

DECONVOLUTION OF ION PAIR FORMATION IN STRUCTURAL DATA FROM
NEUTRON DIFFRACTION WITH ISOTOPIC SUBSTITUTION. PROOF OF PRINCIPLES
VIA MOLECULAR SIMULATION

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ABSTRACT

For more than three decades a great deal of structural information of electrolyte solutions has been collected from x-ray and neutron scattering experiments. In particular, neutron diffraction with isotopic substitution (NDIS) has shown the potential to provide not only the water structure, but also the ion-water (by the *first-order difference* method) and the ion-ion (by the *second-order difference* method) correlations. Although powerful, these scattering techniques have limited capabilities for resolving overlapping peaks associated with ion pair formation¹, and for quantifying effects or pairing on the related determination of hydration numbers.

The NDIS method was originally applied to aqueous electrolyte solutions involving heavy rather than light water, to avoid the large effects of incoherent scattering of the neutrons by the protons. Later, improvements in sources, instrument design, and the operator's ability to correct raw data for incoherent scattering made it possible to use light and heavy mixtures, water to study the structure of aqueous metal chlorides. The alternative use of light and heavy water allowed them to determine the total structural factors, and subsequently, to determine the radial distribution function for the (water hydrogen)-cation, assuming that the partial structural factors for the (water oxygen)-cation and (water hydrogen)-cation interactions are independent of the solvent isotopic nature.

A common approach in the determination of the solvent structure around ions, has been to assume negligibly small contributions of the ion-ion and the ion-counterion contributions to the total structural factor. In practical terms, the above assumption hinges around the fact that the coefficients associated with the ion-counterion and ion-ion partial structural factors are typically an order of magnitude smaller than those

corresponding to the ion-oxygen, as well as the ion-deuterium and ion-hydrogen partial structural factors. However, as noted in our previous work^{1,3}, the product of the coefficients and their associated partial structural factors, may not be negligible even when the coefficients are small.

From a strictly structural viewpoint, a non-negligible coefficient for the ion-counterion structural factor indicates a potential penetration of the ions into the counterion's hydration shells, whose manifestation is an overlapping of the anion-cation with the (water hydrogen)-cation and/or (water-hydrogen)-anion contributions to the corresponding total structural factors¹. The consequence of this potential overlapping appears as a distortion of the normal shape of the second peaks of the *first-order difference* of the cation's neutron-weighted distribution functions, and the first peaks of the anion's neutron-weighted distribution functions, either in the form of inconspicuous inflections or shoulders. These subtle details usually cannot be resolved from Fourier transformation of the total structural factors, a situation that makes it very difficult for anyone to detect the presence of ion-pair formation from the anion's or cation's neutron-weighted distribution functions, and highlights the need for a more direct approach to test the presence of ion pairing and its subsequent measurement.

In this contribution we present the unambiguous and direct assessment of the ion-pair formation, and predicted its contribution to the structural factors of ions in aqueous solution from the molecular dynamics simulation analogue of the NDIS experiments, using null aqueous solutions of lithium and calcium chloride at ambient conditions. The significance of this study resides in the fact that molecular simulation allows the unambiguous resolution of the usual overlapping between the anion-cation and the (water hydrogen)-cation peaks, as well as between the anion-cation and (water hydrogen)-anion peaks in the corresponding neutron-weighted correlation functions for aqueous electrolyte solutions. Furthermore, this resolution makes it possible to assess accurately the magnitude of the predicted ion-pair formation, as well as its contribution to the 'measured' water-hydrogen coordination numbers around the anions and the cations in solution.

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The combination of the proposed method with increasingly more accurate scattering raw data will ultimately provide additional insights into molecular-level structure of aqueous electrolyte solutions.

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