Notes on techniques for the study of molecular adsorption at the solid/liquid interface.

This is in response to the question by Prof. Tait about what other experimental methods there are to characterise molecules at the solid/liquid interface other than STM.

Notes by Stuart Clarke (University of Cambridge):

Here are some notes on a variety of methods that can be used to determine particular aspects of molecular species adsorbed from liquids to solid surfaces. In general a combination of these methods is recommended to give a clear picture of these complex and challenging systems. This is not intended as a full review of all the methods one might consider, but a suggestion of some that might be used to complement STM measurements, as prompted by the question raised at the Faraday meeting. I have not included other techniques that colleagues from a UHV background will be familiar with, that should also be employed to characterise surfaces before and/or after adsorption from solution, such as XPS, SIMS, EDX, BSED, FIB-TEM, EELS, EXAFS etc.. which are generally available through national and local services.

In these notes I have included one or two examples drawn from my own experience and papers on hand. In no way do these reflect the extensive body of literature that each of these approaches represents. I hope that interested parties will perform their own review of these techniques that they might be interested to use.

Structural methods

1) 2D – in plane diffraction (Xrays and neutrons): This approach can be used to determine the in-plane 2D molecular crystal structure of single species and multicomponent combinations. Very high spatial resolution. Xrays and neutrons are ideally combined to address heavy and light components. Powdered substrates used to optimise contribution from the surface (preferential orientation of some substrates can also enhance data collection). A non-invasive approach.

Extensive body of work including adsorbed alkanes, alcohols, fatty acids, amines, amides, ‘spheres’, ‘dipoles’, ‘quadrupoles’ etc.. hydrogen bonded systems, halogen bonded systems..etc. Temperature dependent studies.

Usually done as a coverage dependent measurement from sub monolayer (‘dry’) to multilayer systems (‘wet’). Usually only very limited amounts of ‘liquid/bulk’ are possible without obscuring the 2D crystal pattern. (unless there are peaks in a different region of the pattern to the fluid). Hence most work is at submonolayer coverages, but some have gone to study solid layers coexisting with liquid.

Detailed analysis of the lineshape can give other physical parameters such as 2D domain size, elastic properties and 2D vs 3D nature of the overlayer structure.

The evolution of the 2D diffraction pattern with composition can indicate the mixing in the 2D solid layers.

A number of these solid layers (eg halogen bonded co-crystals) have not been seen with STM (despite trials by us and other more experienced STM users!).
Synchrotron Xray sources are preferred over lab-based source for the high flux. Neutrons require a suitable centralised facility and appropriate access by peer review application.

Examples of Systems:

**Alkanes on Graphite:**


**Haloalkanes on graphite:**


**Nitrogen on graphite:**

Carboxylic acids on graphite:


Alcohols on graphite:


Amides on graphite:


Aldehydes on graphite:


Halogen bonding systems on graphite:


Alkanes on MgO:

Alkanes on BN:
T. Arnold et al, Structure of Normal-Alkanes Adsorbed on Hexagonal-Boron Nitride

**Review**

2) **Truncation rod experiments:**
Surface crystallography: very high resolution studies.

**On Calcite.**


**On Mica.**

3) **Neutron and Xray reflection (structure normal to surface)**

Gives the absolute composition and layer thicknesses of the adsorbed surface layers - in situ. Isotopic contrast to study multicomponent mixtures. Requires large very flat surfaces (ideally several square centimetres) and a neutron source. Recent work includes studies under external fields.

**Silica**

**Minerals:**

**Calcite:**


**Mica:**


**Metals/oxides**

**Iron oxide**


**Steel**


**Nickel**


**Alumina**


**Copper**

**Others**

**Polymer surfaces**


3) Adsorption to the surface of particles/colloids from liquids

Small angle xray (SAXS) and neutron scattering (SANS): Introduction to the method:


Used to quantify composition and layer structure of molecules on small particles in suspension. SANS can again exploit the contrast variation approach to probe each component of mixtures.

**Spectroscopic methods**

1) Sum frequency generation (SFG) – surface specific

Using the break in centrosymmetric symmetry at a surface to characterise the surface IR spectroscopy of adsorbed species. Ideal for determination of adsorbed chemistry (eg CO₂H vs CO₂ -), absolute orientation of molecular dipoles, adsorbate molecular orientation and details of conformational order of alkyl chains. Can get in-plane spatial distribution on micron lengthscales with an SFG microscope. Can probe adsorption in-situ under static and applied fields such as shear, temperature etc. ideally on a flat, reflective surface. Metallic substrates can have some enhancement, relative to dielectrics. E.g.


2) Related spectroscopy – surface sensitive

RAIRS/ ATR are reasonably standard methods that enhance the contribution of IR bands from a surface species, relative to bulk contributions.

Recent method advances such as PM IRRAS (which exploits polarisation to enhance the contribution from a surface) can be helpful.

3) AFM-IR – In outline one might consider that thermal expansion of an adsorbed layer by uptake of IR radiation is detected by an AFM tip. Hence very high in-plane spatial resolution (approx. 10nm). Used for chemical group identification on spatially heterogeneous surfaces. Presently only used for ‘dry’ systems (not under liquids).

**Thermodynamics/Calorimetric methods**

1) Differential Scanning Calorimetry
Thermal transitions arising from a monolayer adsorbed from a liquid on a powdered substrate can be identified and followed with changing conditions/composition.

For example, the melting point of a monolayer adsorbed on a substrate can be identified (‘pre-solidification’). The variation of this monolayer melting point with composition reveals: preferential adsorption from mixtures, non-ideality of mixing in the 2D layer, identification of 2D phase diagram including: ideal mixing, phase separation, non-ideal mixing, peritectics, dystetics (2D stoichiometric complexes). etc. etc.

**Example Systems:**

**Alkanes on Graphite**


Castro, M et al Physical Chemistry Chemical Physics, 1, 5017-5023 (1999). 'The Investigation of Mixed Monolayers Adsorbed from Solution: Octane and Nonane Mixtures on Graphite'.

Alcohols


**Alkanes and alcohols mixtures on graphite**


**Carboxylic acids on graphite**


**Amines on graphite**


**Others**


Can be used to observe layer by layer freezing at a surface and other transitions.


2) Solution depletion adsorption isotherms.

Gives the amount adsorbed as a function of solution concentration. Can infer molecular orientation/structure. With suitable analytical tools can probe competitive adsorption, non-ideal behaviour etc.. Temperature dependence can be used to give ΔH and ΔS of adsorption. Cheap and relatively easy (with appropriate care).

3) Titration/Ph

Means of characterising surface groups in water/non-aqueous systems by their pKa and amount. Extensive literature from water/environmental Chemistry (e.g. Book: Aquatic chemistry, Stumm and Morgan) with equilibrium constants, binding mechanisms of organics on substrates etc..

Used to identify potential determining ions and indifferent electrolytes, etc.

**Dynamic methods**

1) NMR low field

T1/T2 as an indicator of what’s adsorbed and binding enthalpy from relaxation. Lots of interest from catalysis characterisation porous solids etc.. (e.g. Lynn Gladden et al, Cambridge).

e.g. C. D’Agostino, et al, "Effect of paramagnetic species on T1, T2 and T1/T2 NMR relaxation times of liquids in porous CuSO4/Al2O3", *RSC Advances*, 2017.

2) High field NMR and ‘dynamic contrast’

Uses the idea that adsorbed molecules are ‘static’ and molecules in solution are mobile. This mobility difference can be detected by NMR. Isotopic labelling is used to identify preferential adsorption of mixtures. E.g.


Cross polarisation NMR measurements have been used to give the binding and spatial distribution of metal ions on clays (relevant to heavy metal ion capture).


Structural localization of Al$^{3+}$ ions in aluminosilicates: application of heteronuclear chemical shift correlation to 2:1 phyllosilicates

3) Incoherent neutron scattering (IQNS)

As for dynamic contrast NMR, uses the difference in adsorbed species mobility relative to the bulk liquid to characterise what’s absorbed and give preferential adsorption. Exploits contrast variation isotopic labelling to identify the behaviour of mixtures hence can be used to probe combinations of very similar species (e.g. octane and decane)

In favourable cases can be used to characterise the nature of motions of adsorbed species (eg translational vs rotational motion from the Q dependence).


Can be used to observe layer by layer freezing at a surface


adsorbed on graphite ..’The elastic scattering observed above Tm is consistent with the coexistence of solid monolayer clusters with a fluid phase, as predicted by the simulations. For T/Tm>1.3, the elastic scattering vanishes from the neutron spectra where the simulation indicates the presence of a fluid phase alone. ‘..

Others