Toward the Understanding of Hydration Phenomena in Aqueous Electrolytes from the Interplay of Theory, Molecular Simulation, and Experiment

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ABSTRACT

We study the microstructural analysis of aqueous electrolytes and present a detailed account of the fundamentals underlying the neutron scattering with isotopic substitution (NDIS) approach for the experimental determination of ion coordination numbers in systems involving both halide anions and oxyanions. We place particular emphasis on the frequently overlooked ion-pairing phenomenon, identify its microstructural signature in the neutron-weighted distribution functions, and suggest novel techniques to deal with either the estimation of the ion-pairing magnitude or the correction of its effects on the experimentally measured coordination numbers. We illustrate the underlying ideas by applying these new developments to the interpretation of four NDIS test-cases via molecular simulation, as convenient dry runs for the actual scattering experiments, for representative aqueous electrolyte solutions at ambient conditions involving metal halides and nitrates.

Keyword: Molecular simulation, aqueous electrolytes, ion pair association, neutron diffraction with isotopic substitution, heavy water, null-environments

I. INTRODUCTION

Researchers have early recognized that ion-water interactions are determining factors in the behavior of aqueous electrolyte solutions typically encountered in biological, geochemical, environmental, and industrial processes. Consequently, they have focused their attention on the properties of electrolyte solutions in terms of the underlying intermolecular forces and sought their interpretation in terms of experimentally measured structural features via diffraction approaches ¹. While ion hydration has been historically studied in a thermodynamic context whose description of the observables was restricted to concentration domains where they obey simple limiting laws (*e.g.*, Debye-Huckel ²), the lack of microscopic input hindered the development of accurate molecular interpretations. For a long time the “missing link” was the lack of a

clear and unambiguous connection between the hydration process and its corresponding thermodynamics, until Ben-Naim introduced a generalized stepwise and clever approach that allowed identifying the underlying statistical mechanical basis and its relevant hydration thermodynamic quantities³⁻⁴

From a modeling perspective the hydration process can be thought as a local density perturbation (or solute-induced changes of the solvent environment toward the formation of the hydration microstructure) caused by the introduction of solute species into the aqueous environment that plays a fundamental role in determining the thermophysical behavior of solutions⁵⁻⁶. This local perturbation arises from the difference of strength (or interaction asymmetry) between the water-water and the solute-water interactions whose macroscopic outcome is always the manifestation of solution nonideality⁷.

The microstructural changes of water around ionic species in aqueous electrolyte solutions are the unavoidable common denominator for all hydration-related phenomena including ion mobility and conductivity⁸⁻⁹, solvent electrostriction and dielectric saturation¹⁰⁻¹¹, salt solubility and ion speciation¹²⁻¹³, electrodic processes¹⁴, salting-in/out in mixed-solvent electrolytes¹⁵, as well as protein denaturing and folding¹⁶⁻¹⁷. This commonality is not accidental but the manifestation of fundamental links between the microstructure of the system, described in terms of (either radial or spatial) distributions functions, and relevant macroscopic properties¹⁸ that might become the basis for macroscopic modeling and useful engineering correlations¹⁹⁻²⁰. In fact, there are basically two available exact formalisms able to provide rigorous (*i.e.*, cause-effect) connections between the microscopic details of the system and their macroscopic properties, in chronological order, McMillan-Mayer (MM)²¹ and Kirkwood-Buff (KB) fluctuation formalisms¹⁸.

While the two theoretical approaches are based on configurational integrals over grand canonical correlation functions, to date their use as means of guiding the interpretation and modeling of electrolyte solutions has been contrastingly different. As discussed recently by Vafaei *et al.*²² who are attempting to change that trend, the observed usage disparity between the two formalisms might be in part because the original MM manuscript is “hard to read” and the formalism reduces the analysis of the

solution to a solute-only form, *i.e.*, where the solvent degrees of freedom in the corresponding partition function are integrated out. Moreover, because the MM formalism delivers thermodynamic properties as power series of the solute concentrations, whose higher order coefficients are difficult to interpret, the formalism has been useful only for dilute solutions²³⁻²⁵. In contrast, the KB formalism involves all species correlation functions where certain combinations of their configurational integrals (*i.e.*, the so-called KB integrals) can be related directly to macroscopic properties including the solution compressibility, the ion osmotic susceptibilities and corresponding partial molar volumes^{6, 26}.

An immediate practical consequence of such links between microscopic and macroscopic behavior has been the proliferation of the use of coordination (or hydration for that matter) numbers as descriptors of hydration strength or model parameters in the development of macroscopic correlators²⁷⁻³¹. In fact, the conventional view of the structure of electrolyte solutions has been shaped by the schematic description of hydration by Frank and Wen³² and Gurney³³ based on concentric water shells around the ions — innermost or primary, secondary, and outermost — to interpret ion hydration in terms of *structure-breakers* (or chaotropes, *i.e.*, they weaken the hydrogen bonding network) and *structure makers* (or kosmotropes, *i.e.*, they strengthen the hydrogen bonding network)³⁴. With this scheme came the challenge of an adequate metric to discriminate between the two structures according to experimentally measured properties such as the dielectric constant of water in the electrolyte solution and the entropy of ion solvation³⁵. This picture also introduced the idea of the ion-water coordination (*aka* hydration number) as the estimated number of water molecules associated with the ion under consideration, a concept that simplified the interpretation and modeling of aqueous electrolyte systems^{14, 36}.

The ion-water coordination is obviously a natural description for the local water environment around an ion yet, its determination becomes strongly dependent on the methodology of measurement and frequently they become adjustable parameters for modeling purposes^{8, 14, 35, 37-38}. Moreover, even though the concept of *hydration numbers* might be a rather deficient one³⁹ — whose experimental determination by mobility, compressibility, dielectric measurements, and diffraction experiments provides a wide

spread set of results⁴⁰⁻⁴² — and oftentimes differentiated from the *coordination numbers* (for a lengthy discussion see Chapter 29 of Ref. 35), its frequent usage highlights the need for more direct ways to probe the water environment around the ions in solution.

In what follows we will discuss relevant issues underlying the subject of interest to fulfill the premise behind the goal of this manuscript; however, due to obvious scope and length constraints we will focus on aspects that are close to our own past and current research activities. In the next sections we address the microstructural analysis of simple aqueous electrolytes and present a detailed account of the fundamentals underlying the NDIS approach for the experimental determination of ion coordination numbers. Then, we discuss the frequently overlooked ion-pairing phenomenon, identify its microstructural signature in the neutron-weighted distribution functions, and propose novel techniques to deal either with the determination of ion-pairing or the correction of its effects on the measured coordination numbers. Finally, we apply these developments to the interpretation of NDIS outputs from molecular simulation of representative aqueous electrolyte solutions at ambient conditions involving metal halides and nitrates. We close the manuscript with a brief discussion and relevant final remarks.

II. MICROSTRUCTURE OF SIMPLE AQUEOUS ELECTROLYTES

In the last four decades we have witnessed the significant investment of effort toward the development of tools for the extraction and collection of structural information of aqueous electrolyte solutions from scattering experiments, mainly, by x-ray and neutron scattering methods⁴³⁻⁴⁹. In particular, the ability of manipulating the isotopic composition of a targeted ion makes NDIS a powerful tool to extract structural information about the electrolyte solution in terms of ion-water (by the *first-order difference* method)⁴³ and the ion-ion (by the *second-order difference* method) correlations⁵⁰. This approach is made possible because the neutron scattering length is isotope specific, and consequently, neutrons can distinguish different isotopic forms of the same elements, a feature that provides the opportunity to develop novel experimental schemes, especially when an element exhibits isotopic forms, g , whose neutron coherent scattering lengths b_g are of opposite signs. In fact, the most prominent of them is given by the $^1\text{H}/^2\text{H}$ (*aka* H/D) isotopic substitution with $b_H = -3.74 \text{ fm}$ and $b_D = 6.67 \text{ fm}$ ⁵¹,

where this condition makes possible the tuning of the global coherent scattering of the hydrogen element to become transparent to neutron, *e.g.*, in the case of “null water” or “semi-transparent” environments to be discussed in detail below ⁵².

In addition to $^1\text{H}/^2\text{H}$, there are other elements with isotopic variations whose coherent scattering lengths exhibit opposite signs, including $^6\text{Li}/^7\text{Li}$, $^{46}\text{Ti}/^{48}\text{Ti}$, $^{50}\text{V}/^{51}\text{V}$, $^{52}\text{Cr}/^{53}\text{Cr}$, $^{58}\text{Ni}/^{62}\text{Ni}$, $^{112}\text{Cd}/^{113}\text{Cd}$, $^{123}\text{Te}/^{130}\text{Te}$, $^{130}\text{Ba}/^{138}\text{Ba}$, $^{149}\text{Sm}/^{147}\text{Sm}$, and $^{184}\text{W}/^{186}\text{W}$. Below we will discuss how this feature can in principle be used to “erase” some correlation peaks, and consequently, avoid potential peak overlapping that prevents the proper interpretation of water-ion coordination (a full account of this novel approach is given elsewhere ⁵³). In fact, peak overlapping is a phenomenon of common occurrence in aqueous electrolytes, a signature of anion-cation hydration shell penetration (*aka* ion pairing) that can affect the interpretation of the shape, location, and deconvolution of scattering peaks ⁵⁴⁻⁵⁵.

NDIS of aqueous electrolyte solutions typically involves heavy rather than light water, to overcome the large effects of incoherent scattering of the neutrons by the protons ⁵⁶. However, and provided that the significantly larger (than those for heavy water) corrections for incoherent scattering can be properly applied ⁵⁷, the feasibility of using light water and light-heavy water mixtures as aqueous environments increases the power of this tool for the extraction of partial structural factors, and consequently, ion coordination information (*vide infra*).

a) Fundamentals underlying NDIS for the determination of ion coordination

In order to set up the foundations for the ensuing discussion here we identify the link between the measured quantities and the targeted microstructures (*e.g.*, ion coordination environment), and discuss the challenges behind the meaningful interpretation of the experimental evidence, including peak overlapping as the signature of ion-pair formation ⁵⁸⁻⁵⁹. For that purpose we focus on the useful portion of the neutron scattering differential cross section of amorphous aqueous samples, dS/dW , that

provides the desired information on their microstructure, *i.e.*, the total structure factor $F(q)$ defined as ⁴⁶,

$$F(k) = \hat{a}_i \hat{a}_j c_i c_j b_i b_j (S_{ij}(k) - 1) \quad (1)$$

where $k = (4\pi/\lambda)\sin(q/2)$ represents the magnitude of the scattering vector as a function of the wavelength λ of the incident neutrons and the scattering angle q , c_i and b_i denote the atomic fraction and the coherent neutron scattering length of atomic species i , respectively, and $S_{ij}(k)$ is the partial structure factor describing the correlation between atoms of types i and j , *i.e.*,

$$S_{ij}(k) = 1 + (4\pi r/k) \int_0^\infty [g_{ij}(r) - 1] r \sin(kr) dr \quad (2)$$

where r and $g_{ij}(r)$ are the atomic number density of the solution and the radial pair distribution function for ij - interactions.

In order to extract $F(k)$ from the experimentally measured neutron scattering differential cross section dS/dW (or mean intensity), *i.e.*,

$$F(k) = dS/dW - \sum_i c_i S_i^{total} / 4\rho - \text{relevant corrections} \quad (3)$$

we need to subtract the total (coherent plus incoherent) cross section S_i^{total} for all scattering centers i , and then correct for inelastic (Placzek corrections⁶⁰) and multiple scattering, as well as for sample and container adsorption⁶¹. While these corrections are not trivial tasks⁶², for the sake of argument we will assume that the instrument scientist behind the experiments will deal with them properly to be able to determine $F(k)$ accurately from the dS/dW - raw data.

Considering the challenges underlying the NDIS experiments including the processing of resulting raw data, and the fact that there is no need for any of the above corrections for the atomistic simulated $F(k)$ or its real space counterpart $G(r)$, it becomes extremely useful to develop molecular simulation “dry runs” of NDIS experiments to determine the location of relevant diffraction peaks, the presence of peak

overlapping, and ultimately to facilitate the interpretation of the experimental evidence. In fact, this strategy provides the unmatched opportunity to assess the adequacy of neutron-weighted distribution function methodologies for the determination of species coordination in aqueous environments, to identify the presence of ion pairing, and to isolate its effect on the outcome of coordination calculations, regardless of the actual type and nature of the underlying intermolecular forces⁶³.

From the simulation side, it is more advantageous to deal with the neutron-weighted real space distribution function $G(r)$ rather than the structural factor $F(k)$, *i.e.*, its Fourier transform,

$$G(r) = \hat{a}_i \hat{a}_j c_i c_j b_i b_j (g_{ij}(r) - 1) \quad (4)$$

where $g_{ij}(r)$ is the radial pair distribution functions for the ij - pair interactions that results from the corresponding partial structural factor $S_{ij}(k)$ as follows,

$$g_{ij}(r) = 1 + \left(1/2\rho^2 r r\right) \int_0^\infty [S_{ij}(k) - 1] k \sin(kr) dk \quad (5)$$

Therefore, for a simple aqueous electrolyte solution involving an $M^{n+} X^{n-}$ type salt, $G(r)$ will comprise ten different pair correlations, with the largest contribution coming from the (light or heavy) water-water interactions, *i.e.*, from either $g_{OH}(r)$ and $g_{HH}(r)$ or from $g_{OD}(r)$ and $g_{DD}(r)$.

Obviously, since our main goal is to determine the ion-water coordination, we need to decouple the most relevant $g_{ij}(r)$'s from Eqn. (4), in particular, the overwhelming background contribution from water-water correlations to be able to extract some meaningful structural information concerning water around the ions. For that purpose we invoke the *first-order difference* method introduced by Soper *et al.*⁴³, a technique that comprises two diffraction experiments, involving two identical solutions except for the different (g , l) isotopic states of the ion under study. At these conditions, and under the assumption of isomorphic structures upon isotopic substitution (*i.e.*, species correlation functions are independent of the isotopic substitution⁶⁴) such that we are able

to subtract the water-water distribution functions from the total neutron-weighted distribution functions, *i.e.*,

$$\begin{aligned} \text{DG}_I^{\text{solv}}(r) &= G_{lI}^{\text{solv}}(r) - G_{gI}^{\text{solv}}(r) \quad (l \neq g \equiv \text{isotopic species}) \\ &= A_I (g_{Ol}(r) - 1) + B_I (g_{DI}(r) - 1) + C_I (g_{HI}(r) - 1) + \\ &\quad D_I (g_{CI}(r) - 1) + E_I (g_{II}(r) - 1) \end{aligned} \quad (6)$$

In Eqn. (6) we use the superscript *solv* to represent the aqueous environment so that *solv*^o (*lw, hw, nw*) will identify it as being light-, heavy-, or null-water, respectively (obviously we might also have a non-null light-heavy water mixture, though we will not discuss it here). Moreover, the subscripts *I*, *C*, *D*, *H*, and *O* denote ion (either X^{n-} or M^{n+}), counter ion, deuterium, hydrogen, and oxygen sites, respectively. Note that we purposely differentiate the prefactors B_I and C_I , even though we adopted the isomorphic condition $g_{DI}(r) = g_{HI}(r)$, to highlight the power behind the manipulation of the aqueous environment to extract microstructural information (*vide infra*). The five prefactors in Eqn. (6) are given by the isotopic-based difference $c_i c_j b_j \left[b_i^g (2 - d_{ji^g}) - b_i^l (2 - d_{ji^l}) \right]$ where we make explicit the isotopic dependence through the corresponding coherent neutron scattering lengths (b_i^l for $l = l, g$) and invoke Kronecker delta d_{ji^l} for the pair of isotopic species.

Oftentimes it is more useful to work with the normalized version of Eqn. (6) because it allows visualizing the relative contributions of the five terms, *i.e.*,

$$\begin{aligned} \text{DG}_I^{\text{solv}, \text{norm}}(r) &= \left[A_I g_{Ol}(r) + B_I g_{DI}(r) + C_I g_{HI}(r) + \right. \\ &\quad \left. D_I g_{CI}(r) + E_I g_{II}(r) \right] / S_I^{\text{solv}} \end{aligned} \quad (7)$$

where $S_I^{\text{solv}} = A_I + B_I + C_I + D_I + E_I$, so that $\text{DG}_I^{\text{solv}, \text{norm}}(r \rightarrow \text{large}) = 1$. Regardless of the choice, Eqns. (6)-(7) still comprise five linearly independent unknowns suggesting that we would need at least five independent experiments to be able to extract the sought microscopic information. This information would be captured by a portion of either $\text{DG}_I^{\text{solv}}(r_L < r < r_U)$ or $\text{DG}_I^{\text{solv}, \text{norm}}(r_L < r < r_U)$ for the radial region where the relevant

correlation peak is located, under the proviso that the peak comprises the contribution of only one type of pair interactions, *i.e.*, absence of peak overlapping.

In order to comprehend the main issues behind the $DG_I^{solv}(r)$ (or $DG_I^{solv,norm}(r)$ for that matter) profiles we reproduce in Figures 1-2 the experimental curves for Ni^{+2} in a heavy water $NiCl_2$ solution, and for Cl^- in a heavy water $LiCl$ solution, respectively, taken with permission from of the Royal Society ⁶⁵. The main features we need to highlight are the identities of the pair correlations conforming the main two peaks, in particular we should note that $DG_M^{solv}(r)$ exhibits an $O - M$ peak followed by the corresponding $H - M$ (or $D - M$) peak, within the first water-cation hydration shell, which are usually pretty much decoupled. In contrast, $DG_X^{solv}(r)$ displays first an $H - X$ (or $D - X$) peak followed the overlapping between the $O - X$ and the second $H - X$ correlation corresponding to the nearest coordinating water molecules. Moreover, depending on the ion's charge density and the solution's ionic strength these peaks might comprise additional contributions due to their partial overlapping with the $M^{\eta+} - X^{\eta-}$ pair correlations whose first peak (*i.e.*, the *CIP* configuration) usually falls between those of corresponding to the first coordination of the two ions.

From a hydration viewpoint, the $M^{\nu+} \cdots X^{\nu-}$ pair formation results from the penetration of the anion into the cation hydration shells, leads to overlapping of the $M^{\eta+} - X^{\eta-}$ with the $H - M^{\eta+}$ or $H - X^{\eta-}$ correlations, and depending on the extent of the overlap it might appear as a distortion of the normal shape of the second peaks of $DG_M^{hw}(r)$, and the first peaks of the $DG_X^{hw}(r)$ (*vide infra*, Figures 5-8). This distortion in the main peaks of $DG_I^{hw}(r)$ can be usually subtle, and consequently, a visual inspection of the shape of either $DG_M^{hw}(r)$ or $DG_X^{hw}(r)$ might not provide any hint on the $M^{\nu+} \cdots X^{\nu-}$ presence.

The next step has been usually to assume negligibly small contributions to either $DG_I^{solv}(r_L < r < r_U)$ or $DG_I^{solv,norm}(r_L < r < r_U)$ from the ion-ion and the ion-counterion interactions ⁶⁶⁻⁷⁰, *i.e.*, $\left[|D_I|, |E_I|\right] \square \left[|A_I|, |B_I|, |C_I|\right]$. Note however that the actual contributions of the $\left[D_I, E_I\right]$ terms to either $DG_I^{solv}(r_L < r < r_U)$ or $DG_I^{solv,norm}(r_L < r < r_U)$

comprise the factors $[g_{Cl}(r), g_{II}(r)]$ so that for very soluble salts, where increasing ionic strength induce ion-pair formation, neither the coefficients $[D_I, E_I]$ nor the correlation functions $[g_{Cl}(r), g_{II}(r)]$ may be considered negligible as already shown elsewhere^{58, 71}. This scenario highlights several pending issues regarding the ability of current methods of processing NDIS data to extract reliable ion-water coordination numbers involving $M^{\eta+} X^{\eta-}$ aqueous systems that exhibit ion-pair formation, a phenomenon that interferes with the interpretation of either $DG_I^{solv}(r_L < r < r_U)$ or $DG_I^{solv, norm}(r_L < r < r_U)$ peaks. In fact, while often overlooked, the relevant issues here are: (a) how to confirm whether the system exhibits ion pairing, and if present, (b) how to decouple the peak overlapping and/or determine the ion-pairing effect on the “measured” ion-water coordination.

This is precisely the context where molecular-based simulation becomes a powerful tool to assist and guide the accurate interpretation of the scattering raw data, because simulation provides the two ends of the analysis and their rigorous connection, *i.e.*, not only the set of correlation functions for all pair interactions, but also the corresponding neutron weighted distribution functions. In other words, simulation offers answers to precisely defined questions as a direct path to the unambiguous test of consistency and accuracy for the methods and conjectures used in the extraction of structural information from NDIS experiments.

To illustrate this issue, let us start with the statistical mechanical definition of the coordination number as the number of water’s b - site surrounding a central ion I within a hydration shell of radius r_s , *i.e.*,

$$\bar{n}_I^b(r_s) = 4\rho r_b \int_0^{r_s} g_{bI}(r) r^2 dr \quad (8)$$

where $b = H, O$ and r_s typically locates the first valley of the radial distribution function $g_{bI}(r)$. Thus, if we had a way to determine the radial distribution function $g_{bI}(r)$ at the conditions of the system of interest (in practice only possible from simulation or theory), then we would be able to provide an accurate estimate of the corresponding water coordination around the chosen ion according to Eqn. (8). Obviously, this is not possible from scattering experiments even though we can “dig up”

the information from the radial integration of either $DG_I^{solv}(r_L < r < r_U)$ or $DG_I^{solv, norm}(r_L < r < r_U)$ peaks as long as we can ensure the compliance of the indicated constraints (a)-(b) (*vide supra*).

After having attained the *neutron-weighted radial distribution functions* $DG_I^{solv, norm}(r)$ or $DG_I^{solv}(r)$ from some NDIS experiments, and after invoking Eqns. (6)-(7) we can rewrite Eqn. (8) as follows,

$$\begin{aligned}\bar{n}_I^b(r_L, r_U) &= \left(4\rho r_b / I_b\right) \int_{r_L}^{r_U} \left(DG_I^{solv}(r) + S_I^{solv}\right) r^2 dr \\ &= \left(4\rho r_b S_I^{solv} / I_b\right) \int_{r_L}^{r_U} DG_I^{solv, norm}(r) r^2 dr\end{aligned}\tag{9}$$

with $I_b = A_I, B_I, C_I, D_I, E_I$, and $b = O, H, D, I$, where we implicitly assume that either $DG_I^{solv}(r_L < r < r_U)$ or $DG_I^{solv, norm}(r_L < r < r_U)$ exhibits well-defined and resolved peaks, *i.e.*, the integration over for the interval (r_L, r_U) would comprise only $b - I$ pair correlations. Thus, when these assumptions are not obeyed the “measured” coordination numbers would misrepresent the actual water environment around the ion. This is typically the case encountered in the study of the water’s hydrogen environment around simple halide anions (alkaline cations) where we expect to find partial overlapping of the $H - X$ ($H - M$) and the $X - M$ when the aqueous $M^{\eta+} X^{\eta-}$ exhibit contact ion-pair (*CIP*) configurations^{58, 72-73}.

Then, the question is how to detect the presence of anion-cation pairing, and how to correct Eqn. (9) for such occurrence. For the sake of argument let us assume that the solvent is heavy water, *i.e.*, $C_I = 0$, and the isotopic substitution is done on the anion, *i.e.*, $(^g X / ^l X)$. Under those conditions Eqn. (9) would read as follows,

$$\bar{n}_X^D(measured) = \left(4\rho r_D S_I^{hw} / B_X\right) \int_{r_L}^{r_U} DG_X^{hw, norm}(r) r^2 dr\tag{10}$$

where we “suspect” there is a potential peak overlapping within the interval (r_L, r_U) , *i.e.*, $DG_X^{hw, norm}(r_L < r < r_U) @ [B_I g_{DI}(r) + D_I g_{CI}(r)] / S_I^{solv}$, from which it follows that,

$$\begin{aligned}
\bar{n}_X^D(\text{measured}) &= \left(4\rho r_D/B_X\right) \int_{r_L}^{r_U} \left(B_X g_{DX}(r) + D_X g_{MX}(r)\right) r^2 dr \\
&= \bar{n}_X^D(r_s) + \underbrace{\left(4\rho r_D D_X/B_X\right) \int_{r_L}^{r_U} g_{MX}(r) r^2 dr}_{CIP \text{ contribution}}
\end{aligned} \tag{11}$$

The *CIP* contribution to the “measured” water’s hydrogen coordination of the anion, over the true value $\bar{n}_X^D(r_s)$, can be further simplified by invoking the identities of the coefficients D_X and B_X , *i.e.*,

$$\begin{aligned}
\left(4\rho r_D D_X/B_X\right) \int_{r_L}^{r_U} g_{MX}(r) r^2 dr &= \left(4\rho r_M b_M/b_D\right) \int_{r_L}^{r_U} g_{MX}(r) r^2 dr \\
&= \bar{n}_X^M(r_s) (b_M/b_D)
\end{aligned} \tag{12}$$

where, by analogy to Eqn. (8), $\bar{n}_X^M(r_s)$ represents the cation coordination of the anion. Likewise, the cation counterpart to Eqn. (11) becomes,

$$\begin{aligned}
\bar{n}_M^D(\text{measured}) &= \left(4\pi\rho_D/B_M\right) \int_{r_L}^{r_U} \left(B_M g_{DM}(r) + D_M g_{MX}(r)\right) r^2 dr \\
&= \bar{n}_M^D(r_s) + \underbrace{\left(4\pi\rho_D D_M/B_M\right) \int_{r_L}^{r_U} g_{MX}(r) r^2 dr}_{CIP \text{ contribution}}
\end{aligned} \tag{13}$$

where after interpreting its meaning, the *CIP* contribution reduces to the simpler form,

$$\begin{aligned}
\left(4\rho r_D D_M/B_M\right) \int_{r_L}^{r_U} g_{MX}(r) r^2 dr &= \left(4\rho r_X b_X/b_D\right) \int_{r_L}^{r_U} g_{MX}(r) r^2 dr \\
&= \bar{n}_M^X(r_s) (b_X/b_D)
\end{aligned} \tag{14}$$

with $\bar{n}_M^X(r_s) = (c_X/c_M) \bar{n}_X^M(r_s)$ according to the solution composition.

In summary, in order to attain the true water’s hydrogen coordination of the anion $\bar{n}_X^D(r_s)$ (cation $\bar{n}_M^D(r_s)$) from the corresponding $\bar{n}_X^D(\text{measured})$ ($\bar{n}_M^D(\text{measured})$) we need also to estimate the extent of the contact anion-cation coordination, *i.e.*, either $\bar{n}_X^M(r_s)$ or $\bar{n}_M^X(r_s)$. This is a situation where the manipulation of the isotopic composition of the

aqueous environment becomes most powerful, in particular when $B_I = -C_I$ in Eqn. (7), *i.e.*, for $c_D/c_H = -b_H/b_D @ 0.561$ according to the scattering lengths given by Sears ⁵¹. This is the so-called null-water environment that, due to the absence of scattering by the water's hydrogens, in principle allows performing NDIS experiments able to isolate the contact anion-cation coordination contribution to either the $\bar{n}_X^D(\text{measured})$ or $\bar{n}_M^D(\text{measured})$. In fact, from Eqn. (7) and for the null-environment we have that,

$$\text{DG}_I^{nw, norm}(r) = [A_I g_{OI}(r) + D_I g_{CI}(r) + E_I g_{II}(r)] / S_I^{nw} \quad (15)$$

with $S_I^{nw} = A_I + D_I + E_I$, and after invoking the definition of $\bar{n}_X^M(r_s)$ we find that,

$$\begin{aligned} \bar{n}_X^M(r_s) &= 4\rho r_M \int_{r_L}^{r_U} g_{MX}(r) r^2 dr \\ &= \left(4\rho r_M S_M^{nw} / D_M \right) \int_{r_L}^{r_U} \text{DG}_M^{nw, norm}(r) r^2 dr \end{aligned} \quad (16)$$

where we have performed the first-order difference over the cation isotopes, $I = M$. Alternatively, if the first order difference is over the substituted anion, $I = X$, then,

$$\begin{aligned} \bar{n}_M^X(r_s) &= 4\rho r_X \int_{r_L}^{r_U} g_{MX}(r) r^2 dr \\ &= \left(4\rho r_X S_X^{nw} / D_X \right) \int_{r_L}^{r_U} \text{DG}_X^{nw, norm}(r) r^2 dr \end{aligned} \quad (17)$$

so that again $\bar{n}_M^X(r_s) = (c_X/c_M) \bar{n}_X^M(r_s)$, the quantities required to complete the calculation of $\bar{n}_X^D(r_s)$ and $\bar{n}_M^D(r_s)$ in Eqns. (12) and (13), respectively.

To illustrate these developments, in what follows we present a few representative case studies of aqueous electrolytes involving either simple anions (chlorides) or more complex oxyanions (nitrates) and discuss the results in the context of experimental data and *ab initio* results whenever available. In terms of notation we will be using the sub/super-script D interchangeable with H or H_w , *i.e.*, to identify the atomic species water hydrogen in microstructural/correlation/distribution functions. However note that

D and H will not be interchangeable when referring to the scattering length of the isotopic species.

b) Illustration of the methodology for model systems involving monoatomic anions

Case Study 1: Ion hydration in aqueous CaCl_2 solutions

Calcium chloride is an important component frequently found in geological formations and in aqueous solutions involved in industrial processes. For that reason, its aqueous solutions have been the focus of extensive thermodynamic⁷⁴⁻⁸⁰ and structural studies by neutron scattering^{73, 81-85}, X-ray diffraction (XRD)⁸⁶⁻⁹³, extended X-ray absorption fine structure (EXAFS)⁹³⁻⁹⁷, electric conductance⁹⁸⁻⁹⁹, and molecular simulation^{90, 100-106}.

Despite the wealth of experimental and simulation studies of aqueous CaCl_2 there is a persistent uncertainty about the nature of the $\text{Ca}^{+2} \cdots \text{Cl}^-$ pair formation, *i.e.*, *CIP* versus solvent-shared (*SShIP*) configurations, and how ionic strength and state conditions affect its occurrence. For example, after reviewing most experimental datasets for the thermodynamic properties of aqueous CaCl_2 , Rard and Clegg⁷⁷ concluded that the standard Pitzer equations¹⁰⁷ and their empirically extended expressions were able to describe the behavior of CaCl_2 over the entire molality range only when they included explicitly the $\text{CaCl}_{(aq)}^+$ pair formation. However, Pitzer *et al.*⁷⁸ later argued that Rard and Clegg's analysis did not settle the argument on the need to account for speciation, in that the impact of the inaccuracies in the association constant $K^o[\text{CaCl}^+]$ translates into the incorporation of higher virial terms. This scenario highlights the need for a more direct way to assess the presence of ion speciation, *e.g.*, in terms of its microstructural signature via scattering techniques.

On the one hand, early wide angle X-ray scattering (WAXS) experiments on concentrated CaCl_2 solutions by Yamaguchi *et al.*⁸⁹ and their re-interpretation of previous data from Caminiti *et al.*⁸⁸ suggested the presence of *CIP* configuration at $\sim 2.74\text{\AA}$ and a *SShIP* configuration at $\sim 4.8\text{\AA}$ (see brief discussion on this re-interpretation previous to their Table II). More recent experimental studies targeting

specifically this hydration phenomenon provided support to Yamaguchi *et al.*'s findings. For example, the Hungarian team led by Gabor Pálincás^{73, 92} performed XRD of aqueous CaCl_2 in the 1 - 6M range at ambient conditions and concluded that about 4M the solution forms *SShIP* at 4.85Å together with *CIP* at 2.7 - 2.75Å. The appearance of ion pairing was accompanied by a significant decrease of the water coordination of Ca^{+2} , $\bar{n}_{\text{Ca}}^O(r_s)$, with ionic strength, a behavior that follows closely the simulated microstructural results of Chialvo and Simonson⁵⁸ as illustrated in Figure 3. While XRD was unable to detect ion pairing below 4M, the ion-pair association above this concentration followed the trend found by simulation as illustrated in Figure 4.

On the other hand, Fulton *et al.*⁸³ used X-ray absorption fine structure (XAFS) spectroscopy to probe the effects of concentration on the first coordination of aqueous Ca^{2+} , and found no evidence for significant contact $\text{Ca}^{+2} \cdots \text{Cl}^-$ pairs according to the *Ca* K-edge EXAFS spectrum for a 6m CaCl_2 (Figure 4 in Ref. 83), yet the hexahydrate melt, 6.29m solution, exhibits an average of 1.2 Cl^- ions coordinating the Ca^{2+} ion. More recently, Pham and Fulton¹⁰⁸ revisited the subject and introduced a new method for their characterization through the simultaneous data refinement from both XAFS and from high-energy XRD spectroscopy, *i.e.*, x-ray absorption/diffraction simultaneous refinement (XADSR). This analysis for the 6m aqueous CaCl_2 identified ~ 0.26 contact $\text{Ca}^{+2} \cdots \text{Cl}^-$ pairs (*CIP*) separated by $\sim 2.71\text{\AA}$, as well as ~ 3.4 solvent-shared $\text{Ca}^{+2} \cdots \text{Cl}^-$ pairs (*SShIP*) separated by $\sim 4.98\text{\AA}$. These authors also highlighted the underlying challenges behind the XRD spectra for the 6m CaCl_2 resulting from the potential contact $\text{Ca}^{+2} \cdots \text{Cl}^-$ pair peak convolution with those associated with the *O - O* and *O - Cl* correlation peaks (Figure 1b of Ref. 108).

Interestingly, almost at the same time, two new publications revisited the analysis of the potential of mean force (*PMF*) for the $\text{Ca}^{+2} \cdots \text{Cl}^-$ pair according to either *ab initio* constrained dynamics simulations¹⁰⁵, or classical simulation of explicit polarizable models for both water and the ions¹⁰⁹, where the $\text{Ca}^{+2} \cdots \text{Cl}^-$ force fields were adjusted through high level electronic structure calculations targeting the optimized pair structure. While the two studies predict similar profiles for the *SShIP* region centered at $\sim 5.0\text{\AA}$, they show significantly different behavior for the *CIP* region around $\sim 2.75\text{\AA}$. In

particular, Dang *et al.*'s simulations indicate the absence of *CIP* at least for $m < 1.0$, while Timko *et al.*'s *ab initio* *PMF* profile highlights the formation of both *CIP* and *SShIP* configurations with similar strengths, where both outcomes contrast significantly with the predictions from classical simulations involving non-polarizable models (*e.g.*, those based on Dang-Smith force fields^{101, 110-111}).

Although these contrasting *PMF* profiles are not unusual predictions from non-polarizable models of aqueous CaCl_2 (*e.g.*, compare earlier results from Guardia *et al.*¹⁰⁰ against those from Dang-Smith force fields¹⁰¹), the recent results highlight the importance of polarization effects and their dependence with ionic strength. In fact, the recent Car-Parrinello molecular dynamics (CPMD) simulations of $2m$ aqueous CaCl_2 by Todorova *et al.*¹⁰⁴ suggest the presence of stable *CIP* and *SShIP* configurations (note however that these results correspond to $T = 320\text{K}$), where the average dipole moment of the coordinating water is significantly affected by the coordination strength of the Ca^{+2} .

The above state of affairs attests to difficulties encountered when interpreting the hydration behavior of ions according to tools that involve different sets of conjectures and approximations in linking the experimental output and the phenomenon/property under study. In what follows we illustrate the challenges encountered by the scattering practitioners when pursuing the extraction of microstructural information from NDIS on a $6.4m\text{CaCl}_2$ aqueous solution at ambient conditions involving either the $^{nat}\text{Ca}/^{44}\text{Ca}$ or the $^{nat}\text{Cl}/^{37}\text{Cl}$ first-order difference scheme for a particular isotopic form of water. For that purpose we performed molecular dynamics simulation of precisely defined models to extract the ten possible pair distribution functions, to determine the relevant first-order difference $\text{DG}_I^{\text{solv},\text{norm}}(r)$ as a means for the characterization of ion hydration behavior, and to identify the sources of uncertainties and the challenges behind the interpretation of scattering data in the presence of ion-pair formation/peak overlapping/convolution. For details on the simulations, please see the Supplementary Information document.

Peak convolution — the consequence of the interpenetration of anion and cation hydration shells resulting from the decrease of dielectric screening of their electrostatic interactions, in response to an increase of ionic strength, system temperature, or both —

is precisely the scenario where null-water environments becomes most useful. For example, according to Figures 5-6 for a 6.4m CaCl_2 in heavy- (top) and null-water (bottom), the contact $\text{Ca}^{+2} \cdots \text{Cl}^-$ pair contributions overlap significantly the $D_I - \text{Ca}$ contribution to $\text{DG}_{\text{Ca}}^{\text{hw},\text{norm}}(r)$ and becomes sandwiched between the $D_I - \text{Cl}$ and the compound $O_I - \text{Cl} \oplus D_{II} - \text{Cl}$ contributions to $\text{DG}_{\text{Cl}}^{\text{hw},\text{norm}}(r)$, where subscripts I and II denote first and second hydration shell, respectively. The integration of either the first peak of $\text{DG}_{\text{Cl}}^{\text{hw},\text{norm}}(r)$ to determine the coordination number $\bar{n}_{\text{Cl}}^D(\text{measured})$, Eqn. (10), or the second peak of $\text{DG}_{\text{Ca}}^{\text{hw},\text{norm}}(r)$ to assess the coordination number $\bar{n}_{\text{Ca}}^D(\text{measured})$, Eqn. (13), will account for some contributions from the CIP as discussed previously by Chialvo and Simonson⁵⁸ (*vide infra*). By switching to the null-water environment, at the same atomic compositions, we eliminate the $D_I - \text{Cl}$, $D_I - \text{Ca}$, and $D_{II} - \text{Cl}$ peaks, making possible the isolation of the CIP contributions in $\text{DG}_{\text{Cl}}^{\text{nw},\text{norm}}(r)$ and $\text{DG}_{\text{Ca}}^{\text{nw},\text{norm}}(r)$ and the determination of the corresponding $\bar{n}_{\text{Cl}}^{\text{Ca}}(r_s)$ (Eqn. (16)) and $\bar{n}_{\text{Ca}}^{\text{Cl}}(r_s)$ (Eqn. (17)).

Table 1: First water coordination of ions in 6.4m CaCl_2 heavy- and null-aqueous solutions according to the direct and the NDIS-based expressions

<i>pair interactions</i>	<i>direct integral</i> (r_s) ^(c)	<i>NDIS integral</i> (r_s) ^(d)
$O_w - \text{Ca}$	4.8(2.75 Å)	4.75(2.67 Å) ^(b)
$D - \text{Ca}$	10.7(3.5 Å)	12.7(2.17 Å, 3.5 Å) ^(a)
$O_w - \text{Cl}$	8.7(4.25 Å)	---
$D - \text{Cl}$	4.5(2.97 Å)	5.1(2.97 Å) ^(a)
$\text{Ca} - \text{Cl}$	1.9(4.0 Å)	1.8(2.97 Å) ^(b,e)

^(a) heavy-water; ^(b) null-water; ^(c) $\bar{n}_b^a(r_s) = 4\rho r_a \int_0^{r_s} g_{ab}(r) r^2 dr$ (Eqn. (8));

^(d) $\bar{n}_b^a(r_s) = \left(4\rho r_a S_b^{\text{solv}} / I_{ab}^{\text{solv}} \right) \int_0^{r_s} \text{DG}_b^{\text{solv},\text{norm}}(r) r^2 dr$ with $\text{solv} = (\text{hw}, \text{nw})$ and $I_{ab}^{\text{solv}} = \left(A_b^{\text{solv}} \text{ if } a = O_w; B_b^{\text{solv}} \text{ if } a = D \right)$

^(e) From Eqn. (16) $\bar{n}_{\text{Ca}}^{\text{Cl}}(r_s) = 1.8$, while from Eqn. (17) $\bar{n}_{\text{Cl}}^{\text{Ca}}(r_s) = 0.98$, i.e., $\bar{n}_{\text{Ca}}^{\text{Cl}}(r_s) \gg 2\bar{n}_{\text{Cl}}^{\text{Ca}}(r_s)$

As clearly illustrated in Table 1, where we collect all calculated ion coordination numbers, the comparison between heavy-water NDIS-based quantities and the actual values (Eqn. (8)) for precisely the same system microstructure indicates significant

differences. A simple inspection of the individual contributions to the corresponding first-order differences in Figures 5 and 6 reveals the presence of contributions from contact $Ca \cdots Cl$ pairs in $DG_{Cl}^{hw,norm}(r)$ and $DG_{Ca}^{hw,norm}(r)$, whose extent can be evaluated according to the previously derived expressions. In particular, note that the *CIP* coordination, $\bar{n}_{Ca}^{Cl}(r_s)$, contributions to $\bar{n}_{Ca}^D(r_s)$ and $\bar{n}_{Cl}^D(r_s)$ are modified by the prefactors $(b_{Cl}/b_D) @ 1.43$ and $(b_{Ca}/b_D) @ 0.70$, respectively. After correcting the NDIS-based coordination numbers for those *CIP* contributions, Eqns. (11)-(14), we attain the sought values that are now in agreement with the expected values from the direct integration of the corresponding radial distribution functions, Eqn. (8), as illustrated in Tables 2-3. For that purpose we have used the null-water NDIS-based $\bar{n}_{Ca}^{Cl}(r_s)$ and $\bar{n}_{Cl}^{Ca}(r_s)$ values according to Eqns. (16)-(17) (see also bottom of Figures 5 and 6).

Table 2: First coordination numbers of Cl^- in $6.4mCaCl_2$ aqueous solutions from integrals over $DG_{Cl}^{solv,norm}(r)$

$\bar{n}_{Cl}^D(Eqn. 8), r_s$	$\bar{n}_{Cl}^D(Eqn. 10), r_L, r_U$	$\bar{n}_{Cl}^D(Eqns. 11-12)^{(a)}$
4.5, 2.97 Å	5.1, 0.0 Å, 2.97 Å	4.4

^(a) $\bar{n}_{Cl}^D(r_s) = \bar{n}_{Cl}^D(measured) - \bar{n}_{Cl}^{Ca}(r_s)(b_{Ca}/b_D)$ where $\bar{n}_{Cl}^{Ca}(r_s) @ 0.98$ from Eqn. (16)

Table 3: First coordination numbers of Ca^{+2} in $6.4mCaCl_2$ aqueous solutions from integrals over $DG_{Ca}^{solv,norm}(r)$

$\bar{n}_{Ca}^D(Eqn. 8), r_s$	$\bar{n}_{Ca}^D(Eqn. 13), r_L, r_U$	$\bar{n}_{Ca}^D(Eqns. 13-14)^{(a)}$
10.7, 3.5 Å	12.7, 2.17 Å, 3.5 Å	10.1

^(a) $\bar{n}_{Ca}^D(r_s) = \bar{n}_{Ca}^D(measured) - \bar{n}_{Ca}^{Cl}(r_s)(b_{Cl}/b_D)$ where $\bar{n}_{Ca}^{Cl}(r_s) @ 1.8$ from Eqn. (17)

Case Study 2: Ion hydration in aqueous $NiCl_2$ solutions

From the beginning, $NiCl_2$ aqueous solutions have been the target of structural studies by neutron scattering^{67, 112-114} and x-ray diffraction¹¹⁵⁻¹¹⁶. Unfortunately, the collected scattering information provides a conflicting picture of the hydration behavior (*e.g.*, water coordination around ions) due to the potential occurrence of *CIP* and *SShip*

configurations, and calls for a re-examination of both the methods as well as the conclusions.

The proof for the presence of contact $Ni^{+2} \cdots Cl^-$ pairs in aqueous for $NiCl_2$ is as controversial as that for the $Ca^{+2} \cdots Cl^-$ counterpart (*vide supra*), i.e., on the one hand Raman spectroscopy of concentrated $NiCl_2$ aqueous solutions suggests the formation of $NiCl_4^{-2}$ complexes¹¹⁷, on the other hand neither EXAFS¹¹⁸ nor X-ray adsorption near-edge structure (XANES)¹¹⁹ experiments found evidence of contact $Ni^{+2} \cdots Cl^-$ pair configurations. Moreover, while earlier XRD evidence was rather inconclusive¹²⁰, later studies by the same team provided evidence of the presence of $Ni^{+2} \cdots Cl^-$ pair configurations by changing the Ni^{2+}/Cl^- ratio through the addition of $LiCl$ to the system. These authors concluded that the methodology underlying the processing of the XRD data might not always be able to detect a small number of contact anion-cation pairs¹²¹, a conclusion shared also by the work of Licheri *et al.*¹²². More recent XRD work by Waizumi *et al.*¹²³ confirms the formation of contact $Ni^{+2} \cdots Cl^-$ pair configurations, separated by $\approx 2.37 \text{ \AA}$, in aqueous $NiCl_2$ within the concentration range $4.57 \leq c(M) \leq 5.47$ (i.e., $5.05 \leq m \leq 6.15$ along the saturation line) resulting in a $0.4 \leq n_{NiCl} \leq 1.0$ range for the number of $Ni^{+2} \cdots Cl^-$ interactions according to their notation. Interestingly, nuclear magnetic resonance (NMR) studies by Weingärtner *et al.* on $1.0m NiCl_2$ aqueous solutions found a coordination range of $0.14 \leq \bar{n}_{Cl}^{Ni}(r_s) \leq 0.22$, depending on the “mechanism of ligand exchange”¹²⁴, that translates into $0.62 \leq \bar{n}_{Cl}^{Ni}(r_s) \leq 1.0$ at $4.4m$ according to their extrapolations. To be fair we should note that the accuracy of NMR results might be susceptible to significant uncertainties originating in the large number of correlated parameters required in the fitting of relaxation data for the extraction of the degree of $Ni^{+2} \cdots Cl^-$ association. Yet, as highlighted by Weingärtner *et al.*¹²⁴ “there is no obvious explanation why nuclear magnetic relaxation and neutron scattering results should be very different, since both of them observe processes in the first coordination sphere fairly directly” we agree with Weingärtner *et al.*’s concern, and below we provide an explanation for such a dichotomy. Additional support for the existence of contact $Ni^{+2} \cdots Cl^-$ pairs in $NiCl_2$ aqueous

solutions comes from recent far-infrared (FIR) spectroscopy studies of their hydration dynamics by Sharma *et al.*¹²⁵ who determined ion-pair extinction spectra for $0.5 \leq m \leq 4.3$ that confirmed the *CIP* presence.

In order to address the Weingärtner *et al.*¹²⁴ contention here we take advantage of the fact that both ions in this salt exhibit appropriate contrast for neutron scattering experiments, and as for the case of H/D , $^{nat}Ni/^{62}Ni$ also shows a change in the sign of the coherent scattering length with the possibility of a “null-nickel” environment by choosing the isotopic composition $c_{^{62}Ni}/c_{^{nat}Ni} = -\left(b_{^{nat}Ni}/b_{^{62}Ni}\right) @ 1.1839$. This behavior, in principle, affords the opportunity to invoke a “null-nickel” approach that will provide a direct route to $\bar{n}_{Cl}^D(r_s)$ from heavy-water NDIS experiments, avoiding the need for the *CIP* correction to the measured coordination in heavy water environments⁵³, Eqn. (11), whose evidence would be the correlation peak at $r_s \simeq 2.53\text{\AA}$ as highlighted in Figures 7-8. Under this null-nickel environment the relevant distribution function $DG_{Cl}^{hw,norm}(r)$ reduces to a simpler one, *i.e.*,

$$DG_{Cl,nNi}^{hw,norm}(r) = \left[A_{Cl} g_{OCl}(r) + B_{Cl} g_{DCl}(r) + E_{Cl} g_{ClCl}(r) \right] / S_{Cl,nNi}^{hw} \quad (18)$$

as illustrated in Figure 9, where the subscript nNi identifies the null-nickel condition and $S_{Cl,nNi}^{hw} = A_{Cl} + B_{Cl} + E_{Cl}$. Consequently, the coordination number $\bar{n}_{Cl}^D(r_s)$ follows from the counterpart of Eqn. (9) for a heavy-water null-cation environment, *i.e.*,

$$\bar{n}_{Cl}^D(r_s) = \left(4\rho r_D S_{Cl,nNi}^{hw} / B_{Cl} \right) \int_0^{r_s} DG_{Cl,nNi}^{hw,norm}(r) r^2 dr \quad (19)$$

as given in Table 4 for a $3.9m NiCl_2$ solution in comparison with the corresponding values obtained from the corrected heavy-water estimations. Note that the experimental values quoted in the available literature are $5.5 \pm 0.4 \leq \bar{n}_{Cl}^D(\text{Eqn. 10}) \leq 6.4 \pm 0.3$ ^{67, 69, 126}, but under the assumption $A_{Cl}, B_{Cl} \ll C_{Cl}, D_{Cl}, E_{Cl}$ ^{67, 69-70} that precludes the participation of, and correction from, any ion-pair formation. Moreover, after extracting an NDIS-based coordination number $\bar{n}_{Cl}^D(r_s)$ fully independent of the presence of *CIP* contributions by

means of a heavy-water null-cation environment, we can now check explicitly the subtle presence of, and contribution from, contact $Ni^{+2} \cdots Cl^-$ pairs.

Table 4: First coordination numbers of Cl^- in $3.9m NiCl_2$ aqueous solutions from integrals over $DG_{Cl}^{solv,norm}(r)$ and $DG_{Cl,nNi}^{hw,norm}(r)$

$\bar{n}_{Cl}^D(Eqn. 8), r_s$	$\bar{n}_{Cl}^D(Eqn. 10), r_L, r_U$	$\bar{n}_{Cl}^D(Eqns. 11-12)^{(a)}$	$\bar{n}_{Cl}^D(Eqn. 19), r_L, r_U$
3.75, 2.85 Å	5.4, 0.0 Å, 2.85 Å	3.70	3.75, 0.0 Å, 2.85 Å

^(a) $\bar{n}_{Cl}^D(r_s) = \bar{n}_{Cl}^D(measured) - \bar{n}_{Cl}^{Ni}(r_s)(b_{Ni}/b_D)$ where $\bar{n}_{Cl}^{Ni}(r_s) @ 1.1$ from Eqn. (16)

Table 5: First coordination numbers of Ni^{+2} in $3.9m NiCl_2$ aqueous solutions from integrals over $DG_{Ni}^{solv,norm}(r)$

$\bar{n}_{Ni}^D(Eqn. 8), r_s$	$\bar{n}_{Ni}^D(Eqn. 13), r_L, r_U$	$\bar{n}_{Ni}^D(Eqns. 13-14)^{(a)}$
7.05, 3.16 Å	10.2, 2.30 Å, 3.17 Å	7.04

^(a) $\bar{n}_{Ni}^D(r_s) = \bar{n}_{Ni}^D(measured) - \bar{n}_{Ni}^{Cl}(r_s)(b_{Cl}/b_D)$ where $\bar{n}_{Ni}^{Cl}(r_s) @ 2.2$ from Eqn. (17)

In fact, we can either invoke the null-water NDIS-based $\bar{n}_{Ni}^{Cl}(r_s)$ and $\bar{n}_{Cl}^{Ni}(r_s)$ values according to Eqns. (16)-(17) (see also bottom of Figures 7 and 8), or determined the $\bar{n}_{Cl}^D(measured)$, Eqn. (10), from which we can extract $\bar{n}_{Ni}^{Cl}(r_s)$ as follows,

$$\bar{n}_{Ni}^{Cl}(r_s) = \left[\bar{n}_{Cl}^D(measured, hw) - \bar{n}_{Cl}^D(hw, nNi) \right] (b_D/b_{Ni}) \quad (20)$$

where $\bar{n}_{Cl}^D(measured, hw)$ and $\bar{n}_{Cl}^D(hw, nNi)$ are given by Eqns. (10) and (19), respectively. In Tables 4-5 we illustrate these determinations, *i.e.*, where we display $\bar{n}_I^D(measured)$ for $I = (Cl^-, Ni^{+2})$ in the second columns, in comparison with the actual $\bar{n}_I^D(r_s)$ values in the first columns, and either the corresponding *CIP* corrected values in the third columns or the $\bar{n}_{Cl}^D(hw, nNi)$. This comparison clearly highlights the equivalence and self-consistency of the proposed NDIS-based approaches and emphasizes the fact that the validity of Eqns. (11)-(12) and (19) are obviously independent of the presence of ion pairing, *i.e.*, for $\bar{n}_{Ni}^{Cl}(r_s) = 0$, Eqns. (10)-(12) and (19) become identically the same as Eqn. (8).

Case Study 3: Ion hydration in aqueous LiCl solutions

Aqueous lithium chloride solutions have been the target of multiple NDIS over the entire range of solubility^{1, 70, 127-136}, XRD^{48, 137-142}, x-ray Compton scattering¹⁴³⁻¹⁴⁴, infrared spectroscopy (IR)¹⁴⁵, dielectric relaxation spectroscopy (DRS)¹⁴⁶⁻¹⁵⁰, Raman spectroscopy¹⁵¹⁻¹⁵², NMR¹⁵³, as well as *ab initio* and classical molecular simulation studies^{59, 154-166}. Yet, no clear picture of its hydration behavior emerges from those studies, a situation once again linked to the $\text{Li}\cdots\text{Cl}$ pair association and its effect on the interpretation of ion coordination. For instance, reverse Monte Carlo (RMC) analysis of early data from Narten *et al.* x-ray and neutron diffraction experiments¹³⁹ by Harsanyi and Pusztai¹⁶⁷ detected no $\text{Li}\cdots\text{Cl}$ formation even at the highest concentration of $18.5m$. However, the same approach applied to newer diffraction data provided clear evidence for the presence of contact ion pairs characterized as $\bar{n}_{\text{Li}}^{\text{Cl}}(\text{CIP})@0.2$ and $\bar{n}_{\text{Li}}^{\text{Cl}}(\text{CIP})@1.0$ for the $3.0m$ and $14.0m$ solution, respectively¹⁴². The newest RMC outcome becomes consistent with the NDIS studies by Winkel *et al.*¹³⁵ on a $1.38m$ system at ambient conditions that exhibited $0.2 \leq \bar{n}_{\text{Li}}^{\text{Cl}}(\text{CIP}) \leq 0.3$, and by Ichikawa *et al.*¹²⁹ on a $12.8m$ solution at higher temperature as illustrated in Figure 10. Additional support for the existence of contact $\text{Li}\cdots\text{Cl}$ pair formation comes from diverse experimental techniques including NMR and differential thermal analysis (DTA)¹⁵³, DRS¹⁴⁸, IR¹⁴⁵, x-ray Compton scattering¹⁴⁴, as well as *ab initio* molecular dynamics¹⁶³. However, neither DRS¹⁴⁹ nor Raman spectroscopy¹⁶⁸ is able to detect contact $\text{Li}\cdots\text{Cl}$ pairs for concentration below $1m$.

While the spectroscopic evidence for contact $\text{Li}\cdots\text{Cl}$ pair configurations is strong, the diffraction counterpart is not so, and the source of controversy usually hinges around the identification of the structural signature for the *CIP* configuration as we have already discussed it in the previous case studies. To illustrate the point according to proposed developments, and link the literature findings with our simulation results, here we revisit the analysis of the hydration behavior of aqueous LiCl solutions over a wide range of concentration, *i.e.*, $3 \leq m \leq 20$. As a representative example, in Figure 11 we display the first order differences $\text{DG}_{\text{Cl}}^{\text{solv-norm}}(r)$ for the $^{\text{nat}}\text{Cl}/^{37}\text{Cl}$ substitution in heavy- and null-aqueous environments, where we clearly identify and isolate the contact $\text{Li}\cdots\text{Cl}$

pair (*CIP*) configuration. Consequently, we are able to assess its contribution to the corresponding “measured” coordination numbers, Eqns. (11) and (13), and correct them according to the proposed methodology as illustrated in Figure 12 as a function of salt molality, as well as in Tables 6-7.

Table 6: First coordination numbers of Cl^- in 14*m LiCl* aqueous solutions from integrals over $DG_{Cl}^{solv,norm}(r)$ and $DG_{Cl,nLi}^{hw,norm}(r)$

$\bar{n}_{Cl}^D(Eqn. 8), r_s$	$\bar{n}_{Cl}^D(Eqn. 10), r_L, r_U$	$\bar{n}_{Cl}^D(Eqns. 11-12)^{(a)}$	$\bar{n}_{Cl}^D(Eqn. 21), r_L, r_U$
4.39, 2.96Å	3.86, 0.0Å, 2.88Å	4.28	4.3, 0.0Å, 2.96Å

^(a) $\bar{n}_{Cl}^D(r_s) = \bar{n}_{Cl}^D(measured) - \bar{n}_{Cl}^{Li}(r_s)(b_{Li}/b_D)$ where $\bar{n}_{Cl}^{Li}(r_s) @ 1.46$ from Eqn. (16)

Table 7: First coordination numbers of Li^+ in 14*m LiCl* aqueous solutions from integrals over $DG_{Li}^{solv,norm}(r)$

$\bar{n}_{Li}^D(Eqn. 8), r_s$	$n_{Li}^D(Eqn. 13), r_L, r_U$	$\bar{n}_{Li}^D(Eqns. 13-14)^{(a)}$
6.0, 3.05Å	8.1, 2.23Å, 3.03Å	6.0

^(a) $\bar{n}_{Li}^D(r_s) = \bar{n}_{Li}^D(measured) - \bar{n}_{Li}^{Cl}(r_s)(b_{Cl}/b_D)$ where $\bar{n}_{Li}^{Cl}(r_s) = \bar{n}_{Li}^{Cl}(r_s) @ 1.46$ from Eqn. (17)

The take home message from Figure 12 and Tables 6-7 is that while $\bar{n}_{Li}^O(r_s)$ can be determined from the integration of either the heavy water or the null water neutron-weighted radial distribution function without the interference of the potential occurrence of ion pairing, this is not the case for $\bar{n}_{Li}^D(r_s)$, as a consequence of the *CIP* contributions proportional to $\bar{n}_{Li}^{Cl}(r_s)$. The top of Figure 12 also highlights the fact that $\bar{n}_{Li}^O(r_s)$ exhibits a significant concentration dependence at ambient conditions, with a similar trend for $\bar{n}_{Li}^D(r_s)$ after the *CIP* correction. In contrast $\bar{n}_{Li}^D(measured)$, extracted from the heavy-water neutron-weighted distribution function, appears almost constant within the entire range of salt concentration. This behavior prompts us to note that if we did not sort the coordinating atoms around Li^+ according to their identities, *i.e.*, by just counting its nearest interactions sites, Li^+ would exhibit an ‘apparent’ first coordination number $\bar{n}_{Li}^{(Cl\oplus O)}(apparent) @ 4$ while $\bar{n}_{Li}^D(measured) @ 8$ and thus, satisfying the 2:1 (*H/O*)-ratio

for water that is oftentimes loosely used as an indicator of consistency in the extracted coordination results.

Given the challenging nature of the detection of *CIP* configurations, it would be convenient either to avoid altogether the need for its assessment, or to have an alternative approach to test the accuracy and consistency of the NDIS-based ion-water coordination numbers. This scenario makes the aqueous *LiCl* solutions somewhat special in two important ways: (a) both ions in the salt comprise appropriate contrast for neutron scattering experiments, and (b) as for the cases of $^{nat}Ni/^{62}Ni$ and *H/D* substitution, $^{nat}Li/^6Li$ also exhibits a change in the sign of the coherent scattering length so that we can also take advantage of the “null-lithium” environment by choosing the isotopic composition $c_{^6Li}/c_{^{nat}Li} = -\left(b_{^{nat}Li}/b_{^6Li}\right)@0.95$. This behavior, in principle, allows proposing a “null- lithium” approach⁵³ that will provide a direct route to $\bar{n}_{Cl}^D(r_s)$ from heavy-water NDIS experiments, and consequently, will avoid the need for the *CIP* correction, Eqn. (11) for heavy water environments, whose manifestation at $r_s \simeq 2.43\text{\AA}$ is illustrated in Figure 11.

As per the null-nickel case study, the relevant distribution function $DG_{Cl}^{hw,norm}(r)$ in the null-lithium environment reduces to the simpler form,

$$DG_{Cl,nLi}^{hw,norm}(r) = \left[A_{Cl} g_{OCl}(r) + B_{Cl} g_{DCl}(r) + E_{Cl} g_{ClCl}(r) \right] / S_{Cl,nLi}^{hw} \quad (21)$$

with $S_{Cl,nLi}^{hw} = A_{Cl} + B_{Cl} + E_{Cl}$ whose behavior for a 14*m LiCl* is illustrated in Figure 13. Consequently, the coordination number $\bar{n}_{Cl}^D(r_s)$ follows from the counterpart of Eqn. (9) for a null-cation environment, *i.e.*,

$$\bar{n}_{Cl}^D(r_s) = \left(4\rho r_D S_{Cl,nLi}^{hw} / B_{Cl} \right) \int_0^{r_s} DG_{Cl,nLi}^{hw,norm}(r) r^2 dr \quad (22)$$

as given in Table 6 in comparison with the corresponding values obtained from the corrected heavy-water estimations.

c) Illustration of the methodology for model systems involving hetero-atomic anions

Up to this point we have studied simple salts comprising monoatomic ions that have been the most frequently targeted by scattering experiments. However, there is another type of simple salts comprising hetero-atomic anions, such as oxyanions, resulting in ‘complexities’ that are more challenging to interpret experimentally. On the one hand, the major contribution to the scattering originates in the stronger water-cation interactions that overwhelm the rather weaker oxyanion-water interactions. On the other hand, the fact that the anion’s oxygen-water and water’s oxygen-water interactions are comparable, *i.e.*, exhibiting correlation peaks at similar distances, makes it difficult to discriminate anion’s oxygen-water from water’s oxygen-water interactions, consequently, to provide adequate information about the anion coordination.

Here we will take advantage of some very recent developments on $^{nat}O_N/^{18}O_N$ substitution¹⁶⁹⁻¹⁷⁰ that open to the possibility of sequential substitution of two different anion sites. This feature increases our chances for a fuller characterization of the hydration structure of oxyanions, and the potential occurrence of oxyanion-cation pairs as we will discuss below. While oxyanion hydration has been traditionally studied by x-ray and neutron diffraction, as well as ultra-violet/visible (UV/vis), NMR, and Raman spectroscopies, the spectroscopic tools might not be reliable enough for the study of ion pair association in aqueous electrolytes involving non-contact ion pair formation, *i.e.*, *SShIP* and solvent-separated (*SSIP*) configurations¹⁷¹.

Note that for the microstructure of a simple aqueous $M^{n+}[XO_n]^{n-}$ solution (with $X = N, S, Cl, P$) involving s isotopic scattering species, there are $s(s+1)/2$ independent radial distribution functions contributing to the neutron weighted distribution function, Eqn. (4), *i.e.*, between 10 and 15 for these oxyanions. For NDIS experiments involving $^gX/{}^lX$ and ${}^lM/{}^xM$ substitutions we will deal with 10 correlation functions, though if we also introduced the isotopic substitution $^{nat}O_X/^{18}O_X$ on the anion only (*i.e.*, not on the water), then we will have five additional correlation functions. Thus, the original Eqn. (7) for the first-order difference must be supplemented as follows,

$$\begin{aligned} \text{DG}_X^{\text{sol},\text{norm}}(r) = & \left[A_X g_{O_W X}(r) + B_X g_{DX}(r) + C_X g_{HX}(r) + \right. \\ & \left. D_X g_{MX}(r) + E_X g_{XX}(r) + F_X g_{O_X X}(r) \right] / S_X^{\text{sol}} \end{aligned} \quad (23)$$

and,

$$\begin{aligned} \text{DG}_O^{\text{sol},\text{norm}}(r) = & \left[A_O g_{O_W O_X}(r) + B_O g_{DO_X}(r) + C_O g_{HO_X}(r) + \right. \\ & \left. D_O g_{MO_X}(r) + E_O g_{O_X O_X}(r) + F_O g_{XO_X}(r) \right] / S_O^{\text{sol}} \end{aligned} \quad (24)$$

with $S_\ell^{\text{sol}} = A_\ell + B_\ell + C_\ell + D_\ell + E_\ell + F_\ell = -\text{DG}_\ell^{\text{sol}}(0)$.

In what follows we will invoke these expressions for the interpretation of the coordination behavior of oxyanions. Note that, in principle $g_{XO_X} = g_{O_X X}$ will contain intra-molecular correlations centered at the corresponding bond-length distance ℓ_{X-O_X} , *i.e.*, $\sim 1.27 \text{ \AA}$ for NO_3^- . Consequently, the experimental $\text{DG}_O^{\text{sol},\text{norm}}(r)$ and $\text{DG}_X^{\text{sol},\text{norm}}(r)$ will usually contain those intra-molecular correlations, while (by construction) the simulation counterparts will not. As discussed elsewhere⁶³, the intra-molecular contributions to the experimental $\text{DG}_O^{\text{sol},\text{norm}}(r)$ and $\text{DG}_X^{\text{sol},\text{norm}}(r)$ can be used to test the internal consistency of the NDIS rawdata.

Case Study 4: Ion hydration in aqueous LiNO_3 solutions

As an oxyanion, NO_3^- has been characterized as exhibiting mild interactions with water, *i.e.*, weakly hydrated as a result of its small charge and relatively large effective ionic that induce limited distortion of the hydrogen bonding of the surrounding water¹⁷²⁻¹⁷³. These features might have contributed to the large disparity in the reported water coordination of the nitrate anion from different experimental sources, including NMR¹⁷⁴⁻¹⁸⁰, IR¹⁸¹⁻¹⁸⁷, Raman^{173-174, 188-197}, XRD^{172-173, 190, 193, 195-204}, as well as NDIS²⁰⁵⁻²¹⁰, and point to unresolved concerns regarding the determination and interpretation of the hydration microstructure of nitrates in a variety of aqueous environments⁶³.

Some of those concerns point to the potential for ion-pair formation, depending on the cation's identity and the salt concentration. In fact, there is significant

experimental evidence for the occurrence of either contact or water-shared ion pairing in aqueous nitrate solutions involving a variety of cations^{180, 182, 192, 204, 211-215}. In particular, the Raman spectroscopic studies of Irish *et al.*²¹¹⁻²¹² provided strong evidence on the occurrence of *CIP* in NaNO_3 aqueous solutions for $m \geq 2.5$, and the presence of *SShip* in LiNO_3 aqueous solutions with $m > 4.6$. Moreover, the combined Raman spectroscopic and XRD analysis of Smirnov *et al.*²⁰² on $\text{Ca}(\text{NO}_3)_2$ aqueous solutions indicated that ~55% and 37% of the Ca^{+2} in 8.9*m* and 4.5*m* solutions, respectively, are directed bonded to the NO_3^- , *i.e.*, participating in *CIP* configurations.

Therefore, in addition to detecting the presence of ion pair formation, we must isolate their contribution for an adequate assessment of the coordinating nitrate environment, and identify the overlapping of several inter- and intra-atomic correlations within the radial distance, ($2.0 < r(\text{\AA}) < 4.4$), where we expect the occurrence of the $\text{NO}_3^- - \text{H}_2\text{O}$ correlations. Unless we provide ways to identify and deconvolute these contributions, they will obstruct both the XRD determination of the water orientation around the nitrate ion caused by the weak hydrogen scattering, and the interpretation of the coordinating environment from heavy-water NDIS involving $^{14}\text{N}/^{15}\text{N}$ substitution.

We have recently confronted some of those issues by proposing a novel approach for the accurate determination of the coordination behavior of the nitrate ion, based on the interplay between NDIS involving the double isotopic substitution on the nitrate group, *i.e.*, $^{14}\text{N}/^{15}\text{N}$ and $^{nat}\text{O}_N/^{18}\text{O}_N$ in heavy-water and null-water environments⁶³. The proposed approach hinges around two innovations: (i) the use of the nearly six-times larger scattering-length contrast between ^{18}O and ^{nat}O — $0.204 \pm 0.003 \text{ fm}^{169}$ — than the earlier tabulated value⁵¹, *i.e.*, making feasible NDIS experiments using $^{nat}\text{O}/^{18}\text{O}$ substitution¹⁷⁰ specially considering that 3-times larger concentration of scattering *O* - sites than *N* - sites, and (ii) the alternating use of heavy- and null-water as a means to extract coordination information for both the water-hydrogen (not achievable by XRD due to the extremely weak hydrogen scattering) and the water-oxygen around the nitrate sites which has been only possible from XRD experiments.

In what follows we analyze the behavior of the neutron-weighted pair correlation functions for the double $^{14}\text{N}/^{15}\text{N}$ and $^{nat}\text{O}_\text{N}/^{18}\text{O}_\text{N}$ substitutions in nitrate ion in heavy- and null-aqueous solutions, according to the simulated microstructure of 6.16mLiNO_3 and the coherent scattering lengths from the available literature as collected in Table 8.

To facilitate the interpretation of the corresponding first-order difference $\text{DG}_\text{N}^{\text{solv},\text{norm}}(r)$ and $\text{DG}_\text{O}^{\text{solv},\text{norm}}(r)$ for both types of solvents, we plot the individual contributions from each pair interactions in Figures 14-15, and collect the coefficients of the two sets of first-order differences in Tables 9-10 to highlight the contrasting magnitudes of these coefficients not only for the pair interactions, *i.e.*, $A_\ell, B_\ell \gg |D_\ell|, E_\ell, F_\ell$, but also the type of isotopic substitution, *i.e.*, $A_\text{N}, B_\text{N} \gg A_\text{O}, B_\text{O}$. These inequalities highlight the facts that (a) the two most relevant contributions to $\text{DG}_\ell^{\text{solv},\text{norm}}(r)$ come from the pair interactions between the ℓ - substituted species and the surrounding water, and (b) the change of coherent scattering length for the $^{nat}\text{O}_\text{N}/^{18}\text{O}_\text{N}$ substitution is significantly smaller than that for the $^{14}\text{N}/^{15}\text{N}$ substitution.

Table 8: Coherent neutron scattering lengths for aqueous LiNO_3

<i>Species</i>	$b_{\text{coh}}(fm)$	<i>Ref.</i>
^{14}N	9.37	51
^{15}N	6.44	51
^{nat}N	9.36	51
^2H	6.67	51
^{nat}O	5.805	51
^{18}O	6.009	169
^{nat}Li	-1.9	51
^6Li	2.0	51
^7Li	-2.22	51

As we have previously found for the case of $3.5m KNO_3$ ⁶³, $DG_N^{hw, norm}(r)$ exhibits two prominent peaks, in this case at slightly larger distances, *i.e.*, at $\sim 2.77 \text{ \AA}$ and $\sim 3.87 \text{ \AA}$ corresponding to the nearest $D \cdots N$ interactions, and the combination of contributions from the second nearest $D - N$, the $O_w - N$, and the negative contribution from the contact $Li \cdots N$ pair interactions. Moreover, the overlapping of $O_w - N$, $Li \cdots N$, and $D - N$ correlation peaks within $3.2 \leq r(\text{\AA}) \leq 4.7$, precludes the determination of the second $D \cdots N$ coordination by integration of the second peak of $DG_N^{hw, norm}(r)$.

Table 9: Coefficients of the first-order difference of weighted distributions for the $^{14}N/^{15}N$ substitution in $6.16m LiNO_3$ heavy- and null-aqueous solutions

<i>Coefficient</i> ^(a)	<i>heavy - water</i>	<i>null - water</i>
A_N	0.2620122	0.2620122
B_N	0.6021091	0.2163830
C_N	0.0	-0.2163830
D_N	-7.914160E-03	-7.914160E-03
E_N	3.292707E-02	3.292707E-02
F_N	7.253952E-02	7.253952E-02
S_N^{solv}	0.9616738	0.3595647

^(a) In fm^2 units

Table 10: Coefficients of the first-order difference of weighted distributions for the $^{nat}O_N/^{18}O_N$ substitution in $6.16m LiNO_3$ heavy- and null-aqueous solutions

<i>Coefficient</i> ^(a)	<i>heavy - water</i>	<i>null - water</i>
A_O	5.472748E-02	5.472748E-02
B_O	0.1257648	4.519672E-02
C_O	0.0	-4.519672E-02
D_O	-1.653060E-03	-1.653060E-03
E_O	1.541781E-02	1.541781E-02
F_O	8.143496E-03	8.143496E-03
S_O^{solv}	0.2024005	7.663573E-02

^(a) In fm^2 units

Note also that the first peak of $DG_N^{hw,norm}(r)$ in Figure 14 comprises mostly the contribution from the first peak of the corresponding $g_{DN}(r)$, yet there are two compensating (*i.e.*, one negative and the other positive) contributions from the $O_w - N$ and $Li \cdots N$. Thus, the conventional calculation of the first coordination number $\bar{n}_N^D(r_s)$ by integration of $DG_N^{hw,norm}(r)$ as usually done²⁰⁸, *i.e.*,

$$\bar{n}_N^D(r) = \left(4\rho r_D S_N^{hw} / B_N^{hw} \right) \int_{r_L}^{r_U} DG_N^{hw,norm}(r) r^2 dr \quad (25)$$

might result in a corrupted coordination number because the upper limit of integration $r_U \gg 3.16 \text{ \AA}$, corresponding to the location of the first minimum of $DG_N^{hw,norm}(r)$, is slightly smaller than the actual value of $r_s \gg 3.32 \text{ \AA}$ from the $g_{DN}(r)$. In fact, the direct determination of $\bar{n}_N^D(r_s)$ using Eqn. (8) indicates that the (true) first coordination number $\bar{n}_N^D(r_s = 3.32 \text{ \AA}) @ 7.0$ while the estimated value from Eqn. (25) is $\bar{n}_N^D(r_U = 3.16 \text{ \AA}) @ 6.3$. Note that we found slightly smaller values for the corresponding coordination numbers for the less concentrated $3.5m KNO_3$ aqueous solution studied previously, *i.e.*, $\bar{n}_N^D(r_s = 3.32 \text{ \AA}) @ 5.9$ and $\bar{n}_N^D(r_U = 3.17 \text{ \AA}) @ 5.2$, respectively. This comparison highlights a frequently overlooked fact that the equivalence between the true coordination, Eqn. (8), and the NDIS-related coordination, Eqn. (25), relies on the absence of any contribution from any other correlations in the $[r_L, r_U]$ radial interval.

For the null aqueous environment there is no contribution from hydrogen interactions to $DG_N^{nw,norm}(r)$, Figure 14 (bottom), whose first peak centered at $r \gg 3.72 \text{ \AA}$ comprises two main components, *i.e.*, a major contribution from $O_w \cdots N$ interactions that overlap with the contact $Li \cdots N$ pair configurations. As for the case of $\bar{n}_N^D(r_U)$ from $DG_N^{hw,norm}(r)$, Eqn. (25), other smaller contributions from the $N - N$ and $O_N - N$ pair correlation peaks affect the outcome of the conventional determination of the water coordination around the nitrogen site, *i.e.*,

$$\bar{n}_N^{O_w}(r_U) = \left(4\rho r_{O_w} S_N^{nw} / A_N^{nw} \right) \int_0^{r_U} DG_N^{nw,norm}(r) r^2 dr \quad (26)$$

as illustrated in table 11 where we collect the resulting water-oxygen coordination around the nitrogen site of the nitrate ion, $\bar{n}_N^{O_w}(r_U)$ according to the direct integration of the $g_{O_w N}(r)$, integral ^(c) below, and the NDIS-based estimate based on Eqn. (26).

In Figure 15 we display the corresponding $DG_O^{hw,norm}(r)$ and $DG_O^{nw,norm}(r)$ counterparts to Figure 14. Note that $DG_O^{hw,norm}(r)$ exhibits an almost completely decoupled first peak associated with the $D - O_N$ correlations centered at $r \gg 1.82\text{\AA}$ resembling the $D - O_w$ peak for pure water ²¹⁶, except for the small negative contribution from the contact $Li \cdots O_N$ pair, followed by a wider multi-peak from the overlapping of the second $D - O_N$ coordination and the two $O_w - O_N$ correlation peaks.

Table 11: First water coordination of the nitrate ion in 6.16m $LiNO_3$ heavy- and null-aqueous solutions according to the direct and the NDIS-based expressions

<i>pair interactions</i>	<i>direct integral(r_s)</i> ^(c)	<i>NDIS integral(r_U)</i> ^(d)
$O_w - N$	14.7(4.91 $\text{\AA}$)	17.9(4.98 $\text{\AA}$) ^(b)
$D - N$	7.0(3.32 $\text{\AA}$)	6.3(3.16 $\text{\AA}$) ^(a)
$O_w - O_N$	4.0(3.56 $\text{\AA}$)	3.8(3.48 $\text{\AA}$) ^(b)
$D - O_N$	2.4(2.53 $\text{\AA}$)	2.2(2.45 $\text{\AA}$) ^(a)
$Li - N$	0.5(3.64 $\text{\AA}$)	---
$Li - O_N$	0.19(2.61 $\text{\AA}$)	0.18(2.45 $\text{\AA}$) ^(b)

^(a) heavy-water; ^(b) null-water; ^(c) $\bar{n}_b^a(r_s) = 4\rho r_a \int_0^{r_s} g_{ab}(r) r^2 dr$;

^(d) $\bar{n}_b^a(r_U) = \left(4\rho r_a S_b^{solv} / I_{ab}^{solv} \right) \int_0^{r_U} DG_b^{solv,norm}(r) r^2 dr$ with $solv = (hw, nw)$ and $I_{ab}^{solv} = \left(A_b^{solv} \text{ if } a = O_w; B_b^{solv} \text{ if } a = D \right)$

If we ignore the small $Li \cdots O_N$ CIP contribution to the first peak of $DG_O^{hw,norm}(r)$, then its integral will provide an adequate estimate — by comparison against the corresponding integral ^(c) below — for the first coordination $\bar{n}_{O_N}^D(r_s)$ as clearly depicted in

Table 11. This number can then corrected for any $Li \cdots O_N$ contribution by taking advantage of the complete deconvolution of this peak in $DG_O^{nw,norm}(r)$, i.e.,

$$\bar{n}_{O_N}^{Li}(r_s) = \left(4\rho r_{Li} S_O^{nw} / D_O^{nw}\right) \int_0^{r_U} DG_O^{nw,norm}(r) r^2 dr \quad (27)$$

so that,

$$\begin{aligned} \bar{n}_{O_N}^D(measured) &= \left(4\rho r_D S_O^{hw} / B_O^{hw}\right) \int_0^{r_U} DG_O^{hw,norm}(r) r^2 dr \\ &= \left(4\rho r_D / B_O^{hw}\right) \int_0^{r_U} \left(B_O^{hw} g_{DO_N}(r) + D_O g_{LiO_N}(r)\right) r^2 dr \\ &= \bar{n}_{O_N}^D(r_s) + \underbrace{\left(4\rho r_D D_O / B_O^{hw}\right) \int_0^{r_U} g_{LiO_N}(r) r^2 dr}_{CIP\ contribution} \\ &= \bar{n}_{O_N}^D(r_s) + (b_{Li}/b_D) \bar{n}_{O_N}^{Li}(r_s) \end{aligned} \quad (28)$$

Table 12: First coordination numbers of NO_3^- in $6.16m LiNO_3$ aqueous solutions from integrals over $DG_O^{sol,norm}(r)$ and $DG_N^{sol,norm}(r)$

$\bar{n}_{O_N}^D(Eqn. 8), r_s$	$\bar{n}_{O_N}^D(Eqn. 28), r_U$	$\bar{n}_{O_N}^D(Eqns. 27-28)^{(a)}$
2.4(2.53 Å)	2.2(2.45 Å)	2.25

^(a) $\bar{n}_{O_N}^D(r_s) = \bar{n}_{O_N}^D(measured) - \bar{n}_{O_N}^{Li}(r_s)(b_{Li}/b_D)$ where $\bar{n}_{O_N}^{Li}(r_s) @ 0.18$ from Eqn. (27)

Moreover, note that the second peak of $DG_O^{nw,norm}(r)$ centered at $r \gg 4.75 \text{ Å}$, from a combination of the smaller solvent-shared $Li \cdots O_N$ pair and $N - O_N$ contributions, describes the corners of a deformed tetrahedral configuration locating the water-oxygens and the nitrate counterparts. Should this tetrahedral distribution between the nitrate-oxygens and water-oxygens exist, as suggested by Caminiti *et al.*¹⁷² (see their Figure 3) and Dagnall *et al.*¹⁹⁹, we would find each nitrate-oxygen coordinating 3 water-oxygens. According to Table 11, the current molecular models describe a tetra- rather than the tri-coordination suggested by these authors, yet, the nature of the cation (and its own hydration behavior) might play an important role on this outcome. In fact, our recent study of the hydration of NO_3^- in a $3.5m KNO_3$ aqueous solution under the same nitrate

potential model description resulted in a nitrate-oxygen coordinating 2 water-oxygens⁶³. Therefore, according to these results (*i.e.*, Table 5 of Ref. 63 and Table 11 of the present work) the frequently used assumption $\bar{n}_N^{O_w}(r_s^{O_wN}) @ 3\bar{n}_{O_N}^{O_w}(r_s^{O_wO_N})$ in the interpretation of XRD data^{199, 217-218} should not necessarily be taken for granted, given the fact that the radii of the coordination shells for these two types of interactions are significantly different (*i.e.*, $r_s^{O_wN} \neq r_s^{O_wO_N}$, see Table 11).

The hydration behavior of nitrates has been usually described in terms of the weakness of the water-oxyanion interactions whose immediate assumption is the absence of a second water-nitrate coordination in the modeling of XRD experiments²¹⁹. However, as Kameda *et al.*²⁰⁸ conjectured the location of the second-nearest $D - N$ correlation peak centered at $4.1 < r(\text{\AA}) < 4.2$, we found that the $g_{DN}(r)$ exhibits two prominent peaks centered at $r \approx 2.77 \text{\AA}$ and $r \approx 4.19 \text{\AA}$, respectively, as clearly illustrated in Figure 14 (similar behavior was observed in the study of $3.5mKNO_3$ solution, see Figure 1 in Ref. 63). Yet, the conventional heavy-water based NDIS experiment will not be able to provide information about the corresponding coordination due to the peak overlapping between $O_N - N$, $O_w - N$, and $D - N$. For that purpose we have recently proposed an NDIS route that in principle will provide an estimation of the second coordination number $n_D^N(r_L, r_U)$ as follows (see Appendix A of Ref. 63 for details),

$$\bar{n}_N^D(r_L, r_U) = \left(4\rho r_D / B_N^{hw}\right) \int_{r_L}^{r_U} \left[S_N^{hw} DG_N^{hw, norm}(r) - S_N^{nw} DG_N^{nw, norm}(r) \right] r^2 dr \quad (29)$$

where $DG_N^{hw, norm}(r)$ and $DG_N^{nw, norm}(r)$ are given in Figure 14, while r_L and r_U are the location of the minima defining the second peak of the $g_{DN}(r)$.

The resulting second coordination numbers $\bar{n}_N^D(r_L, r_U)$ from Eqn. (29) are compared in Table 13 against those from the direct integration of $g_{DN}(r)$, Eqn. (8), for two alternative r_U values to highlight the presence of a shoulder in the relevant integration domain of $DG_N^{hw, norm}(r)$. Note that these coordination numbers are comparable to those found for $3.5mKNO_3$ aqueous solutions.

Table 13: Second water-hydrogen coordination of the nitrate ion according to the direct and the derived NDIS-based expressions

<i>pair interactions</i>	<i>direct integral</i> (r_L, r_U) ^(a)	<i>NDIS integral</i> (r_L, r_U) ^(b)
$D - N$	22.4(3.32 Å, 4.90 Å)	23.3(3.16 Å, 4.90 Å)
$D - N$	34.5(3.32 Å, 5.54 Å)	35.4(3.16 Å, 5.54 Å)

$$^{(a)} \bar{n}_N^D(r_s) = 4\rho r_D \int_{r_L}^{r_U} g_{DN}(r) r^2 dr \text{ (Eqn. (8))}$$

$$^{(b)} \bar{n}_N^D(r_L, r_U) = \left(4\rho r_D / B_N^{hw} \right) \int_{r_L}^{r_U} \left[S_N^{hw} D G_N^{hw, norm}(r) - S_N^{nw} D G_N^{nw, norm}(r) \right] r^2 dr \text{ (Eqn. (29))}$$

III. LINK BETWEEN THE DEGREE OF $M^{v+} \cdots X^{v-}$ PAIR FORMATION AND THE $M^{v+} \cdots X^{v-}$ PAIR RADIAL DISTRIBUTION FUNCTION

The developments in the previous sections have given us the tools to not only detect the presence of *CIP* between an anion (or an oxyanion site) and the cation, but also to isolate it, and finally estimate a representative coordination number. The unresolved question at this point concerns the extent of such an ion-pair association — described as a degree of ion pairing and linked to an association constant, rather than as a coordination number $\bar{n}_X^M(r_L, r_U)$ — and discriminated by the type of configuration as *CIP*, *SShIP*, and *SSIP* according to the Eigen-Tamm classification²²⁰. Thus, in what follows we invoke a somewhat less-known rigorous formalism to make such a connection²²¹.

The degree of $M^{v+} \cdots X^{v-}$ pair association $\mathcal{A}_{-+}$ can be expressed in terms of the corresponding $M^{v+} \cdots X^{v-}$ pair distribution function $G_{-+}(r)$ (to be derived and not to be confused with the conventional $g_{-+}(r)$), as follows,

$$\mathcal{A}_{-+}(d_{-+}) = \int_0^{d_{-+}} G_{-+}(r) dr \quad (30)$$

under the condition that, in the thermodynamic limit, $\lim_{d_{-+} \rightarrow \infty} \mathcal{A}_{-+}(d_{-+}) = 1.0$, where d_{-+} typically denotes the largest distance where the $M^{v+} \cdots X^{v-}$ pairs are counted, such as the location of the first (for contact ion pairs) or second valley (for contact plus solvent-

shared ion pairs) of $g_{-+}(r)$. In Eqn. (30) $G_{-+}(r)Dr$ measures the probability of finding the X^{n-} species in the spherical shell of thickness Dr , separated by a distance r from the M^{n+} species, when neither X^{n-} nor M^{n+} participates in any additional pairing within the radial distance r . From a statistical mechanical point of view, $G_{-+}(r)$ can then be written as an integral equation,

$$G_{-+}(r) = 4\rho r_{+} g_{-+}(r) r^2 P_{-}(r) P_{+}(r) \quad (31)$$

where $P_{-}(r)$ ($P_{+}(r)$) denotes the probability that an X^{n-} (M^{n+}) separated by a distance r from an M^{n+} (X^{n-}) does not engage in an ion pair with any other ion of the opposite charge, *i.e.*,

$$P_{-}(r) = 1 - \int_0^r G_{-+}(s) ds \quad (32)$$

$$P_{+}(r) = 1 - \int_0^r G_{+-}(s) ds$$

Therefore, the entire formalism hinges around being able to determine $P_{-}(r)$ and $P_{+}(r)$, through the simultaneous solution of Eqns. (31)-(32) under the required conditions of system electroneutrality and species conservation. The explicit form of these conditions depends on the type of ionic formula; consequently, here we will illustrate the simplest case of symmetric salts (for the case of asymmetric ion-pairs please see the original manuscript), *i.e.*, where electroneutrality requires $g_{-+}(r) = g_{+-}(r)$, so that the species conservation reads,

$$r_{-} G_{-+}(r) = r_{+} G_{+-}(r) \quad (33)$$

From Eqns. (32)-(33), it becomes obvious that $P_{-}(r) = P_{+}(r)$ because $r_{+} = r_{-}$, and by solving the integral equation it follows that,

$$P_{-}(r) = \left[1 + 4\rho r_{+} \int_0^r g_{-+}(s) s^2 ds \right]^{-1} \quad (34)$$

Finally, from Eqn. (31)-(34),

$$G_{-+}(r) = 4\rho r_+ g_{-+}(r) r^2 / \left[1 + 4\rho r_+ \int_0^r g_{-+}(s) s^2 ds \right]^2 \quad (35)$$

which satisfies the required normalization, *i.e.*,

$$\int_0^\infty G_{-+}(r) dr = 1 - \left[1 + 4\rho r_+ \int_0^\infty g_{-+}(r) r^2 dr \right]^{-1} = 1 \quad (36)$$

Note that the corresponding association constant becomes,

$$K_a = \left(g_{-+} / r_+ g_{\square}^2 \right) \int_0^{d_{-+}} G_{-+}(r) dr / \left(1 - \int_0^{d_{-+}} G_{-+}(r) dr \right)^2 \quad (37)$$

where g_{-+} and $\gamma_{\mp}$ denote the ion-pair activity and free ion mean activity coefficients, respectively. As the electrolyte concentration approaches infinite dilution, $\lim_{r_+ \rightarrow 0} r_+^{-1} \int_0^r G_{-+}(s) ds = 4\rho \int_0^r g_{-+}(s) s^2 ds$ and consequently Eqn. (37) converges to the most frequently used expression²²²,

$$\begin{aligned} K_a &= 4\rho \int_0^{d_{-+}} g_{-+}^\infty(r) r^2 dr \\ &= \lim_{r_+ \rightarrow 0} \left[a_{-+} r_+^{-1} / (1 - a_{-+})^2 \right] \end{aligned} \quad (38)$$

since, $\lim_{r_+ \rightarrow 0} a_{-+} = 1$. While usually we can derive an expression to determine $G_{-+}(r)$ from the corresponding (theoretical or simulated) pair distribution function $g_{-+}(r)$ such as Eqn. (35), there could be cases for which there is no analytical solution to the corresponding integral equation²²³. For those cases we are still able to extract $G_{-+}(r)$ directly from simulation by accumulating the required histogram according to the principles underlying its definition, Eqn. (31), as illustrated and briefly explained in the Appendix of Ref. 223.

The important message here is twofold. On the one hand, for systems with finite electrolyte concentration we can use the anion-cation radial distribution function $g_{-+}(r)$ to assess the extent of the ion-pair association according to Eqn. (30). This equation, in

conjunction with Eqn. (35) for the case under consideration, tells us that the relevant quantity for the assessment of ion pair association is an integral over $G_{-+}(r)$ rather than $g_{-+}(r)$, a fact that is usually overlooked. On the other hand, for the system at limiting concentrations, the relevant distribution $g_{-+}^{\infty}(r)$ is not experimentally accessible, *i.e.*, it requires an indirect simulation route (via potential of mean force) for its evaluation as discussed elsewhere²²².

Moreover, while the second scenario provides a way to estimate the ion-pair association constant of electrolytes, something that has been achieved successfully for many relevant systems²²⁴⁻²²⁶, the first scenario might also be a viable approach to provide an estimate of the corresponding association constant, should we have a way to assess the corresponding activity coefficients, through the experimentally determined ion-pair coordination numbers $n_{-+}^+(r_s)$. In fact, after recalling its definition, Eqn. (8), Eqn. (37) reduces to,

$$K_a(r_{IP}) \equiv \gamma_{-+} n_{-+}^+(r_{IP}) / (\gamma_{+}^2 \rho_{+}) \quad (39)$$

Note that Eqn. (39) defines the association constant for the ion-pairs separated by a distance r_{IP} , therefore, it should not be confused with the full association constant involving all ion pair configurations, *i.e.*, $CIP + SShIP + SSIP$ ²²².

In Figures 16-19 we display the radial anion-cation radial distribution functions $g_{-+}(r)$, as well as their corresponding ion-pair radial distribution functions $G_{-+}(r)$ and degree of ion-pair association $\alpha_{-+}(r)$. Among other features, note the significant differences in magnitude between $G_{-+}(r)$ and $g_{-+}(r)$ functions, as well as the correspondence between their two main peaks associated with the *CIP* and *SShIP* configurations. All four systems exhibit significant $M^{v+} \cdots X^{v-}$ pair association characterized by $\alpha(CIP) @ 0.76, 0.77, 0.6$ and 0.36 with $\alpha(CIP + SShIP) \approx 0.8$ for the $CaCl_2$, $NiCl_2$, $LiCl$, and $LiNO_3$, respectively.

Based on the discussed ion-pair formalism we can also make a direct comparison between the simulated degree of ion-pair association and the corresponding values extracted from experimentally measured stability constants, more appropriately, their

mass action ‘concentration products’ $K_d^{\circ} \circ K_a(g_{\square}^2/g_{-+}) = a_{-+} r_{+}^{-1} / (1 - a_{-+})^2$. For that purpose we invoke data from the tabulation of Rard and Clegg⁷⁷ for the aqueous $CaCl_2$ systems, and plot the resulting $a_{CaCl^+}(CIP)$ as a function of the system ionic strength $I(m)$ in comparison with values from molecular simulation in Figure 20. The most obvious feature of this comparison is given by the underestimation of $a_{CaCl^+}(CIP)$ by the aqueous models, an outcome that fuels the need for more accurate determinations of association constants^{74, 77}, novel tools to interpret diffraction and spectroscopic experiments, as well as unambiguous modeling approaches.

It is also instructive for the understanding of the nitrate coordination, and its ion-pairing ability, to analyze the microstructural behavior of cation-nitrate interactions in terms of the $Li \cdots N$ spatial distribution function, $g_{LiN}(r, q, f)$ ²²⁷, where the polar angle q is defined between the principal z - axis (direction perpendicular to the plane defining the nitrate geometry) and the vector position $\mathbf{r}$ (relative to the molecule at the origin of the principal axes) of the neighboring Li^+ , while the azimuthal angle f describes the angle formed between the principal y - axis and the projection of $\mathbf{r}$ onto the $z = 0$ plane as depicted in Figure 21. For that purpose we invoke the methodology described in our previous work⁶³ where we analyzed the spatial distribution of water around the nitrate ion, though here we are only interested in the spatial distribution of Li^+ around the anion.

Note that the radial distribution function involved in the definition of the ion-pair distribution function, Eqn. (35), is simply an orientational averaged $g_{LiN}(r) \circ \langle g_{LiN}(r, q, f) \rangle_{q, f}$ counterpart as illustrated at the top of Figure 19, *i.e.*, it describes the mean interaction between the nitrate’s nitrogen core and the lithium ion represented by at least three nearest-neighbor shells whose peaks are located at $r \approx 3.12 \text{ \AA}$, $r \approx 5.1 \text{ \AA}$, and $r \approx 7.6 \text{ \AA}$, respectively. In contrast, the actual spatially distributed $Li \cdots N$ pair interactions exhibit a preference for specific orientations that translate into strong correlations several times larger than the corresponding angle-averaged quantities. This behavior becomes explicit by displaying spatial distribution function $g_{LiN}(r, q)_{f=const}$ at the representative azimuthal angles $f = 0^\circ$ and $f = 60^\circ$ as illustrated in Figure 21a. These azimuthal angles can be taken as reference orientations

since $\mathcal{F} = 0^\circ$ represents the distributions in the plane perpendicular to the nitrate's rigid geometry containing the $N - O_1$ bond (this distribution is identical to that defined by $\mathcal{F} = 120^\circ$ due to molecular symmetry), while $\mathcal{F} = 60^\circ$ defines the distribution on the plane bisecting the $\angle O_1 - N - O_2$ angle and containing the $N - O_3$ bond, *i.e.*, it describes a plane of symmetry.

In Figures 21b-c we illustrate how the main correlation peak in $g_{LiN}(r, \theta)_{\phi=0^\circ}$ evolves as we increase the azimuthal angle from $\mathcal{F} = 0^\circ$ to $\mathcal{F} = 60^\circ$, where the most significant changes occur at the base of the *CIP* peak and centered at $r \approx 3.12 \text{ \AA}$. The strong single peak $g_{LiN}(r > 2.1 \text{ \AA}, \theta \sim 120^\circ)_{\phi=0^\circ}$ centered at $\theta \sim 120^\circ$, transitions to a double peak centered at $\theta \sim 60^\circ$ and $\theta \sim 120^\circ$, while decreasing its strength as $\mathcal{F} \rightarrow 60^\circ$. Note however that these peaks reach their maximum strength at $r \sim 2.45 \text{ \AA}$ and $r \sim 3.0 \text{ \AA}$, *i.e.*, at distances smaller than the actual location of the *CIP* peak. Similarly, while the radial location of the *SSHIP* peak is about $r \approx 5.1 \text{ \AA}$ with $g_{LiN}(r \sim 5.1 \text{ \AA}) \sim 2$, the corresponding spatial distribution counterparts $g_{LiN}(r \sim 5.1 \text{ \AA}, 80^\circ < \theta < 100^\circ)_{\phi=0^\circ} \sim 1$ and $g_{LiN}(r \sim 5.1 \text{ \AA}, \theta \sim 90^\circ)_{\phi=60^\circ} \sim 3$. These features attest to the highly inhomogeneous nature of the aqueous environment around the nitrate as illustrated previously⁶³.

IV. FINAL REMARKS

We have provided a detailed account of the fundamentals underlying the microstructural analysis of aqueous electrolytes based on the NDIS approach toward the experimental determination of ion coordination numbers in systems involving both halides anions and oxyanions. In particular, we focused on the potential occurrence of ion-pair formation — a significant hydration phenomenon that is typically overlooked or assumed negligible — identified its microstructural signature in the neutron-weighted distribution functions, suggested new techniques for the direct estimation of the ion-pairing magnitude and the consequent correction of its effects on the experimentally measured coordination numbers, and proposed novel approaches to determine anion

coordination numbers free of ion-pairing contributions through the implementation of null-cation environments.

We illustrated these new developments aimed at the interpretation of four NDIS study cases via molecular simulation, as convenient dry runs for the actual scattering experiments, involving representative electrolyte solutions at ambient conditions comprising aqueous metal halides and nitrates. We should emphasize the challenging nature of the diffraction experiments, especially those involving null environments, and for that reason, we should highlight once more the power of molecular simulation tools that allows taking an atomistic “peek” at the local environment around the isotopically-labeled species before any experiment is attempted.

The formidable value of that interplay stems from the ability of molecular simulation to provide all pair distribution functions that describe the system microstructure, that allows us to “reconstruct” the NDIS output from the relevant distribution functions, and consequently, to test the accuracy of the “measured” NDIS-based coordination numbers against the “direct” counting (true values) from the simulated microstructure. In this context, the novel tools we have recently introduced offer versatile ways (a) to identify the individual partial contributions to the total neutron weighted distribution function (peak size and radial location), (b) to isolate the contributions of ion pair configurations, (c) to “dig up” the hydration behavior of the oxygen-site in oxyanions, and consequently, to assess the actual water coordination around them.

The reader might be rightfully concerned about the realism of the interaction potentials used in the study and how that could affect the outcome of the present analysis. While fixed-charge (*i.e.*, non-polarizable) models have been rather successful in describing the behavior of water and aqueous electrolytes in bulk and interfaces systems, and the models used in this work have shown adequacy to describe the systems of interest, we must also recognize that non-polarizable models are obviously not able to capture some subtleties underlying the inhomogeneous nature of the polarization phenomena in aqueous environments as attested by our ongoing effort in this matter²²⁸⁻²³⁰. Yet, we should also note that, because the molecular simulation in this study provides all the radial distribution functions that fully characterize the system microstructure, we

can also “reconstruct” the NDIS output from the relevant distribution functions; consequently, we can test the accuracy of the “measured” NDIS-based coordination numbers (*e.g.*, Eqns. (12) and (14)) against the “direct” counting (*i.e.*, Eqn. (8)) from the simulated microstructure. In this sense, the validity of our NDIS-simulation interplay analysis becomes independent of the force field inaccuracies.

In summary, we have offered our assessment on the current state of affairs regarding the understanding of hydration behavior in aqueous electrolytes, and discussed ways to pursue a fruitful interplay between fundamentals, molecular simulation, and experiment. In our view the main challenge now is to confront the difficulties associated with these NDIS experiments and translate the proposed novel schemes into versatile tools for the accurate characterization of ion hydration, a task that is currently being pursued by our research group.

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FIGURE CAPTIONS

Figure 1: Radial profile of $\Delta G_M^{solv}(r) \equiv G_{Ni}(r)$ in our notation for a heavy water $NiCl_2$ solution at ambient conditions taken from Ref. 65 with permission of the Royal Society

Figure 2: Radial profile of $\Delta G_X^{solv}(r) \equiv G_{Cl}(r)$ in our notation for a heavy water $LiCl$ solution at ambient conditions taken from Ref. 65 with permission of the Royal Society

Figure 3: Comparison between molecular-based simulation results ⁵⁸ and XRD experiment data ⁹² for the concentration dependence of the Ca^{+2} – coordination, $\bar{n}_{Ca}^O(r_s)$

Figure 4: Comparison between molecular-based simulation results ⁵⁸, XRD experiment data ⁹², and EXAFS-XANES data from Fulton *et al.* ⁸³ for the concentration dependence of the $Cl^- \cdots Ca^{+2}$ – coordination, $\bar{n}_{Ca}^{Cl}(r_s)$

Figure 5: Normalized first-order difference of neutron weighted distribution functions for the $6.4mCaCl_2$ in heavy- and null-water solution at ambient conditions under $^{nat}Ca/^{44}Ca$ substitution.

Figure 6: Normalized first-order difference of neutron weighted distribution functions for the $6.4mCaCl_2$ in heavy- and null-water solution at ambient conditions under $^{nat}Cl/^{37}Cl$ substitution.

Figure 7: Normalized first-order difference of neutron weighted distribution functions for the $3.94mNiCl_2$ in heavy- and null-water solution at ambient conditions: under $^{nat}Ni/^{62}Ni$ substitution.

Figure 8: Normalized first-order difference of neutron weighted distribution functions for the $3.94m\text{NiCl}_2$ in heavy- and null-water solution at ambient conditions under $^{nat}\text{Cl}/^{37}\text{Cl}$ substitution.

Figure 9: Normalized first-order difference of neutron weighted distribution functions for the $3.94m\text{NiCl}_2$ heavy-water solution at ambient conditions under “null-nickel” environment and $^{nat}\text{Cl}/^{37}\text{Cl}$ substitution.

Figure 10: Normalized first-order difference of neutron weighted distribution functions for the $14m\text{LiCl}$ in heavy- and null-water solutions at ambient conditions under $^{nat}\text{Cl}/^{37}\text{Cl}$ substitution.

Figure 11: Concentration dependence of the coordination numbers of aqueous LiCl solutions according to conventional integration of the neutron-weighted distribution functions, Eqn. (9), their *CIP* corrected (“corr”) counterparts, and the corresponding degree of *CIP* association.

Figure 12: Concentration dependence of the contact $\text{Li}\cdots\text{Cl}$ coordination $\bar{n}_{\text{Cl}}^{\text{Li}}(\text{CIP})$ and the corresponding degree of pair association $\alpha_{\text{LiCl}}(\text{CIP})$ in aqueous LiCl solutions from molecular simulation and a variety of experimental approaches.

Figure 13: Normalized first-order difference of neutron weighted distribution functions for the $14m\text{LiCl}$ heavy-water solution at ambient conditions under “null-lithium” environment and $^{nat}\text{Cl}/^{37}\text{Cl}$ substitution.

Figure 14: Normalized first-order difference of neutron weighted distribution functions for the $6.16m\text{LiNO}_3$ in heavy- and null-water solution at ambient conditions under $^{14}\text{N}/^{15}\text{N}$ substitution.

Figure 15: Normalized first-order difference of neutron weighted distribution functions for the $6.16m LiNO_3$ in heavy- and null-water solution at ambient conditions under $^{nat}O/^{18}O$ substitution.

Figure 16: Radial pair distribution function $g_{-+}(r)$, as well as their corresponding ion-pair radial distribution functions $G_{-+}(r)$ and degree of ion-pair association $\alpha_{-+}(r)$ for the $6.4m CaCl_2$ aqueous solution at ambient conditions.

Figure 17: Radial pair distribution function $g_{-+}(r)$, as well as their corresponding ion-pair radial distribution functions $G_{-+}(r)$ and degree of ion-pair association $\alpha_{-+}(r)$ for the $3.94m NiCl_2$ aqueous solution at ambient conditions.

Figure 18: Radial pair distribution function $g_{-+}(r)$, as well as their corresponding ion-pair radial distribution functions $G_{-+}(r)$ and degree of ion-pair association $\alpha_{-+}(r)$ for the $14m LiCl$ aqueous solution at ambient conditions.

Figure 19: Radial pair distribution function $g_{-+}(r)$, as well as their corresponding ion-pair radial distribution functions $G_{-+}(r)$ and degree of ion-pair association $\alpha_{-+}(r)$ for the $6.16m LiNO_3$ aqueous solution at ambient conditions.

Figure 20: Ionic strength dependence of the estimated degree of ion-pair association $\alpha_{CaCl^+}(CIP)$ from the corresponding experimentally measured ‘concentration products’ in comparison with microstructure-based values from molecular simulation of model $CaCl_2$ aqueous solutions.

Figure 21: Spatial pair distribution functions $g_{LiN}(r, \theta)_{\phi=const}$ for the $6.16m LiNO_3$ aqueous solution at ambient conditions: top at $\phi = 0^\circ$ and bottom at $\phi = 60^\circ$ according to the set of axes described on the right.

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