Near-Infrared Spectral Studies for Investigating the Hydration of 18-Crown-6 in Aqueous Solutions

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Received: August 27, 1998; In Final Form: January 8, 1999

The near-infrared difference spectra of 18-crown-6 in aqueous solutions have been obtained in the 1350−1650 nm region. Resolution of the difference spectra yielded the spectra of hydrated 18-crown-6 molecule and with the help of density data has allowed the determination of hydration numbers of 18-crown-6 at different concentrations (0.5−4 *m*). The hydration number obtained at 1 *m* concentration of 18-crown-6 is about ∼20, while at higher concentrations the value is around 4. These results have been interpreted in terms of hydrophobic hydration of 18-crown-6 in the dilute concentration region, resulting in clathratelike equilibria, while at higher concentrations, four water molecules remain hydrogen-bonded to the crown ether ring having D_{3d} conformation. These complexed water molecules have been further differentiated into two types: (i) two water molecules doubly hydrogen-bonded (bridging) to the crown ether oxygen atoms and (ii) the other two singly hydrogen-bonded to the remaining oxygen atoms and rapidly exchangeable.

Introduction

Recently, there has been much interest in large macrocyclic polyethers owing to their ability to complex alkali metal ions specifically in variety of solvents.[1−3] It has been indicated that the studies of functional properties of these supermolecules and their interaction with solvent or guest ion/molecules may shed light on the complicated biological processes involving molecular recognition, catalysis, and transport. The interactions of water molecules with crown ethers, especially 18-crown-6 (18C6), have attracted attention through computer simulation and molecular dynamic studies.[4−10] It has been well established that 18C6 molecules attain D_{3d} conformation in the presence of certain guest or solvent molecules in the solid state, while the same has been indicated in the liquid phase through Raman spectroscopic studies[11−13] and simulation studies.[4−10] In contrast, pure 18C6 exists in C_i conformation in the gas and solid phases. Therefore, it is certain that the electrostatic, hydrophobic, and hydrogen-bonding interactions must be playing a major role in stabilizing a particular type of conformation in the liquid phase. With water as a solvent, it has been proposed that at least two water molecules are firmly bound to the 18C6 ring. In addition to this Kowall and Geiger[9] have indicated from their molecular dynamic studies that at lower concentrations of 18C6, there is enhancement of water structure around the hydrophobic part of the molecule. Similarly, the results of neutron scattering and self-diffusion coefficient measurements have indicated a faster conformational dynamics of 18C6 aided by particular structural effects of water in terms of complexation and hydrophobic interaction.[14−16] The importance of hydrophobic hydration of 18C6 was also revealed in our recent volumetric studies[17] of 18C6 + water solutions. The partial molal volume of 18C6 goes through a minimum as a function of crown ether concentration.

To gain more insight into the complexation process, the role of water molecules in stabilizing the cavity, hydrophobic hydration, and hydrogen bonding of water molecules to the crown ether oxygen atoms, we have studied the differential NIR (near-infrared) spectral properties of aqueous solutions of 18C6 (0.5−4 *m*) at 25 °C in the overtone and combination region of 900−1800 nm of water. The results of the study are analyzed in the 1350−1650 nm region for the ($2\nu_{13}$) combination band of water using the McCabe−Fisher method to resolve the differential spectra into the normal water spectrum and the hydration spectrum.[18−20] The findings of our investigations are presented and discussed below.

Experimental Section

18C6 procured from Merck-Schuchardt (99%) was used without further purification. It was dried in a vacuum oven for 24 h. All the solutions in the concentration range 0.5−4.0 m were prepared by weight (molality) using doubly distilled, deionized water. The solutions were filtered before recording the spectra.

The NIR spectra were recorded using Hitachi model 330 spectrophotometer in a temperature-regulated room (25 ± 1 °C). In the 1350−1650 nm region, use was made of absorption-matched quartz cells having a path length of 0.1 ± 0.0001 cm. The calibration of the spectrophotometer was carried out by recording the spectrum of pure water against air and also by recording the differential spectrum of water dissolved in acetone against acetone diluted with an equivalent amount of CCl_4. In both these cases satisfactory agreement was observed between the recorded band maxima and those reported in the literature.[19] The CCl_4 used was the middle fraction collected during the distillation. The NIR spectrum of CCl_4 did not show any significant absorption in the spectral region under study.

Each spectrum was recorded with aqueous solutions of 18C6 in a sample cell against either air or pure water in the reference cell. The variation of temperature between the sample and the reference cells is a major source of error when the spectra are recorded with air as reference, but the error is minimum when water is used as reference solvent. The absorption baseline was obtained by recording the spectrum of water against water. The baseline was found to be constant with time, indicating the absence of significant temperature fluctuations between the

10.1021/jp983548p CCC: $18.00
Published on Web 03/11/1999

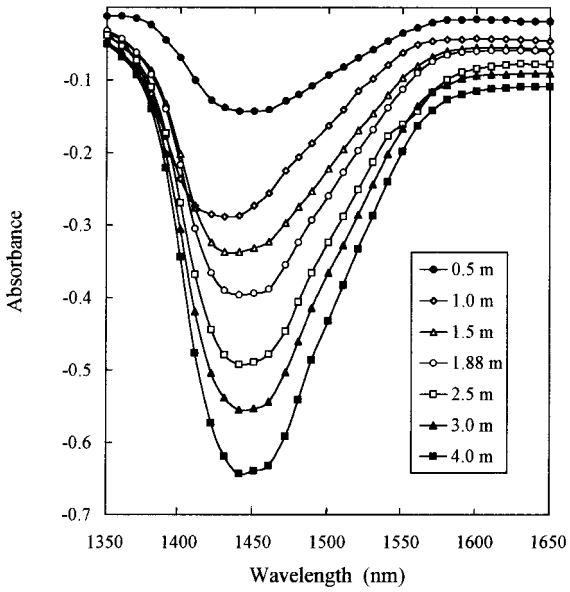

Figure 1. Differential spectra for different concentrations of 18C6 in aqueous solution at 25 °C.

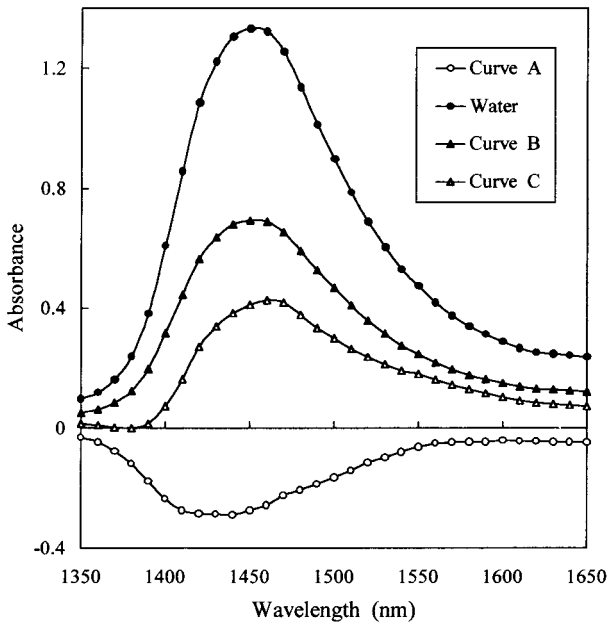

Figure 2. Resolution of the differential spectrum of 1 *m* 18C6 solution using McCabe−Fisher method.

sample and reference absorption cells. The difference spectra with 18C6 solutions in water in the sample cell and pure water in the reference cell were recorded under similar conditions. The reproducibility of the absorbance measurements are estimated to be on the order of ±2%.

To investigate the absorption properties of 18C6 in the overtone and combination region, a spectrum of 1 *m* 18C6 solution in CCl_4 was recorded in the 1350−1650 nm region; there is no appreciable absorption by 18C6 in this region. The density data required for the analysis were obtained using the Anton-Paar Digitale densitometer at 25 ± 0.02 °C. The details of the measurements are described elsewhere.[17]

Results

The differential spectra recorded at 25 ± 1 °C for different concentrations (0.5−4.0 m) of 18C6 in water against water are reproduced in Figure 1. Each of the spectrum was analyzed following the McCabe and Fisher method of resolution[18] to obtain the parameters related to 18C6−water interactions. According to this method, the observed differential spectrum (curve A) (Figure 2) arises owing to the overall effect of the following events. (i) Absorption by water molecules in the sample cell is always less than that in the reference cell because of the dilution of water in the sample cell on addition of the solute (excluded volume effect). (ii) The added solute molecule causes changes in the water structure, and if such water molecules in the hydration sheath of the solute are spectroscopically different from the normal water molecules in the reference cell, then there will be a positive contribution to curve A. (iii) There can also be a positive contribution to the curve A when the added solute itself absorbs in the studied spectral region.

It was found that 18C6 does not show any appreciable absorbance in the region 1350−1650 nm, and hence, the third event does not have any role to play in the differential spectra obtained for the aqueous solutions of 18C6. This makes the application of the method fairly easy.

Event i indicates the volume effect (due to hydrated solute = solute + affected water molecules) and can be quantitatively described by the method. More insight can be gained regarding such effects and the effect of 18C6 on the water structure by resolving the differential spectrum into the normal water spectrum (due to excess normal water molecules in the reference cell) (curve B) and the hydration spectrum (curve C) (Figure 2). The contribution to the differential spectrum by the water molecules in the reference cell that are in excess over the water molecules (not influenced by the presence of the solute) in the sample cell can be obtained by normalizing or reducing the pure water absorbance at all the wavelengths in proportion to the dilution caused (event i). The normalization factor can be obtained by taking the ratio of absorbencies of the differential spectrum to that of the pure water spectrum at a certain wavelength. The choice of the wavelength is guided[18] by the fact that the normalized or normal water spectrum (curve B) so obtained should have an appearance similar to that of the pure water spectrum, and the absorbance values must be either zero or positive for curve C. The normal water spectrum (curve B) is then obtained by multiplying the absorbance values of the pure water spectrum at all the wavelengths by the normalization factor. The hydration spectrum (curve C) can be evaluated by adding the absorbance values of curves A and B (i.e., the normal water contribution is canceled out) at different wavelengths. Thus, the hydration spectrum gives the spectrum of water molecules that are directly hydrogen-bonded to 18C6 and the water molecules in the hydration sheath of the 18C6 molecule. The resolution of curve A at all concentrations was carried out using the above procedure, and in Figure 2 the results of the resolution are presented for 1 *m* 18C6 concentration.

The volume effect can be quantitatively described in terms of the excluded volume ($V_{excl.}$), which can be defined as the volume unavailable for occupancy of the normal water molecules or the volume occupied by the hydrated solute. The excluded volume can be evaluated by using the following expression:

$$V_{excl} = 1000(FV)/c \qquad (1)$$

where c is the concentration of 18C6 in mol L^{-1} while FV is the fractional volume. The fractional volume can be obtained by taking the ratio of absorbance value of curve B to that of the pure water spectrum at any wavelength. It indicates the fraction by which the amount of the normal water molecules is

TABLE 1: Hydration Parameters of Excluded Volume, Apparent Molal Volume, and Hydration Number of 18C6 in Water at 25 °C

molality of 18C6 (mol kg^{-1})	concn of 18C6 (mol L^{-1})	V_{excl} (cm^3 mol^{-1})	ϕ_v (cm^3 mol^{-1})	n
0.5678	0.5026	270.6	223.4	2.6
1.1392	0.9065	574.7	222.7	19.5
1.5142	1.1302	343.3	222.2	6.7
1.8815	1.3111	311.2	221.8	5.0
2.5180	1.6138	299.3	221.1	4.3
3.0037	1.8024	309.6	220.7	4.9
4.1353	2.1581	281.7	221.1	3.4

decreased. The method further allows us to calculate the hydration number (n) of 18C6, using the apparent molal volumes (ϕ_v) of 18C6 in the studied concentration range, which were evaluated from the density data[17] by using the equation[21]

$$\phi_v = 1000(d_o - d)/(mdd_o) + M_2/d \quad (2)$$

where d and d_o are the densities of solution and solvent (water), respectively, m is the concentration of 18C6 in mol kg^{-1}, and M_2 is its molecular weight. The hydration numbers (n) in the studied concentration range were calculated using the equation

$$n = (V_{excl} - \phi_v)/V^o \quad (3)$$

where V^o is the molal volume of water (18.069 cm^3 mol^{-1} at 25 °C). The values of excluded volume, ϕ_v, and hydration number at different concentrations of 18C6 are collected in Table 1. It is difficult to assign unambiguous meaning to the parameter hydration number. It is assumed that the water molecules hydrogen-bonded to oxygen atoms of 18C6, as well as those (not directly H-bonded to 18C6) that are different from the bulk water molecules, cause the effect. The number may simply signify the water molecules affected by the presence of 18C6 molecules.

The effect of 18C6 molecules on the water molecules can be understood from the analysis of the hydration spectrum (curve C), which shows two distinct bands with the band maxima at 1460 and 1560 nm, respectively. The hydration spectra (curves C) were subjected to band resolution into Gaussian curves using the FORTRAN computer program.[22] It was found that the bands can be resolved into two Gaussian curves at the above-indicated wavelengths with the help of the equation

$$A_i = A_i^o \exp\left\{-\left[\frac{\lambda_i^o - \lambda_i}{0.601(\Delta\lambda_{1/2})}\right]^2\right\} \quad (4)$$

where A_i is the absorbance of the species i at wavelength λ_i, A_i^o is the absorbance at wavelength λ_i^o corresponding to the band maximum, and $\Delta\lambda_{1/2}$ is the bandwidth at half the peak intensity of the band under consideration. The parameters for the Gaussian components at the different 18C6 concentrations are compiled in Table 2. The area (nm^2) under the curves was evaluated using the expression

$$\text{area} = \frac{1}{2}[0.601(\pi)^{1/2}A_i^o(\Delta\lambda_{1/2})] \quad (5)$$

The resolution of curve C for 1 and 1.5 m concentrations of 18C6 are represented in parts a and b of Figure 3, respectively.

TABLE 2: Summary of the Parameters of Gaussian Curve Resolution at Various Concentrations of 18C6

molality of 18C6 (m)	λ_{max} (nm)	band 1			band 2		
		λ_{max} (nm)	$\Delta\lambda_{1/2}$ (nm)	area (nm^2)	λ_{max} (nm)	$\Delta\lambda_{1/2}$ (nm)	area (nm^2)
0.5678	1460	1460	66.5	2.2	1560	132.1	3.4
1.1392	1460	1460	88.0	36.9	1559	134.2	21.5
1.5142	1460	1460	73.8	12.9	1555	134.2	11.0
1.8815	1460	1460	73.4	10.7	1560	128.8	10.3
2.5180	1460	1460	75.5	11.0	1560	150.0	10.1
3.0037	1460	1460	73.7	13.8	1559	125.8	11.8
4.1353	1460	1460	70.3	11.7	1560	115.3	10.1

Discussion

Examination of Figure 1 reveals that there is no positive absorption contribution around 1400 nm, that the differential spectra are negative at all wavelengths, and that the negative contribution increases with an increase in the concentration of 18C6 (excluded volume effect). McCabe and Fisher[23] have shown that such differential spectra are observed in the case of aqueous solutions of solutes such as sucrose, proteins, etc. The molecular volume of sucrose is smaller in magnitude compared to that of a protein, but a negative differential spectrum similar to that of the latter is obtained, indicating similarity in the solvation behavior of the two solutes. Though the volume effect plays an important role, this gives the first evidence for the large hydrophobic hydration of the 18C6 molecule.

The resolution of the differential spectra was carried out by normalizing the pure water spectrum at 1380 nm, since the normalization factor at this wavelength satisfies the criteria discussed earlier. It can be observed from Figure 2 that the normal water spectrum (curve B) has an appearance similar to that of the pure water spectrum. This is true for all other concentrations of 18C6. The magnitude of the excluded volume (V_{excl}) decreases as a function of concentration of 18C6. These further yield the hydration numbers (Table 1) at various concentrations of 18C6. The hydration number at 1 m 18C6 concentration is found to be ~20, which further decreases and remains almost constant around the value of 4 in the concentration range 2.5−4.0 m of the crown ether. The hydration number of 18C6 in 1 m solution is high but is not an unexpected one.

It is well-known that the hydration numbers of sugars determined by the NIR spectroscopic technique[24] lie in the range 6−25. The Raman spectroscopic and thermal analysis studies carried out by Matsuura et al.[11,13] indicate that the 20 wt % composition of 18C6 (1 m) in the 18C6 + water system corresponds to a eutectic point (−2.4 °C). The long-range order at this composition may persist to some extent even up to 25 °C. The molecular dynamic study carried out by Kowall and Geiger[9] (254 water molecules, 0.219 m) has revealed that a large number of water molecules ($n \approx 44$) are present in the hydration sheath of 18C6 molecule and indicate that at least four water molecules are hydrogen-bonded to oxygen atoms of the 18C6 molecule. The 1:4 18C6 hydrate is also known to exist and has been analyzed by X-ray diffraction studies.[25] Further, the Monte Carlo study[5] of the 18C6 + water system (100 water molecules, 0.555 m) also reveals that the first hydration shell of 18C6 in the D_{3d} conformation consists of about 20 water molecules (and additional five water molecules in the first hydration shell of the crown ether oxygen atoms, $n = 25$). The large hydration of 18C6 molecule in the low-concentration region is also supported by the volumetric[17] and compressibility studies[26] of the 18C6 + water system.

It can be inferred from the values of hydration numbers that at all concentrations of 18C6 at least four water molecules remain H-bonded to oxygen atoms of the crown ether. These are the only water molecules distinguishable spectroscopically from the bulk water molecules in the higher concentration

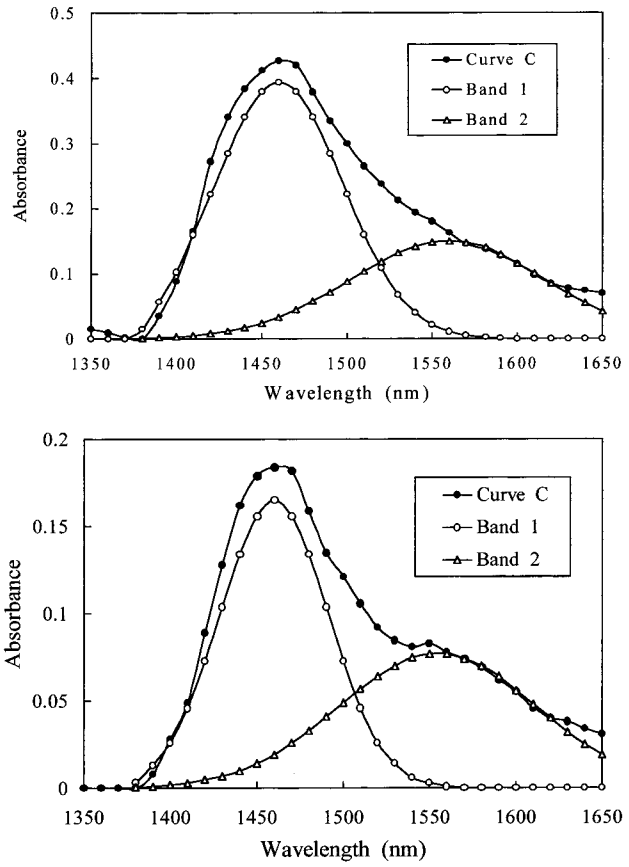

Figure 3. Resolution of hydration spectra of 18C6 into two Gaussian curves having band maxima at 1460 and 1560 nm: (a) 1 *m* 18C6, (b) 1.5 *m* 18C6.

region. In the dilute concentration region some of the remaining water molecules may be H-bonded to these four water molecules and so on to create a three-dimensional network of water molecules, H-bonded among themselves, around the 18C6 molecule. In other words at lower concentrations clathratelike equilibria may exist. Further increase in concentration causes a large decrease in the hydration number, which can be explained on the basis of cosphere overlap and hydrophobic interactions. At higher concentrations the cosphere of one 18C6 molecule overlaps with that of the other 18C6 molecule and the water molecules in the overlap region are lost to the bulk of the solution and are no longer spectroscopically distinguishable from water molecules in the bulk of solution. The results of quasielastic neutron scattering studies[14] have indicated that the frequency of conformational motion at low concentrations of 18C6 is high compared to the constant values obtained at higher concentrations. The low hydration number of 18C6 at 0.5 *m* may be due to such faster conformational dynamics. This fast motion may cause distruction of the hydration sheath of 18C6 on the time scale under investigation.

The hydration spectra were resolved into two Gaussian components (Figure 3) centered at 1460 and 1560 nm. The latter band is found to be broader, and the bandwidth is almost constant around ~130 nm (534 cm^{-1}), while the former has a bandwidth of ~70 nm (329 cm^{-1}), which is nearly constant in the studied concentration region. Therefore, it seems that there are at least two types of water molecules that can be differentiated spectroscopically.

There have been extensive vibrational spectroscopic studies of interactions of water with various bases such as ethers, ketones, amines, etc. The studies of Mohr et al.[27] indicate that the strength of the hydrogen bond between a base and a water molecule is dependent on the nature of the base. By comparison of the fundamental band positions of water molecules H-bonded to ethers with the similar bands of the water molecules complexed with 18C6 in CCl_4, it was found that the hydrogen bonds between water and 18C6 are weak.[28] Bryan et al. have further reported that the water molecules may be complexed to 18C6 oxygen atoms either through one H bond or two H bonds (bridged water molecules). The strength of the hydrogen bond formed by a singly hydrogen-bonded water molecule is greater than those formed by the bridging water molecules.[28] With examination of the results of the present study, it must be remembered that the fundamental band positions of these water molecules in aqueous medium cannot be compared with those in CCl_4. This is because it is well-known that 18C6 exists as a mixture of conformers[29] in CCl_4 and that the presence of a guest molecule, which favorably interacts with 18C6, may cause 18C6 molecule to attain D_{3d} conformation forcefully. In aqueous solution, however, the D_{3d} conformation is energetically more favorable, and since the O···O distance in the gauche conformation of 18C6 is very close to the closest O···O distance in liquid water at 25 °C,[26] the H bonds formed by bridging water molecules would be expected to have strength greater than that of the singly H-bonded water molecules.

The analysis of the IR band of water in the fundamental region indicates a band maximum at 3425 cm^{-1}, which can be resolved into five Gaussian components[30] (3215 and 3420 cm^{-1} for H-bonded and 3555 and 3645 cm^{-1} for non-H-bonded O−H stretching components, and the fifth component appears at 3050 cm^{-1}). In the absence of a detailed study in the fundamental IR region, it would be difficult to say which of these components is enhanced by the presence of the 18C6 molecule. There can be no doubt that H-bonded components will be enhanced in intensity because of the structure-making effect of 18C6 molecule on water. We therefore assume the fundamental O−H stretching frequency of water as $\nu_{13} \approx 3425$ cm^{-1}.

Using these arguments and the other factors to be discussed below, we assign tentatively the 1560 nm band to the water molecules that are singly H-bonded to 18C6 and the 1460 nm band to the bridging water molecules. At 1 *m* concentration of 18C6, as discussed earlier, the water molecules, which are not directly H-bonded to the 18C6 molecule, form an H-bonded network and must contribute to the differential curve in the spectral region where the overtone of O−H stretching vibrations for icelike water molecules[31,32] appear, i.e., in the region 1460−1500 nm. This is also supported by the fact that the area under the 1460 nm band at this concentration is large (36 nm^2 compared to 21 nm^2 for the 1560 nm band). The presence of such a band does not cause any asymmetry of either the 1460 or 1560 nm band, and hence, we did not attempt to resolve any such component. Furthermore, the resolution of such a component will not have any effect on the hydration number, since the contribution due to these water molecules is already taken into account by the parameter, excluded volume.

The NIR spectral study of interactions of water with acetone carried out by McCabe et al.[19] revealed the fact that in addition to a major peak at 1413 nm two minor peaks are observed at 1460 and 1540 nm and were assigned to a 1:2 water−acetone complex. Burneau and Corset[33,34] studied acetone−water interactions in CCl_4 as well as in pure acetone in the fundamental and near-infrared regions. They concluded that the 1540 nm band cannot be assigned only to the vibrations of water molecules but must arise because of a combination transition

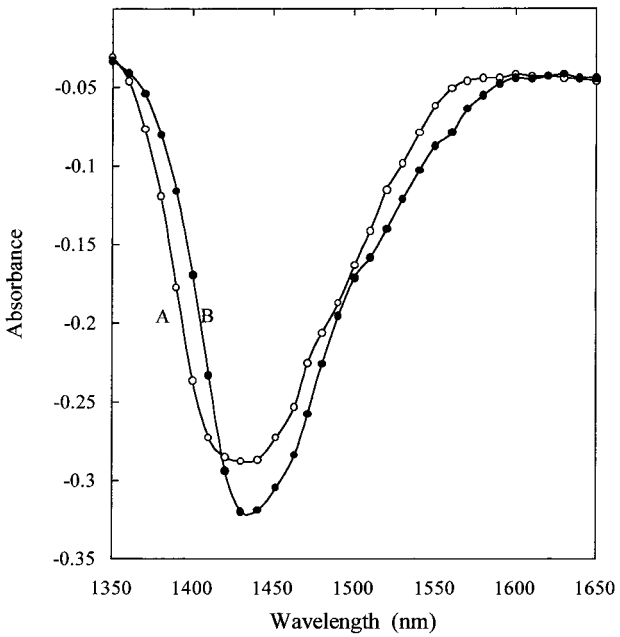

Figure 4. Differential spectra of 1 *m* 18C6 (A) and 1 *m* 18C6 + 2 *m* KBr (B) at 25 °C.

simultaneously involving the vibrations of the H-bonded water and acetone molecules.

The 1560 nm band observed in the hydration spectrum of 18C6 aqueous solutions can be attributed[38] to a similar combination of a transition of H-bonded water (singly H-bonded to 18C6; the other −OH group may be interacting with bulk water molecules or the bridged water molecules) O−H stretching vibration (ν_{13} = 3425 cm^{-1}) and the C−H stretching vibration of 18C6 (∼3000 cm^{-1}). It is a well-known fact that the IR bands broaden on hydrogen bonding. The bandwidth of the 1560 nm band, however, is larger and is not only due to H-bonding, but it must also include the conformational dynamic effects. The large bandwidth also indicates that the lifetime of the singly H-bonded water molecules is short and leads to a conclusion that such water molecules are rapidly exchangeable in conformity with the simulation[9] and neutron scattering studies.[14]

The 1460 nm band can be assigned to the ($2\nu_{13}$) overtone band in accordance with the assignment of the 1450 nm band of liquid water.[36] The 1460 nm band is shifted toward longer wavelength compared to that of pure water.

Since the hydration number of 18C6 at higher concentrations remain constant around 4 and since the aread under the 1460 and 1560 nm bands in the studied concentration range are about the same, it can be said that there are two water molecules of each type (singly H-bonded and bridged) H-bonded to 18C6 oxygen atoms. The bridging water molecules are firmly held to the ring, one on either side, while the singly H-bonded water molecules are rapidly exchanged with the bulk water molecules. The bandwidth of the 1460 nm band, ∼70 nm (329 cm^{-1}) is in good agreement with the bandwidths of H-bonded water molecules reported for pure water or for water in aqueous solutions of different solutes.[30]

The NIR difference spectrum of 1 *m* 18C6 + 2 *m* KBr against 2 *m* KBr was recorded at 25 °C and is reproduced in Figure 4 along with the difference spectrum of 1 *m* 18C6 + water against water for comparison. The effect of Br^- anions in the sample and reference cells may be assumed to be almost equal and hence canceled. Thus, the resulting difference spectrum indicates the effect of complexation of the K^+ ion with 18C6. The K^+ ion replaces (partially or completely) the water molecules H-bonded to 18C6 and itself occupies the 18C6 cavity. The positive contribution of the replaced water molecules (in 1 *m* 18C6 + water system) does not appear in the 18C6 + KBr + H_2O system, which is evident from increased negative absorbance values around 1460 and 1560 nm compared to the absorbance values in the difference spectrum of 1 *m* 18C6 + H_2O against H_2O. The replaced water molecules, since they now behave like normal water molecules, nullify the volume effect to some extent as can be observed from the increase in absorbance values (in positive sense) below 1410 nm. This supports the resolution of the hydration spectrum into the two Gaussian components at 1460 and 1560 nm. Also, the assignment of these bands to the water molecules H-bonded to 18C6 can be justified.

Conclusions

The results of the NIR studies reported here indicate that the overtone band ($2\nu_{13}$) of water in the presence of 18C6 molecules subtly differentiates the mode of interaction of water molecules inside the cavities of the crown ether rings, as well as with the exterior of the cavities. In the dilute concentration region the 18C6 molecules exhibit extensive hydrophobic hydration, while at higher concentrations the complexation effect with the ring oxygen atoms dominates the interactions. The complexed water molecules can be differentiated into two types: two water molecules, each H-bonded to two oxygen atoms of the 18C6 ring, remaining firmly bound to the ring (band at 1460 nm) while the other two are singly H-bonded to the remaining oxygen atoms of 18C6 (band at 1560 nm) and are rapidly exchangeable with the bulk water molecules. The stoichiometry of the complex in the liquid phase is 1:4 18C6−water. It is known that the stability constant of the 18C6−K^+ complex in aqueous medium is lower than that in nonaqueous media.[37] This may be attributed to the fact that the K^+ ions have to replace these four water molecules either completely or partially for the formation of the complex.

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(38) The NIR spectral study of the O−H stretching overtone of HDO in the region 1300−1600 nm carried out by Worley and Klotz[35] indicate an H-bonded O−H stretching overtone at 1525 nm and an H-bonded coupled overtone band at 1556 nm. We may also assign the 1560 nm band to such a coupled overtone of H_2O (2×3220 cm^{-1}) instead of assigning it to a combination band. It is felt that the differentiation in terms of overtone or combination band for such systems needs further experimentation.