Elucidating aqueous structure and the crystallisation narrative using X-ray total scattering

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Crystallisation is one of the most important physical phenomena within modern chemistry, with large areas of materials science and organic chemistry being indebted to this process, yet little is known about the narrative from aqueous to solid. Understanding this fundamental mechanism will not only allow for a greater understanding of the crystallisation route but also understanding of the key elements that dictate physical structure, properties, and attributes. This will ultimately allow for the fine-tuning of the crystallisation process and allow for higher quality, more bespoke functional materials for diverse applications such as catalysis, hydrogen storage, electrochemical cells, and pharmaceuticals.

Using developments in both synchrotron (such as the new ARC detector at the I15-1 beamline at Diamond [1]) and laboratory-based instruments [2], it is now increasingly possible and accessible to measure and determine aqueous structure using an X-ray total scattering approach. Here I will introduce the current state of, and future directions for, aqueous structure and crystallisation studies. Focussing on specific samples: magnesium sulfate, propylene carbonate and 3-methylcyclopentanone, will highlight both the recent advances in X-ray total scattering and the advantages over more traditional techniques such as neutron scattering, Raman, and computational studies. [3–5] Experimental considerations needed to obtain good quality data with good time resolution will be highlighted.

Analysis of the total scattering data can be conducted via a variety of analysis routes including non-negative matrix factorization (NMF), small-box modelling via software such as TOPAS [6], and large-box modelling using EPSR and Dissolve. [7–8] Each analysis route pays a key role in unlocking further information, such as experimental conditions under which significant changes the scattering data are observed, identification and characterisation of molecular fragments, short- and long-range structures, as well as average motifs within the model. I will show how consideration of all of these analyses is required to provide the necessary information to determine the aqueous structure, common structures in the crystallising system, key interactions between fragments and solvent structure. Combining the outcome of these routines and the information acquired allows one to understand the ‘bigger picture’ such as the crystallisation narrative at a molecular level, what can cause glassy transitions and how varying synthesis, solvent and conditions can dictate a final product of basic salts, co-crystals and functional materials such as catalysts, zeolites, perovskites, and metal-organic frameworks (MOFs).

Figure 1. Key structures dictating the crystallisation narrative for magnesium sulfate defined using various concentrations with structure, extracted from a large-box EPSR X-ray refinement.