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Neutron Scattering Studies of the Hydration Structure of Li^+

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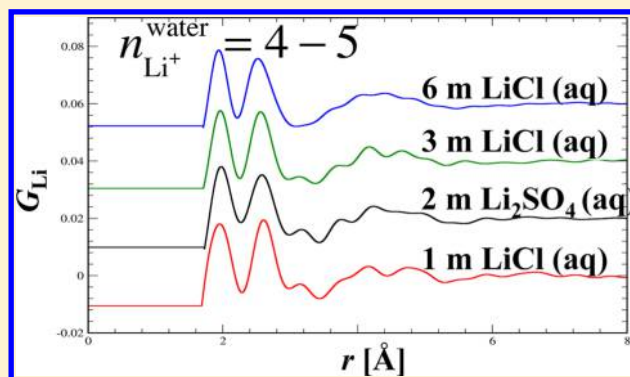
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ABSTRACT: New results derived from the experimental method of neutron diffraction and isotopic substitution (NDIS) are presented for the hydration structure of the lithium cation (Li^+) in aqueous solutions of lithium chloride in heavy water (D_2O) at concentrations of 6, 3, and 1 m and at 1.5 m lithium sulfate. By introducing new and more-accurate data reduction procedures than in our earlier studies (I. Howell and G. W. Neilson, *J. Phys: Condens. Matter*, **1996**, 8, 4455–4463), we find, in the first hydration shell of Li^+ , $\sim 4.3(2)$ water molecules at 6 m, $4.9(3)$ at 3 m, $4.8(3)$ at 1 m in the LiCl solutions, and $5.0(3)$ water molecules in the case of Li_2SO_4 solution. The general form of the first hydration shell is similar in all four solutions, with the correlations for $\text{Li}-\text{O}$ and $\text{Li}-\text{D}$ sited at $1.96(0.02)$ Å and $2.58(0.02)$ Å, respectively. The results resemble those presented in 1996, in terms of ion–water distances and local coordination, but the hydration number is significantly lower for the case at 1 m than the $6.5(1.0)$ given at that time. Thus, experimental and theoretical results now agree that lithium is hydrated by a small number of water molecules (4–5) in the nearest coordination shell.



■ INTRODUCTION

For several decades, we have been interested in determining the hydration structure of Li^+ ,^{1–4} not least because of its importance in the technological development of batteries and its use in medicine to treat certain illnesses. As the primary ion in the alkali series, Li^+ is also of deep theoretical interest, thus motivating *ab initio* simulations to probe hydration structure.^{5,6} In previous papers, we presented results derived from the method of neutron diffraction and isotopic substitution for lithium chloride salts at several concentrations.^{1–4} We showed that the Li^+ cation is relatively strongly hydrated with a characteristic hydration shell that could accommodate more than 6 water molecules at the lowest concentration of 1 m at which we worked.³ Because the $\text{Li}-\text{O}$ and $\text{Li}-\text{H}$ distances could be ascertained with a high degree of accuracy, those geometric results along with ion hydration free energies and vibrational spectra provided validation points for *ab initio* theoretical studies.

Ab initio approaches are appropriate for probing solution structure, because they do not rely on empirical parametrization of particle interactions. Consensus emerged in the theoretical community that 4 water molecules preferentially coordinate Li^+ in infinitely dilute water under standard conditions.⁷ This conclusion was based on a series of *ab initio* computations, including *ab initio* molecular dynamics (AIMD),^{5,6,8} coupled *ab initio* and classical molecular dynamics,^{9–11} coupled *ab initio* static calculations with dielectric continuum solution models,^{5,8,12} and static *ab initio* studies of microhydration.^{13–16}

In one theoretical test of 6-fold coordination of Li^+ versus 4-fold coordination of Li^+ , a hexa-coordinated Li^+ ion in liquid water relaxed to tetra-coordination within the first 112 fs of

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AIMD simulation,⁵ with chemical shielding,¹⁶ hydration geometry,⁷ and hydration free energy^{17,18} consistent with experiments. In another test, water droplets with hexa-coordinated Li⁺ were found to be inconsistent with solution structure and vibrational spectra, whereas tetra-coordinated Li⁺ species were consistent.¹⁵ Given these discrepancies, the theoretical results motivated us to carry out new experiments to revisit the problem of Li⁺ solution structure undertaken in ref 3.

Data analysis methods of neutron scattering have improved dramatically over the past decade. These advanced techniques are of particular importance to Li neutron diffraction and isotopic substitution (NDIS) measurements, because the correction factors that arise between the highly absorbing ⁶Li isotope and the low-absorption ⁷Li are very different. For other isotopes, NDIS measurements result in a reduction of the overall systematic error because the data correction errors from each isotopic sample cancel. In the case of Li, the mismatch between the ⁶Li and ⁷Li samples, in terms of the strong geometric effect due to the attenuation of the incident beam and marked difference in the multiple scattering correction, result in a large systematic error in the NDIS difference function. This error is further increased when coupled with the inelastic scattering of water. Therefore, the systematic error that manifests from the traditional data reduction methods becomes even more significant at lower concentrations.

These challenges prompted us to advance our neutron correction procedures to provide one of the first full Monte Carlo neutron transport simulations for the data correction. It is also noteworthy that commensurate improvements in neutron instrumentation, such as that on the D4C diffractometer at Institut Laue–Langevin (ILL) in Grenoble, France, have provided data of much greater statistical accuracy than in our earlier experiments on ionic solutions.

The Neutron Isotopic Difference Method. The technique of neutron diffraction and isotopic substitution (NDIS) has already been well-established¹⁹ as the most direct method for the determination of hydration structure around ions in aqueous solution as the information sought can be directly related to the experimental data. Recall that the structure factor of a solution is written as

$$F(Q) = \sum_{\alpha} \sum_{\beta} c_{\alpha} c_{\beta} \bar{b}_{\alpha} \bar{b}_{\beta} (S_{\alpha\beta}(Q) - 1) \quad (1)$$

where c_{α} is the atomic concentration of species α , and \bar{b}_{α} is its corresponding mean coherent neutron scattering length, and $\hbar Q$ is the momentum transfer in the scattering process. $S_{\alpha\beta}(Q)$ is the partial structure factor for atoms α and β and is related, via Fourier transformation, to the corresponding radial pair distribution function, $g_{\alpha\beta}(r)$:

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

where ρ is the atomic number density of the solution and has a value typically of $\sim 0.1 \text{ \AA}^{-3}$. Equation 1 can be written explicitly for solutions of salts (M^+X^-) in heavy water (D_2O) as

$$\begin{aligned} F(Q) = & c_O^2 \bar{b}_O^2 (S_{OO}(Q) - 1) + c_D^2 \bar{b}_D^2 (S_{DD}(Q) - 1) \\ & + 2c_D c_O \bar{b}_D \bar{b}_O (S_{DO}(Q) - 1) + 2c_D c_M \bar{b}_D \bar{b}_M (S_{DM}(Q) - 1) \\ & + 2c_D c_X \bar{b}_D \bar{b}_X (S_{DX}(Q) - 1) + 2c_O c_M \bar{b}_O \bar{b}_M (S_{OM}(Q) - 1) \\ & + 2c_O c_X \bar{b}_O \bar{b}_X (S_{OX}(Q) - 1) + c_M^2 \bar{b}_M^2 (S_{MM}(Q) - 1) \\ & + c_X^2 \bar{b}_X^2 (S_{XX}(Q) - 1) + 2c_M c_X \bar{b}_M \bar{b}_X (S_{MX}(Q) - 1) \end{aligned} \quad (3)$$

The first-order difference method relies on the fact that if one atom in the solution is replaced by its isotope in a second identical solution, there is no difference in the structures of the two solutions. Consequently, a difference between the neutron scattering structure factors ($F_1(Q)$ and $F_2(Q)$) of two solutions will give a function $\Delta_M(Q)$ that contains a linear sum of the partial structure factors $S_{M\beta}(Q)$ associated with the substituted ion. Specifically, for an aqueous electrolyte solution of lithium salt in heavy water (D_2O), which is usually used in preference to water itself because of the large incoherent scattering due to the protons, we can write

$$\Delta_{Li}(Q) = AS_{LiO}(Q) + BS_{LiD}(Q) + CS_{LiX}(Q) + DS_{LiLi}(Q) + E \quad (4)$$

where $A = 2c_{Li}c_O\bar{b}_O\Delta\bar{b}_{Li}$, $B = 2c_{Li}c_D\bar{b}_D\Delta\bar{b}_{Li}$, $C = 2c_{Li}c_X\bar{b}_X\Delta\bar{b}_{Li}$, $D = c_{Li}^2(\bar{b}_{Li}^2 - \bar{b}_{Li'}^2)$, $E = -(A + B + C + D)$, and $\Delta_{Li} = \bar{b}_{Li} - \bar{b}_{Li'}$, where \bar{b}_{Li} and $\bar{b}_{Li'}$ are the scattering lengths of Li⁺ in the two solutions.

Because the coefficients of the partial structure factors are not dependent on Q (in contrast to the situation for X-rays), eq 4 can be Fourier-transformed directly to give the structural information required

$$G_{Li}(r) = Ag_{LiO}(r) + Bg_{LiD}(r) + Cg_{LiX}(r) + Dg_{LiLi}(r) + E \quad (5)$$

The analysis of $G_{Li}(r)$ can then be undertaken to describe the pairwise structure around the lithium cation. Information concerning ion–oxygen, ion–deuterium distances and hydration numbers can be calculated directly. For example, the coordination for oxygen atoms around the Li⁺ cation is given by integration over the Li–O correlation and has the form

$$n_{Li}^O = \frac{4\pi}{\rho} \int_{r_1}^{r_2} r^2 g_{LiO}(r) dr \quad (6)$$

EXPERIMENTAL SECTION

Sample Preparation. Similar procedures were used to prepare all solutions. Here, only the preparation of the 6 m LiCl solutions is described in detail. Note that 1 m = 1 mole of solute/1.105 kg D_2O . Solutions of both naturally abundant lithium and the ⁶Li isotope (^{nat}LiOH and ⁶LiOH) were prepared by dissolution of the metal in water (Sigma–Aldrich, 95 at. % ⁶Li and Sigma–Aldrich, 99% for ^{nat}Li $\approx 230 \text{ mg}$ in 5 mL, $\sim 6 \text{ m}$ LiOH). Aliquots (250 μL) from each of these solutions were then calibrated by titration against a 0.962 m HCl standard. The correct amount of each of these LiOH solutions was then taken ($\sim 2 \text{ mL}$) and titrated exactly versus the same HCl standard solution in a flask of known weight. The water was then removed using a rotary evaporator. D_2O was added and the LiCl dissolved prior to the water being removed using a rotary evaporator. This process was repeated three more times to remove any residual ¹H before the correct amount of D_2O was added to effect the correct concentration. This process was used for all of the LiCl solutions, while a similar process (but using H_2SO_4 instead of HCl) was used for the preparation of the Li_2SO_4 solutions. Each sample was allowed to equilibrate for 1 h in a sealed vial prior to being transferred to the Ti/Zr null scattering container.

The isotopic purities for the 1 and 3 m LiCl, and 1.5 m Li_2SO_4 solutions, were 95 at. % ⁶Li and 100% ⁷Li, respectively. For the 6 m solutions, the isotopic enrichments were 95 at. % ⁶Li and natural abundance Li (91% ⁷Li).

Data Collection and Analysis. Neutron diffraction data were collected on the D4C diffractometer at the ILL in Grenoble,

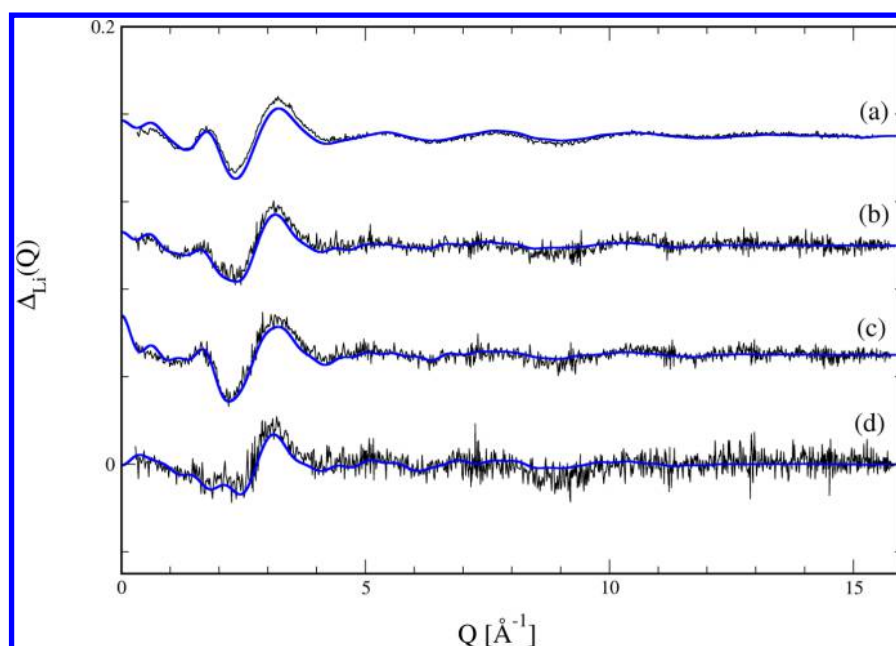


Figure 1. $\Delta_{\text{Li}}(Q)$ (presented in units of barns str^{-1}) for the heavy water solutions: (a) 6 m LiCl shifted up by 0.01 barns str^{-1} , (b) 3 m LiCl shifted up by 0.1 barns str^{-1} , (c) 1.5 m Li_2SO_4 shifted up by 0.05 barns str^{-1} , and (d) 1 m LiCl. The lines through the data are the “back” Fourier transforms of the results shown in Figure 2.

France. The instrument is situated at the hot source of the ILL. We used neutrons of wavelength $\lambda = 0.7 \text{ \AA}$ for all the experiments. The instrument comprises 9 multidetectors, each composed of 64 detector elements, and is swept over a range of Q , where $Q = 4\pi/\lambda \sin(\theta)$ and 2θ is the scattering angle. Normalization of the data in terms of barns str^{-1} is achieved relative to the scattering from a vanadium standard rod. [Note that 1 barn = 10^{-28} m^2 ; str represents steradians or degrees of solid angle.] The relative efficiencies of detector elements is achieved with reference to vanadium, which is an element whose scattering properties are well understood.

Although the data reduction procedures are generally straightforward and involve corrections for multiple scattering, absorption processes in the sample and the container, and for inelastic or Placzek effects, there are three aspects of the present work that required particular attention. The first two of these involved the samples themselves and the third concerned the instrument configuration, which affected the resolution. For the case of lithium, isotopic substitution of the natural sample, which is predominantly ^7Li , by the highly absorbing ^6Li means that special care must be taken when correcting for absorption. Moreover, since both isotopes are only slightly more massive than a neutron, differing inelastic effects between the solutions were also taken into account. The third consideration we addressed concerned the collimation and positioning of the sample container relative to the 9 multidetector banks, each with 64 elements of the D4C instrument. A new suite of computer programs was developed²⁰ to provide a more accurate method of correcting the experimental data. This new procedure has been facilitated by the thousand-fold increase in processing and order-of-magnitude increases in computer memory since the earlier data were taken in the late 1980s. By using Monte Carlo methods, we have been able to carry out a fully self-consistent data correction procedure that improves upon the previous approximation methods of Paalmann and Pings,²¹ Blech and Averbach,²² Placzek,²³ and, independently, Powles²⁴ to account for the absorption and multiple scattering

of the sample and its container, and inelastic scattering, respectively.

The specific component to the correction of the data from the Monte Carlo procedure of both the ^6Li and ^7Li samples is reported in the Appendix, where we show the difference between the standard correction methods and the complete Monte Carlo analysis that we have performed here.

While writing this paper, it was noted that Dawidowski and colleagues had analyzed water data obtained on the D4 diffractometer. Their result is now published in the open literature.²⁵ The difference between their work and ours is in the form of the scattering law model used to represent water in the Monte Carlo simulation. In our case, we used the model produced at the Los Alamos Experimental Data Facility (ENDF, Los Alamos, New Mexico USA).²⁰

RESULTS AND DISCUSSION

The Li^+ cation total partial structure factors $\Delta_{\text{Li}}(Q)$ and corresponding total radial distribution functions $G_{\text{Li}}(r)$ are presented in Figures 1 and 2. Although little can be inferred structurally from the Q -space data, it is worth noting the general trend in the data between $1 < Q (\text{\AA}^{-1}) < 2$. The data shows an increase in structure with increasing concentration, which is usually taken to be indicative of ion–counterion association.

Analysis of the results in Figure 2 is straightforward, with peaks at ~ 1.95 and 2.58 \AA being readily identified with Li–O and Li–D correlations of the first hydration shell (Table 1). Integration over these peaks individually according to eqs 5 and 6, or collectively according to eq 5 and the values in Table 1, give the coordination numbers shown in Table 2.

The results can be compared with our previous work on this ion and others in the alkali series. It is seen that the overall structure of water around Li^+ is almost identical to that found previously, in terms of interatomic distances; however, the amplitude of the peaks at 3 m and 1 m are smaller. As a consequence of the diminished peak amplitudes, the hydration numbers are also smaller in these solutions. The higher hydration numbers

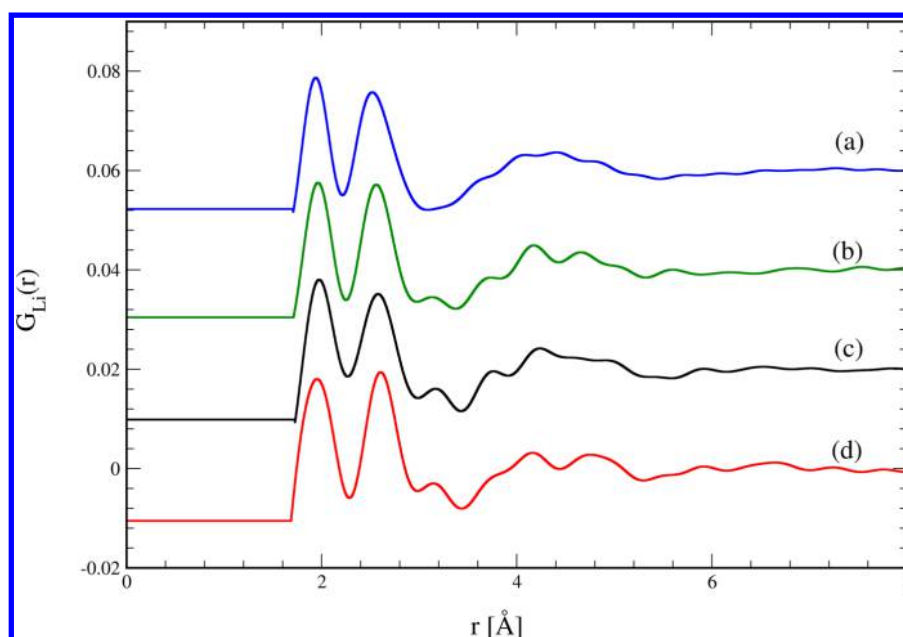


Figure 2. $G_{\text{Li}}(r)$ (in units of barns str^{-1}) for the heavy water solutions: (a) 6 m LiCl shifted up by 0.06 barns str^{-1} , (b) 3 m LiCl shifted up by 0.04 barns str^{-1} , (c) 1.5 m Li_2SO_4 shifted up by 0.02 barns str^{-1} , and (d) 1 m LiCl.

Table 1. Values of Coefficients in eq 5 for Each Solution

solute and molality	Coefficient Value (mbarn str^{-1})				
	A	B	C	D	E
LiCl (6 m)	4.477	10.293	0.797	−0.005	−15.563
LiCl (3 m)	2.602	5.983	0.232	−0.003	8.812
Li_2SO_4 (1.5 m)	2.738	5.683	0.033	−0.005	−8.449
LiCl (1 m)	0.909	2.090	0.027	0.000	−3.025

Table 2. Structural Results Obtained for Li^+ Hydration^a

solute (and molality)	r_{LiO} (Å)	r_{LiD} (Å)	n_{Li}^{O}	n_{Li}^{D}	$n_{\text{Li}}^{\text{D}_2\text{O}}$
LiCl (6 m)	1.94(2)	2.54(2)	4.4(2)	8.6(2)	4.3(2)
LiCl (3 m)	1.97(2)	2.58(2)	5.0(3)	9.5(3)	4.9(3)
LiCl (1 m)	1.96(2)	2.56(2)	4.7(3)	9.5(3)	4.8(3)
Li_2SO_4 (1.5 m)	1.96(2)	2.56(2)	5.1(3)	9.6(3)	5.0(3)

^aInteratomic distances were read directly from Figure 2, and coordination numbers were calculated by integration of eq 6 over the peaks and between successive minima.

published in previous papers are likely a consequence of the poorer statistics at that time and less-accurate correction procedures.

Since the experiments produce calculated hydration numbers for Li^+ that are greater than 4, and $G_{\text{Li}}(r)$ is nonzero beyond the first hydration shell, between 4 and 5 water molecules on average solvate Li^+ in the nearest hydration shell. This lower coordination number is generally in agreement with *ab initio* calculations.^{5,6,8,12,16,18} The coordinating waters reside in the first hydration shell for time scales of 10^{-11} s, or tens of picoseconds, as determined experimentally and also indicated by *ab initio* molecular dynamics (AIMD) simulations. For example, one AIMD simulation sampled trajectories in a 1 M solution over 45 ps¹⁸ and another sampled a more concentrated solution for 25 ps.⁶ Both reported highly structured pair (Li –O) distribution functions that drop near zero at the first minimum, which indicates few water exchanges between hydration shells. Longer time scales to obtain better sampling of water exchange

are challenging for AIMD simulations and may affect structural analyses. Yet, static calculations of hydration structure^{5,7,8,13–17} bypass those time-scale limitations and produce the same hydration numbers as AIMD simulations.

The residence time of water molecules in the first hydration shell of Li^+ can be contrasted with that for more strongly hydrated ions such as hexa-coordinated Ni^{2+} and Fe^{3+} , and tetra-coordinated Be^{2+} ,^{26,27} where water molecules exchange with the bulk solution much more slowly, residing in the first hydration shell on time scales $\geq 10^{-9}$ s. In these cases, the $G_{\text{M}}(r)$ does indeed vanish in the range beyond the first hydration shell. Inspection of Figure 2 in the region just beyond the first hydration shell confirms this point for Li^+ . An interesting observation is that $G_{\text{Li}}(r)$ is close to zero just beyond the first hydration shell for the highest concentration. That result implies that the large Cl^- ions might well be in a position to stabilize Li^+ and its first hydration shell as a relatively long-lived complex. NDIS experiments at the second-order difference level,²⁸ which would allow the determination of $g_{\text{LiCl}}(r)$, would help confirm this proposition.

Table 3. Structural Results for the Hydration of Alkali-Metal Ions (M^+), As Determined from Neutron and X-ray Scattering Experiments

ion	solute (molality)	r_{MO} (Å)	r_{MD} (Å)	$n_{\text{M}}^{\text{D}_2\text{O}}$	ref
Li^+	LiCl (3 m)	1.97(2)	2.58(2)	4.9(3)	this work
	LiCl (1 m)	1.96(2)	2.56(2)	4.8(3)	this work
Na^+	NaClO_4 (4 m)	2.4(2)		4.9(1.0)	Skipper and Neilson ³⁰
	NaCl (3 m)	2.34(2)		5.1(1.0)	Mason et al. ³¹
K^+	KCl (4 m)	2.9–3.4		5.3(6)	Neilson and Skipper ³²
Rb^+	RbCl (4 m)	3.1(2)		6.9(4)	Ramos et al. ³³

Another interesting observation is that the hydration number of Li^+ is independent of ion concentration up to 3 m. That result reflects the strong interactions between Li^+ and inner-shell water, strong enough that Cl^- has difficulty penetrating. That result also seems to imply that the water-mediated potential of mean force between the Li^+ ion and the Cl^- counterion is sufficiently repulsive to negate the Coulombic attraction between the bare ions. Furthermore, the potential of mean force is also repulsive enough to reduce the probability of direct ion-counterion contact to a level below that between comparable-sized neutral solutes dissolved in water.²⁹

In comparison with other alkali-metal ions, it is clear that Li^+ , with its higher charge density, is unsurprisingly more strongly

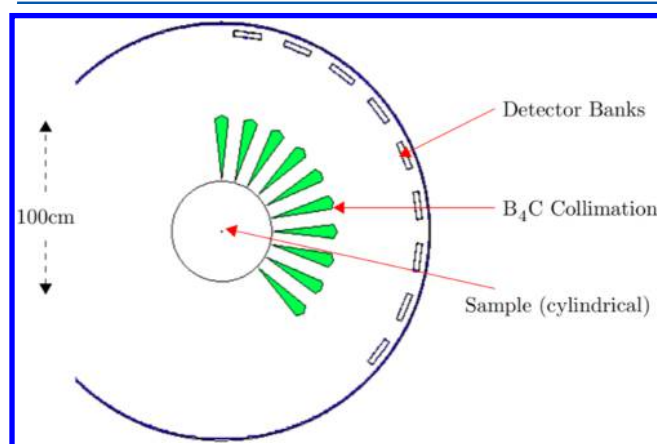


Figure A1. Monte Carlo (MCNP(X)) simulation model for the D4C diffractometer showing the sample within the belljar, detector banks, and the collimation composed of boron carbide (B_4C) to screen the neutrons.

hydrated than Na^+ , K^+ , and Rb^+ . All of those ions have been studied either by the NDIS method, or the equivalent anomalous X-ray scattering method (see Table 3).^{30–33} Although hydration numbers are similar in magnitude, more water molecules coordinate at distances further from the ion, and peaks diminish in sharpness as the ions become larger. Those trends are consistent with a general weakening of the hydration structure with increased ion size, which is also apparent in *ab initio* studies of these ions.^{7,17,34–43}

CONCLUSIONS

The new results clearly show that Li^+ retains a well-defined hydration shell at concentrations of 1 m with a hydration number of $\sim 4.8(3)$, which is significantly less than that reported in an earlier paper. Furthermore, the hydration number is independent of ion concentration. These new results generally agree with *ab initio* calculations. The results also show that the tremendous increase in computer power and memory, and significant improvements in neutron technology over the past two decades facilitates NDIS experiments on ever more complex liquids and solutions. The target of these developments is improved structural information to be used hand-in-hand with theoretical analyses to give new insights into solvation behavior.

APPENDIX

Separate Monte Carlo simulations were carried out for each sample and detector position, to correct each dataset. The total scattering cross sections were treated independently for each detector angle before combining to make the total difference scattering cross sections. The simulations were carried out using a modified MCNP(X)/Geant code base running models produced using CombLayer [https://github.com/SAansell/CombLayer]. The model geometry included the D4C sample

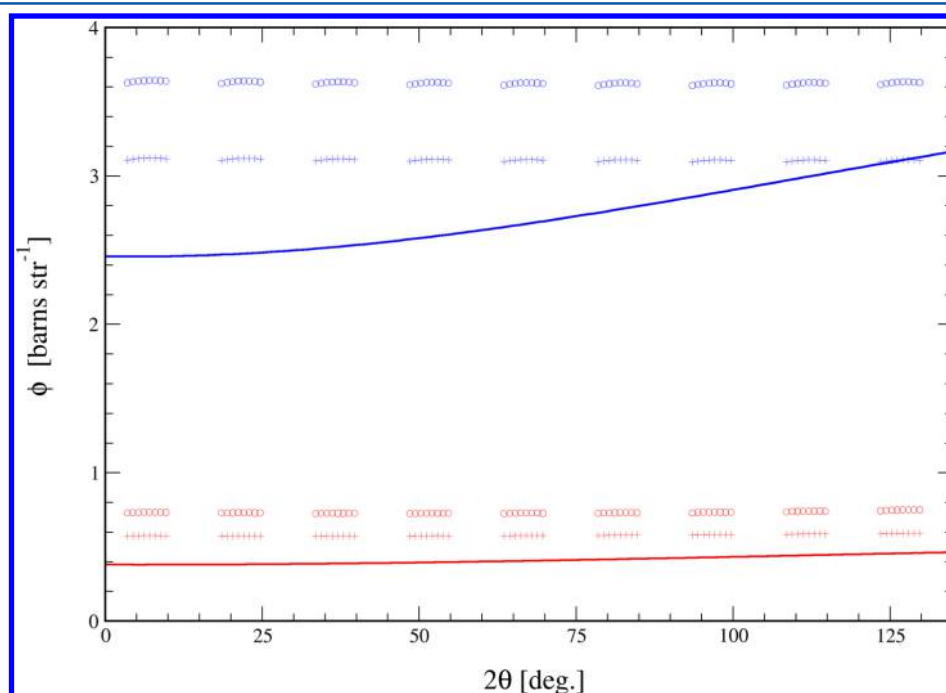


Figure A2. Comparison of scattering flux (ϕ) per scattering angle (2θ) between the Monte Carlo calculation and the standard Palmann and Pings results for one location of the detector arrangement. The top three curves are for $^{\text{nat}}\text{LiCl}$ in 6 m D_2O (crosses (+), single scattering; circles (O), multiple scattering; and solid line (—), standard calculation of multiple and single scattering). The bottom three curves are for $^6\text{LiCl}$ in 6 m D_2O (crosses (+), single scattering; circles (O), multiple scattering; and solid line (—), standard calculation of multiple and single scattering). The curves are normalized, in terms of barns str^{-1} , relative to vanadium.

environment (belljar), sample and container, and detectors (see Figure A1). For each simulation, the separate coherent, incoherent, and multiple scattering contributions to the detectors, from both the sample and the sample container, were isolated. The incoherent scattering functions were simulated using Granada's synthetic $S(\alpha, \beta)^{44}$ for water, He, and Ti/Zr. For aluminum, the Los Alamos ENDF-VII high-angle binned $S(\alpha, \beta)$ was used.

The D4C instrument has banks of 64 detectors over an 8° arc separated by trapezoidal collimation dividers that cover 7° , as shown in Figure A1. Because of the geometric layout of the B₄C collimation and the use of a cylindrical sample, the outside detectors of each bank see only a partial view of the sample.

The total single (incoherent + coherent) and full multiple scattering calculations from both the standard and Monte Carlo analysis methods are shown in Figure A2. The single scattering flux from the standard analysis follows a quadratic form between 0° and 165° (shown from 0° to 135°). This curvature is caused by attenuation of the beam in the cylinder and the Placzek correction. The curvature is less pronounced for the Monte Carlo result because of the treatment of the inelastic spread of the scattering. The standard model also overestimates the ^6Li attenuation in the central angles. In addition, the outside detectors of each 8° bank are obscured by the collimation, resulting in a rapid drop to null values in the single scattering contribution, which are not taken into account in the standard model.

The multiple scattering function is approximated by a simple fraction of the total scattering function in the standard Blech and Averbach method. In reality, the true multiple scattering for lithium samples is a convolution of the scattering probability with the geometric attenuation contribution. Monte Carlo simulations naturally include those contributions. For example, the Monte Carlo corrections sample over the cylindrical volume and higher-order multiple collisions are considered. The significance of including those contributions for lithium samples is shown by the difference between ^6Li and $^{\text{nat}}\text{Li}$ multiple scattering levels (see Figure A2). Also, a smoother curve is produced by the Monte Carlo treatment, compared to the standard treatment, which minimizes artificial structural features in the multiple scattering results. Given all the effects accounted for in the Monte Carlo data correction procedure, in addition to the improved neutron instrumentation, we are confident that the hydration results presented here represent a significant improvement over prior work.

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Notes

The authors declare no competing financial interest.

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