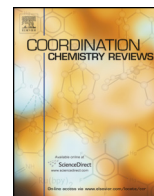




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Review

Using synchrotron X-ray and neutron methods to investigate structural aspects of metal ion solvation and solution structure: An approach using empirical potential structure refinement

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ABSTRACT

The microscopic structure of solutions and the interactions of their constituent chemical species are topics of long standing interest and importance in the chemical sciences. Like many fields of condensed matter research, techniques developed at large scale facilities such as X-ray synchrotrons and pulsed or reactor based neutron sources have, over the past few decades, played a significant role in unravelling many of the mysteries that underpin the chemical, physical and biochemical properties of these systems. In this article we set out to review a subset of these methods, specifically X-ray diffraction, neutron diffraction and X-ray absorption spectroscopy, as well as their combined application to the investigation of structural questions on aqueous electrolyte solutions. Particular emphasis will be given to the use of analytical approaches based on atomistic computer modelling of the experimental data.

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1. Introduction

The microscopic structure of liquids plays an important role in solution chemistry, where the choice of solvent medium can significantly affect chemical reaction equilibria and rates. These effects result from the diverse range of solute–solvent interactions that

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can be experienced [1,2], and underline the importance of understanding the atomic and molecular details of solvation and solvent structure if rational chemical control is to be obtained. Recent decades have seen the development of state of the art X-ray and neutron facilities that have significantly increased the availability and utility of valuable tools suitable for directly addressing many of the scientific issues in the field. Over the same period, concomitant developments in advanced computational methods have revolutionized our ability to extract the maximum information from the resulting experimental data. In particular and for the purposes of this review, three experimental techniques with highly complementary characteristics have been chosen to form the heart of this contribution, these are: X-ray diffraction (XRD), neutron diffraction (ND) and X-ray absorption spectroscopy (XAS).

The strength of the X-ray and neutron diffraction techniques is that they probe the entire structure of a solution. However unlike crystallography, where the method measures sharp Bragg scattering features arising from the single body correlation functions of regular periodic lattices, the diffuse diffraction pattern of a liquid only contains information about the pair correlations between the system's constituent atoms. If a liquid solution is formed from N distinct atom types, then a single diffraction experiment will measure a total pair correlation function formed from a linear sum of $N(N+1)/2$ partial pair contributions, and the analytical challenge for the scientist is then to identify how these structural correlations are distributed between the various atom pair combinations. In the absence of small angle scattering information, which most commonly falls outside the measurement range of most liquids diffractometers, the structural insight of a liquid diffraction experiment is generally restricted to atomic pair correlations that occur over length scales less than 10 \AA .

In contrast to the ability of the diffraction methods to probe the entire structure of a system, X-ray absorption spectroscopy is a chemically specific technique that is tuned to probe the local structural environment of a selected constituent element predominantly through the atomic pair correlations with the photo-absorbing atom. This chemical specificity reduces the complexity of the measured total correlation function of an N component system, to a signal that contains N or fewer pair correlation terms centred on the atomic species of interest, that fall within a typical distance range of less than 4 \AA . Additionally, because this chemical specificity is derived from the resonant absorption signal of a photoabsorbing atom, the technique also allows structural information to be obtained on the environments occupied by very dilute components in the system.

The complementary viewpoints of the diffraction and X-ray spectroscopy techniques make their combination particularly powerful for unravelling the microscopic structural complexities of solutions. This is because the varying sensitivities of each method to the $N(N+1)/2$ partial pair correlations improves the chances of a reliable separation of the specific structural terms. To illustrate the capabilities of these analytical methods we will use examples drawn from studies of aqueous electrolytes, as these are classic systems of continuing contemporary interest, and we will demonstrate how a unified analytical framework based on atomistic computer simulation allows us to maximize their effectiveness.

2. Experimental techniques

As we aim to build quantitative structural models of liquids and solutions that are consistent with experimental data, it is very important to have a comprehensive understanding of the information that is contained in the available data sets, but also knowledge of how the data is normalized in relation to the theoretical functions that will be calculated from the model ensembles. Many

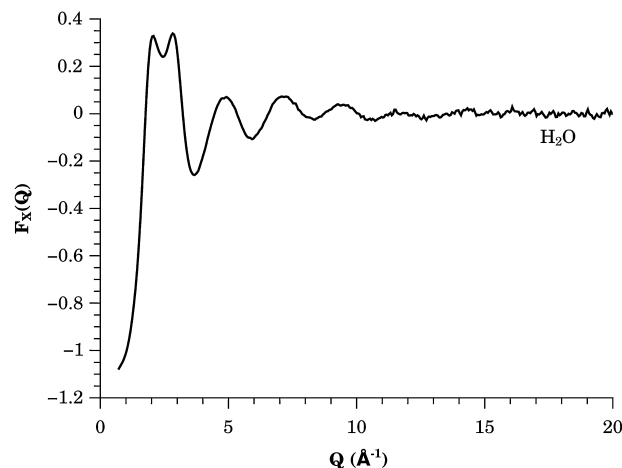


Fig. 1. X-ray interference differential scattering cross section for liquid water (H_2O) measured at 298 K using X-rays of wavelength 0.559 \AA on a X'pert Pro diffractometer (Panalytical, Almelo, The Netherlands). This function has been normalized to the single atom scattering as $F_X(Q) = ((1/N)(d\sigma/d\Omega) - \sum_{\alpha} c_{\alpha} f_{\alpha}^2(Q)) / \sum_{\alpha} c_{\alpha} f_{\alpha}^2(Q)$.

normalization schemes exist in the literature, so here we take a little time to outline the formalisms that we have chosen to adopt.

2.1. X-ray diffraction

An X-ray diffraction experiment measures the total differential scattering cross section $(1/N)(d\sigma/d\Omega)$ of a system where N is the number of atoms, σ the scattering cross section and Ω the solid angle [3,4]. This function is defined as

$$\frac{1}{N} \frac{d\sigma}{d\Omega} = \sum_{\alpha} c_{\alpha} f_{\alpha}^2(Q) + \sum_{\alpha} \sum_{\beta \geq \alpha} (2 - \delta_{\alpha\beta}) c_{\alpha} c_{\beta} f_{\alpha}(Q) f_{\beta}(Q) [S_{\alpha\beta}(Q) - 1] \quad (1)$$

Q is the magnitude of the momentum transfer vector of the scattering process defined as, $Q = (4\pi/\lambda)\sin\theta$, where 2θ is the scattering angle and λ is the wavelength of the incident X-ray photon. The $S_{\alpha\beta}(Q)$ terms are the partial structure factors encoding the pairwise correlations between atoms of type α and β , whilst c_{α} , c_{β} and $f_{\alpha}(Q)$ and $f_{\beta}(Q)$ are their concentrations and atomic scattering form factors [5], respectively. $\delta_{\alpha\beta}$ is the Kronecker delta function to avoid double counting the like-atom pair correlations.

The two terms to the right of the equality in Eq. (1) correspond to the single atom scattering and the interference differential scattering cross section or total structure factor. It is the latter function, henceforth called $F_X(Q)$, that contains the structural information that is sought in a liquid diffraction measurement, see Fig. 1 for an example.

$$F_X(Q) = \sum_{\alpha} \sum_{\beta \geq \alpha} (2 - \delta_{\alpha\beta}) c_{\alpha} c_{\beta} f_{\alpha}(Q) f_{\beta}(Q) [S_{\alpha\beta}(Q) - 1] \quad (2)$$

Each partial structure factor that contributes to this total structure factor is related to its corresponding partial pair distribution function $g_{\alpha\beta}(r)$ by a Fourier transform that is weighted by the atomic density of the system, ρ ,

$$S_{\alpha\beta}(Q) - 1 = 4\pi\rho \int_0^{\infty} r^2 (g_{\alpha\beta}(r) - 1) \frac{\sin Qr}{Qr} dr \quad (3)$$

The partial pair distribution functions are formally defined by

$$g_{\alpha\beta}(r) = \frac{n_{\alpha\beta}(r)}{c_{\beta}\rho 4\pi r^2 dr} \quad (4)$$

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