Studies of the Ion Distribution in the Surface of a Liquid Solution of Sodium Iodide in Tetramethylguanidine–Water using Electron Spectroscopy

Ove Bohman,[a]* Per Ahlberg,[b]* Martin Lundholm,[c] Sven Holmberg,[c] Robert Moberg,[c] Mats Arbman,[c] and Hans Siegbahn[c]*

[a] *Department of Organic Chemistry, University of Uppsala, P.O. Box 531, S-751 21 Uppsala, Sweden*
[b] *Department of Organic Chemistry, University of Göteborg, S-412 96 Göteborg, Sweden*
[c] *Department of Physics, University of Uppsala, P.O. Box 530, S-751 21 Uppsala, Sweden*

Enhanced signals from sodium iodide in tetramethylguanidine containing water indicate that sodium and iodide ions are concentrated in the surface layer of the liquid solution.

During the last few years, the scope of ESCA (electron spectroscopy for chemical analysis) has expanded further to sample situations which include a liquid-phase component. The techniques and applications of liquid ESCA have been described in a series of papers primarily concerned with bulk phenomena of liquids and solutions.[1] The present communication reports results with solutions of sodium iodide in 1,1,3,3-tetramethylguanidine (TMG) containing water. Use has been made of the extreme surface sensitivity of ESCA and the fact that the signals detected originate from a layer of the solution which is only $\sim$25 Å thick. The signals from sodium iodide are found to be strongly enhanced compared to the signals expected for the bulk solution. This is suggested to be due to a difference in solution composition of the surface layer and the bulk.

The experimental arrangement for recording of the liquid electron spectra is shown in Figure 1. The essential feature is the rotating stainless steel trundle which is submerged in a cup containing the liquid sample. Through its rotation the metal surface of the trundle is covered by a film of the sample, which is subject to irradiation by monochromatized X-rays (Al-K_α, $h\nu$ = 1486.6 eV). The sample and trundle are enclosed in a differentially pumped compartment, whose effective pressure during the experiment is equal to the vapour pressure of the liquid sample.

The solutions were prepared from TMG which had been refluxed for 5 h over calcium hydride, distilled *in vacuo* from calcium hydride and stored over molecular sieves.[2] Samples were syringed into the sample compartment through a specially designed system under inert atmosphere. Owing to the high vapour pressure of TMG at room temperature, the spectra were recorded at −35 °C.

A typical spectrum in the energy range containing the Na 2s and I 4d signals from a 0.1 M NaI solution in TMG containing water (2 M) is shown in Figure 2(a). In Figure 2(b) is shown a spectrum of a 0.4 M NaI ethanol solution. As can be seen, the relative intensities of the Na 2s and I 4d signals differ considerably between the two spectra. Also, the overall intensities of these signals compared to the solvent signal (C 1s) are substantially increased in the spectrum from the TMG solution. This enhancement of the solute intensity in TMG solution was found to be stable in time over the recording period ($>$1 h). The expected intensity ratio between the I 4d and Na 2s signals is $\sim$10 based on theoretical relative subshell cross sections.[3] The spectrum from the ethanol solution is seen to be in good agreement with this figure ($I_{\mathrm{I\ 4d}} : I_{\mathrm{Na\ 2s}} = 8.8$).

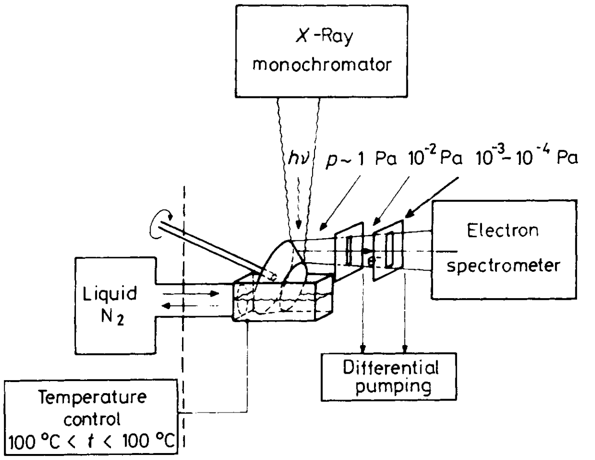

Figure 1. Diagram of the experimental arrangement for liquid electron spectroscopy.

Also, based on solute concentration and relative cross sections, the observed solute-to-solvent signal intensity ratio is found to agree well with expectation for the ethanol spectrum. The ethanol solution spectrum intensities are thus equal to those expected for the bulk solution. Similarly, expected 'bulk' intensities were obtained with solutions of NaI in formamide and dry TMG, respectively.

As evidenced in Figure 2, the 0.1 M NaI solution containing 2 M water has a surface layer composition which differs from that of the bulk. The enhancements of the solute intensities compared to expected values for solvent lines are 110 times for Na 2s and 7 times for I 4d. This corresponds to $[Na^+] \sim 11$ M and $[I^-] \sim 0.7$ M respectively, in the surface layer. Thus, there are much larger concentrations of Na^+ and I^- than in the bulk and furthermore, there are many more sodium ions than iodide ions in the surface layer. These results contrast with our earlier results obtained with surface layers of solids of alkali metal halide–crown ether and –cryptand complexes.[4]

Furthermore, for the TMG solutions containing water a high-energy O 1s peak (at 535.5 eV) was observed. This peak is ascribed to hydroxide ion (OH^-) which may be formed in an acid–base reaction between water and TMG which is a strong nitrogen base. The results thus indicate an $Na_x{}^+I_y{}^-\,(OH^-)_z$ composition of solute in the surface layer. However, in all cases $x > (y + z)$. This indicates a net positively charged surface layer within the small sampling depth of the photoelectrons. The enhancements of the solute signals were only observed when small amounts of water had been added and were always accompanied by an OH-peak and an increased intensity of the O 1s peak from water compared to that expected for the bulk.

Solutions of the kind used in the present investigation have previously been studied by ^{23}Na n.m.r. spectroscopy.[5] From these investigations it is concluded that in formamide sodium iodide is present as free solvated ions. In ethanol the ions may be present as free solvated ions and/or as solvent-separated ion-pairs. Sodium iodide in TMG, on the other hand, appears to be present as contact ion-pairs.

Thus, it is likely that ion-~~pairing plays a rô~~le also in the present context. Possibly we are dealing with larger ion aggregates which happen to be concentrated in the surface layer. Normally, one would expect particle formation to lead to decreased solute signal intensities, since in such a case a large fraction of the solute becomes inaccessible for photoelectron emission owing to the small escape depth of the photoelectrons. However, the formation of particles of larger size means that the rate of diffusion of the solute also decreases (roughly inversely proportional to the particle radius). This implies that the rate of continuous removal by pumping of the solvent from the solution surface may, at a certain particle radius, exceed the particle diffusion rate. This in turn means that the particle concentration will increase substantially near the solution–vacuum interface. Eventually larger crystals could be formed. However, our data do not yield any estimates of the size of the ion aggregates. Another possible explanation is that a new liquid phase with larger concentrations of ions and water than in the bulk has been formed, *e.g.* in the form of a microemulsion. Visual inspection of the solutions used in the experiments did not show the presence of a separate liquid phase.

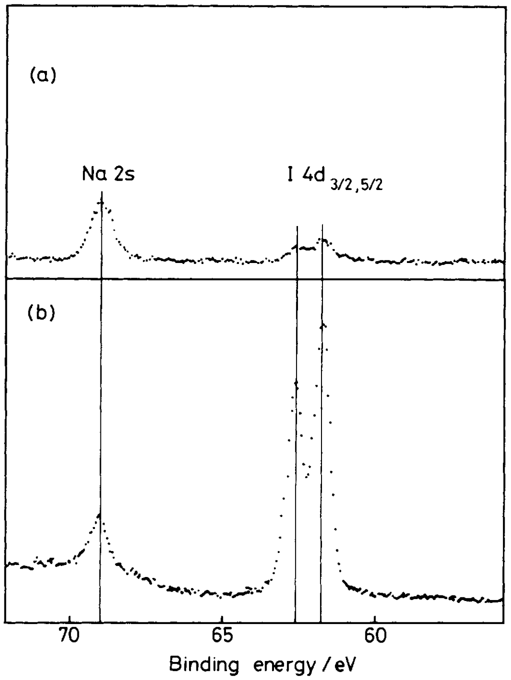

Figure 2. (a) Na 2s and I 4d ESCA lines from a 0.1 M solution of NaI in TMG containing 2 M H_2O recorded at 238 K. (b) Na 2s and I 4d ESCA lines from a 0.4 M solution of NaI in EtOH recorded at 200 K. The spectra have been normalized to each other for this figure so that the Na 2s peaks have equal heights. Thus, the lower spectrum is 110 times weaker in intensity compared to the solvent lines than the top spectrum. The background levels are not directly comparable between the two spectra owing to different running conditions. The recording time for the top spectrum was 30 min, which gave 1000 counts on the Na 2s peak.

We are grateful for support from the Swedish Natural Science Research Council.

Received, 14th April 1986; Com. 487

References

1 *Cf.* H. Siegbahn, *J. Phys. Chem.*, 1985, **89**, 897, for a review.
2 D. S. Kemp, S. J. Wrobel, Jr., S.-W. Wang, Z. Bernstein, and J. Rebeck, Jr., *Tetrahedron*, 1974, **30**, 3969.
3 J. A. Scofield, *J. Electron Spectrosc.*, 1976, **8**, 129.
4 R. Nyholm, O. Bohman, P. Ahlberg, and J. M. Lehn, *Chemica Scripta*, 1984, **23**, 212, and references therein.
5 M. S. Greenberg, R. L. Bodner, and A. I. Popov, *J. Phys. Chem.*, 1973, **77**, 2449.