Surface Structures of Solutions of Tetrabutylammonium Nitrate Studied by Core Electron Spectroscopy

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Dedicated to Professor Göran Bergson on the occasion of his 65th birthday

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Angular resolved core electron spectroscopy has been applied to the study of solutions of a surfactant onium salt (tetrabutylammonium nitrate) in formamide. The effect of dissolving CsI into the surfactant system was studied as a function of concentration. The electron spectra, correlated to observed surface tension changes, were interpreted in terms of direct involvement of iodide ions in double-layer screening at the vacuum–solution interface.

The concept of double layer formation at liquid interfaces is well established in a variety of fields in chemical physics; cf. Ref. 1. Colloidal stability, electrode processes, biological membranes and detergency are a few of the areas where double layers play a fundamental role. In organic synthesis, electric double layer systems formed by so-called phase transfer catalysts (PTC), e.g. tetraalkyl-ammonium and -phosphonium salts, act as transfer agents of ions from aqueous to organic phase and facilitate reactions in the latter phase.

The structure of the double layer is a function of several parameters which may be broadly divided into non-specific electrostatic interactions (i.e. those that do not depend on the internal structure of the ions and may be treated within a classical Poisson–Boltzmann type of double layer description or development thereof) and those interactions that depend specifically on the chemical character of the ions involved. The latter give rise to short-range ion-pairing effects in the topmost surface layers of the solution. We have previously demonstrated[2-5] that electron spectroscopy may be successfully used to identify such ion-pairing effects. In this contribution we present further experimental results using core level spectroscopy in the angular resolved mode, which provides in-depth information on the ionic distribution within the electron escape depth of ≈ 25 Å from the

solution–vacuum interface. The system studied in the present case is tetrabutylammonium nitrate (Bu_4NNO_3), for which we have previously established a diffuse double layer structure at the interface. In particular, the effects of introducing additional ions (CsI), which are believed to act as ion-pairing agents, are studied.

Experimental

In several papers[2-5] we have applied core electron spectroscopy to study structures at liquid surfaces. The technique developed by us for such studies is based on the use of a continously wetted metal substrate inside a differentially pumped sample cell introduced into the electron spectrometer analysis chamber. Figure 1 shows the sample arrangement schematically. The liquid sample is contained in a specially designed box surrounding the metal substrate disk. The box is built in a sandwich fashion such that the box and the disk may be electrically insulated from each other and from the spectrometer ground by means of Teflon layers. There are several reasons for this arrangement. First, the disk (and hence the liquid film created by rotating the disk) may thus be put on an externally defined potential with respect to the entrance aperture of the spectrometer. As we have shown in previous work,[6] this implies that the spectrum due to the liquid surface can be effectively removed from disturbing spectral contributions from the gas phase.
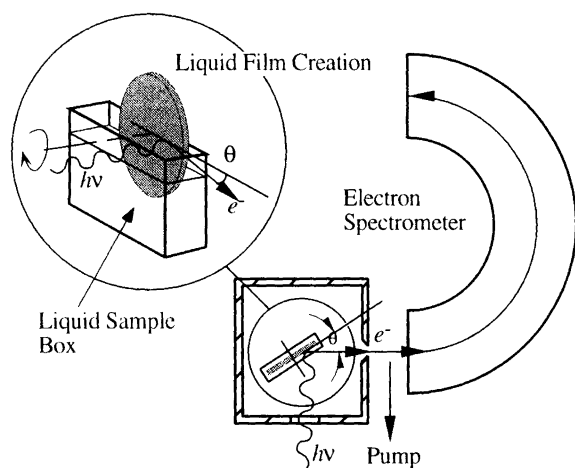
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Fig. 1. Schematic of the experimental set-up for core electron spectroscopy of liquid surfaces.

Fig. 2. C1s spectrum of a formamide solution containing 0.25 mol dm^{-3} tetrabutylammonium nitrate obtained at 90 take-off angle of the electrons.

Fig. 3. Surface tension of formamide solutions as a function of CsI concentration containing no tetrabutylammonium nitrate (empty circles) and 0.25 mol dm^{-3} tetrabutylammonium nitrate (filled circles).

Second, the construction also implies thermal insulations which means that the liquid samples can be subjected to controlled cooling. This is achieved by continous circulation of a cooling medium (liquid methanol) through the body of the liquid box. Excitation of the spectra is performed by means of monochromatized Al Kα radiation and the take-off angle of the photoelectrons is varied via rotation of the disk through an axis coincident with the X-ray line focus.

The arrangement described, which is fixed to a sample rod attached to a linear transport device, forms part of a spectrometer designed for the study of high-vapor substances in our laboratory. Typically, the liquid sample is precooled and carefully prepumped in a separate preparation chamber prior to the introduction into the analysis chamber. Differential pumping in this chamber is performed in two stages in front of the separately pumped spectrometer. At sample pressures ≤0.1 mbar this leads to spectrometer pressures ≤10^{-5} mbar. The electron spectra and surface tension data presented here were recorded at a sample temperature of 10 °C.

Results and discussion

Figure 2 shows a typical C1s spectrum, in this case obtained from a 0.25 mol dm^{-3} Bu$_4$NNO$_3$ solution in formamide. First, the solute signal is clearly resolved into two components (with the expected intensity ratio of 1:3) originating, respectively, from the nitrogen-bound, inner carbons and the more neutrally charged, outer carbons of the solute Bu$_4$N$^+$ cation. Second, it can be concluded that a substantial relative intensity enhancement is observed for the surfactant Bu$_4$NNO$_3$ with respect to calculated relative intensity values from bulk molecular ratios. In this case, the enhancement is approximately threefold, indicating a substantial surface excess.

The surface excess in these systems is confirmed by measurements of the surface tensions for the solutions
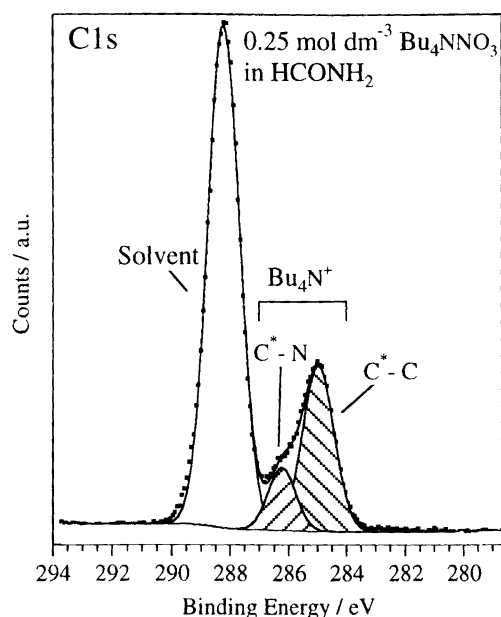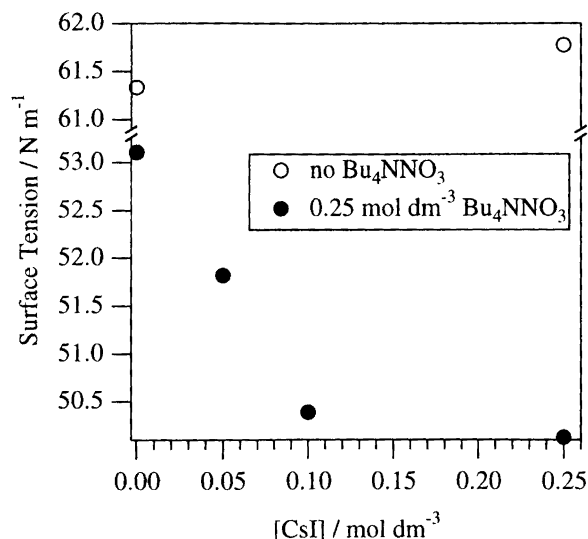
(cf. Fig. 3). Values have been plotted as a function of CsI concentration in formamide solutions, containing either no content of Bu$_4$NNO$_3$ (empty circles) or 0.25 mol dm^{-3} Bu$_4$NNO$_3$ (filled circles). As can be seen, the trends observed are opposed depending on the presence of the surfactant. Thus, whereas a slight increase in surface tension is observed in the former case, the surface tension in the latter case drops significantly in the range up to 0.1 mol dm^{-3} concentration above which a leveling-off occurs. This difference in behavior may be accounted for in terms of different mechanisms in the

two cases. For the pure CsI solutions the negative surface excess, implied by the increasing surface tension, is readily explained as a solvent screening effect of the ions close to the liquid–vacuum interface. In the latter system other effects take over due to the interaction between the surfactant Bu₄NNO₃ and CsI both at the surface and in the bulk. The bulk interaction effectively leads to a salting-out effect of the surfactant, whereas the surface interaction implies a lowering of the electrostatic free energy within the solution–vacuum interface.[7]

Turning next to the 3d signals of cesium and iodine in these solutions, Fig. 4 shows the 5/2 component obtained for two different solutions. Normalization of the components is made against the solvent C1s line. Referring to the 0.25 mol dm⁻³ CsI solution, the addition of the Bu₄NNO₃ surfactant leads to opposing behavior of the cesium and iodine signals. Thus, for 90° take-off angle of the photoelectrons the iodine signal increases by a factor of ≈2 and the cesium signal slightly decreases. A qualitative explanation for these changes in the signal intensities is clearly the presence of an electric double layer at the solution surface due to the surfactant, a major effect being the segregation of negative counterions from the substrate bulk towards the positively charged overlayer at the solution–vacuum interface. Conversely, the positively charged cesium ions are repelled from the surface. The effect is further enhanced for a take-off

angle of 30° and thus increased surface sensitivity. These observations show that the surface tension behavior in Fig. 3 is not only due to competing solvation in the solution bulk (salting-out) but also direct involvement of the iodide ions in the electric double layer at the surface. This corroborates theoretical expectations,[7] which predict the surface electrostatic screening mechanism to be dominant in systems of the present type.

Figure 5 summarizes the results over the CsI concentration range up to 0.25 mol dm⁻³ (with constant concentration of Bu₄NNO₃ of 0.25 mol dm⁻³). The trend observed in Fig. 4 is seen to persist over this entire range, the iodide signal being enhanced by approximately a factor of two for all concentrations. The signal of the Bu₄N⁺ ion is seen to increase by around 30% with addition of CsI up to 0.25 mol dm⁻³ corroborating the surface tension data. Comparing the relative enhancements of the Bu₄N⁺ and iodide signals it may be concluded that the iodide ions do not fully compensate the positive charge of the overlayer. We have previously established contact ion pairing at the surface between iodide ions and onium cations for a similar system [Bu₃(PrI)N⁺I⁻].[2] However, in this case the situation is probably more complex. Thus, the screening of the overlayer seems also to involve the nitrate ions. This latter screening is likely to occur in terms of a diffuse layer consisting of iodide and nitrate ions.

Further support for the above assertion of a double mechanism in the overlayer screening is provided by the observation in Fig. 4 of the decrease in the Cs signal. Such behavior is predicted from a diffuse-layer Poisson–Boltzmann treatment of electric double layers. Observation of such an effect of coion repulsion implies
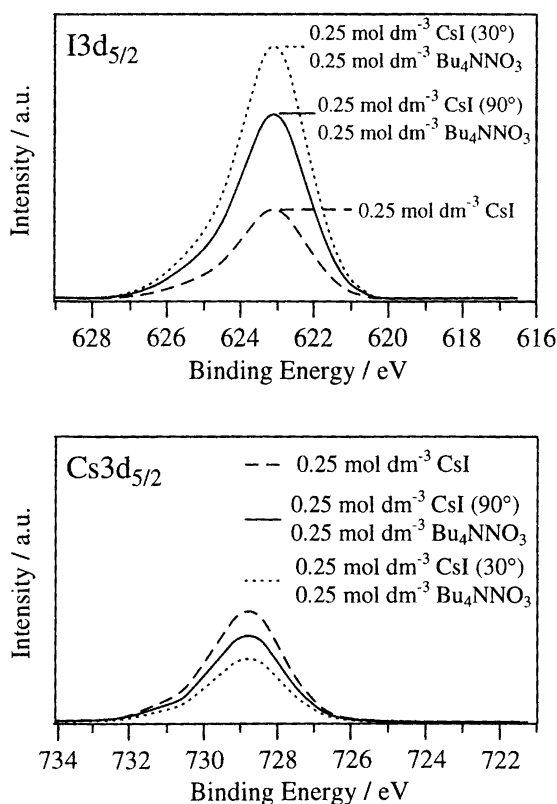

Fig. 4. I3d₅/₂ and Cs3d₅/₂ lines obtained from the formamide solutions indicated in the insets. Normalization of the lines has been made against the solvent C1s line for each solution.
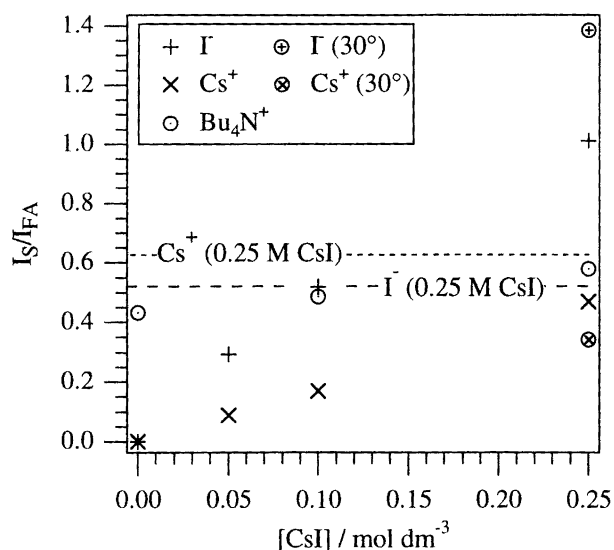
Fig. 5. Intensity ratios (referred to the solvent C1s line: I_{FA}) as a function of CsI concentration. In all cases the tetrabutylammonium nitrate concentration was 0.25 mol dm⁻³. The dashed horizontal lines correspond to the intensity ratios of the Cs3d₅/₂ and I3d₅/₂ lines in a 0.25 mol dm⁻³ solution of CsI without tetrabutylammonium nitrate.

that there exists a longer-range unscreened potential from the charged overlayer. This in turn implies that the overlayer cannot be fully screened by direct contact ion pairing alone.

Conclusions

Core level spectroscopy has been applied to the study of the electric double layer formed at the liquid-vacuum interface of a solution of tetrabutylammonium nitrate in formamide. Lowering of the surface tension was observed upon dissolution of CsI into the solution. The photoelectron spectra show that the surface tension lowering in this case is accompanied by opposed segregation tendencies of the iodide and cesium ions with respect to the interface. Thus, the iodide ions contribute directly to the screening of the positively charged overlayer. We interpret the observed behavior in terms of a double screening mechanism consisting both of contact ion pairing and diffuse layer screening. The latter mechanism is confirmed by the repulsion of the cesium ions from the interface, which is in line with a Poisson-Boltzmann diffuse layer description.

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