**Crown Ethers at the Aqueous Solution-Air Interface: 1. Assignments and Surface Spectroscopy**

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The surface of aqueous solutions of 4-Nitro Benzo-15-Crown-5 (NB15C5) and Benzo-15-Crown-5 (B15C5) has been studied using the surface sensitive technique vibrational sum frequency spectroscopy (VSFS). The NO, CN, COC and CH vibrational modes of these compounds at the air-water interface as well as OH vibrational modes of the surface water hydrating this compound have been targeted in order to obtain molecular information about arrangement and conformation of the adsorbed crown ether molecules at the air-water interface. The CH2 vibrational modes of crown ethers have been identified and found to be split due to interaction with ether oxygen. The spectra provide evidence for the existence of a protonated crown complex moiety at the surface leading to the appearance of strongly ordered water species. The interfacial water species are influenced by the resulting charged interface and by the strong Zundel polarizability due to tunneling of the proton speciesbetween equivalent sites within the crown ring.

Introduction

The unusual ability of crown ethers to non-covalently bind cations has excited continuous interest since this family of molecules was discovered by Pedersen in 19671. Typically, crown ether consists of three to twenty oxygen atoms, separated by two or more carbon atoms. Most common are the macrocyclic oligomers of ethylene oxide units which appear to have the most effective complexing ability.2 The complexing ability arises from the geometrically advantageous arrangement of the electron pair donating oxygen atoms to form a binding site (often misleadingly referred to as a cavity.)

Crown ethers are interesting in a range of contexts, for example in biomedicine. Synthetic crown ether modified amphipathic peptide structures have been shown to selectively target the membranes of cancerous cells and disrupt them.3 Additionally, crowns have the ability to self-assemble in membranes, forming ion channels4 with a water core. Another important use of crown ethers is in environmental management. Fission products like 90Sr and 137Cs can be separated from nuclear waste by solvent extraction using crown ethers5, 6 which are thus required to cross the interface, so their interfacial behaviour is crucial from a mass transfer perspective.

The behaviour of the crowns depends markedly on the nature of the solvent. In non-aqueous solvents the oxygen site provides an ideal home for cationic species2. The cation is surrounded by the oxygen ligands while the CH2 groups are presented outwards to the solvent. In aqueous solvents, crowns are nonetheless capable of binding cations; in this case the crowns compete with ordinary aqueous hydration of the ions. Note that the H3O+ species can also bind to the crown7 so the pH becomes an important parameter.

Attaching aromatic rings to crown ethers provides interesting functionality for encapsulation. For instance, some aromatic crowns emit strong fluorescence on capturing a cation;8 others may alter the fluorescence wavelength depending on the nature of the cations captured.9 The benzo-crowns are more rigid than simple crown rings. The flexibility is reduced not only by the structural rigidity of the planar benzene ring but also due to the extended delocalization of the π-system with the adjacent oxygen lone pairs. Thus, the ethers of the crown ring adjacent to the benzene ring are co-planar with it and the resultant increase in stiffness somewhat reduces the cation binding.2

The hydration of crown ethers is of great interest and has been a source of discussion since Ranghino *et al.*10 proposed a model for ethylene oxide (EO) crown hydration based on a computer simulation of the interaction of water with 18-crown-6. It was reported that there should be at least two distinct types of water molecules hydrating the crown in aqueous solution. In the first, the two hydrogens from a single water molecule bridge to two next-nearest ether oxygens. In the second, one hydrogen of water bonds to an oxygen from EO and the other hydrogen bonds to an oxygen from a second water molecule. On the other hand Kusaka *et al*.11, 12 have studied the structure and its hydrated clusters of jet cooled 18-crown-6, benzo 18-crown-6 and dibenzo 18-crown-6 using IR UV double resonance spectroscopy. They found different conformers for the bare crown ethers and moreover, for the monohydrated clusters they found that the water is of a bidendate type with the O atoms adjacent to the benzene ring. Nickolov *et al.* 13 have studied the hydration of 15-Crown-5 and 18-Crown-6 in aqueous solution with FTIR-ATR spectroscopy and assigned the water modes using a model proposed by Walrafen.14 The two features from the region 3200 cm-1 - 3450 cm-1 were assigned to water H-bonded to other water molecules and the two features from 3500 - 3600 cm-1 to water molecules bridging the two second nearest O from the ether. Furthermore, Brzezinski *et al.* 15 have also investigated the one-to-one complex of H+ with crown ethers and proved that the complex shows a large proton polarizability.

The adsorption behaviour and hydration structure of neutral ethylene oxide (EO) based compounds in water solution have been studied by Tyrode *et al.* 16 using Vibrational Sum Frequency Spectroscopy (VSFS). They observed no signal from the CH2 species belonging to the surfactant head group and thus were able to conclude that the EO head groups are randomly oriented. (This conclusion was supported by studies of the ordered water at the interface). Other VSFS 17-19 studies of interfacial water structure in the presence of soluble cationic and anionic surfactants have demonstrated great enhancement of the OH stretching peaks due to alignment of water molecules in the sub-surface layers by the electric charge associated with the surface layer.

The focus in this work is twofold: firstly, to study the interfacial behaviour of crown ethers and secondly, to examine the hydration of the ethylene oxide moiety in a constrained conformation where the random configuration of Tyrode16 is prevented . The target crown ethers of the present study are nitrobenzo-15-crown-5 (NB15C5) and Benzo-15-Crown-5 (B15C5), which are shown schematically in .

a) b)

4

5

O

O

O

O

O

NO

2

O

O

O

O

O

1

2

3

6

Figure . Diagrams representing a) NB15C5 and b) B15C5.

Background Theory

VSFS is a second-order nonlinear optical technique capable of providing molecular information about molecules present at any interface accessible by light. The theory behind VSFS has been described in detail in the literature20-22 so only a short description is provided here.

Two incident laser beams, one fixed in the visible and one tuneable in the infrared, are overlapped in space and time at the interface. A third beam, at the sum of the frequencies of the two incoming beams, is generated at the interface, bearing the fingerprint of the molecules present at any interface. The intensity of the detected beam (*ISFG*) is proportional to the intensities of the incoming visible (*IVIS*) and infrared (*IIR*) beams and the square of the second order nonlinear susceptibility *χeff*(2) as follows:

 (1)

Information about surface molecules is carried in *χeff*(2) which is a third rank tensor with 27 elements. It can be divided into two contributing components:  - a nonresonant contribution from the substrate and - resonant contributions from the νthvibrational modes of the molecule under study.

 (2)

The resonant part of this contribution is proportional to the number of the molecules at the interface - *N*, and the orientationally averaged molecular hyperpolarizability 

 (3)

where  is the dielectric permittivity. The molecular hyperpolarizability is a function of the Raman tensor -  and IR transition moment -  as shown in the following equation:

 (4)

where  is the frequency of the νth vibrational mode,  is the frequency of the IR beam, *i* is the imaginary unit, *Γ*ν is the damping constant, and α, β and γ are the molecular coordinates. The transformation of the molecular hyperpolarizability coordinates into laboratory coordinates is done using an Euler transformation matrix.23

In order to determine the elements of the second order nonlinear susceptibility tensor several polarization combinations are employed. The polarization combinations used in this study are SSP, PPP and SPS, where P polarized light refers to light polarized parallel to the plane of incidence and S polarized light refers to light polarized perpendicular to the plane of incidence. The first letter corresponds to the polarization of the sum frequency beam, the second to that of the visible beam and the third to the infrared beam. In our study SPS spectra were limited to regions above 1250 cm-1.

Materials and Methods

Nitrobenzo-15-crown-5 was purchased from Anatrace and benzo-15-crown-5 was purchased from Fluka, both with purity greater than 99%. They were further purified by columned chromatography. The water used in the VSFS experiments was obtained from a Millipore RiOs-8 and Milli-Q Plus purification system with a resistivity of 18 MΩ cm and a pH of 5.5. The areas of the molecules obtained from SPARTAN-08 calculations based on the crystral structure of benzo-15-crown-5 are 288 Å2 (B15C5) and 315Å2 (NB15C5).

VSFS Spectrometer

A Nd:YAG laser system (Ekspla PL2143A/20) was used to pump an optical parametric generator/optical parametric amplifier OPG/OPA (LaserVision, USA) to produce the fixed visible beam at 532 nm and the tuneable IR beam. The laser system has an output of 1064 nm with a pulse length of 24 ps and a repetition rate of 20 Hz. The OPG/OPA produces the visible beam by frequency doubling of the fundamental 1064 nm in a nonlinear KTP crystal. Part of the visible beam is further used in pumping the first stage of the OPG/OPA which consists of two angle-tuned nonlinear KTP crystals where an idler beam of 1.2 -1.6 μm is produced. In the second stage, consisting of two angle-tuned nonlinear KTA crystals, this idler beam is then combined with the second part of the fundamental 1064 nm through difference frequency mixing in order to produce a mid-IR beam. The output of the second stage is tuneable in the range of 1.5 – 5.0 μm with a bandwidth of about 8 cm-1 and energy per pulse of 100 – 450 μJ depending on the wavelength. When targeting the region above 5.0 μm that is below 2000 cm-1, a fifth crystal (AgGaSe) was used in a third OPA stage. The output of this stage is the result of difference frequency mixing of the signal and idler from the second stage and it covers the region 5.0 – 12.0 μm with a bandwidth smaller than 15 cm-1. The movement of all five crystals is computer controlled and the IR frequency is scanned with increments of 1 cm-1/second.

The collected spectra are fitted using the program Igor. A Lorentzian profile was used as described in Equation 5:

 (5)

where *Aν*- is the relative amplitude of the fitted peak.

Linear Spectroscopy.

IR spectra were recorded using a Perkin Elmer Spectrometer (ATR). The IR spectrum of water is considered as background and subtracted. Raman spectra could not be obtained for the solutions due to insufficient signal but were obtained from the solid materials.

Solution purity

For spectra recorded in the CH region an extra purification step was performed using the Lunkenheimer surfactant purification unit. The CH region is highly sensitive to organic contaminants. Three different types of surface aspiration were used. The first type was for fast contaminant adsorption to the surface (a few seconds after the surface area was diminished) then intermediate contaminant adsorption time (2 minutes after the surface area was diminished) and slow adsorption (5 minutes after the surface area was diminished). The spectra recorded after purification in the Lunkenheimer Unit were indistinguishable from those obtained without using this instrument. Atomic Absorption/Emission Spectroscopy (AAS) was used to establish whether sodium ions were present in solution since these might bind to crown complexes and complicate the spectra were they to adsorb. AAS established that there is no Na+ ion contamination within the resolution of the instrument, (ppm). A possible further source of sodium contamination might be leaching from the borosilicate glassware (Pyrex) used during, and in preparing, the experiments. Thus repeat measurements were performed where all preparation and experiment were performed in Teflon containers and the same features were observed.

Pendant drop Method

In order to recordsurface tension isotherms a Pendant Drop Instrument (First Ten Angstroms, USA) was used. For each data point recorded an independent solution was prepared. The adsorbed amount at each concentration was estimated using Gibbs adsorption equation.

Results and Discussion

Surface tension measurements

To obtain insight into the adsorption process of NB15C5 and B15C5 compounds at the water - air interface it is useful to combine the information given by surface tension measurements with that provided by sum frequency spectroscopy. Surface tension measurements are used as an independent method to estimate the number of molecules present at the interface. The surface excess or adsorbed amount is calculated using the Gibbs equation assuming a single adsorbing neutral species, which is expressed as:

 (6)

where γ is the surface tension, *c* is the molar concentration in the bulk, R is the gas constant, *T* is the temperature and Γ is the surface excess. The area per molecule *A* is calculated using *A****=****1****/*** Γ*N****A*** where *N****A*** is Avogadro’s number. Despite the fact that crowns contain water soluble ethylene oxide units, their solubility is not high.



Figure . a)Surface tension isotherms of nitro benzo-15-crown-5 (NB15C5) and benzo-15-crown-5 (B15C5). The curve between the points is a polynomial fit (a logarithmic scale is used for the concentration). b) Area occupied by a molecule at different concentrations calculated from eq.6. The lines between points are a guide to the eye.

The surface tension isotherms are shown in and reveal the extent to which these compounds are surface active.

At higher concentrations than shown here, erratic results were observed for surface tension data, particularly a few hours after recrystallization (the time frame needed for VSFS measurements) indicative of solubility issues. Thus the spectroscopic studies have been limited to the range 0-10 mM concentration, where surface tension and VSFS data are highly reproducible. A 4th order polynomial equation was used to fit the surface tension data shown in Figure 2a. Using the surface excess obtained from the polynomial fit, the area per molecule was calculated as a function of concentration and is shown in b.

As expected, at low concentrations each molecule occupies a large area on the water surface. The driving force to the surface is presumably the hydrophobicity of the benzene group, which displaces water molecules from the interface. It is also known that while the interior of the crown is hydrophilic, the *exterior* of the crown is hydrophobic so the EO groups may also contribute to the reduction of the free energy. At concentrations below 10mM where most of the sum frequency (SF) spectra were taken, the area occupied by each molecule is of the order of hundreds of Å2. Considering the size of crown ether molecules, this implies that they are far apart from one another and thus are unlikely to interact very strongly. However, island formation or dimerisation cannot be ruled out on the basis of the surface tension data alone.

Sum Frequency Spectra

The NO and CO Stretching Region 1000 – 1800 cm-1.

Not only do both compounds adsorb at the air-water interface, they also adsorb in an ordered fashion as the sum frequency data testifies. In order to identify the bonds corresponding to the peaks observed in our sum frequency spectra, standard IR and Raman spectra were acquired. The IR spectra presented in Figure 3 show vibrational features of both B15C5 and NB15C5. Both the Raman (not shown) and IR shown in Figure 3 reveal many active species (C-O, C=C and N-O) between 1000 cm-1-1600 cm-1.



Figure . IR Spectra of water solution NB15C5 and B15C5 both normalized to highest peak intensity. The NB15C5 spectrum is offset by +0.3 units The water spectra are considered as background in the IR normalization.

Based on literature results the feature in the IR spectra at about 1128 cm-1 of both B15BC and NB15C5 () belongs to the symmetric C-O-C stretch of the ethylene oxide unit νs(C-O-C)24 and the peak at about 1260 cm-1 of both compounds belongs to the symmetric C-O stretch from the phenyl ring νs(PhO). 25 The feature at 1280 cm-1 is the C-N vibration of the NB15C5 25; the symmetric νs(NO2) and antisymmetric νa(NO2) vibrations of NB15C5 are positioned at 1341cm-1 and 1517cm-1 respectively 26. Finally the peak at about 1590 cm-1 of both NB15C5 and B15C5 spectra is assigned to the skeletal benzene vibration skl(C=C). 25



Figure .SFG spectra of B15C5 (a) and NB15C5 (b) under different polarization combinations. The spectra are normalized to unity since the SSP spectra are more intense than the PPP and SPS ones. They are also off-set for better clarity.

Figure 4 shows the VSFS spectra of both B15C5 (Figure 4 a) and NB15C5 (Figure 4 b) in different polarization combinations: SSP, PPP and SPS. The interface of B15C5 gives a signal only in SSP polarization while the interface of the NB15C5 displays signal in all polarizations. The SSP spectrum of B15C5 ( Figure 4 a) displays a well defined peak centred at 1260 cm-1; based on IR results 24, 25 we assign this to the C-O symmetric stretching mode of C 1 and 2 from benzene νs(PhO). This peak is also present in the spectrum of NB15C5 but is not obvious due to the strong signal at 1279 cm-1; it is, however, clearly distinguishable at low NB15C5 concentrations. (The concentration dependence is discussed in the next paper.27 )

The peak at 1279 cm-1 shown in the SSP, PPP and SPS spectra of Figure 4 b is assigned to the ν(CN) vibrational mode 25 and overlaps the νs(PhO) mode since it is much more intense. The most prominent feature of the SSP spectra is the symmetric νs(NO2)26 which appears at 1341 cm-1. This peak is also present in PPP and SPS polarizations. Moreover, a small and well defined peak appears at about 1121 cm-1 which can also be seen in IR spectra of both B15C5 and NB15C5. This peak could be either νa(C-O-C) aliphatic stretch or C-H in-plane bending.24 The PPP spectrum contains multiple nonlinear susceptibility terms and is thus the most complex, showing four well defined and separated vibrational modes. Besides the νs(NO2) and ν(CN) peaks, the PPP combination shows two additional peaks: νa(NO2) and skl(C=C) at 1521 cm-1 and 1592 cm-1 respectively.25, 28 The latter peak also manifests in the SPS spectrum. The IR spectrum of NB15C5 shows the aromatic C-O mode at 1263 cm-1 and the aliphatic C-O mode at 1129 cm-1, while in the SFG spectra the aromatic C-O mode is at 1260 cm-1. Therefore, we assign the 1121 cm-1 peak as being an aliphatic C-O since the separations between these two modes are very similar. When comparing the IR spectra of the two compounds (Figure 3) one can note that the aromatic C-O stretch of the NB15C5 is shifted about 7 cm-1 to higher energy; however, the aliphatic stretches overlap well for both spectra suggesting that the NO2 group has a slight effect on the ether ring, changing the macrocyclic conformation. This has been previously observed by Rogers *et al.*29 who characterized a series of nitrated benzo crown ethers. All transitions are summarized in shown below.

Table . Assignments for transitions in N-O and C-O region

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Nr | Vibrational mode | IR  wavenumbers  (cm-1)  NB15C5 | Ref. | SFG  wavenumbers  (cm-1)  NB15C5 |
| 1 | νs(C-O-C) | 1129 | 24 | 1121 |
| 2 | νs(PhO) | 1263 | 25 | 1260 |
| 2 | ν(CN) | 1280 | 25 | 1279 |
| 3 | νs(NO2) | 1341 | 26 | 1341 |
| 4 | νa(NO2) | 1517 | 26 | 1521 |
| 5 | skl(C=C) | 1590 | 25 | 1592 |

Note: s = symmetric, a = asymmetric, skl = skeletal

The structural orientation of a certain molecule can be revealed by examining the relative intensities of the studied vibrational mode under different polarization combinations. Dipole moment projections on the surface normal are probed using SSP polarization, while SPS polarization probes projections of the dipole moment on the surface plane. Therefore the fact that the νs(NO2) and ν(CN) stretches appear in both SSP and SPS implies that the NB15C5 molecule adopts a position at an angle between the surface plane and the normal to the interface. B15C5 appears to adopt a more upright configuration since the ν(PhO) stretch is practically absent from the SPS spectra, a result which will be further discussed together with the spectra from the CH region.

The CH Spectral Region 2800 – 3100 cm-1

Traditional IR and or Raman spectroscopy alone cannot resolve all the peaks that contribute to spectral features in the CH region of the crown ethers. While IR UV double resonance is capable of distinguishing several bands in the CH region of crown ethers,30, 31 no specific assignments of the different CH vibrational modes have yet been made. Using VSFS it is possible both to resolve the peaks that contribute to the spectral features in the CH region and to obtain an *indication* of their origin.



Figure 5 ATR spectrum of 10mM NB15C5 in the CH stretching region



Figure . (a) SFG spectra of 5 mM NB15C5 under SSP, PPP and SPS polarization combinations (SSP shifted +0.3 units and PPP shifted +0.15 units) and (b) Spectra of 4mM B15C5 under SSP, PPP and SPS (SPS shifted -0.1 units SSP shifted +0.2 units).

Ffitting of the spectra reveals the presence of six features in the alkyl region. Complete, unambiguous assignment verges on the impossible, as there are at least two published explanations for these features. Firstly Zwier31 has recently published gas phase spectra of B15C5 and has discussed this spectral region in terms of different conformations of the crown ring with varying capacity of the methylene to interact with the phenyl oxygen *across the ring.* We note that the difference in electronegativity of the phenyl and ether oxygen atoms should be enough to differentiate the methylene attached to them and that this alone is sufficient to cause complexity in this region. In this case there would be two distinct types of methylene groups in the ratio 2:6. Were there then to be different conformations at the surface this would render any further assignment impossible; however the conformational richness in the gas phase may not be reflected in solution where the interaction with water molecules is likely to constrain the ring. In a different study Rong Lu *et al.*32 studied a series of diols using a polarization spectroscopic technique to assign the CH2 features. They attribute the appearance of two kinds of methylene group frequencies to the fact that there are two distinguishable methylene moieties: those which are directly attached to OH groups and those that are not.

An alternative assignment is due to Zhelyaskov33 who proposed a sequence of coupling mechanisms – firstly the coupling between two isolated CHs on adjacent carbon atoms and then considering in-phase and out-of-phase oscillations of the symmetric and antisymmetric stretches. Finally Zhelyaskov invokes coupling with a Fermi resonance of the CH bend to obtain the requisite amount of splitting. However, this approach ignores anharmonicity effects. It may in fact be that these effects, coupled with the first-mentioned coupling above, would be sufficient to explain the spectrum.

Nonetheless certain unambiguous assignments can be made independently of which model is used. Figure 5 displays the ATR spectrum of NB15C5 in the CH stretching region. Examination of the spectrum reveals that the only features appearing in this region are the CH2 vibrational modes. SFG spectra of NB15C5 are shown in Figure 6 a) in three different polarizations SSP, PPP and SPS. The most obvious feature of the SSP spectra is the increased baseline level which arises from interference with water band tails. Assuming C2v symmetry for the methylene vibration we use the polarization selection rule32 in an attempt to assign the observed CH features. The two peaks present at 2857 cm-1 and 2879 cm-1 dominate the SSP spectra but are practically absent in the SPS spectrum; thus, both of them are assigned to the symmetric CH2 stretch. Given that the CH stretch shifts to higher frequency when it interacts with an electronegative atom,34, 35 we can safely assign the vibrational mode at 2857 cm-1 to symmetric ether CH2 while the 2879 cm-1 mode is assigned to a symmetric CH2 connected to phenyl oxygen. The peak at 2966 cm-1 which has slightly stronger intensity in PPP spectra than in SSP or SPS spectra is consistent with the antisymmetric ether CH2. The peak at 2887 cm‑1 in the PPP spectrum appears as a dip in the SSP spectrum because it destructively interferes with the symmetric peak at 2879 cm-1. It might therefore be assigned to an antisymmetric CH2 although it appears at too low a wavenumbers. Based on an IR study of the same compound we assign the small dip in the SSP spectrum at 3090cm-1 to aromatic CH.25

The spectra of B15C5 under different polarization combinations are shown in Figure 6 b). It is clear that both SSP and PPP spectra have similar features to those of NB15C5 (Figure 6 a). However, there are two well defined peaks in the PPP spectrum of B15C5 which appear as dips in the SSP spectrum at 3020 cm-1 and 3060 cm-1 and these are assigned to aromatic CH stretch modes.36-39

There is no defined assignment (in terms of symmetry type) for the benzene CH stretches in the benzo crowns molecules, thus, our assignment must rely on similar compounds (monosubstituted39 or ortho substituted benzene36) from the literature. Thus, the observed band in B15C5 at 3060 cm-1 is assigned to symmetric HC4 – C5H of the benzene ν20 (e1u in ref36). The small 3020 cm-1 peak is tentatively assigned to the adjacent C3H-C6H symmetric stretch. Obviously, when the NO2 is added to the benzene in pos 4 the ν20 mode is displaced and therefore is not visible in either the IR25 or the SFG spectra. These peaks are not well distinguished in the SPS spectrum and since they are relatively strong in SSP polarization this provides further support to the conclusion from the lower wavenumbers region that the B15C5 molecule undertakes an upright position at the interface. All assignments are summarized in Table 2 listed below.

Table . CH peak assignments for NB15C5

|  |  |  |  |
| --- | --- | --- | --- |
| Fitted peak  wavenumbers  (cm-1) | Polarization | IR peak  wavenumbers  (cm-1) | Assignment |
| 2857 | SSP | 2856 | CH2 sym |
| 2879 | SSP, PPP | - | CH2 sym next to PhO |
| 2887 | PPP | - | CH2 asym |
| 2914 | SSP | - | FR of CH |
| 2927 | SSP, PPP | 2926 | FR of CH next to PhO |
| 2966  3020  3060  3090 | PPP, SPS, SSP  SSP, PPP  SSP, PPP  SSP | 2957  -  -  - | CH2 asym  Aromatic CH stretch  Aromatic CH ν20  Aromatic CH stretch |

The OH Spectral Region 3000 – 3800 cm-1.

Prior to all measurements a spectrum of the air-water interface was collected to ensure that no contaminants were adsorbed. Figure 7 a) shows the spectra of NB15C5 and pure water under SSP and PPP polarization combinations. The SSP and PPP spectra of water are in agreement with spectra reported before by other groups.40, 41 The most important features revealed by the water spectra in this region are a broad band extending for more than two hundred wavenumbers and centred at around 3350 cm-1 followed by a sharp peak at 3700 cm-1.

The assignment of the broad band is still a source of debate. One view is that the broad band is attributed to hydrogen bonded water molecules of varying strength and coordination and is separated into two broad peaks centred at 3200 cm-1 and 3400 cm-1, loosely referred to as “ice-like’’ and “liquid-like’’ respectively.40, 42, 43 A more recent suggestion is that the doubled peaked structure originates from vibrational coupling between the stretch and the bending overtone of water modes.44

The strong peak at 3700 cm-1 is referred to as “free-OH’’ and is assigned to the uncoupled OH stretching mode of surface water molecules with one OH bond protruding out into the gas phase. The PPP polarization spectrum of pure water shows only the free-OH feature and is consistent with PPP spectra previously reported.40



Figure 7. Spectra of NB15C5 under SSP (a) and PPP (b) polarization combinations in the OH region. Both a) and b) spectra are normalized to the intensity of the free OH. Water spectra are shown for reference. The lines are guides to the eye.

When fitting spectra with adsorbed NB15C5, three peaks were used for the 3000-3850 cm-1 region which, for the SSP spectrum, which are located at 3250 cm-1, 3382 cm-1 and 3700 cm-1.

The most obvious difference between the SSP spectra of pure water and NB15C5 in Figure 7 a) is the dramatic increase in the OH features. Similar effects for bonded OH have been reported before in the literature. Adsorption of cationic surfactants17-19, 45 at water-air interface, charged lipids spread on water subphase46 and lipid supported bilayers47 induces a remarkable increase in the water bands of the SFG spectrum due to highly aligned water in the electrical double layer created at the interface. Moreover, solvated hydrogen ions in water solutions48 show great enhancement of the OH bands at 3200 cm-1 and 3330 cm-1 which is attributed both to water directly solvating the protons and the enhanced ordering within the created electric field .49

It is obvious that the addition of the crown ether to the surface perturbs this region. The topmost free OH layer (protruding, freely vibrating OH bonds) is affected by the presence of crown ethers similarly to what is observed in the case of surfactants50 but slightly more intensely. The subsequent layers of water below the top monolayer but within the surface region are also perturbed. The low frequency water mode is blue-shifted about 30 cm-1 to 3250 cm-1 which indicates a weakening in the H bond strength. The peak is assigned to the strong intermolecular coupling water molecules.51, 52 The peak at 3382 cm-1 is well separated from the peak at 3250 cm-1. It corresponds to a more weakly bonded water feature40 and is associated with molecules vibrating in a more disordered hydrogen bonded environment in correlation with the Raman spectra of water.53

The feature at 3700 cm-1 forms a relatively broad band at high energies. This broadening of the band in comparison to pure water free OH might be viewed as an increase in the number of geometries and strengths (dynamically varying) in which the OH is vibrating.54 This has been observed for other surfactant systems, but to a lesser extent. The apparent broadening may also be due to a weak feature at about 3630 cm-1 for which there is slight evidence in both SSP and PPP. While it is emphasised that the evidence here is weak, such a peak has previously been assigned to a “free OH” modified by the presence of hydrocarbon.54 Finally, it may also be subject to the delocalisation effect discussed in an ensuing paragraph.

Figure 7 (b) shows the PPP spectra of pure water for reference and NB15C5 in solutions at 5mM. The feature present in the PPP spectra centred at 3560 cm-1 has been seen by Tyrode *at al.* 16 in the hydration of polyoxyethylene surfactants. It was assigned to water molecules vibrating against hydrocarbon tails. Assuming that the CH2 groups face the exterior of the ring and oxygens are oriented towards the inside of the ring, we argue that the band at 3560 cm-1 is the OH stretching of water molecules in close proximity to hydrocarbon. summarizes all the vibrational modes in the 3100-3950cm-1 region presented in this study.

Table . Vibrational modes in 3000-3900 cm-1 spectral region.

|  |  |  |
| --- | --- | --- |
| Fitted peak wavenumbers  (cm-1) | Polarization | Assignment |
| 3250 | SSP | ‘ice – like ’ water |
| 3382 | SSP | ‘liquid –like’ water |
| 3560 | PPP | non-donor OH against hydrocarbon phase |
| 3700 | SSP | Uncoupled/Free OH |

In comparison to the findings of Tyrode *et al.*16 in relation to the strength of the water signal hydrating the ethylene oxide groups a much stronger water signal is observed when NB15C5 or B15C5 is adsorbed at the water-air interface. The intensity of the bonded OH signal increases significantly, at concentrations just above the limit at which the water surface starts to be perturbed by crown ether. A more detailed description of the difference between NB15C5 and B15C5 in this spectroscopic region as a function of temperature and concentration is considered in the next paper.27

Since it is known that the hydronium ion can be stabilized by crown ethers2, 7, 55 we therefore propose that the increased OH bonded signal of the spectra is caused by the presence of the crown-H3O+ species at the interface. Their presence would explain the spectrum through the formation of an electric double layer and resulting water ordering.19, 56-60 The protonic charge is considered to be delocalized across the 15-crown-5 ring (and not associated with a specific oxygen). This significantly increases the polarisability and potentially this renders it more “anion like”,61 permitting enrichment at the interface. MD simulations also predict that highly polarisable ions are enriched at the surface.62 This delocalization effect has been shown by Brzezinski *et al.*15 to give raise to a continuum from about 1500 – 3700 cm-1 in the IR spectra of crown complexes. A similar type of signal enhancement was found by Allen *et al.* 63 in their work on methane sulfonic acid which was also ascribed to delocalization of the proton in the acid system.

The suggestion of stable protonic charge at the interface is indirectly related to suggestions by Saykally and Petersen64 that hydronium species may be enriched at aqueous interfaces.   There is currently much discussion as to which aqueous species are favoured at the interface62, 65-67 and much research remains to be done in that exciting area. In the current case the stabilisation mechanism is related to a delocalisation within the crown moiety and thus has a somewhat different mechanism.



Figure 8. SFG spectra of 5 mM NB15C5 in SSP polarisation in protonated and deuterated water. All features are normalized to the highest peak in D2O spectrum. The H2O spectrum is shifted +0.3 units for clarity.

Figure 8 shows the SSP spectra of 5 mM NB15C5 in both protonated and deuterated water for comparison. The baseline of the spectrum in deuterated water goes down to zero intensity and the entire broad band is now shifted to lower wavenumbers over the OD stretching region; therefore, the enhancement of the water band is clearly not due to the nonresonant contribution.

This rules out any enhancement of the water band by a nonresonant contribution and strongly supports the contention that the spectral feature arises from the delocalisation in a charged interfacial crown complex.

The presence of charge at the interface is somewhat unexpected. In fact, it was this observation which led to the extensive purification procedures described earlier and which had no effect on the experiments. (We had considered the ability of the crown ethers to coordinate to Na+ a serious possible complication, but exclusion of Na+ from the system did not influence the OH peaks.) At this stage we can only speculate as to the reasons why the charged species should be surface active – in general one would expect the charges to be repelled from the interface due to the lower local dielectric constant and commensurately less favourable solvation energy.

However, since crowns are known to transport ions across interfaces between high and low dielectric constant media68, it is implicit that in some manner they evade this apparent energy penalty. It may be that the loss of hydrogen bonding associated with the ether groups when they occupy the interfacial film, is at least partially offset by the favorable interaction with the ion. There is both an enthalpic and entropic benefit to “dehydrating” a charge at the interface.

The solvation energy penalty is also dramatically ameliorated by the diffusion of the charge over a much larger volume. Finally it is also conceivable that the crowns align in such a way that a proton can be delocalized over several rings69 which would reduce the effective charge density even further, though the areas per molecule estimated from surface tension would speak against such a structure.

Conclusions

It is clear that both the crown ether species examined in this study have a certain surface specificity, and the correlation with vibrational sum frequency measurements reveals that they adsorb with preferred, though slightly different orientations. The successful assignment of the vibrational modes (performed with the assistance of IR and Raman spectroscopy) means that the door is now open for a broader examination of the interfacial properties of crowns, both at the aqueous-air interface and the buried oil-water interface, where this behaviour has important implications for metal ion extraction.

The addition of the nitro group to the benzo group has no significant effect on the crown properties *per se* but imparts a higher degree of ordering at the surface, and from a spectroscopic perspective imparts an invaluable fingerprint in the lower wavenumbers region, which will allow for the probing of orientational behaviour in the following paper.

Most importantly, the results have clearly implicated a protonated, charged form of the crown as at least one of the surface active species, which indicates that the charge delocalization associated with crown complexes is sufficient to offset much of the energy penalty associated with charges at interfaces. This has implications both for ion channels and ion transfer to nonaqueous media. Finally, this charged complex at the surface has such a profound influence on the water spectrum that the hydration structure of the crown itself cannot be isolated, and the hydration of ethylene oxide thus remains no less of a mystery.

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Notes and references

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