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The Relative Diffusive Transport Rate of SrI_2 in Water Changes over the Nanometer Length Scale as Measured by Coherent Quasielastic Neutron Scattering

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Abstract

X-ray and neutron scattering have been used to provide insight into the structures of ionic solutions for over a century, but the probes have covered distances shorter than 8 Å. For the non-hydrolyzing salt SrI_2 in aqueous solution, a locally ordered lattice of ions exists that scatters slow neutrons coherently down to at least $0.1 \text{ mol}\cdot\text{L}^{-1}$ concentration, where the measured average distance between scatterers is over 18 Å. To investigate the motions of these scatterers, coherent quasielastic neutron scattering (CQENS) data on D_2O solutions with SrI_2 at 1, 0.8, 0.6, and 0.4 mol L^{-1} concentrations was obtained to provide an experimental measure of the diffusive transport rate for the motion between pairs of ions relative to each other. Because CQENS measures the motion of one ion relative to another, the frame of reference is centered on an ion, which is unique among all diffusion measurement methods. We call the measured quantity the pairwise diffusive transport rate D_p . In addition to this ion centered frame of reference, the diffusive transport rate can be measured as a function of the momentum transfer q , where $q = (4\pi/\lambda)\sin \theta$ with a scattering angle of 2θ . Since q is related to the interion distance ($d = 2\pi/q$), for the experimental range $0.2 \text{ \AA}^{-1} \leq q \leq 1.0 \text{ \AA}^{-1}$, D_p is, then, measured over interion distances from 40 Å to $\approx 6 \text{ \AA}$. We find the measured diffusional transport rates increase with increasing distance between scatterers over the entire range covered and interpret this behavior to be caused by dynamic coupling among the ions. Within the model of Fickian diffusion, at the longer interionic distances D_p is greater than the Nernst-Hartley value for an infinitely dilute solution. For these nm-distance diffusional transport rates to conform with the lower, macroscopically measured diffusion coefficients, we propose that local, coordinated counter motion of at least pairs of ions is part of the transport process.

Abbreviations used:

QENS, quasielastic neutron scattering

IQENS, incoherent quasielastic neutron scattering

CQENS, coherent quasielastic neutron scattering

HWHM, half width at half maximum

FWHM, full width at half maximum

SANS, small angle neutron scattering

SLD, scattering length density

M, molar (mol L^{-1})

Introduction

As is well known, ionic diffusion coefficients in solution can be measured in many ways. The classic ones are well established,^{1,2} and of these, NMR provides the shortest lengths over which bulk diffusion coefficients are measured: lengths in the 1 μm range limited by the .100 ms time scale of the experiment. On the other hand, by measuring collisional properties with paramagnetic ions, average solvent diffusion coefficients near the ions have been inferred.^{3,4}

A less well known method to measure diffusive transport uses the scattering of cold neutrons.⁵⁻⁷ The technique called quasi-elastic neutron scattering (QENS)—not only can measure diffusion coefficients, but also measures them as a function of length scale from about 10 Å to 40 Å. (1 nm = 10Å.) These measurements are possible because the neutrons' kinetic energies are in the range of the changes in energy imparted to them by the scatterers in solution.⁷ Most such diffusion coefficient measurements have been made for motion in the laboratory frame of reference, such as diffusion of the water in a solution,⁸⁻¹¹ or the diffusion of a hydrogen-containing solute such as tetraalkylammonium ions.¹² The method of QENS that relies on scattering from single nuclei—a phenomenon called incoherent scattering—is used, and the incoherent type is often abbreviated IQENS.

A second type of QENS relies on scattering from two centers at a time—this is called coherent scattering and, hence, coherent QENS (CQENS). Previously, only a few liquid solutions have been amenable to measuring the distance dependence of the average, pairwise relative diffusive transport as a function of solute-solute spacing.¹³⁻¹⁶ Unique among these few are the aqueous (D_2O) solutions of SrI_2 presented here that show scatter from the individual ions= nuclei and not from polyatomic molecules.¹⁷ The CQENS measurement of diffusion reported here is unique in that the reference frame is anchored on a scattering ion and independent of an external frame.

For ionic solutions that are not dilute, their diffusion coefficients are classified as being collective diffusion coefficients with the assumption that motions of anions and cations to some degree move in the same direction to preserve electroneutrality.¹⁸ Under that assumption, the Nernst-Hartley collective diffusion coefficient is somewhat smaller than the weighted average of the single-ion values. (See Discussion.) Because CQENS measures the motion of one ion relative to another, we call the quantity measured the pairwise diffusive transport rate, D_p . In addition to

this ion-distance frame of reference for D_p , the rate can be measured as a function of that interparticle distance over lengths from 40 Å to ≈ 6 Å. These distances correspond to the experimental range of $0.2 \text{ \AA}^{-1} \leq q \leq 1.0 \text{ \AA}^{-1}$, where $q = (4\pi/\lambda)\sin \theta$ for a scattering angle of 2θ and $d = 2\pi/q$. CQENS has, for the first time, allowed such information to be collected from an aqueous ionic solution. As described here, our CQENS measurements give surprising results for the D_p values as they change with interion distance in D_2O solutions of SrI_2 that are 0.4 M (1 M = 1 mol L⁻¹), 0.6 M, 0.8 M, and 1.0 M in the salt.

The equations describing the ability to measure relative diffusion coefficients by coherent quasi-elastic neutron scattering can be found in a succinct summary in the paper by Faraone, et al.¹⁵ and from other viewpoints by Vineyard⁵, by Kneller,¹⁹ and by Roe²⁰ The underlying molecular processes and the way the interaction of the solution with the cold neutrons produces the scattering are described phenomenologically in the body of the paper. In addition, a brief description of the equation showing the relationship between the time-dependent coherent scattering between two centers and the measured scattering intensities can be found in the Supplementary Material.

Materials and Methods[†]

Strontium iodide solutions

Anhydrous SrI₂ (99.99% metals based, Alfa Aesar, Ward Hill, MA) was both measured out and weighed in a dry N₂ atmosphere. D₂O (99.9%, Cambridge Isotope Labs) was added to produce a 2.00 M stock solution. The appropriate D₂O volume needed was calculated by subtracting the volume of the salt from the desired total volume, since the densities of aqueous SrI₂ solutions were found to be reproduced by the reverse of this calculation using the density of solid, anhydrous SrI₂ (4.55 g cm⁻³). All experiments were run on solutions of this stock diluted with D₂O at least 24 hours before the scattering experiment, and subsequently degassed under vacuum just prior to the run.

Both the anion and cation species scatter, and their scattering length densities are estimated to be approximately equal in the following way. Using the density of Sr metal (2.65 g cm⁻³) and the density of I₂ liquid (4.933 g cm⁻³), and isotope-weighted coherent cross sections of, respectively, 6.19 barns and 3.5 barns,²¹ the NCNR scattering length density calculator (<http://www.ncnr.nist.gov/resources/activation/>) gives the coherent strontium SLD as $(1.28 \pm 0.01) \times 10^{-6} \text{ \AA}^{-2}$ and that for iodide as $(1.24 \pm 0.01) \times 10^{-6} \text{ \AA}^{-2}$. Some adjustment for the differences between the atomic and ionic dimensions and the solvent electrostriction would be necessary to estimate more accurate values. Nevertheless, the cations and anions are calculated to possess nearly equal scattering length densities.

The pD values of the solutions were those recorded by a glass electrode calibrated in H₂O. No isotope correction was made, with the assumption that the unmodified value was more accurate since it is likely that the buffer pD and electrode surface's pK_a shifted approximately the same amount with the level of D-H substitution. The measured pD values of the samples lay in the range 7.1 to 7.4. One reason strontium iodide was chosen for the measurement is that it is a nonhydrolyzing salt, *i.e.* it does not produce either protons or hydroxide ions upon hydration, and so leaves the pD near neutral for all concentrations. This property means that hydroxyl coordination is not expected for the cation, and we can anticipate only water in the hydration shells—properties that minimize the possible number of different species that are present. Both the strontium²² and iodide²³ have been characterized by EXAFS scattering under such

conditions.^{22, 23}

The coherent quasielastic scattering experiment

A neutron can scatter pairwise from two solute scatterers in solution, and theory shows how two points separated in three dimensional space scatter to produce interference fringes.^{24, 25} This phenomenon is called coherent scattering. Any two scatterers fixed in separation in the solution are, in general, randomly oriented in space, and the average of all these orientations produces a scattering pattern of intensity versus angle that can be interpreted to find the distance between the two points.^{24, 25} The scattering can be thought of as a transfer of momentum that kicks the neutron from its incoming direction of travel and displaces it to an angle 2θ away from the axis defined by the neutron's original line of travel. The small-angle neutron scattering (SANS) contains the structural information, but not the time dependence of the scattering. In the case of the SrI_2 in D_2O , the published SANS shows a single peak at an angular position for which the q -value marks the average distance between nearest-neighbor scattering centers.²⁶ The shape of the peak reports the distribution of distances around the most probable one after an appropriate three-dimensional Fourier transform.

In addition to the separation distance distribution of SANS, the QENS measurement shows the distribution of energy gained or lost due to the $k_B T$ -induced diffusional motion. (See eq. 1.) The distribution of the energy after scattering is often observed as a single Lorentzian line centered at the elastic scattering energy value. The phenomenon producing this result is called quasielastic scattering. (Not all QENS spectra are pure, single Lorentzians.)

The incoming and scattered neutrons are characterized by their wavevectors and energies: \mathbf{k}_i and E_i , \mathbf{k}_f and E_f , respectively. The wavevector and energy of the neutrons are linked: $E_{i/f} = \hbar^2 k_{i/f}^2 / 2m_n$, where m_n = the neutron mass, $\hbar = h/2\pi$, E_i is the initial neutron energy, and E_f is the final energy.

The exchanged wavevector, q , and energy, E , are defined as $\mathbf{q} = \mathbf{k}_i - \mathbf{k}_f$ and $E = E_i - E_f$. The cosine rule of triangles (see Figure 1) yields Equation 1.

$$q^2 = 2 \frac{m_n}{\hbar} \left[E_i + E_f - 2\sqrt{E_i E_f} \cos 2\theta \right] \quad (1)$$

{Figure 1 near here. Vector diagram.}

Quasielastic neutron scattering (QENS) data collection

The QENS experiments were run on the Disk Chopper Spectrometer (DCS) on beamline NG4 at the NIST Center for Neutron Research (NCNR).²⁷ This time-of-flight spectrometer was used with an incoming wavelength of 10 Å, with data collected in the range $0.2 \text{ \AA}^{-1} \leq q \leq 1.0 \text{ \AA}^{-1}$. In that range, the coherent signal from the average interion structure dominates. Using the low resolution configuration, the instrument had an energy resolution of $\approx 20 \text{ \mu eV}$, which allowed study of the collective coherent dynamics of the solution over times between 1 ps and 50 ps.

Data were collected from annular samples held in aluminum cans with indium metal seals. The inner diameter of the annulus measured 18.3 mm, and the outer diameter 19.9 mm, yielding a sample thickness of 0.8 mm and a length of 100 mm. With the instrument geometry, this sample thickness is equivalent to a $\approx 2.4 \text{ mm}$ pathlength flat sample. A measurement performed on a vanadium standard was used for detector normalization. Using the package MSlice of the software DAVE,²⁸ the data were reduced to dynamical structure factor spectra, $S(q, E)$, at 15 fixed wavevector transfers, q .

In contrast to the vast majority of QENS measurements that have utilized incoherent scattering from individual scatterers,^{10, 11, 29} we measured the coherent quasielastic CQENS scatter from pairs of scatterers. The experimental intensities result from the ensemble of sets of structures that exist in the solution.

A question arises whether multiple scatter might distort the data. The samples' transmissions were about 0.9, which indicates that only 10% of the intensity would be multiple scatter (double scatter/scatter = 0.01/0.1). The multiply scattered intensity lies within the uncertainty of the statistical uncertainty of the data.

Separating the Contributions from Incoherent and Coherent Neutron Scattering

Incoherent scatter results from the interaction of the neutron with the nuclear magnetic spin of an isotope. Since iodine has a nuclear spin (5/2), its neutron scattering has an incoherent contribution, which increases the scattering background signal but does not produce any structural distance information. Strontium has a number of isotopes, and, by abundance, 93% of

them have no nuclear spin. So the incoherent scatter from strontium is only 20% of the total incoherent scatter from the SrI_2 solute. More quantitatively, the incoherent scattering cross sections for thermal neutrons are: ^{127}I (natural abundance 100 %, 0.31 barns, stoichiometry 2 for total 0.61 barns); ^{87}Sr (n.a. 7%, 0.5 barns), which gives for the total stoichiometry 1Sr, (100 %, 0.06 barns). As a result, the incoherent contribution of the strontium lies within the experimental uncertainty and is not included in the data fitting. The contribution of the incoherent scatter from the D_2O solvent is removed by subtracting the scattering from a pure (99.9%) D_2O sample multiplied by its volume fraction after correction for self shielding for each SrI_2 concentration. More on this correction appears below.

A preliminary neutron spin echo (NSE) study at the NCNR on another 1.0 mol L^{-1} solution of SrI_2 in D_2O showed that at the maximum of the observed solvent-subtracted scattering peak, the incoherent and coherent static contributions of the D_2O -solvent-subtracted SrI_2 scattering are equal within the instrumental uncertainty. In addition, the structural relaxation caused by diffusion as measured by NSE was complete before the 100 ps short-time limit for that experiment.

Because the interpretation of the diffusion coefficient derived from CQENS can be distorted by contributions from incoherent scatter, the latter must be removed to obtain the correct Lorentzian line. The incoherent contribution has two major sources: one is the scattering from deuterium, and, as mentioned above, the iodide also contributes. For the former, a question of the accuracy of the solvent subtraction for the QENS experiment does arise, since the lineshape of the incoherent scatter of D_2O does depend on the chemical environment—more specifically, the dynamics—of the deuterons.

We judge that the environment of the D_2O is not of importance in the solvent subtraction for the QENS data for two reasons. First, the ions in the solvent do not change the dynamics to a large extent. For example, recent IQENS work on aqueous ionic solutions has shown that the single particle dynamics of water changes less than 15 % up to concentration of 1 M.¹¹ And second, the vibrational deuterium dynamics and the water's structure and density are not greatly changed by the presence of the SrI_2 . This is supported by the small shift in the D_2O Raman O-H frequencies due to the presence of the ions,[Unpublished data] and by the absence of electrostriction as shown by the additivity of the volumes of pure water and the salt to give the

final solution volume.²⁶

As a result, after the solvent subtraction equal to the partial volumes of D₂O in the solutions (for 1.0 M, 0.8 M, 0.6 M, and 0.4 M these are 0.925, 0.940, 0.955, and 0.970 of pure D₂O), the signal remaining is from the SrI₂ alone. Any incoherent scattering observed originates mostly from the iodide, as described earlier.

The total incoherent scatter due to the SrI₂ was evaluated from the change in baseline with different concentrations in SANS experiments and knowledge of the coherent-to-incoherent ratio measured by NSE.²⁶ The SrI₂ incoherent scattering lineshape was determined using a Fickian self-diffusion model as a Lorentzian with a full width at half maximum (FWHM) equal to $2D_s q^2$. The self diffusion coefficients, D_s , were determined using published diffusion results (see Table 1 below). The diffusion *versus* distance results reported here have been corrected for this SrI₂ concentration-dependent incoherent contribution.

Results and Discussion

As can be seen in the representative, solvent-corrected data in Figure 2, the line broadening of the CQENS measurements increases with q . (The experimental lineshape shown here is a convolution of a sample's scattering and a Gaussian due to instrumental broadening.) The three representative scattering curves are from a 0.8 M solution of SrI_2 in 99.9% D_2O . The heights of all three lie on the same arbitrary linear scale within the accuracy of the calibration between channels of the DCS detector. The contributions from the coherent and incoherent scattering are also shown.

{Figure 2 near here. QENS data plots}

Obtaining the relative diffusion coefficient from a Lorentzian linewidth

The relationship between the QENS Lorentzian linewidth and the diffusion coefficient is described through a simple relationship involving the half width at half maximum (HWHM).^{5, 19, 30, 31}

$$\text{HWHM} = D(q) \cong q^2 \quad (2)$$

As can be seen from the units on the horizontal axes in Figure 3, commonly the HWHM from a QENS is expressed in units of meV. With q in \AA^{-1} , the units of $D(q) = \text{HWHM}/q^2$ are $\text{meV}\cdot\text{\AA}^2$. Typical aqueous ion diffusion coefficients at room temperature show HWHM in the region of $0.1 \text{ meV}\cdot\text{\AA}^2$.

To convert the QENS Lorentzian linewidth to a diffusion coefficient with the usual units of $\text{cm}^2 \text{As}^{-1}$ ($1 \text{ cm}^2 \cdot \text{s}^{-1} = 10^{-4} \text{ m}^2 \cdot \text{s}^{-1}$) used in chemistry requires that the distance be converted from \AA to cm, and the energy in meV be converted into units of time. The latter is done by recognizing that $E = (\hbar/2\pi)\omega$, where ω has units of s^{-1} . From the value of $\hbar = 6.582 \times 10^{-13} \text{ meV}\cdot\text{s}$, we calculate that $1 \text{ meV}/\hbar = 1.5192 \times 10^{12} \text{ s}^{-1}$. Then, $1 \text{ meV}\cdot\text{\AA}^2 = 1.5192 \times 10^{-4} \text{ cm}^2\cdot\text{s}^{-1}$.

Origin and linewidth of the Lorentzian scattering peak

For spatially unlimited diffusion, the width of the Lorentzian is expected to increase linearly as a function of q^2 . The reason for this behavior is straightforward in concept.³¹ The presence of a scattering structure can alternatively be described as having the scatters' positions

fixed in space relative to each other so that pairs of scatterers remain in the same relative positions. Then each pair's positions are said to be correlated, and for a fixed structure, pairwise they have correlation coefficients of unity. If the pairs then move randomly, that spatial correlation is lost, the correlation decreases until it can reach zero, where the atoms originally located together are then randomly related in space compared to their original relative positions.

In a liquid, the mechanism moving the atoms away from their initial positions is diffusion which moves them toward a structure uncorrelated with the initial one. In addition, the measured length scale of the original ordering—which is another way to say the length also equals the spatial resolution of the original measurement—depends on q . The key point to understanding this q dependence of the linewidth is that the shorter the resolution length, d , the faster the structure escapes from the original ordering. When the mechanism of escape is Fickian diffusion, the distance moved is given by $(\Delta x)^2 = 2Dt$. So the time to escape is proportional to $(\Delta x)^2 = d^2 \propto 1/q^2$.

A corollary of this relationship is if the Lorentzian linewidth is divided by q^2 , the quotient is proportional to the diffusion rate at the inverse distance q : that is, $D(q) = \text{HWHM}/q^2$. In this way, the quasielastic scattering supplies a diffusion coefficient as a function of length scale, and the length scale for cold neutrons is in the range of a few nm and below.

This relationship results from a model where the distance $d = 2\pi/q$ over which Fickian diffusion occurs has the distance precisely defined by q . The physical process can be envisioned as the scattering of the neutron wave packet by the two centers separated by d , and the dephasing of that scattering by the Fickian diffusion while the wave packet passes by. The equality of a macroscopically measured Fickian diffusion coefficient and the CQENS-measured diffusive transport rate D_p is a matter of discussion. Here, we assume the two are equal.

The nature of the diffusion coefficients of SrI₂ measured by CQENS

The CQENS measurements provide a new and unique measurement of diffusive motion for ionic solutions. Unlike other measurement methods that inherently depend on either a laboratory or solvent frame of reference,³² the diffusion reported here is the ensemble average from individual ions as each moves relative to another ion within the solution.

Here, the diffusion in this ionic solution occurs without macroscopic concentration

gradients, so that the measurements do not need compensation for free energy gradients. The diffusion measurement occurs within the distribution of structures that exist with the $k_B T$ driving force for fluctuations on the nm scale. Other studies using CQENS to measure diffusion have been done,¹³⁻¹⁶ but not for aqueous salt solutions.

{Figure 3 near here. Four diffusion coeffs vs distance}

As is clear from the graphs of Figure 3, CQENS has the unique ability to measure the pairwise relative diffusion as a function of interion distance on the nm length scale, which has not been possible until now. However, for the SrI_2 in free solution, hydrodynamics should explain the behavior when the solvent can be validly viewed as a continuum and where viscosity can be used as a measure both of the transfer of momentum and the loss part of the complex mechanical properties of a solution. In that case, as exemplified by, e.g., the Stokes-Einstein equation, rates of diffusion are inversely proportional to the measured viscosity. As can be seen from the graphs in Figure 3, the diffusion coefficient changes with the interionic distance under conditions where the macroscopic viscosity remains constant. We must conclude that the concepts of macroscopic hydrodynamics do not apply on this length scale with aquated ions where both the ions and the nearest-neighbor distances are on the order of the molecular size of the solvent.

Nevertheless, numerous studies of colloids and of the water in ionic solutions have been shown to behave as expected, with their QENS linewidths increasing linearly with q^2 .³³ If that behavior were followed by SrI_2 , the graphs as plotted in Figure 3 would be horizontal lines over the full length range.

It is worth noting that the motions of the individual ions locally was suggested from the SANS results from SrI_2 in D_2O at concentrations down to 0.1 M.²⁶ The baseline widths of the distributions of ion distances remained essentially independent of concentration with a value around 10 Å. This was interpreted to mean that the process of diffusion—and the necessary counterflow of the solvent—involved rotations of ion-water clusters that has the effect of switching the positions of a water and the ion while minimally disrupting the rest of the lattice.

This rotational exchange of positions by the ion and water appears to provide a mechanism to elucidate the dielectric decrement (or kinetic polarization deficiency) to be expected as derived by Hubbard et al.³⁴ That is, the static dielectric constant is reduced relative

to the pure solvent in a manner proportional to the product of the dielectric relaxation time of the solvent alone and the low frequency conductivity of the solution. The mechanism for transport by water-ion-cluster rotation appears to comport with such a phenomenon. The conductivity is proportional to the ion concentration, and the relaxation time should correlate with the rate or amount of rotation.

Comparing the macroscopic and pairwise diffusive transport rates

For macroscopic length scales, ionic solutions must be electrically neutral, and so one useful comparison of the values of the measured D_p is to the Nernst-Hartley mutual diffusion coefficient^{18, 35} at infinite dilution, D_m^0 .³⁶ The value of D_m^0 can be found from the limiting diffusion coefficients of the anion with charge z_- and cation with charge z_+ of a single salt in solution.³⁶

$$D_m^0 = \frac{(z_+ - z_-)D_+^0 D_-^0}{z_+ D_+^0 - z_- D_-^0}$$

For SrI_2 , the limiting diffusion coefficients³⁷ are $D_{I^-}^0 = 2.045 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and

$D_{\text{Sr}^{2+}}^0 = 0.792 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, which then yield $D_m^0 = 1.34 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at 25°C. This is

lower by only 18% from the simple, number-weighted average of the limiting diffusion coefficients for strontium ion and iodide, which is $1.63 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. We also use this latter value in comparison and show them on Figure 3. This value is greater than averages of the single-ion diffusion coefficients at the concentrations used here (see column 4, Table 1). Tracer diffusion coefficients that are equal to these have been reported but with lower precision.³⁸

{Table 1 near here. Diffusion coeffs}

Magnitudes of the diffusion coefficients

As noted just above, the Nernst-Hartley mutual diffusion coefficient^{35, 36} for SrI_2 at infinite dilution, $D_m^0 = 1.34 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at 25°C. That value is shown on the top graph of Figure 3. The values of D_p for much of the range lie above the Nernst-Hartley limiting value and also above the macroscopic number average values for each concentration, which are listed in the fourth column of Table 1.

The classically determined self diffusion coefficients of the strontium ions and the iodide ions as they change with concentration in aqueous solutions have been enumerated by Matuura and Koga.³⁷ The single-ion diffusion coefficients associated with the concentrations in the four solutions measured by CQENS are listed in Table 1, and they are all smaller than the respective limiting average values.

One further qualifier follows from the near equality of the SLDs of Sr^{2+} and I^- . The contribution to the measured average D_p by both Sr^{2+} and I^- are expected to be proportional to their individual concentrations, but only to the extent that their scattering length densities (SLDs) are, in fact, equal as calculated in the methods section. If they are not, their contributions to the measured value will be weighted by their relative SLD values.

As is well established, collective diffusion coefficients are larger than those of isolated, charged *particles*. A clear demonstration of the effect is described by Appell, et al.³⁹ for colloids of a fixed size but with varied total surface charges. The colloids with greater charge showed a greater measured diffusion coefficient. However, diffusion coefficients in most aqueous ionic solutions differ in that they tend initially to decrease linearly as the square-root of the concentration—following Onsager's Limiting Law—but then increase to levels higher than the limiting diffusion coefficient around the molar-concentration range.⁴⁰ That is, only around 0.2 M to 0.5 M do their Fickian diffusion coefficients turn around and increase with increasing concentration as expected for collective diffusion coefficients.^{40, 41} For SrI_2 , the range of decreasing values continues even to molar solutions.³⁷ The distance dependence of D_p found here furnishes new insights

Distance dependence of D_p

As seen in Table 1, even in the molar range, the macroscopic collective diffusion coefficients of SrI_2 still follow a decreasing trend with increasing concentration, although significant ion-ion interactions are present as indicated by the distance dependence of D_p within the nanometer length scale. The molecular picture for this variation is as follows. When the ions are dilute, an isolated ion is subject to a random force (thought of as random kicks) from the waters surrounding it, which then results in the motions of the diffusive process. But when not dilute, and the ions are not isolated, each is surrounded by distant ions that are also subject to

random, short impacts by their local waters. However, these more remote neighbors interact with the original ion effectively generating additional kicks to the local ones. This process increases the number of the random forcing events in a given time. In other words, the higher total impulse frequency means more motion in a given time: a faster diffusion process. A quantitative description of these concepts is not straightforward, and to the best of the authors' knowledge no theory has been developed for the collective diffusion of concentrated ion solutions.⁵⁰

The increase of D_p with increasing separation distance occurs because the number of ions that create the extra forcing fluctuations increases with the distance between the probed pair of ions. However, when ignoring the dropoff at short-range, i.e., where $d < 7 \text{ \AA}$, log-log plots of the diffusion coefficients against interparticle distance for all four concentrations have slopes between 0.4 and 0.6. Any geometric and molecular framework to explain this log-log slope is well beyond the data to discern.

Interpreting the details of the diffusion coefficients' distance dependence

{Table 2 near here. Short-distance break}

At the left-hand side of the graphs, the diffusion rate rises rapidly up to a break at about 7 Å. (The break points are listed in Table 2.) This break coincides closely with the 6.3 Å separation expected for a solvent-separated strontium-iodide ion pair. This expected separation distance comes from the distances within the crystal structure of strontium iodide dihydrate.⁴² We combine the I-H-O distance of 3.6 Å with the Sr-O distance of 2.7 Å to project the solvent-separated ion pair internuclear distance (linear Sr-O-D-I) of 6.3 Å. The sharp decrease of relative diffusion with closing distance is expected both from having the intervening water difficult to remove to let the ions approach more closely and also likely from the rotational motion of the intact solvent-separated ion pair. The projection of the rotational motion along the neutron scattering axis can extend to zero distance, i.e., when one ion eclipses the other in that direction. As can be seen, at distances less than 7 Å, the values for D_p versus interion distance are nearly the same for all the concentrations. The reason for the anomalous value at 0.6 M is uncertain.

A second feature is a dip in the diffusion coefficient around 10 Å to 12 Å, which is the average distance between nearest neighbors.²⁶ We interpret these as originating from the slowing of the relative motions when the ions naturally reside as nearest neighbors of the reference central

ion. As can be seen, this slowing is greater with increasing concentration. In the scattering literature, this behavior is referred to as deGennes narrowing.

The values of D_p continue to increase up to between 20 Å and 40 Å, the latter being the longest distance within the experimental range. Except for the 1 M solution, their magnitudes rise to nearly twice the Nernst-Hartley limiting diffusion coefficient.

For these nm-separation relative diffusion coefficients to be compatible with the macroscopic measurements, the motions of the ions in one direction must be coordinated with motions in the opposite direction. This can be accomplished by having circulation (or rotation) of regions within the solution containing at least two ions, which means that at least part of their joint motions extend in opposite directions. Among the possible mechanisms are the rotations of the solvent-separated ion pairs or the coordinated motions within traveling chains of ions/solvent moving in a circle; such motions can occur with a minimum of disturbance of the remaining solution.⁴³ A third possibility would be to have coordinated countermotions through the tendency toward electroneutrality over some electroneutrality coherence distance, although this is contrary to the basic idea of the Nernst-Hartley calculation that anions and cations tend to follow one another. Asked as a question, would the counterflowing ions have the same charge or be of opposite charge as facilitated by the ionic structures in the solution?

Conclusions

The causes of the complex behavior of the average diffusive transport rate as it changes with interparticle distance cannot be clarified with this set of SrI_2 data alone. It is not possible to eliminate any of the numerous factors that are recognized to affect the diffusion process. Decades ago, Straub et al.⁴⁴ mentioned four probable influences on the variation of mutual diffusion coefficients with distance. The first one listed below follows from the simple fact that the ions and the waters are about the same size and not many can fit into the distances probed here. That is,

- 1) The hydrodynamic description of frictional forces involved in diffusion must be

replaced by a solvent consisting of molecules.

This molecular contribution to frictional forces means that

2) The total friction along the reaction coordinate results from the magnitudes of the collisional impacts, and that, in turn, is a function of the local solvent structure.

If the molecular solution's collective modes are viewed as playing a part,

3) The collective modes will vary depending on the particle separation, and that influences the decay time of the structure and, consequently, the diffusion.

Also, since another part of our understanding of the cause of diffusion involves the random force,

4) The variation of the diffusion coefficient can result from the equilibrium average mean-square of the force being dependent on the distance from the ions as well as the distance between the ions (or clusters).

In addition to the above four influences, we add that the complexity of modeling will be difficult because of a fifth factor.

5) Although the experiment measures only the change of the average diffusion coefficient with the distance between two centers, for equally spaced particles in solution each scatterer has twelve nearest scattering neighbors.²⁶ Such geometries have proven to be nearly intractable even for hydrodynamic simulation.

Further, it is well known that ion pairing or clustering does occur in strontium iodide solutions and depends on concentration. For example, Aggarwal⁴⁵ long ago showed evidence for such ion association in molar-level SrI₂ solutions. However, that chemistry does not seem to have a major effect on the diffusion coefficients given their similarities with distance at all four concentrations. One caveat remains: the absolute values of the distance measured as $2\pi/q$ and the actual spatial structural motion that the loss of correlation measures are as yet not calibrated against macroscopic measurements. This calibration is ongoing. Nevertheless, the measures of the relative rates of diffusion with distance will remain proportionally the same. Consequently, we present this unique data for ionic solutions found by SANS and CQENS and leave explanations for the behavior to be found from future modeling.

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Footnotes**Disclaimer**

Certain commercial materials are identified in this paper, but such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Table 1. Self Diffusion Coefficients ($\text{cm}^2 \text{s}^{-1}$) and Relative Viscosities of Strontium Iodide Solutions

SrI ₂ Concentration/M	I ⁻ Self Diffusion Coeff ^a /10 ⁻⁵	Sr ²⁺ Self Diffusion Coeff ^b /10 ⁻⁵	SrI ₂ Number Average Diffusional Transport Rate ^c /10 ⁻⁵	Relative Viscosity SrI ₂ Solutions ^d
0.0	2.045	0.79	1.63	1.000
0.4	1.68	0.71	1.36	1.059
0.6	1.60	0.69	1.30	1.096
0.8	1.52	0.66	1.23	1.139
1.0	1.44	0.63	1.17	1.186

a. Non-zero concentrations estimated from fitting the self diffusion coefficients from Matuura³⁷ from the linear portion of their Figure 4 and correcting for (η/η_0) . Equation used: $D \cdot (\eta/\eta_0) = (1.9058 \pm 0.004) - (0.1997 \pm 0.007) \cdot [\text{SrI}_2]^2$. Estimated uncertainty $\pm 5\%$ ($\pm \sigma$). Temperature 25 °C.

b. Non-zero concentrations estimate from interpolation of the data from Matuura³⁷ for strontium between 0.125 M and 0.985 M. Fitting equation: $D(\text{Sr}^{2+}) = \{0.64502 - 0.09103 \cdot \exp([\text{SrI}_2])\}^2$. Estimated uncertainty $\pm 5\%$. Temperature 25 °C.

c. For each concentration, $(2D_I + D_{\text{Sr}})/3$.

d. At 25 °C relative to pure water.

Table 2. Estimated break points at short distance

SrI ₂ concentration/ M	Break point/Å ^a
1.0	7.2 \pm 0.2
0.8	7.0 \pm 0.2
0.6	6.6 \pm 0.3
0.4	7.0 \pm 0.3

a. From the intersection of straight lines on opposite sides of the point. Uncertainties are the estimated full range

Figure Captions

Figure 1. Definitions of terms used to describe quasielastic scattering with conservation of energy and momentum.

Figure 2. QENS scattering curves for the 0.8 M solution at three representative q values together with the inelastic and quasielastic component fits. Error bars ($\pm\sigma$) are those of the counting statistics only.

Figure 3. Plots of the ensemble average D_p versus interparticle distance for the four concentrations of SrI_2 in D_2O . Error bars ($\pm\sigma$) are those of the counting statistics only. The same set of graphs plotted as D_p versus q are shown in the Supplement.

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50. In colloidal physics the lengthscale dependence of the measured diffusion coefficient

(most often through light scattering), commonly referred as the effective diffusion coefficient, is expressed as: $D_{\text{eff}}(q) = D_0 H(q)/S(q)$ where D_0 is the infinite dilution diffusion coefficient, $H(q)$ is the hydrodynamic function, and $S(q)$ is the static structure factor. This expression describes the data from QENS of some protein solutions.^{46, 47} However its applicability here is questionable

where the scattering centers (the ions) are comparable in size with the waters. On the other hand, the empirical Sköld approach^{48, 49} has been used for describing the coherent scattering of molecular liquids as a function of their incoherent counterpart: $S_{\text{coh}}(q,E)/S(q) = S_{\text{inc}}$. Although successful in some cases⁵¹ this approach has been questioned.⁵²

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