IUPAC Technical Report

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Experiments on adsorption at hydrous metal oxide surfaces using attenuated total reflection infrared spectroscopy (ATRIRS) (IUPAC Technical Report)

<https://doi.org/10.1515/pac-2019-0211>

Received February 15, 2019; accepted July 19, 2019

Abstract: This article seeks to encourage the adoption of modern methods of surface analysis in teaching contexts by introducing the use of attenuated total reflection infrared spectroscopy (ATRIRS) in analysis of adsorption reactions at hydrous metal oxide thin films. The first experiment shows how outer-sphere adsorption of perchlorate ion is distinguished from inner-sphere adsorption of ethanedioate (oxalate) ion at TiO_2 surfaces. The second experiment shows how the nature of adsorption of sulfate ion to iron oxide surfaces changes with pH. In the third experiment, the variation of the amount of benzene-1,2-diol (catechol) adsorbed to TiO_2 with solution concentration enables an adsorption constant to be derived from the adsorption isotherm.

Keywords: adsorption; attenuated total reflection; hydrous metal oxides; infrared spectroscopy; surface chemistry.

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Article note: Sponsoring body: IUPAC Physical and Biophysical Chemistry Division: see more details on page 2060

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1 Introduction

This technical report is an outcome of IUPAC project 2006-050-3-100, Wet Surface Vibrational Spectroscopy Experiments, which aimed to encourage the uptake of modern vibrational spectroscopic methods in the teaching of surface chemistry. This report is confined to the use of attenuated total reflection infrared spectroscopy (ATRIRS) to study adsorption reactions at hydrous metal oxide surfaces. The included three experiments were chosen to illustrate the different types of information about adsorption obtainable using ATRIRS. During the course of this project, a related undergraduate chemistry laboratory experiment on adsorption using attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy was published [1].

1.1 Scope of ATRIRS adsorption studies

During the past two decades, the development of ATRIR spectroscopy to study adsorption reactions at particulate metal oxide film/water interfaces [2–4] has led to considerable advances in understanding the surface chemistry of these systems. Although corresponding IR studies of reactions with dry particulate oxide surfaces have been carried out for more than 50 years, advances in Fourier transform IR spectrometers, digital data processing, and internal reflectance sampling methods provided the critical impetus for wet surface studies. TiO₂ was an early substrate studied [2], not only because of its fundamental importance to surface chemistry, but also due to its significance in many practical contexts, such as in solar cells [5], the biocompatibility of titanium [6], and photocatalysis [7]. Addressing the surface chemistry of ferric oxide [8, 9] was also an early focus due to its environmental importance, *e.g.* in sequestration of arsenate (AsO₄³⁻) [10] and antimonate (Sb(OH)₆⁻) [11] mine waste species. The ATRIR method has been applied to various oxide species and can in principle be applied to any solid for which a stable nanoparticle film can be formed on an internal reflection prism immersed in solution. Solid-water interfaces are widespread in nature and in technology, but many have poorly understood surface chemistry, making ATRIRS an effective method of research in this field.

1.2 Principles of the ATRIRS method

When an IR beam undergoes total internal reflection at an interface between a solid and a less dense medium (sample), there exists an evanescent IR wave in the less dense medium, which can be attenuated by interacting with (sample) dipolar molecular motions and thereby give rise to a measurable IR absorption spectrum [12]. The simplest experimental situation that satisfies these conditions involves total internal reflection within a 45 ° prism, as shown in Fig. 1a, a configuration now commonly used in ATR accessories for FTIR spectrom-

Fig. 1: (a) Single internal reflection prism coated with a particle film and covered with a glass solution flow cell. (b) Schematic of single internal reflection and decay of evanescent wave through a particle film immersed in solution. Adapted with permission from [13] Copyright 1997 American Chemical Society and [2] Copyright 2001 Wiley-VCH.

eters. Total internal reflection requires a high refractive index (RI) prism and the common prism materials, ZnSe and diamond: both have RI of 2.4. For such prisms, samples having RI up to about 1.7 will sustain total internal reflection and yield IR spectra. These samples include water (RI 1.33) and aqueous solutions, but also, surprisingly, most hydrous metal oxide particle films. Metal oxides, such as TiO_2 and Fe_2O_3 , have RI greater than 2, but the effective RI of a hydrous TiO_2 particle film is around 1.5, which is critical in enabling wet adsorption ATRIRS studies with thin coatings of such materials on ATR prism surfaces.

The intensity of the evanescent wave decays exponentially away from the prism interface, as shown schematically in Fig. 1b. The penetration depth ($1/e$) of the evanescent wave into the sample is about $1\ \mu\text{m}$, which is a typical particle film thickness. Spectral sensitivity is inversely related to particle size. For nm-scale particles, the large surface area of their porous particle films results in highly sensitive wet surface spectroscopy. Evonik Aeroxide P25 TiO_2 , with a specific surface area of $50\ \text{m}^2\ \text{g}^{-1}$ and 21 nm primary particle size, is a typical adsorbent material for ATRIR studies.

1.3 Experimental procedures for adsorption studies by ATRIRS

Spectra of solution and adsorbed species are usually presented as functions of absorbance (A) vs wave-number ($\tilde{\nu}$) spectra. The measurement of the FTIR spectrum of a species in solution requires a background (blank) single beam (SB) spectrum ($I(\tilde{\nu})_b$) and sample SB spectrum ($I(\tilde{\nu})_s$) to construct an absorbance spectrum ($A(\tilde{\nu})$).

$$A(\tilde{\nu}) = \log_{10} \frac{I(\tilde{\nu})_b}{I(\tilde{\nu})_s} \quad (1)$$

Thus, absorbance spectra arise from ratios of SB spectra. Absorbance spectra are effectively difference spectra between the absorptions of the sample and of the background. For solution spectra, the background spectrum is obtained from the same solution without the IR absorbing species of interest. Absorbance spectra of aqueous solutions involve the subtraction of substantial water absorptions present in both sample and background SB spectra. Constructing absorbance spectra of species adsorbed on metal oxides from solutions involves similar considerations, with the background including the metal oxide absorptions.

With some FTIR instruments, rather than defaulting to single beam (SB) measurements, the software is designed around collecting a background (blank) spectrum and then automatically taking a ratio of all sample spectra to that background. In this case, the initial spectra throughout the experiments will resemble those in Fig. 2b, rather than those in Fig. 2a. If your instrument defaults to this collection method, the typical approach is to collect a background spectrum of the unreacted metal oxide thin film with aqueous electrolyte flowing through the system prior to addition of the adsorbate.

Because ATRIRS is a reflectance measurement, there are some considerations when using it for quantitative analysis. Unlike transmission mode measurements, there is a wavelength dependence in sample penetration depth that complicates use of the Beer-Lambert equation. However, as long as all measurements are

Fig. 2: An example of the data collection and processing of ATRIR spectra for aqueous solutions of sulfate on an ATR crystal. (a) Raw single beam (SB) ATR spectra that include peaks, either the diamond ATR crystal (dashed) or from water, diamond ATR crystal, and sulfate (solid). (b) Absorbance spectra from ratioing the background (with H₂O) SB spectrum from sulfate solution samples from 0.5 to 25 mmol L⁻¹ SB spectra. (c) ATRIRS spectra from 2b after selecting the spectral region where S-O vibrations occur and performing a baseline correction on the data set using a linear offset from 1250 to 900 cm⁻¹.

performed on the same crystal, it is possible to use ATRIRS for solution quantitative analysis by constructing a calibration curve of absorbance vs concentration. The specific case of sulfate ion in a 0.1 mol L⁻¹ KCl background is shown below (Fig. 3). This example illustrates the utility of spectroscopic information, giving both molecular symmetry (a single S-O vibration at 1100 cm⁻¹ indicates an undistorted tetrahedron) and quantitative information (absorbance is linearly related to concentration *via* the Beer-Lambert equation over a wide range of sulfate concentration).

For IR spectra of adsorbed species, a stable metal oxide particle film deposited on an appropriate ATR prism is required. First, a background spectrum of the film immersed in solution without adsorbate is collected, followed by a sample spectrum of the film immersed in adsorbate-containing solution over sufficient time for adsorption to take place. Normally, the spectra from the solutions with- and without-adsorbate are used to construct absorbance spectra, revealing the spectral features of the adsorbed species with minimal influence from the strong water absorption, which is almost entirely subtracted. The absorbance of spectra from adsorbed species is proportional to the surface concentration, which facilitates data analysis.

Formation of the particle film is the main task before carrying out the adsorption experiment.

Small particles of many oxides are now commercially available due to intense interest in both nanoparticles and nanotechnology. Very small amorphous particles of TiO₂ and iron (III) hydroxide (ferrihydrite) are readily prepared by hydrolysis of TiCl₄ or Ti(OR)₄ and aqueous Fe³⁺, respectively, and give strong adsorbed species spectra. Generally, hydrothermal methods are needed to prepare small particles of well-defined crystalline phases. Suspensions of particles in water or electrolyte can be prepared with the aid of sonication and small volumes (10 to 100 μL range) of suspensions with concentrations of about 1 mg mL⁻¹, transferred to an ATR prism surface for drying in air or under an inert gas to form about 1 micrometer thick films. Dip coating

Fig. 3: (a) Sulfate aqueous solutions from 0.5 to 25 mmol L⁻¹ measured with single internal reflection prism cell. (b) Integrated absorbance from 900 to 1250 cm⁻¹ of spectra from (a) plotted against sulfate concentration to produce a calibration curve (dotted line).

or spin coating gives films with more uniform thickness, which is assessable by AFM or SEM measurements. Drying in air tends to accumulate adsorbed carbonate from atmospheric CO₂ and the use of inert gas for drying and storing particle suspensions is recommended. Washing films before experiments with alkaline solutions aids adsorbed carbonate removal.

ATRIRS accessories are available with single and multiple reflection prisms, where each reflection gives increased absorption of the evanescent wave by the sample. Both ZnSe and diamond prisms have wide infrared spectral ‘windows’, making these the most useful ATR prism materials for IR spectroscopy. Diamond has advantages for acidic systems, as ZnSe is attacked by acid below pH of about 3. However, diamond can have a spectral cutout at 1900 to 2400 cm⁻¹ due to its phonon absorptions. The greater sensitivity from multiple reflection prisms comes at the cost of total water absorption in the OH stretching region and a more restricted spectral range below 1000 cm⁻¹. Single reflection prisms have the advantage that the strong water OH stretching and bending absorptions do not completely absorb the IR beam and thus provide continuous spectra over a wide spectral range.

Multiple reflection prisms mounted in the form of shallow troughs facilitate solution measurements. Deposition of particle films in such troughs allows spectra of adsorbed species to be collected simply by pipette replacement of background solutions with adsorbate solutions. Better control of adsorption conditions is obtained by mounting a flow cell on the prism or trough and using a peristaltic pump for 1 to 2 mL min⁻¹ flow of solutions across a thin film surface. Both multiple and single bounce ATR setups are suitable for deposition of metal oxide films, as demonstrated with Fe₂O₃ in Fig. 4.

1.4 Types of experiments and limitations

For room temperature adsorption experiments monitored by ATRIRS, the principal experimental variables are adsorbate concentration, solution pH, and mass transport conditions at the solid/solution interface. For strongly adsorbed species, adsorbed monolayers are typically reached with 10⁻⁴ mol L⁻¹ adsorbate solutions. For such conditions the solution contributions to IR signal are negligible, so that the observed spectrum may be entirely from the adsorbed species. The advantages of using a flow cell are control of mass transport by maintaining constant adsorbate concentration close to the surface and having a known bulk concentra-

Fig. 4: Thin film depositions of Fe_2O_3 on common ATR prisms (a) Multiple ZnSe internal reflection prism coated with a particle suspension, allowed to dry, and then rinsed to remove non-adhering particles. (b) Diamond-coated ZnSe single internal reflection prism masked with tape, coated with particle suspension, and then tape removed leaving a Fe_2O_3 film coated prism. Photos courtesy Courtney Phillips and Dr. Derek Peak.

tion at equilibrium. Single pass experiments ensure constant environmental conditions but recirculation of solutions from a reservoir can also be used if there are insignificant changes in solution composition during experiments.

Absorbance of characteristic bands of adsorbed species is proportional to surface concentration, which allows surface concentration to be directly monitored. When an adsorbate solution is introduced to the metal oxide film, an initial rapid increase in absorbance of an adsorbed species band signifies adsorption (e.g. Fig. 5 shows the first 60 minutes of sulfate adsorption onto a Fe_2O_3 film at pH 4). The rate of absorbance increase declines to eventually give constant absorbance when equilibrium is reached. The disadvantage of an adsorption experiment from a static solution, as in batch adsorption experiments, is an unknown final solution concentration unless the volume of the solution is high and/or the adsorbed amount low.

Control of solution pH is important in determining the metal oxide surface charge relative to its point of zero charge (PZC). However, most buffer solutions contain ligand species, such as carboxylic acids, which also adsorb to metal oxides. Thus, typical buffer mixtures are to be avoided and pH control is generally limited to strong acids and strong bases. Anionic adsorption is favoured by low pH, where positive surface charge generally prevails. Determination of the variation of surface concentration with pH is often the initial investigation in any study of adsorption behaviour and may reveal changes in the nature of adsorbed species in different pH ranges. Such experiments are best carried out with an initial background spectrum at high pH, followed by a succession of spectra of solutions with the same adsorbate concentration but decreasing

Fig. 5: (a) ATRIR spectra during sulfate adsorption on Fe_2O_3 as a function of time at pH 4 with an initial sulfate concentration of 0.1 mmol L^{-1} . Spectra were collected in 10 s intervals for 60 minutes. (b) Integrated band absorbance from 950 to 1250 cm^{-1} of adsorbed sulfate from (a) plotted as a function of time.

pH. If one begins instead at low pH with high amount adsorbed and systematically raises solution pH, slow desorption rates of strongly-bound adsorbed species can complicate the experiment.

Under certain conditions, some adsorbate-induced dissolution of the substrate can occur [14, 15]. Adsorption without significant dissolution is observed if adsorbate concentrations are sufficiently low.

1.5 Nature of adsorption and adsorption isotherms

For hydrous metal oxides, two main types of adsorption can be distinguished. Outer-sphere adsorption arises from electrostatic attraction of opposite charges where the interaction occurs *via* solvent-separated species. This type of adsorption is dominant in situations where the adsorbate has little tendency to form coordinated bonds with the metal ions at the oxide surface and is strongly affected by variation of ionic strength. Inner-sphere adsorption involves the formation of metal-ligand coordinated bonds, for which outer-sphere adsorption is often a precursor stage. Ionic strength typically has much less influence on inner-sphere adsorption. IR spectroscopy allows these forms of adsorption, which often occur together, to be readily distinguished. The IR spectrum of an outer-sphere adsorbed species is almost identical to that of its free solution form, while the IR spectrum of an inner-sphere adsorbed species is generally altered from that in solution by the molecular perturbation of covalent bonding. The spectrum of oxalate adsorbed to a metal oxide is quite distinct from that in solution, while that of the adsorbed catechol is little altered from that of the catecholate dianion in solution.

Measuring an adsorption isotherm allows the derivation of an adsorption constant which indicates adsorption affinity. An adsorption isotherm is a plot of equilibrium surface concentration against the equilibrium solution concentration of the adsorbate. For ATRIRS, absorbance at a chosen wavenumber or integrated absorbance over a spectral region can be plotted against concentration. The experiment is generally performed at a fixed pH and constant solution ionic strength. Results are obtained by first measuring a background spectrum of the deposited film immersed in solution not containing the adsorbate, then obtaining equilibrium spectra for a series of adsorbate solutions of increasing concentration. An example is shown in Fig. 6a below for sulfate on Fe_2O_3 at pH 4 and 0.01 mol L^{-1} KCl. This sequence of experiments requires a good deal of time to achieve near constant absorbance corresponding to equilibrium.

The simplest model which can be applied to adsorption isotherm data like those in Fig. 6 is the Langmuir adsorption isotherm. This model assumes that there are no lateral interactions of molecules which adsorb to

Fig. 6: (a) ATRIR spectra during sulfate adsorption on Fe_2O_3 at pH 4 with increasing sulfate concentration (0 to 2 mmol L^{-1}) measured with Fe_2O_3 deposited on a single internal reflection prism in a flow cell. (b) Integrated absorbance from 900 to 1250 cm^{-1} from Fig. 5a spectra plotted against sulfate concentration to produce an isotherm that has been modeled with the Langmuir equation (dotted line).

a surface containing identical sites and which is saturated by a single molecular adsorbed layer. The Langmuir equation expresses the Langmuir adsorption constant (K_L) in terms of fractional surface coverage (θ) and solution concentration (c)

$$\theta = \frac{A}{A_{\max}} = \frac{K_L c}{1 + K_L c} \quad (2)$$

K_L is best obtained by non-linear regression (curve-fitting) of the data to the Langmuir equation, from which the standard error for K_L is obtainable. K_L can also be obtained from a simple linear regression. Langmuir adsorption constants are a measure of adsorption affinity of the adsorbate for the adsorbent, and Langmuir adsorption constants are commonly used to relate adsorption affinities of different adsorbates on the same adsorbent.

1.6 FTIR spectrometer performance

Monolayers on surfaces correspond to much smaller molecular samples than in bulk phase spectroscopy studies and this has been the primary challenge in surface spectroscopy. The practicability of carrying out ATRIRS wet particle film adsorption experiments depends not only on the use of high surface area particle films but also on the sensitivity of the FTIR spectrometer employed. Absorbance signals from species adsorbed on particle films in some ATRIRS experiments can be as low as 0.001 using single reflection prisms. In such experiments, the spectrometer absorbance noise needs to be about 10^{-4} for useful mid-infrared measurements. Use of multiple reflection prisms with less sensitive spectrometers can make some ATRIRS experiments feasible, but it is important to check that the performance of available laboratory spectrometers is adequate before setting up to carry out the experiments in this report.

2 Experiment 1. Modes of adsorption of ethanedioate (oxalate) and of perchlorate to TiO_2

2.1 Learning objectives

This laboratory exercise uses IR spectroscopy to address the influence on TiO_2 surface charge of coordinative adsorption of ethanedioate ion in the presence of perchlorate ion. The outer-sphere adsorption of perchlorate ion on TiO_2 is reduced when inner-sphere adsorption of ethanedioate occurs, which illustrates the distinction between these different adsorption modes.

2.2 Introduction

Adsorption to metal oxide surfaces is a common phenomenon that can profoundly influence the surface chemistry. Perchlorate ion adsorbs to metal oxides in response to surface charge as a solvated species with IR spectrum (Fig. 7b) almost unchanged by the adsorption [16]. The amount of perchlorate outer-sphere adsorption, evident in the 1100 cm^{-1} antisymmetric Cl-O stretch band of surface IR spectra, is therefore an indicator of positive surface charge. Oxalic acid (OxH_2) adsorbs to metal oxides as the bidentate oxalate ligand (Ox^{2-}), usually *via* an inner-sphere interaction [13], which is similar to that in the corresponding coordination compounds of the metal ion [17]. Inner-sphere adsorption of an ionic species changes surface charge. Additionally, the strong chemical interaction of the small oxalate ion with metal ions in the oxide surface significantly alters the IR spectrum of inner-sphere adsorbed oxalate ion (Fig. 7a) from that in solution. This molecular perturbation allows the coordinatively adsorbed oxalate to be readily distinguished in IR spectra from outer-sphere adsorbed oxalate also present due to net positive surface charge.

All adsorption experiments are carried out in solutions at pH 4, determined by strong acids (HCl or HClO_4), under which conditions TiO_2 has a positive surface charge. Oxalic acid, with $\text{p}K_a$ of 1.23 and 4.19, is in pH 4 solution a mixture of hydrogen oxalate (OxH^-) and oxalate (Ox^{2-}) species. However, the predominant

Fig. 7: (a) Comparison of oxalate and (b) perchlorate ATRIR spectra from aqueous solutions at pH 4 (black) and adsorbed on TiO_2 (red).

adsorbed species are not determined by solution equilibria, as the IR spectra show. The first part of the experiment, with only perchlorate present, shows that perchlorate ion exhibits outer-sphere adsorption. In the second part of the experiment, with both perchlorate and oxalate in solution, the influence of oxalate adsorption on the TiO_2 surface charge is evident in the smaller adsorbed perchlorate signal.

2.3 Materials

Titanium dioxide powder (Evonik Aeroxide P25 (about 80 % anatase, about 20 % rutile), anatase) or colloidal amorphous TiO_2 (e.g. from TiCl_4 or Ti(IV) isopropoxide hydrolysis), sodium oxalate, sodium perchlorate, hydrochloric acid.

2.4 Equipment

Reflectance accessory for IR spectrometer e.g. single or multiple internal reflection ZnSe or diamond. Solution spectra recorded with drop of solution covering bare ATR prism surface.

Flow cell, tubing, and peristaltic pump.

Aluminium oxide powder $0.015\ \mu\text{m}$ for cleaning of ZnSe or diamond.

Safety – For polishing of ZnSe use gloves and wash well with water. Used tissues go to toxic disposal. Avoid contact of ZnSe with acidic solution having $\text{pH} < 3$.

2.5 Experimental procedures

The following sequence of experiments is suggested. It is advantageous if a series of single beam (SB) spectra can be acquired and subsequently processed into absorbance spectra. While it is possible to record spectra with static solutions on the ATR prism, it is preferable to acquire spectra during solution flow. With this approach, background (SB) and sample (SB) spectra can be acquired sequentially by a simple change of solution reservoir, giving near constant measurement temperature. Each IR absorbance spectrum requires an appropriate background spectrum. To record a spectrum of a solution species or adsorbed species, the solution conditions need to be nearly identical for background and sample spectra, apart from the low concentration of solution species or adsorbate in the sample solution. Data acquisition for SB spectra should be for at least a minute at $4\ \text{cm}^{-1}$ resolution to acquire good quality background and sample spectra.

Solution spectra are initially recorded to compare with the spectra of adsorbed species subsequently obtained. For solution absorbance spectra a flow time of 5 to 10 min at about $1\ \text{mL min}^{-1}$ should be sufficient to obtain unchanging signals for both background and sample spectra.

2.5.1 Record a solution SB spectrum of $10^{-4}\ \text{mol L}^{-1}\ \text{NaClO}_4$ on the bare ATR prism preceded by a background SB spectrum from water. The resulting absorbance spectrum should give an undetectable signal for ClO_4^- at $1100\ \text{cm}^{-1}$. However, this serves to illustrate the effective enhancement of this weak signal when adsorption occurs at a high surface area positively-charged metal oxide thin coating as will be observed in 2.5.3. Secondly, record an IR spectrum of $0.1\ \text{mol L}^{-1}\ \text{NaClO}_4$ following the same procedure to obtain a detectable ClO_4^- absorption at $1100\ \text{cm}^{-1}$ to be compared with data from 2.5.4.

2.5.2 Record a solution IR spectrum of $0.1\ \text{mol L}^{-1}$ sodium oxalate with a water background.

2.5.3 Prepare a TiO_2 particle film from $1\ \text{mg mL}^{-1}$ aqueous dispersion of TiO_2 by shaking or sonication followed by spreading about $0.1\ \text{mL}$ of dispersion over about $1\ \text{cm}^2$ on the prism surface and drying under low vacuum about $5\ \text{kPa}$ ($50\ \text{mbar}$), e.g. water pump or by gentle nitrogen flow. Avoid rapid and complete film drying, as this can weaken film adhesion to the prism surface when subsequently exposed to solution. Remove the film at the end of an experiment using wet tissue paper followed by light polishing with the fine alumina supported on a tissue or polishing cloth.

2.5.4 Record the background spectrum from 10^{-4} mol L $^{-1}$ HCl solution over the TiO $_2$ film surface, followed by the sample spectrum from 10^{-3} mol L $^{-1}$ NaClO $_4$ solution containing 10^{-4} mol L $^{-1}$ HCl. The resulting absorbance spectrum shows the outer-sphere adsorbed ClO $_4^-$ signal at 1100 cm $^{-1}$.

2.5.5 Continue the above experiment by switching the solution flow to 10^{-4} mol L $^{-1}$ oxalate solution in 10^{-3} mol L $^{-1}$ NaClO $_4$ containing 10^{-4} mol L $^{-1}$ HCl and record SB spectra at 5 min intervals for up to an hour. In this period, the growth of the inner-sphere adsorbed oxalate spectrum and the consequences of the oxalate adsorption on the adsorbed ClO $_4^-$ signal will be recorded. To obtain the absorbance spectra during the adsorption process, use the background spectrum from 10^{-4} mol L $^{-1}$ HCl solution over the TiO $_2$ film surface recorded for 2.5.4.

2.6 Results and discussion

2.6.1 Solution spectra

Perchlorate ion has a fairly broad band at about 1100 cm $^{-1}$ (Fig. 8a) related to the antisymmetric Cl-O stretching mode. Oxalate ion (Ox $^{2-}$) has bands at about 1580 cm $^{-1}$ (broad) and 1308 cm $^{-1}$ (sharp). The oxalate solution species vary from the dominance of Ox $^{2-}$ at pH 6 to a mixture of OxH $^-$ and OxH $_2$ at lower pH (Fig. 8b). Use the system pK $_a$ and the given spectra to identify the wavenumbers of the major IR absorptions of the three different oxalate species.

2.6.2 Adsorbed species spectra

IR spectra from part 2.5.5 are shown in Fig. 9, where the initially present 1100 cm $^{-1}$ ClO $_4^-$ peak at 1100 cm $^{-1}$ is gradually diminished with the growth of adsorbed oxalate bands at 1698, 1419, and 1270 cm $^{-1}$, corresponding to oxalate coordinatively adsorbed to Ti(IV). The IR spectrum of coordinatively adsorbed oxalate is quite different from the IR spectrum of solution Ox $^{2-}$, indicating a strong interaction. A comparison of the observed adsorbed oxalate IR bands with published data for coordination compounds confirms the bidentate mode of the binding.

Fig. 8: (a) ATRIR solution spectra from (a) 0, 10, 25, 50, 75, and 100 mmol L $^{-1}$ sodium perchlorate solutions and (b) 50 mmol L $^{-1}$ oxalate solutions over the pH range between 1.6 and 6.0.

Fig. 9: Red data - ATRIR spectra of 10^{-3} mol L $^{-1}$ NaClO $_4$ solution containing 10^{-4} mol L $^{-1}$ HCl (pH 4) in contact with a P25 TiO $_2$ thin film. Black data - ATRIR spectra with solution components same as (a) plus 1.1×10^{-4} mol L $^{-1}$ sodium oxalate. Background spectra for both experiments are from 10^{-4} mol L $^{-1}$ HCl (pH 4) in contact with TiO $_2$ film.

Account for the observed ClO $_4^-$ absorption under pH 4 conditions (2.5.4) from such a low concentration of perchlorate solution in contact with the TiO $_2$ thin particle film. Further account for the diminished ClO $_4^-$ absorption when oxalate is introduced (2.5.5) while the original solution species at the same concentrations remain.

2.6.3 Adsorption kinetics

Plot the temporal variation of absorbance for adsorbed oxalate at 1419 cm $^{-1}$ in the 2.5.5 spectra and account for its general form in terms of factors influencing the rate of an adsorption reaction.

3 Experiment 2. Influence of pH on sulfate adsorption onto iron oxides

3.1 Learning objectives

This laboratory exercise will demonstrate the importance of solution pH and adsorbent surface structure on adsorption mechanisms that occur at the iron oxide/water interface.

3.2 Introduction

Iron oxides and hydroxides are ubiquitous in natural environments and are extremely important sorbents for ions in soils, groundwater, and sediments. In fact, sorption on iron oxide surfaces is known to control the availability and mobility of a range of chemicals, including both contaminants, such as uranyl (UO $^{2+}$) ions and arsenic oxoanions, and plant macronutrients, such as phosphate and sulfate. The strong interactions between iron oxide surfaces and aqueous ions also mean they are commonly used as part of water treatment

strategies. Iron oxide as $\text{Fe}(\text{OH})_3$ is also known as iron (III) hydroxide or ferrihydrite. The explanation for the high reactivity of iron oxides with a variety of ions lies in the amphoteric surface functional groups that are present at the iron oxide surface and that protonate and deprotonate depending upon solution pH:

For oxyanion adsorption, the most important protonation states are the $\text{Fe}-\text{OH}_2^+$ and FeOH sites, whereas at pH greater than the oxide's point of zero charge, PZC, the deprotonation to form FeO^- can become important for cation adsorption. These sites participate in a variety of complexes with ions, including outer-sphere, hydrogen-bonding, and inner-sphere complexation (*via* a ligand exchange mechanism). One good ion for probing the surface chemistry of iron oxides is the oxyanion sulfate [18]. This experiment will study adsorption of sulfate on iron oxide surfaces as a function of pH.

3.3 Background on sulfate IR spectra

Vibrational spectra of sulfate have been extensively studied and clear relationships exist between peak wave-number, number of peaks, relative intensity, and molecular symmetry (Fig. 10). This makes sulfate an excellent choice for studying oxyanion bonding to iron oxide surfaces.

3.4 Materials

N_2 purge gas, iron (III) nitrate, sulfuric acid, sodium sulfate, sodium chloride, hydrochloric acid, potassium hydroxide, and sodium hydroxide. Iron (III) nitrate and potassium hydroxide will be used to synthesize the amorphous mineral ferrihydrite, $\text{Fe}(\text{OH})_3$, *via* the method of Schwertmann and Cornell [19]. Ferrihydrite synthesis is readily accomplished by titrating 1 mol L^{-1} iron (III) chloride to pH 7.5 with 1 mol L^{-1} KOH and holding the resulting suspension at pH 7.5 for 30 min. The $\text{Fe}(\text{OH})_3$ precipitate should then be washed *via* centrifugation and de-ionized water to remove any residual iron and nitrate and then dialyzed for 3 days with regular replenishments of deionized water. The mineral suspension can then be directly utilized in experiments or, alternatively, freeze-dried and ground.

Fig. 10: Possible sulfate species at hydrous iron oxide surfaces, their symmetry species, vibrational mode splitting, and observed IR spectra [18].

Synthetic hematite, Fe_2O_3 , can be purchased or, alternatively, synthesized according to Schwertmann and Cornell [19]. Hematite is synthesized by dropwise addition of 60 mL of 1 mol L⁻¹ iron (III) nitrate solutions into 750 mL of boiling deionized water. The resulting suspension is then removed from heat, cooled for 24 hours, dialyzed, and freeze-dried.

3.5 Equipment

ATR (single or multiple reflection) accessory with a crystal attachment designed for liquids. A flow cell type accessory, tubing, and a pump is ideal for these experiments, but it is possible to conduct them with a normal trough by exchanging the solutions with a Pasteur pipette.

3.6 Experimental procedures

Note the general experimental instructions at the start of 2.5, especially the preference for flow-through experimentation over static measurements.

3.6.1 Make a 0.01 mol L⁻¹ NaCl solution in a beaker. Add a magnetic stir bar, adjust the pH to 9, and sparge it with N_2 gas while stirring. Use a pump to recirculate this solution through the flow cell for the adsorption envelope experiments at a constant rate.

3.6.2 Deposit a thin layer of either $\text{Fe}(\text{OH})_3$ or Fe_2O_3 solid particles on the ATR crystal and allow it to dry. Rinse the dried film once carefully with H_2O to remove non-adhering iron oxides. When the rinsed surface has again dried, place the ATR crystal into the flow cell (or trough onto the reflectance accessory). Flow a pH 9 solution of 0.01 mol L⁻¹ NaCl that is N_2 purged to exclude CO_2 through the assembled flow cell. Initially, the particulate system in contact with the ATR crystal will be changing rapidly as the metal oxide rehydrates, adsorbed carbonate is released, and its surface functional groups dehydronate (deprotonate). You can monitor these transformations by regularly collecting single beam (SB) spectra and comparing them by difference as the system stabilizes. If there are no changes in the system, the absorbance spectrum produced *via* difference of successive scans would yield a flat line over the full spectral region at 0.00 absorbance; this will not initially be the case. Instead, you will initially observe large changes in the water bands, a large decrease in the region typical of absorbed carbonate, and other changes caused by small amounts of the metal oxide eroding from the surface. It is typical that, after 60 minutes, successive scans have very little difference in the 900 to 1300 cm⁻¹ region used for the experiments. When you are confident that the deposit on the ATR surface is stable, then collect a SB spectrum that will be used for the remainder of the experiments as an unreacted surface.

3.6.3 Next, add enough 1 mol L⁻¹ sulfate stock solution to your beaker from 3.6.1 to produce a final concentration of 250 $\mu\text{mol L}^{-1}$ sulfate and adjust the final pH of your reaction vessel to 6.0. There will be an initial lag time as this sulfate travels through the tubing and reaches the flow cell, and then there will be a gradual increase in the absorbance of sulfate as it adsorbs on the iron oxide surface and slowly reaches equilibrium. Collect SB spectra every 10 minutes, and when successive scans have an absorbance (after background subtraction) that is within 95 % of one another, then consider the reaction at an operationally defined steady state and adjust the pH to 4.5. Repeat this process and collect SB spectra of sulfate adsorbed on the iron oxide surface at pH 6.0, 4.5, and 3.5. When you have completed the studies for both metal oxides, the background subtracted data should look something like Fig. 10.

The overall experiment takes several hours to complete, as each pH can require 30-60 minutes to reach adsorption equilibrium. If more time is available, then it is possible to collect spectra in smaller pH increments from pH 9 (unreacted surface cleaned of carbonate) to pH 3 (See Fig. 11). Examples of more detailed pH envelopes of this type can be seen for sulfate adsorption on Fe_2O_3 [8], FeOOH [18], and $\text{Fe}(\text{OH})_3$ [20], as well as on TiO_2 [1].

Fig. 11: Example adsorption envelopes collected by stepwise lowering of pH from pH 9 (unreacted) to pH 3.5 in the presence of 0.25 mmol L^{-1} sulfate and a deposit of either ferrihydrite, $\text{Fe}(\text{OH})_3$ (a) or hematite, Fe_2O_3 (b).

3.7 Results and discussion

3.7.1 Given what is known about these metal oxides, why is the absorbance of adsorbed sulphate so much larger on ferric hydroxide compared to hematite?

3.7.2 What is the dominant mechanism of surface complexation between sulfate and (a) $\text{Fe}(\text{OH})_3$ and (b) Fe_2O_3 ?

3.7.3 What are possible explanations why complexation mechanisms differ between these two surfaces? What are the implications of this observation to the field of surface chemistry in general?

4 Experiment 3. Adsorption isotherm for benzene-1,2-diol (catechol) adsorbed to TiO_2

4.1 Learning objectives

This laboratory exercise shows how the adsorption isotherm for inner-sphere adsorption of catechol to TiO_2 may be obtained using attenuated total reflection infrared spectroscopy and how the Langmuir adsorption constant (K_L) of the catechol/ TiO_2 system may be deduced.

4.2 Introduction

Benzene-1,2-diol, or catechol, and its derivatives are found widely amongst natural and synthesised chemicals. It is a well-known bidentate ligand in coordination chemistry and the same coordination to metal ions is evident when catechol adsorbs to the surface of metal oxides in aqueous environments [21]. This coordinative interaction is also the basis of bacterial siderophore sequestration of iron [22].

The hydroxyl groups on catechol with $\text{p}K_{\text{a}1} = 9.45$ and $\text{p}K_{\text{a}2} = 12.8$ indicate the free catecholate dianion can exist at high pH, but rigorous exclusion of solution oxygen is needed to prevent oxidation to 1,2-benzoquinone. The IR spectrum of the catecholate dianion in solution is dominated by strong absorptions at 1482 and 1258 cm^{-1} , arising from benzene ring and C-O stretch modes, respectively. When catechol adsorbs to metal oxides, the presence of these strong absorptions indicates that catechol adsorbs as the catecholate dianion. Fig. 12 shows these peaks at 1481 and 1257 cm^{-1} for catechol adsorbed to TiO_2 .

An adsorption isotherm is the variation of adsorbed amount with variation in solution concentration at equilibrium and constant temperature. Measuring an adsorption isotherm provides the means of deriving an adsorption constant, which is a measure of the adsorption affinity between the adsorbate and the adsorbent. The variation with concentration of the absorbance of either of the strong IR bands of adsorbed catechol near 1480 and 1260 cm^{-1} can be used to obtain an adsorption isotherm (See Fig. 13).

In this experiment, a series of catechol solutions in pH 3 solution ($10^{-3} \text{ mol L}^{-1} \text{ HCl}$) of increasing concentration will be successively flowed over the same TiO_2 thin film on an ATR prism and, at each concentration, the maximum (equilibrium) absorbance of adsorbed catechol will be recorded. Note that the rate of adsorption depends on the solution concentration and that for the more dilute solutions equilibrium may take some time to be reached. Therefore, this experiment is best carried out, if the spectrometer is

Fig. 12: ATRIR spectrum of catechol adsorbed to TiO_2 from $10^{-3} \text{ mol L}^{-1}$ catechol solution [23].

Fig. 13: Non-linear fitting of the Langmuir equation to the adsorption isotherm from absorbance at 1481 cm^{-1} yielding $K_L = 1.2 \times 10^4 \text{ L mol}^{-1}$. Inset IR spectra for catechol adsorbed to TiO_2 from 1×10^{-6} , 5×10^{-6} , 1×10^{-5} , 2.5×10^{-5} , 5×10^{-5} , 1×10^{-4} , 2.5×10^{-4} , 5×10^{-4} , $1 \times 10^{-3} \text{ mol L}^{-1}$ aqueous pH 3 solutions containing $0.01 \text{ mol L}^{-1} \text{ KCl}$. Background: $0.01 \text{ mol L}^{-1} \text{ KCl}$ (pH 3) solution over TiO_2 film [23].

available, over an extended period of time, such as by involving more than one laboratory period on successive days.

4.3 Materials

Titanium dioxide powder (Evonik Aeroxide P25 (about 80 % anatase, about 20 % rutile)) or anatase, or colloidal amorphous TiO_2 (eg from TiCl_4 or Ti(IV) isopropoxide hydrolysis), catechol, potassium chloride, hydrochloric acid.

4.4 Equipment

FTIR spectrometer with absorbance noise about 10^{-4} or less in mid IR region.

ATR reflectance accessory for IR spectrometer containing single or multiple reflection ATR prism of diamond or ZnSe.

Flow cell to cover TiO_2 film to be attached to prism surface *via* O-ring.

Peristaltic pump and tubing (eg pvc) to provide about 1 mL min^{-1} flow through flow cell and over TiO_2 thin film on prism.

4.5 Experimental procedures

Note the general experimental instructions at the start of 2.5.

4.5.1 Measure the IR spectrum of a 0.1 mol L^{-1} solution of catechol in $10^{-3} \text{ mol L}^{-1}$ HCl aqueous solution (pH 3) on a bare prism surface with $10^{-3} \text{ mol L}^{-1}$ HCl aqueous solution as a background. The high solubility of catechol in aqueous solution allows the solution spectrum to be readily obtained. The corresponding spectrum of pure catecholate dianion solutions is difficult to obtain due to the ready oxidation of catechol by oxygen at high pH. Dissolving catechol in high pH solutions pre-purged with nitrogen or a noble gas can help.

4.5.2 Prepare a TiO_2 particle film on the ATR prism as specified in 2.5.3.

4.5.3 Record a background SB spectrum for 0.01 mol L^{-1} KCl containing $10^{-3} \text{ mol L}^{-1}$ HCl on the TiO_2 film from (b). Then record SB spectra for a sequence of catechol-containing solutions with the same KCl and HCl concentrations. It is suggested the following sequence of catechol concentrations be used: 1×10^{-5} , 2.5×10^{-5} , 5×10^{-5} , 1×10^{-4} , 2.5×10^{-4} , 5×10^{-4} , and $1 \times 10^{-3} \text{ mol L}^{-1}$ aqueous solutions containing 0.01 mol L^{-1} KCl and $10^{-3} \text{ mol L}^{-1}$ HCl. Finally, use the prerecorded background spectrum to construct absorbance spectra at each concentration. The peak absorbance in these spectra show the dependence of the amount of adsorbed catechol on the solution concentration.

4.6 Results and discussion

4.6.1 Use the pK_a data to estimate the catechol speciation expected in the 0.1 mol L^{-1} (pH 3) catechol solution of 4.5.1. Compare the spectra of catechol adsorbed on TiO_2 with that in a 0.1 mol L^{-1} catechol solution and account for the differences in absorbance and in spectral features.

4.6.2 Fit absorbance (A) at 1481 cm^{-1} for the concentrations (c) measured to the Langmuir equation (Section 1.6) by non-linear regression analysis using data analysis software e.g. Origin, OriginLab, to obtain a Langmuir

adsorption constant, K_L . If data analysis software is unavailable, an alternative is to plot A/c vs c and obtain K_L from the slope/intercept.

4.6.3 Using the Langmuir adsorption isotherm equation, show that K_L could be obtained from either the $c \rightarrow 0$ limiting slope of the isotherm or the solution concentration at which the absorbance reaches 50 % of maximum absorbance. Would you expect the K_L values obtained from these alternative analyses to be as precise as that from the regression analysis of the isotherm fitted in 4.6.2?

5 Conclusion

The use of *in situ* attenuated total reflection infrared spectroscopy to study the surface chemistry of hydrous metal oxides clearly reveals the distinction between inner sphere and outer sphere adsorption processes and allows the variation of adsorbed species surface coverage to be readily monitored with time, with solution pH, as well as with solution concentration which enables adsorption isotherms to be obtained. The ATRIRS approach enables both classical and molecular aspects of hydrous metal oxide surface chemistry to be addressed in a single experiment.

Funding: International Union of Pure and Applied Chemistry, Funder Id: <http://dx.doi.org/10.13039/100006987>, Grant Number: 2006-050-3-100.

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