chain is all trans and extended, when of course, gauche conformers could be present. Given that the cross-sectional area of an alkyl chain is approximately 20 Å 2 ,³⁵ the chain could be folded back on itself once, but no more, allowing for some gauche conformers. Equally, the dodecane may penetrate the alkyl chain region of the 4NP. In summary, there are three possible arrangements: the alkyl chains are upright and extended, the chain is folded back on itself once, and/or the chains are extended with penetrating solvent molecules. A scanning tunneling microscopy study, presented in the Supporting Information, proved inconclusive in determining the molecular conformation of 4NP.

A comparison of the adsorption isotherms for 4NP in several binary and ternary solutions on iron oxide is shown in Figure 3. The adsorption isotherm for 4NP in dodecane (45 %) and iso-octane (55 %) on iron oxide shows the same rise in adsorption with concentration towards a plateau as for dodecane alone. The extracted area per molecule of (33 ± 4) Å 2 molecule $^{-1}$ is somewhat smaller than for dodecane alone, suggesting a more upright orientation.

This difference in area per molecule in the different solvents may be attributed to the more effective packing of dodecane in the 4NP alkyl chain region, pushing the 4NP apart. In contrast, iso-octane is somewhat bulkier and less convenient for packing among the 4NP tails, leading to some exclusion of the iso-octane from the 4NP alkyl chain region. In this case, a smaller area per molecule is expected, rather closer to that for fully upright, close packed 4NP.

In a solution of dodecane (95 %) and ethanol (5 %) the isotherm in Figure 3 shows that very much less phenol is adsorbed in the presence of the ethanol. Hence, we conclude that the ethanol competes strongly with the phenol since the addition of just 5 % ethanol essentially excludes the phenol from the surface.

Similar behavior is evident for the three component oil, dodecane (40 %), iso-octane (55 %) and ethanol (5 %), shown in Figure 3, where again we find that the ethanol effectively competes with the phenol for the surface.

Figure 3. Comparison of 4NP adsorption from pure dodecane (red), dodecane (45 %) and iso-octane (55 %) (black), dodecane (95 %) and ethanol (5 %) (green) and dodecane (40 %), iso-octane (55 %) and ethanol (5 %) (blue) on iron oxide. Data are shown as points and Langmuir fits are shown as a solid line. The $\overline{\text{NRMSD}}$ values are 0.07 (black) and 0.05 (red).

The adsorption isotherms of carvacrol and 4NP from dodecane are illustrated in Figure 4. The carvacrol isotherm shows the characteristic rise from low concentrations to a plateau like that of the 4NP isotherm. In this case however, the area per molecule is found to be approximately $(66 \pm 6) \text{ \AA}^2$, somewhat larger than that for the 4NP above. Geometric estimates, shown in the Supporting Information, suggest that the dimensions of carvacrol are approximately $(7.5 \times 3.8 \times 9.2) \text{ \AA}$. If the molecule is flat on the surface one might expect an area of $69 \text{ \AA}^2$, in contrast to an upright molecule with an area of $28 \text{ \AA}^2$. Hence, these data indicate a flatter adsorption geometry in contrast with that observed for 4NP. This geometry is confirmed by a lack of bands in the SFG spectrum, presented in the Supporting Information.

Figure 4. Adsorption isotherm of 4NP (black) and carvacrol (red) from dodecane on iron oxide. Data are shown as points and Langmuir fits are shown as solid lines. The $\overline{\text{NRMSD}}$ values are 0.05 (black) and 0.02 (red).

At this stage we cannot be certain of the underlying mechanism for the differences in molecular orientation between carvacrol and 4NP. Typically, one might expect an aromatic ring to lie flat on the oxide surface³⁶. Hence, it is 4NP that is atypical. The upright orientation likely arises from the preference for effective alkyl chain

packing, which is clearly not a dominant effect for carvacrol. The interdigitation of the solvent, dodecane, may also be significant. However, as will be presented later, we have seen evidence for gauche defects in the 4NP alkyl chain, suggesting that the alkyl chain packing is not optimized.

The temperature-dependent adsorption isotherms of 4NP from dodecane onto iron oxide are given in Figure 5. We note that the amount adsorbed at high concentrations is essentially constant with changing temperature. Rather, it is the concentration at which this plateau is obtained that changes. We can fit these isotherms to a Langmuir-type adsorption isotherm³⁷ and obtain an approximate adsorption constant as a function of temperature. A van't Hoff plot³⁸ is then used to estimate the enthalpy and entropy of binding of the 4NP to the iron oxide surface. These thermodynamic parameters are found to be $\Delta H_{\text{ads}} = -29.9 \text{ kJ mol}^{-1}$ and $\Delta S_{\text{ads}} = -44 \text{ J K}^{-1} \text{ mol}^{-1}$. These values suggest that the exchange of adsorbed dodecane for 4NP is exothermic and that the adsorption of 4NP leads to a more ordered monolayer than the dodecane. This finding might be rationalised if the dodecane adsorbs flat taking up a relatively large area (at $\sim 150 \text{ \AA}^2$) on the surface. Hence, on desorption one dodecane molecule is released but two or three 4NP molecules are bound (at $\sim 50 \text{ \AA}^2$), leading to a net reduction in translational entropy.

Figure 5. Temperature dependent adsorption isotherms of 4NP from dodecane on iron oxide at 20 °C (black), 40 °C (red) and 60 °C (green). The $\overline{\text{NRMSD}}$ values are 0.04 (black), 0.06 (red) and 0.07 (green).

SFG study of 4NP on iron oxide

SFG spectra for 4NP adsorbed onto iron oxide from d26-dodecane are presented in Figure 6. They were collected in the range $2800\text{--}3200 \text{ cm}^{-1}$ to capture the C–H stretches³⁹. The PPP and SSP polarization spectra were recorded and are given in Figures 6a) and b) respectively. The step in intensity at 3125 cm^{-1} , indicated by a *, is due to an artifact of the SFG machine, arising from the re-orientation of the diffraction grating. The peaks and their assignments are summarized in Table 1.

As a resonance must be both IR and Raman active to be sum frequency allowed¹⁵, obtaining spectral assignments for the methyl and methylene stretches has been aided by comparison with the bands of polymethylene in its IR and Raman spectra^{40,41}.

Table 1. Summary of SFG peaks in the C–H stretching region, shown in Figure 6, and corresponding assignments.

Frequency / cm ⁻¹		Assignment
PPP	SSP	
2846	2848	CH ₂ symmetric stretch (d ⁺)
2870	2876	CH ₃ symmetric stretch (r ⁺)
2910	-	Mixture of CH ₂ anti-symmetric stretch (d ⁻) and d ⁺ Fermi resonance
2958	-	CH ₃ anti-symmetric stretch (r ⁻)
-	2934	Fermi resonance of overtone of methyl bending mode with CH ₂ symmetric stretch ^{42,43}
2992	-	CH ₂ shifted due to aromatic ring ⁶
-	3010	Olefinic contamination ⁴⁴

Figure 6. SFG spectra of 4NP on iron oxide from d26-dodecane in a) PPP and b) SSP polarizations between 2800–3200 cm⁻¹. The * indicates an instrumental jump in laser intensity.

The bands at 2992 and 3010 cm⁻¹ in the PPP and SSP spectra respectively are somewhat low in frequency to be assigned to an aromatic C–H stretch. As such, we tentatively attribute these bands to a CH₂ stretch shifted due to proximity to the aromatic ring⁶ and an olefinic contamination respectively⁴⁴.

The presence of a strong CH₂ symmetric stretch at ~2850 cm⁻¹ indicates some degree of conformational disorder in the alkyl chain⁴⁵, typically manifested as gauche defects. If the molecules

were well-packed and all-trans, the methylene groups would be locally centrosymmetric and hence not observed.

The SSP polarization combination, which has a *p*-polarized infrared laser beam, probes only the $\chi_{yyz}^{(2)}$ component of the second order non-linear optical susceptibility. Therefore, only vibrational modes with a transition moment that contains a component parallel to the surface normal will contribute to the SFG intensity. In this case the SSP spectrum features a strong symmetric methyl resonance (r⁺), but the anti-symmetric methyl resonance (r⁻) is absent. This observation indicates that the C₃ axes of the terminal methyl groups are orientated, on average, parallel to the surface normal⁴⁶, in good agreement with the isotherm results above. It is noted that the r⁻ mode is, however, observed in the PPP. Because of symmetry considerations, there are four components of the susceptibility that contribute to the PPP spectra. Hence, orientational conclusions are not as straightforward to obtain from the PPP.

The SFG spectrum for the 1100–1700 cm⁻¹ region, recorded in a PPP polarization, is presented in Figure 7. The strong peak at 1270 cm⁻¹ is assigned as a $\nu(\text{CO})$ band, characteristic of a phenolate anion⁴⁷. This assignment is further confirmed by a shift of ~20 cm⁻¹ from the $\nu(\text{CO})$ band measured in the bulk solution IR at 1250 cm⁻¹, consistent with the literature as indicative of the formation of a phenolate species^{48,49}. The peaks at 1506 and 1610 cm⁻¹ are assigned to $\nu(\text{CC})$ ring vibrations^{50,51} and the peak at 1180 cm⁻¹ is assigned to a C–CH₃ stretch⁵². Interference bands from atmospheric water vapor can be seen in the 1300–1700 cm⁻¹ region.

This slightly unexpected result not only confirms the presence of 4NP on the surface, but gives us an insight into the chemistry of the adsorption behavior, suggesting that adsorption takes place through a phenolate anion despite the non-polar alkane solvent. It is not possible to tell what happens to this proton from the SFG spectrum. However, we tentatively speculate that it could form hydroxylated termination groups⁵³ on the iron oxide, diffuse into the metal in a similar fashion to the phenomenon of hydrogen embrittlement⁵⁴ or perhaps react with a surface OH group, which are typically found at iron oxide surfaces⁵⁵, to form water.

Figure 7. SFG spectrum of 4NP adsorbed onto iron oxide from d26-dodecane in PPP polarization between 1100–1700 cm^{-1} .

qNMR as a novel technique for adsorption analysis

In order to verify that qNMR could be used as a robust, quantitative analytical technique suitable for measuring adsorption isotherms, the 4NP in dodecane onto iron oxide isotherm was repeated (shown in the Supporting Information). The curve shape is similar and the area per molecule is calculated to be $(42 \pm 3) \text{ \AA}^2 \text{ molecule}^{-1}$ which is within experimental error of results obtained using UV/Vis as an analytical technique. Therefore we conclude that qNMR can be successfully used in order to measure adsorption isotherms.

Figure 8 shows the adsorption isotherm of ethanol onto iron oxide from dodecane, the measurement of which was only possible using qNMR. These data cannot be fit to a Langmuir adsorption model; instead a Freundlich model^{56–58} must be used. This model, unlike the Langmuir model, assumes there are lateral interactions between additives such that the probability of adsorption is a function of surface coverage. This fit indicates that for our system the ethanol-ethanol interactions are a significant factor in its adsorption behavior.

We also do not observe the characteristic plateau of Langmuir-like adsorption, indicating that we are not forming well defined monolayers. Dashed lines indicate approximately where a complete monolayer and bilayer would be expected, demonstrating that the system adopts a multilayer interfacial structure. Additionally, ethanol/alkane systems, while miscible, have been shown to be close to phase separation⁵⁹. Therefore, instead of forming a solid phase, Langmuir-like monolayer at the surface, we suggest that the ethanol is partitioning onto the surface in a liquid phase. We interpret this interfacial behavior as a surface enhanced local phase separation, which is qualitatively consistent with molecular dynamics simulations of ethanol adsorption onto an iron (III) oxide surface^{60,61}.

Figure 8. Adsorption isotherm of ethanol adsorbed from dodecane onto iron oxide. Data are shown as points. A Freundlich fit is shown as a solid line. Dashed lines indicate the approximate amount adsorbed corresponding to a monolayer and a bilayer of ethanol. The $\overline{\text{NRMSD}}$ value is 0.03.

Summary and Conclusions

The adsorption of 4NP onto iron oxide from non-aqueous solvents was observed. The molecules are seen to adsorb in an essentially upright orientation, but with significant conformational disorder. There is some evidence that the binding takes place through a phenolate anion despite the non-polar and non-aqueous solvent, shown as a schematic in Figure 9.

The adsorption of 4NP is affected by the nature of the solvent such that the branched iso-octane leads to a lower area per molecule. This result is possibly attributed to exclusion of the solvent from the 4NP alkyl region, where the linear alkane dodecane may be able to enter. The introduction of 5 % ethanol greatly affects the amount of 4NP present at the surface. Indeed, at this concentration the 4NP is essentially excluded from the surface. We expect that the much larger mole fraction of ethanol leads to the exclusion of the phenol from the surface.

The hindered phenol carvacrol also adsorbs as a monolayer from dodecane. This molecule adopts a higher surface area which suggests the molecular orientation is instead flat on the surface.

The temperature dependent adsorption behavior was used to extract an estimate of $\Delta H_{\text{ads}} = -29.9 \text{ kJ mol}^{-1}$ for the enthalpy and $\Delta S_{\text{ads}} = -44 \text{ J K}^{-1} \text{ mol}^{-1}$ for the entropy of exchange of dodecane for 4NP.

The adsorption of ethanol onto iron oxide from dodecane was investigated, from which it was concluded that ethanol does not form adsorbed monolayers but instead partitions onto the iron oxide surface as a liquid phase multilayer structure.

Figure 9. Schematic illustration of 4NP adsorbing onto iron oxide from an alkane solvent.

ASSOCIATED CONTENT

Supporting Information

Comparison between UV/Vis and qNMR as analytical techniques for measuring adsorption isotherms, characterization of iron oxide substrates, attempt to determine molecular conformation using scanning tunneling microscopy (STM), 4NP area estimations, carvacrol area estimations, carvacrol SFG study. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Brown, M.; Fotheringham, J. D.; Hoyes, T. J.; Mortier, R. M.;

- (2) Orzulik, S. T.; Randles, S. J.; Stround, P. M. *Chemistry and Technology of Lubricants*, 2nd ed.; Springer Netherlands: Dordrecht, 1997.
- (3) Varatharajan, K.; Pushparani, D. S. Screening of Antioxidant Additives for Biodiesel Fuels. *Renew. Sustain. Energy Rev.* **2018**, *82*, 2017–2028.
- (4) Priest, M.; Ehret, P.; Flamand, L.; Dalmaz, G.; Childs, T. H. C.; Dowson, D.; Berthier, Y.; Taylor, C. M.; Lubrecht, A.; Georges, J. M. *Lubrication at the Frontier: The Role of the Interface and Surface Layers in the Thin Film and Boundary Regime*, 1st ed.; Elsevier Science, 1999.
- (5) Barker, J.; Langley, G. J.; Richards, P. Insights into Deposit Formation in High Pressure Diesel Fuel Injection Equipment. *SAE Int. J. Fuels Lubr.* **2010**.
- (6) Wood, M. H.; Welbourn, R. J. L.; Charlton, T.; Zarbakhsh, A.; Casford, M. T.; Clarke, S. M. Hexadecylamine Adsorption at the Iron Oxide–Oil Interface. *Langmuir* **2013**, *29* (45), 13735–13742.
- (7) Wood, M. H.; Casford, M. T.; Steitz, R.; Zarbakhsh, A.; Welbourn, R. J. L.; Clarke, S. M. Comparative Adsorption of Saturated and Unsaturated Fatty Acids at the Iron Oxide/Oil Interface. *Langmuir* **2016**, *32* (2), 534–540.
- (8) Wood, M. H.; Browning, K. L.; Barker, R. D.; Clarke, S. M. Using Neutron Reflectometry to Discern the Structure of Fibrinogen Adsorption at the Stainless Steel/Aqueous Interface. *J. Phys. Chem. B* **2016**, *120* (24), 5405–5416.
- (9) Jones, D. A. *Principles and Prevention of Corrosion*, 2nd ed.; Pearson, 1996.
- (10) Cornell, R. M.; Schwertmann, U. *The Iron Oxides: Structure, Properties, Reactions, Occurrences and Uses*, 2nd ed.; Wiley-VCH Verlag GmbH & Co., 2004.
- (11) Fink, J. K. *Additives for High Performance Applications*, 1st ed.; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2016.
- (12) Bharti, S. K.; Roy, R. Quantitative ^1H NMR Spectroscopy. *Trends Anal. Chem.* **2012**, *35*, 5–26.
- (13) Simmler, C.; Napolitano, J. G.; McAlpine, J. B.; Chen, S.-N.; Pauli, G. F. Universal Quantitative NMR Analysis of Complex Natural Samples. *Curr. Opin. Biotechnol.* **2014**, *25* (312), 51–59.
- (14) Kovacs, H.; Moskau, D.; Spraul, M. Cryogenically Cooled Probes—a Leap in NMR Technology. *Prog. Nucl. Magn. Reson. Spectrosc.* **2005**, *46*, 131–155.
- (15) Bain, C. D. Sum-Frequency Vibrational Spectroscopy of the Solid/Liquid Interface. *J. Chem. Soc. Faraday Trans.* **1995**, *91*, 1281–1296.
- (16) Lambert, A. G.; Davies, P. B.; Neivandt, D. J. Implementing the Theory of Sum Frequency Generation Vibrational Spectroscopy: A Tutorial Review. *Appl. Spectrosc. Rev.* **2005**, *40* (2), 103–145.
- (17) Tian, C. S.; Shen, Y. R. Recent Progress on Sum-Frequency Spectroscopy. *Surf. Sci. Rep.* **2014**, *69* (2–3), 105–131.
- (18) Humphreys, E. K.; Casford, M. T. L.; Allan, P. K.; Grey, C. P.; Clarke, S. M. SFG Study of the Potential-Dependent Adsorption of the p-Toluenesulfonate Anion at an Activated Carbon/Propylene Carbonate Interface. *J. Phys. Chem. C* **2017**, *121* (38), 20567–20575.
- (19) Sharma, V. K.; Anquandah, G. A. K.; Yngard, R. A.; Kim, H.; Fekete, J.; Bouzek, K.; Ray, A. K.; Golovko, D. Nonylphenol, Octylphenol, and Bisphenol-A in the Aquatic Environment: A Review on Occurrence, Fate, and Treatment. *J. Environ. Sci. Heal. Part A* **2009**, *44* (5), 423–442.
- (20) Al-Ahmari, S. D.; Watson, K.; Fong, B. N.; Ruyonga, R. M.; Ali, H. Adsorption Kinetics of 4-n-Nonylphenol on Hematite and Goethite. *J. Environ. Chem. Eng.* **2018**, *6* (4), 4030–4036.
- (21) McBride, M. B.; Kung, K.-H. Adsorption of Phenol and Substituted Phenols by Iron Oxides. *Environ. Toxicol. Chem.* **1991**, *10* (4), 441–448.
- (22) Iwasaki, S.; Fukuhara, T.; Abe, I.; Yanagi, J.; Mouri, M.; Iwashima, Y.; Tabuchi, T.; Shinohara, O. Adsorption of Alkylphenols onto Microporous Carbons Prepared from Coconut Shell. *Synth. Met.* **2002**, *125* (2), 207–211.
- (23) Yamada, K.; Tamura, T.; Azaki, Y.; Kashiwada, A.; Hata, Y.; Higashida, K.; Nakamura, Y. Removal of Linear and Branched P-Alkylphenols from Aqueous Solution by Combined Use of MelB Tyrosinase and Chitosan Beads. *J. Polym. Environ.* **2009**, *17* (2), 95–

- (23) Barhoumi, M.; Beurroies, I.; Denoyel, R.; Saïd, H.; Hanna, K. Coadsorption of Alkylphenols and Nonionic Surfactants onto Kaolinite. *Colloids Surfaces A Physicochem. Eng. Asp.* **2003**, *219* (1–3), 25–33.
- (24) Kurinobu, S.; Tsurusaki, K.; Natui, Y.; Kimata, M.; Hasegawa, M. Decomposition of Pollutants in Wastewater Using Magnetic Photocatalyst Particles. *J. Magn. Magn. Mater.* **2007**, *310* (2), e1025–e1027.
- (25) Düring, R. A.; Krahe, S.; Gäth, S. Sorption Behavior of Nonylphenol in Terrestrial Soils. *Environ. Sci. Technol.* **2002**, *36* (19), 4052–4057.
- (26) Gundogdu, A.; Duran, C.; Senturk, H. B.; Soylak, M.; Ozdes, D.; Serencam, H.; Imamoglu, M. Adsorption of Phenol from Aqueous Solution on a Low-Cost Activated Carbon Produced from Tea Industry Waste: Equilibrium, Kinetic, and Thermodynamic Study. *J. Chem. Eng. Data* **2012**, *57* (10), 2733–2743.
- (27) Wu, H.; Lin, Y.; Wu, J.; Zeng, L.; Zeng, D.; Du, J. Surface Adsorption of Iron Oxide Minerals for Phenol and Dissolved Organic Matter. *Earth Sci. Front.* **2008**, *15* (6), 133–141.
- (28) de la Luz-Asunción, M.; Sánchez-Mendieta, V.; Martínez-Hernández, A. L.; Castaño, V. M.; Velasco-Santos, C. Adsorption of Phenol from Aqueous Solutions by Carbon Nanomaterials of One and Two Dimensions: Kinetic and Equilibrium Studies. *J. Nanomater.* **2015**, *2015*, 1–14.
- (29) Brunauer, S.; Emmett, P. H.; Teller, E. Adsorption of Gases in Multimolecular Layers. *J. Am. Chem. Soc.* **1938**, *60* (2), 309–319.
- (30) Everett, D. H. Thermodynamics of Adsorption from Solution. Part 1.—Perfect Systems. *Trans. Faraday Soc.* **1964**, *60*, 1803–1813.
- (31) Giles, C. H.; MacEwan, T. H.; Nakhwa, S. N.; Smith, D. 786. Studies in Adsorption. Part XI. A System of Classification of Solution Adsorption Isotherms, and Its Use in Diagnosis of Adsorption Mechanisms and in Measurement of Specific Surface Areas of Solids. *J. Chem. Soc.* **1960**, No. 0, 3973.
- (32) Wang, J.; Chen, C.; Buck, S. M.; Chen, Z. Molecular Chemical Structure on Poly(Methyl Methacrylate) (PMMA) Surface Studied by Sum Frequency Generation (SFG) Vibrational Spectroscopy. *J. Phys. Chem. B* **2001**, *105* (48), 12118–12125.
- (33) Zheng, G.; Price, W. S. Solvent Signal Suppression in NMR. *Prog. Nucl. Magn. Reson. Spectrosc.* **2010**, *56* (3), 267–288.
- (34) Levenberg, K. A Method for the Solution of Certain Non-Linear Problems in Least Squares. *Q. Appl. Math.* **1944**, *2* (2), 164–168.
- (35) Ben-Shaul, A. Molecular Theory of Chain Packing, Elasticity and Lipid-Protein Interaction in Lipid Bilayers. In *Handbook of Biological Physics*; Elsevier, 1995; Vol. 1A, pp 359–401.
- (36) Grabowska, H.; Miśta, W.; Syper, L.; Wrzyszczy, J.; Zawadzki, M. Alkylation of 1-Naphthol with Alcohols over an Iron Oxide Catalyst. *Angew. Chemie Int. Ed. English* **1996**, *35* (1314), 1562–1565.
- (37) Langmuir, I. The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum. *J. Am. Chem. Soc.* **1918**, *40* (9), 1361–1403.
- (38) van't Hoff, M. J. H. Etudes de Dynamique Chimique. *Recl. des Trav. Chim. des Pays-Bas* **2010**, *3* (10), 333–336.
- (39) Snyder, R. G.; Hsu, S. L.; Krimm, S. Vibrational Spectra in the C-H Stretching Region and the Structure of the Polymethylene Chain. *Spectrochim. Acta Part A Mol. Spectrosc.* **1978**, *34* (4), 395–406.
- (40) Snyder, R. G.; Scherer, J. R. Band Structure in the C-H Stretching Region of the Raman Spectrum of the Extended Polymethylene Chain: Influence of Fermi Resonance. *J. Chem. Phys.* **1979**, *71* (8), 3221–3228.
- (41) MacPhail, R. A.; Strauss, H. L.; Snyder, R. G.; Elliger, C. A. Carbon-Hydrogen Stretching Modes and the Structure of n-Alkyl Chains. 2. Long, All-Trans Chains. *J. Phys. Chem.* **1984**, *88* (3), 334–341.
- (42) Bain, C. D.; Davies, P. B.; Ward, R. N. In-Situ Sum-Frequency Spectroscopy of Sodium Dodecyl Sulfate and Dodecanol Coadsorbed at a Hydrophobic Surface. *Langmuir* **1994**, *10* (7), 2060–2063.
- (43) Ward, R. N.; Duffy, D. C.; Davies, P. B.; Bain, C. D. Sum-Frequency Spectroscopy of Surfactants Adsorbed at a Flat Hydrophobic Surface. *J. Phys. Chem.* **1994**, *98* (34), 8536–8542.
- (44) Casford, M. T. L.; Davies, P. B.; Smith, T. D.; Bracchi, G. L. The Adsorption of Synovene on ZDDP Wear Tracks: A Sum Frequency Generation (SFG) Vibrational Spectroscopy Study. *Tribol. Lett.* **2016**, *62* (1), 11.
- (45) Conboy, J. C.; Messmer, M. C.; Richmond, G. L. Dependence of Alkyl Chain Conformation of Simple Ionic Surfactants on Head Group Functionality As Studied by Vibrational Sum-Frequency Spectroscopy. *J. Phys. Chem. B* **1997**, *101* (34), 6724–6733.
- (46) Conboy, J. C.; Messmer, M. C.; Richmond, G. L. Investigation of Surfactant Conformation and Order at the Liquid/Liquid Interface by Total Internal Reflection Sum-Frequency Vibrational Spectroscopy. *J. Phys. Chem.* **1996**, *100* (18), 7617–7622.
- (47) Popov, A.; Kondratieva, E.; Gilson, J. P.; Mariey, L.; Travert, A.; Mauge, F. IR Study of the Interaction of Phenol with Oxides and Sulfided CoMo Catalysts for Bio-Fuel Hydrodeoxygenation. *Catal. Today* **2011**, *172* (1), 132–135.
- (48) Kotorlenko, L. A.; Aleksandrova, V. S. Spectral Manifestations of Change in Electronic Structure in Phenol-Phenolate Anion-Phenoxy Radical Series. *Theor. Exp. Chem.* **1982**, *18* (1), 97–99.
- (49) Rao, Y.; Subir, M.; McArthur, E. A.; Turro, N. J.; Eissenthal, K. B. Organic Ions at the Air/Water Interface. *Chem. Phys. Lett.* **2009**, *477*, 241–244.
- (50) Roth, W.; Imhof, P.; Gerhards, M.; Schumm, S.; Kleinermanns, K. Reassignment of Ground and First Excited State Vibrations in Phenol. *Chem. Phys.* **2000**, *252*, 247–256.
- (51) Evans, J. C. The Vibrational Spectra of Phenol and Phenol-OD. *Spectrochim. Acta* **1960**, *16*, 1382–1392.
- (52) Yadav, B. S.; Tyagi, S. K.; Seema. Study of Vibrational Spectra of 4-Methyl-3-Nitrobenzaldehyde. *Indian J. Pure Appl. Phys.* **2006**, *44* (9), 644–648.
- (53) Rochester, C. H.; Topham, S. A. Infrared Study of Surface Hydroxyl Groups on Haematite. *J. Chem. Soc. Faraday Trans. 1* **1979**, *75* (0), 591–602.
- (54) Bhadeshia, H. K. D. H. Prevention of Hydrogen Embrittlement in Steels. *ISIJ Int.* **2016**, *56* (1), 24–36.
- (55) Cornell, R. M.; Schwertmann, U. *The Iron Oxides: Structures, Properties, Reactions, Occurrences and Uses*, 2nd ed.; Wiley-VCH Verlag GmbH & Co., 2003.
- (56) Jaroniec, M. Adsorption on Heterogeneous Surfaces: The Exponential Equation for the Overall Adsorption Isotherm. *Surf. Sci.* **1975**, *50* (2), 553–564.
- (57) LeVan, M. D.; Vermeulen, T. Binary Langmuir and Freundlich Isotherms for Ideal Adsorbed Solutions. *J. Phys. Chem.* **1981**, *85* (22), 3247–3250.
- (58) Freundlich, H. Über Die Adsorption in Lösungen. *Zeitschrift für Phys. Chemie* **1907**, *57U* (1), 385.
- (59) Hongo, M.; Tsuji, T.; Fukuchi, K.; Arai, Y. Vapor–Liquid Equilibria of Methanol + Hexane, Methanol + Heptane, Ethanol + Hexane, Ethanol + Heptane, and Ethanol + Octane at 298.15 K. *J. Chem. Eng. Data* **1994**, *39* (4), 688–691.
- (60) Chia, C. L.; Avendano Jimenez, C.; Siperstein, F.; Filip, S. Liquid Adsorption of Organic Compounds on Hematite α -Fe₂O₃ Using ReaxFF. *Langmuir* **2017**.
- (61) Chia, C.-L.; Alloway, R. M.; Jephson, I.; Clarke, S. M.; Filip, S. V.; Siperstein, F. R.; Avendaño, C. Competitive Adsorption of a Multifunctional Amine and Phenol Surfactant with Ethanol on Hematite from Nonaqueous Solution. *J. Phys. Chem. B* **2019**, *123* (6), 1375–1383.