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Hydration of Aprotic Donor Solvents Studied by Means of FTIR Spectroscopy

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The paper attempts to explain the mutual influence of nonpolar and electron-donor groups on solute hydration, the problem of big importance for biological aqueous systems. Aprotic organic solvents have been used as model solutes, differing in electron-donating power. Hydration of acetonitrile, acetone, 2-butanone, and triethylamine has been studied by HDO and (partially) H_2O spectra. The quantitative version of difference spectra method has been applied to determine solute-affected water spectra. Analysis of the data suggests that solvent−water interaction via the donor center of the solute is averaged between water−water interactions around the solute. Such behavior can be simply explained by the model of solute rotating in a cavity of water structure, which is formed by clathratelike hydrogen-bonded water network. On the basis of the band shape of solute-affected HDO spectra and the corresponding distribution of intermolecular distances, the criterion for hydrophobic type hydration has been proposed. From that point of view, all the studied solutes could be treated as hydrophobic ones. The limiting band position and the corresponding intermolecular distance of affected water, gained with increasing electron-donating power of solutes, has been inferred from the data obtained. These observations are important for interpretation of vibrational spectra of water as well as for volumetric measurements of solutions. The simple model of hydration, proposed to better justify the results, connects the values obtained from the methods providing microscopic and macroscopic characteristics of the system studied.

1. Introduction

Knowledge about mutual influence of different structural groups on hydration of biomolecules is very important for understanding molecular recognition and native structures present in biological systems. The manner of hydration determines the structure and thus the activity of macromolecules of biological importance.[1] Knowledge concerning hydration itself in mixed type affinity of solute surface to water as a solvent is still incomplete and rather intuitive.

The goal of this paper is recognition of mixed types of hydration, i.e., the mutual influence of nonpolar and electron-donor groups on solute hydration. The results we have obtained hitherto for hydrophobic ions Bu_4N^+,[2] Et_4N^+,[3] and Ph_4P^+ [4] indicate that population of water hydrogen bonds (H-bonds) in the surrounding of such solutes is higher than for bulk water. That increase is carried on at the expense of weak and so-called “free” OH groups of water. Simultaneously, average energy of H-bonds does not change considerably because some weakening of H-bonds takes place inside the hydration layer. In other words, water molecules from hydration sphere of hydrophobic solute form more, but weaker H-bonds, when compared to bulk water. The observed difference consists of different distribution of H-bonds energies and corresponding intermolecular distances. Recently,[5] we have characterized, how hydrophobic effect of alkyl side chain is influenced by polarizing power exerted on water molecules by the electrophilic group of 2-butylamine. This effect is cooperatively transmitted to the interactions inside the clathratelike water “cage” around the alkyl group, effectively strengthening it.

Different aprotic organic solvents with widely varying electron-donating power have been used presently as components of hydration model systems studied. Their electron donor properties, which determine H-bond strength, can be characterized with different scales. They generally refer to reaction of the $X-H + B = X-H\cdots B$ type, for which the Gibbs energy or enthalpy have been measured; for references, see ref 6. Components of such model H-bonded system are in the gas phase or in solution diluted in an “inert” solvent. In that respect, all scales are not closely related to the systems studied in this work, namely, our base B (a solute) has been highly diluted in water (H-bond donor). Since the work of Taft et al.[7] and Arnett et al.,[8] 4-fluoro-phenol has proven to be a reference H-bond donor for the establishment of a thermodynamic hydrogen-bond basicity scale for organic bases B, denoted by pK_{HB} (negative logarithm of the formation constant of complex of 4-fluorophenol with B in CCl_4 at 298 K).[6] Another attempt is represented by the donor number scale (DN), proposed by Gutmann,[9] which corresponds to the negative enthalpy value (in kcal mol^{-1}) for 1:1 adduct formation of the electron donor solvent with $SbCl_5$ (as electron acceptor) in a highly diluted solution in 1,2-dichloroethane. We have already adopted this scale to some extent to the infrared characteristic of water diluted in organic solvents, qualified by the DN parameter.[10] The solvents, studied in this work as solutes, differ substantially with respect to their donor numbers: acetonitrile (DN = 14.1), acetone (DN = 17.0), 2-butanone (DN = 17.5), and triethylamine (TEA, DN = 61.0). For comparison, DN for monomeric water equals 18; however, the value for bulk water is considerably higher (DN = 26.7).[10]

Vibrational spectroscopy, which we have used in this work, is a valuable tool for the investigation of solute hydration.[11,12] Spectra of isotopically diluted HDO in H_2O are free from most

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of experimental and interpretative problems connected with H_2O spectra.[13−15] The decoupled OD water vibrations appear to be the most sensitive and ideally suited probe of ionic hydration. Spectra of H_2O, although more inconvenient in experiment and subject to various interpretations, ensure valuable structural information about hydration sphere of solutes.[16−19]

To extract information about the interactions inside the hydration sphere, the contribution of bulk water should be eliminated from the solution spectrum to obtain the solute-affected water spectrum. The corresponding method of spectral data analysis originates from Kristiansson, Eriksson, and Lindgren works.[20,21] The quantitative version of this method was formulated later by these authors and independently in our laboratory.[22,23]

The solute-affected water spectra allow registering even relatively short-lived species formed by water molecules influenced by a solute, because of the time scale of response of vibrational spectroscopy ($\sim10^{-14}$ s^{-1} in the range of water vibrations). Simultaneously, they give valuable information about the energetic states of perturbed water on the basis of empirical Badger−Bauer rule,[24] which states that the position of the water stretching band changes proportionally with the energy of a hydrogen bond. HDO vibrational spectra provide also basic structural characteristics of the solute-affected water, as the OD band position can be correlated with interatomic oxygen−oxygen distance. Several correlations linking R_{OO} with ν_{OD} have been published[22,23] and successfully used in the studies on ion hydration.[2,20,27]

2. Experimental Section

2.1. Chemicals and Solutions. Acetonitrile (99.5%, Aldrich), acetone (analytical amount, POCh S.A.), 2-butanone (99.9%, Aldrich), and TEA (99.5%, Aldrich) were used as supplied. D_2O (99.84% deuterium) was produced by Institute of Nuclear Investigation, Poland. The surface active agent $C_{13}H_{27}(OC_2H_4)_9$-OH has been kindly provided by Dr. Halina Szeląg from Department of the Technology of Fats and Detergents of the Chemical Faculty, Gdańsk University of Technology, Poland. H_2O used for measurements was twice distilled.

Stock solutions with H_2O were prepared for each solution series for HDO and H_2O spectra. Sample solutions for the HDO spectra were made by adding 4% (by weight) of D_2O relative to H_2O ($H_2O + D_2O = 2HDO$, $K \approx 4$) and the reference solutions (without D_2O) by adding the same molar amounts of H_2O. All solutions have been prepared by weight and their densities were determined with Anton Paar DMA 5000 densitometer at 25.000 ± 0.001 °C.

2.2. IR Measurements and Analysis. FTIR spectra were recorded on an IFS 66 Bruker or Nicolet 8700 spectrometer. For each spectrum, 256 scans were made with a selected resolution of 4 cm^{-1}. For HDO spectra, a cell with CaF_2 windows and a Teflon spacer was used; the path length was 0.0296 mm, as determined interferometrically. For H_2O transmission spectra, a cell with adjustable optical path length of ca. 0.002 mm with BaF_2 windows was also used. The temperature was kept at 25.0 ± 0.1 °C by circulating thermostated water through the mounting plates of the cells used. The temperature was monitored by a thermocouple inside the cell.

HDO spectra have been measured for solution molalities (m) in the range between 0 and 1, in less than 0.2 mol kg^{-1} steps. Approximation of molar absorptivity vs molality at each wavenumber measured has been verified to be the most justified by using linear regression ($R^2 > 0.9999$).

The procedure used for H_2O spectra has been described previously.[28] To improve adhesion of the very thin film of aqueous solutions to BaF_2 cell windows, a small addition of the surface active agent $C_{13}H_{27}(OC_2H_4)_9OH$ was applied. Because of the very small optical path length of the cell for H_2O solutions (~0.002 mm), the spectra have been additionally calibrated on the basis of the absorption of the same solutions measured in the thick cell with CaF_2 windows, with the precisely known optical path length. H_2O spectra have been measured for TEA aqueous solutions of molalities as follows: 0, 0.316, 0.320, 0.531, 0.533, 0.647, and 0.676 mol kg^{-1}. Approximation of molar absorption coefficient values vs m at each wavenumber measured has been done using linear regression; $R^2 > 0.9997$ and the maximum scatter of experimental data points from regression line did not exceed 0.5 in the scale of molar absorption coefficient. Practically, equally good fit could be obtained with a second-order polynomial.

The method of analysis of the spectral data toward extraction of solute-affected water spectrum has been described in ref 2. Accordingly, solute-affected water spectra in molar absorptivity scale is defined for each wavenumber as

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

where ϵ is the spectrum of water in solution at molality m (mol kg^{-1}) and ϵ_b is the spectrum of bulk water identical to the spectrum of pure water. Thus, $(\epsilon - \epsilon_b)$ denotes classical "difference spectrum". N parameter, called "affected number", equals to the number of moles of water affected by one mol of a solute, and M is the mean (4% D_2O in H_2O in the case of HDO spectra) molecular weight of water (kg mol^{-1}). Equation 1 makes the basis for extraction of solute-affected water spectrum at molality m. When $m \to 0$, eq 1 reduces to

$$\epsilon_a = \frac{1}{NM}\left(\frac{\partial\epsilon}{\partial m}\right)_{m=0} + \epsilon_b \tag{2}$$

Passing the procedure of approximation of ϵ vs m by the least-squares method, eq 2 enables the determination of solute-affected water spectrum extrapolated to infinite dilution, when the affected number (N) is known. The proper value of N can be found basing on spectra deconvolution, according to the published algorithm.[2]

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

3. Results and Discussion

Derivatives shown in Figure 1, together with the bulk HDO band for better comparison, have been used to determine solute-affected HDO spectra according to eq 2 and the band shape analysis performed following the previously published procedure.[2] Derivatives correspond to linear regression of $\epsilon(\nu)$ values vs solution molalities. Acetonitrile, the weakest electron-donor solvent studied, shows decrease in HDO absorption in the low wavenumber region, corresponding to strong H-bonds in liquid water structure. Accompanying increase of absorption at high wavenumber region corresponds to weak water H-bonds. Absorption increase in the region 2200−2320 cm^{-1} is due to incompletely compensated the ν(CN) band of acetonitrile, because a subtracting factor used in the procedure of determination of HDO spectrum for subtraction of H_2O in the sample and the reference solution is smaller than the factor for

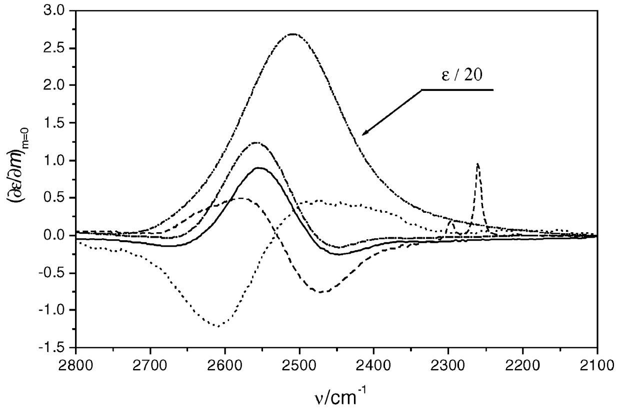

Figure 1. Derivatives $(\partial\epsilon/\partial m)_{m=0}$ for HDO spectra of aqueous solutions of acetonitrile (dashed line), acetone (solid line), 2-butanone (dash-dot line), TEA (dotted line), and the bulk HDO spectrum for comparison purposes (dash-dot−dot line; in molar absorptivity scale divided by 20).

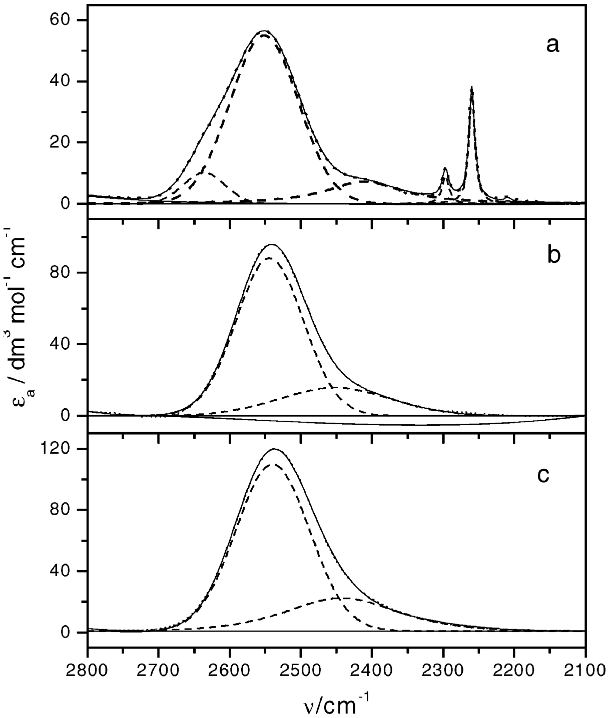

Figure 2. Decomposition of HDO spectra affected by (a) acetonitrile, (b) acetone, and (c) 2-butanone. Solid line, original affected spectrum; dashed lines, component bands; dotted line, sum of the component bands.

subtraction of solute absorption. Acetone and 2-butanone, stronger electron-donors than acetonitrile, and only slightly differing from each other, show similar course of derivatives. They reveal less absorption decrease in low wavenumber region than acetonitrile, the minimums correspond to ca. 2450 cm^{-1}, but at the position characteristic to icelike water (2420 cm^{-1}), the derivative value is about zero. That means stronger segregation of water H-bonds, when compared to bulk water: almost the same population of strong H-bonds, less of moderate strength, and much more of weak strength, as indicated by significant increase of absorption at high wavenumber region. TEA, which is a much more stronger electron-donor than the rest of aprotic solvents studied as solutes, shows also very different derivative course: significant increase in the region corresponding to strong water H-bonds with accompanying decreasing in the region of weak H-bonds.

Spectra of HDO affected by acetonitrile ($N = 1.5 \pm 0.3$), acetone ($N = 1.1 \pm 0.3$), and 2-butanone ($N = 1.5 \pm 0.5$) have been shown in Figure 2.

The acetonitrile−water system is unusual in some respects. Both components of mixture are known as favoring significant preferential solvation. There is a broad mixture composition range where acetonitrile molecules are unaffected by water molecules and strong tendency for self-association of water molecules has been evidenced.[29] Acetonitrile-affected HDO spectrum shown in Figure 2a reveals a shoulder at 2636 cm^{-1}. Its position corresponds to the band attributed to HDO diluted in acetonitrile.[29] Thus, discussed band component in the affected spectrum is most probably due to HDO molecules diluted in acetonitrile microphase. Another peculiarity concerns the low wavenumber component band at ca. 2410 cm^{-1}. In most cases such an analytical component is necessary to adequately approximate the band shape of solute affected HDO spectrum, as a correction of band asymmetry normally occurs. As such, this component does not carry any special physical meaning in a sense of an additional absorbing species. Decomposition of bulk HDO spectrum into analytical components also reveals a low wavenumber component.[20] However, in the case of acetonitrile its presence does appear like a shoulder, which takes place for acetonitrile-affected spectrum. On the other hand, in that case we do not have any suspicions regarding new absorbing species, so the shoulder appears as a result of especially strong segregation of water H-bonds surrounding acetonitrile molecule. According to discussion of derivatives in Figure 1, the population of strong icelike H-bonds is now smaller than for bulk water, but even smaller is the population of weaker H-bonds, giving the observable shoulder. This result is compatible with already mentioned strong tendency of water molecules to self-association in acetonitrile aqueous solutions.

Acetone- and 2-butanone-affected HDO spectra, shown in parts b and c of Figure 2, respectively, are very similar to each other and the solutes influenced the same number of water molecules, within experimental error. Both affected spectra also need a low-wavenumber component to approximate their band shape, as discussed previously. However, now it forms the “tail” of the band rather than a shoulder, as in the case of acetonitrile. It seems to be the result of a red shift of the main band for acetone and 2-butanone affected spectrum relative to the acetonitrile one.

The spectrum of HDO affected by TEA has been determined for $N = 6.1 \pm 0.3$, Figure 3a. The spectrum of H_2O affected by TEA corresponds to $N = 5.8 \pm 0.3$, Figure 3b. The band of HDO affected by TEA resembles the ones for bulk water, 2-butylamine-affected HDO previously determined,[5] as well as the liquid trimethylamine hydrate $(CH_3)_3N{\cdot}10.25H_2O$ HDO spectrum.[30] The main difference in affected spectrum between TEA and 2-butylamine is a small and narrow band observed at 2456 ± 7 cm^{-1} in the last case. We formerly ascribed[5] this band to a HDO molecule hydrogen bonded directly to a lone electron pair of nitrogen atoms of amine. Now we have corrected that interpretation, ascribing discussed band to vibrations of isotopically substituted N−D bond. Below pH 10 the protonated form of amine dominates in solution and this band disappears: coordination of D^+ to the electron pair of nitrogen atom cause significant red-shift of N−D vibration of 2-butyl-ammonium cation to ca. 2240 cm^{-1}, as observed.[5] In the case of TEA there is no possibility for the isotopic substitution, and we do not observe corresponding N−D vibration band of the free amine. In Figure 3a we can observe, however, the residual N−D vibration of the protonated amine at 2278 ± 18 cm^{-1}. By comparison with 2-butylamine results,[5] it can be estimated that

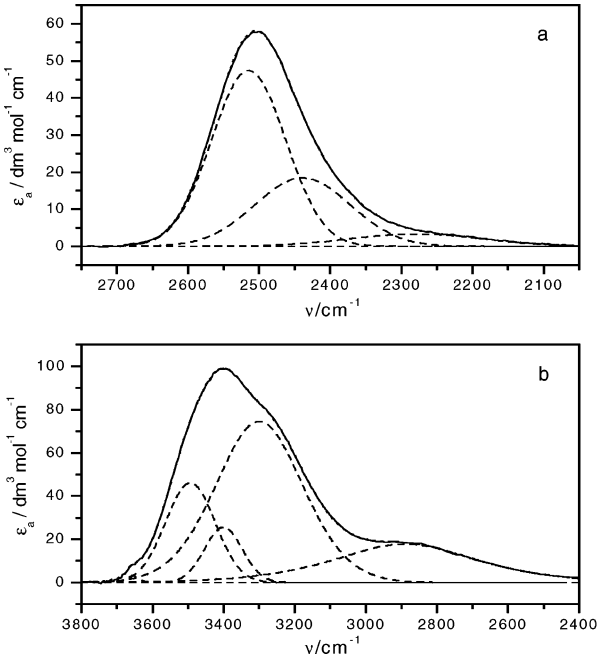

Figure 3. Decomposed (a) HDO and (b) H_2O spectra affected by TEA. Solid line, original affected spectrum; dashed lines, component bands; dotted line, sum of the component bands.

ca. 5% of TEA is protonated in diluted aqueous solution. The corresponding band is even more pronounced in H_2O spectrum affected by TEA. The low-wavenumber component band at 2890 ± 20 cm^{-1}, shown in Figure 3b, is due to ν(N−H) vibration of the TEA cation. The own absorption of TEA in the 2800−3000-cm^{-1} spectral range, attributed to C−H vibrations of ethyl groups, has been removed from Figure 3b.

The H_2O spectrum affected by TEA can be interpreted in a similar way, as we previously did for the spectrum of H_2O affected by tetrahydrofuran (THF)[28] and also by tetraethylammonium tetrafluoroborate.[3] Ascriptions of component bands shown in Figure 3b, most probably corresponding to the respective ones for bulk water (not shown in the figure), are based on previously published in ref 19 and references cited therein. To compare population of water molecules of different types in bulk and TEA-affected water, the correction of band intensity relative to band position has been applied. This is necessary because integral intensity of water stretching vibration bands increases with band shift toward lower wavenumbers.[31] In Table 1, a correction of band intensity for bulk and TEA affected water has been performed, so they represent molar contributions of H_2O molecules in different states.[32]

On the basis of the band component *D* (Table 1), which describes the state of OH oscillators in tetrahedral icelike water network, two important conclusions can be inferred. There is significant increase of icelike water around TEA relative to bulk but with weaker H-bonds (the blue shift of TEA-affected band component), perhaps because of less favorable arrangement of water molecules around the solute. This increase of icelike water population has been done with the expense of band component *C* (Table 1), which means, with the expense of water molecules population having their OH oscillators in distorted tetrahedral environment, which do not form all four H-bonds. The red shift of this band influenced by TEA can be attributed to water molecules in the hydration sphere, which interact additionally with lone electron pair of TEA. The band component *B* (Table 1) describes the state of OH oscillators, which form H-bonds belonging to molecules outside the tetrahedral network of water. The red shift of this band influenced by TEA can be attributed to H-bond formation with lone electron pair of the amine. We can see from Table 1 that the respective component band *B* is more intensive for TEA-affected water. The band component *A* (Table 1) describes another oscillator of the same water molecule that was already considered within component *B*. For TEA-affected water, component *A* reveals a blue shift because of the anti-cooperativity effect[33] of the second OH group of H_2O molecule forming H-bond with TEA.

TABLE 1: H_2O Band Parameters of Bulk and TEA-Affected Water (N = 5.8 ± 0.3) at 25.0 °C

band component[a]	ν^{o} [b]	fwhh[c]	I[d]	I_c[e]
		Bulk Water		
A (G)	3634 ± 2	81 ± 2	2.04 ± 0.08	3.6 ± 0.1
B (G)	3557 ± 2	151 ± 2	12.7 ± 0.3	19.6 ± 0.4
C (G)	3425 ± 2	205 ± 2	37.3 ± 0.3	43.9 ± 0.4
D (GL)	3253 ± 2	268 ± 2	47.1 ± 0.1	32.9 ± 0.4
		TEA-Affected Water		
A (L)	3656 ± 4	36 ± 4	0.56 ± 0.1	1.0 ± 0.2
B (G)	3503 ± 6	158 ± 4	21.0 ± 0.6	29.4 ± 0.6
C (G)	3405 ± 4	140 ± 6	16.4 ± 0.8	18.6 ± 1.0
D (GL)	3288 ± 6	295 ± 15	62.1 ± 0.8	51.0 ± 1.2
ν(N−H) (GL)	2883 ± 5	471 ± 25		

[a] Ascription given in text; band shape has been shown in parentheses: G, Gaussian band; L, Lorentzian band. [b] Band position at maximum/cm^{-1}. [c] Full-width at half-height/cm^{-1}. [d] Integral intensity of the component band relative to the integral intensity of the whole band; in the case of TEA-affected water, the band attributed to ν(N−H) has not be taken into account (%). [e] Corrected integral intensity of the component band relative to the corrected integral intensity of the whole band, corresponding to the mole fraction of water in the distinct state (%).

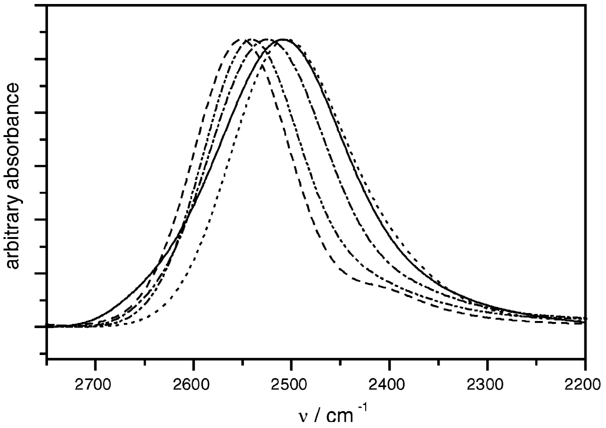

Figure 4. Affected HDO spectra for acetonitrile (dashed line), acetone (dash-dot−dot line), 2-butanone (dash-dot line), and TEA (dotted line) along with the bulk HDO spectrum (solid line). Height of the spectra has been scaled to the same value for better comparison.

Figure 4 summarizes results obtained for several aprotic organic solvents in water. In essence, these solvent-affected HDO spectra show features characteristic to electron-donor abilities of solvents, as well as of their nonpolar groups. Height of bands has been scaled to the same value, to enable better comparison. Spectra differ generally in the band position and the half width (Table 2). Their common feature appears as lower intensity at the high wavenumber slope when compared to the bulk HDO band. Acetonitrile-affected HDO band shown in Figure 2a has been devoided of high wavenumber component at 2636 cm^{-1}, which corresponds to water molecules included in acetonitrile microphase, as already discussed before, as well as of incompletely compensated acetonitrile own absorption in the range 2200−2300 cm^{-1}.

It is evident that solvents, which are characterized by DN higher than DN value for monomeric water (DN = 18), have

TABLE 2: Solvent-Affected and Bulk OD Band Positions and the Respective Interatomic Oxygen−Oxygen Distances at 25.0 °C

solute	N[a]	ν^{o}_{OD}[b]	ν^{c}_{OD}[c]	fwhh[d]	R_{OO}^{o}[e]	R_{OO}^{c}[f]	ref
bulk water		2509 ± 2	2505 ± 2	160 ± 2	2.829 ± 0.003	2.843 ± 0.003	this work
acetonitrile	2.5 ± 0.2	2551 ± 8	2544 ± 8 (2549 ± 8)[g]	119 ± 8 (131 ± 8)[g]	2.889 ± 0.005	2.891 ± 0.005	this work
acetone (AC)	1.1 ± 0.2	2540 ± 2	2532 ± 2	124 ± 6	2.872 ± 0.005	2.875 ± 0.005	this work
2-butanone (BN)	1.5 ± 0.5	2536 ± 2	2526 ± 2	138 ± 8	2.865 ± 0.005	2.870 ± 0.005	this work
tetrahydrofuran (THF)	3.3 ± 0.2	2525 ± 2	2502 ± 2	149 ± 6	2.835 ± 0.003	2.837 ± 0.003	28
dimethylacetamide (DMA)	2.9 ± 0.2	2519 ± 2	2497 ± 2	166 ± 6	2.835 ± 0.003	2.833 ± 0.003	34
tetramethylurea (TMU)	6.4 ± 0.2	2511 ± 2	2497 ± 2	167 ± 6	2.833 ± 0.003	2.828 ± 0.003	35
dimethylsulfoxide (DMSO)	2.8 ± 0.2	2519 ± 2	2497 ± 2	169 ± 6	2.828 ± 0.006	2.830 ± 0.006	36
2-butylamine (BA)	6.0 ± 0.2	2511 ± 10	2496 ± 10	148 ± 6	2.836 ± 0.005	2.832 ± 0.005	5
TEA	6.1 ± 0.2	2500 ± 2	2490 ± 2	151 ± 5	2.827 ± 0.003	2.824 ± 0.003	this work

[a] Affected number. [b] Band position at maximum/cm^{-1}. [c] Band position at gravity center/cm^{-1}. [d] Full-width at half-height/cm^{-1}. [e] The most probable oxygen−oxygen distance/Å. [f] Mean oxygen−oxygen distance/Å. [g] Taking into account the high wavenumber component band, see text.

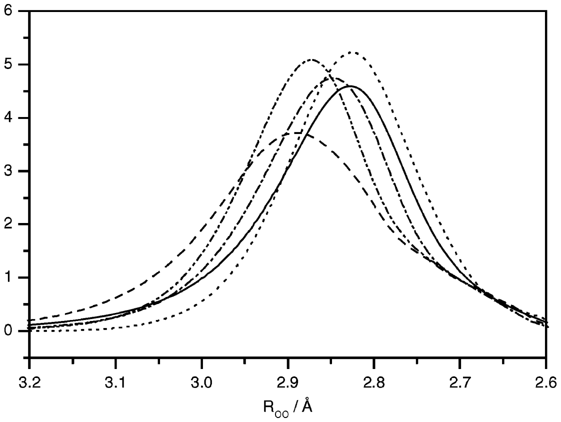

Figure 5. Interatomic oxygen−oxygen distance distribution derived from the HDO spectra affected by acetonitrile (dashed line), acetone (dash-dot−dot line), 2-butanone (dash-dot line), and TEA (dotted line) along with the bulk HDO (solid line) distance distribution curve.

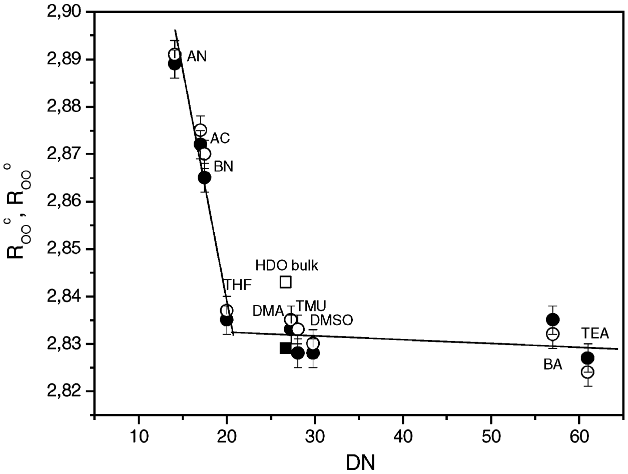

Figure 6. Correlation of the mean interatomic oxygen−oxygen distance (R_{OO}^{c}, open symbols) and the most probable interatomic oxygen−oxygen distance (R_{OO}^{o}, full symbols) of affected water relative to the DN of aprotic solvents as solutes from Table 2. The respective distances for bulk water have been marked and shown by square symbols. Errors shown correspond to ±0.003 Å.

affected HDO spectra, which differ only slightly, irrespective of significant difference in electron-donor abilities of these solvents. It is suspicious that acetone (DN = 17.0) and 2-butanone (DN = 17.5), which have similar donor number values but lower than the donor number for monomeric water, differ distinctly in shape and band position from the band of bulk water, whereas the band of HDO affected by TEA (DN = 61) differs only slightly. In on attempt to explain this behavior, the interatomic oxygen−oxygen distance distribution function, $P(R_{OO})$, for water affected by solvents has been shown in Figure 5, as well as the correlation of selected oxygen−oxygen distances, R_{OO}, with the donor number of solvent, shown in Figure 6.

We used the R_{OO} vs ν_{OD} correlation curve of Berglund et al.,[25] which allowed calculation of distance probability distribution function from absorption band shapes,[2,27] as proposed before.[21] In Figure 5 we have used two simple distances from the probability distribution curves, namely, the mean distance (corresponding to the gravity center of the area under the distance distribution curve, R_{OO}^{c}) and the most probable distance (corresponding to the maximum of the distance distribution curve, R_{OO}^{o}) to correlate them with donor number of solvent.

The state of water molecules is characterized not only by the band position in the maximum or in the gravity center but also by the band shape - all available information should be extracted. The band contour is generally asymmetric and differs between the systems studied. The asymmetry can be explained by the well recognized increase of the integrated intensity of water band with the shift to lower wavenumbers.[31,37] This means that infrared spectrum overestimates strongly H-bonded water molecules relative to weakly H-bonded ones. This effect has been already corrected when the spectral band contour has been transformed into the oxygen−oxygen distance probability distribution function, $P(R_{OO})$. These are the reasons for which the parameter R_{OO}^{c} seems to be the most rational measure (arising from infrared data) of the structural-energetic state of hydrated water.

When we compare HDO band shape of bulk water with that of affected water in Figure 4, it appears that the latter are more asymmetric, with the low-wavenumber tail. When these spectra are transformed to distance distribution curves, as in Figure 5, it appears that now solvent-affected HDO spectra give much more symmetric distribution function than the one for bulk HDO does. This manifests by close position of the R_{OO}^{o} and R_{OO}^{c} values in Figure 6 (the same within experimental error) for affected spectra and distinct separation of corresponding values for bulk water, with longer mean oxygen−oxygen distance relative to the most probable distance. This means that bulk water has larger population of weakly H-bonded molecules with respect to strongly H-bonded ones. For hydrated aprotic organic solvents, these populations are practically the same. We observed the same effect for symmetric tetralkylammonium cations, studied previously as model hydrophobic solutes.[2,3] They decrease population of weakly H-bonded water molecules in their surroundings, when compared with bulk water. On average, the energy of H-bonds and corresponding distances can be the same, slightly lower or higher than for bulk water, depending on the details of chemical superstructure of a solute. For "purely hydrophobic" solutes, previously studied,[2,3] it depends on solute size − in the case of already studied organic aprotic solvents, it depends on electron-donor ability of a solute.

We do not observe for solvent-affected HDO spectra the band component attributed to water molecules directly H-bonded to electron pair of donor atom of solvent molecule. Such interaction can be, however, inferred from the H_2O spectra of TEA solutions. These suggest that solute−water interaction is averaged between water−water interactions around a solute. The results can be simply explained by the model of a solute rotating in a cavity of water structure, which is formed by clathratelike network of water H-bonds. This model is in accordance with the results of rotational correlation times analysis of symmetric tetraalkylammonium ions determined in water and other solvents by the NMR method.[38]

From above discussion a spectral criterion for hydrophobic hydration can be inferred. The qualitative indicator of it for solute-affected HDO spectra is less absorption in high-wavenumber slope of the band, giving stronger asymmetry with pronounced low-wavenumber "tail", when compared to the bulk HDO band. A more univocal and quantitative test can be based on transformation of HDO band shape into probability distribution function of water oxygen−oxygen distances, which should show approximately the same values for the mean ($R_{OO}{}^{o}$) and the most probable distance ($R_{OO}{}^{c}$), within experimental error. In the light of formulated criterion, all aprotic organic solvents included in Figure 4 should be treated as hydrophobic solutes. The question could be asked, which solute in this group is the most hydrophobic? There is no univocal answer to this question solely on the basis of infrared spectra. As hydrophobic hydration phenomena is mainly controlled by entropy, more negative entropy change for the hydration should mean more hydrophobic solute. Infrared HDO spectra primarily deliver energetic characteristics the states of water molecules. Taking into account that for hydrophobic hydration, stronger interaction (more negative enthalpy change) causes generally even stronger decrease of entropy (more positive part in Gibbs energy of hydrated water),[39] we are forced to claim that TEA is the most hydrophobic solute in the studied series.

Another very important observation concerns the course of correlation R_{OO} vs DN values in Figure 6. It reveals that starting from the donor number value characteristic for monomeric water (DN = 18), solutes having stronger electron donating ability do not change HDO band position considerably and thereby do not change corresponding intermolecular distances of hydrated water. Qualitatively the same effect can be obtained by correlating R_{OO} vs pK_{HB} values,[40−42] instead of DN ones. pK_{HB}, as the thermodynamic measure of hydrogen-bond basicity, should be by definition even more closely related to hydration effects.

The subject discussed above seems to have more general nature. To prove that the discussed correlations are not an effect of some specific viewpoint of infrared spectroscopy, we compare the data obtained for molecular level characteristics with macroscopic volumetric measurements, such as limiting apparent molar volume of solutes in water. The intention of relations described below is to find correlation between limiting apparent molar volume (corresponding to the limiting partial molar volume) of the solutes in water and their FTIR spectroscopic data.

The limiting apparent molar volume of studied solutes in water, $V_\Phi{}^{o}$, can be approximated as a sum of three contributions: (*a*) the "intrinsic" volume of a solute, V_i, (*b*) the change of solvent volume resulting from perturbation by a solute which leads to change of hydrogen bond distances of water (structural effect), V_s, and (*c*) the empty volume, V_e, (also known as free, void, or dead volume) associated with packing of solvent molecules around a solute

$$V_\Phi{}^{o} = V_i + V_s + V_e \tag{3}$$

In our simplified model, the contributions b and c have been linked to the parameter N (affected number), used in our procedure of obtaining solute-affected spectra. The V_e contribution can be approximately expressed as

$$V_e = aSN \tag{4}$$

where S denotes the surface area of a solute molecule, a the thickness of empty volume space between the surface of a solute and the surface marked by average positions of solvent molecules in the first layer, and the N parameter is already discussed.

The V_s contribution can be expressed as a difference of volume of affected water in hydration sphere, V_a, and the volume of the same number of water molecules surrounding a solute with the structure of bulk water, V_b, (a hypothetical state of solution, where solute−solvent interactions do not exist)

$$V_s = V_a - V_b \tag{5}$$

therefore V_s can be approximated as

$$V_s = [NS\,(1 + 2a/r)bR_{OO}{}^{s}] - [NSbR_{OO}{}^{b}] = NSb[(1 + 2a/r)R_{OO}{}^{s} - R_{OO}{}^{b}] \tag{6}$$

where $R_{OO}{}^{s}$ and $R_{OO}{}^{b}$ denote oxygen−oxygen distance of water in the solution and bulk water, respectively, taken from spectral data (transformed to R_{OO}), r the effective radius of solute molecule, b the correction constant of R_{OO} value as to obtain oxygen−oxygen distance between nearest layers of water molecules measured logway to the solute radii (R_{OO} refers only to these oxygen−oxygen distances, which are collinear with hydrogen bond directions), it has been assumed to be the same for solution and bulk water. The relations can be easily derived for a spherical solute. Rearrangement of eq 3 gives

$$(V_\Phi{}^{o} - V_i)/NS = b[(1 + 2a/r)R_{OO}{}^{s} - R_{OO}{}^{b}] + a \tag{7}$$

In our case the radius of a solute is rather much higher than parameter a, so the term $2a/r$ can be neglected. As a result

$$(V_\Phi{}^{o} - V_i)/NS = b(R_{OO}{}^{s} - R_{OO}{}^{b}) + a \tag{8}$$

Equation 8 shows simple linear relationship between volumetric data of a solution and the change of the oxygen−oxygen distance in water structure due to solute−solvent interactions

TABLE 3: Volumetric Data and Calculated Molecular Parameters for the Studied Solutes

solute	V_{Φ}^{oa}	V_{vdW}^{b}	V_{vdW}^{c}	S_{SAS}^{d}
acetonitrile	47.42^{e}	46.69	28.12	108.7
acetone	66.9^{e}	63.31	38.13	128.5
2-butanone	82.6^{f}	79.95	48.15	146.2
tetrahydrofuran	76.8^{g}	75.83	45.66	137.3
dimethylacetamide	89.65^{h}	91.46	55.08	154.4
tetramethylurea	115.3^{e}	115.74	69.70	115.3
dimethylsulfoxide	68.92^{h}	69.96	42.13	139.1
TEA	120.9^{e}	125.33	75.47	187.2

[a] Limiting apparent molar volume/cm^3 mol^{-1}. [b] Calculated van der Waals volume/Å^3. [c] Calculated van der Waals volume/cm^3 mol^{-1}. [d] Calculated solvent accessible surface/10^4 cm^2 mol^{-1}. [e] Data from ref 53. [f] Data from ref 54. [g] Data from ref 55. [h] Data from ref 56.

($\Delta R_{OO} = R_{OO}^{s} - R_{OO}^{b}$), as well as the N parameter, obtained from infrared spectra.

There are many ways for obtaining molecular parameters like intrinsic volume and surface area of a solute.[43−50] We have used van der Waals volume as a measure of intrinsic volume ($V_i \equiv V_{vdW}$) and the solvent-accessible surface (SAS) as better corresponding to the considered model than the van der Waals surface ($S \equiv S_{SAS}$). The SAS measures only the surface area of a solute exposed to contact with solvent molecules. On the other hand, SAS is a surface that includes a value of radius equal to the van der Waals radius of a solute plus the radius of solvent molecule (1.4 Å in our case), thus the parameter a in our model is already accounted for this value.

The solute parameters, V_{vdW} and S_{SAS}, have been calculated by the grid method described by Bodor et al.,[51] using the atomic radii of Gavezotti,[52] implemented in HyperChem Release 6 for Windows program for molecular modeling by Hypercube Inc. Data used for correlations have been included in Table 3.

Correlations shown in Figure 7 generally give linear relationship with the correlation coefficient $R^2 = 0.98$, excluding the point for acetonitrile. This solute, as considerably smaller than the rest, apparently does not match the assumptions of our model. The slopes of the correlation lines, which are equal to the b parameter, have the value of ca. 3, instead of expected $b \leq 1$ and close to 1. This could be the result of the van der Waals volume taken for correlations, which is smaller than the volume included within the solvent accessible surface of a solute, but with the radius that does not include the radius of solvent molecule. Parameter a, calculated from correlation lines, equal to ca. 0.10 Å for ΔR_{OO}^{c} and ca. 0.06 Å for ΔR_{OO}^{o}, and must be increased by 1.4 Å, which corresponds to the radius of the solvent molecule, as already mentioned.

To recapitulate discussed correlations, electrically neutral aprotic solute cannot substantially decrease intermolecular distances of surrounding water with respect to the most probable distance of bulk water, as shown in Figure 7b. These observations can be justified by restricted water compressibility. This statement is not descriptive of the mean distance, as can be seen in Figure 7a, because there are much more weak H-bonds in bulk water than in water surrounding hydrophobic solutes, for which the mean and the most probable distances are almost equal, within experimental error. To achieve contraction of water volume, additional energy is necessary, which may be provided as electric work of inserting a charged solute into the water medium. The phenomenon of volume contraction of solvent around ions is well-known as electrostriction effect. The corresponding spectral conditions for ion hydration will be discussed in the following paper.

As a consequence of limiting value of the intermolecular distance (Figure 6) or the band position, the conclusion important for interpretation of water spectra may be reached. For solutions of electrically neutral aprotic solutes, HDO band attributed to water−water interactions cannot be expected at lower wavenumber than the position in maximum of bulk HDO band. It should be at least true for solutes which can rotate in water cavity, in conditions which allow averaging of water H-bonds around the solute. Up till now we have observed in the infrared only one group of solutes which do not obey the above statement, namely amino acids in the zwitterionic form. These examples are very specific, however, and will be discussed separately.

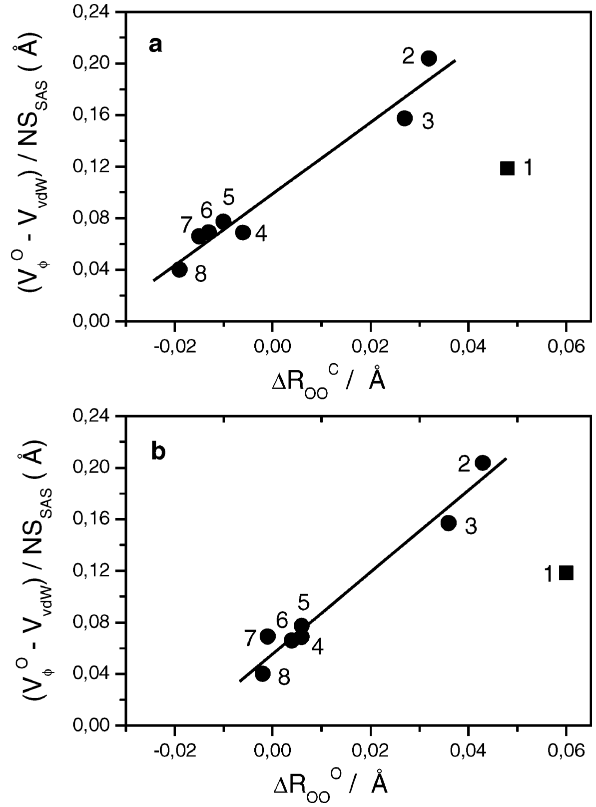

Figure 7. Correlation between limiting apparent molar volume (V_{Φ}^{o}), molecular parameters for a solute, van der Walls volume (V_{vdW}), and solvent accessible surface (S_{SAS}) and solute-affected number of solvent molecules (N) and the change of oxygen−oxygen distance of affected and bulk water molecules for (a) the mean distance (ΔR_{OO}^{c}) and (b) the most probable distance (ΔR_{OO}^{o}). Numbers shown correspond to the solutes: 1, AN; 2, AC; 2, BN; 4, THF; 5, DMA; 6, TMU; 7, DMSO; 8, TEA. Data taken for correlations have been included in Table 2 and Table 3.

4. Conclusions

Hydration of electron-donor aprotic organic solvents, studied as model solutes, implies averaging between solute-water interaction via its donor center and water−water interactions around a solute. In that respect the hydration is not specific in character. Such behavior can be simply explained by the model of a solute rotating in a cavity of water structure, which is formed by clathratelike H-bonded water network.

On the basis of the band shape of solute-affected HDO spectra and the corresponding distribution of intermolecular distances, the criterion for hydrophobic type hydration can be proposed. From that point of view, all the studied solutes should be treated as hydrophobic ones. To order their hydrophobic properties, one has to take into account energetic aspect of interaction: stronger average water H-bonds and thus shorter corresponding intermolecular distances should mean stronger hydrophobic character of a solute. This is because, for hydrophobic hydration, stronger interaction (more negative enthalpy part) causes generally even stronger increase of the entropy part ($-T\Delta S$) in Gibbs energy of hydrated water, as this phenomenon is mainly entropic in nature (ref 39 and references cited therein).

The band position and the corresponding most probable intermolecular oxygen–oxygen distance of hydrated water approach a limit with increasing electron-donating power of solutes. This observation, which can be justified by restricted water compressibility, is important for interpretation of vibrational spectra of water as well as for volumetric measurements of solutions. The simple model of hydration, which has been proposed for comparison of the results obtained by FTIR and other experimental techniques, connects the values from the microscopic and macroscopic methods of characterization of the studied system.

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(32) According to the Glew and Rath work[28] with regard to water diluted in a number of organic solvents, the composite H_2O band intensity is directly proportional to the red-shift of the asymmetric stretching frequency, ν_3, and can be ascribed by the formula $I = 131.3(3756 - \nu_3)$. The starting wavenumber 3756 cm^{-1} is the gas phase value for ν_3. In our method, the calculated total area of the composite H_2O band (I^g), referred to the position of the gravity center (ν^g), represents one mole of H_2O in the hypothetical state characterized by ν^g. The measured area of each component of H_2O spectrum, S_i, characterized by its band position at maximum, ν_i^o, (coincident with the gravity center for analytical symmetric band), can be corrected (obtaining S_i^c) using appropriate factors: $S_i^c = S_i(I^g + \Delta I_i)/I^g$, where ΔI_i denotes intensity change with respect to ν^g position. This equation can be expressed in another form: $S_i^c = S_i(1 + \Delta I_i/I^g) = S_i[1 + (\nu_i^o - \nu^g)/(3756 - \nu^g)]$, where $[1 + (\nu_i^o - \nu^g)/(3756 - \nu^g)]$ is a correction factor k_i. The corrected total band area is equal to $\Sigma S_i k_i$ and corresponds to one mole of H_2O. The contribution of *i*th component band in the corrected intensity, determined as $S_i k_i/\Sigma S_i k_i$, denotes mole fraction of water in the distinct state.
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