Hydration Sphere of Tetrabutylammonium Cation. FTIR Studies of HDO Spectra

Janusz Stangret* and Teresa Gampe

Department of Physical Chemistry, Technical University of Gdańsk, 80-952 Gdańsk, Poland

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The hydration of tetrabutylammonium cation (Bu_4N^+) has been studied in aqueous solutions of Bu_4NBr, Bu_4NCl, and Bu_4NF salts by means of the FTIR method. Isotopically diluted HDO in H_2O has been applied by using the stretching vibration OD band as a probe of the solutes' hydration. The spectra have been analyzed in a way that led to removal of the contribution of the bulk water and thus to the separation of the spectra for salt-affected HDO. In several steps of a curve-fitting procedure the Bu_4N^+- and the respective anion-affected OD bands have been refined from the salt-affected HDO spectra. The Bu_4N^+-affected OD band profile and the bulk spectrum have been converted to a probability distribution function of interatomic O···O distances for influenced water, by the use of a correlation curve. Comparison of the band for HDO affected by cation with that of the bulk water, as well as the derived respective distributions of O···O distances, leads to the conclusion that "iceberg formation" is a wrong expression for the effect of hydrophobic groups in water. The results have been discussed with respect to enthalpy and entropy effects.

Introduction

Since the iceberg hypothesis by Frank and Evans,[1] the molecular basis and the nature of the so-called hydrophobic hydration have not been well understand yet. According to Finney,[2] there is no evidence from recent neutron scattering measurements that the structure of the hydration water close to a nonpolar group of a solute is more ordered than that of water in the bulk. Thus, there is also lack of strong arguments for the conventional explanation of the entropic and/or enthalpic driving force for hydrophobic hydration phenomenon.

In this paper we compare the energy distribution of hydrogen bonds within the hydration sphere of a hydrophobic solute with that of the bulk water by means of the FTIR method. The spectral data enable us also to express these interactions in terms of the distribution of water interatomic distances by using experimental frequency−distance correlation functions.

Vibrational spectroscopy is a well-suited method for investigation of solute hydration.[3,4] Spectra of isotopically diluted HDO in H_2O prevent a number of experimental and interpretative problems connected with H_2O spectra.[5−7] To receive information about the structure and interactions inside the hydration sphere, the contribution of the bulk water to the spectrum should be removed to obtained the solute-affected water spectrum (refs 8 and 9 and literature therein). The time scale of the response of vibrational spectroscopy, $\sim 10^{-14}$ s^{-1} in the range of water vibrations, allows us to register even relatively short-lived species formed by water molecules influenced by a solute. They give rise to respective water absorption bands with a characteristic band position and band shape profile.[10] The most important factor in the interpretation of HDO spectra is the band position. The experimental Badger−Bauer rule, valid in most cases, states that the position of the water stretching band changes proportionally with the energy of a hydrogen bond.[11−14] Thus, the solute-affected HDO spectra give valuable information about the energetic states of perturbed water and are naturally suited for the aim of this work.

One of the practical problems in experimental studies of hydrophobic hydration is the selection of an adequate object for investigations. Nonpolar and nonionic solutes do not dissolve sufficiently in water, whereas polar or having hydrophilic group solutes demonstrate mixed types of hydration. In the case of ionic solutes the problem with the co-ion arises. Recently, a published paper[15] on the hydration of tetraphenylborate (Ph_4B^-) and tetraphenylphosphonium (Ph_4P^+) ions has also shown that water interaction depends on the kind of electric charge of an ion. It appears that only positively charged ions, like Ph_4P^+, could organize surrounding water molecules in a way we call hydrophobic hydration.

Aqueous solutions of symmetrical tetraalkilammonium cations (R_4N^+) have been long considered to provide model systems for a study of hydrophobic hydration; for the review see ref 16. From the number, thermodynamic, and transport properties investigations and from spectroscopic, ultrasonic, and dielectric relaxation studies, it has been concluded that tetrapropylammonium (Pr_4N^+) and especially tetrabutylammonium (Bu_4N^+) ion increase the structure of water, whereas the tetramethylammonium (Me_4N^+) ion diminishes the structure. The term "structure" is generally poorly defined as well as poorly translated into a molecular parameter characteristic of water around hydrophobic cation. The organization pattern of water in the vicinity of ions in dilute solution also remains questionable; icelike formation, clathratelike, or nontetrahedral hydrogen bonds have been considered.

Tetrabutylammonium cation (Bu_4N^+) has been studied as a model for investigation of hydrophobic hydration in aqueous solutions of Bu_4NBr, Bu_4NCl, and Bu_4NF. The selection of the respective salts was restricted by their solubility in water. For Br^--, Cl^--, and F^--tetrabutylammonium salts the problem with the considerable overlapping of cation- and anion-affected water bands occurred. This has been solved by bands division by using a multisteps self-consistent curve-fitting procedure.

Experimental Section

D_2O (99.84% deuterium) was produced by Institute of Nuclear Investigation, Poland. H_2O used for measurements was twice-distilled. Tetrabutylammonium bromide, $(C_4H_9)_4NBr$ (Flu-

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ka, puriss.), and tetrabutylammonium fluoride trihydrate, $(C_4H_9)_4$-NF·$3H_2O$ (Merck, more than 98% pure, for synthesis), were used without further purification. Tetrabutylammonium chloride, $(C_4H_9)_4NCl$, was obtained from tetrabutylammonium hydroxide (Serva, pure, 40% solution in water) and hydrochloric acid (reagent-grade purity) followed by crystallization. The crystals were dried in vacuo at 35 °C to a constant weight.

Stock solutions with H_2O were prepared for each tetrabutyl-ammonium salt. Sample solutions were made by adding 4% (by weight) of D_2O relative to H_2O ($H_2O + D_2O = 2HDO$, $K \approx 4$) and reference solutions (without D_2O) by adding the same amounts of H_2O. All solutions were prepared by weight, and their densities were measured using a bicapillary pycnometer at 25.0 °C.

FTIR spectra were recorded on an IFS 66 Bruker spectrometer. A cell with CaF_2 windows and a Teflon spacer was used. The path length was 0.0296 mm, as determined interferometrically. Five-hundred scans were made with a selected resolution of 4 cm^{-1}. The temperature was kept at 25.0 ± 0.1 °C by circulating thermostated water through the mounting plates of the cell. The temperature was monitored by a thermocouple inside the cell.

The spectra have been handled and analyzed by the commercial PC programs GRAMS/32 (Galactic Industries Corporation, Salem) and RAZOR (Spectrum Square Associates, Ithaca) run under GRAMS/32.

Analysis of Spectral Data. The method of analysis of the spectral data toward extraction of solute-affected solvent spectrum has been described in ref 9. It is based on the assumption that water in solution may be divided into bulk (*b*) and solute-affected (*a*) water. Accordingly, the total concentration of water in solution (c/mol dm^{-3}) is equal to $c_a + c_b$, then mean molar absorptivity of water in solution (ϵ) is equal to ($\epsilon_a c_a + \epsilon_b c_b$)/$c$. Hence,

$$\epsilon_a = \frac{c}{c_a}(\epsilon - \epsilon_b) + \epsilon_b \qquad (1)$$

or in molalities,

$$\epsilon_a = \frac{1}{NMm}(\epsilon - \epsilon_b) + \epsilon_b \qquad (2)$$

where m denotes the molality of solution (mol kg^{-1}), M is the mean molecular weight of water (H_2O + 4% D_2O) (kg mol^{-1}), N is the affected number that denotes the number of moles of water molecules influenced by 1 mol of solute, and ($\epsilon - \epsilon_b$) is the difference spectrum of the aqueous solution and pure water.[17]

Owing to the main assumption, the above equations are better performed for low molalities of solutions. When $m \rightarrow 0$, eq 2 reduces to

$$\epsilon_a = \frac{1}{NM}\left(\frac{\partial \epsilon}{\partial m}\right)_{m=0} + \epsilon_b \qquad (3)$$

Passing the procedure of approximation ϵ vs m at each wavenumber, relation 3 makes the basis for extraction of a solute-affected solvent spectrum extrapolated to infinite dilution when the affected number (N) is known.

Adjusting the N value, and thus the $\epsilon_a(\nu)$ spectrum, has been performed by band shape analysis of the data for the right side of eq 3 with varied N. The maximum value of N for which the data do not contain a shape of the bulk spectrum (HDO in pure H_2O) is regarded as the affected number and the corresponding $\epsilon_a(\nu)$ spectrum as the solute-affected spectrum. The procedure of finding this spectrum consists of computer simulation
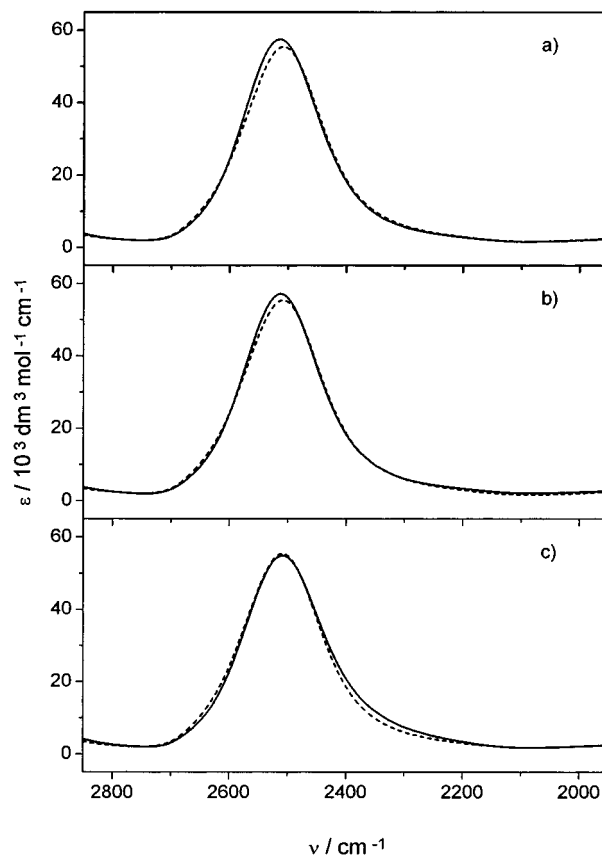

Figure 1. FTIR spectra of HDO in H_2O (dashed line) and in the most concentrated aqueous solution studied (solid line) of (a) Bu_4NBr at molality 1.019, (b) Bu_4NCl at molality 1.028, and (c) Bu_4NF at molality 1.015.

described in ref 15. The spectral data of the right side of eq 3 have been fitted as a sum of a linear baseline, analytical bands, and the bulk spectrum. With the minimum number of analytical band components the product of Gaussian and Lorentzian peak functions has been found as best-fitting the data. The intensity of the component of bulk spectrum in the simulated spectral data decreases with decreasing N value and reaches zero for the affected spectrum $\epsilon_a(\nu)$.

Results and Discussion

Figure 1 shows the spectra of HDO, in the range of OD stretching vibration, for the most concentrated aqueous solutions studied ($m \cong 1.02$) of Bu_4NBr, Bu_4NCl, and Bu_4NF, along with that in pure water. Each spectral series contains additional spectra for molalities of 0.346, 0.535, and 0.724. The absorption of H_2O has been eliminated by subtracting the absorption of the reference solution (without D_2O), recalculated for the same concentration of H_2O as in the sample solution.

Slopes $(\partial\epsilon/\partial m)_{m=0}$. An approximation of ϵ values vs m has been performed using both linear and quadratic regression. The linear relationship reflects the additivity for cation- and anion-affected water (salt-affected water does not change with molality), whereas the quadratic (and higher degree polynomial) relationship means lack of additivity. Both approximations work comparably well.[18] However, quadratic regression does not seem to be justified enough because of the small experimental difference between the spectra.[19] In Figure 2 the slopes $(\partial\epsilon/\partial m)_{m=0}$ have been shown for linear regression. They illustrate the intensity changes of the bands as the fraction of salt-affected HDO increases. In the case of linear relationship ϵ vs m, the
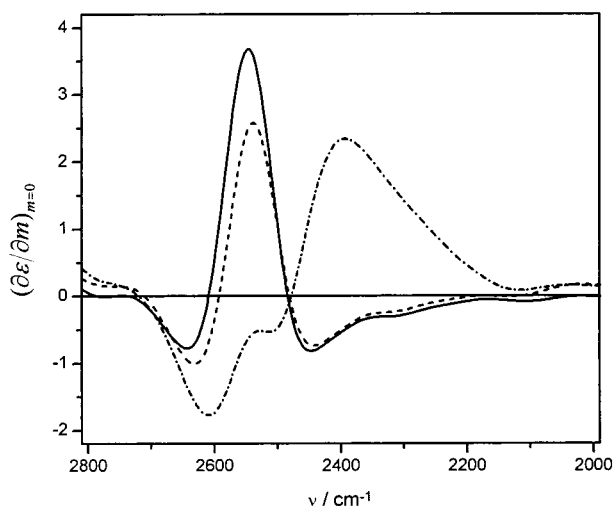
Figure 2. Derivatives $(\partial\epsilon/\partial m)_{m=0}$ for aqueous solutions of Bu4NBr (solid line), Bu4NCl (dashed line), and Bu4NF (dashed−dotted line). The derivatives have been shown for the linear relationship ϵ vs m, so they correspond in values to the difference $\epsilon(m) - \epsilon_b$ at $m = 1$ (see text).

Figure 3. HDO spectra affected by $Bu_4N^+Br^-$ (solid line), $Bu_4N^+Cl^-$ (dashed line), and $Bu_4N^+F^-$ (dashed−dotted line) together with the bulk HDO (dotted line).

derivatives in Figure 2 correspond in values with the difference spectrum $\epsilon(m) - \epsilon_b$, where $\epsilon(m)$ is an interpolated mean molar absorptivity of HDO in solution at molality m equal to 1. It is evident that the intensity most strongly increases with molality around 2546 cm^{-1} for $Bu_4N^+Br^-$, around 2538 cm^{-1} for $Bu_4N^+Cl^-$, and 2393 cm^{-1} for $Bu_4N^+F^-$. This enhancement is superimposed upon a general decrease in the intensity of the unaffected (bulk) water. In the case of $Bu_4N^+F^-$ the additional intensity-growing region has been observed around 2527 cm^{-1}, within the range of bulk water depletion, which is a sign of Bu_4N^+-affected water band.

Salt-Affected Spectra. After the adjusting procedure, the affected numbers,[20] N, were found to be equal to 7.4 ± 0.7 for $Bu_4N^+Br^-$, 8.1 ± 0.8 for $Bu_4N^+Cl^-$, and 9.7 ± 1.0 for $Bu_4N^+F^-$. The ranges of error for N values has been estimated from the results of the quadratic regression of ϵ vs m and from different starting parameters for analytical component bands in the curve-fitting procedure. Estimated N values increase in the order Br$^-$, Cl$^-$, F$^-$ salts, according to the polarizing power of the anions. The N values are small in comparison to the hydration numbers expected for the salts investigated. Even a hydration number of 46 has been published for the Bu_4N^+ cation;[21] Br$^-$, Cl$^-$, and F$^-$ tetrabutylammonium salts are known to form solid clathrate hydrates with the ideal formula $Bu_4N^+X^-{\cdot}32.8H_2O$.[22,23] Affected numbers generally do not have to correspond to hydration numbers; they show a number of solvent molecules statistically influenced by a solute, in comparison to the bulk solvent. One can assume that N equals the hydration number known from other techniques, having correspondingly affected the spectrum according to relations 2 or 3. Such treatment, in some cases, is accomplished in Lindgren's laboratory (ref 10, for instance). In our approach, only a few water molecules appear to be influenced by the proximity of dissolved ions; the rest resembles bulk water circumstances. This way, salt-affected spectra in Figure 3 show the water status in "concentrated form".

Figure 3 summarizes the band shape analysis, showing the salt-affected spectra for the solutions investigated along with the bulk HDO.[24] The $Bu_4N^+Cl^-$-affected spectrum resembles the one previously studied[15] for $Ph_4P^+Cl^-$. Figure 3 is very meaningful because of the following reason. The salt-affected spectra consist of cation- and anion-affected HDO, and it is

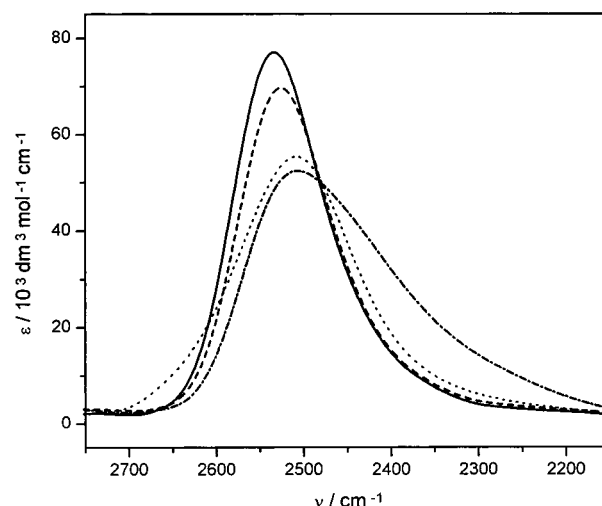known that Br$^-$- and Cl$^-$-affected bands have their maximum at higher wavenumbers than bulk HDO and that the F$^-$-affected band has the maximum at a lower wavenumber than bulk HDO.[10] Thus, from Figure 3 the observation is evident that Bu_4N^+-affected HDO has less absorption at the high wavenumber side than bulk HDO. That means fewer very weak H-bonds in water around the cation in comparison to bulk water. More detailed analysis of this effect has been performed by division of salt-affected spectra into anion- and cation-affected bands.

Ion-Affected Bands. The isolation of anion- and cation-affected bands from salt-affected spectra have been obtained by a curve-fitting procedure, which consisted of several steps.[25]

The results of the curve-fitting procedure have been shown in Figure 4, the consistency of it can be checked by the correlation in Figure 5 and by ref 26; the ion-affected band parameters have been placed in Table 1. Along with the band position of the maximum, the centers of gravity of the bands have been considered because of two reasons: (i) to have a measure of band asymmetry in relation to the band position at maximum; (ii) to have a better measure of the energetic state of water H-bonds than a band position at the maximum can deliver in the case of an asymmetric or a complex shape of water spectrum. As can be seen from Table 1, the asymmetry is rather negligible for the Br$^-$-affected band and increases distinctly with the low-wavenumber shift of the anion-affected band. Especially high asymmetry is shown for the Bu_4N^+-affected band.

The correlations of Figure 5 show positions of the maximum, ν_o, or gravity center, ν_g, for salt-affected spectra (y-axis) relative to the refined anion-affected band positions of the maximum, ν_o (x-axis). The points for bulk water have been also shown in the correlation to help find the band positions of Bu_4N^+-affected HDO. The idea is that the x-axis position for bulk water stands for the position of a hypothetical anion for which the affected water is bulk water (no anion-affected band). The intersection of this position with the correlation of ν_o and ν_g determines the respective positions for the Bu_4N^+-affected band. The correlation indicates that the position of the maximum for the Bu_4N^+-affected band is shifted toward higher wavenumber (2524 cm^{-1}) relative to that of bulk water (2509 cm^{-1}) and that the center of gravity position is the same as that for the bulk (2504 cm^{-1}) within the range of spectral and procedure errors. The values for the refined Bu_4N^+-affected band are equal to 2523 and 2502 cm^{-1} for ν_0 and ν_g, respectively (Table 1).

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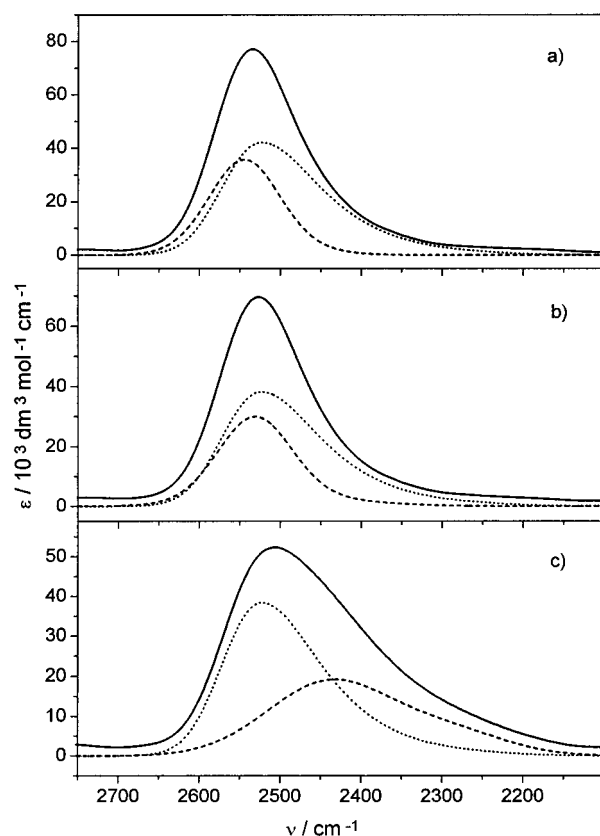*J. Phys. Chem. B, Vol. 103, No. 18, 1999* **3781**

Figure 4. Division of salt-affected HDO spectra (solid line) between Bu$_4$N$^+$-affected (dotted line) spectrum and the respective anion-affected (dashed line) spectrum for (a) Bu$_4$N$^+$Br$^-$, (b) Bu$_4$N$^+$Cl$^-$, and (c) Bu$_4$N$^+$F$^-$.
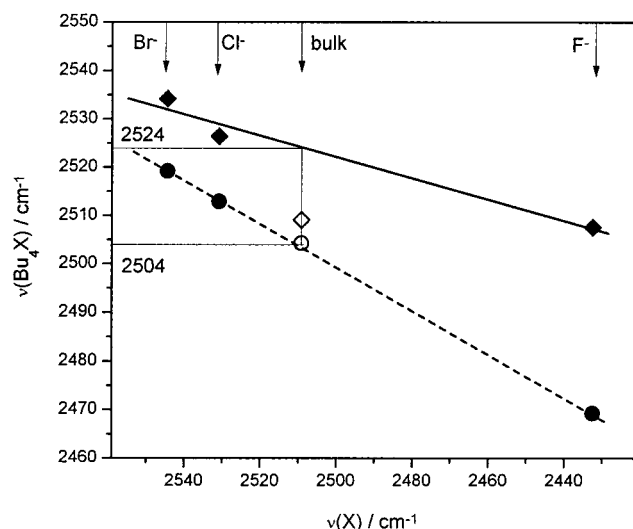

Figure 5. Correlation of OD band position of the maximum (solid diamond points, solid line) and of the gravity center (solid circle points, dashed line) Bu$_4$N$^+$X$^-$-affected band vs band position in maximum of X$^-$-affected band. Open points correspond to the bulk OD band (see text). X denotes the relevant anion.

The observed band positions of anion-affected bands (Table 1) reproduce the trend of the calculated frequencies for HDO in the OH region (as recalculated for OD region).[27] The anion-affected band parameters obtained can be directly compared with those already published by Bergström, Lindgren, and Kristiansson,[10] refined from aqueous solutions of Ni(II) and Na(I) salts. Perhaps the observed difference for Br$^-$ is within expected error, but for F$^-$ it exceeds that arising from the experimental and

TABLE 1: Ion-Affected and Bulk OD Band Parameters[a]

	ν_o,[b] cm^{-1}	ν_g,[c] cm^{-1}	$\Delta_{1/2}$,[d] cm^{-1}
Br$^-$	2544 ± 6	2543 ± 6	106 ± 8
	2556(8)[e]		147(8)[e]
Cl$^-$	2531 ± 4	2528 ± 4	112 ± 8
	2530(8)[e]		154(8)[e]
F$^-$	2433 ± 18	2414 ± 16	226 ± 10
	2472(8)[e]		203(10)[e]
Bu$_4$N^{+f}	2523 ± 6	2502 ± 8	146 ± 14
bulk	2509 ± 2	2504 ± 2	160 ± 2

[a] The estimated errors shown are based on experimental uncertainties and on results for different handling procedures of spectral data. [b] The band position of the maximum. [c] The band position of the gravity center. [d] The halfwidth. [e] The values of Bergström, Lindgren, and Kristiansson.[10] Estimated standard deviation is shown in parentheses. [f] The contour of the band can be approximated by the sum of three Gaussian components with the following band position, ν_o, and halfwidth, $\Delta_{1/2}$: (1) ν_o = 2542 cm^{-1}, $\Delta_{1/2}$ = 93.5 cm^{-1}; (2) ν_o = 2487 cm^{-1}, $\Delta_{1/2}$ = 129.0 cm^{-1}; (3) ν_o = 2409 cm^{-1}, $\Delta_{1/2}$ = 208.6 cm^{-1} and with the relative heights (1):(2):(3) = 3.675:3.436:1.

curve-fitting procedure. Another meaningful observation should be taken into account for the F$^-$ anion. It has been shown[10,28] that the F$^-$-affected HDO spectrum from NaF aqueous solution has a significant high-wavenumber component (2596 cm^{-1}). According to the authors,[10] this shoulder arises from OD of the HDO oscillator, which is pointing away from the anion when the OH oscillator interacts with the anion; the OD oscillator interacting with F$^-$ in the opposite direction gives the band at 2472 cm^{-1}. Similar behavior has been published for the SO$_4^{2-}$ anion from NiSO$_4$ aqueous solution.[10] However, we have not observed any such effect for Bu$_4$N$^+$F$^-$. It seems rather clear that F$^-$ hydration in both cases is different. For us, the published[10,28] results for Na$^+$F$^-$ could also mean that water molecules that interact with the anion do not form at the same time hydrogen bonds are formed via their lone electron pairs, suggesting the existence of a disorganized second hydration shell, like in the Frank–Wen zone model,[29] around anions of strong polarizing power. On the other hand, the effect observed for Bu$_4$N$^+$F$^-$ could be in accordance with the models considered by Narten and Lindenbaum[30] for X-ray scattering data of concentrated Bu$_4$N$^+$F$^-$·41H$_2$O solution at 25 °C. For the models, F$^-$ ions are part of a hydrogen-bonded network with butyl chains of the cations located inside the cavities formed by such framework. Thus, HDO molecules can interact more symmetrically through hydrogen atoms (between F$^-$ and another water molecule), having their electron pairs also involved in the network. Owing to the additional polarizing effect of interaction via lone electron pairs, HDO molecules should show a low-frequency shift[31,32] of the OD band relative to the position reported[10] for the Na$^+$F$^-$ system. We are aware that as a further consequence of the above-mentioned model, the Bu$_4$N$^+$- and anion-affected bands should not be completely independent of each other. Although the Bu$_4$N$^+$-affected band could be considered as an average of the polarizing power of anions under study, we did not find any direct evidence for it from the respective steps of the curve-fitting procedure.

Bu$_4$N$^+$-Affected Band. Figure 6 compares Bu$_4$N$^+$-affected with bulk HDO. The absorptivity of the Bu$_4$N$^+$-affected band has been scaled in Figure 6a to the same value for the maximum as the bulk band. As it can be seen, the affected band clearly shows higher asymmetry than the bulk does, with a lower absorption on the high-wavenumber slope of the band and the band position of the maximum shifted toward higher wavenumbers. At the same time the centers of gravity for both bands have the same position within expected error.
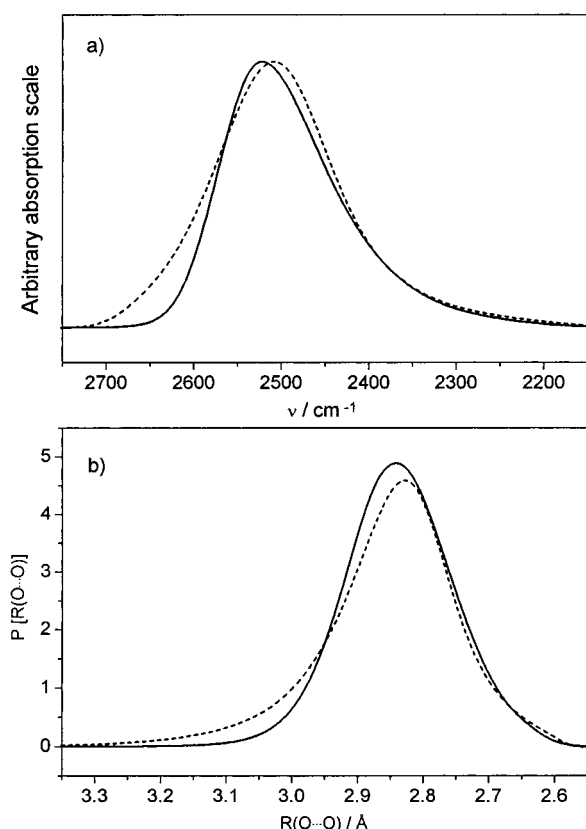
Figure 6. Comparison of the Bu_4N^+-affected HDO (solid line) and the bulk HDO (dotted line): (a) in OD absorption band; (b) in interatomic O···O distance distribution.

A comparison of the resulting Bu_4N^+-affected band position with that for bulk water can be performed from the point of view of water H-bond energy, using the experimental Badger–Bauer rule.[11-14] Originally, the rule deals with the band position at its maximum. We suggest that the center of gravity of a band could be a better measure of H-bond energy for asymmetric and complex shape water bands; at least it could provide a better comparison with respect to the bands considered.

In conclusion, an average H-bond energy of water surrounding the Bu_4N^+ cation is the same as that for bulk water. This result is in agreement with the effect of cooperative influence of cations on water, which has been comprehensively shown and disscused by Luck and coauthors.[32] At that point it is noteworthy that the above statement does not concern directly the energetic state of water in both cases because HDO spectra are much more sensitive to the energy of hydrogen bonds than to that of van der Waals interactions,[33-36] so the latter effect may be completely masked. Another important observation concerns the different distribution of H-bonds in the case of cation-affected and bulk water. This effect will be discussed subsequently in more detail.

More structural information, dealing with interatomic distances in solution, can be obtained from water band contours.[37,38] A number of experimental data may be used to construct a correlation between interatomic distances, known from solid hydrates, versus the wavenumber of water stretching (refs 37 and 39 and references therein). To convert the refined band-shape of the Bu_4N^+-affected HDO to the distribution of O···O distances, R, of surrounding water, we have used the procedure described in ref 38. The correlation equation in the form of $R = [16.01 - \ln(2727 - \nu_{OD})]/3.73$, obtained in ref 39, has been applied. The equation for the probability distribution[38] of the O···O distances, $P(R)$, versus ν_{OD} is

$$P(R) = Ca(\nu)(d\nu/dR)$$

where

$$\int_0^\infty P(R)\, dR = 1$$

C is the normalization constant, and $a(\nu)$ is the absorbance. This procedure can be used if the variation of the absorptivity across the band is constant with wavenumber. On the basis of the correlations shown in Bergström, Lindgren, and Kristiansson's work[10] for (i) the integral OD band intensities of HDO around different anions versus OD band position and (ii) the halfwidths of the OD bands with the band position, roughly linear plots for the band parameters can be obtained. Both the intensities and halfwidths proportionally increase with the low-wavenumber shift of the band. An approximately constant absorptivity across an OD band can be deduced from the above-mentioned plots taking into account that the absorptivity of a band is proportional to the quotient (*integral intensity*)/(*halfwidth*), which has a constant value.

Figure 6b shows the probability distribution of the O···O distances for Bu_4N^+-affected water as well as for bulk water. The distribution function for affected water is practicaly symmetrical. The O···O distance at the maximum of the function (the most probable distance) equals 2.842 ± 0.008 Å, wheras in the gravity center (mean distance) equals to 2.839 ± 0.010 Å. The function for bulk water is clearly asymmetrical with higher probability for long distances; the most probable distance equals 2.829 ± 0.003 Å and the mean distance 2.843 ± 0.003 Å. The three decimal numbers have been shown for better comparison between both types of water, whereas the uncertainties of distances shown arise only from the spectral uncertainties of band positions. The results obtained for bulk water are in good agreement with the value obtained from X-ray scattering studies;[40] the O···O distance changes gradually from 2.82 Å at 4 °C to 2.94 Å at 200 °C; the value 2.83−2.84 Å can be inferred at 25 °C. It is also worth to noting that the X-ray peak corresponding to the near-neighbor O···O interaction is not symmetrical and cannot be described by a single Gaussian distance distribution.

The observed difference between the hydration spheres of the Bu_4N^+ cation and of bulk water is contained in different distributions of water H-bond energy and of interatomic O···O distances for both species. On average, energetic states of water H-bonds and O···O distance are the same for both types of water. However, the population of H-bonds around the Bu_4N^+ cation is greater than for bulk water. This has been achived by an increase of the most probable intermolecular distance of water, perhaps because of H-bond deformation. Such phenomenon seems to be in accordance with the famous statement of Hertz:[41] "It thus follows that the structure increase must be such as to be attended by rupture or deformation of hydrogen bridges." The second possibility appears to be right. The structural observations obtained can be translated to thermodynamic characteristics of water transfer between pure water and aqueous Bu_4N^+ solution. The enthalpy change expected should be approximately equal to zero for the contribution of the H-bond energy (negative with the contribution of water−solute van der Waals interactions). The negative change for entropy transfer is expected because of the negative translational−rotational and orientational entropy contribution caused by the greater number of water H-bonds in the hydration sphere of the Bu_4N^+ cation.

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Conclusions

IR spectroscopy seems to provide valuable information about hydrophobic hydration if spectral data are analyzed in a way that leads to the separation of the solute-affected water spectra. In that respect the method appears to be a very sensitive tool for detecting subtle differences in structure and interactions of solvent molecules.

A comparison of the profile of the OD band for HDO affected by the Bu_4N^+ cation with that of bulk water as well as with the derived respective probability distribution functions of O···O distances leads to the conclusion that the energetic state of water H-bonds and water O···O distances are on average the same as for bulk water, but at the same time the population of H-bonds around the cation is greater. Qualitatively, the same kind of hydration was revealed for the Ph_4P^+ cation as recently reported[15] and also for the nonionic molecule of tetrahydrofuran.[42] Although the H-bond energy or O···O distances distribution do not give the full molecular particulars of hydrophobic hydration, our results support the opinion that the so-called hydrophobic hydration is mainly an entropy effect. This conclusion is in agreement with the suggestion anticipated by Luck.[43]

The differences detected for bulk and Bu_4N^+ hydration water are very important for the hydrophobic hydration phenomenon but not very pronounced in terms of structure and interactions characteristics. Taking into account that the applied method of the spectral analysis can see only some distinguished water molecules, which carry the effect of more molecules surrounding a hydrophobic solute (the reason for high sensitivity of the method), the observations seem to be in accordance to that from the neutron scattering method for the hydrophobic aqueous system studied.[2,44] They have shown no evidence that the structure of the hydration water close to a nonpolar group of the solute is more ordered than that of bulk water. This general observation agrees well with our results with respect to the mean H-bond energy and O···O distances of hydrated water. The detection of increased population of water H-bonds, which is presented in this work, additionally shows the nature of the entropic driving force of hydrophobic hydration. We suppose that the results obtained for the hydration sphere of Bu_4N^+ are more general for hydrophobic solutes. It should be again stressed that "iceberg formation" is a wrong and confusing expression for the effect of hydrophobic groups in water.

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(17) Equation 2 can be expressed in another form by inserting subtraction constant k for the difference spectrum of the aqueous solution and pure water: $\epsilon_a = (\epsilon - k\epsilon_b)/(1 - k)$, where $k = 1 - NMm$.[15] Subtraction constant k corresponds in fact to the parameter k_3 used by Lindgren and coauthors[8] in their method.
(18) The discriminant coefficient R^2 is generally higher than 0.9999, and the experimental scatter is less than 0.1 on the molar absorptivity scale, for points lying above 20% of the total height of the bands and less than 0.3 for points below this limit.
(19) In the range of the main OD band ($2700-2300$ cm^{-1}) there are only minor differences in comparison with the results of quadratic regression. Higher differences are observed for the low-wavenumber range ($2300-1800$ cm^{-1}) where libration water overtones dominate and absorption is very low.
(20) As a criterion, less than 0.5% of the bulk component in the total band area has been considered as the final point of band shape analysis.
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(24) The minimum number, three or four, of analytical band components has been used to fit adequately the presented salt-affected spectra in the range of the HDO band. Additional two or three analytical bands, along with a linear baseline, were necessary to correct the background.
(25) As a start point, the band for the Bu_4N^+ cation has been approximated to the low-wavenumber slope of the $Bu_4N^+Br^-$-affected spectrum and to the high-wavenumber slope of the $Bu_4N^+F^-$-affected spectrum, using one log-normal analytical contour. This way the asymmetry of the cation-affected band has been roughly described, which appeared as the critical parameter for adequate resolving of the spectra. In the next step, the cation contour obtained, along with a linear baseline and two (for Br^- and Cl^--affected bands) or three (for F^--affected band) Gaussian components, has been used to fit the salt-affected spectra in the range of the main HDO band. Additional components were used to correct the background. At this stage one of the three cation-band parameters, band position, halfwidth, and asymmetry factor, was fixed for all the salts and the rest of the obtained parameters were averaged. After the three cation band parameters have been adjusted for the first time, the procedure was continued and the progress was controlled by the correlation type shown in Figure 5 until consistency within the expected error have been attained.
(26) Taking into account the adjusted salt-affected numbers, N, the estimated uniformity of the height of the Bu_4N^+-affected band obtained from the salts studied is ca. 6%.
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