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Tetrabutylammoniumiodide in formamide and hydroxypropionitrile: the temperature dependence of segregation studied by metastable induced electron spectroscopy

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Abstract. Metastable induced electron spectroscopy is used to investigate the surface segregation of tetrabutylammoniumiodide in the solvents formamide and hydroxypropionitrile. In formamide no temperature dependence of the amount of salt found in the topmost surface layer can be traced. The segregation in hydroxypropionitrile is favoured by low solvent temperatures. Comparing the given bulk concentration with the particle ratio in the surface shows a larger enhancement in formamide. With the aid of surface tension measurements and under the assumption of a simple depth profile it is possible to estimate the thickness of the surface layer with an enhanced salt concentration.

1. Introduction

Liquids have been extensively studied by means of Raman, infrared and NMR spectroscopy, which make mainly bulk properties accessible. Since the surface of liquids is interesting because of its behaviour in catalytic reactions, electron spectroscopy has been established to study the liquid–vapour interface during the last two decades. The pioneering work was carried out in [1] using XPS (ESCA). The results presented here are obtained by using MIES (metastable induced electron spectroscopy), a method first applied in 1986 [2]. Due to its perfect surface sensitivity, MIES is an ideal tool for studying surface segregation. In contrast to the above-mentioned XPS study and other works using UPS [3] where the excitation energy is supplied by photons, we use metastable helium atoms. This projectile He* with thermal velocities does not penetrate into the liquid and excites electrons only in the topmost layer. The systems studied are solutions of an organic salt in two organic solvents. The surface activity depends strongly on the nature of the salt. Whereas small inorganic substances like NaI are not seen within the sampling depth of UPS [3], organic salts like tetrabutylammoniumiodide (TBAI, $(C_4H_9)_4N^+I^-$) are very surface active due to their hydrophobic butyl groups. For this reason we obtain MIES results for TBAI in the polar liquids formamide (FA, $HCONH_2$) and hydroxypropionitrile (HPN, $CN(CH_2)_2OH$).

A solution of TBAI in formamide has already been investigated by our group using MIES [4]. The main result of this study consists of the ratio of salt molecules versus solvent molecules in the top surface layer as function of salt concentration. Near concentrations of 0.2 mol kg^{-1} we observed a change in the slope of this ratio which we attributed to a change in surface topology. The data in that regime particularly showed a large scattering

and we found a correlation between the solvent temperature and the amount of salt traced in the surface with MIES: the lower the temperature the more TBAI molecules seemed to segregate into the topmost surface layer. This seemed reasonable since a change in topology in a liquid could be influenced by its temperature. In order to check this assumed effect in detail we recorded a large set of new data; the conclusions drawn in this paper are therefore based on new experimental material. The new results show much smaller data scattering, so the effect of temperature can be carefully studied.

2. Experimental details

2.1. The apparatus

Since details of the experimental set-up are mentioned in [4] only a short description will be given here. Metastable helium atoms and He I photons are produced simultaneously in a cold-cathode gas discharge. Separating the two types of projectile by a time-of-flight method allows the recording of MIES and UPS data at the same time. The liquid target consists of a vertical beam flowing down a stainless steel needle. Via a manipulator, it can be moved in all three directions allowing any part of the free liquid surface to be investigated. The substances were purchased from Janssen Chimica with a guaranteed purity of 99%. They were used without further purification.

The subject of this paper is the temperature dependence of segregation. Unlike in experiments with solid surfaces we are not free to choose any temperature we want. Rather, one has a small window with a lower limit determined by the melting point of the liquid. The upper limit of the temperature is due to the vapour pressure of the solvent, which prevents the He* from reaching the surface. The saturation pressure is described by the Antoine law [5]:

$$\ln p = \frac{a}{T} + b \ln T + c$$

with p the vapour pressure (mm mercury), T the absolute temperature (K), and a, b, c the constants for the liquid.

Table 1. Properties of the investigated species. Constants for temperature dependence of pressure according to the Antoine law are taken from [10]. Other sources are listed. The molecular volume is calculated under the assumption of a spherical symmetry.

| | Formamide | Hydroxypropionitrile | TBAI |
|--|--------------|----------------------|-------------|
| a | -6826.6 | -5637.1 | |
| b | 2.53 | 2.55 | |
| c | 5.09 | 2.18 | |
| Molar weight (g mol ⁻¹) | 45.05 | 71.08 | 369.37 |
| Density (g cm ⁻³) | 1.133 | 1.05 | |
| Molecular volume (Å ³) | 66.1 [17] | 112.4 [6] | 500 [18] |

When calculating these values for FA one ends up with an increase of vapour pressure by a factor 5 for a temperature variation from the freezing point (~3 °C) to room temperature.

Under this latter condition the number of metastable helium atoms reaching the surface is strongly reduced preventing the taking of spectra in an acceptable time.

The lower limit of the temperature depends on the salt concentration. In general the addition of salt lowers the melting point but this effect is contrary to the temperature dependence of the solubility product. Depending on the concentration of TBAI the temperature of the solvent may have to be increased in order to prevent the salt from falling out. Data for the saturation concentration cannot be found in the literature, and we have therefore measured some experimental values, listed in table 2. At the temperature at which the salt starts to fall out, the liquid becomes turbid which can be easily seen, giving a clear criterion for the limiting temperature.

Table 2. Highest salt concentration for a given temperature.

| Concentration (mol kg ⁻¹) | Temperature (°C) |
|--|---------------------|
| 0.56 | 5.5 |
| 0.75 | 10.5 |
| 0.9 | 15 |

For this reason the data presented in figure 6 cover a larger temperature interval for a lower salt concentration. The results for a molality of 0.9 are therefore not shown since the error bars are larger due to bad counting statistics at such high temperatures.

2.2. The transmission function

Quantitative analysis requires the correction of instrumental functions (e.g. e⁻ transmission) and taking into account the detection probability of the species investigated. The first point means that one has to take care that the probability for an electron to reach the detector does not depend on the energy of the electrons being considered when analysing results gained with electron spectroscopy. Since this transmission is not constant over a large energy interval it means that the spectra have to be corrected for this effect. Whereas we assumed a constant transmission function in [4], we found an exponential transmission function in the energy regime of interest [6]. UPS measurements carried out at the Berlin Electron Storage Ring for Synchrotron Radiation (BESSY) showed that spectra of the liquids remained unchanged when the energy of the exciting beam was varied between 30 and 80 eV [7]. Therefore we assume a constant transmission in these experiments and take the spectra as references to gauge our UPS and thereby our MIES data. This is possible due to the simultaneous measurement of the two sets of data, so conditions are identical. For the comparison of two peaks separated by ΔE the correcting factor f amounts to

$$f = \exp \frac{\Delta E \text{ (eV)}}{2.94}.$$

3. Comments on former studies

A solution of tetrabutylammoniumiodide in formamide has already been investigated by our group [4]. Since the present paper is focusing on temperature effects in the segregation behaviour (a point left open in paper [4]) the results of that former study are briefly discussed in the light of the new results: figure 1 shows MIE spectra of pure formamide

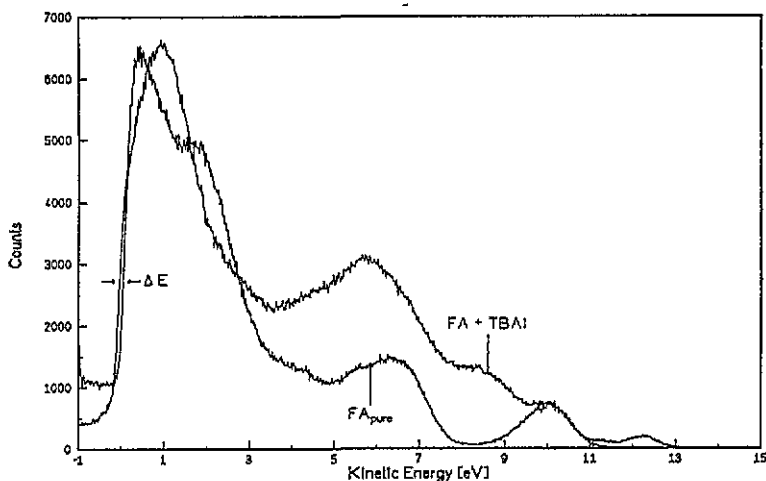


Figure 1. MIE spectrum of pure formamide and of a 0.52 molal solution of TBAI (all spectra are not corrected for transmission in the plot). The spectra are scaled at $E_{kin} = 10$ eV for calculating the salt spectrum as a difference. We observe a slight energy shift ΔE of peaks relative to the 0 eV edge.

and of a 0.52 molal solution of TBAI in FA. When TBAI in FA was investigated for the first time in [4] the shape of the electron spectra below $E_{kin} \sim 4$ eV was not constant over different runs. Since it was a new apparatus we had to learn how to handle this parameter and we restricted ourselves to interpreting only bands at higher energy. Meanwhile, the shape of the spectra can be reproduced over the whole energy region, so the shoulder at about 2 eV in the spectrum of the pure formamide is taken as real. This structure is apparently strongly reduced when adding the salt TBAI. The reduction of the peak increases with the salt concentration. We found the same behaviour for all tetraalkylammonium salts with a symmetric arrangement of the hydrocarbon chains (namely $(C_3H_7)_4N^+I^-$, $(C_4H_9)_4N^+I^-$, $(C_4H_9)_4N^+Br^-$, $(C_5H_{11})_4N^+I^-$). In contrast, the structure at 2 eV is unaffected when tetraalkylammonium salts with one extremely long chain and three shorter ones are dissolved in FA. This has been observed for $C_{16}H_{33}(CH_3)_3N^+Br^-$ and $C_{13}H_{27}(CH_3)_3N^+Br^-$. Neither does the structure seem to decrease when a symmetric salt contains phosphonium instead of ammonium. So far this has only been checked for $(C_4H_9)_4P^+Br^-$. The reason for this behaviour is not clear at the moment but it is obvious that the secondary electrons are influenced in different ways.

Gas phase measurements [3] cannot trace evaporated salt molecules or fragments so no spectrum of the pure salt can be obtained experimentally. Therefore, the TBAI-MIE spectrum was calculated by subtracting the FA reference spectrum from that of the solution (cf. figure 2). This spectrum is cut at 3 eV because the origin of the shoulder at $E_{kin} = 2$ eV is not known. In case of alkyl iodides the binding energy of the highest occupied orbital ($5p^-$) is separated by a few eV from the next one. In addition, an increase of the TBAI concentration leads to a monotonic decrease of the intensity at the highest FA band. Thus we assign the structure at about 10 eV kinetic energy exclusively to FA. This criterion leads to the scaling of the reference data before subtraction in figure 1. The spectra are shifted horizontally in order to fit the maximum and right side of the $FA(n_N, n_O)$ band. After this correction an energy difference at the 0 eV edge can be observed. It is not discussed further within the context of this paper. The structure between the 11 and 13 eV electron energies

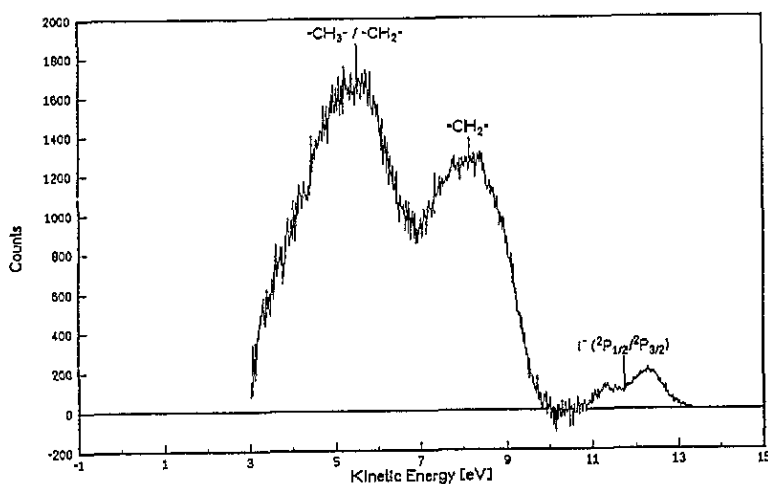


Figure 2. The TBAI MIE spectrum given as a difference. The structures can be assigned to the $\text{CH}_2\text{-CH}_3$ groups of the butyltetrahedron. It is remarkable that the anion I^- can also be traced in the topmost surface layer.

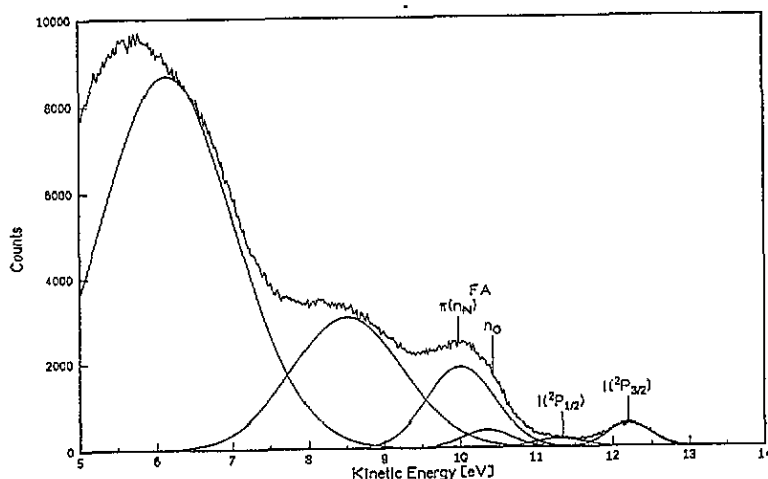


Figure 3. MIES of FA, enlarged with fitted Gaussians. They are used to determine the ratio I/FA and the amount of the spin splitting $\text{I}^-(^2\text{P}_{1/2}\text{-}^2\text{P}_{3/2})$.

can be identified as fine-structure splitting $^2\text{P}_{1/2}/^2\text{P}_{3/2}$ of the neutral iodine, produced by electron detachment of I^- . Comparison with other molecules containing CH_2 and CH_3 groups leads to the assignment of the peaks at $E_{kin} = 8.1$ eV and 5.4 eV as being caused by hydrocarbon groups. Therefore MIES is capable of monitoring anions and cations in the surface.

The fact that the anions can be traced with MIES shows that the common picture of a hydrophilic I^- remaining at a certain distance from the surface-active TBA^+ has to be rejected. Rather, it must be visible in the topmost layer accessible to the metastable helium atoms. From the fitted Gaussians, as shown in figure 3, two results can be extracted. (i) The area ratio of $\text{FA}(n_N, n_O)/\text{I}(^2\text{P})$ is a measure of the amount of salt in the surface shown in figure 4. The fine-structure splitting of the iodide signal can be interpreted in terms of

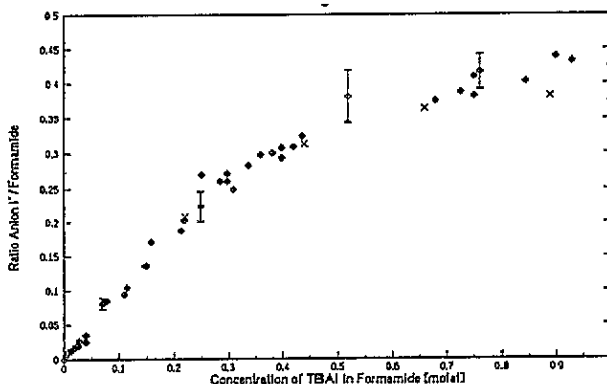


Figure 4. Ratio of I^- versus FA in the top layer as function of bulk concentration. The data indicated with crosses (\times) are XPS values taken from [18].

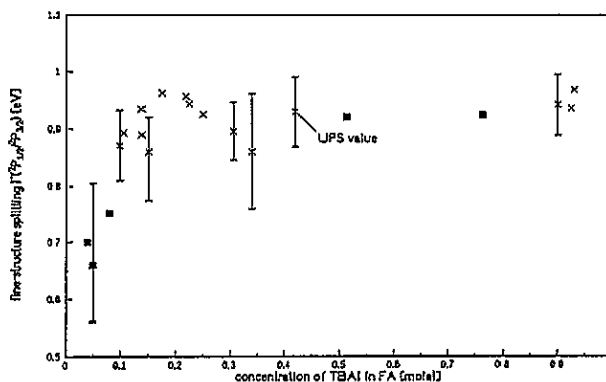


Figure 5. Fine-structure splitting of I^- ($^2P_{1/2}/^2P_{3/2}$) dependent on the bulk concentration. The filled squares are newly measured compared to [4]. An additional UPS value from [10] is assigned.

the electrostatic environment seen by the anion. The first aspect will be discussed in detail later; the consequences of the spin splitting plotted in figure 5 are briefly reported. (ii) For concentrations between 0.1 and 1 mol kg^{-1} the difference in energy between $^2P_{1/2}$ and $^2P_{3/2}$ is about 0.9 eV which is close to the atomic value for a free iodine atom of 0.943 eV [8]. The investigation of low concentrations is new compared to [4] for the following reasons. (a) Below $c = 0.1 \text{ mol kg}^{-1}$ the value decreases but errors in the fitting procedure increase at the same time. The change of the splitting is due to the intramolecular Stark effect [9]. (b) For an I^- in an ionic bond this additional E field results in a lowering of the $^2P_{1/2}/^2P_{3/2}$ splitting. In the case of TBAI this can be interpreted as follows: for a wide concentration range I^- is embedded in a surprisingly isotropic electrostatic environment, analogous to an isolated I^- . The lower splitting at $c \leq 0.1$ indicates an electrostatic anisotropy as seen within a molecule.

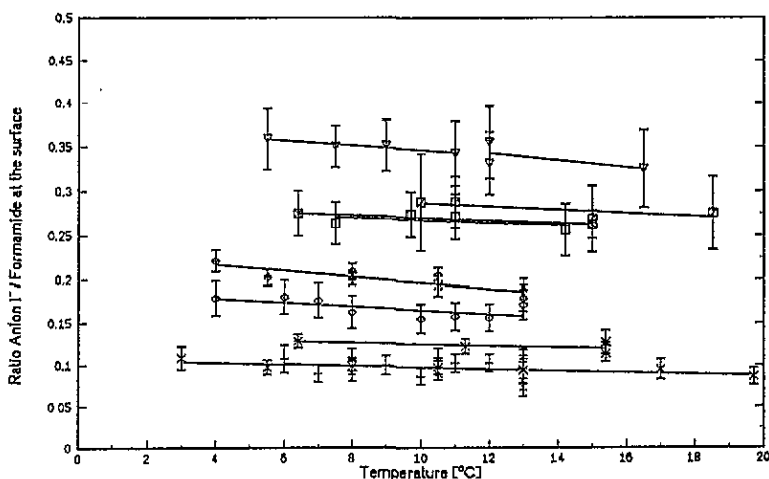


Figure 6. Ratio of I^- versus FA in the top layer for different bulk concentrations as function of temperature. Different symbols indicate different bulk concentrations of TBAI.

4. Results

Fitting Gaussians to the spectra of TBAI dissolved in FA leads to the following (transmission-corrected) peak area ratios: We find $I^-/\text{solvent} = 0.46 \pm 10\%$ for a concentration of 0.5 mol kg^{-1} (N_{TBAI}/N_{FA} which corresponds to $x = 0.023$). A concentration of 1.0 mol kg^{-1} ($x = 0.045$) leads to $I^-/FA = 0.66 \pm 10\%$; cf. table 4. These values have only been corrected with the factor resulting from the transmission function discussed in section 2.2. Figure 6 shows the ratio of I^- versus FA in the topmost surface layer for a given bulk concentration as a function of temperature. One result extracted from this plot is that the segregation hardly depends on temperature. This could have been expected for salt concentrations around 0.2 mol kg^{-1} at which the TBAI clusters break up to form one-dimensional chains [10]. The calculated regression lines have a negative slope which seems to indicate that segregation is favoured at low temperatures (17% enhancement for lowering T about 9°C , $c = 0.25 \text{ mol kg}^{-1}$). One has to mention that this effect is not due to the slow evaporation of formamide during the measurement. This could happen if the amount of solvent vaporizing was high enough to change the concentration of the salt (which does not vanish and therefore accumulates in the liquid) noticeably. In this case one would not be able to distinguish whether the increased ratio of salt/solvent is due to evaporation or to changes in temperature. For FA the temperature was therefore not varied linearly from high to low T but randomly, thus excluding this falsifying effect. (In the case of the second solvent discussed later this effect has to be considered.) To judge the regression line one has to take into account the error bars and the scattering of the data. Therefore we calculated the lowest and highest segregation gradient compatible with the experimental data. One has to state that the uncertainty of the slope exceeds the value of the slope of the regression line by an order of magnitude. When going to higher temperatures these errors even increase. The final conclusion that can be drawn at the moment is that no enhancement of the segregation can be supposed for any temperature within the experimental error.

After formamide had been investigated by electron spectroscopy several times we used hydroxypropionitrile (HPN) as a second polar solvent. UPS data for HPN have already been published in 1985 [11], but only the signals of dissolved substances have been exploited.

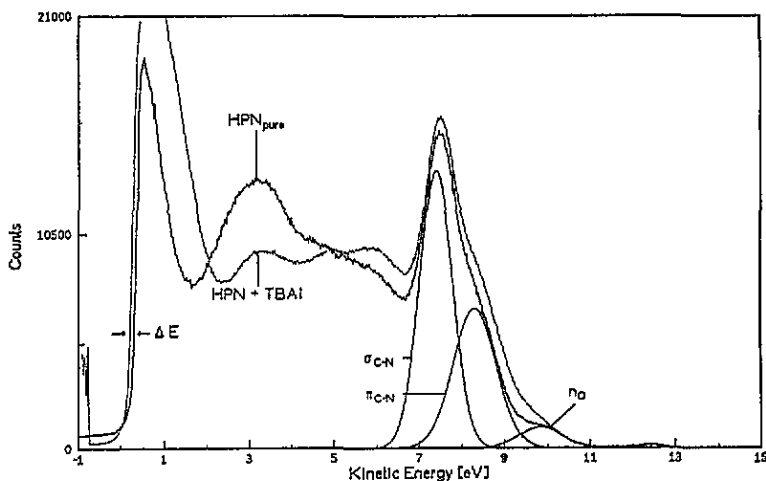


Figure 7. MIES of HPN and a 0.69 molal solution of TBAI, Gaussians for n_O , $\pi_{C=N}$, $\sigma_{C=N}$ of pure HPN. We again observe an energy shift ΔE when dissolving salt.

The first structure information was obtained by MIES when investigating lipid and tenside layers on HPN [12]. The MIE spectra of pure HPN and of a 0.63 molal solution of TBAI at a temperature of -6°C are shown in figure 7. We have chosen this concentration since the particle ratio is $N_{TBAI}/N_{sol} = 0.043$ and thus compatible with TBAI/FA for a concentration of 1 mol kg^{-1} . The Gaussians for the pure HPN spectrum can be assigned as follows. The highest orbital with a kinetic energy of 9.6 eV originates from the lone-pair orbital of the oxygen. The structure at 8.1 eV kinetic energy is due to the $\pi_{C=N}$ bond. Emission from the $\sigma_{C=N}$ orbital leads to the dominating structure at 7.1 eV kinetic energy. The highest n_O state has a binding energy which is 0.5 eV higher than in the case of the highest state in FA ($E_{kin}(n_n, n_O) = 10.0\text{ eV}$). Therefore one expects a signal originating from the I^- to be better separated from the solvent orbitals in HPN. Adding TBAI of 0.63 molal concentration leads to changes in the spectra shown in figure 7. A closer look at the interesting energy region is plotted in figure 8. At kinetic energies of 11.27 and 12.2 eV one can trace the iodine fine-structure states $^2P_{1/2}$, $^2P_{3/2}$. The splitting amounts to $\Delta E = 0.93 \pm 0.06\text{ eV}$, the ratio of $^2P_{1/2}/^2P_{3/2}$ being 1.9. This means that for HPN I^- is embedded in an electrostatically isotropic environment, as in the case for FA, for concentrations above 0.25 mol kg^{-1} . In addition, the spectrum shows that alkane chains of the butyltetrahedron $(\text{C}_4\text{H}_9)_4\text{N}^+$ are also visible in MIES. The band at a kinetic energy of 8.1 eV is strengthened by dissolving TBAI in HPN. Whereas the ratio $\sigma_{C=N}/n_O$ has endured minor changes [$(\sigma/n_O)_{pure}/(\sigma/n_O)_{TBAI} = 100/84$] the second orbital was enhanced by a factor of 1.71 compared to the HPN reference spectrum. One should mention that at both energies the spectra contain an unknown salt contribution so that it is difficult to separate effects from changes in the solvent structure and from those in the surfactant. Assuming the energy separation between signals from the alkane chains in the butyltetrahedron and iodide I^- is 3.5–4 eV, as in FA, the orbital indicated by $\pi_{C=N}$ contains an additional contribution of CH_2 groups. Evaluation of the different Gaussians and calculating TBAI spectra for all measured temperatures shows that within the experimental error no differential segregation for anions and cations can be found. For a temperature of -17.7°C in figure 9 one calculates $\text{I}^-/\text{HPN} = 0.0235 \pm 10\%$. The corresponding spectrum (No 7) shows an enhanced amount of salt in the surface due to evaporation of solvent (see

below). It was therefore chosen to minimize errors in the fitting procedure. In order to correct for evaporation the salt concentration of No 1 (=82% of No 7) has to be taken for further calculations. With the transmission factor f (=4.6; cf. section 2.2) this leads to $I^-/HPN = 0.0235 \times 0.82 \times 4.6 = 0.09$.

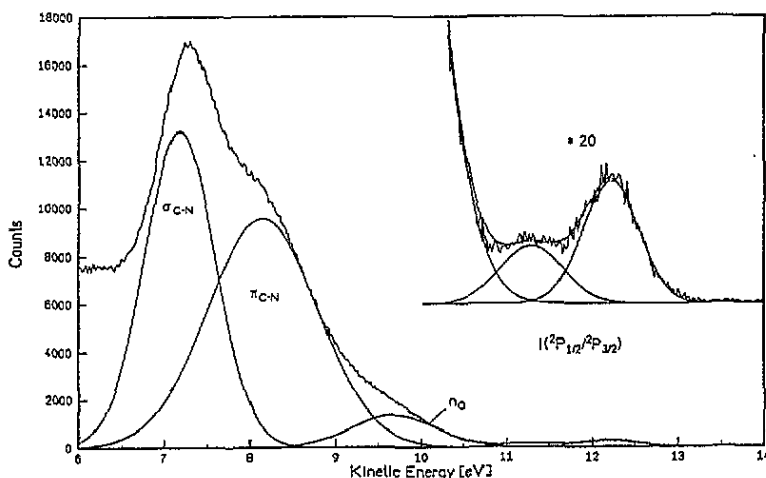


Figure 8. MIES of the TBAI/HPN range of n_0 , $\pi_{C=N}$, $\sigma_{C=N}$ and $5p(I)$. The ratio I^-/HPN is calculated by means of the fitted Gaussians and the spin splitting.

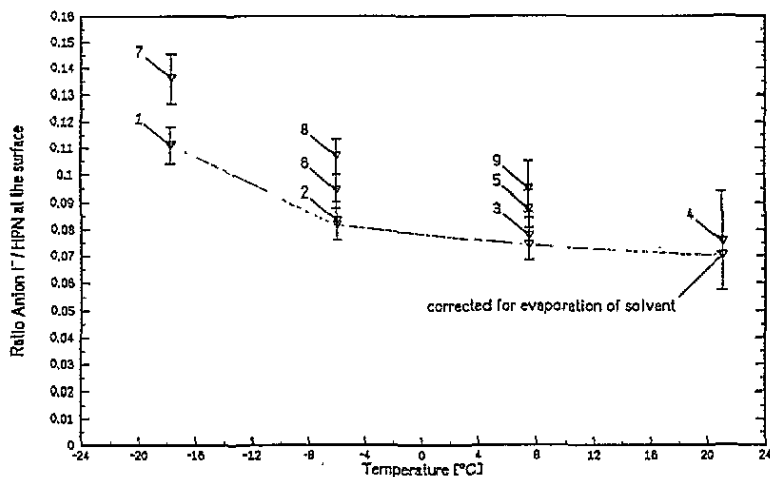


Figure 9. I^-/HPN ratio as a function of temperature. The full line represents the temperature dependence when the falsifying evaporation of solvent is corrected.

Since HPN shows a different segregation behaviour to FA, it is interesting to measure the temperature dependence. These measurements are shown in figure 9, again for a salt concentration of 0.63 mol kg^{-1} . The line assigns data points corrected for evaporation of the solvent (see below). Apparently the T -dependence cannot be characterized by a linear progression but the reaction to changes in T is enhanced when approaching the freezing point of the solvent, i.e. $-46 \text{ }^\circ\text{C}$ [5]. Lowering the temperature from $21 \text{ }^\circ\text{C}$ to $-6 \text{ }^\circ\text{C}$

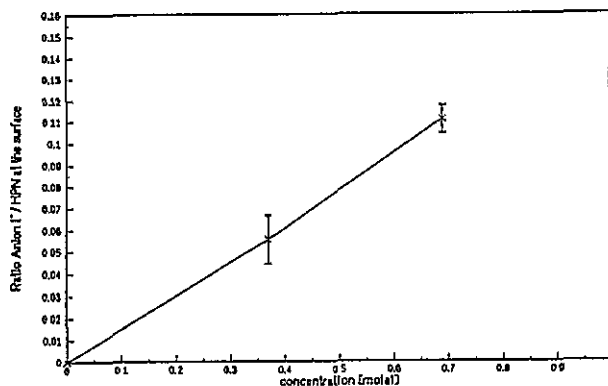


Figure 10. Segregation profile for two concentrations. Within the measured concentration regime we can assume a linear dependence of the ratio I^-/HPN in the surface.

increases the I^- signal by about 19%. Further cooling from -6°C to -18°C leads to an additional enhancement of 50%. Immediately the question arises of why this behaviour has not been studied for temperatures closer to the freezing point; this is simply due to the limited capacity of the cooling device used. So at the moment it is not known whether saturation sets in or whether the segregation gradient still increases when approaching the freezing point. An effect of the long measuring period for HPN is made visible by the chronological indication of the different runs. The temperature was varied up and down a few times between spectra 1 and 9. If one value is measured repeatedly (e.g. 2, 6, 8) the amount of salt is higher the later the data are taken. A reason for this fact lies in the slow evaporation of solvent between two points (the time at which the temperature was adjusted and the time when the spectrum was taken). The total measuring time from 1 to 9 adds up to 31 h. Such an effect obviously exists for all solvents but it was not seen in the case of FA since the time for each run only amounts to a few hours. These errors due to the evaporation can be avoided in two ways: one is the minimization of measuring time and the other is minimizing the time taken adjusting the temperature. This requires the improvement of the e^- yield (mainly the detection system) and a newly designed cooling circuit and device. These changes cannot be carried out using the existing apparatus within a reasonable time period. The only possible solution is to control the gas density so that the amount of solvent remaining in the liquid circuit can be calculated by means of the temperature-dependent evaporation rate. These calibration measurements require a mass spectrometer attached to the apparatus used so that the gas influences can be studied in detail and results from the liquid surface can be extrapolated to zero vapour pressure. Such an extrapolation was used to gauge our reference data. For the time being one can state that the surface activity of TBAI in HPN is strongly favoured by low HPN temperatures.

5. Discussion

In section 2.2 the factor f used to correct transmission effects in both solvents was derived. If the ratio I^-/FA determined in [4] were just multiplied by f it would lead to a salt contribution in the FA surface of $0.66 \pm 10\%$ for a molality of 1.0 and 0.46 for $c = 0.5 \text{ mol kg}^{-1}$. With this particle ratio and the size of the molecules (I^- : 14.7 \AA^2 , TBA^+ : 71.8 \AA^2 , FA: 19.8 \AA^2 as a projection of spherical symmetry [17]) one calculates the surface covered by TBAI to be 78% for $c = 0.5 \text{ mol kg}^{-1}$ and 90% for $c = 1.0 \text{ mol kg}^{-1}$.

From other experiments carried out with angle-resolved photoemission [7] a depth profile for the TBAI molecules can be derived. A problem arises because the fraction in the topmost surface layer is given according to the C 1s signal. The step size in that profile is about 1.5 Å meaning that a complete TBAI molecule extends over about six layers (approximately 10 Å). Within these six layers the internal distribution of the carbon atoms is reflected. Since only one iodide belongs to all layers, we do not know the exact location of the anion. In a liquid it will not be fixed at only one position. As a first estimate we therefore take the molar fraction of the C 1s atoms within the outermost surface layer which amounts to $N_{TBAI}/N_{FA} = 0.29 \pm 10\%$ for a 0.5 molal solution. Therefore 64% of the surface is covered by TBAI. Obviously the number of anions cannot exceed the amount of TBA^+ since the cation is the hydrophobic part of the molecule.

Thus we have a discrepancy between the amount of salt in the surface evaluated from UPS or from MIES data: whereas the surface area covered by TBAI amounts to 64% ($TBAI/sol = 0.29$) in the case of UPS, MIES leads to a value of 78% ($TBAI/sol = 0.46$) (both for a concentration of 0.5 mol kg⁻¹). In order to judge this deviation one has to ask for the models these calculations are based on. It must be stated that in the case of liquid surfaces the topology is not as well established as for solids. In [7] a depth profile for the C 1s signal was recorded; assuming a tetrahedron-like arrangement of the alkane chains leads to the above-mentioned amount of salt in the topmost surface layer. MIES is so surface sensitive that the spectra are a direct measure of the area covered by the respective molecules, provided that the detection sensitivities are known. We have developed a technique to gauge the detection probabilities of the two species relative to each other, but it is applicable only in the case when both species are liquids [14]. In the present case, one of the species is a salt. This means that the pure substance cannot be studied in our machine under the same conditions as a liquid. Theoretical calculations based on a model containing domains of salt and solvent lead to a covered area between 64% and 66%; including error bars the values never exceeded 70% [13] meaning that $TBAI/sol \sim 0.30$. We therefore think that it is legitimate to scale the detection probability of I⁻ with MIES in order to reach the UPS value. This probability then amounts to 1.59 (0.46/0.29) instead of 1. It is reasonable to do so not only because of the above-mentioned calculation and UPS data. When the metastable helium atoms approach a surface they are attracted by negatively charged ions. This is known for many molecules and may also be valid for I⁻. In addition part of the solvent might be shielded by the alkane chains so that FA is not reached by He*. This would also lead to an enhanced salt contribution in the MIES signal.

After gauging the iodide signal, the enhancement of the salt in the surface compared to the given bulk ratio can be calculated. In FA the bulk particle ratio for $c = 0.5$ mol kg⁻¹ is 0.023. In the surface we find a ~13-fold amount of salt (0.29/0.023 = 12.6). At a concentration of 1 mol kg⁻¹ this amounts to a factor of ~9 (0.42/0.045 = 9.3). The respective enhancement in the case of TBAI in HPN has to be compared with the above value. The detection probability for iodide and for both solvents cannot be compared directly. In order to compare the ratios I⁻/FA and I⁻/HPN one has to check the electron yield FA/HPN. This task has recently been carried out in this laboratory [6, 14]. The method is based on a set of reference spectra for the pure solvent taken at different vapour pressures in the target chamber. The relation of count rate versus pressure can be evaluated and extrapolated for $p = 0$ meaning now disturbing the gas phase. After treating FA and HPN in the same way, the solvent peak intensities can be compared. [14] shows that $HPN(\sigma_{C=N})/FA(n_N, n_O) = 4.0$ meaning that in the HPN case the e⁻ emission compared to FA is fourfold. This value has to be corrected for transmission effects with $\Delta E = 2.2$ eV between the respective FA and HPN peaks. The factor f is calculated as 2.1 and the above-

calculated particle ratio of I^-/HPN then amounts to 0.11 ($= 0.06 \times 4.0/2.1$). With a size of 28.1 \AA^2 for HPN [6] 28% of the liquid surface is covered by TBAI. The analogue calculation for a solvent temperature of $21 \text{ }^\circ\text{C}$ corrected for evaporation leads to $I^-/HPN = 0.07$ with a salt-covered area of 19%.

If the change of segregation with time in figure 9 is explained by continuous evaporation of the solvent, the real salt content after evaporation has to be calculated in order to check whether this leads to a reasonable rate of evaporating molecules. The segregation recorded at a fixed temperature for different concentrations shows a linear dependence of the amount of salt in the surface in that concentration regime. Between measurements 1 and 7 in figure 9 the amount of salt was enhanced by a factor of 1.22. Thus 82% of the starting volume of the solvent is left in the liquid circuit after the total measuring time of 1107 min. With the molar weight of 71.08 g one calculates that 0.28 mol ($=19.6 \text{ g}$) evaporate in 66 420 s. The free liquid surface exposed to vacuum can be estimated as 0.94 cm^2 ($\varnothing 1.5 \text{ mm}$, length 20 mm). In total one ends up with an evaporation rate of $4.4 \times 10^{-6} \text{ mol cm}^{-2} \text{ s}$. For the other solvent FA the value of $5.2 \times 10^{-6} \text{ mol cm}^{-2} \text{ s}$ is found in the literature [15]. Therefore the calculated value for HPN can be judged as a reasonable estimate. Assuming a spherical symmetry of the HPN molecule the number of monolayers leaving the surface can be given as 4350 monolayers per second; thus the rate of evaporation amounts to $220 \text{ }\mu\text{s}$ per monolayer.

6. Comparison with macroscopic properties

The segregation of surfactants leads to an enhanced amount of these species in the surface region. This surface excess Γ is connected with the surface tension and the chemical potential of the investigated compound via the Gibbs equation:

$$d\gamma = - \sum_i \Gamma_i d\mu_i \quad (1)$$

with $d\gamma$ the change in the surface tension, Γ_i the surface excess of compound i , $d\mu_i$ the variation of the chemical potential of i .

Therefore a comparison between the enrichment studied by MIES on a microscopic scale and the macroscopic property surface tension can be made. This correlation can be used to evaluate the thickness of the surface region.

Molecules are accommodated in the surface as long as this leads to a minimization of the Gibbs energy. The change in surface tension $d\gamma = -RT \sum_i \Gamma_i d(\ln x_i + \ln f_i)$ depends on the molar fraction x_i of TBAI and on the activity coefficient of the salt f_i . We assume Raoult's law [16] to hold in our case and, thus, get $a_i \sim x$. In this case the latter equation can be transformed into:

$$-\frac{x}{RT} \frac{d\gamma}{dx} = \Gamma_T - \frac{x}{1-x} \Gamma_S \quad (2)$$

that is

$$-\frac{x}{RT} \frac{d\gamma}{dx} = \Gamma_T \left(1 - \frac{x}{1-x} \frac{\Gamma_S}{\Gamma_T} \right) \quad (3)$$

via the definition

$$\Gamma_i = n_i^{surf} d \quad (4)$$

and we get:

$$-\frac{x}{RT} \frac{d\gamma}{dx} = \Gamma_T \left(1 - \frac{x}{1-x} \frac{n_S^{surf}}{n_T^{surf}} \right) \quad (5)$$

where the ratio $n_{solv}^{surf}/n_{TBAI}^{surf}$ is directly supplied by MIES; cf. table 3. Since the left-hand side of equation (5) is determined from surface tension measurements we can calculate the quantity Γ_T . Via equation (4) we can then evaluate the layer thickness d provided we know the surface density n_{TBAI}^{surf} . This latter quantity can be calculated by assuming a compact liquid which leads to

$$n_{TBAI}^{surf} v_{TBAI} + n_{solv}^{surf} v_{solv} = 1 \text{ cm}^3 \tag{6}$$

where n is given in units of molecules per cm^3 .

Table 3. Comparison of MIES results and data obtained by measurement of surface tension. x denotes the molar fraction of TBAI. MIES values from figures 4 and 9 and table 4 are indicated with †. The abbreviations used in the table are as follows: $A = 1 - [x/(1-x)]/(n_T^{surf}/n_S^{surf})$, $B = -(x/RT)(dy/dx)_{10^\circ\text{C}}$, $E = \Gamma_{TBAI}/n_{TBAI}^{surf} = d =$ depth of layer with enhanced amount of salt.

| TBAI conc. (molal) | Solvent | x_{TBAI} | $n_T^{\dagger}/n_S^{\dagger}$ | A | B ($10^{-11} \text{ mol cm}^{-2}$) | Γ_{TBAI} ($10^{13} \text{ mol cm}^{-2}$) | n_{TBAI}^{surf} (10^{20} cm^{-3}) | E (10^{-8} cm) |
|--------------------|---------|------------|-------------------------------|-------|--|---|---|------------------------------|
| 0.5 | FA | 0.023 | 0.29 | 0.995 | 14.7 | 8.90 | 13.7 | 6.5 |
| 1.0 | FA | 0.045 | 0.42 | 0.986 | 5.9 | 3.60 | 15.2 | 2.4 |
| 0.6 (21 °C) | HPN | 0.043 | 0.04 | 0.998 | | 2.78 | 3.02 | 9.2 |
| 0.6 (-18 °C) | HPN | 0.043 | 0.06 | 0.998 | 4.6 (10 °C) | 2.78 | 4.2 | 6.6 |

This is transformed into:

$$n_{TBAI}^{surf} = \frac{v_{solv}}{1 \text{ cm}^3} \left(\frac{v_{TBAI}}{v_{solv}} + \frac{n_{solv}^{surf}}{n_{TBAI}^{surf}} \right) \tag{7}$$

with the molar volumes v_i listed in table 1.

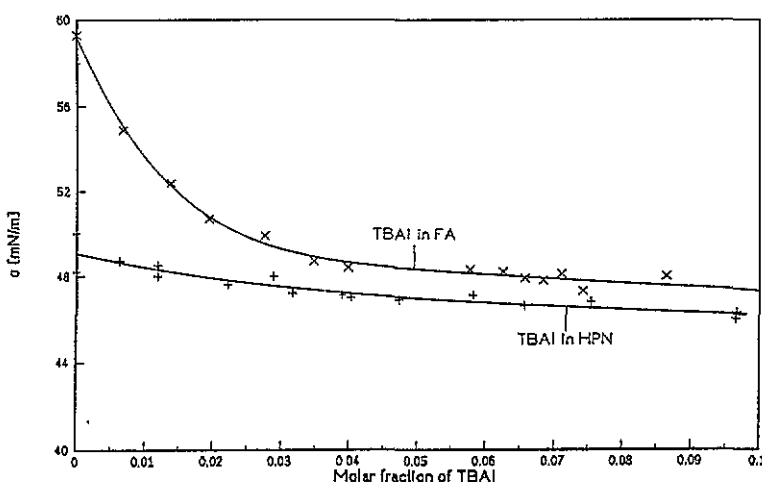


Figure 11. Surface tension of TBAI in FA/HPN, temperature = 10 °C. The line represents an analytic function which was fitted to allow calculation of the derivative dy/dx_{TBAI} .

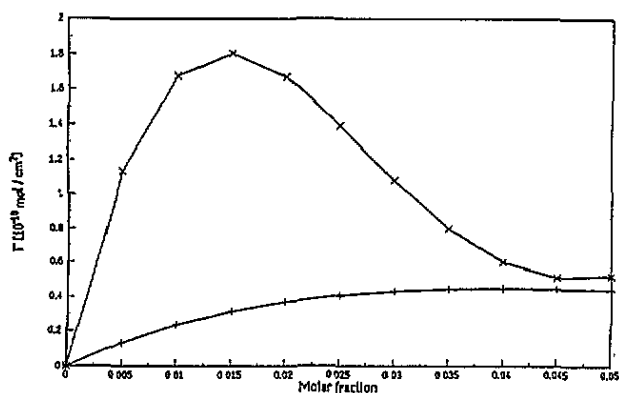


Figure 12. Surface excess for TBAI in both solvents. This is used to determine the thickness of the layer with enhanced salt concentration.

Table 4. Composition of the topmost surface layer for different solvents. The rows marked [a] refer to the peak areas of the respective Gaussians in figures 3 and 8. After correction these values are identical with the ratio of particle numbers marked with [b]. The area marked [c] in the second to last row is the actual area of the liquid surface covered by the respective molecules.

| Concentration <i>c</i> (mol kg ⁻¹) | Formamide | | Hydroxypropionitrile | |
|---|--------------|--------------|----------------------|--------------|
| | 0.5 | 1.0 | 0.6 | |
| <i>x</i> _{TBAI} | 0.023 | 0.045 | 0.043 | |
| <i>T</i> (°C) | | | -17.7 | 21 |
| Γ ⁻ /sol [a] uncorrected | 0.21 ±10% | 0.30 ±10% | 0.02 ±7% | 0.01 ±24% |
| Γ ⁻ /sol [a] transmission corrected | 0.46 | 0.66 | 0.09 | 0.06 |
| Γ ⁻ /sol [b] transmission + detection probability corrected | 0.29 | 0.42 | 0.06 | 0.04 |
| Γ ⁻ /sol transmission + detection probability + FA → HPN corrected | | | 0.11 | 0.07 |
| Area [c] [TBAI] | 64% | 76% | 28% | 19% |
| Enhancement surface/bulk | 12.6 | 9.3 | 2.6 | 1.6 |

In figure 11 the surface tension of two solutions, namely TBAI in formamide and in hydroxypropionitrile at a constant temperature of 10 °C is plotted. The full line is a function fitted to calculate the derivative $d\gamma/dx$. The respective surface excess is shown in figure 12; conclusions drawn from these values are listed in table 3. MIES monitors the particle ratio only in the topmost surface layer (column 4 in table 3) whereas the surface excess represents the total amount of salt molecules in the depth profile behind it. Combining the MIES and

surface tension data with the assumption of a rectangular shape of the depth profile gives an estimate for the thickness of the salt layer at the surface; cf. column *E* in table 3.

7. Summary

The surface segregation of tetrabutylammoniumiodide in formamide (FA) and hydroxypropionitrile (HPN) was measured with special attention to temperature dependence. This point was left open in a previous paper [4]. No temperature influence could be confirmed in the case of FA. In HPN the amount of salt found in the topmost surface layer with MIES is higher for lower solvent temperatures. Due to the limited capacity of the cooling device used, how the slope changes under further approach to the melting point of HPN is still in question. A macroscopic overview on the total amount of segregated molecules is given by the surface excess determined by measurement of the surface tension. This excess gives the integral of all salt molecules in a surface region with an enhanced salt concentration compared to the bulk value. We assumed a rectangular shape to the depth profile for TBAI and could thus calculate a first estimate for the thickness of this surface layer. The MIES value gives the salt concentration in the topmost surface layer as one side of this rectangular profile, whilst with the integral via the surface excess we can determine the layer thickness *d*. In FA it roughly extends to 3–7 Å whereas it is 7–9 Å in HPN. This means that we have more or less one monolayer of TBAI in both solvents but that the profile is smeared out somewhat in HPN. The higher the solvent temperature, the larger the extension.

When dissolving salt we observed a slight energy shift of the peaks with respect to the zero eV edge. This is not discussed further within the present paper but will be subject of additional experiments.

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