Electrolytes and Interfaces

in Nature and in Technology

Research group of Susan Perkin

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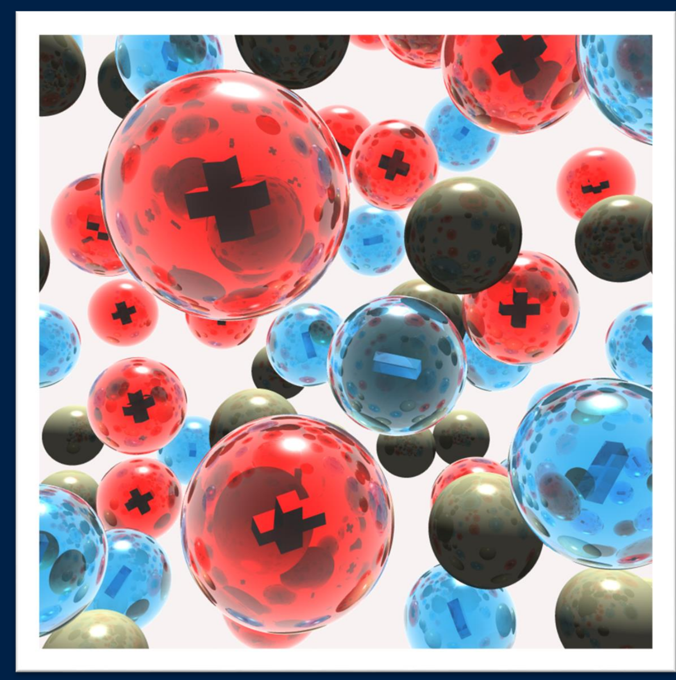
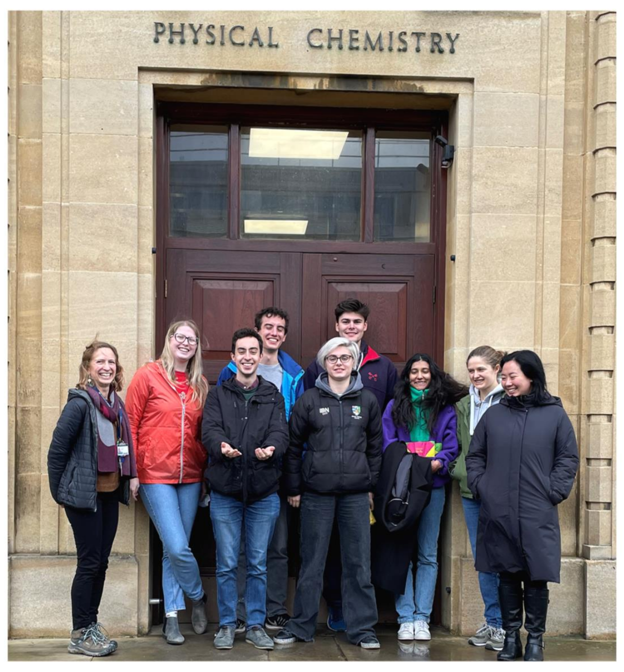


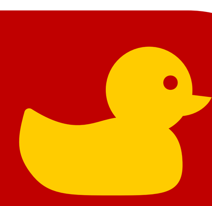


We are motivated to contribute towards solving problems of environmental sustainability and energy storage through fundamental research involving the physical chemistry of electrolytes.

Electrolytes are all around us: they are the fluid solvent for life on earth, both within living organisms and surrounding us as oceans and rivers. They are also key ingredients in energy storage devices such as batteries, supercapacitors, and fuel cells. Remarkably, fundamental physical chemistry of electrolytes still presents serious challenges to our understanding of the liquid state.

For more information or to arrange a visit, contact: susan.perkin@chem.ox.ac.uk

2023 Scholarships and positions available:

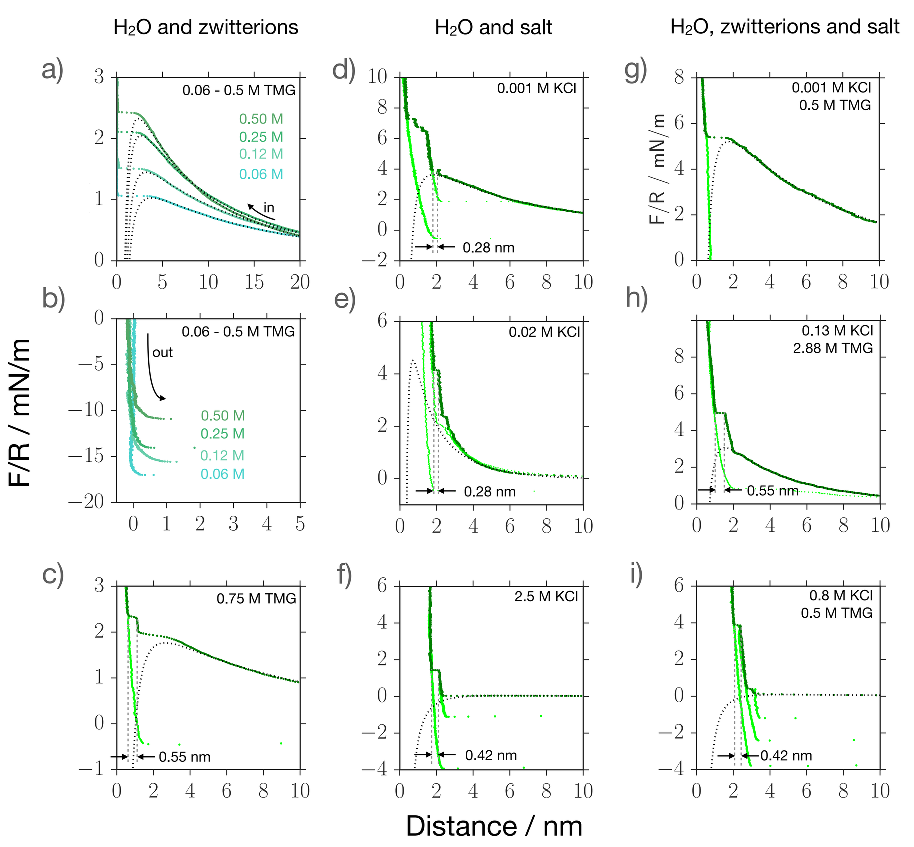


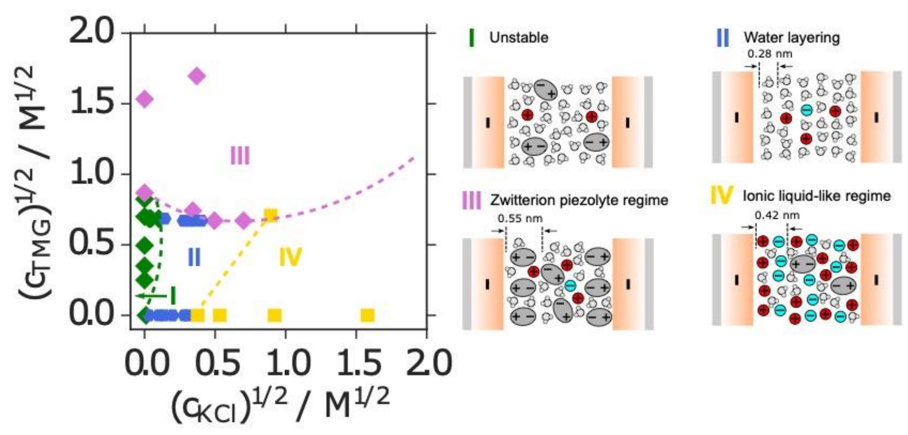
- **Part II:** We offer up to two Part II places every year
- **DPhil:** Two DPhil scholarships (including fees at UK rate) are available for autumn 2023 start.

Osmolytes and Natural Electrolytes

Natural electrolytes consist of multiple ionic, zwitterionic, and molecular components. Organisms maintain appropriate osmotic pressure by accumulating specific components. What is the effect of this complexity on the interactions occurring in this mixed environment?

By investigating the effect of zwitterions on the interaction between charged surfaces, we show that these osmolytes are far from passive observers of electrostatic interactions: they play a significant role in defining the range and form of interaction potentials between charged particles.



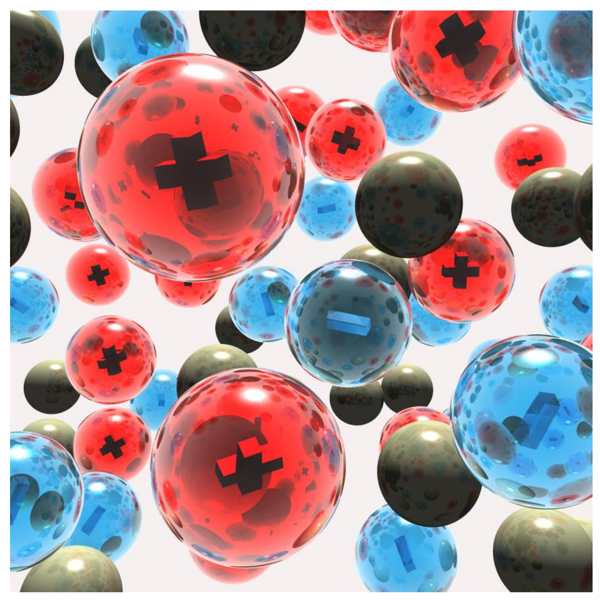


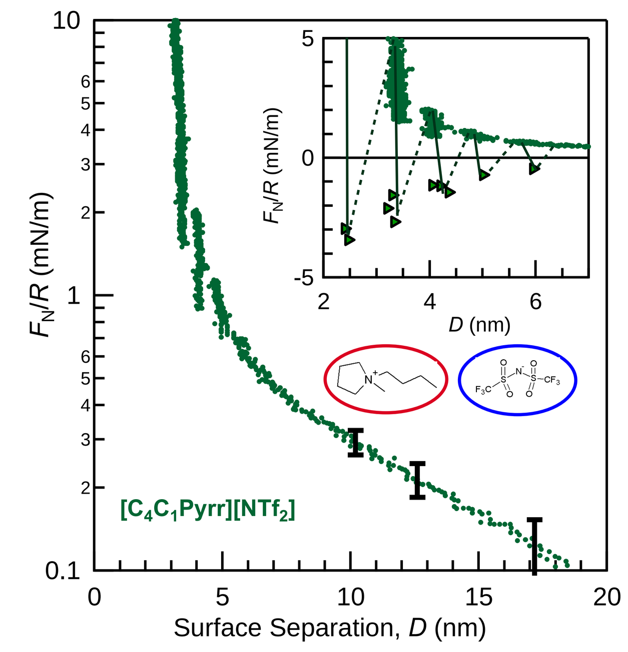
Top, (a)-(i): example measurements of interaction force vs. distance between charged surfaces across electrolytes containing different amounts of KCl salt and TMG zwitterions. Bottom left: phase map indicating that interactions fall into four delineated 'phases' depending on the concentration of KCl and TMG; these are interpreted in terms of the interfacial electrolyte structure as shown in the cartoons (bottom right). [Hallett, Agg, Perkin; submitted 2022]

Dense Electrolytes and Ionic Liquids

Energy storage relies on **highly concentrated electrolytes** with finely tuned physical and electrochemical properties. However, many fundamental aspects of the chemical physics of concentrated electrolytes remain unclear or difficult to explain due to the complexity of ion correlations and excluded volume effects at high (charge) density.

We carry out delicate high resolution measurements of surface forces across dense electrolytes to determine the **electrostatic screening** properties and **structural arrangement of ions and solvent**. The aim is to build an understanding of electrostatics in dense electrolytes equivalent to the Debye-Hückel theory appropriate at low concentration.

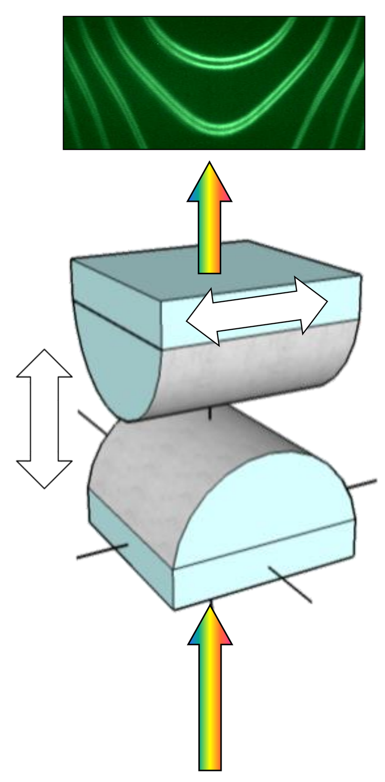




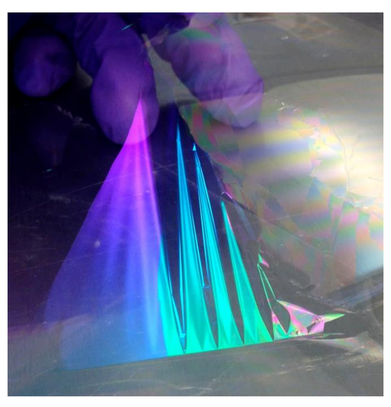
Left: Cartoon of a high concentration electrolyte; solvent and ions are present in similar number. Right: measured force vs. separation distance between negatively charged plates across a pure ionic liquid (liquid salt with no solvent; structure shown in inset). At short range oscillations are due to structure; at longer range the monotonic decay is electrostatic screening. [From: Smith et al. JPCL 2016; Lee et al. PRL 2017]

Measurement of Surface Forces

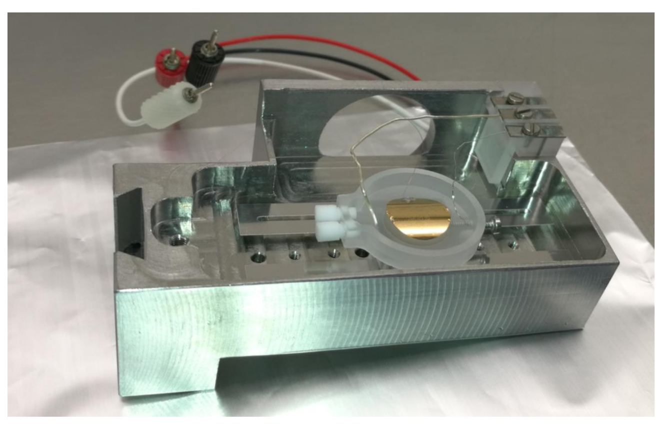
We are an experimental research team, with special expertise in using a **Surface Force Balance** (SFB) to study fluids, interfaces, and surface forces. The **interaction force** is measured between two solid cylinders, **atomically smooth** and mounted in crossed orientation, as a function of their separation distance with **~ 0.1 nm resolution**. Mirrors behind the solid substrates are used to create an **interferometer** for the precise distance and force measurement. Various modes and electrochemical attachments allow us to apply symmetric and asymmetric voltages to the surfaces.



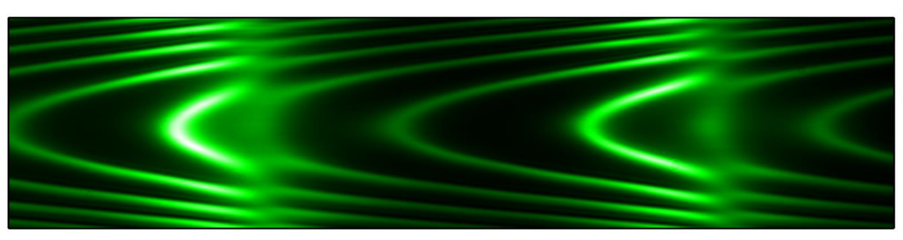
Schematic view of the Surface Force Balance



Mica crystal cleaved along a single crystal plane revealing bright interference colours



One gold cylindrical lens mounted in the inner chamber and showing electrode connections



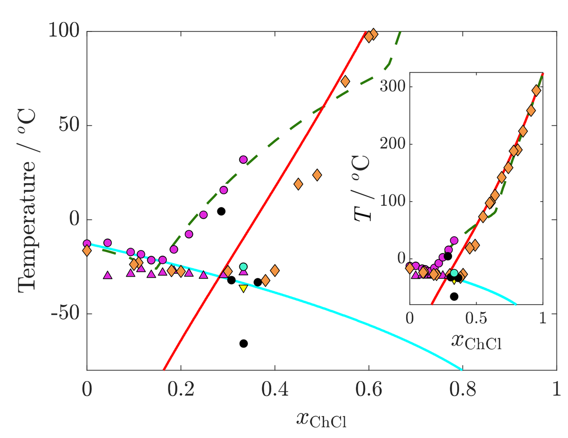
A FECO interference pattern arising from reflections between a triple-layer gold interferometer

Projects open to new students 2023

Upcoming projects open to students starting in 2023 include:

(1) **Fundamental studies of the interfacial science involved in CO_2 mineralization:** Carbon mineralization, also called enhanced weathering, refers to the process of speeding up the natural process of CO_2 reaction with rocks rich in Ca^{2+} or Mg^{2+} to create carbonates. We will investigate the influence of chemo-mechanical forces, hydration, and alkalinity on interfacial processes related to mineralisation.

(2) **The phase behaviour and physico-chemical properties of eutectic electrolyte mixtures:** Eutectic mixtures of salts and polar solvents (often involving chelating ligands) are of interest as electrolytes for energy storage devices and many other applications. In some cases the eutectic point is deeper than predicted based on ideal mixing, and these mixtures are called 'deep eutectic solvents'. We will characterize new eutectic mixtures and investigate their electrochemical and thermodynamic properties.



Left: Collected literature measurements of the liquidus and solidus lines for the mixture of ethylene glycol and choline chloride. Right: new measurements of the phase diagram for the same system, revealing strikingly different eutectic features. [Hayler & Perkin, ChemComm 2022]