

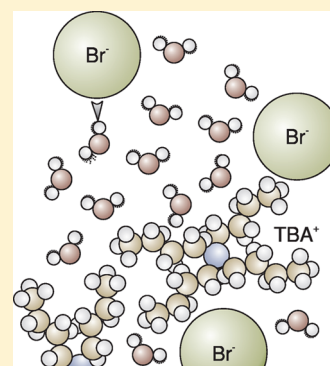
Water Dynamics in Aqueous Solutions of Tetra-*n*-alkylammonium Salts: Hydrophobic and Coulomb Interactions Disentangled

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S Supporting Information

ABSTRACT: We studied the effects of tetra-*n*-alkylammonium bromide ($\text{N}(\text{C}_n\text{H}_{2n+1})_4^+\text{Br}^-$) salts on the dynamics of water using polarization-resolved femtosecond infrared spectroscopy. With this technique, we are capable of distinguishing the response of water solvating the hydrophobic cations from that of water solvating the bromide anion. We observe that both types of ions slow down the orientational dynamics of the water molecules in their solvation shells. However, the nature of this slowdown is different for both ions. For the hydrophobic cation, we find an increasing number of retarded water molecules, scaling with the alkyl chain length. Water in the bromide solvation shell experiences a partial decay of its orientation by a fast wobbling motion, after which the remaining anisotropy decays much slower. The dynamics of the wobbling motion are observed to be dependent on the nature of the cation. For Me_4NBr , the slow reorientation time is not concentration-dependent, and no aggregation is observed. This is in contrast to the tetra-*n*-alkylammonium salts with longer alkyl chains, for which the slow reorientation time of bromide-bound water molecules increases dramatically with concentration, and clusters of cations and anions appear to be formed.

**■ INTRODUCTION**

Many processes in biological systems involve a subtle interplay between hydrophilic and hydrophobic molecular groups and water. A detailed understanding of the effect of hydrophobes on water is therefore crucial to understand processes like protein folding and membrane formation. Although “the hydrophobic effect” and “hydrophobic hydration” have become common language nowadays, still many controversies exist regarding the exact nature of the structural and dynamical properties of water around hydrophobes and their role in biological processes.

Symmetrical tetra-*n*-alkylammonium (TAA, $\text{N}(\text{C}_n\text{H}_{2n+1})_4^+$) salts are good model systems for hydrophobic hydration because they are often very soluble in water and their hydrophobicity is easily increased by increasing *n*. Moreover, tetramethylammonium (Me_4N^+) is biologically very relevant as it forms the positively charged moiety in polar head groups of a common class of phospholipids. Frank and Evans used TAA salts in their famous work in which they proposed so-called iceberg formation around hydrophobes, thereby explaining the counterintuitive thermodynamic behavior that is common for hydrophobic solutions.¹ The formation of more structured ice-like water around hydrophobic moieties provided an explanation for the increased heat capacity of solutions containing amphiphiles. In later work, the iceberg theory was disputed as hardly any changes in the hydrogen-bond structure of water were observed upon the addition of amphiphilic solutes.² However, recent Raman spectroscopy studies did find a more ordered hydration structure around hydrophobic groups.³ In other work, the *dynamics* rather than the structure of water were found to be affected; water molecules are observed to reorient

much more slowly in solutions containing amphiphilic molecules.^{4–6}

The ionic nature of TAA salts offers an interesting opportunity to study the combination of coulomb and hydrophobic effects. Not only does the cation carry both charge and hydrophobic groups in different ratios depending on the length of the alkyl chains, the system also necessarily includes counterions. The combined ionic and hydrophobic character of the TAA cations is often used to explain the structure-making/breaking differences between the shorter and longer chains.^{7–10} The *n* = 1 salts were found to be structure breakers, the *n* ≥ 3 salts structure makers, and the *n* = 2 salts neutral intermediates.⁷ This change in character with increasing alkyl length is believed to result from the competition between coulomb and hydrophobic interactions.¹⁰ Some recent studies suggested that the water structure around the TAA hydrophobic moieties is enhanced³ and that this is less the case for Me_4NBr and Et_4NBr compared to Pr_4NBr and Bu_4NBr .^{2,10}

In this work, we study the reorientation of water in solutions of TAABr salts for four different chain lengths (*n* = 1–4) using polarization-resolved femtosecond pump–probe spectroscopy. This technique has proven to be a very versatile tool to study the reorientation of water molecules in both aqueous salt solutions and solutions containing amphiphiles.^{4,5,11,12} We will demonstrate that the technique also allows one to disentangle the effects of the hydrophobic cation on water from those of

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the anion. We compare the data with results on solutions of NaBr, for which the coulomb effects will dominate.

EXPERIMENT

In our polarization-resolved femtosecond infrared pump–probe experiment, we use infrared pump and probe pulses that are resonant with the OD stretch vibration of HDO molecules in isotopically diluted water (4% D₂O in H₂O). The OD stretch absorption band in solutions containing bromide shows a blue shift with respect to neat HDO/H₂O, for which the OD band has its maximum at 2500 cm^{−1}. For this reason, we center the pump–probe spectrum around 2525 cm^{−1}. The infrared light is generated using the 800 nm output of a Ti:Sapphire pulsed laser (Hurricane, Spectra Physics), with a pulse duration of 110 fs and pulse energy of 0.9 mJ; 60% of this light is used to pump a commercial optical parametric amplifier (OPA, Spectra Physics), in which 2000 nm pulses are generated in a β-barium borate (BBO) crystal. After frequency-doubling in a second BBO crystal, the 1000 nm pulses are difference-frequency mixed with the remaining 40% of the 800 nm output of the Ti:Sapphire laser to generate ~4 μm pulses with an energy of 5 μJ and a duration of 150 fs.

Most of the generated 4 μm light is used as a pump to promote the vibrational stretch mode of a fraction of the OD oscillators to their first excited state. After excitation, the OD oscillators exhibit a modified absorption spectrum, caused by three effects. Because fewer molecules are in the ground state, a decreased absorption is observed at the $\nu = 0 \rightarrow 1$ frequency, the so-called ground-state bleach. A second effect contributing to the decreased absorption is stimulated emission from the excited state back to the ground state, induced by the probe pulse. Finally, the excited molecules can be excited to their $\nu = 2$ state, which causes an increased absorption at the $\nu = 1 \rightarrow 2$ frequency. This induced absorption spectrum is red-shifted by ~200 cm^{−1} due to the anharmonicity of the OD stretch vibration. The pump-induced (transient) absorption changes are monitored by a weak time-delayed probe pulse.

The pump pulse preferentially excites HDO molecules that have their OD stretch transition dipole moments aligned parallel to the pump polarization. The probe polarization is set either parallel or perpendicular to the pump polarization. The delay-time-dependent transient absorption spectra thus contain information on the reorientation of the OD transition dipole as well as the vibrational relaxation. The so-called isotropic transient absorption spectra $\Delta\alpha_{\text{iso}}(\omega, t)$ contain only information on the vibrational relaxation and are constructed as

$$\Delta\alpha_{\text{iso}}(\omega, t) = \frac{\Delta\alpha_{\parallel}(\omega, t) + 2\Delta\alpha_{\perp}(\omega, t)}{3} \quad (1)$$

where $\Delta\alpha_{\parallel}(\omega, t)$ and $\Delta\alpha_{\perp}(\omega, t)$ are the parallel and perpendicular transient absorption spectra, respectively. The typical lifetime of the OD stretch vibration in 4% D₂O in H₂O was found to be 1.8 ± 0.2 ps.¹³

The anisotropy parameter R is a quantity that depends exclusively on the orientational dynamics of the molecules and is given by the normalized difference between $\Delta\alpha_{\parallel}(\omega, t)$ and $\Delta\alpha_{\perp}(\omega, t)$,

$$R(\omega, t) = \frac{\Delta\alpha_{\parallel}(\omega, t) - \Delta\alpha_{\perp}(\omega, t)}{\Delta\alpha_{\parallel}(\omega, t) + 2\Delta\alpha_{\perp}(\omega, t)} \quad (2)$$

Theoretically, the anisotropy starts at a maximum of 0.4 and decays exponentially. The reorientation time constant of OD groups in HDO/H₂O is found to be 2.5 ± 0.1 ps.¹³

Samples. We prepared solutions containing different concentrations (0.25, 0.5, 1, 2, 3, 4, and 6 mol/kg) of TAABr in isotopically diluted water (4% D₂O in H₂O). We used bromide salts with tetra-alkylammonium cations with four different alkyl chain lengths, 4-methylammonium (Me₄NBr), 4-ethylammonium (Et₄NBr), 4-propylammonium (Pr₄NBr), and 4-butylammonium (Bu₄NBr). An obvious choice of a reference sample without any hydrophobicity in the cation would have been solutions of ammonium bromide. However, the protons of the ammonium cation exchange with the deuterium in the solvent. The ND group formed absorbs at nearly the same frequency as the OD groups in the solvent. As a result, the observed dynamics would no longer exclusively represent the dynamics of the water molecules. We therefore used solutions of NaBr as a reference. All salts were purchased from Sigma Aldrich and had a purity of ≥98%. The sample cell consisted of two calcium fluoride windows (dimensions $W \times H \times D = 20 \times 39 \times 4$ mm³) pressed against each other with a Teflon spacer in between. The thickness of the spacer was varied between 25 and 100 μm for different compounds and concentrations to obtain about 10% transmission in the OD stretch region in all measurements. To prevent heat accumulation during the measurement, the sample cell was slowly moved up and down with an oscillation period of a few seconds.

RESULTS AND ANALYSIS

Experimental Results. Figure 1 displays linear spectra of the OD stretch absorption band of neat 4% D₂O in H₂O and 4

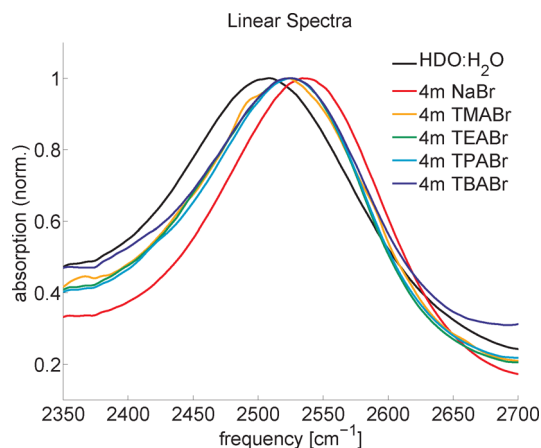


Figure 1. Comparison of the linear spectra of 4 m TAABr solutions in the OD stretch region in isotopically diluted water (4% D₂O in H₂O). The spectra are blue-shifted compared to neat 4% D₂O in H₂O due to the bromide ions but not as much as those for 4 m NaBr.

mol/kg solutions of the different salts. The TAA salt solutions show a blue shift with respect to neat HDO/H₂O, without any clear dependence on the nature of the cation. The blue shift increases with concentration. In previous work, this blue shift was assigned to the OD oscillators of HDO molecules that are hydrogen-bonded to the anions (OD⋯Br[−]).¹⁴ Because this bond is weaker than water–water hydrogen bonds (OD⋯O), the coupled OD stretch resonance frequency is blue-shifted by ~50 cm^{−1}. We centered the pump and probe spectrum in our experiment at 2525 cm^{−1} to have them optimally overlapping

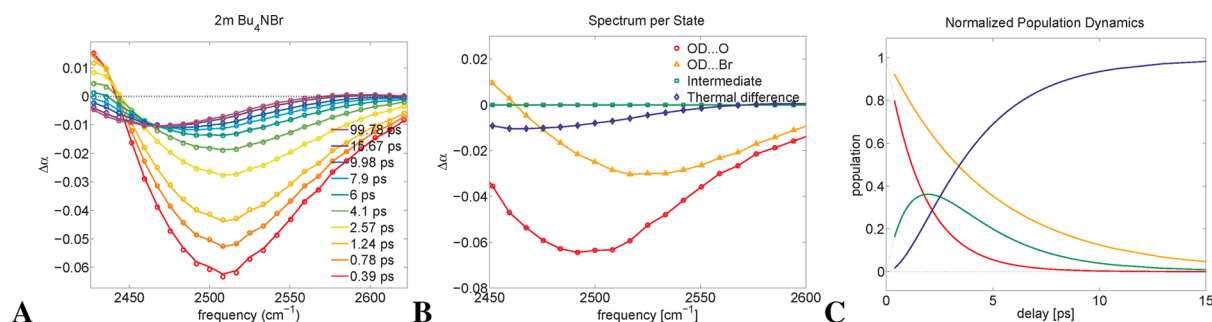


Figure 2. (A) Transient spectra measured for different delay times for a 2 mol/kg solution of Bu_4NBr . The solid lines represent a fit of the kinetic model described in the Modeling section. The fitted state spectra and population dynamics for this data set are in (B) and (C), respectively. The vibrational decay is very slow and is incomplete after 15 ps.

with both contributions to the absorption band. The linear spectrum of the same concentration NaBr shows a significantly larger blue shift of the OD stretch compared to the TAA salt solutions.

Figure 2 shows transient spectra at different pump–probe delay times for a 2 mol/kg solution of Bu_4NBr . For early delays, a bleach due to the depleted ground state and stimulated emission is observed in the center and at the blue side of the spectrum. At lower frequencies, the induced absorption $\nu = 1 \rightarrow 2$ is seen. For the following analysis, we consider only the bleaching contribution to the transient spectra in the spectral range of 2450–2600 cm^{-1} . The absorption changes decay to a spectral feature that remains constant on the time scale of the experiment (<100 ps). This final spectrum is a thermal difference spectrum that results from the heating of the sample by a few degrees due to the thermalization of the excitation energy.¹⁵ To properly calculate the anisotropy dynamics of the excited OD oscillators, we subtract this thermal contribution by fitting the isotropic data with a kinetic model for the vibrational decay.

Modeling. For pure 4% D_2O in H_2O , it was found that the rise of the thermal difference spectrum was somewhat delayed with respect to the decay of the excited state.¹³ This behavior was modeled with an intermediate state without any spectral signature. Because the spectrally shifted $\text{OD}\cdots\text{Br}^-$ oscillators have a longer vibrational lifetime than the $\text{OD}\cdots\text{O}$ oscillators,¹⁶ we extend this model with a second excited state (for more information on the model used, see ref 17). The isotropic data can be written as

$$\Delta\alpha_{\text{iso}}(\omega, t) = \sum_{i=1}^n N_i(t)\sigma_i(\omega) \quad (3)$$

where $N_i(t)$ is the population dynamics and $\sigma_i(\omega)$ is the spectral response of state i . The two excited state spectra represent a bleach due to the $\nu = 0 \rightarrow 1$ reduced ground-state absorption and $\nu = 1 \rightarrow 0$ stimulated emission and a $\nu = 1 \rightarrow 2$ induced absorption, $\sigma_1(\omega)$ for the $\text{OD}\cdots\text{O}$ and $\sigma_2(\omega)$ for the $\text{OD}\cdots\text{Br}^-$ species. The sum includes the two excited states and the thermalized state. The introduction of the intermediate state leads to a delay of the rise of the thermal response with respect to the vibrational relaxation. A delay of the thermal response has been observed in previous work.^{13,18} The intermediate state has no transient spectral signature, meaning that we assume its spectrum to be the same as that of the ground state. Therefore, the intermediate state does not contribute to the isotropic signal; it only changes the kinetics of the absorption changes. The delay of the thermalization can

be explained from the relatively slow adaptation of the coordinates of low-energy degrees of freedom (hydrogen-bond bend and stretch) to the higher-energy content that results from the relaxation of the OD stretch vibration. The relaxation of the OD stretch vibration leads to a rapid increase of the energy content of the lower-energy degrees of freedom, and these coordinates need some time to evolve to the new equilibrium positions corresponding to this higher-energy content. The decay time of the intermediate state can thus be regarded as the thermalization time.

Because we have two types of excited OD oscillators with different spectral response and vibrational lifetimes, the total anisotropy as expressed in eq 2 contains the reorientation dynamics of both species with time- and frequency-dependent weighting factors. Following the notation of eq 2, the total anisotropy can be written as the sum of its separate contributions according to

$$R(\omega, t) = \frac{\sum_{i=1}^n R_i(t)N_i(t)\sigma_i(\omega)}{\sum_{i=1}^n N_i(t)\sigma_i(\omega)} \quad (4)$$

where $R_i(t)$ is the anisotropy in state i at a given time t . In this decomposition, it is implicitly assumed that no significant frequency dependence of the anisotropy exists within any of the bands σ_i . This independence can be assigned to fast spectral diffusion and is in agreement with previous results on the reorientation dynamics in solutions with amphiphiles and salts.^{17,19} Furthermore, it is assumed that the reorientational diffusion is identical in the $\nu = 0$ and $\nu = 1$ states. Because the anisotropy in the thermalized ground state is zero, the sum of eq 4 is only over the two excited states representing the $\text{OD}\cdots\text{O}$ and $\text{OD}\cdots\text{Br}^-$ oscillators.

We assume a functional form for the anisotropy decays of these two species. Several studies showed that in solutions containing amphiphilic solute molecules, the reorientation of water takes place on two different time scales.^{4,6,20} The fast time scale is associated with OD groups hydrogen-bonded to water that have bulk-like reorientation dynamics, and the slow time scale is associated with OD groups hydrogen-bonded to water hydrating the hydrophobic group of the solute. We thus model the $\text{OD}\cdots\text{O}$ anisotropy decay by

$$R_{\text{OD}\cdots\text{O}}(t) = A_f e^{-t/\tau_f^{\text{O}}} + A_s e^{-t/\tau_s^{\text{O}}} \quad (5)$$

where A_f and A_s are the relative amplitudes of the fast and slow relaxation processes and τ_f^{O} and τ_s^{O} are the fast and slow relaxation time constants.

In other work, the anisotropy of OD groups bound to anions was found to decay by different processes:^{21–23} (1) a very fast

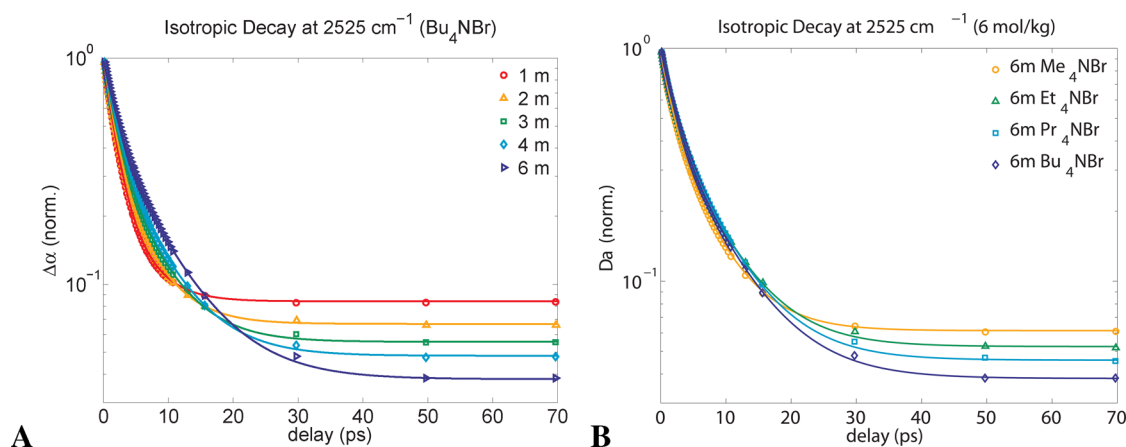


Figure 3. The vibrational decay dynamics becomes slower for increasing concentrations of Bu_4NBr (A) and for increasing chain lengths at a concentration of 6 m (B). The delay traces shown are taken at 2525 cm^{-1} . The solid lines in the figures are the fit of the kinetic model described in the text to the data.

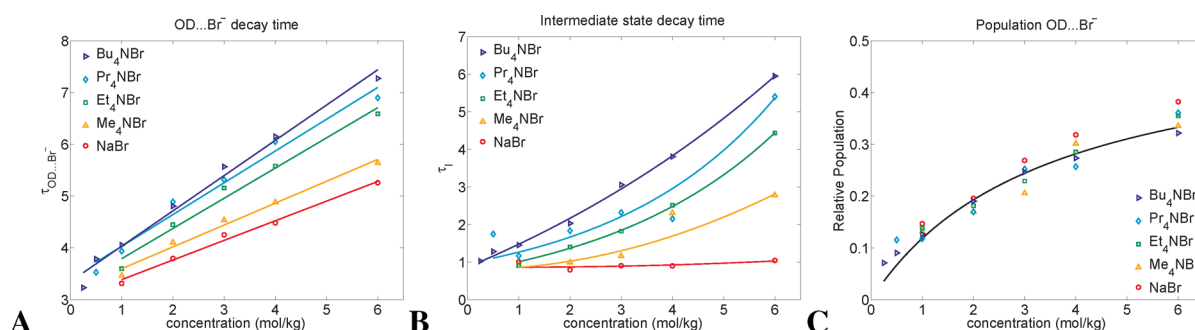


Figure 4. For all measured salts and concentrations, the vibrational decay time of the $\text{OD}\cdots\text{Br}^-$ oscillators (A), the decay time of the intermediate state (B), and the $\text{OD}\cdots\text{Br}^-$ population (C). The vibrational lifetime of bromide-bound water becomes very slow for high concentrations of the salts with longer alkyl chains. The solid lines are guides to the eye.

decay due to librational motions ($\sim 150\text{ fs}$), (2) a contribution due a wobbling motion that is caused by the reorganization of the hydrogen-bond network outside of the first solvation shell ($\sim 2\text{ ps}$), and (3) a much slower decay due to rotational diffusion of the solvating water over the anion surface ($\sim 10\text{ ps}$). Therefore, we choose the following functional form for the $\text{OD}\cdots\text{Br}^-$ anisotropy decay

$$R_{\text{OD}\cdots\text{Br}^-}(t) = B_f(Ce^{-t/\tau_{\text{lib}}^{\text{Br}}} + (1 - C)e^{-t/\tau_i^{\text{Br}}}) + B_s e^{-t/\tau_s^{\text{Br}}} \quad (6)$$

where B_f and B_s are the relative amplitudes of the fast and slow orientational relaxation processes described above and $\tau_{\text{lib}}^{\text{Br}}$, τ_i^{Br} , and τ_s^{Br} are their corresponding time constants. The very fast librational decay has an amplitude $B_f C$. The anisotropy dynamics in (eq 6) thus contains a fast decaying part and a slow decaying part analogous to the $\text{OD}\cdots\text{O}$ anisotropy decay in eq 5.

Both the kinetic model for the vibrational decay and the functions for the two excited-state anisotropy decays are fitted to the data simultaneously in a self-consistent fit (more information on the modeling can be found in the Supporting Information). To limit the freedom in the fit, we fix several parameters entering eqs 5 and 6. Because the vibrational lifetime of the $\text{OD}\cdots\text{O}$ oscillators in pure $\text{HDO}/\text{H}_2\text{O}$ is 1.8 ps ,¹³ the $\text{OD}\cdots\text{O}$ anisotropy can only be measured accurately up to about 10 ps . We therefore model the slow component of the $\text{OD}\cdots\text{O}$ reorientation as an end level of the anisotropy, that is, we set the slow time constant to $\tau_s^{\text{O}} = \infty\text{ ps}$. In previous

work, it was found that the fast time constant in $R_{\text{OD}\cdots\text{O}}$ is $\tau_{\text{lib}}^{\text{O}} = 2.5\text{ ps}$, and the fast time constant in $R_{\text{OD}\cdots\text{Br}^-}$ is $\tau_i^{\text{Br}} = 2\text{ ps}$,^{17,19} and we fix those constants accordingly. Finally, the time resolution of our experiment is limited to the cross correlate of the pump and probe pulses ($\sim 250\text{ fs}$). For this reason, we fix the amplitude to $C = 0.25$ and the time constant of the librational decay to $\tau_{\text{lib}}^{\text{Br}} = 170\text{ fs}$, corresponding to the value found in previous work on alkali halide solutions.²³ The freely fitted parameters are thus the parameters of the kinetic model describing the isotropic decay, the amplitudes A_f , A_s , B_f , and B_s , and the slow reorientation time τ_s^{Br} of bromide-bound water.

Modeling Results. The solid lines in Figure 2A represent the isotropic results of a fit of the model to the data obtained for a 2 m Bu_4NBr solution. Figure 2B presents the fitted state spectra $\sigma_i(\omega)$, and the corresponding population dynamics $N_i(t)$ are shown in Figure 2C. The excited $\text{OD}\cdots\text{Br}^-$ spectrum shows a blue shift of about 30 cm^{-1} with respect to the excited $\text{OD}\cdots\text{O}$ spectrum, significantly smaller than the value of 50 cm^{-1} that was found for alkali bromide salts.¹⁴ The vibrational decay time of the $\text{OD}\cdots\text{Br}^-$ is slow, as is the decay of the intermediate state, leading to a long delay of the rise of the thermal difference signal. Delay traces show that the vibrational decay becomes slower with increasing concentration (Figure 3). Equal concentrations of different TAA salts show the same trends.

The fit results of the isotropic model are summarized for all measured data sets in Figure 4. The vibrational lifetime of $\text{OD}\cdots\text{Br}^-$ increases both with TAA salt concentration and

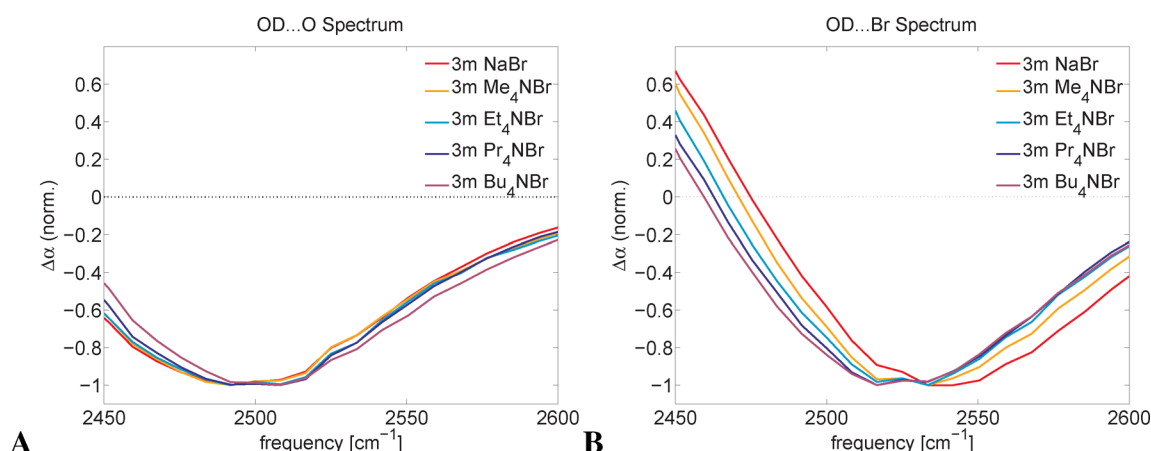


Figure 5. The spectra of OD...O (A) and OD...Br[−] (B) oscillators obtained by fitting the kinetic model to all 3 mol/kg solutions. Depending on the alkyl chain length, the resonance frequency of the bromide-bound oscillators blue shifts less compared to that of aqueous NaBr.

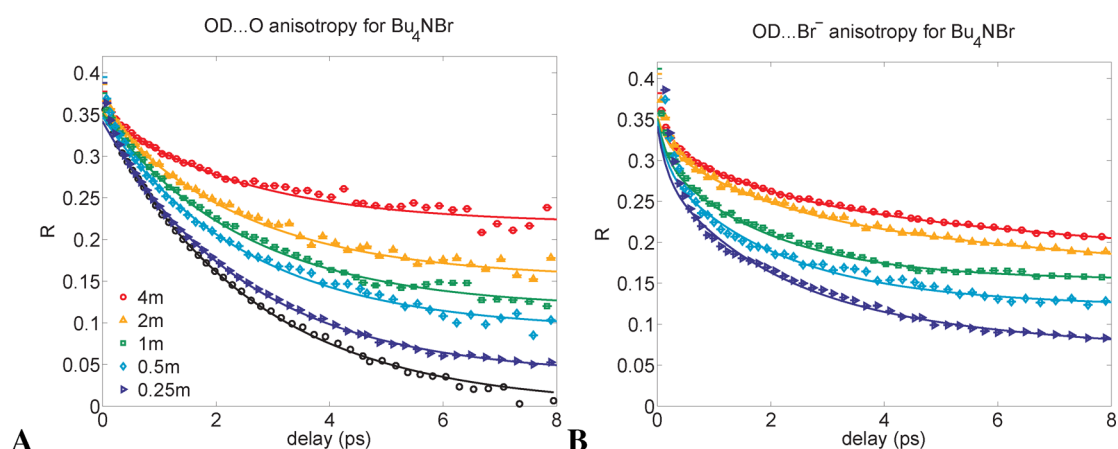


Figure 6. The anisotropy decay in solutions of different concentrations of Bu₄NBr, decomposed in its components OD...O (A) and OD...Br[−] (B). Already for 250 mmol/kg Bu₄NBr, the anisotropy decay shows a substantial slow component (the anisotropy decay in neat water is shown in black circles). The OD...Br[−] anisotropy decay shows a saturation effect for the higher concentrations.

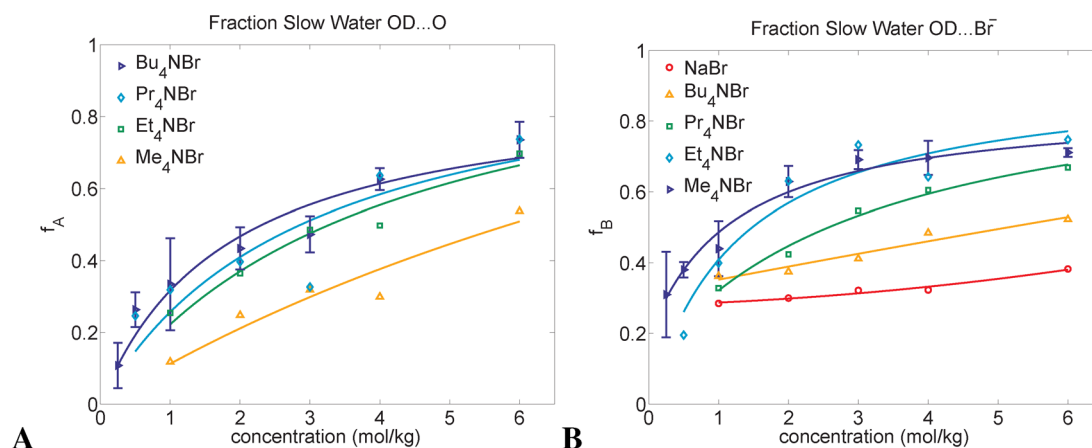


Figure 7. The fractions of OD groups with slow reorientation for OD...O (A) and OD...Br[−] (B) oscillators. Bromide-bound OD groups have an intrinsic slow fraction, which becomes more retarded in solutions with many or large hydrophobic cations. The solid lines are guides to the eye.

with alkyl chain length and becomes as long as 7.3 ± 0.3 ps for the highest concentration of Bu₄NBr. The dynamics of the ingrowing heat depends on both the concentration and the alkyl chain length. The right panel shows the population of OD...Br[−] relative to that of OD...O. When calculating these values, we took into account that the cross section of OD...Br[−]

is ~ 1.5 times higher than the cross section of OD...O. (The ratio between the OD...O and OD...Br[−] cross sections was determined by taking linear spectra of various concentrations of NaBr in 8% HDO in H₂O from which the linear spectrum of the same concentrations in pure H₂O was subtracted. These difference spectra show the background-free OD stretch

absorption band, containing contributions of both OD \cdots O and OD \cdots Br $^-$ that vary with concentration. The total cross section (the surface of the absorption band) was found to increase with concentration. Using a coordination number of 8 for Br $^-$,²⁴ we obtained the relative amplitudes of the OD \cdots O and OD \cdots Br $^-$ contributions and thus could relate the increase in total cross section of the OD stretch band to the relative cross section increase of OD \cdots Br $^-$ compared to OD \cdots O.) From the slope, we determine a hydration number of 7 ± 2 , consistent with earlier work^{22,24,25} and independent of the nature of the counterion (Figure 2C). For the 3 mol/kg solutions, all fitted spectra are shown in Figure 5. The blue shift of the OD \cdots Br $^-$ spectrum clearly depends on the nature of the cation, while the OD \cdots O spectrum is the same for all cations. This is surprising because the linear spectra of the solutions do not show a clear dependence on the length of the alkyl chains.

Figure 6 shows the $R_{\text{OD}\cdots\text{O}}$ (A) and $R_{\text{OD}\cdots\text{Br}^-}$ (B) anisotropy decays and corresponding fits for different concentrations of Bu $_4$ NBr (a detailed description of how the data points of the anisotropy decays were obtained can be found in the Supporting Information). Both anisotropy decays show a slow component of which the amplitude increases with increasing concentration. The fraction of this component is determined from the fitted amplitudes. More specifically, we determine the fraction of slow OD groups $f_A = A_s/(A_f + A_s)$ in the case of OD \cdots O. For the OD \cdots Br $^-$ anisotropy decay, the fraction $f_B = B_s/(B_f + B_s)$ represents the part of the anisotropy that decays by the slow process. The fractions are plotted for all measured data in Figure 7. The f_A and f_B increase with increasing alkyl chain length and with concentration. Toward infinite dilution, the OD \cdots Br $^-$ slow fraction assumes a nonzero value that is roughly 0.25 for all salts. In Figure 8, the slow

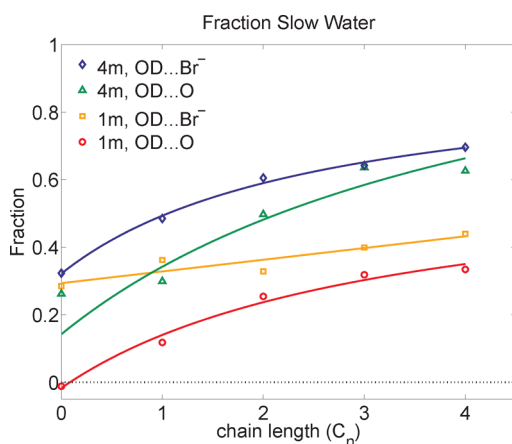


Figure 8. The fraction of slow water for different alkyl chain lengths decomposed in its components for 1 and 4 mol/kg solutions. The solid lines are guides to the eye.

water fraction of the two components is plotted against the number of carbons in the cation alkyl chains for two concentrations. The increase of the alkyl chains is shown to increase the fraction of water with slower dynamics, both for the OD \cdots O and the OD \cdots Br $^-$ oscillators.

The time constant τ_s^{Br} was a free fit parameter and is shown in Figure 9. The slow reorientation time of water bound to bromide is 14 ± 2 ps for Me $_4$ NBr, independent of the concentration. This time constant can be well determined thanks to the very slow vibrational relaxation of the OD \cdots Br $^-$

oscillators (T_1 up to 7 ps for the highest concentration). For Et $_4$ NBr, τ_s^{Br} depends strongly on the concentration, increasing from 20 ± 2 ps for the lowest concentrations up to 40 ps for the highest concentration. In the case of the cations with the longest alkyl chains (Pr $_4$ NBr and Bu $_4$ NBr), the slow reorientation time exceeds 40 ps already at low concentrations.

DISCUSSION

Hydrophobic Effects on the Anion Hydration Shell.

One of the characteristic features of the halide series is that water molecules bound to these anions (apart from fluoride) show an OD stretch resonance that blue shifts with increasing anion size. This is a result of the weaker bond between an OD group and the bromide ion (OD \cdots Br $^-$) compared to the average OD–water hydrogen bond (OD \cdots O).¹⁴ The blue shift of OD \cdots Br $^-$ oscillators enables us to disentangle the anisotropy dynamics of these two species.

In recent work, it was suggested that the reorientation of water is highly concerted, and a separation between OD groups solvating ions and OD groups hydrogen-bonded to other water molecules is invalid for this observable at the concentrations studied.²⁶ The argument used was that the total anisotropy for MgBr $_2$ did not show a noticeable dependence on frequency as the OD \cdots O and OD \cdots Br $^-$ oscillators have a different linear absorption spectrum. A difference in reorientation dynamics should have led to a frequency dependence of the overall anisotropy decay. There are a number of points missing in this argument. First, the discussion does not address the influence of the population dynamics on the total anisotropy. Because the stretch vibrations of OD \cdots Br $^-$ oscillators have a considerably longer lifetime, their relative contribution to the total anisotropy does not only depend on the distributions in the linear spectrum. At short delay times, the anisotropy is dominated by the orientation of OD \cdots O oscillators, while at 8 ps delay time, the anisotropy is almost exclusively representing the orientation of OD \cdots Br $^-$ oscillators, irrespective of the probe frequency (see also Figure 2B and C). Hence, the lack of frequency dependence in the overall anisotropy dynamics of ref 26 is mostly due to the fact that at later delays, only the OD \cdots Br $^-$ dynamics are observed. In case both species have highly different reorientation dynamics, a large frequency separation of their resonances, and not too different lifetimes, as is the case for the core and shell water of reverse micelles,²⁷ the total anisotropy dynamics clearly shows a frequency dependence. This is also the case for NaClO $_4$ solutions, for which also a strong frequency dependence of the total anisotropy dynamics was found.¹⁷ For systems with a smaller spectral separation of the two species, a spectral decomposition as was performed in our work yields a more accurate method to obtain the reorientation dynamics of the different water species. If the proposition in ref 26 were correct, then the decomposed anisotropy dynamics of both species as obtained by our method would be equal. This is not what we observe.

The dynamics of water around the TAA cations, included in the OD \cdots O component, is strongly perturbed (Figure 7A). The slope of a straight line fitted to the first, linear part of the slow water fraction in Figure 7A yields the number of OD group that have slower reorientation dynamics per solute molecule. With increasing alkyl length, the number of retarded OD groups per cation we found are 12, 20, 32, and 44. For Pr $_4$ NBr and Bu $_4$ NBr, these numbers are in good agreement with the estimated number of water molecules in the hydration shells of

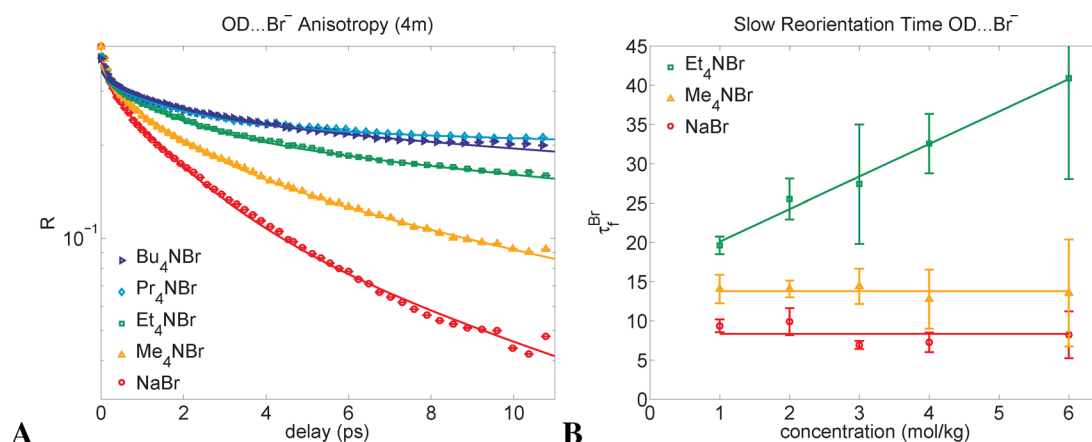


Figure 9. (A) A comparison of the anisotropy decay of bromide-bound OD groups for salts with different alkyl chain lengths. The vertical axis is logarithmic. (B) The slow reorientation time becomes slower for higher concentrations of Et₄NBr. All fitted time constants for Pr₄NBr and Bu₄NBr were longer than 40 ps (data points not shown). At such a long time scale, our experiment is not sensitive enough to determine this time constant accurately.

these ions as obtained from GHz dielectric relaxation spectroscopy and molecular volumes.^{20,28} The fact that the slow water fraction for the lower concentrations scales nearly linearly with the number of CH_{*n*} (*n* = 2,3) groups in the solution is evidence that the retardation is caused by a hydrophobic effect. This is in line with previous studies on amphiphilic molecules in water, where a similar retardation was found of about three water molecules per methyl group.^{4,5} It may be expected that such an immobilization of the hydrogen-bond network is accompanied by structural changes, and indeed, it was shown in recent work that the hydrophobic solvation shell is slightly more ordered compared to bulk water.³

The slow fraction of water around the bromide ion (Figure 7B) shows the same qualitative behavior compared to water outside of the bromide hydration shell. Extrapolation toward infinite dilution suggests that there is an intrinsic effect of the bromide on the reorientation dynamics. This fits the picture of previous work on alkali halide salts in water, where the reorientation dynamics of OD groups bound to an anion were found to have two main contributions. A fast decay process (~2 ps) is caused by the wobbling motion of a water molecule while keeping its hydrogen bond to the anion intact. As the anion restricts the wobbling motion to a certain angle, this process does not lead to a full decay of the anisotropy, and the remaining part decays by the much slower process of rotational diffusion of the molecules over the anionic surface.^{17,29} The latter slow component is the intrinsic anionic effect that is present in Figure 7B. For increasing alkyl chain lengths and concentrations, the amplitude fraction of the slow process becomes larger (see also Figure 8). $R_{\text{OD}\cdots\text{Br}^-}$ must therefore be interpreted as a combination of an anionic effect and a hydrophobic effect, and the latter can be understood as follows. The wobbling motion of an OD group bound to the bromide anion is caused by the reorganization of the hydrogen-bond network outside of the first solvation shell. For this reason, the wobbling reorientation time is close to that of normal hydrogen-bond network reorganization (2.5 ps). In the TAABr solutions, the dynamics of the hydrogen-bond network is dramatically retarded by the presence of the hydrophobic cations. This decreased mobility is reflected in the dynamics of the OD groups that are hydrogen-bonded to the bromide ion.

The OD \cdots Br⁻ wobbling motion thus becomes slower for increasing alkyl chain lengths and concentrations.

The vibrational lifetime of the OD stretching mode of anion-bound water is in general observed to be longer than that for bulk water.^{16,30} It depends on the salt concentration and was reported to be as long as 4.8 ps for a 6 mol/kg NaBr solution,¹² in agreement with our current findings (Figure 4). The increased vibrational lifetime is generally caused by a decrease of the hydrogen-bond interaction.³⁰ The dependence on the concentration may in part be due to exchange events between OD \cdots Br⁻ and OD \cdots O species.³¹ An initially excited OD \cdots Br⁻ oscillator can rotate out of the solvation shell and become OD \cdots O, thereby decreasing the effective vibrational lifetime. In salt solutions, these exchange effects have been observed to take place on a time scale of ~10 ps depending on concentration.^{32,33} For the TAABr salts, the OD \cdots Br⁻ vibrational lifetime becomes even longer than that found for NaBr, up to 7.3 ps for a 6 mol/kg concentration of Bu₄NBr (Figure 4). We interpret this long lifetime as a result of a considerably slower exchange rate out of the bromide solvation shell in solutions with big hydrophobic cations. This picture is consistent with the decreased mobility of the OD \cdots Br⁻ wobbling component; a more slowly wobbling OD group will jump out of the solvation shell at a lower rate.

For all solutions, we observe that the thermalization is delayed with respect to the vibrational relaxation. This delay is ~800 fs in pure water and was interpreted to reflect the adaptation of the hydrogen-bond network to the new energy distribution after relaxation.^{13,34} Figure 4B shows that the thermalization dynamics, expressed in the decay time of the intermediate state, becomes very slow upon the addition of Bu₄NBr. Apparently, at high concentrations, the hydrogen-bond network is less capable of adapting to the new energy distribution after the vibrational excitation has relaxed into thermal modes. The effect is weaker for the shorter alkyl chains, indicating that this effect is correlated with the hydrophobicity in the solution.

The OD \cdots Br⁻ oscillators show a smaller blue shift in solutions of TAABr than in solutions of NaBr, as seen in both the linear spectra (Figure 1) and the transient spectra (Figure 5). A smaller blue shift means stronger OD \cdots Br⁻ hydrogen bonds, which in this case should be induced by the presence of the hydrophobic cations. The stronger OD \cdots Br⁻ interaction

can be explained if, on average, fewer OD groups are hydrogen-bonded to bromide per anion as the anion charge is in such case less screened. The depletion of the bromide solvation shell can be caused by the large hydrophobic chains of the cations that stick into the bromide solvation shell. This explanation is supported by the $\text{OD}\cdots\text{Br}^-$ populations shown in Figure 4C that show that the number of OD groups in the bromide solvation shell is systematically lower in solutions of TAABr than that in solutions of NaBr. This interpretation is also in agreement with MD simulations that find a tendency of weaker hydrated halide anions to form ion pairs with TAA cations³⁵ and GHz dielectric relaxation results that find evidence for the presence of penetration ion pairs in which the bromide anion approaches the methylene groups of the alkyl chains of the larger ($n > 2$) cations.²⁰

Formation of Aggregated Ion Clusters. The fraction of slow water in Figure 7 saturates for increasing concentrations of Et_4NBr , Pr_4NBr , and Bu_4NBr , which means that there is a decreasing number of slow OD groups per solute molecule. This can partly be explained by overlapping hydration shells; with 44 OD groups per Bu_4N^+ solvation shell, this overlap is bound to happen already at concentrations of 2 mol/kg. In addition, MD simulations and neutron diffraction experiments show that large hydrophobic cations tend to aggregate strongly.^{8,36} The aggregation leads to a reduced hydrophobic surface that is exposed to water and hence effectively decreases the slow fraction. Me_4NBr does not seem to aggregate much, which was also predicted by MD simulations.³⁷ A very similar situation occurs when aqueous solutions of tetra-methylurea (TMU) or tert-butyl alcohol (TBA) are compared to solutions of trimethylamine N-oxide (TMAO). TMU and TBA show saturation behavior due to aggregation starting at concentrations of 3 mol/kg.³⁸ The very polar TMAO molecule, on the contrary, has little tendency to aggregate, and the slow water fraction for TMAO solutions is accordingly observed to saturate only at very high concentrations (>8 mol/kg) due to inevitable overlap of the hydration shells at these high concentrations.^{38,39} The lack of aggregation for Me_4NBr solutions is therefore attributed to the charged nature of the Me_4N^+ cation. Nevertheless, there is also a fraction of slowly reorienting water molecules around the Me_4N^+ due to the hydrophobicity of the methyl groups. This observation is in line with the results of NMR,^{7,40} neutron scattering,⁴¹ and GHz dielectric relaxation spectroscopy,²⁰ in which it was found that Me_4N^+ , other than Na^+ , is not capable of aligning the static dipoles of its solvating water molecules. These findings are in agreement with its qualification as a hydrophobe.

We observe that the slow reorientation time of $\text{OD}\cdots\text{Br}^-$ (τ_s^{Br}) has a constant value of 15 ps for all measured concentrations of Me_4NBr , while for Et_4NBr , τ_s^{Br} increases from 20 to more than 40 ps (Figure 9). The reorientation time constants τ_s^{Br} of Pr_4NBr and Bu_4NBr are longer than 40 ps for all concentrations, somewhat larger than the values obtained from dielectric relaxation studies for concentrations of these salts lower than 3 m.²⁰ For alkali halide salts, the slow reorientation was found to occur with a time constant of ~ 10 ps and is primarily due to rotational diffusion of OD groups over the anionic surface while keeping their $\text{OD}\cdots\text{Br}^-$ hydrogen bond intact.^{11,17} The exchange of water between the hydration shell and the bulk can also contribute to the anisotropy dynamics, but this will be a minor contribution.¹⁷ The exchange mainly affects the amplitude of the anion-bound spectral component, that is, the T_1 time constant. We observe that the

presence of the hydrophobic cations leads to a severe retardation effect in the anisotropy dynamics. Rotational diffusion over the anionic surface requires the reorganization of the hydrogen-bond network outside of the solvation shell. The hydrophobic cations appear to slow down this reorganization and thereby slow down the rotational diffusion.

The results for Me_4NBr are distinct from those for the other TAABr salts in the sense that no concentration dependence for the slow reorientation time of $\text{OD}\cdots\text{Br}^-$ is found. This is related to the previous observation that Me_4NBr has no tendency to aggregate. From classical MD simulations, it was shown that whether amphiphilic solute molecules tend to aggregate or not has a strong effect on the dynamics of the solvating water molecules.⁴² Weakly aggregating molecules like TMAO mix better with the solvent, resulting in water molecules confined in thin films in between the big solute molecules. Aggregating molecules like TMU form clusters at higher concentrations, with nanopools of bulk-like water in between. In the case of water films around TMAO, the reorientation time is further slowed down due to the nanoconfinement in addition to a hydrophobic effect. A retardation effect of nanoconfinement on the reorientation dynamics of water has also been observed for reversed micelles^{27,43} and ionic liquids.⁴⁴ With this in mind, we can interpret our results on τ_s^{Br} as follows. For increasing concentrations of Et_4NBr , the slow water fraction saturates, which points toward a decrease in the exposed hydrophobic surface and hence aggregation. At the same time, we find increasing values of τ_s^{Br} , which point toward an increasingly slower reorientation of the hydrogen-bond network around the anions. The distortion of the hydrogen-bond network can be caused by nanoconfinement of the solvating water in between the clustering cations. In concentrated solutions of Et_4NBr , domains are likely formed in which bromide anions and Et_4N^+ cations cluster together with a restricted number of water molecules in between. For Pr_4NBr and Bu_4NBr , this type of clustering already happens at the lowest concentrations measured. The affinity of large halide anions for TAA cations was shown in MD simulations.³⁵ The existence of ion aggregates has been proposed before.^{20,36} In dielectric relaxation experiments, it was found that the concentration of ion pairs decreases for increasing concentrations (>0.5 M) of Pr_4NBr or Bu_4NBr . In addition, the reorientation time of both the ion pairs and the water molecules hydrating the cations in solutions of Pr_4NBr or Bu_4NBr was found to become exponentially slower for concentrations larger than 2.2 and 1.7 M, respectively.²⁰ Such behavior points to the formation of large ion aggregates. In the case of Me_4NBr , there is no decrease in the exposed hydrophobic surface and hence no aggregation. The values of τ_s^{Br} remain constant up to 6 mol/kg, similar to the results for NaBr, indicating that aggregation and confinement do not play a role. The Me_4N^+ cation is thus unique in the sense that the coulomb interactions are strong enough to prevent it from aggregating, but the hydrophobic nature is still slowing down the reorientation of the water molecules hydrating the methyl groups. The reason why even at low concentrations the slow reorientation time of bromide-bound OD groups is affected by the cations may find its origin in ion pair formation, which is indeed observed for these solutions.^{20,35}

CONCLUSIONS

We studied the dynamics of water in aqueous TAABr solutions for different lengths of the alkyl chains (Me_4NBr , Et_4NBr ,

Pr₄NBr, and Bu₄NBr). Using the blue shift of the OD stretch resonance of HDO molecules bound to bromide, we can distinguish the dynamics of the bromide solvation shell from the bulk water dynamics. The number of slow water molecules increases with the length of the alkyl chains and corresponds to the solvation numbers of these ions found in other work. For Me₄NBr, we find that about 12 OD groups per cation have slower dynamics, consistent with the picture of hydrophobic hydration. This means that not the charged but the hydrophobic nature of the cation governs the water dynamics of its solvation shell. For the larger TAA ions, this dominance of the hydrophobic effect is even stronger.

The slower dynamics of the hydrogen-bond network is reflected in the solvation shell of the bromide anion as well. The dynamics of OD groups that remain hydrogen-bonded to bromide is partially governed by a wobbling motion that roughly follows the reorganization of the hydrogen-bond network outside of the solvation shell. We find that this wobbling motion acquires a slow component due to the presence of the hydrophobic cations. We also find that the blue shift of both the linear and transient spectra of OD⋯Br[−] compared to those of OD⋯O is much smaller for solutions of TAABr compared to NaBr solutions. This observation can be explained from the partial hydration of the Br[−] hydration shell by the protruding hydrophobic chains of the TAA cations. This picture also explains the increase of the vibrational lifetime for the OD stretch excitation of OD⋯Br[−] with increasing TAA concentration and increasing alkyl chain length. For alkali halide salt solutions, this lifetime is partly determined by exchange events between OD groups bound to bromide and water outside of the solvation shell. These exchange events take place on a time scale of ~10 ps but will be much slower in concentrated TAABr solutions due to the effect of the nearby hydrophobic TAA cations on the dynamics of the surrounding liquid.

From the saturation behavior of the fraction of slowly reorienting water and the increasing reorientation time of OD⋯Br[−] oscillators, we infer that cations with long alkyl chains form clusters with bromide ions and water molecules. The clustering effectively decreases the total exposed hydrophobic surface, which leads to a saturation effect in the observed slow water fraction. The water molecules inside of these clusters are highly confined, causing the reorientation of OD groups bound to the bromide ions that penetrated such a cluster to become even slower than 40 ps. Normally, such slow reorientation processes are difficult to probe in this type of experiments due to the short lifetime of the OD stretch vibration. However, the long OD⋯Br[−] lifetime allows for an accurate determination of such long reorientation time constants. The aggregation effect is not observed for Me₄NBr even at concentrations of 6 mol/kg, probably because for this ion, the repulsive coulomb interaction is strong enough to prevent the formation of large aggregated ion clusters.

■ ASSOCIATED CONTENT

● Supporting Information

The modeling of the data is described in more detail. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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