

Cite this: *Phys. Chem. Chem. Phys.*, 2011, **13**, 7939–7947

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Crown ethers at the aqueous solution–air interface. Part 2.† Electrolyte effects, ethylene oxide hydration and temperature behaviour‡

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Received 13th October 2010, Accepted 4th March 2011

DOI: 10.1039/c0cp02144j

Vibrational Sum Frequency Spectroscopy (VSFS) was employed to study adsorbing films of 4-Nitro Benzo-15-Crown-5 (NB15C5) and Benzo-15-Crown-5 (B15C5) at the aqueous solution–air interface. The surface of the solution is strongly influenced by the presence of crown ether species. Changes in the orientation of NB15C5 were monitored as a function of solution concentration, by targeting the ratio of peak intensities of the CN and NO₂ vibrational modes. The water of hydration has also been probed as a function of crown concentration, salt concentration, and temperature. The latter study strongly suggests that the surface can be treated as a charged interface, and that the associated ordered water decreases with increasing ionic strength of the bulk solution.

Introduction

This paper concerns the surface spectroscopy of crown ethers adsorbed at the aqueous solution interface and as such builds on a preceding paper.¹ In that paper the different vibrational modes belonging to two benzo-crown ethers and the ordered water of hydration in the slab interface[§] were identified and studied. Clear evidence was found that the crown–H₃O⁺ complex exists at the surface and leads to the appearance of highly ordered water species.

Having assigned the peaks it is interesting to further probe the interfacial behaviour of these unusual molecules. The fact that both the more polar moiety (crown) and the hydrophobic moiety (aromatic group) are cyclic rather than linear raises questions as to the expected interfacial conformation. This structure should be compared to more conventional surface active species, which in general consist of an unbranched alkyl tail and a polyoxyethylene chain of varying size as the hydrophilic moiety.² (For ionic surface active agents the hydrophilic group is usually more compact, consisting for example of a

charged species such as an amine, sulfate or carboxylic acid).^{3–6} Moreover, the hydration of ethylene oxide is known to be temperature dependent.⁷ Since its surface activity in water is related to the degree of hydration, it would be interesting to establish whether there is a similar temperature response for the crown structure that may affect the affinity for the interface. This might in turn influence the ability of the crown to transport ions across the water–oil interface in, for example, solvent extraction.^{8,9} To gain insight into interfacial affinity and orientation, it is possible to perform a series of experiments where the concentration (controlling the density at the interface), the temperature (potentially controlling hydration and orientation distribution) and the salt concentration (affecting the density of charged interfacial species and the interfacial hydration spectrum) are systematically varied.

The orientation of crown ether moieties at the water–air interface for different solute concentrations has therefore been studied by probing the prominent vibrational modes in the spectra with Vibrational Sum Frequency Spectroscopy. This technique also allows the hydration properties of the interface to be studied for the different crown species and under different solution conditions. The structures of the two crown ethers studied are presented in Fig. 1, in which their planar nature is apparent.

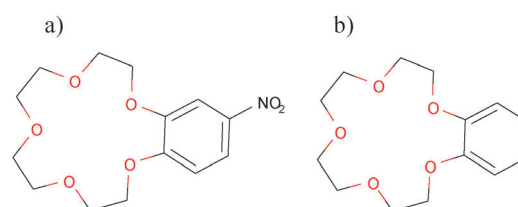


Fig. 1 Diagrams representing (a) NB15C5 and (b) B15C5.

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† For Part 1 see ref. 1.

‡ Electronic supplementary information (ESI) available. See DOI: 10.1039/c0cp02144j

§ A slab interface is one where the adsorbate can be thought of as a “slab” of finite thickness between the bulk liquid and the vapour phase. Surfactant films, for example, are typically treated in this way. On the other hand a single component liquid interface is not ordinarily considered to have a finite thickness.

Theory

A detailed explanation of the Vibrational Sum Frequency Spectroscopy (VSFS) theory can be found in other sources.^{1,10–13} Briefly, it is a nonlinear technique that provides information about the identity and orientation of species present at the interface with no contribution from the bulk solution, as well as their orientation. Under the electric dipole approximation, only molecules present in a noncentrosymmetric environment give a Sum Frequency (SF) response. The intensity of the SF beam is proportional to the second-order susceptibility, which carries information about the species present at the interface as well as their average orientation.

To obtain orientational information about specific molecular bonds in addition to distinguishing molecular species at the interface, spectra with different polarization combinations of the incoming and outgoing beams are required.

Materials and methods

4-Nitro Benzo-15-Crown-5 (NB15C5) and Benzo-15-Crown-5 (B15C5) with purity greater than 99% were purchased from Anatrache and Fluka, respectively. Further purification was done by column chromatography. Millipore RiOs-8 and Milli-Q Plus systems were used as water supply with a pH of 5.5. For certain experiments a Lunkenheimer surfactant purification unit was employed for more extensive purification of crown ethers. NaCl was purchased from Merck with purity greater than 99.5% and used as received.

The experimental VSFS setup has been described in the previous paper,¹ however we provide a brief description here. A Nd:YAG with 1064 nm output pumps a Laser Vision Optical Parametric Generator/Optical Parametric Amplifier (OPG/OPA) in order to obtain both the visible 532 nm and the tuneable IR in the range 2.5–10.0 μm . The optical set up is in a copropagating geometry and the angles of the IR and the visible beams are 63° and 55° , respectively, from the surface normal. The collected SF beam is passed through a monochromator before being directed to a photomultiplier tube (PMT), after which the signal is processed by an integrated boxcar and finally a computer LabView program.

All the spectral features analyzed in this study were fitted using a Lorentzian profile using the program Igor as described in our previous paper.¹

Results and discussion

Concentration dependence

Both compounds, NB15C5 and B15C5, were studied over a range of concentrations in both the NO–CO and CH–OH spectral regions. In order to better understand and correlate the information from the two spectral regions the discussion of the results is divided into two sections.

CO–NO spectral region 1100–1400 cm^{-1}

The peak assignments of the observed features present in this region for NB15C5 and B15C5 have been discussed in detail in the preceding paper.¹ Only NB15C5 was used to study the relationship between concentration and orientational response

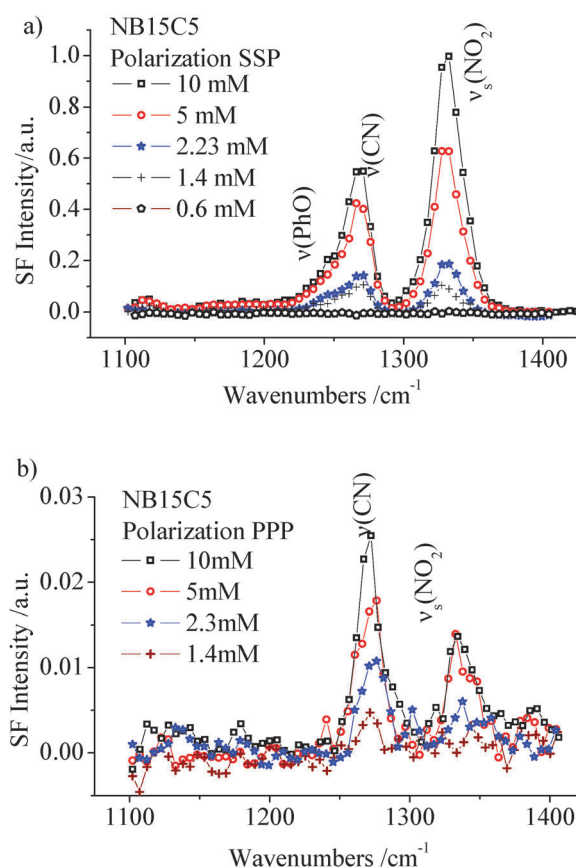


Fig. 2 SFG spectra of NB15C5 taken under SSP (a) and PPP (b) polarization combinations for 0.6, 1.4, 2.3, 5, 10 mM.

at the water–air interface. NB15C5 displays a good signal to noise ratio in both SSP and PPP polarization combinations[¶] in the region associated with the nitro moiety ($\nu_s(\text{NO}_2)$ and $\nu(\text{CN})$). These features are of course lacking for B15C5.

The minimum concentration at which peaks were clearly resolved in the CO–NO region in both the SSP and PPP polarization combinations was 1.4 mM NB15C5. The spectra were fitted using three resonant vibrations at 1260 cm^{-1} , 1279 cm^{-1} , and 1341 cm^{-1} . The peak positions and the bandwidth remained constant over the concentration range studied. Only a very small nonresonant background was obtained in the fitting procedure, which is generally the case for the water–air interface.¹⁴

Fig. 2 shows the $\nu(\text{CO})$, $\nu(\text{CN})$ and the symmetric $\nu_s(\text{NO}_2)$ vibrational modes for SSP and PPP polarization combinations at varying concentrations. Changes of the fitted amplitudes of the $\nu(\text{CN})$ and $\nu_s(\text{NO}_2)$ as a function of the NB15C5 concentration are shown in Fig. 3(a). The fitted amplitudes initially increase as the concentration is increased up to 5 mM after which they appear to level off. Since the intensity of the SFG signal is determined both by the number of the molecules present at the interface and their average orientation, an increase in the signal strength could therefore be due to an

[¶] The letters refer to the polarizations of the sum frequency, visible and IR beams, respectively; S and P refer to polarizations, respectively, perpendicular to and parallel to the plane of incidence.

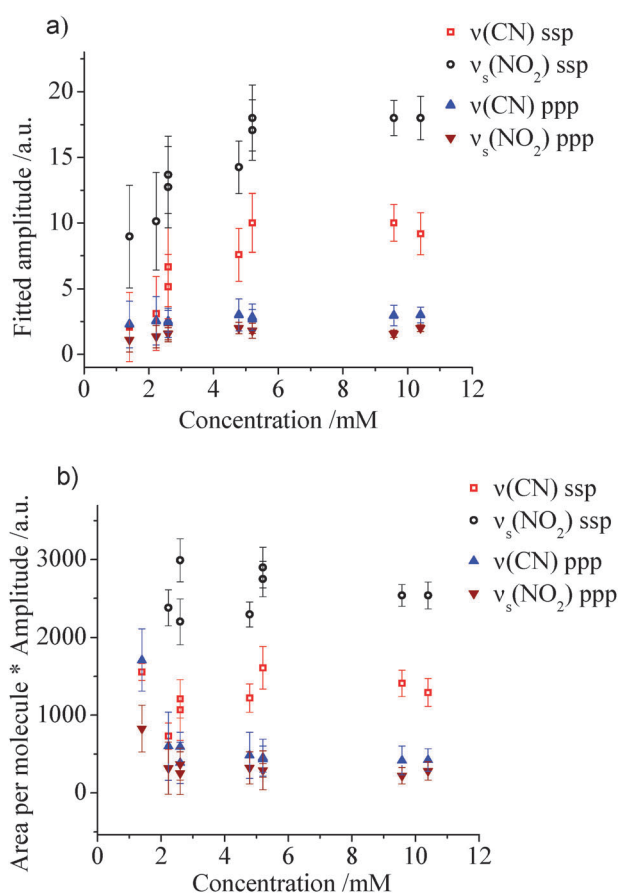


Fig. 3 Fitted amplitudes (a) and fitted amplitudes normalized by the number of the adsorbed molecules (b) of the CN stretch and symmetric NO₂ stretch modes in SSP and PPP polarization combinations as a function of NB15C5 concentration.

increase in the adsorbed amount, an increase in the molecular order/orientation or a combination of both.

In order to account for the contribution of the adsorbed amount to the detected signal one can normalize the intensity of the fitted amplitude by the square of the number of molecules present at the surface. Fig. 3(b) shows the fitted amplitudes normalized by the surface density; in this way the contribution of the adsorbed amount to the detected signal is excluded. The number density has been obtained from the Gibbs adsorption equation and isotherms shown in the previous paper¹ which are not reproduced here. The amplitude of both peaks under both polarization combinations *appears* to remain roughly constant over the whole concentration range. However, since different polarization combinations probe different projections of the molecular dipoles any change in the orientation of the molecules with concentration would engender a change in the *ratio* of the fitted amplitudes for each vibration and this ratio should be more sensitive to orientational changes.

Fig. 4 shows the ratio of the SSP to the PPP fitted amplitudes with varying crown concentration in the bulk solution. The ratio increases slightly with increasing concentration for both the CN and NO₂ vibrations.

The sum frequency intensity is dependent on the average molecular orientation with respect to the planes of polarization

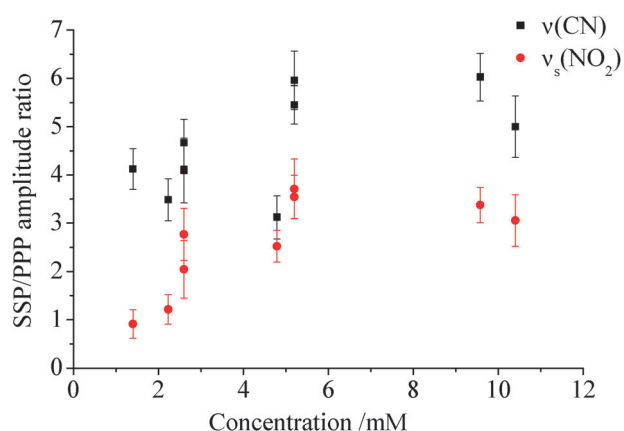


Fig. 4 Ratio of the fitted amplitudes ssp/ppp for the CN and NO₂ vibrational modes. The $\nu(\text{CN})$ is offset -4 units for clarity.

of the input beams. The ratio of the peak amplitudes for two different polarization combinations can thus reveal orientational changes. Further, if this value can be compared to theoretical curves (requiring intimate knowledge of molecular parameters) then the average orientation can be determined in terms of an angle to the surface normal.¹⁵

The polarization data could conceivably be used to determine the orientation angle of the two vibrations, since the geometry of the molecule is such that the projections of the dipoles for the two vibrations are coincident.

Such analysis has been extensively described in the literature^{16–18} however in this case, it is untenable. Firstly the NO₂ and CN stretches are strongly coupled.¹⁹ More importantly, there is significant mixing of the bands. For example it has been shown from PED calculations of nitrobenzene that for the band assigned to the CN stretch, for example, only 26% of the energy is in fact associated with the CN stretch.²⁰ The situation is somewhat better for the NO₂ band, but under these circumstances it would be inappropriate to apply orientation analysis to these bands—even if reliable hyperpolarizability parameters could be obtained. We note that we have made several attempts to obtain “indications” of how the polarisation ratios of the two stretches should vary as the tilt angle is varied. To do this we have taken depolarisation ratios²⁰ and refractive indices²¹ from the literature, and assumed C_{2v} symmetry for the NO₂ stretch. However, the values of the ratios actually observed are not predicted theoretically, indicating that the treatment is rather inaccurate. The NO₂ and CN curves also seem to indicate that the orientations are changing in opposite directions, which is impossible since the two groups are collinear. Finally the fitted curves are extremely sensitive to the refractive index of the interfacial film, which can only be coarsely approximated. (The refractive index values are required to convert amplitudes to molecular parameters. There are thus several factors conspiring against the possibility of sensible theoretical analysis.)

While the absolute orientation cannot be extracted, a *change in orientation* is clearly followed. As the concentration is increased the magnitude of the SSP/PPP ratio (shown in Fig. 4) also increases. This detectable orientational change with concentration is consistent with the conventional picture of film

formation where a decreasing area per molecule leads to orientational changes of the adsorbing species. The physical area of the molecules in plane of the ring structure is much larger than the area available per molecule at the highest densities.¹ Thus the molecules are significantly tilted at high densities and it would seem unlikely that the changes in the SSP/PPP ratio indicate a decreasing tilt with density.

CH–OH spectral region 2800–3800 cm^{−1}

Once again the *assignment* of the CH and OH spectral features for both compounds was undertaken in the preceding work.¹ Here we will address the differences in hydration, complexation with Na⁺ ions and temperature behaviour for the two compounds.

The pure water spectra are in agreement with spectra reported in the literature.^{4,18,22,23} In order to compare spectra of different systems taken on different days, normalization of spectra to the intensity of the free OH peak of the day was performed.

All studies in the literature thus far concur that the free OH peak centred at 3700 cm^{−1} (the uncoupled OH that protrudes into the gaseous phase) appears only at the interface. This provides an unambiguous probe for the perturbation of the topmost water monolayer by any added solute. The bonded OH water region—the ‘liquid like’ band centred at 3382 cm^{−1} and the ‘ice like’ band centred at 3250 cm^{−1}—gives information about the subsequent ordered water layers present at the interface.²⁴

Fig. 5(a) and (b) show the SSP polarization spectra of NB15C5 and B15C5 in the spectral region of water. It is not uncommon to fit such spectra by assuming the presence of certain peaks associated with different ‘‘hydrogen bonding water species’’,^{22,25–29} Such fitting depends on the model of water used, and it is not always unambiguous. Nonetheless, fits are necessary to quantify changes, for example with temperature, and have thus been included. In addition to the conventional peaks at 3250 cm^{−1}, 3382 cm^{−1} and 3700 cm^{−1}, the peak positioned at 3560 cm^{−1}, which is evident in PPP spectra, was introduced into the fitting procedure. An orientation analysis of the water features suggests that the ‘ice like’ and ‘liquid like’ water appear to have a symmetric character while the 3560 cm^{−1} feature has a more asymmetric character. The theoretical model for the broad feature present at 3700 cm^{−1} shows that either *C*_{∞v} or *C*_{2v} symmetry is consistent with this water vibration. The details of the orientation analysis of the water bands are provided in the ESI.† The broadening of this band and of that shifted to slightly lower wavenumber associated with adsorption has been assigned to a heterogeneous distribution of the ‘dangling’ OH bonds caused by the disruption to the local water structure as well as to water molecules participating in weak complexation.^{2,30,31} Very few studies exist of the 3700 cm^{−1} feature other than at the surface of pure water. In this case though, if the adsorbate is tilted with respect to the interface there is the possibility of interfacial water constrained between the molecule and the air, and free OH stretches from such species would be expected to have a range of angles and energies. Indeed it may be that the increased broadening associated with the NB15C5, compared

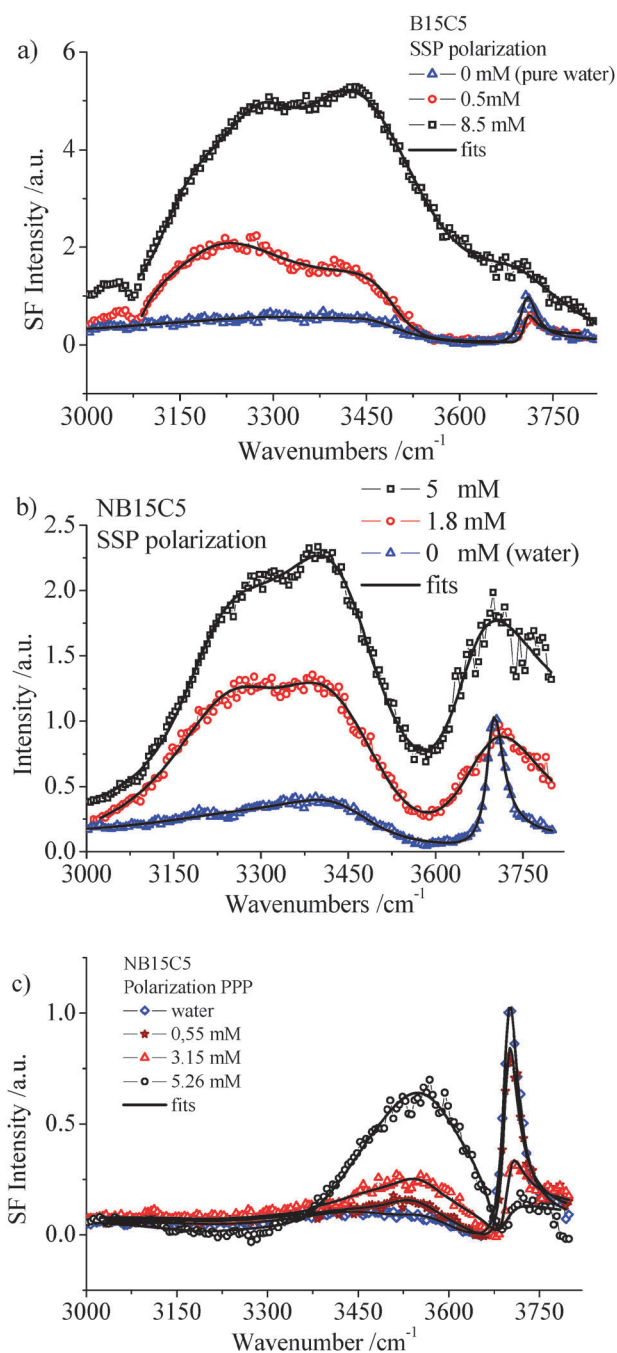


Fig. 5 (a and b) Comparison of spectra of B15C5 and NB15C5 at 0.5 mM and 8.5 mM for B15C5 and 1.8 mM and 5 mM for NB15C5, including fitting curves; (c) PPP polarization conditions of NB15C5 at 0.55 mM, 3.15 mM and 5.26 mM.

to B15C5, is due to interaction of just such a constrained water species with the nitro group. Evidence for such weak interactions has earlier been advanced by the Richmond group for SO₂.³⁰ Finally, it is also possible to speculate about the water and H₃O⁺ complexes involved in bridging the crown. For 18-crown-6, both calculations and the results of IR, NMR and XRD experiments are consistent with a pyramidal hydronium complex centred over the crown ring and hydrogen bonded to 3 ether oxygen atoms in a fluxional complex.^{32–35} In the somewhat

smaller ring used here and given the presence of aromatic ether oxygen atoms, a slightly different bridging conformation might be expected,^{36,37} with only two hydrogen bonds to the crown ring. This would constrain one of the hydronium OH to protrude, and a corollary would be the presence of a second water molecule with only a single donor bond to the crown, leading to another potential source of unbonded OH.

As the concentration of the crown ethers in solution is increased, the amount adsorbed to the surface also increases, which in turn gives rise to a strong OH signal characteristic of a charged interface.^{23,38,39} In the preceding paper this is related to the presence at the interface of a charged crown- H_3O^+ complex. This signal enhancement appears at lower concentrations for B15C5 than for NB15C5. At 0.5 mM B15C5 the intensity of the water signal is twice that of pure water. In the case of NB15C5 a similarly high intensity of the water signal is not reached until a concentration of 2 mM. Moreover, at higher concentrations the B15C5 hydrogen bonded water feature overlaps the broad band at 3700 cm^{-1} . The most obvious difference between the two crowns is thus that the hydrogen bonded water hydrating the B15C5 provides more signal than the H-bonded water hydrating the NB15C5 at similar bulk concentrations.

This increase in the water intensity, which depends upon both the adsorbed amount and surface charge, is reflected in the surface tension measurements,¹ which indicate that B15C5 has a somewhat higher surface excess at low concentration. Thus, it seems clear that at lower concentrations, B15C5 has a greater affinity for the surface, which may reflect the absence of the more polar nitro group. Given that there is a slight difference in both adsorbed amount and molecular polarity, the fact that the intensity of the hydrogen bonded water region is different for the two molecules is not surprising; small differences in charge will have a marked effect on the water ordering. The affinity of the hydronium for the site, and thus the net charge, may be affected by the interfacial orientation—this affects how close the site resides to the low dielectric constant vapour phase. While the difference between the two moieties is thus difficult to tie down, the fact remains that this is secondary to the primary observation: the ordered water signal increases by an order of magnitude compared to pure water for both species.

Another interesting observation is the fact that the peak at 3382 cm^{-1} shifts to higher frequency with increasing concentration. Higher frequency is associated with a lower degree of hydrogen bonding which is to be expected as the interface becomes less “water like”.

The PPP polarization spectrum of NB15C5 is presented in Fig. 5(c). Increasing the bulk concentration induces an increase in intensity of the band at 3560 cm^{-1} . (The B15C5 also displayed the prominent feature 3560 but no concentration study was performed.) This band has been observed before for analogous species and is associated with non-donor OH bonds which vibrate towards non-polar species.² The increase in intensity with concentration reflects the increased number of hydrocarbon moieties at the surface. Furthermore, the two features present in the PPP spectra centred at 3560 cm^{-1} and 3700 cm^{-1} interfere destructively revealing that both modes must have the same phase. This implies that the water

molecules responsible for the 3560 cm^{-1} vibration on average have their H atoms directed upwards. The fact that this interference persists, even at the highest concentration, shows that the water surface is not fully covered with solute molecules and that interfacial water molecules are still found surrounding the surface regions occupied by crown ether molecules. (For completeness we note that a broad band has also been observed between $3500\text{--}3600\text{ cm}^{-1}$ in the case of pure water by Wei and Shen¹⁸ which has subsequently been assigned by Hong-fei Wang to single hydrogen bonded water associated with the free water molecules.⁴⁰ However, the polarization ratios in that case were completely different, and as discussed by Hong-fei Wang *et al.*,³¹ this peak thus has a different origin. The fact that the free OH peak and the 3560 band have completely different concentration dependence further confirms the assignment.) A much smaller broadening effect of the 3700 cm^{-1} feature is also observed at increasing solute concentration, visible on the right hand tail of the peak. We note that the concentration behaviour of this feature in PPP is opposite to that in ssp, which coupled with the fact that consistent fits cannot be performed, strongly implies that this peak corresponds to the conventional “free OH” of the water surface rather than any of the potential species discussed above. (This implies that some of the signal observed in ssp also originates from the free OH, which would further explain the broadening in ssp.)

As discussed in paper 1¹ concerning the spectral assignments, the water region is affected by a broad resonance feature associated with delocalisation of protonic charge in the crown ring, which leads to significant broadening of the spectral features. The PPP spectra shown here are unaffected by this delocalisation effect. It would thus appear that the hydrogen bonded water revealed by PPP is confined to the water in contact with, but not complexed by, the crown molecule. This peak increases in intensity with concentration exactly as expected from earlier studies on PEO.⁴¹ This fact, coupled with the fact that there is no “ice like” water component to the spectrum, indicates that these molecules are primarily hydrating the interfacial crown species, rather than participating in a conventional “aqueous hydrogen bonding network”.

Effect of sodium chloride

Prior to investigating the effect of the NaCl ion on the hydrating water and crown adsorption, it was first deemed necessary to perform experiments to observe how the water interface is perturbed by addition of NaCl ions in the absence of crown ether species. These spectra are not shown here since they reflect earlier findings in the literature.^{23,27,42–44} Briefly, the bonded OH region shows only a slight decrease in intensity in the presence of NaCl, with negligible change to the *spectral lineshapes*.^{27,45}

The effect of addition of NaCl to the crown ether solution is shown in Fig. 6(a) and (b) for B15C5 and NB15C5, respectively. The bonded OH features (both “weak” and “strong”) appear to decrease in intensity with increasing NaCl concentration for both compounds. On the other hand in Fig. 6(c), it can be seen that the CH fitted intensity increases slightly for all CH modes as the salt concentration is increased. Thus, the addition

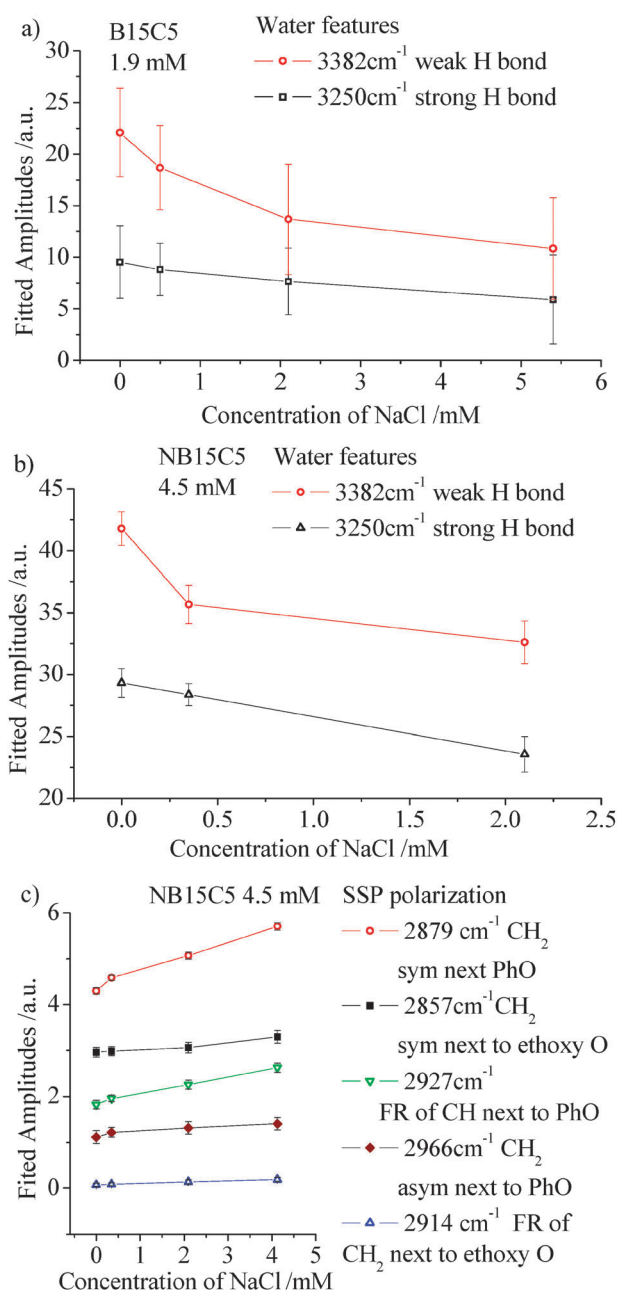


Fig. 6 Fitted amplitudes of B15C5 and NB15C5 spectra (a) in SSP polarization and (b) in OH spectral regions and (c) fitted amplitudes of NB15C5 in the CH region. In (b) the 'ice like' characteristic is offset by +15 units for clarity. The peak at 2857 cm⁻¹ in (c) is offset by +2 units for clarity. Lines are guides to the eye.

of NaCl to crown ether solution causes changes to the surface which affect both the interfacial water and alkyl bands; the implications of which are now addressed.

Aqueous crown ethers form complexes in the form of Crown-H₃O⁺, and the adsorption of such moieties to the solution-air interface promotes the formation of an electrical double layer. The thickness of a double layer is dependent on the concentration of electrolyte, becoming thinner at higher concentrations and thus addition of Na⁺ and Cl⁻ ions should promote screening of the interfacial charge. It is also

known that both B15C5 and NB15C5 form complexes with Na⁺ ions in solution which raises the possibility of several adsorbing species at the interface. The crown species which could conceivably be present at the water interface are thus (i) uncomplexed crown, (ii) crown-Na⁺ complex and (iii) crown-H₃O⁺ complex.

We can speculate that the crown-Na⁺ complex will not be as surface active as the hydronium crown complex, since the sodium ion is too large to be accommodated in the binding site.⁴⁶ This fact would result in a larger hydration shell with ensuing entropy costs associated with adsorption.

The data in Fig. 7 appear to be consistent with double layer screening for two reasons. The decrease in signal from ordered water is consistent with a reduction in surface charge (for example due to depletion of charged crowns from the surface) or a reduction in the range of the electric field with a commensurate reduction in the depth of the water film oriented by the field. In the former case a reduction in the number of molecules at the surface would lead to a reduced signal in the alkyl region but in fact the reverse is observed. The increasing signal in the CH region implies an *increase* in the adsorbed amount and this is consistent with the repulsion between charged species being screened with added salt, allowing a closer approach of the molecules. Screening of the electric field by spectator ions of sodium and chloride thus satisfactorily explains both the observations.

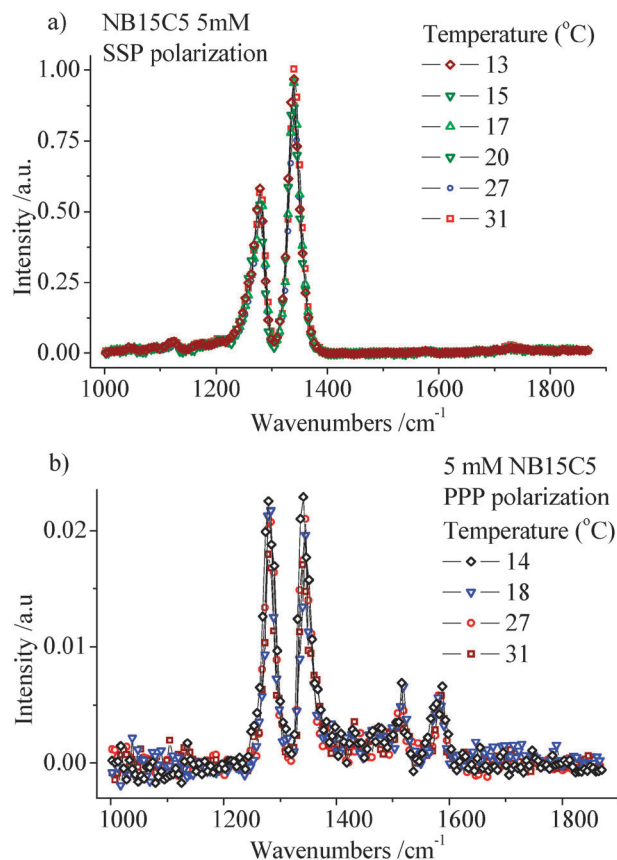


Fig. 7 VSFS spectra of NB15C5 under (a) SSP and (b) PPP polarization combinations at 13, 15, 17, 20, 27, 31 °C for SSP and 14, 18, 27, 31 °C for PPP.

A corollary of this result is that ions penetrate very close to the interface (at 10 mM the Debye length is 3 nm) despite the potentially unfavourable hydration implications in this region. It is also consistent with the earlier observation of a detectable orientational change with concentration increase being due to increased electrostatic interaction between surface species.

Effect of temperature

There are several models in the literature which attempt to explain the unusual behaviour of polyethylene oxide-based compounds which phase separate with increasing temperature.^{47–49} These models variously invoke temperature based configurational changes and entropic considerations associated with dehydration of the ethylene oxide. Crown ethers have the same chemical composition as the linear molecules, but the ring structure precludes the possibility of configurational changes with temperature. This fact thus potentially offers a means of shedding light on the driving forces for ethylene oxide dehydration at elevated temperatures. The following section describes the effect of temperature on the interfacial behaviour of the crown ethers.

CO–NO spectral region 1000–1800 cm^{−1}

Only NB15C5 was studied for temperature effects in the CO–NO₂ region, since the signal to noise ratio for the spectral features associated with the nitro groups is rather good.

In Fig. 7 the VSFS spectra of NB15C5 under (a) SSP and (b) PPP polarization conditions and at temperatures ranging from 13 to 31 °C in the CO–NO₂ stretching range are presented. This temperature range was chosen as the phase transitions in polyoxyethylene moieties of this size tend to occur in this range.⁵⁰ The assignments of the recorded features and their fitting procedure were discussed in the preceding paper.¹ The intensity of the two prominent peaks $\nu(\text{CN})$ and $\nu_s(\text{NO}_2)$ appears to be constant in both SSP and PPP when the solution is heated.

The fitted amplitudes of the peaks in Fig. 7 are displayed in Fig. 8(a). The intensities are invariant within error over the entire temperature range studied. As discussed earlier the VSFS signal contains information about both the average orientation and the number of molecular species present at the interface. Since no apparent change in intensity occurs, the results of Fig. 9(a) imply that no change occurs in either the adsorbed amount or the average orientation over the temperature range studied.

Once again, a further test, which decouples any possible contribution to the intensity from the density, is to simply compute the ratio of the fitted relative amplitudes of the same vibrational mode in two different polarization combinations. The ratio of the fitted amplitudes for the two vibrational modes considered ($\nu(\text{CN})$ and $\nu_s(\text{NO}_2)$) is thus plotted in Fig. 8(b) as a function of the temperature. Even here it appears that the ratio remains constant for both modes within the experimental error (We observe once again that full orientation analysis is prohibited by the coupling and mixing between $\nu(\text{CN})$ and $\nu(\text{NO}_2)$).^{19,20} The interfacial orientation of the CN and NO₂ bonds thus remains essentially constant over the

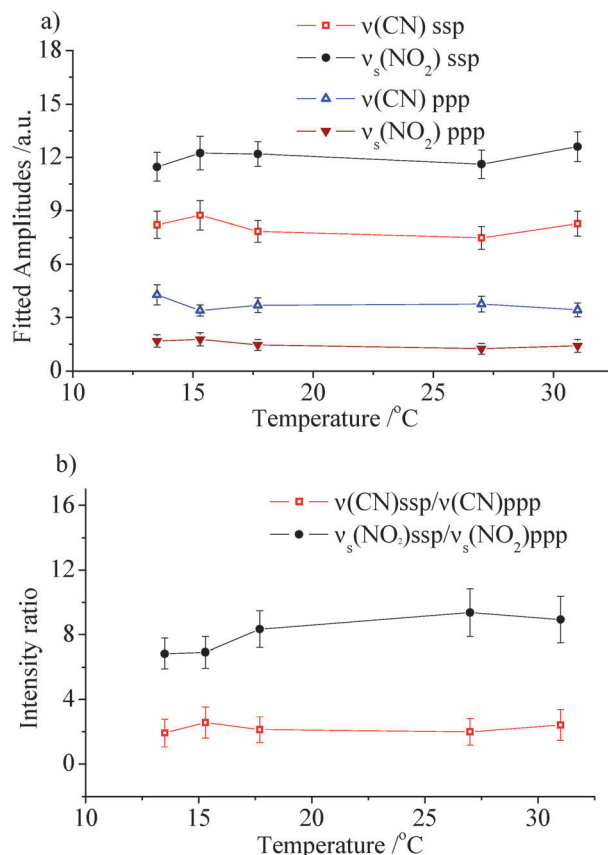


Fig. 8 (a) Change in the fitted amplitude with temperature and (b) SSP to PPP ratio of the fitted amplitudes with temperature. Lines are guides to the eye. A $\nu(\text{CN})$ ppp in (a) is offset +2 units for clarity.

temperature interval ranging from 13 to 31 °C and given the intrinsic rigidity of the molecule this also applies to the crown species as a whole.

OH spectral region 3000–3800 cm^{−1}

The effect of temperature on the spectra of pure water has been studied before^{41,51} and it was found that there is only a very small decrease in the intensity with increasing temperature. This is attributed to a broadening of the preferred orientation of the surface water molecules, related to an increased disorder of the water surface structure.

Long acquisition times combined with condensation issues on the cell windows limited the experimental temperature range for these measurements to 26–36 °C.

The VSFS spectra of NB15C5 under SSP and PPP conditions at different temperatures are displayed in Fig. 9(a) and (b), respectively, where the pure water spectra are also shown for reference. There are no dramatic changes in the shape of the SSP spectra with increasing temperature, and the intensity of the free OH and weakly bonded regions remains almost unchanged. The signal corresponding to the “ice like” or more strongly hydrogen bonded water molecules (at around 3250 cm^{−1}) however decreases measurably at elevated temperature. While not apparently a large effect on this scale, it should be noted that the magnitude of the decrease is comparable with the entire intensity of the pure water interface, and

must therefore be considered significant. This effect is also evident in the B15C5 spectra (not shown). Thus, there is a change in the highly ordered water associated with the interface.

The non-donor OH band at 3560 cm^{-1} which is the only significant feature of the PPP spectra appears to be even less dependent on the temperature. As mentioned before, these water molecules interact with non-polar species, and since there is no evidence for any change in the adsorption (Fig. 7) one would not expect any significant change in this band either. (Further evidence for the lack of change in adsorption density, conformation or orientation lies in the spectra of the CH region, where no variation is observed with T . Data not shown).

Thus one can conclude that interfacial water molecules that reside in proximity to the adsorbed crown ether at the interface have little temperature dependence over the range studied. An increase in the temperature from 26 to $36\text{ }^{\circ}\text{C}$ causes a reduction in the ordered water signal. As mentioned before a surfactant with the same number of ethylene oxide units (linear, OH terminated) and of similar molecular weight to the crown ethers used here has a cloud point of $30\text{ }^{\circ}\text{C}$ which is in the range studied here.⁵⁰

The observed temperature dependence of hydration now permits speculation about the various mechanisms proposed in the literature to explain the anomalous temperature behaviour of ethylene oxide based compounds. The “conformational model”⁴⁷ attributes the reduced solubility at elevated temperature to a reduced polarity associated with a change in the preferred ethylene oxide conformation. Such a conformational change is unfeasible for the case of crown ethers since the ethylene oxides are constrained to a ring and the required change in conformation from *gauche* (low T) to *trans* (high T) around the C–C bond is impossible.

Other models attribute the change in solubility with T to the hydration shell affinity and invoke a highly ordered hydration at low T . The more convincing of these models—the Kjellander model⁴⁸—argues that the ethylene oxide chains are surrounded by water molecules in a highly ordered, hydrogen bonded clathrate structure. The solubility is then determined by the balance between the energy and entropy terms associated with the hydration. At higher temperatures the entropy gain associated with dehydration of the chains dominates over the entropy of mixing and the enthalpy of hydration terms in the expression for the free energy. Thus the experimental system provides a potentially powerful means of discriminating between the models—the conformational transition is prohibited, so if dehydration is observed it can only be due to the hydration/Kjellander model.

There is plenty of evidence of highly ordered water in the spectra, though most of this is thought to be associated with the surface charge. The significant reduction in the ordered water signal in Fig. 9 however would appear to be solely associated with the ethylene oxide hydration. Any change in surface charge or orientation would have been apparent in Fig. 8. This evidence thus supports the Kjellander model but is by no means overwhelming.

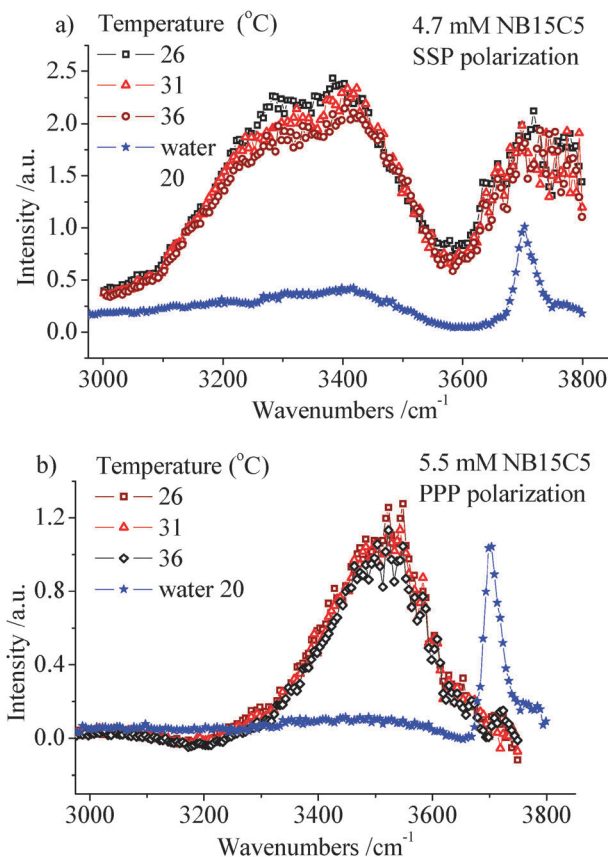


Fig. 9 VSFS spectra of NB15C5 under SSP (a) and PPP (b) polarization combination at different temperatures: 26, 31, and $36\text{ }^{\circ}\text{C}$.

Conclusions

The adsorption of 4-Nitro Benzo-15-Crown-5 (NB15C5) and Benzo-15-Crown-5 (B15C5) at the water–air interface has been successfully investigated using Vibrational Sum Frequency Spectroscopy. Probing the change in relative amplitude of polarization combinations of CN and NO_2 vibrational modes of the 4-Nitro Benzo-15-Crown-5 (NB15C5) at varying concentration of the solute indicates that the orientation relative to the surface changes measurably over the concentration range studied. Despite the rather low surface excess, this indicates that the molecules are nonetheless interacting, probably *via* repulsive electrostatic interactions since it is the charged crownate species which occupies the surface.

The water–air interface is strongly perturbed by the presence of the crown despite the fact that the monolayer regime is not achieved in the concentration range studied. The earlier observation that B15C5 is able to decrease the surface tension more readily at low concentrations in comparison to NB15C5 is reflected in the water spectral analysis and is consistent with the greater hydrophobicity of the aromatic group engendered by the absence of the nitro group. The water signal is enhanced in this region and this is due partly to the hydration of the crown moiety but mainly to the formation of a charged proton crown complex, which orients water molecules in the proximity of the interfacial layer. The response to increased electrolyte permits the conclusion that the surface density of crowns *increases* while the fact that apparent ordered hydration

decreases is of course explained simply by the fact that the surface potential is screened so the orienting effects of the surface charge are curtailed.

None of these observations are inconsistent with the suggestion that regions of aligned crowns⁵² may exist which would also give rise to the delocalization phenomena characterizing the water region of the spectrum.

The temperature dependence of the hydration was studied in the hope of shedding light on the hydration of ethylene oxide since the constrained conformation of the crown is in contrast to the configurational freedom of surfactants.⁴¹ A reduction of the hydration, albeit small, was observed as the temperature was raised and since the majority of the hydration is due to charge orientation effects, this suggests that the intrinsic hydration of the ethylene oxide was indeed being reduced. Since the alkyl region of the spectrum shows that there is no conformational change of the crown (which is essentially ruled out by the pinned configuration) these observations provide weak support for the Kjellander model of clouding in ethylene oxide systems, over the so-called conformation model.

Acknowledgements

Financial support from European Union FP6 Marie Curie Program through SOCON—'Self Organization Under Confinement' Training Network grant nr. 321018 607307, Swedish Research Council and the UK Engineering and Physical Sciences Research Council (EPSRC) for support under grants EP/C008863 and GR/R67729/01 is gratefully acknowledged. MR is a fellow of the Swedish Research Council and gratefully acknowledges support from SSF Materials program. Discussions with Dr Steve Baldelli (University of Houston, USA) are gratefully acknowledged. MR and MJ are members of and receive financing from The Swedish Center for Biomimetic Fiber Engineering.

Notes and references

- P. Niga, W. King, J. Hedberg, C. M. Johnson, J. G. Frey and M. W. Rutland, *Phys. Chem. Chem. Phys.*, 2011, DOI: 10.1039/C0CP00604A.
- E. Tyrode, C. M. Johnson, A. Kumpulainen, M. W. Rutland and P. M. Claesson, *J. Am. Chem. Soc.*, 2005, **127**, 16848–16859.
- C. M. Johnson and E. Tyrode, *Phys. Chem. Chem. Phys.*, 2005, **7**, 2635–2640.
- C. M. Johnson, E. Tyrode, S. Baldelli, M. W. Rutland and C. Leygraf, *J. Phys. Chem. B*, 2005, **109**, 321–328.
- C. M. Johnson, E. Tyrode, A. Kumpulainen and C. Leygraf, *J. Phys. Chem. C*, 2009, **113**, 13209–13218.
- E. Tyrode, C. M. Johnson, M. W. Rutland, J. P. R. Day and C. D. Bain, *J. Phys. Chem. C*, 2007, **111**, 316–329.
- U. M. Meguro and K. Esumi, *Nonionic Surfactants: Physical Chemistry*, New York, 1987.
- W. A. Charewicz and R. A. Bartsch, *Anal. Chem.*, 1982, **54**, 2300–2303.
- S. Shinkai, T. Nakaji, T. Ogawa, K. Shigematsu and O. Manabe, *J. Am. Chem. Soc.*, 1981, **103**, 111–115.
- C. D. Bain, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 1281–1296.
- Y. R. Shen, *Nature*, 1989, **337**, 519–525.
- N. Bloembergen and P. S. Pershan, *Phys. Rev.*, 1962, **128**, 606–622.
- A. G. Lambert, P. B. Davies and D. J. Neivandt, *Appl. Spectrosc. Rev.*, 2005, **40**, 103–145.
- R. Superfine, P. Guyot-Sionnest, J. H. Hunt, C. T. Kao and Y. R. Shen, *Surf. Sci.*, 1988, **200**, L445–L450.
- C. Hirose, N. Akamatsu and K. Domen, *Appl. Spectrosc.*, 1992, **46**, 1051–1072.
- Y. Rao, Y.-s. Tao and H.-f. Wang, *J. Chem. Phys.*, 2003, **119**, 5226–5236.
- W. Gan, D. Wu, Z. Zhang, Y. Guo and H. F. Wang, *Chin. J. Chem. Phys.*, 2006, **19**, 20–24.
- X. Wei and Y. R. Shen, *Phys. Rev. Lett.*, 2001, **86**, 4799–4802.
- R. D. Kross and V. A. Fassel, *J. Am. Chem. Soc.*, 1956, **78**, 4225–4229.
- V. A. Shlyapochnikov, L. S. Khaikin, O. E. Grikina, C. W. Bock and L. V. Vilkov, *J. Mol. Struct.*, 1994, **326**, 1–16.
- D. Fulvio, B. Sivaraman, G. A. Baratta, M. E. Palumbo and N. J. Mason, *Spectrochim. Acta, Part A*, 2009, **72**, 1007–1013.
- Q. Du, R. Superfine, E. Freysz and Y. R. Shen, *Phys. Rev. Lett.*, 1993, **70**, 2313–2316.
- S. Baldelli, C. Schnitzer, M. J. Shultz and D. J. Campbell, *J. Phys. Chem. B*, 1997, **101**, 10435–10441.
- N. Ji, V. Ostroverkhov, C. S. Tian and Y. R. Shen, *Phys. Rev. Lett.*, 2008, **100**, 096102.
- C. S. Tian and Y. R. Shen, *Chem. Phys. Lett.*, 2009, **470**, 1–6.
- R. K. C. Maria Sovago, G. W. H. Wurpel, M. Muller, H. J. Bakker and M. Bonn, *Phys. Rev. Lett.*, 2008, **100**, 173901.
- D. F. Liu, G. Ma, L. M. Levering and H. C. Allen, *J. Phys. Chem. B*, 2004, **108**, 2252–2260.
- B. M. Auer and J. L. Skinner, *J. Phys. Chem. B*, 2008, **113**, 4125–4130.
- E. C. Brown, M. Mucha, P. Jungwirth and D. J. Tobias, *J. Phys. Chem. B*, 2005, **109**, 7934–7940.
- T. L. Tarbuck and G. L. Richmond, *J. Am. Chem. Soc.*, 2005, **127**, 16806–16807.
- Z. Zhang, D.-s. Zheng, Y. Guo and H.-f. Wang, *Phys. Chem. Chem. Phys.*, 2009, **11**, 991–1002.
- M. Buhl, R. Ludwig, R. Schurhammer and G. Wipff, *J. Phys. Chem. A*, 2004, **108**, 11463–11468.
- P. I. Nagy and P. W. Erhardt, *J. Phys. Chem. A*, 2006, **110**, 13923–13932.
- R. Chenevert, A. Rodrigue, P. Beauchesne and R. Savoie, *Can. J. Chem.*, 1984, **62**, 2293–2298.
- E. S. Stoyanov and C. A. Reed, *J. Phys. Chem. A*, 2004, **108**, 907–913.
- J. Kriz, J. Dybal, E. Makrlík and J. Budka, *J. Phys. Chem. A*, 2008, **112**, 10236–10243.
- R. Chenevert, D. Chamberland, M. Simard and F. Brisse, *Can. J. Chem.*, 1990, **68**, 797–803.
- S. Baldelli, C. Schnitzer, M. J. Shultz and D. J. Campbell, *Chem. Phys. Lett.*, 1998, **287**, 143–147.
- D. E. Gragson and G. L. Richmond, *J. Am. Chem. Soc.*, 1998, **120**, 366–375.
- W. Gan, D. Wu, Z. Zhang, R. R. Feng and H. F. Wang, *J. Chem. Phys.*, 2006, **124**, 114705.
- E. Tyrode, C. M. Johnson, M. W. Rutland and P. M. Claesson, *J. Phys. Chem. C*, 2007, **111**, 11642–11652.
- C. Schnitzer, S. Baldelli and M. J. Shultz, *Chem. Phys. Lett.*, 1999, **313**, 416–420.
- S. Baldelli, C. Schnitzer, D. J. Campbell and M. J. Shultz, *J. Phys. Chem. B*, 1999, **103**, 2789–2795.
- E. A. Raymond and G. L. Richmond, *J. Phys. Chem. B*, 2004, **108**, 5051–5059.
- C. Schnitzer, S. Baldelli and M. J. Shultz, *J. Phys. Chem. B*, 2000, **104**, 585–590.
- G. W. Gokel, *Crown Ethers and Cryptands*, Royal Society of Chemistry, 1994.
- G. Karlstrom, *J. Phys. Chem.*, 1985, **89**, 4962–4964.
- R. Kjellander, *J. Chem. Soc., Faraday Trans. 2*, 1982, **78**, 2025–2042.
- S. Bekiranov, R. Bruinsma and P. Pincus, *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.*, 1997, **55**, 577–585.
- F. Harusawa, S. Nakamura and T. Mitsui, *Colloid Polym. Sci.*, 1974, **252**, 613–619.
- P. B. Miranda and Y. R. Shen, *J. Phys. Chem. B*, 1999, **103**, 3292–3307.
- A. Cazacu, C. Tong, A. van der Lee, T. M. Fyles and M. Barboiu, *J. Am. Chem. Soc.*, 2006, **128**, 9541–9548.