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FTIR-ATR Studies of the Hydration of 15-Crown-5 and 18-Crown-6 in Aqueous Solutions

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The hydration of 15-crown-5 (15C5) and 18-crown-6 (18C6) in aqueous solutions has been studied by FTIR-ATR spectroscopy. A model of decomposition of the O−H stretching band of water into four components, accounting for bound and bulk water in the solutions, has been employed in the analysis of the spectra. The dependencies of the relative areas and peak wavenumbers of the resolved components on concentration reveal similarities and differences in the hydration of the two crown ethers. The number of water molecules influenced by the hydration is ca. 18−20 for 18C6 solutions and ca. 12−15 for 15C5 solutions at sufficiently high dilutions. The immediate hydration shell for both crown ethers consists of 4−5 water molecules directly H-bonded to the crown ring. The most probable hydration structure around 18C6 is composed of two bridging water molecules and two other water molecules singly bound to the ring, while, due to differences in its conformational structure, 15C5 is hydrated mostly by singly H-bonded water molecules.

1. Introduction

The solvation, or more specifically the hydration, of simple crown ethers such as 12-crown-4 (12C4), 15-crown-5 (15C5), and 18-crown-6 (18C6) is of particular interest to understanding chemical recognition phenomena and the stability of host−guest complexes. The hydration has a strong effect on the conformation of the crown ring, which is best expressed for 18C6 aqueous solutions and has been well documented by a number of experimental techniques including Raman spectroscopy,[1−6] infrared spectroscopy,[7] X-ray diffraction,[8] quasielastic neutron scattering,[9] and ultrasonic velocity.[10,11] Computer simulations employing molecular mechanics,[12,13] molecular dynamics,[14−17] and Monte Carlo calculations[18,19] have successfully complemented the experimental studies. It is now well accepted that in water an 18C6 molecule has a predominant D_{3d} conformation of a centrosymmetric type which is most favorable for complexation with a guest.

Recent X-ray diffraction studies of the solid hydrates of 18C6 (tetra-, hexa-, octa-, and dodecahydrates)[20,21] have shown an immediate hydration structure consisting of four water molecules per crown ring in the D_{3d} conformation. Two water molecules (type W1) bridge two second nearest oxygen atoms on each side of the ring, forming donor H-bonds. Another two water molecules W2 (one per each side) form donor H-bonds to the remaining oxygen atoms of the crown ether and with the oxygen atom of W1.[20] This hydration structure probably extends to aqueous solution but is dynamically modified with respect to the bonding sites in the crown ring and exists for the lifetime of the respective H-bonds. Evidence for such behavior is provided by recent molecular dynamics and quantum mechanical simulations.[14,15] According to them, one bridging water molecule is strongly bound on each side of the crown to two oxygen atoms during the simulation time, forming a 1:2 ether−water complex. The third ether oxygen on each side, vacant at a given moment, is coordinated by a singly and loosely bound water molecule. Similar hydration patterns indicating two types of bound water molecules have been experimentally verified by FTIR spectroscopy for the isolated case of 18C6 hydration in carbon tetrachloride.[7] The analysis of the O−H stretching band in that study showed that two types of 1:1 adducts can be formed with equal probability. In the first case, one water molecule is bound in a bidentate (bridging) fashion between two of the ether oxygens of the crown, while in the second case, the water molecule is attached by a single H-bond in a monodentate fashion. Both types of bound water are characterized by specific bands at ca. 3685, 3600, and 3535 cm^{-1}.[7]

Our recent comparison of conformational changes around the C−C bond in aqueous solutions between crown ethers (15C5 and 18C6) and the corresponding short open-chain poly(oxyethylene)s (POE)[22] also showed a much higher population ratio gauche/trans for the crowns, which was attributed to H-bonding of the ether oxygens with bridging water molecules.

Experimental studies and computer simulations on 12C4 and 15C5 are not so abundant as on 18C6 and do not show a predominant conformation in the liquid state.[3,23−25] Rather, several conformers are found to exist for both 12C4 and 15C5 in the liquid state and in solution. Two extensive molecular mechanics calculation studies of these compounds[26,27] showed that there are four conformers in solution for 12C4, which constitute about 90% of the total population. These observations find partial confirmation from Raman spectral studies which show the existence of at least two conformers in solution. The analysis of 15C5 gives much more definite conclusions, especially for aqueous solutions, where the three conformers (3, 4, and 22) account for more than 98% of the total population of crown molecules.[27] Conformer 3 has a predominant population of 83.3% in water solution, which makes 15C5 similar in this respect to 18C6.

Summarizing all available data on the hydration of simple crown ethers, we felt that there is a necessity to study experimentally their hydration structure from the viewpoint of the changes in the H-bonded structure of the solution. These changes should be reflected in changes of the shape of the water O−H stretching band.

Fourier transform infrared (FTIR) spectroscopy is a quite popular method nowadays to study aqueous solutions especially

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after the commercial introduction of attenuated total reflection (ATR) accessories. However, studies of the water O−H stretching band region in a wide concentration range from dilute to concentrated solutions are not so numerous, because studying dilute solutions presents a difficult problem due to the high absorption cross section of water even when an ATR accessory is used. Hydration studies in wide range like this, on the other hand, are very interesting because of the existence of different concentration ranges, where the hydration changes. Obviously, at low concentrations, the bulk water contribution is dominant, while, on the contrary, at high concentrations, bound water is the dominant species.

It is the aim of the present paper to report on the results of hydration structure studies of 15C5 and 18C6 in a wide concentration range from ca. 1:1 to ca. 50:1 mole ratio of water to crown ether. The resolution of the IR O−H stretching band into components is chosen as an analytical approach.

Deconvolution of the water O−H stretching band into components has proven to be a powerful method for analysis of the structure of liquid water and water solutions with changes in temperature and concentrations of solutes.[28−34] We have recently applied a method of decomposition of the Raman O−H stretching band in aqueous solutions of simple open-chain POE ($C_1E_1C_1$ and $C_1E_2C_1$)[35,36] into two main components, corresponding to tetrabonded and not tetrabonded water, to analyze the dependence of the hydration structure on concentration. Unfortunately, no clear difference between bound and bulk water can be made in the frame of this model, although it gives a satisfactory picture of the hydration structure. In this work, we refine our analytical procedure and resolve the O−H stretching band into four components corresponding to different types of bound and bulk water.

2. Experimental Section

2.1. Materials and Recording of Spectra. 15C5 and 18C5 were commercial products supplied by Tokyo Kasei Kogyo. Aqueous solutions of these cyclic POE compounds were prepared for mole fractions ranging from 0.02 to 0.5 with doubly distilled deionized water. The FTIR-ATR spectra were recorded on a Nicolet Impact 400 spectrometer equipped with a DTGS detector using the CIRCLE ATR cell (Spectra-Tech) with a ZnSe cylindrical element of length ca. 7.5 cm and $^{1}/_{4}''$ diameter. To obtain high quality spectra even in the case of dilute solutions, especially in the O−H stretching region characterized with very high absorbance, the CIRCLE cell was filled only partially with the studied solutions. The spectra were recorded by coaddition of 400 interferograms at a resolution of 8 cm^{-1} and data points spacing 3.85 cm^{-1}. The spectra were corrected for the wavelength dependence of the penetration depth of the evanescent wave by using the Impact 400 software capabilities.

2.2. Processing of Spectra. To check if changes in the signal due to different levels of filling of the CIRCLE cell influence the results, we decided to normalize the FTIR-ATR spectra to some band area, which is considered linearly dependent on concentration in the whole studied range. The C−H deformation band of the crown ethers at ca. 1460 cm^{-1}, which should be conformation independent with changes in concentration, was chosen for this purpose. We normalized every spectrum to the total area of its C−H deformation band integrated after baseline correction between 1420 and 1505 cm^{-1}. In fact, proper normalization with respect to water should result in linear dependence of the integrated total area of the O−H stretching band, S_{OH}, on the mole ratio, as the total absorption cross section for the O−H stretching band is not expected to be concentration dependent as predicted by Beer's law. The dependencies of S_{OH} in 15C5 and 18C6 aqueous solutions on mole ratio, calculated after simultaneous curve fitting of the C−H and O−H stretching bands (see below), are shown in Figure 1. The high linearity with linear regression coefficients 0.9982 and 0.9994, respectively, proves that our experimental method is correct. Examples of the normalized spectra in the C−H and O−H stretching regions are shown in Figure 2.

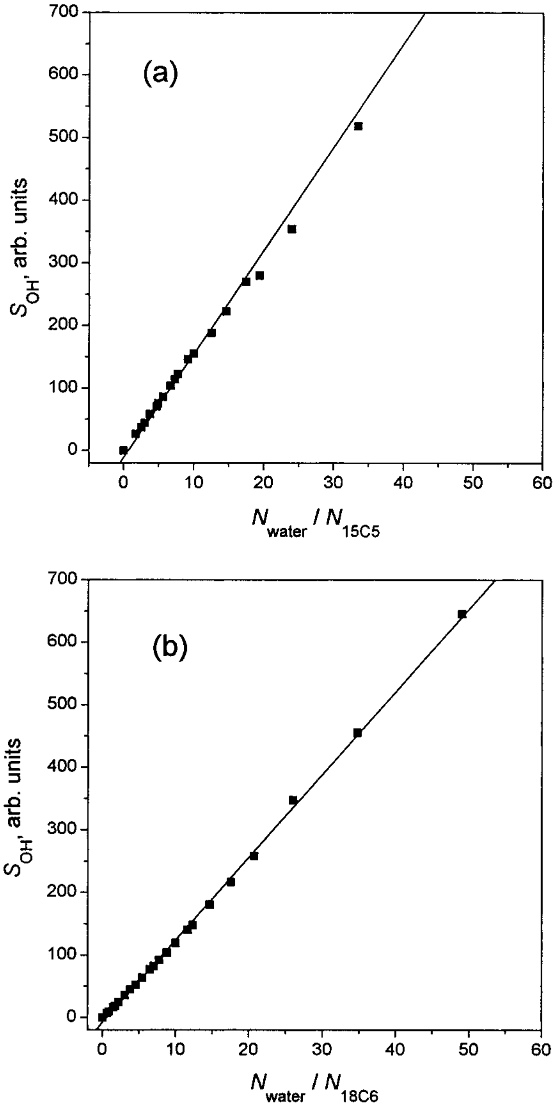

Figure 1. Dependencies of the integrated total area of the O−H stretching band on the mole ratio of water to crown ether: (a) 15C5 aqueous solution and (b) 18C6 aqueous solution. The lines correspond to a linear fit with regression coefficients 0.9982 for (a) and 0.9994 for (b).

A problem which arises in the analysis of the spectra is the partial overlapping of the C−H and O−H stretching bands. To separate both bands and at the same time to resolve the O−H stretching band into components, we chose to resolve simultaneously the C−H and the O−H stretching bands into six and four components, respectively, for 15C5 and into five and four components for 18C6. The best results were obtained, as shown in Figure 3, when the bands were fitted with fixed shape components of 70% Gaussian + 30% Lorentzian functions with all other parameters being varied upon iteration. Four components for the O−H stretching band describe correctly the existing types of H-bonded O−H oscillators in the whole range of concentrations studied. We have examined the shape of the

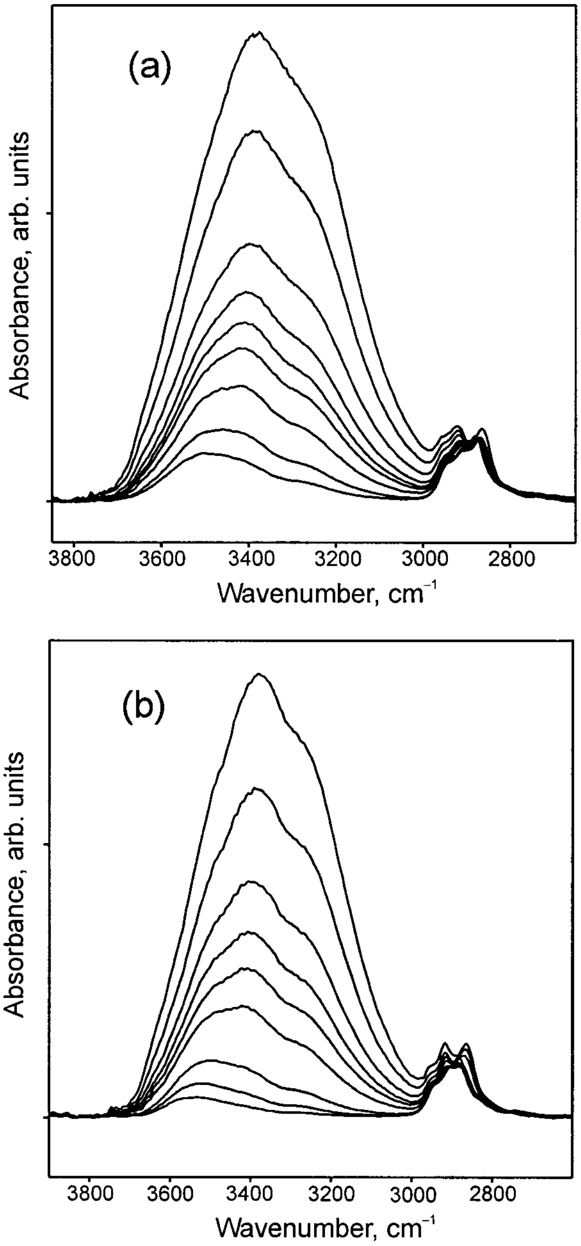

Figure 2. Examples of IR spectra in the C−H and O−H stretching region normalized to the integrated intensity of the C−H deformation band: (a) 15C5 aqueous solution and (b) 18C6 aqueous solution. Mole fractions in (a) are, from top to bottom, 0.029, 0.054, 0.074, 0.098, 0.114, 0.130, 0.168, 0.249, and 0.361, and mole fractions in (b) are, from top to bottom, 0.037, 0.046, 0.064, 0.079, 0.091, 0.124, 0.245, 0.360, and 0.514.

O−H bands at the lowest water content for both crown ether solutions and found that, although there is a basic contribution in the region centered around 3500 cm^{-1}, which should be due to bound water molecules, a shoulder around 3300 cm^{-1} is also observed and should correspond to bulklike water molecules. Therefore, in accordance with the present understanding of 18C6 immediate hydration[7,14,15,18] and the vibrational structure of bulk water, we fitted the O−H stretching band with four components. The two low-wavenumber components at ca. 3290 (component I) and 3400 cm^{-1} (component II) (Figure 3), which are of low magnitude in the highly concentrated crown ether solutions, but dominate the absorbance spectra at low concentrations, are traditionally connected with the H-bond network of bulk liquid water.[37,38]

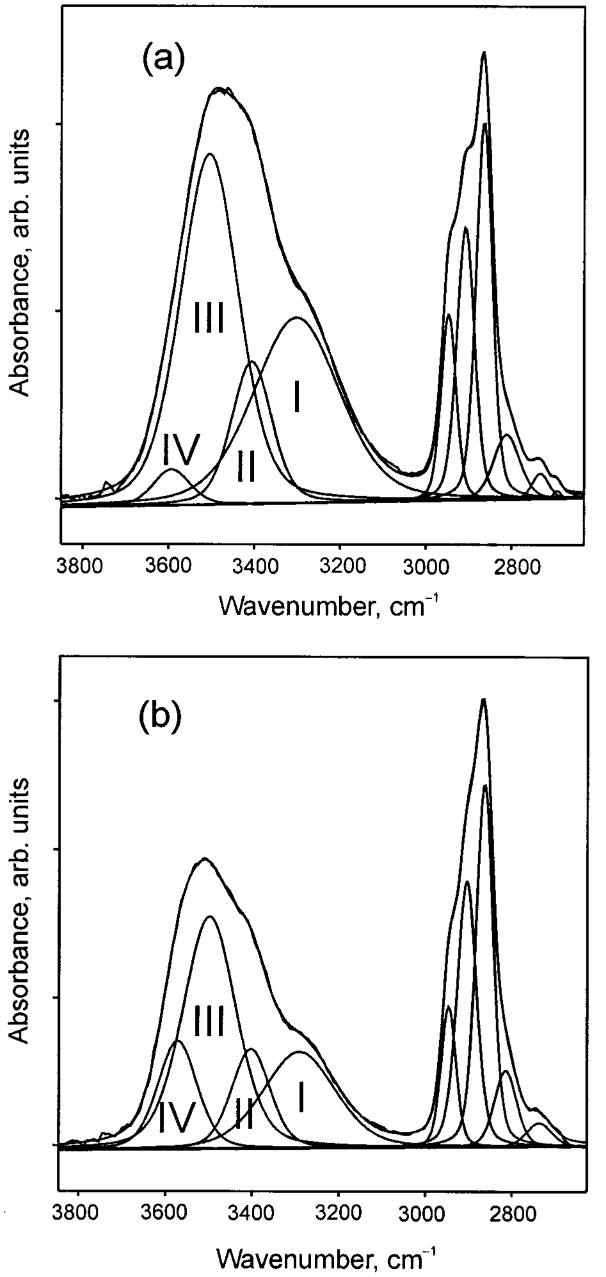

Figure 3. Examples of simultaneous decomposition of the C−H and O−H stretching bands into components: (a) 15C5 aqueous solution with 0.285 mole fraction and (b) 18C6 aqueous solution with 0.310 mole fraction.

We assume, adhering to the model based on Raman spectral measurements initially proposed by Walrafen[39] and subsequently developed by Green et al.[31] and Hare and Sorensen,[29] that component I at ca. 3290 cm^{-1} (3240 cm^{-1} in the Raman spectra[35,36]) corresponds to the collective in-phase O−H stretching vibrations of H-bonded aggregates consisting of a water molecule and its nearest and higher order neighbors. The relative intensity of this collective mode is an indicator of the extent to which strong and uniform H-bonding exists in the liquid. Thus, it usually describes the collective in-phase stretching vibrations of large clusters of tetracoordinated water molecules in liquid water. The Fermi resonance of the bending overtone ($2\nu_2$) with the symmetric (ν_1) O−H stretching vibration has been considered in the past as one of the reasons for the appearance of this low-wavenumber feature in the O−H stretching spectrum. However, the influence of Fermi resonance has recently been

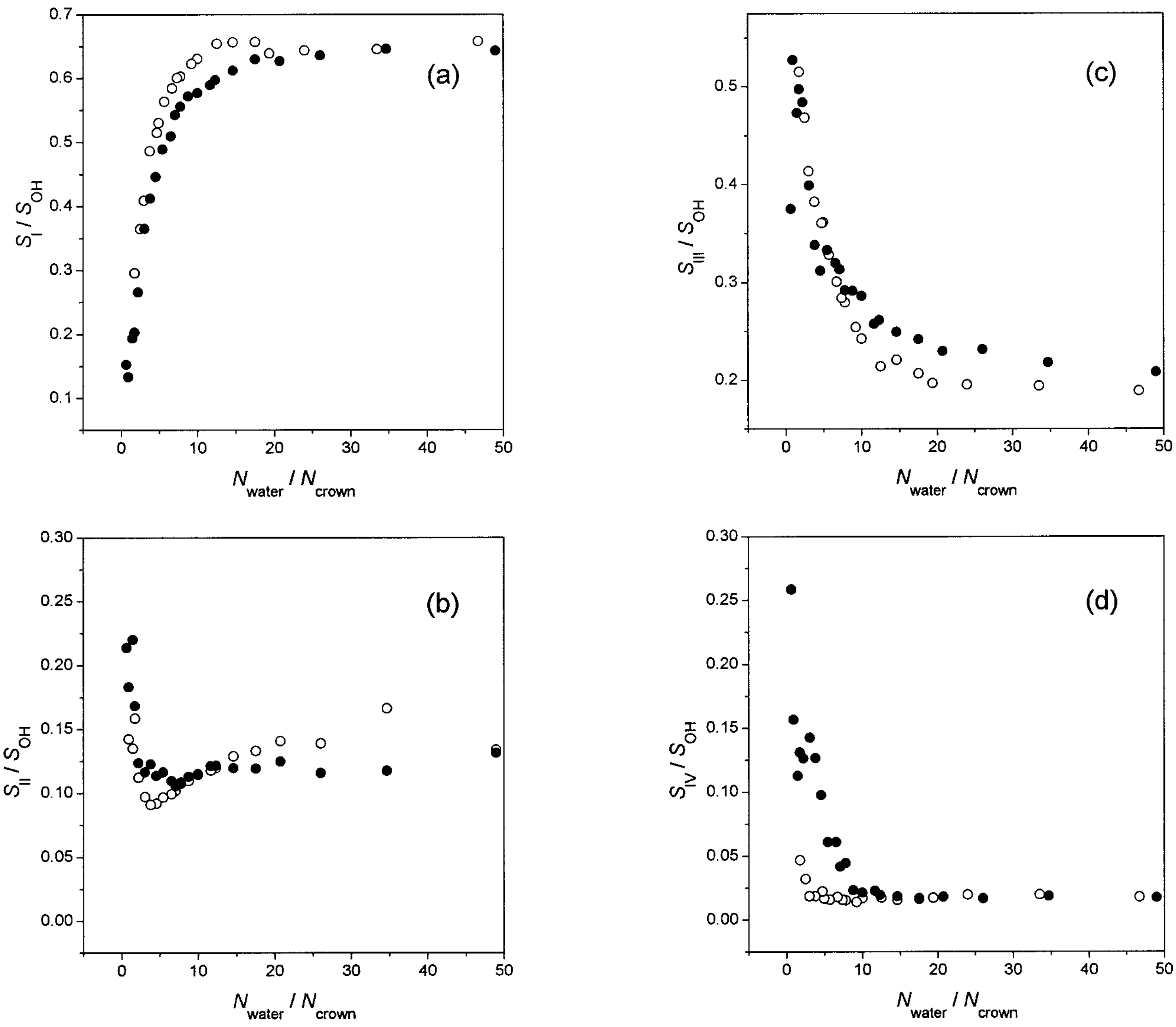

Figure 4. Dependencies of the relative areas of the respective components of the O−H stretching band on the mole ratio for 15C5 aqueous solution (open circles) and 18C6 aqueous solution (filled circles): (a) component I, (b) component II, (c) component III, and (d) component IV.

shown to be weak or absent.[29,40] Supporting the assignment of component I is its highly polarized nature in the Raman spectrum[31] and the fact that it evolves into the main component in the spectrum of supercooled water.[29] Component II at ca. 3400 cm^{-1} (3420 cm^{-1} in the Raman spectra[35,36]) is attributed to O−H stretches which are not in-phase between nearest or higher neighbor molecules in bulk water and can be considered as not fully tetrabonded. Marechal[41] and Libnau et al.[42] have also derived definite conclusions supporting the above two-state model of water based on precise FTIR-ATR measurements of the O−H vibrational spectrum. At higher crown ether concentrations, component II will eventually also reflect the properties of water molecules influenced by the hydration. The existence of aggregates of water molecules (cyclic dimers and polymers) as structures with more distorted and energetically unfavored H-bonds has been suggested to explain its origin.[43−45]

Two components at ca. 3500 (component III) and 3600 cm^{-1} (component IV) were assumed to contribute to the band absorbance in the high-wavenumber region of the O−H stretching band (Figure 3). In accordance with the recent studies of 18C6 immediate hydration,[7,14,15,18] we assigned component III to the symmetric O−H stretching vibration of bidentate water molecules H-bonded to two second nearest oxygens in the ring, overlapped with the bonded O−H stretch of monodentate (singly bonded to the ring) water molecules. Component IV was assigned to the asymmetric O−H stretching vibration of bidentate water molecules.[7] Both these components correspond to water molecules directly connected with H-bonds to the crown ether ring and therefore can be considered as bound water. We assume that a similar decomposition can be employed also for 15C5 because of the dominance of a single conformation,[27] in which favorable conditions for H-bonds of both kinds exist, although there is still no experimental evidence to support this. Thus, in the whole range of concentrations studied, a division between “bound” and “bulk” water molecules can be made in a somewhat conditional sense. Components II, III, and IV express the contribution of the water molecules influenced by the hydration and are considered as bound water, and component I corresponds only to bulk water.

At low concentration of the crown ethers, components III and IV should preserve the contribution of bound water, but due to the dominance of bulk water, they will reflect mostly its structure. Therefore, a change in the assignment of these bands should be adopted. We have assumed that the decomposition into four components should be preserved, but in the region above mole ratios of about 20 (see below), components III and IV will reflect mainly the behavior of bulk water. An assignment of these components, based on a recent review of the Raman spectra in the O−H stretching region of liquid bulk water by Walrafen et al.,[46] is that the 3500 and 3600 cm^{-1} components correspond to the O−H stretching vibrations of water molecules, in which one proton is not engaged in linear or nearly linear H-bonding. The 3500 cm^{-1} component corresponds to the H-bonded O−H oscillator of such molecules, while the 3600 cm^{-1} vibration is attributed to the "free" O−H oscillator.

3. Results

We have chosen to analyze the results of the curve fitting of the water O−H stretching band in terms of the mole ratio (mr) of water to crown ether, N_{water}/N_{crown}, where N_{water} and N_{crown} are the mole amounts of water and crown ether, respectively, at a given composition. This ratio gives a better picture of the interactions in the solution and of the hydration in particular, as it is a direct measure of the total number of water molecules which correspond to one crown ether molecule at a given concentration. Two parameters of the resolved components, relative area and peak wavenumber, have an important meaning in studying the hydration behavior. The relative areas of the components S_i/S_{OH}, where i = I−IV and $S_{OH} = S_I + S_{II} + S_{III} + S_{IV}$, are representative of the variations of the different fractions of H-bonded water molecules assigned to each component. The peak wavenumbers express the strength of the respective H-bonds as well as the variations in the average O···O distances between the water molecules in the H-bond network of bulk water.[47,48]

3.1. Dependencies of the Relative Areas. The dependencies of the relative areas of components I−IV on the mole ratio are shown in Figure 4. The dependencies of component I corresponding to bulk water showed two characteristic regions for both crown ether solutions (Figure 4a). Up to around 10−15 mr, there is a continuous steep increase in the fraction of bulk water molecules. After ca. 15 mr, the fraction of bulk water remains almost constant up to the highest dilutions studied. The mole ratio at which the relative area of component I assumes constant behavior is around 13−15 for 15C5 and around 18−20 for 18C6.

The general behavior of the other three components for 15C6 and 18C6 solutions follows an opposite tendency (Figure 4b−d). Their areas have their maximum values at very high concentrations of crown ether or at very low values of the mole ratio. Then, they quickly decrease down to around 5−7 mr and after this remain almost constant or slowly decreasing up to higher dilutions. The similarities in the general behavior of S_{II}/S_{OH}, S_{III}/S_{OH}, and S_{IV}/S_{OH} with increase in mole ratio for both crown ethers, following an opposite tendency to the behavior of S_I/S_{OH}, suggest that we can view components II, III, and IV as corresponding to bound water or water affected by the hydration at least in the range up to ca. 20 mr. Figure 5 shows plots of the relative areas S_I/S_{OH} and $(S_{II} + S_{III} + S_{IV})/S_{OH}$ for both solutions.

A more detailed comparison between the dependencies of the relative areas of the different components reveals some interesting peculiarities. The fractions of the bulk water components, corresponding to S_I/S_{OH}, for both solutions at higher dilution (above 30 mr) have very close values (0.62−0.65), and the same is true, of course, for the total bound water components, $(S_{II} + S_{III} + S_{IV})/S_{OH}$ (0.35−0.38).

The dependencies of S_{II}/S_{OH} are more noisy (Figure 4b) due most probably to the high degree of overlapping of component II with the other components (Figure 3). Nevertheless, an initial steep decrease from the values at very concentrated solutions and a shallow minimum at around 5−7 mr can be observed for both crown solutions, the one for 15C5 being deeper. After this the dependencies are almost constant.

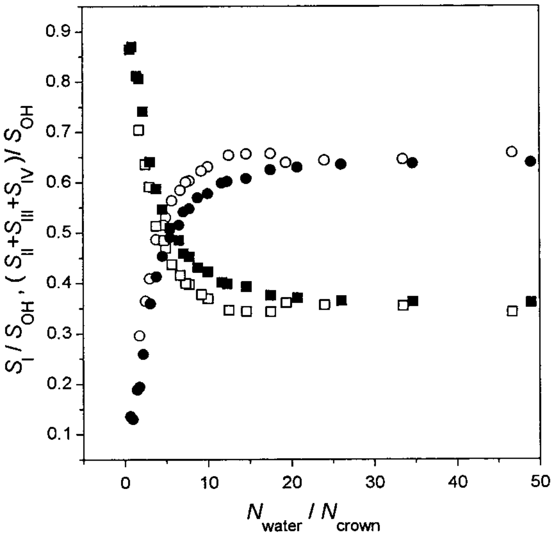

Figure 5. Dependencies of the relative areas S_I/S_{OH} and $(S_{II} + S_{III} + S_{IV})/S_{OH}$ on the mole ratio: (open circles) S_I/S_{OH} of 15C5 aqueous solution; (open squares) $(S_{II} + S_{III} + S_{IV})/S_{OH}$ of 15C5 aqueous solution; (filled circles) S_I/S_{OH} of 18C6 aqueous solution; (filled squares) $(S_{II} + S_{III} + S_{IV})/S_{OH}$ of 18C6 aqueous solution.

The fractions of bidentate and monodentate bound water molecules, reflected in S_{III}/S_{OH}, have a different rate of decrease for the two solutions. After the initial steep drop (Figure 4c), the relative area of component III of 18C6 assumes a more gradual decrease compared to that of 15C5. Thus, the greater changes in the hydration structure of the 18C6 solution influenced by both types of water molecules bonded to the crown ring might be assumed, in comparison to 15C5 solutions, in the range of higher dilutions (above 10 mr). The comparison of the dependencies of S_{IV}/S_{OH} on concentration is even more interesting (Figure 4d). As a whole, the relative area of the bridging water component in 18C6 solutions down to around 10 mr is 4−5 times greater than the corresponding area for 15C5. This suggests that the relative fraction of bridging water molecules is much higher for 18C6. Moreover, a small but well-defined maximum at around 3−4 mr can be observed for 18C6 solutions, suggesting that there is probably an optimal hydration configuration at these concentrations. This is not observed for 15C5 solutions. After about 10 mr, the normalized areas of component IV for both solutions approach a constant value of ca. 0.02.

3.2. Dependencies of the Peak Wavenumbers. The dependencies of the wavenumbers of the resolved components show more characteristic behavior on concentration changes, as shown in Figure 6. The wavenumbers of component I, corresponding to tetrabonded bulk and bulklike water molecules, pass through a well expressed maximum at ca. 4−5 mr and then decrease to almost constant values of ca. 3270 cm^{-1} at high dilutions (Figure 6a). The wavenumber dependencies of component II are quite noisy, due to the severe overlapping with neighboring components, but nevertheless, a small minimum in the range 3−5 mr could be clearly observed in their generally decreasing behavior (Figure 6b).

The wavenumbers of component III for both crown solutions exhibit a sharp decrease to a minimum at ca. 4−5 mr (Figure 6c). This minimum can be connected with increased strength of the H-bonds of water molecules of both types (bidentate and monodentate bonded to the ether ring) in this range. A similar minimum is observed also for the wavenumber of component

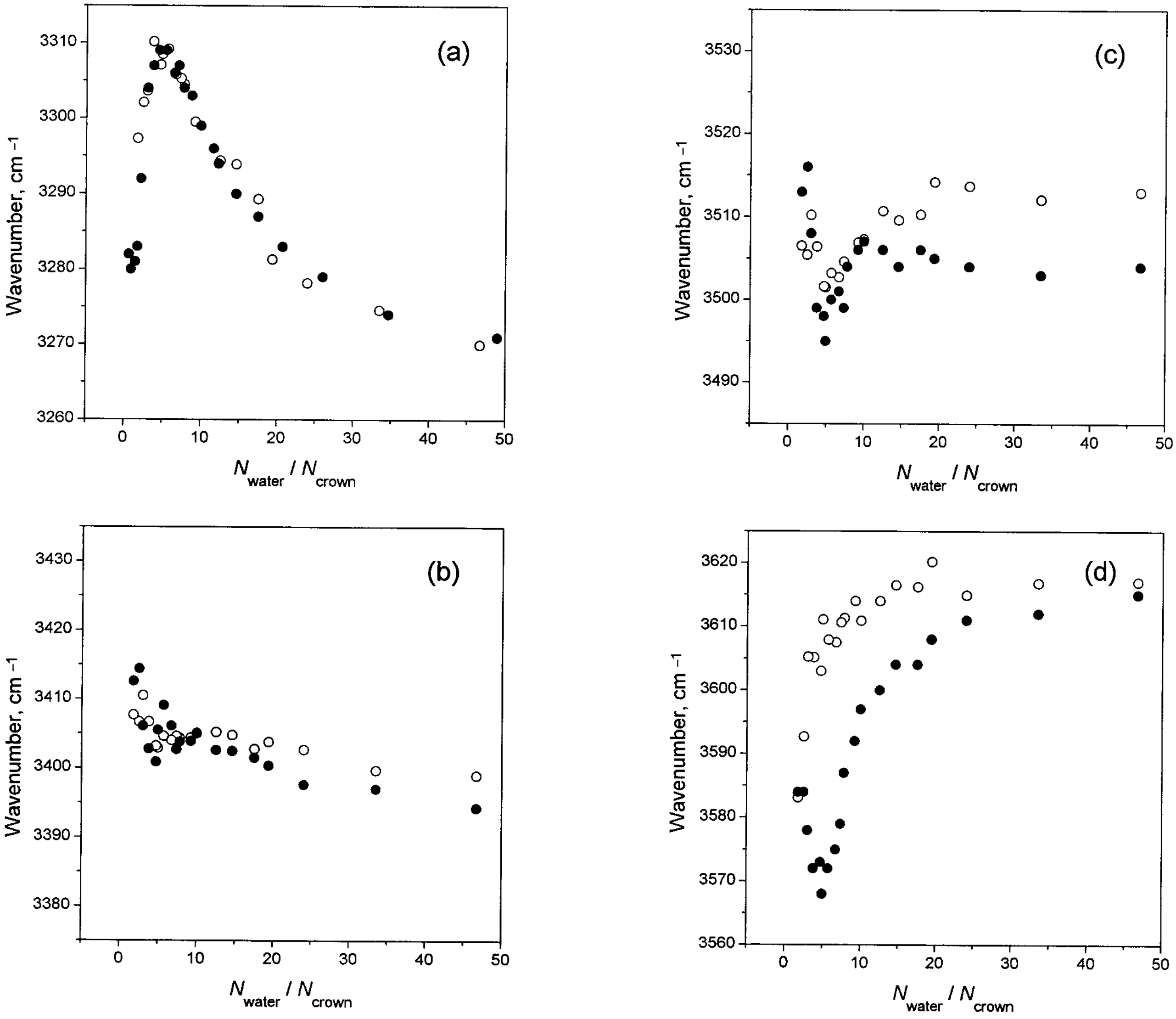

Figure 6. Dependencies of the peak wavenumbers of the respective components of the O−H stretching band on the mole ratio for 15C5 aqueous solution (open circles) and 18C6 aqueous solution (filled circles): (a) component I, (b) component II, (c) component III, (d) component IV.

IV in the 18C6 solutions, while it is absent in the dependence of component IV for 15C5 (Figure 6d). It is reasonable to suppose that the H-bonding of water molecules of the bidentate type for 15C5 is quite different than in the case of 18C6. The same conclusion is evident from the dependencies of the areas of component IV for both crown solutions (Figure 4d).

4. Discussion

The dependencies of the parameters of the resolved O−H stretching band components, i.e., relative areas and wavenumbers, on the mole ratio of water to crown ether, demonstrate that the hydration of 15C5 and 18C6 can be analyzed on a common basis, using a model of 18C6 hydration substantiated in a series of recent works[7,14,15,18] and a model for the H-bond structure of bulk water.[35,36,39,46] Nevertheless, there are similarities and differences in the hydration behavior of both crown ethers which need further attention.

In general, there are two hydration-sensitive concentration ranges, as shown in Figure 5. The first extends from very low to about 15−20 mr. It is characterized with a noticeable increase of bulk water contribution corresponding to a decrease in the relative areas of components II, III, and IV. The second is from 15−20 mr upward and is characterized with almost constant values of the relative areas of bulk water. To be more accurate, the transition between the two ranges is at ca. 12−15 mr for 15C5 solutions and at ca. 18−20 mr for 18C6 solutions. These two mole ratios can be viewed as the maximum number of water molecules per one crown ether molecule influenced by the hydration. Therefore, they can be accepted as the number of water molecules building the hydration shells of both crown ethers. Hydration complexes with a similar number (around 20) of water molecules are assumed to form the first hydration shell of 18C6 as shown by Monte Carlo calculations,[18] and it is suggested that the hydrophobic hydration plays a determining role for their formation.[15] According to the present results, a number of ca. 12−15 water molecules most probably builds the hydration shell of 15C5 at higher dilutions. A mechanism of hydrophobic hydration at lower concentrations of 15C5 in water might be suggested to explain this result.

The immediate hydration of the two crown ethers is best reflected in the dependencies of the relative areas of components III and IV on the mole ratio (Figure 4c,d). After around 7 mr, the relative area of component III of 18C6 follows a considerably higher level than the corresponding component of 15C5. We can conclude that the primary hydration of 18C6, which is due to bridging (bidentate) and singly bound (monodentate) water molecules, is stronger than that of 15C5 in the region above 7 mr. Of course the contribution of bulk water components to component III has to be recognized after ca. 15−20 mr, but still the dominance of a more stable primary hydration of 18C6 should be assumed even at higher dilutions, being in accord with the suggested hydration patterns.[15,18]

At concentrations higher than 10 mr, the relative area of component IV of 18C6 is drastically higher than that of 15C5 (Figure 4d). Taking into account that this component belongs only to bridging water molecules, we can conclude that they are much more abundant in concentrated 18C6 solutions. On the other hand, the low relative area of this component for 15C5 solutions and the similar values of the areas of components III for both crown ethers in the range below 7 mr (Figure 4c) can be explained with a dominant role of the singly bound water molecules to the 15C5 ring compared to 18C6.

The behavior of the wavenumbers of the components in the region around 4−5 mr seems to support the results from the area studies, especially the dependencies of the peak wavenumbers of components I, III, and IV. Similarly to the area dependencies, there is a clear difference in the behavior of the wavenumbers of component IV belonging to bridging water. The minimum at 4−5 mr in the dependency of the 18C6 wavenumber contrasts sharply with the smooth increase in the 15C5 wavenumber (Figure 6d). The minimum in the wavenumber dependence of component IV of 18C6 shows that a more stable H-bonded structure is formed between the bridging water molecules and the crown ring. Similar structure cannot be accepted for 15C5 in view of its wavenumber behavior. The behavior of the wavenumbers of component III for both crown ethers, exhibiting minima at 4−5 mr (Figure 6c), proves that immediate hydration structures with stronger H-bonds are formed in this concentration range. The behavior of component III, belonging to both bridging and singly bound to the crown ring molecules, can be explained by a major contribution from the singly bound waters in the case of 15C5, as a similar minimum does not exist for component IV. For 18C6, the minimum is deeper, suggesting stronger H-bonds than for 15C5 between bound water molecules and the ring (Figure 6c). The peak wavenumbers of component I for both crown ethers also exhibit similar behavior in the whole studied range—an initial increase, a maximum at ca. 4−5 mr, and then a gradual decrease to almost constant values at higher dilutions (Figure 6a).

Thus, in general, we can conclude that there is an interesting hydration region around 4−5 mr for both crown ethers. According to the differences in the obtained parameters of the O−H stretching band for 15C5 and 18C6 aqueous solutions in our results, and data from the literature,[14,15,18,20,21] we can propose the following immediate hydration structures.

A hydration structure of 18C6, in which 3.5 to 5.5 water molecules are directly H-bonded to the ether oxygens, with four to five molecules on the average being involved in the most stable hydration complex, seems to explain the experimentally obtained values of the O−H stretching band parameters. This is in very good agreement with results from the computer simulations[14,15,18] and the experimental evidence for 18C6 crystal hydrates,[20,21] which show that two or three water molecules can be directly bound by H-bonds to one side of the 18C6 ring in the D_{3d} conformation. Thus, we can envisage that two different immediate hydration patterns with a total of four and five water molecules, respectively, exist for 18C6 in the D_{3d} conformation. In the first, one bridging water molecule and one singly bound water molecule hydrate the 18C6 oxygens on each side of the ring.[15,20] In the second, one water molecule bridges two second-nearest oxygens in the ring and two others form bridges between the first bridging water molecule and the third oxygen on one side of the ring,[21] while on the other side the hydration pattern of two water molecules is formed. Of course, a diversity of conformations exists in highly concentrated aqueous solutions as was experimentally shown,[1] but the analysis of the parameters of the water O−H stretching band proves that at a mole ratio around 4, an enhanced H-bonded structure exists which is dominated by water molecules forming bridges to the next nearest oxygens of the crown ring.

The immediate hydration pattern for 15C5 is not so readily disclosed from our data as in the case of 18C6. The most abundant conformer of 15C5 in water (conformer 3),[27] which accounts for 83% of the total population, is characterized, according to our estimates, with a structure in which only two possibilities for connection of bridging water molecules exist. As they originate both at one of the oxygen atoms, only one bridging water at a time can be assumed. This is 2 times less compared with the number of directly bonded bidentate waters to 18C6 in the D_{3d} conformation for which six possible bonding sites are available. Moreover, while in 18C6 in the D_{3d} conformation a complex of four water molecules directly H-bonded to the ring and between each two of them is assumed, the conformation of 15C5 obviously will not facilitate a similar hydration pattern. We can expect that the other oxygens of 15C5 are hydrated by singly bound water molecules on both sides of the ring, so that the maximum number of directly bound water molecules is four. One of them might form an H-bond with the bidentate bonded water molecule. However, the residence time of the other two singly bound water molecules can be much shorter than in the case of 18C6, as no second H-bonds with bidentate bonded water molecules can be assumed. This picture of immediate 15C5 hydration explains the difference in the behavior of the relative areas and wavenumbers of components III and IV in comparison with 18C6, especially at high concentrations (Figures 4c,d and 6c,d).

It is interesting to note that at the highest concentration of 18C6 studied (0.672 mr) there is a considerable increase in the relative area of the component of the bridging water molecules, which is related to the significant decrease in the component III area (Figure 4c,d), as the total area of components III and IV remains almost the same. Unfortunately, solutions of 18C6 with lower mole ratios could not be studied due to dissolution problems, but it is reasonable to suppose that bridging water molecules should dominate the bound water population at hypothetically very high concentrations. They could include not only water molecules bridging internally oxygen atoms within a crown ether molecule but also water molecules bridging between two crown ether molecules. The possibility of direct vibrational spectroscopic studies of immediate hydration in highly concentrated aqueous POE solutions is intriguing and can be realized for simple open-chain POE compounds. Studies of this kind will be reported by us in forthcoming papers.

5. Conclusions

The method of decomposition of the IR O−H stretching band of water applied in this study reproduces faithfully the hydration structure in crown ether aqueous solutions. It gives better results at low mole ratios of water to crown ether, where the immediate H-bonding of water to the crown ether ring can be studied. The results obtained for 18C6 hydration are in good agreement with the predictions from computer simulation models[14,15,18] and with the experimental data on 18C6 crystal hydrates.[20,21] They can be explained on the basis of the predominant D_{3d} conformation in which 18C6 exists in aqueous solution. At mole ratios higher than 10, the contribution of bridging water molecules directly H-bonded to the crown ring is relatively much higher for 18C6 solutions than for 15C5 solutions. The hydration of 15C5 differs from that of 18C6 most probably as a result of the different conformational structure it assumes in water solution.[27] As a result, a stable structure, similar to 18C6, of four to five water molecules bonding to the crown ether oxygen atoms and between themselves in a bridging fashion cannot be formed. Nevertheless, our results show that both crown ethers are optimally hydrated by about four directly bonded water molecules at high concentrations. At low concentrations (mole ratio higher than 15−20), the formation of a first hydration shell of ca. 18−20 water molecules around 18C6 and of ca. 12−15 water molecules around 15C5 can be assumed. Hydrophobic hydration seems to explain satisfactory the hydration in this range.

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