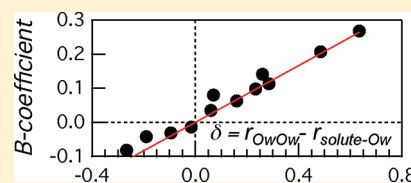


Viscosity of Aqueous Solutions and Local Microscopic Structure

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ABSTRACT: The effect of solutes on the structure of water has been debated intensively over the past years. Typical scenarios label different ions as water structure “makers” or “breakers”: this is a quite elusive definition, which has been first introduced in the description of the effect of solutes on the viscosity of water and, although criticized, is still used in the current literature. Here, using a combination of neutron diffraction and computer modeling, we present a possible relation between the viscosity B coefficient and a local structural property of the solution. In particular, B appears in the Jones–Dole relation and its sign is traditionally used to characterize a solute as “structure maker” or “breaker”. We find that B is linearly correlated to the difference between the average solute–water distance and the water–water distance in the pure liquid, in the case of monovalent electrolyte solutions.



INTRODUCTION

Ion–water interactions represent a central topic in chemistry and biology. As first suggested by Cox and Wolfenden¹ in 1934, the structure and dynamics of water, and in particular of its hydrogen bond network, are perturbed by ions, yet the extent and nature of this ion induced modification are still far from being resolved after more than 70 years of intense research.^{2–5} Moreover, although experimental and theoretical approaches now allow a microscopic insight of the water structure and hydrogen bonding in the presence of solutes, a consensus connection between such a microscopic investigation and macroscopic properties of the aqueous solution is still lacking.

The traditional and accepted view⁶ distinguishes ions as being either kosmotropes, structure-makers (from Greek *kosmos* meaning order), or chaotropes, structure-breakers (from Greek *chaos* meaning disorder), on the basis of their ability to increase or decrease water structure, although it has to be said that what is meant by structure in this context is somewhat ambiguous. One measure of whether a solute is a structure maker or breaker is the effect it has on the viscosity of the solution compared to the viscosity of pure water: solutes that increase the viscosity compared to that for pure water are considered structure makers (kosmotropes), whereas those that decrease the viscosity of the solution compared to that for pure water are considered structure breakers (chaotropes). This kind of empirical evidence has led to a distinction between kosmotropes and chaotropes based on the sign of the viscosity B coefficient appearing in the well-known Jones–Dole expression for the relative viscosity of a solution:^{7,8}

$$\eta/\eta_w = 1 + Ac^{1/2} + Bc \quad (1)$$

Here η_w is the viscosity of pure water, c is the solute concentration, and A and B are coefficients that depend on the solute and the solvent. The A term depends on interionic forces and is always positive. In practice, this term is negligible, compared to the B term, for the univalent solutes in the concentration range examined (see ref 8 and Table 1). The B term depends on ion–solvent interactions; it can be positive or negative and is

Table 1. Parameters of the Aqueous Solutions Used in the Empirical Potential Structure Refinement

sample	N_w	N_s	box size (Å)	ρ (atoms/Å ³)	m (mol/kg)
LiOH	830	10	29.18	0.1014	0.67
	951	34	30.53	0.1038	1.85
NaOH	835	10	29.00	0.1013	0.67
	900	18	30.00	0.1022	1.11
	948	25	30.50	0.1028	1.47
KOH	819	10	29.12	0.1007	0.68
	964	34	30.87	0.1017	1.96

related to the volumes of the ions, but so far in a theoretically inaccessible manner.^{2,4,8} Do ions that create greater viscosity in water actually give rise to enhanced structural features? Equally the observation that negative B values are found almost exclusively in water as a solvent⁸ is puzzling and suggests a closer look at the kind and range of perturbation of water structure caused by dissolved ions.

To date a coherent picture of whether dissolved ions lead to increased or decreased water structure is lacking. On the one hand, after a series of femtosecond pump–probe spectroscopic studies on dilute and concentrated $\text{Mg}(\text{Cl}_4)_2$, NaClO_4 , and Na_2SO_4 aqueous solutions, Bakker and colleagues^{9,10} argued that the presence of ions does not lead to an enhancement or a breakdown of the hydrogen-bond network in liquid water, therefore challenging the notion that ions affect bulk water structure. As a consequence, it was claimed that, using the Einstein–Stokes equation, “a 30% increase of the viscosity, as observed for a 1 M $\text{Mg}(\text{ClO}_4)_2$ solution, can be obtained with a solution of 1 M suspended spheres that have a radius of about 3.6 Å. This radius is

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similar to the radius of an ion and its first solvation shell of water molecules". Hence, the increase in viscosity upon adding ions to water can be fully explained^{9,10} from the rigid nature of the solvation structure formed by the ion and its first solvation shell. Although the same argument cannot be used to explain the reduction of viscosity due to addition of solutes, more recent work by the same group has modified the claim on the negligible perturbation brought by solutes.¹¹

On the other hand, structural data derived from the neutron diffraction method and modeled using empirical potential structure refinement (EPSR) have shown that the effect of monovalent ions in solution extends beyond the first hydration shell of the ions.¹²

In particular, the perturbation due to ions is visible as a clear change of the water oxygen–oxygen correlation function, compared to the case for neat water, in a manner closely analogous to what happens in bulk water under external pressure.¹³ The straightforward conclusion is that the hydrogen bond network of water molecules is altered by the presence of solutes even at relatively large distance from the solute. Such intriguing similarity between pressure and solute effects on water has also been found in Raman spectroscopy¹⁴ and in a recent molecular dynamics simulation study,¹⁵ which went as far as to claim that pressure and solute effects could be taken as "two sides of the same coin". Yet all solutes determine an increase of what has been named "equivalent pressure", irrespectively of the sign of B .

In this work we present the analysis of new and already published neutron diffraction data on aqueous solutions of monovalent electrolytes, aimed at identifying a structural parameter which may be correlated with B , and changes sign as B does.

EXPERIMENTAL AND NUMERICAL METHODS

Our approach is to combine experimental neutron diffraction data with an appropriate computer simulation method (EPSR),¹⁶ which refines the molecular structure against the diffraction data.

The new data have been taken on alkali hydroxide solutions with different cations (Li^+ , Na^+ , and K^+) at solute concentration, ranging from 1 solute to 28 water molecules to 1 solute to 83 water molecules (Table 1), at ambient conditions. Each experiment required three diffraction measurements on samples with different H/D contents.^{17,18} This allowed the extraction of three differential cross sections (DCS),

$$F(Q) = \sum_{\alpha} \sum_{\beta \neq \alpha} w_{\alpha\beta} [S_{\alpha\beta}(Q) - 1] \quad (2)$$

where Q , the momentum transferred in the interaction between a neutron and a nucleus, is defined as a function of the neutron wavelength λ and the scattering angle 2θ by

$$Q = \frac{4\pi}{\lambda} \sin \theta \quad (3)$$

and the weighting factors $w_{\alpha\beta} = c_{\alpha}c_{\beta}b_{\alpha}b_{\beta}(2 - \delta_{\alpha\beta})$ depend on the atomic fractions, c_{α} and c_{β} , and on the neutron scattering lengths,¹⁹ b_{α} and b_{β} , of the $\alpha\beta$ atom pairs. The Kronecker $\delta_{\alpha\beta}$ avoids double counting of like terms in the summation. The $S_{\alpha\beta}(Q)$ are called partial structure factors (PSF) and are defined as Fourier transforms of the corresponding radial distribution

functions of the $\alpha\beta$ pair, $g_{\alpha\beta}(r)$;

$$S_{\alpha\beta}(Q) - 1 = 4\pi\rho \int_0^{\infty} r^2 [g_{\alpha\beta}(r) - 1] \frac{\sin Qr}{Qr} dr \quad (4)$$

In pure water with only two distinct atomic sites, H and O, three site–site radial distribution functions, namely O–O, O–H, and H–H, can in principle be calculated as Fourier transforms of the corresponding partial structure factors, making the experiment fully exhaustive. The aqueous solutions investigated in the present report contain five distinct atomic components, namely the cation, H and O of the hydroxide anion, and the water hydrogen and water oxygen. A full structural characterization of the system therefore requires the determination of 15 site–site radial distribution functions, which is well beyond the possibility of any existing diffraction techniques by themselves. Therefore, a complete picture of the solutions can only be obtained by means of an appropriate computer simulation, as described below.

The experiment was performed on the small angle neutron diffractometer for amorphous and liquid samples (SANDALS)²⁰ diffractometer at the ISIS spallation neutron source. The sample containers were standard Ti–Zr flat cells (1 mm wall thickness, 1 mm sample thickness), accommodated in the sample changer available on SANDALS.

Details of correcting the raw diffraction data for absorption, multiple scattering, and inelasticity effects are fully described in ref 21 and briefly outlined in refs 17 and 22. The output of the analysis routines are the three differential cross sections (DCS) (Figure 1). These functions contain ion–water and ion–ion correlations as well as the water–water correlations.

The complete set of DCS is used to drive the EPSR routine, which has lately been tested¹⁶ and used to analyze data on both aqueous and nonaqueous solutions.^{12,13,17,18,22–32} Briefly, this routine starts by building a simulation box with the same density and composition as the real sample (Table 1) using a reference pairwise-additive effective potential that attempts to catch the distinctive characteristics of the system under investigation (such as the presence of hydrogen bonds, and ionic charges, for instance). The parameters for this potential are typically drawn from previous computer simulations of the system in question, such as those used in ref 22 (Table 2). Periodic boundary conditions are imposed. A perturbation to this reference potential, called the empirical potential, is then introduced and adjusted iteratively until the simulated DCS converges to a satisfactory fit of the measured ones (Figure 1). In the EPSR routine the acceptance of a move is based on the usual Metropolis condition, according to the probability $p = \exp(-\Delta U/k_{\text{B}}T)$, where ΔU is the change in potential energy of the system as a result of the move. This procedure ensures that the system proceeds along a Markov chain covering a wide range of phase space compatible with the data. The resulting molecular ensembles, representing a model of the solution investigated, can be used to derive site–site radial distribution functions, as well as many further features of the microscopic structure not directly accessible from diffraction data.

RESULTS

What then determines if an ion is labeled as a structure maker or breaker? In trying to answer this question, we have analyzed the results of the present experiment along with those already published for other aqueous solutions.^{12,18,22–29}

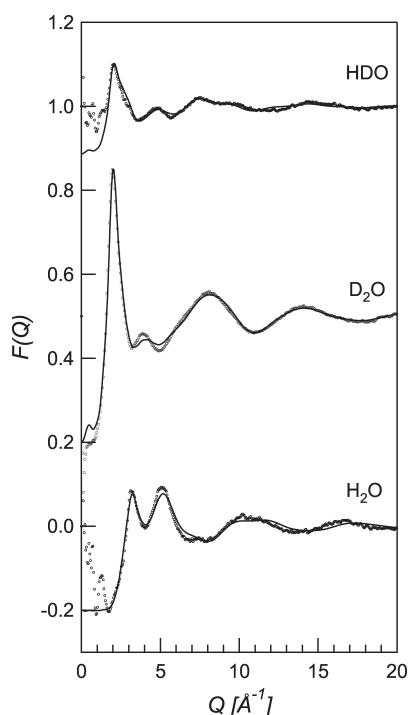


Figure 1. Differential cross sections for the 0.67 *m* NaOH aqueous solution (dots) along with the fit (solid line) obtained with the EPSR code. The labels H-solution, D-solution, and HD-solution indicate a fully hydrogenated, a fully deuterated, and an equimolar HD hydroxide solution, respectively. Small misfits in the low-*Q* region are likely due to a failure of the data reduction to completely remove the large recoil effects due to the interaction of neutrons with the hydrogens. However, this recoil effect is expected to have only a monotonic dependence on *Q* and so is unlikely to influence the model structure to any significant extent. It should be noted that small misfits near $Q = 4 \text{ \AA}^{-1}$ and above, observable for the deuterated and the hydrogenated solutions, are due to a small difference in length between the intramolecular OH and OD bonds³² and as such do not affect the intermolecular structure. Both D- and HD-solution DCS have been vertically shifted for clarity. Similar agreement between simulated and experimental DCS are obtained for all the hydroxide solutions examined in the present study.

Table 2. Lennard-Jones Parameters, Fractional Charges, and Atomic Mass Used in the Empirical Potential Structure Refinement Simulation Code^a

atomic site	ϵ/k (kJ/mol)	σ (Å)	q/e	m
Li	0.690	1.51	0.6791	7
Na	0.125	2.50	0.6791	23
K	0.500	3.00	0.6791	39
O	0.251 (0.50)	2.75 (2.30)	−1.1029	16
H	0.184 (0.30)	1.44 (1.00)	0.4238	2
O_w	0.650	3.17	−0.8476	16
H_w	0.00	0.00	0.4238	2

^a Values shown in parentheses have been used for the KOH solutions.²² O_w and H_w indicate water oxygen and hydrogen, respectively.

A measure of the extent of the effect of solutes on the water hydrogen bond network might be obtained by performing a cluster analysis on the simulated molecular distributions. The rationale here is that the distinction between solutes as structure makers or breakers might be linked to the “making” or “breaking”

of the hydrogen bond network of water, and consequently to the dimension of the largest water cluster in the solution, with respect to the case of pure water. The details of the cluster analysis are given in the Appendix. Briefly, the main outcome is that the hydrogen bond network percolates at any ion concentration and the distortion or fragmentation of the percolating water cluster is enhanced with concentration, without distinction for all the solutes analyzed. This means that the dimension of the water clusters cannot be correlated with the behavior of the viscosity (i.e., with the *B* coefficient), being monotonic with respect to the solute, as the already mentioned “equivalent pressure”. As a consequence, according to the above criterion, all solutes should be considered as “structure breakers”.

The puzzling picture that emerges from the experimental evidence so far is that of solutes that do not alter considerably the size of the water hydrogen bond network, yet they increase (or decrease) considerably the viscosity of water. To tackle this question, here we propose to put aside the hydrogen bond network and look instead for a different description.

The Macedo–Litovitz model for the viscosity and diffusivity of liquids^{33,34} puts into evidence the relevance of the local environment of a molecule in determining each diffusive step in dense liquids, resulting in two independent terms. These are energy fluctuations, which allow us to overcome the energy barrier between two minima of the configurational energy, and density fluctuations, which leave enough free volume in which to move. Both these fluctuations may be favored or disfavored by the presence of ions. When an ion substitutes a water molecule in the solution, it may push in or draw out its first neighboring water molecules, relative to their original position, depending on its charge and size. This local change of the microscopic structure does affect both the energy landscape experienced by neighboring water molecules and their local density. We have identified a useful parameter for measuring this effect, by comparing the average ion–water oxygen distance to the oxygen–oxygen distance in pure water. This is done by looking at the corresponding site–site radial distribution functions and introducing the quantity δ , defined as the difference between the first neighbor oxygen–oxygen distance in neat water ($O_w-O_w = 2.81 \text{ \AA}$) and the average solute–water oxygen distance in solution:

$$\delta = r_{O_w - O_w} - r_{\text{solute} - O_w} \quad (5)$$

The solute–water oxygen distance is obtained by averaging the anion–water oxygen and the cation–water oxygen distances taken from the corresponding site–site radial distribution functions. For solutes like NaCl this is straightforward, as the distances between each monatomic ion and the first neighbor water oxygen are easily identified in the corresponding site–site radial distribution functions. In other words, the position of the first peak of the ion–water oxygen radial distribution function is taken as the ion– O_w distance. For solutes like NaOH or KSCN, dissociating in polyatomic ions like OH^- and SCN^- , the calculation of δ requires additional information related to the identity of the atomic site of the ion that is actually interacting with first neighbor water oxygen. Earlier studies on the hydration of the hydroxyl ion^{22,23} and of the SCN^- ion¹⁸ indicated that the atomic site interacting with the closest O_w is the oxygen of the hydroxyl ion and that the negative charge on the SCN^- ion is equally distributed on the S and N sites, and consequently, this ion can coordinate a water molecule at both ends. The

Table 3. *B* Coefficients and First-Neighbor Distances between Water Oxygen and Cation (C) or Anion (A) for All the Solutes Here Considered, along with the Values of $\delta = r_{\text{O}_w-\text{O}_w} - r_{\text{solute}-\text{O}_w}$ ^a

solute	<i>B</i> (dm ³ /mol)	<i>r</i> _{O_wC} (Å)	<i>r</i> _{O_wA} (Å)	δ (Å)
KI	−0.08	2.62	3.54	−0.27
KBr	−0.04	2.65	3.35	−0.19
KSCN	−0.03	2.65	3.16	−0.10
KCl	−0.01	2.62	3.04	−0.02
HBr	0.04	2.10	3.40	0.06
HCl	0.06	2.10	3.20	0.16
NaCl	0.08	2.33	3.15	0.07
KF	0.10	2.65	2.50	0.23
KOH	0.11	2.80	2.25	0.29
LiCl	0.14	1.95	3.15	0.26
NaOH	0.21	2.40	2.25	0.49
LiOH	0.27	2.10	2.25	0.64

^a $r_{\text{O}_w-\text{O}_w} = 2.81$ Å and $r_{\text{solute}-\text{O}_w} = 0.5 \cdot (r_{\text{O}_w\text{C}} + r_{\text{O}_w\text{A}})$.

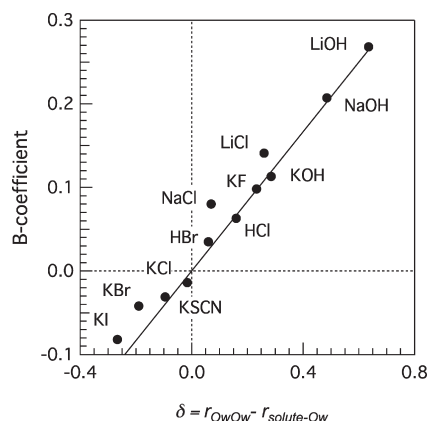


Figure 2. Viscosity *B* coefficient, appearing in the Jones–Dole expression, as a function of δ , namely, the distance difference between two first neighbor oxygens in neat water and solute–first neighbor oxygen in solution. The quantity δ is a measure of the ability of a given ion to draw in or draw out water molecules in its first hydration shell. The solute–water oxygen distance is obtained by averaging the anion–water oxygen and the cation–water oxygen distances taken from the corresponding site–site radial distribution functions. *B* coefficient of the solute, on the vertical axes, is the sum of the *B* coefficients of the ionic species in solution.⁸ The graph shows a linear fit with a slope $(0.416 \pm 0.024) \times 10^7$ m²/mol and the intercept set to 0. If the linear fit is done without the constraint on the value of the intercept, then this is equal to $(0.01724 \pm 0.0060) \times 10^{-3}$ m³/mol and the slope $(0.388 \pm 0.021) \times 10^7$ m²/mol. The linear correlation factor of both linear regressions is very close to unity and acceptable within the confidence level of 95%, and consequently, statistical analysis via the *F*-test confirms that the fit with the constraint on the intercept is to be preferred.

water–solute (KSCN) distance can be therefore averaged over K–O, S–O, and N–O distances. For HCl and HBr, the distances between water oxygen and their cations have been obtained by considering the distance between H₃O⁺ and the nearest water oxygen,^{24,28} i.e., by averaging the hydronium oxygen and hydrogen distances from the water oxygen, as in the case of SCN[−]. All the ion–water oxygen distances of interest are reported along with the corresponding *B* and δ values, in Table 3.

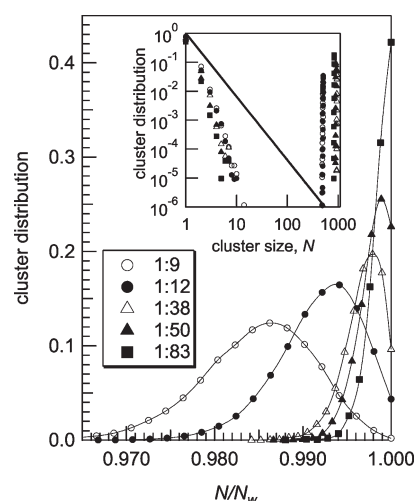


Figure 3. Cluster size distribution for all the NaOH solutions investigated in the present study (solute/water ratios 1:83, 1:50, and 1:38) and in a previous article.²³ The enlarged view of the percolating cluster distribution of hydrogen bonded water molecules in the simulation box, normalized by the total number of water molecules *N_w* in the box (Table 1). Similar results are obtained for all solutions investigated. This cluster analysis has been applied to EPSR configurations obtained with simulation boxes having either different numbers of water molecules, as in the present report (Table 1), or a fixed number of water molecules (see, for instance, ref 12), thus ruling out the possibility that the shift of the peak position (in reduced *N/N_w* units) as a function of a solute concentration increase is simply due to size effect of the simulation. The variance in these percolating cluster peaks arises from the large number of configurations on which the cluster analysis is based: in the limit of an infinitely large simulation box (macroscopic limit) this variance would diminish to zero, but the peak position, identifying the average cluster size *M* (see caption of Figure 4), would not change. Inset: Cluster size distribution for all the NaOH solutions investigated in the present study (solute/water ratios 1:83, 1:50, and 1:38) and in a previous article.²³ The thick solid line represents the prediction for random percolation on a 3D cubic lattice. The sharp peak at *N* ~ 1000 indicates a cluster of hydrogen bonded water molecules with dimensions of the order of the entire simulation box. The sharp peak at *N* ~ 500 indicates a cluster of hydrogen bonded water molecules resulting from an earlier work²³ where a smaller simulation box was used.

Figure 2 shows the *B* coefficient of the solute, namely the sum of those of the ionic species in solution,³ as a function of δ . The observed linear relationship between *B* and δ describes all solutes investigated in the present report as well as those whose data have been taken from similar neutron diffraction studies.^{12,18,22–29} As expected, the straight line shown in Figure 2 has an intercept equal to 0, indicating that if a solute can replace a water molecule at the same distance ($\delta = 0$), there will be a negligible effect on the relative viscosity of the solution (see also the caption of Figure 2). Solutes with a relatively large δ , such as NaOH and LiOH, will determine a large increase of the relative viscosity while retaining a large and connected water network, as shown in Figures 3 and 4 of the Appendix.

Those solutes identified by positive *B* and δ values will alter the water viscosity by drawing in water molecules: these will be in deeper minimum of the energy landscape and at the same time will have lesser free volume around, so that their diffusivity will be restricted. On the contrary, solutes with negative *B* and δ values will push out water molecules, distorting the hydrogen

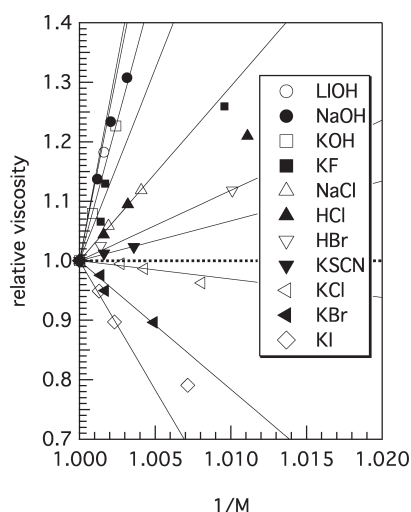


Figure 4. Relative viscosity η/η_w as a function of the reciprocal of the average size of the cluster distribution $1/M$ for several univalent solutes. Relative viscosity data are calculated as a function of solute concentration according to the Jones–Dole expression.⁸ We define M as the average size of the percolating cluster, divided by the total number of water molecules in the simulation box (Table 1). Average size of the cluster distribution M are obtained by a cluster analysis of the corresponding EPSR configurations. Lines are fit to data in the region $1/M < 1.005$. We underline that the average size M is scale invariant, as it can be defined as

$$M = 1 - \frac{N_n}{N_w} \quad (6)$$

where N_n is the number of water molecules in nonpercolating clusters. Upon increasing the size of the simulation box, N_n will increase in proportion to N_w for any given solute concentration. Therefore, M does not depend on N_w and, as a consequence, on the size of the simulation box.

bonds between neighboring water molecules and leaving a larger free volume for the diffusive step in their vicinity.

CONCLUSIONS

In conclusion, we have shown that the univalent solutes examined in the present report have a similar effect on the water hydrogen bond network; namely they all reduce the size of the percolating cluster, even though to a different extent depending on the particular solute. Conversely, we have found that we can relate a structural quantity, such as the difference between oxygen–oxygen distance in pure water and oxygen–solute distance in a solution to a dynamical quantity, namely the relative viscosity. This connection is based on the observation that when an ion is solvated, it may occupy a larger or lesser volume compared to that of a water molecule and the δ parameter may be a reasonable measure of this effect. Moreover, this local structural effect brings along local density and energy fluctuations, which may promote or be unfavorable to the diffusive step, thus increasing or decreasing the relative viscosity of the solution.

An important consequence of this work is that viscosity changes are not caused by changes in the bulk liquid, but they must be associated with the water molecules that are directly interacting with the ions. Namely, we observe an increase or decrease of the relative viscosity according to the sign of δ . Therefore, it is the local environment of a water molecule in the

ion solvation shell, relative to its environment in bulk water, that determines whether the viscosity of the solution increases or decreases relative to bulk water. The distortion of the HB network and loss of tetrahedrality that we observed in earlier work^{12,22} have minor effects on the diffusivity and viscosity.

Incidentally, the way the solutes are placed along the straight line in Figure 2 is reminiscent of the well-known Hofmeister series,^{35–37} as ions on one side of the series are usually labeled as structure makers (B positive) and ions on the other side structure breakers (B negative).⁶ Nevertheless, one of the most effective solutes in the salting in of proteins, namely KSCN, has a relatively small δ and, consequently, a relatively small B (Figure 2). The solute–water oxygen distance in this case is not greatly different from the O_w – O_w distance in water. These observations suggest that the traditional view, according to which the Hofmeister series reflects ion effects on the structure of water, is incorrect. All the solutes investigated in the present report can be described in terms of their ability to draw in or push out water molecules: the latter characteristics affect the viscosity of the solution but do not appear related to their ability to salt-in or salt-out proteins. As a consequence, the particular effect of solutes ranked in the Hofmeister series must be looked at in terms of specific ion interactions with hydrophilic or hydrophobic surfaces, as suggested by recent work.^{4,37–40}

APPENDIX

Here we give details about the cluster analysis mentioned in the main text. The cluster analysis is based on the following criteria. Two water molecules are regarded as bonded if the intermolecular distance between the oxygen atom on one molecule and the hydrogen atom of another is less than or equal to the position of the first minimum of the corresponding intermolecular water oxygen–water hydrogen radial distribution function (i.e., 2.4 Å). Obviously, other definitions involving bond angles and bond energies as well as distances could have been employed here, but practically this would not have affected the underlying conclusions. In particular, the oxygen–hydrogen coordination number obtained by this definition in pure water is ~ 1.8 atoms, which is similar to what is obtained with more sophisticated definitions. The above criterion for hydrogen bonding makes no distinction between a water molecule bonded to an ion and one that is not, but of course the ion is not included in the cluster definition. For a group of molecules to be classified as forming a cluster, each pair of water molecules in the group has to be bonded to at least one other molecule in the same group. Obviously in the case of pure water the overwhelming majority of molecules exist in a single cluster that percolates across the simulation box.

Figure 3 shows the probability of finding a cluster of H bonded water molecules of size N/N_w in the NaOH water solution simulation box at different concentrations, N being the number of water molecules in the cluster and N_w the number of water molecules in the simulation box (Table 1). The predicted power law for random percolation on a 3D cubic lattice⁴¹ is also shown in Figure 3 (inset) as a thick solid line. Depending on the concentration, there are a number of very small clusters that lie below the percolation line, with (usually) just one very large cluster containing most of the molecules in the simulation that spans the entire box. The size of this percolating cluster fluctuates slightly from configuration to configuration, giving rise to the distribution of cluster sizes shown in this figure. Most of the water in solution occurs in this single, percolating network of hydrogen

bonds, as in pure ambient water,^{17,42} as shown by the sharp peak near $N \sim 1000$. This will be here called the percolation peak.

Figure 3, main panel, reveals a systematic dependence of the percolation peak on solute concentration. In particular, the peak moves to lower N/N_w with increased solute concentration and becomes broader. Nevertheless, the size of the percolation peak is always larger than that predicted by theory, indicating that most of the water molecules belong to a single large and long-spanning cluster even at the relatively high solute concentration examined (9 water molecules per NaOH), and similar results have been obtained for all solutes investigated).

The observed robustness of the hydrogen bond network in response to the addition of solutes cannot be taken obviously as a yardstick to define a given solute as being water “structure maker” or “structure breaker”. Yet in the presence of a reduction of the cluster size dimension as small as 1 or 2%, as shown in Figure 4, we have an increase (or decrease) of the viscosity of a solution by as much as 40%.

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