PHYSICAL REVIEW B **74**, 094201 (2006)

Structure of 2 molar NaOH in aqueous solution from neutron diffraction and empirical potential structure refinement

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(Received 20 March 2006; revised manuscript received 5 June 2006; published 11 September 2006)

Neutron diffraction with isotopic substitution has been used to investigate aqueous solutions of $2M$ NaOH in the liquid state. The data were modeled using empirical potential structure refinement which allows for the extraction of the ion-water and water-water correlations. The data show that the ion-water radial distribution functions are in accordance with those found by previous studies on NaOH solutions and follow a trend which is dependent on the concentration of the solute. In particular, the shape of the hydroxide hydration shell is found to be concentration independent, but the number of water molecules occupying this shell increases with dilution. Additionally, the water-water correlations show that there is still a measurable effect on water structure with the addition of ions at this concentration, as the second shell in the water oxygen radial distribution function is compressed relative to the first shell. The data are also used to discuss the recent claims that the published radial distribution functions of water are unreliable, showing that data taken at different neutron sources, with different diffraction geometry and systematic errors lead to the same structural information when analyzed via a realistic modeling regime.

DOI: 10.1103/PhysRevB.74.094201 PACS number(s): 61.20.Ja, 61.12.−q

I. INTRODUCTION

Given the importance of electrolytic solutions in many biological, chemical, and industrial processes there is not yet full accordance on the extent to which ions may influence the structure of water.[1] A variety of hydroxides in aqueous solutions have been recently studied using neutron diffraction combined with empirical potential structure refinement (EPSR) computational modeling.[2–4] Both the effect of concentration and cationic size (Li, Na, K) have been investigated, but only in highly concentrated solutions, ranging from $4M$ to $12M$. In those studies, the hydration shell around the hydroxide ion was experimentally determined. The shape of this hydration shell was found to be independent of the concentration of the ion, although the number of water molecules occupying this shell was concentration dependent. Additionally, a concentration dependent shortening of the second neighbor water-water distance due to the presence of the ionic charges was observed at concentrations higher than $4M$ where all water molecules in the solution are engaged in the first hydration shells of ions. In order to understand whether this disturbance to the water structure affects the molecules in the second hydration shell as well as those in the first hydration shell, it is important to study solutions at lower concentrations.

Here we report neutron diffraction experiments on a $2M$ $NaOH/H_2O$ solution, corresponding to about 1 solute molecule per 28 water molecules, which utilize the technique of hydrogen isotope substitution to vary the diffraction contrast for the hydrogen atoms, combined with empirical potential structure refinement (EPSR) modeling. At this concentration, not only are both ions fully hydrated but there is also a sufficient number of water molecules present to ensure that there are water molecules present beyond the first hydration shells.

The measurements reported here can be distinguished from the previous data in that they were measured on a different diffractometer at a steady state reactor neutron source (the D4c diffractometer at the Institut Laue Langevin, France), compared to the previous data which were measured on the SANDALS diffractometer at the ISIS pulsed neutron source, U.K. These two different techniques of neutron diffraction, the former fixed energy and angle dispersive, the latter fixed angle and energy dispersive, lead to quite different inelastic responses from materials containing hydrogen. As a result the corrections for these inelastic responses are different, so these data are invaluable not only in their ability to provide further insight into the solvation of sodium hydroxide in aqueous solution, but also to provide a reliability check on the interpretation of data collected at different neutron sources, using angle dispersive versus energy dispersive diffraction, with different sample containment and sizes, and subsequently modeled using EPSR.

This has particular relevance in regard to a recent study which, by using reverse Monte Carlo simulation (RMC), came to the conclusion that widely different radial distribution functions (RDFs) could be extracted from analogous neutron diffraction data on pure water.[5,6] In that work the reliability of published RDFs of water was called into question, and it was stated at the end of the paper that "a definitive set of partial pair correlation functions…of liquid water may remain hidden for long." It was also stated in that work that "a method is needed that could characterize/quantify the reliability of a given measurement."[5] Given the different source of the data reported here compared to our previous published results on the NaOH-water system, it would seem that the present data provide an excellent opportunity to characterize and quantify the reliability of the measurements.

II. THEORETICAL BACKGROUND

A. Neutron diffraction

Neutron diffraction augmented by H/D substitution is the premier technique by which the structure of hydrogen containing liquids can be determined.[7–14] This is largely due to the fact that hydrogen and deuterium give rise to different scattering intensities when probed by neutrons. In addition, and unlike x-ray scattering, both isotopes have scattering intensities of the same order of magnitude as heavier elements.[15] The quantity obtained, after appropriate corrections,[16] in a neutron diffraction experiment is the interference differential scattering cross section, $F(Q)$, which is defined as

$$F(Q) = \sum_{\alpha\beta \geqslant \alpha} (2 - \delta_{\alpha\beta}) c_\alpha c_\beta b_\alpha b_\beta [S_{\alpha\beta}(Q) - 1], \tag{1}$$

where Q is the magnitude of the change in wave vector by the scattered neutrons, $Q=4\pi \sin\theta/\lambda$, c_α is the atomic fraction, and b_α is the scattering length of isotope α. $F(Q)$ is the neutron weighted sum of the Faber-Ziman partial structure factors, $S_{\alpha\beta}(Q)$, weighted by their composition and scattering intensity. $S_{\alpha\beta}(Q)$ is in turn related to the corresponding site-site radial distribution function RDF $[g_{\alpha\beta}(r)]$ via

$$S_{\alpha\beta}(Q) = \frac{4\pi\rho}{Q} \int r[g_{\alpha\beta}(r) - 1]\sin(Qr)dr, \tag{2}$$

where ρ is the atomic number density of the sample.

The object of the neutron diffraction experiment with isotope substitution is to vary the scattering contrast in (1) by substituting different isotopes for some or all of the atoms and so produce a set of diffraction patterns in which different partial structure factors have different weights. Then if the isotope substitutions are chosen carefully some or all of the partial structure factors can be extracted in favorable cases by inverting the scattering matrix,[17] to yield partial structure factors or composite partial structure factors as in the previous work.[3,4] However in the present work the extraction of partial structure factors has not been performed, but instead we model the interference differential cross section, (1), directly and then use the model to extract the relevant site-site radial distribution functions.

In order to understand the average local structure of a liquid, $g_{\alpha\beta}(r)$ can be integrated over a specified distance range to give the coordination number of atoms β around α atoms between two distances, r_1 and r_2, as

$$n_\alpha^\beta(r) = 4\pi c_\beta \rho \int_{r_1}^{r_2} g_{\alpha\beta}(r) r^2 dr. \tag{3}$$

B. EPSR

Empirical potential structure refinement (EPSR) was used to model the collected diffraction data. EPSR is a computational device created for modeling disordered materials such as liquids and glasses,[18,19] which allows a three-dimensional model to be constructed that is consistent with a set of one-dimensional structure factor measurements. EPSR begins with a standard Monte Carlo simulation using an initial reference potential consisting of an intramolecular harmonic potential to define the geometry of the molecules being modeled, and an intermolecular potential, which in this case consisted of Lennard-Jones 12-6 potentials with appropriate Coulomb potentials for the site-site interactions. This reference potential is used to generate a starting configuration of molecules. EPSR then iteratively introduces a perturbation to this reference potential to obtain the best possible agreement between the computed and experimental structure factors. As is the case with RMC,[5] EPSR provides a molecular ensemble which is consistent with the measured diffraction data, but it does not *a priori* guarantee a unique model for the structure of the liquid in question. There may be several distinct structures which give equally reasonable agreement between data and simulation.

By definition, ambiguities can only be removed by introducing as much known information into the problem as possible. In the present instance, for example, as the intramolecular structure of a water molecule is well known it is not necessary to rely solely on the diffraction data to provide this information given that the intramolecular water distances and standard deviations about these distances are well characterized by other measurements and calculations. However the diffraction data might help to *refine* that structure. Equally it seems fairly plausible in the present case that the Na and OH ions in solution will have charges, and that the water molecules will form hydrogen bonds with each other and with the ions. All this information can be built into the reference potential energy function at the outset. If the assumptions in this prior information are incorrect, a satisfactory fit to the data may still be obtained but, as stated above, obtaining a satisfactory fit to the diffraction data does not necessarily *guarantee* that the structure obtained is correct as there may be structural features which are not well measured using neutron diffraction. For example if the charges on the ions in the EPSR simulation were removed and the water molecules were prevented from forming hydrogen bonds, though a satisfactory fit to the diffraction data might be obtained, the resultant model would be physically meaningless as most of the known physics of the problem in question would have been ignored.

In this regard it is important to be quite clear about the technical distinctions between EPSR and RMC. Although in principle they are closely analogous, the two techniques are in fact approaching the problem from two rather different viewpoints. EPSR attempts to assume as much prior information as possible, in the hope that by pinning down the uncertainties at the outset, one has less chance of developing spurious or incorrect structures. RMC on the other hand, as a general rule, is attempting to assume as little as possible prior information about the structure of the system before structure refinement,[20,21] and in that sense will produce the most disordered structure consistent with the data. The RMC method works well for many atomic liquids and glasses, where the local structure is well defined by pair correlations. However when investigating molecular liquids, this approach runs into difficulties, because the pair approximation is not usually an adequate assumption in those cases. Molecules are governed by complex, many body forces, which in general cannot be defined purely by pairwise additive correlations as there are almost always significant overlaps between intramolecular and intermolecular distances.

When modeling a molecular fluid with RMC, it is usual to define molecules via a series of coordination constraints,[5,13,22] to account for intramolecular bonds. Such "square well" interactions are highly unphysical since the near neighbor intramolecular forces are believed to be quasiharmonic in form, and the resulting atom-atom intramolecular distribution functions are Gaussian in nature.[23] Furthermore in RMC the only constraint on atomic overlap is a hard sphere potential which prevents atoms lying on top of one another. Yet in water it is widely believed that water molecules interact via hydrogen bonds. These hydrogen bonds produce attractive and repulsive forces in different directions and depending on the orientation of neighboring molecules. Therefore if the model specifically ignores hydrogen bonding, it is not surprising if the result consists of widely variant structures which are strongly dependent on the particular set of data being analyzed. This is because for molecular systems the one-dimensional diffraction data by themselves, where only the pairwise interactions are directly measured, do not contain all the necessary information to characterize the full three-dimensional and orientational structure, even in the rare instance that a full set of partial structure factors can be extracted. This point has been discussed extensively by many authors—see, for example, the discussion in Gray and Gubbins,[24] and the point was also proven in a recent test.[25] Additionally, another recent work[26] studied pure heavy water under extreme pressures and temperatures, but nonetheless useful data on the site-site RDFs were extracted because the structural model assumed at the outset that the water molecules had a specified structure and that hydrogen bonding would occur between them. Without those assumptions, the outcome of the structure refinement would have been meaningless. Hence RMC cannot be expected to give meaningful results when used to interpret molecular diffraction data without constraints, since in general it ignores fundamental aspects of the intermolecular forces that might be present right from the outset. On the other hand when refining a structure *without* assuming prior information, RMC can be very helpful in identifying structural aspects of the system to which the data are truly sensitive.

TABLE I. Samples measured by neutron diffraction and the appropriate sample size for each measurement.

Sample	Composition	Sample size (nm)
I	$2M$ NaOH in H_2O	2.40
II	$2M$ $NaOH_{1/2}D_{1/2}$ in HDO	4.10
III	$2M$ NaOD in D_2O	4.10

III. EXPERIMENTAL AND MODELING PROCEDURES

Ultra-pure NaOH (99.99%), 40 wt. % $NaOD/D_2O$, and D_2O (99.8%) were purchased from Sigma-Aldrich Chemical Company and were used without further purification. The NaOD solution was diluted to the appropriate concentration with D_2O. The samples measured are listed in Table I where in each case the concentrations of the solution were $2M$ giving the composition of $\sim 1:28$ $NaOH:H_2O$ molecules. The samples were measured in cylindrical containers constructed from a *null* Ti/Zr alloy. The use of this alloy allows for minimal coherent scattering from the sample container leading to a more tractable data analysis for the samples themselves. In addition each of the containers was lined with 0.05 mm wall thickness PTFE® tubing. Each sample container has a 1 mm wall thickness and the internal sample diameter of each sample is listed in Table I. Note the different sample geometry used in this work compared to the previous work on hydroxide solutions.[3,4,27]

The neutron diffraction data were collected on the D4c diffractometer on the high flux reactor source at the Institut Laue Langevin in Grenoble, France. Measurements were taken for each of the samples as well as for the empty sample containers in order to ensure an effective background subtraction. The raw data for the NaOH solutions (Table I) have been converted to the structure factor, after correcting for absorption, multiple scattering, and inelasticity effects, by using a program, Gudrun, which is a new version of the previous ATLAS suite of programs available at ISIS.[16] In the diffraction pattern the level of $d\sigma/d\Omega$ was checked after the application of corrections by comparison with theoretical values based on the known density and composition of the sample in question.[15] In each case the level of scatter was below the expected level, likely due to machining uncertainties on the interior of the sample container given the PTFE® liners. For this reason in each diffraction pattern the effective thickness of each sample was adjusted until the scattering level was within 1% of the expected value at low Q values.

The EPSR model was begun by building a box of molecules at the appropriate density, namely 0.1 atoms Å^{-3}, which contained 20 Na^+, 20 OH^- ions, and 560 water molecules. The starting potentials used for the EPSR fits to the data are listed in Table II where the potentials for NaOH were taken from Botti *et al.*[3] and the SPC/E potentials were used for water.[28] O_w and H_w refer to the oxygen and hydrogen atoms on the water molecule, respectively. The potential parameters for Na^+ and OH^- were chosen to ensure that the charge on the H site in the OH^- ion is identical to the charge on the hydrogen site in water H_w. The other parameters for

TABLE II. EPSR reference potentials for fits to the neutron diffraction data.

Atom	ε (kJ·mol^{-1})	σ (Å)	q_e
O_w	0.65	3.166	−0.8476
H_w	0.0	0.0	0.4238
Na	0.125	2.5	0.6791
O	0.87864	2.96	−1.0290
H	0.184	1.443	0.42380

NaOH have subsequently been adjusted accordingly to not only to charge balance the system but also to drive the simulation towards a good fit. Nevertheless a good fit can also be achieved by using a different parameter set, given that EPSR can compensate for small differences in the starting reference potentials and empirical potential, provided that the reference potential is reasonably realistic. It should be noted that the three measured data sets were simultaneously fit by *one* EPSR model.

IV. RESULTS

The measured diffraction data $F(Q)$ along with the EPSR fits to the data are shown in Fig. 1. The EPSR fits to the data are excellent in each case except at low Q ($Q \leqslant 2.0$ Å^{-1}) in the hydrogen containing samples (I and II) where the background and inelasticity corrections to the data are most difficult to remove. The diffraction data are the sum of all of the partial structure factors for each atom-atom interaction and it is not possible to extract each individual structure factor and thereby atom-atom correlations from measurement of the data alone. However from the EPSR model it is possible to extract each of the individual site-site radial distribution functions (RDF's) and in the present study the RDF's relevant to the discussion below are shown.

A. Water structure

Figure 2 shows the RDF's for the water-water interactions in the NaOH/H_2O system compared with those from pure water, and Table III shows the respective coordination numbers for these functions.[7] In each of the three RDF's the first peak has become broader and shorter upon the addition of NaOH. In the $g_{\mathrm{OwOw}}(r)$ function the first nearest neighbor distance (2.8 Å) is not affected by the presence of the ions. However the second nearest neighbor peak maximum is at a shorter distance than in the case of pure water, specifically, this peak shortens by 0.3 ± 0.1 Å upon the addition of NaOH. Figure 3 shows a comparison between the $g_{\mathrm{OwOw}}(r)$ function from the present study (Fig. 2), compared with the same function for higher concentration solutions measured previously.[3,4] It is clear from this figure that the second peak position shortens at higher concentrations and moreover that this shift is concentration dependent, with the shortest distance being seen in the 12M concentration. The shortening of this peak is similar to the effect seen in pure water under

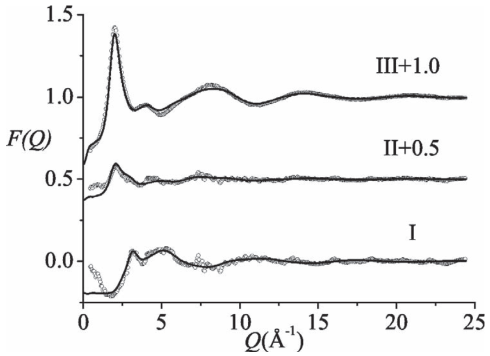

FIG. 1. Measured diffraction data (circles) and subsequent EPSR fits to the data (solid line) for (I) 2M NaOH in H_2O, (II) 2M $NaOH_{1/2}D_{1/2}$ in HDO (+0.5), and (III) 2M NaOD in D_2O.

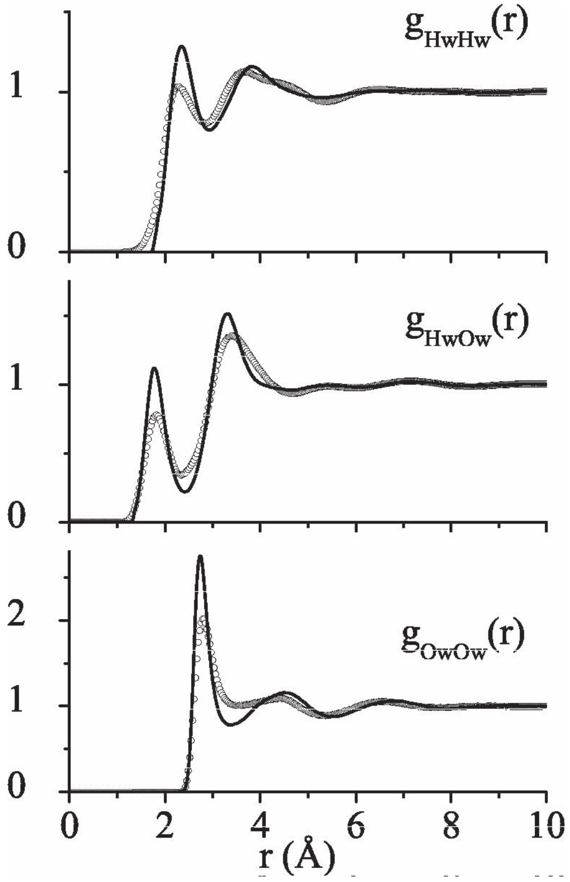

FIG. 2. Water-water RDF's from the EPSR fits 28:1 NaOH:water data (circles) compared with water-water RDF's for pure water (lines) (Ref. 7).

TABLE III. Coordination numbers for the water radial distribution functions for the NaOH/water system and pure water (Ref. 7).

RDF	$n_\alpha^\beta(r)$ water	$n_\alpha^\beta(r)$ NaOH/water	$r_{\min}$ (Å)
$g_{\mathrm{OwOw}}(r)$	~4.5–5	4.2	3.36
$g_{\mathrm{OwHw}}(r)$	~1.8	1.6	2.37
$g_{\mathrm{HwHw}}(r)$	~4–5	4.1	2.85

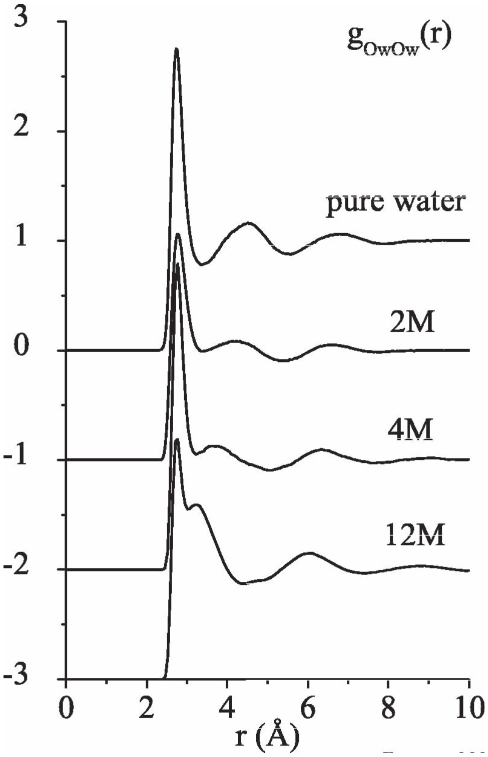

FIG. 3. $g_{\mathrm{O}w\mathrm{O}w}(r)$ functions for pure water (Ref. 7) and different concentration NaOH/H_2O solutions (4M and 12M are taken from Ref. 3).

pressure.[18,29] Figure 4 shows the equivalent pressure which needs to be applied to pure water in order to obtain the same shift in the peak position. Structurally, there is little difference between the water-water correlations in the 2M electrolytic solution under ambient pressure and pure water under a pressure of ~100 MPa.[30] Moreover, the net electrostrictive pressure on water molecules increases with increasing concentration of ions,[4] until the number of water molecules is unable to fully hydrate all the ions present in the solution at which point the pressure reaches a plateau. It should be noted that the 12M concentration is quite concentrated and as such there are insufficient water molecules present to solvate each ion.

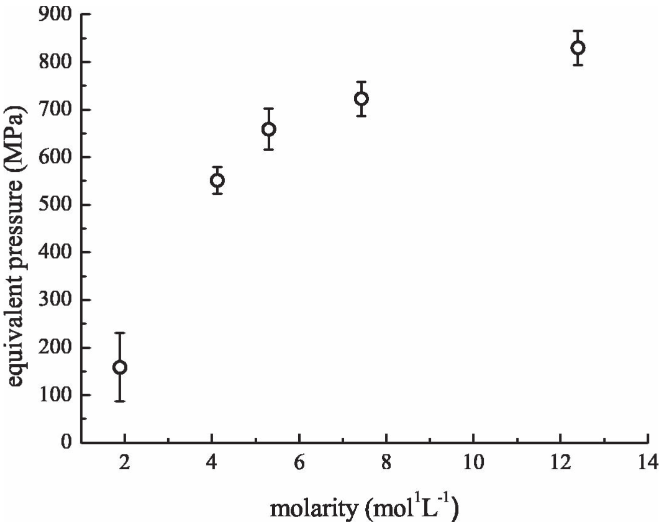

FIG. 4. Equivalent pressures for different NaOH solutions vs molarity calculated according to Ref. 2; the 2M solution is compared with points obtained from Ref. 3.

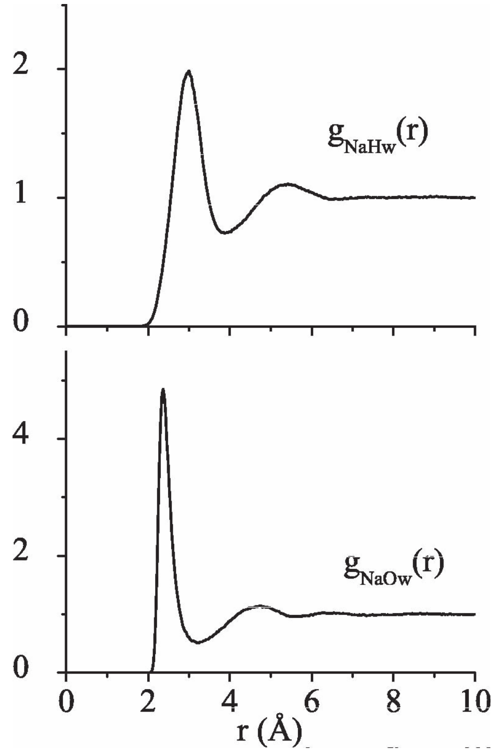

FIG. 5. Na^+-water RDF's from the EPSR fits to the diffraction data.

B. Ion-water interactions

Figure 5 shows the RDF's from the EPSR fits to the data for the Na^+-water interactions and Table IV shows the coordination numbers for these functions. The first peak in $g_{\mathrm{NaO}w}(r)$ is located at ~2.4 Å, while the first peak in $g_{\mathrm{NaH}w}(r)$ is around 3.0 Å, similar to the previously reported 4M solution. In the higher concentration solutions (4M–12M) there was a small feature present in the $g_{\mathrm{NaH}w}(r)$ function *before* the main peak at 3 Å which increased in intensity with increasing molarity. This peak was attributed to water molecules being shared between the two hydration shells, namely the OH^- first hydration shell and the Na^+ first hydration shell as a result of the high concentration. This peak is completely absent when the solution is diluted to 2M; implying that each ion is fully hydrated.

Figure 6 shows the RDF's from the EPSR fits to the data for the hydroxide-water interactions and Table V shows the

TABLE IV. Coordination numbers for Na^+-water RDF's.

RDF	$n_\alpha^\beta(r)$	$r_{\min}$ (Å)
$g_{\mathrm{NaO}w}(r)$	5.3	3.24
$g_{\mathrm{NaH}w}(r)$	15.2	3.87

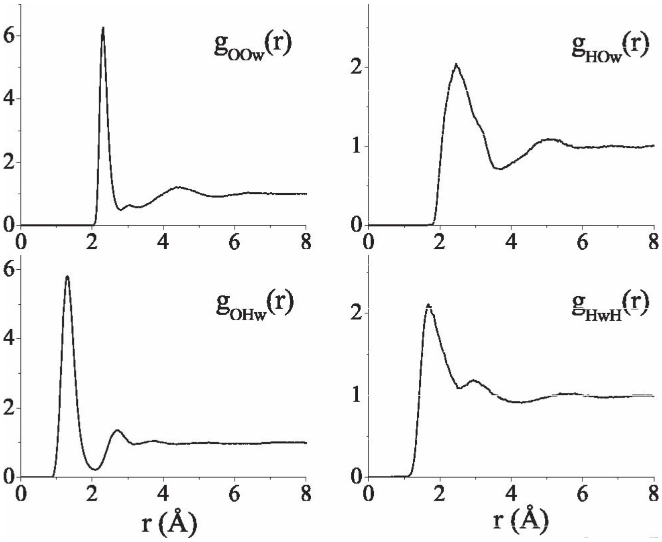

FIG. 6. OH$^-$-water RDF's from EPSR fits to the data.

coordination numbers for these functions. The first peak in $g_{\mathrm{OO}w}(r)$ appears at 2.3 Å while the second peak is located at ~4.4 Å. The coordination number for the first peak is 4.2 (Table V) showing a higher coordination than is seen in the more concentrated solutions where the coordination number of the first peak in the $g_{\mathrm{OO}w}(r)$ function varies from 3.9 at 4*M* to 2.9 at 12*M*. Additionally there is a small feature present in this function between the two primary peaks at approximately 3 Å. The coordination number indicates there is one water molecule present at this location. This water molecule contributes to the intensity of the broad peak in the $g_{\mathrm{HO}w}(r)$ function, starting from 2 Å, which can be attributed to the hydrogen bonding distance between hydroxide hydrogen and the water oxygen (O_w). This hydrogen bond is weak, as was shown in the previous studies,[4] given its distance, compared to the hydrogen bond length seen in water.[18]

V. DISCUSSION

In the results presented here we have deliberately refrained from repeating material already published in the previous papers in this series, unless it is pertinent to the present discussion. For example the spatial density function of water around the hydroxide ion is not shown in the present work though this function is similar to what has been shown previously. What is of primary importance here is that the present solutions contain a lower concentration of sodium hydroxide than has been measured previously. Additionally, the data in the present study were measured on a different neutron source with angle dispersive neutron diffraction instead of energy dispersive neutron diffraction, and are nonetheless consistent with the previous data measured. Also, in this case the $F(Q)$ diffraction data have been fitted by the EPSR model as opposed to the composite partial structure factors in the previous studies on these systems.[3,4] However, it has recently been shown that both of these functions can be fit with equivalent accuracy, and lead to equivalent structural conclusions.[31] Moreover, the EPSR model of the diffraction data shows trends with increasing dilution which are consistent with the previous results on the NaOH in aqueous solution. In particular, the effect of reduced electrostriction in these more dilute solutions can be clearly seen (Figs. 3 and 4), a trend which is closely mirrored in a first principles computer simulation study of hydroxide ions in solution.[32] The trend in hydroxide hydration with increased dilution is towards larger coordination numbers, rather than smaller coordination numbers as has been predicted in some cases.[33,34] This therefore reinforces the ideas of Tuckerman *et al.*[35] based on *ab initio* simulations that the nature of proton exchange with a hydroxide ion is different compared to the proton in solution, and does not follow the traditional view that the two types of exchange should be symmetric with each other, involving just three water molecules around both hydroxide or hydrogen ion.[33,34]

TABLE V. Coordination numbers for water-OH-RDF's.

RDF	$n_{\alpha}^{\beta}(r)$	r_{min} (Å)
$g_{\mathrm{OO}w}(r)$	4.2	2.82
	5.2	3.3
$g_{\mathrm{HO}w}(r)$	7.4	3.69
$g_{\mathrm{OH}w}(r)$	4.1	2.10
	9.9	3.15
$g_{\mathrm{HH}w}(r)$	5.9	2.58
	19.8	4.05

A second feature of this study is that in spite of the different data correction regimes between the two types of neutron diffraction techniques,[17] the outcome after empirical potential structure refinement is quite consistent with previous analyses on similar solutions. This is in contradistinction to the analysis of Pusztai,[5] which concluded after RMC simulation that a range of quite different site-site RDFs might be consistent with the available diffraction data on pure water. The obvious difference between the previous RMC analyses[5,6] and the present EPSR analysis is the reference potential which in RMC contains limited prior information about both the molecular structure and the interactions between molecules. In fact in our earlier study of pure water[25] we deliberately omitted one or more of the diffraction data sets for the structure refinement, and found that unless the hydrogen bonding interaction was included in the reference potential, attempting to refine the structure with only one or two data sets could indeed lead to spurious results. This does not negate the structure refinement method but rather reinforces it. Structure refinement in such cases serves to provide information on the dependency of the diffraction data on the site-site RDF's.

It is undoubtedly true that most neutron diffraction data, particularly those from materials containing hydrogen, are subject to systematic uncertainties. These are believed to arise primarily from the inelastic response of the material to collisions with the neutron. The theory of neutron scattering states that these inelasticity effects will appear as a background to the interference diffraction pattern being sought,[17] Eq. (1) and Fig. 1. Since they are not structural in origin, they are generally unlikely to be fit by a structural model of the system. For pulsed neutron diffraction the inelasticity effects appear mostly as a rise in the scattering at small Q ($Q < 2$ Å^{-1}). In fixed incident energy, angle dispersive, neutron diffraction data these effects appear as a very marked fall off in the scattering level at high scattering angles. Currently it is difficult or impossible to estimate these inelasticity effects with sufficient accuracy to be able to remove them quantitatively, and typically the procedure is to use a polynomial or equivalent expression to remove the main inelastic contribution approximately, with the aim that any residual inelastic scattering in the data will not cause an excessive perturbation to the refined structural model. Here we have used a completely different data set from a different source, compared to the previous work on this system, and obtained results that are clearly consistent with the previous analysis. Since the inelastic contributions in the present work are different in nature to those of the earlier work, yet the outcomes are similar, this lends support to the idea that EPSR with its heavily constrained molecules and starting reference potentials is able to extract useful structural information concerning the local order in solution, even in the presence of systematic inelasticity effects in the data. Without these constraining potentials and defined molecules, it is likely the outcome would be far less certain as was demonstrated by Pusztai.[5,6]

VI. CONCLUSIONS

In comparison with more concentrated solutions of NaOH previously measured by neutron diffraction,[3,4] the number of water molecules in the 2M NaOH solution is sufficient in number to fully hydrate both ions as well as providing enough molecules for a second hydration shell. The effect of adding these ions to water results in a marked compression of the second shell towards the first and by comparison with the analysis of the previously measured concentrations shows that the degree of this compression is concentration dependent.

The hydroxide ion hydration shell, as described by the present data, confirms previous results,[3] namely that the first hydration shell of water molecules directly bonded to the hydroxide oxygen contains about four molecules at lower concentrations and one water molecule weakly bonded to the hydroxide hydrogen. This is particularly relevant because it is known that the water molecule at this location plays a key role in the transport mechanism of hydroxide ions in water, as predicted by *ab initio* simulations.[35] There is no sign of the predicted decrease in this coordination number with increasing dilution.[34] The measurements presented here are in agreement with the trends seen in the water-water correlations and the solute-solvent interactions upon the addition of NaOH to water in previous work. They demonstrate the consistency not only of the experimental data on isotopomeric samples collected on different diffraction sources but also of the EPSR method itself. The previously reported concentrations were collected at the ISIS spallation source with flat plate sample geometry, while here the samples were of a cylindrical shape and measured at a reactor source. This is indicative that the structures of hydrogen containing fluids as measured by neutron diffraction and when interpreted via a realistic modeling regime are indeed reliable.

ACKNOWLEDGMENTS

The authors would like to thank the U.S. National Science Foundation for financial support for S.E.M. (Grant No. OISE-0404938) and G. Cuello (ILL), A. Wright, and R. Haworth (both from University of Reading, UK) for assistance with the neutron diffraction measurements.

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