Imaging Ion Pairs Forming Structural Arrangements in Interfacial Regions

Omar Teschke,* José Roberto de Castro, and David Mendez Soares

UNICAMP, IFGW, DFA, Laboratório de Nanoestruturas e Interfaces, 13083-859 Campinas, São Paulo, Brazil

ABSTRACT: A technique to image ion pairs in solution is reported. We investigated structural and dynamic properties of ion-pair distributions deposited on highly oriented pyrolytic graphite (HOPG) surfaces in electrolyte solutions. Atomic force microscopy images of HOPG immersed in NaCl and KCl solutions display regular arrangements on top of the hexagonal carbon rings forming the HOPG atomic structure. These arrangements are the result of the low value of the aqueous interfacial dielectric constant ($\varepsilon_i \approx 3–11$). The measured ion-pair radius is a function of the salt present in the solution; for KCl, the ion-pair radius is equal or smaller than 0.42 nm; for NaCl, the ion-pair radius is 0.36 nm. A comparison of these values with their crystalline lattice dimensions indicates that both KCl and NaCl ion pairs in solution at the HOPG/solution interfacial region exist as tight contact ion pairs in quasistationary distributions. The NaCl ion-pair distribution forms an aligned arrangement, and the KCl distribution is formed by intercalated pairs.

1. INTRODUCTION

Interfacial regions in aqueous salt solution are relevant to various physicochemical processes with implications ranging from biology to the environment.1–6 Aqueous salt solution interfaces utilizes the Gibbs isotherm equation7 and the higher surface tension of aqueous salt solutions relative to pure water to describe the classical form of an interface devoid of ions.8,9 However, recently experimentalists suggested that the presence of ions at the interface of NaI and NaBr solutions could account for the diatomic iodine and bromine gas10 measured uptake coefficients. Recent molecular dynamics simulations have studied the propensity of ions11–12 at the air–solution interface. Dynamics simulations locate the carboxylate group anchored in the liquid and the methylated benzene ring tilted away from the aqueous phase.13,14 Other molecular dynamics study of the interfacial structure of aqueous solutions showed the anomalous dependence of surface tension on concentration.15 The relatively high concentration of ions at the air–water interface compared to that in the bulk solution contradicts the traditional model of the surfaces of electrolytes within which atomic ions are repelled from the air–water interface.16 The ability of water to stabilize ions is associated with its high dielectric constant. As a consequence ions in aqueous solution are expected to be repelled from a hydrophobic medium interface. However, experimental evidence to the contrary was obtained by measurements that indicated a substantial negative charge at the surface of oil droplets, solid hydrophobic polymers, gas bubbles and thin-liquid films.17

One of the main problems in theories for electrolytes has been the account for ion–ion and ion–solvent interactions. In 1903, Arrhenius18 made the assumption that electrolytes were completely dissociated into ions for an infinitely dilute solution, which accounts for the thermodynamic properties of electrolyte solutions, as shown by Debye and Huckel19 in 1923. In 1926, Bjerrum20 introduced the ion-pair concept and how the mass action constant of the equilibrium between ions and ion pairs was a function of the dielectric constant of the solvent. The Bjerrum theory was strongly supported by the work of Kraus,21 Freiser,22 Szwarc,23 and Atherton and Weissman.24

Ion-pair formation between organic ions in solution has been shown to produce a stable, nondissociating species, although no chemical bond is formed between the two components.21,25 Liquid–liquid extractions,26,27 ion-exchange resins,28 solubilizing lipophilic drug molecules,29,30 and polymerization31–33 processes are associated with the presence of stable ion pairs. Ion pairs have also been shown to influence molecular assembly at air–liquid interfaces34 and at the solid–liquid interface.35

A description of ion pairing is only possible after the development of adequate experimental methods. Previous methods have included conductivity measurements of the electrolyte solution followed by potentiometry and measurements of the solution thermodynamic properties. Spectroscopic measurements and relaxation methods have also provided insights into the nature of the ion pair. Atomic force microscopy (AFM) is an experimental method that has been shown to be capable of accessing, at liquid aqueous interfaces, the details of ionic and molecular interactions by the observation of deposited patterns with angstrom resolution.34 Collisions of oppositely charged ions...
due to their thermal motion in solution are not considered to produce stable ion pairs per se, unless they are immersed in a region with a low dielectric permittivity where they are stable. Ions are repelled from interfacial regions, but the ion pairs are attracted, so in this work, we report an AFM technique developed to image these ion pairs formed in interfacial regions.

2. RESULTS AND DISCUSSION

2.1. Imaging Structures in Electrolyte Solutions. The standard calibration procedures described in our previous work were followed by a finer scale calibration using a freshly cleaved highly oriented pyrolytic graphite (HOPG) substrate. The scanners were recalibrated by setting the standard periodicity equal to the measured periodicity.

Lateral force images show a substantial improvement in the signal-to-noise ratio when compared to the topographic image. Figure 1a displays an image of HOPG in air. The periodicity indicated in Figure 1b is 0.25 ± 0.5 nm. A schematic diagram of this structure will be employed to determine the deposited ion-pair arrangement.

To measure the crystalline lattice parameter $2 \cdot (r^+ + r^-)$, where $r^-$ and $r^+$ correspond to the radius of $\text{Cl}^-$ and $\text{Na}^+$, respectively, the crystalline structure of NaCl was scanned in air. Figure 2 shows an image of a NaCl deposit on silicon (100) (optically polished). A drop of 0.154 M NaCl solution was deposited onto the substrate and dried in air (60% RH, 25 °C); then, the surface was scanned. It should be noted that the structure corresponds to an interpenetrating face-centered cubic lattice with a lattice parameter of ~0.56 nm. The larger chloride ions are arranged in a cubic close packing structure, while the smaller sodium ions fill the octahedral gaps between them. KCl has the same structure as NaCl but with a different lattice parameter (0.623 nm).

After measuring the crystalline lattice parameters of KCl and NaCl, KCl and NaCl ion-pair deposits were imaged on HOPG surfaces immersed in water electrolytes.

Evidence for the presence of ionic pairs on HOPG comes from the observation of regular structures equally spaced in the $x$-direction obtained while scanning the substrate. Figure 3 depicts the pattern observed by scanning the HOPG surface immersed in a 1 M NaCl solution for a scanning speed of 200 nm/s. The image does not show clear periodicity in the vertical direction; however, in the horizontal direction, a periodicity of 0.73 nm is observed. The tip is scanned in the horizontal direction ($x$-axis) which is measured, in our figure, in nm. In diagram (b) the image depicts the $z$-axis. The $z$-direction

Figure 1. (a) AFM contact image of HOPG scanned in air (35% RH at 25 °C). (b) Lateral force profile between the tip and the HOPG substrate scanned over a distance of 2.5 nm at a scanning speed of 250 nm/s. The HOPG lattice periodicity of 0.25 nm is indicated in the lateral force profile. The force profile vertical direction ($x$-axis) corresponds to the $z$-direction. In the image shown in (a) the horizontal ($x$-axis) and the vertical ($y$-axis) dimensions have the same scale as indicated in the figure. The scale in the $z$-axis is given in nm but it is associated with the up and down movement of the tip where force $F$ and displacement $z$ ($z$-direction) are related by the cantilever spring constant.

Figure 2. AFM contact image of a crystalline NaCl film grown on a (100) Si wafer scanned in air over a distance of 4.0 nm at a speed of 200 nm/s. The measured NaCl crystal lattice periodicity of 0.56 nm is indicated.

Figure 3. (a) AFM contact image of an ion-pair deposit observed at a HOPG surface immersed in 1 M NaCl solution for a scanning speed of 200 nm/s. Identical $x$-axis and $y$-axis units, shown in (b). (b) Lateral force horizontal profile.
displacement is associated with the up and down movement of the tip and is related to the force necessary to raise the tip when it gets in contact with a structure. The units of this displacement are nN (nano newton) but the tip is placed on a cantilever with a spring constant of \( \sim 0.03 \text{ N/m} \). The units of these displacements can also be nm because they are related by the spring constant.

The scanning velocity was then increased to 300 nm/s; an image with a distinct periodicity was registered, which is shown in Figure 4. The measured periodicity of the pattern is now 1.06 nm, as shown in the lateral force horizontal profile below. The scanning speed was further increased to 500 and 600 nm/s, and the corresponding images are shown in Figures 5 and 6, respectively.

HOPG surfaces were then scanned following immersion in 1 M KCl solutions, and the result for a scanning speed of 400 nm/s is shown in Figure 7. The pattern shows the formation of columns separated by a distance of 1.5 nm.

Figure 4. (a) Same as that shown in Figure 3 for a scanning speed of 300 nm/s. Identical x-axis and y-axis units, shown in (b). (b) Lateral force horizontal profile.

Figure 5. (a) Same as that shown in Figure 3 for a scanning speed of 500 nm/s. Identical x-axis and y-axis units, shown in (b). (b) Lateral force horizontal profile.

Figure 6. (a) The same as that shown in Figure 3 for a scanning speed of 600 nm/s. Identical x-axis and y-axis units, shown in (b). (b) Lateral force horizontal profile.

Figure 7. (a) AFM contact image of an ion-pair deposit observed at a HOPG surface immersed in 1 M KCl solution for a scanning speed of 400 nm/s. Identical x-axis and y-axis units, shown in (b). (b) Lateral force horizontal profile.

Figure 8 shows the image registered for a scanning speed of 500 nm/s, with columns separated by \( \sim 2.0 \text{ nm} \) and an internal columnar separation of 0.73 nm. Finally, as shown in Figure 9, the image was registered at a scanning speed of 600 nm/s, and the observed periodicity for the separation of columns was \( \sim 2.0 \text{ nm} \) and the internal columnar separation was 0.73 nm.

2.2. Force Versus Distance Profiles Measured in the Interfacial Region. After imaging the structure of the ion-pair deposits on HOPG surfaces by measuring their periodicities, the ion-pair formation mechanism was investigated. The starting point was to measure the force versus distance profiles. Figure 10 shows the measured force between a neutral tip and a hydrophobic surface (HOPG) immersed in NaCl solution plotted against surface separation (\( D \)). Attraction was observed starting at a separation of \( D \approx 20 \text{ nm} \).
By probing various regions of the HOPG/water electrolyte interface of various substrates using different tips, we obtained force versus separation patterns for increasing immersion times, as shown in Figures 11 and 12. These curves are very similar to those measured for hydrophobic surfaces shown in our previous work. In the approaching curve with a cantilever with $k \approx 0.03$ N/m a large repulsive step appears at $D \approx 25$ nm as shown in Figure 11. This profile was obtained by scanning the substrate $\sim 240$ min after the immersion of HOPG in 1 M NaCl solution. At large distances, $D > 80$ nm, the force is negligible. Figure 12 shows a curve with a smaller repulsive component at the origin compared to that shown in Figure 11. This image was registered $\sim 260$ min after HOPG immersion in the solution.

Figure 8. (a) Same as that shown in Figure 7 for a scanning speed of 500 nm/s. Identical x-axis and y-axis units, shown in (b). (b) Lateral force horizontal profile.

Figure 9. (a) Same as that shown in Figure 7 for a scanning speed of 600 nm/s. Identical x-axis and y-axis units, shown in (b). (b) Lateral force horizontal profile.

Figure 10. Force vs separation curve measured for the HOPG surface in 1 M NaCl solution with a cantilever with a spring constant of 0.03 N/m at $t \approx 0$ min after HOPG immersion in the solution.

Figure 11. Same as that shown in Figure 10 measured at $t = 240$ min after HOPG immersion in the solution, showing the time evolution of the curve.

Figure 12. Same as that shown in Figure 10 measured at $t = 260$ min after HOPG immersion in the solution, showing the time evolution of the curve.
2.3. Shape Analysis of the Force Curves. Here, by using nanosized diameter tips, we have measured force versus distance curves, which are associated with the spatial variations of the interfacial dielectric constant at a HOPG surface immersed in electrolyte solutions. Typical force curves include various steps in the regions close to the aqueous/air interface. These steps have been measured by various authors.\textsuperscript{36,37} To calculate the dielectric constant profile, we modelled the energy change involved in the immersion of the tip inside the interfacial layer by the product of the immersed tip volume, dielectric permittivity variation and square of the electric field vector.\textsuperscript{34} The tip was modelled with a conical shape flat end structure with an area of \(\pi R^2\). The volume element \(dv\) immersed in the interaction region is given by \(dv = \pi[R + (\tan \alpha)z]^2dz\), where \(z\) is the integration variable of the conical volume, and \(d\) is the distance between the substrate and the tip. The change in the electric energy involved in the immersion is associated with the exchange of the dielectric permittivity of the polarization layer with that of the tip. It is calculated by integrating the exchange energy expression over the immersed tip volume in the polarization layer region. The force is obtained from the gradient of the energy expression.

Figures 11 and 12 shows different scenarios with various attractions and repulsions. The calculated dielectric permittivity profile obtained by a best fit to the experimental curves starts at \(\varepsilon_t \approx 4\) at the interface and increases to a value of 11 at a distance of \(\sim 50\) nm away from the surface.

2.4. Models of the Interfacial Ion-Pair Measured Arrangements. The permittivity varies from \(\varepsilon_t \approx 4\) at the interface to \(\varepsilon_t \approx 11\) at a distance of \(\sim 30\) nm away from the surface, indicating a potential region for the formation of ion pairs. The ion-pair-deposit distribution at the interface is described below. Initially, the polytetrafluoroethylene (PTFE) surface was scanned but no arrangement was observed, then we used HOPG surfaces as substrates, and the images are shown in Figures 3–9. This result indicates that in order to image ion-pair formation, another condition besides the scanning regions with a low dielectric permittivity is necessary: substrate matrices, where ion pairs can be orderly bound to the surface. This fixing of pairs in an orderly manner allows the dimensions of the ion pair to be measured.

Because the tip substrate interaction during scanning results in an applied force in the \(x\) direction (scanning direction) and not in the orthogonal direction (\(y\) axis), the images show arrangements without a definition in the \(y\) axis. The measured profiles indicated by yellow in the figures reflect the ion-pair distribution, which is modeled as follows: ion pairs indicated by blue circles are distributed in such a way that the spatial periodicity along the scanning horizontal direction (\(x\)-axis) is in agreement with the measured periodicity and the aggregation of ion pairs given by the width of each individual column. The scale in the vertical direction (\(y\)-axis) is the same as the \(x\)-axis but the image does not show a clear pattern in the \(y\)-direction because the scanning action takes place only along the \(x\)-direction. The periodicity of the substrate which induces the deposit patterns was used. Using this procedure we constructed the patterns in blue. By drawing various arrangements we found distributions with the smallest separation in both \(x\)- and \(y\)-directions is a constant and we claim that it corresponds to the diameters of the ion pairs. Ion pairs forming the deposited structure are imaged as large yellow patches forming vertical lines; the superimposed blue circles indicate the modeled ion-pair positions. The pattern of the carbon atoms, as observed by scanning bare HOPG surfaces, is indicated by small circles, which form a hexagonal structure, and there is matching between these two structures.

Figure 9 shows the measured profile for an image scanned in NaCl solution with a 200 nm/s scanning speed. There is only one observed periodicity in this profile: \(\sim 0.73\) nm. The arrangement of the ion pairs that satisfies this measured pattern is shown in Figure 13. Ion pairs are equally spaced in the \(x\) and \(y\) directions with separations of 0.73 and 0.83 nm, respectively. The pattern adjusted to the profile measured in 1 M NaCl using a scanning speed of 300 nm/s is shown in Figure 14. The measured periodicity of the profile is 1.06 nm and the ion-pair distribution that fits this pattern has an ion-pair separation of 0.73 nm in the \(y\) direction. For a higher scanning velocity of \(\sim 500\) nm/s, a distinct profile is obtained, as shown in Figure 15. The measured periodicities in the \(x\) and \(y\) directions are 0.79 and 0.73 nm, respectively. The proposed ion-pair profile for a higher scanning speed of 600 nm/s is shown in Figure 16. Ion pairs are separated by 0.82 nm, but the separation of the ion pairs in the \(y\) direction is the same as that shown in the previous Figures 13–15. The separation of the pairs is \(\sim 2.0\) nm.

Next, let us analyze the profile measured for KCl ion pairs. Figure 7 shows the profile that corresponds to the image obtained for a scanning speed of 400 nm/s. The modeled profile is shown in Figure 17.

Here, two periodicities are clearly observed: one periodicity formed by a pair of ion pairs with a separation of 1.47 nm and a second periodicity for a pair of ion with a separation of 1.09 nm. The separation in the \(y\) direction is 0.83 nm, which is distinct from the value measured for NaCl (0.73 nm).

Figure 18 shows the arrangement that fits the profile for 500 nm/s scanning speed shown in Figure 8. The width of the measured profile indicates that KCl ion pairs form intercalated
structures that are distinct from the isolated ion pairs formed for NaCl. As in the previous image, the separation of the ion pairs in the y direction is 0.83 nm. Finally, Figure 19 shows the profile and the suggested pattern for the KCl ion-pair distribution obtained when scanning the HOPG surface with a speed of 600 nm/s. Intercalated ion pairs are formed with a horizontal separation of 0.73 nm, as indicated in the figure, and the distance between the ion pairs in the y direction is the same as those shown in Figures 12 and 13. Therefore, our results show two differences between the KCl and NaCl ion-pair arrangements: KCl ion pairs aggregate, forming intercalated ion-pair arrangements, while NaCl ion pairs form aligned pairs. The second difference lies in the ion-pair diameters.

Ions cannot approach each other more closely than the distance of the closest approach $a$ due to the strong repulsive forces of the electron shells of the ions. The distance $a$ is understood to bear some relation to the sum of the crystal ionic radii of the positively charged $r^+$ ions and the negatively charged $r^-$ ions, with $a \geq r^+ + r^-$. By comparing the size of the measured ion-pair radii with the sum of the crystal ionic radii, we can determine the solvent distribution in the observed ion-pair patterns.

The work of Sadek and Fuoss later confirmed by Roberts and Szwarc, showed that an ion pair can exist in two forms: as a tight or intimate ion pair, or as a loose or solvent-separated ion pair, depending on the nature of the solvent–ion interaction. An ion possessing a tight solvation shell may approach a counter ion without hindrance until its solvation shell contacts the partner. Then either the associate maintains its structure as a loose, solvent-separated ion pair or the solvent molecules separating the partners are squeezed out and a tight contact ion pair is formed. Here, measurements of the ion pair distribution patterns in various electrolyte solutions determine the separation of two ion pairs in solution, and it is then possible to define if ions are at the distance of closest approach, not hydrated solvent separated, or solvent shared. Arrangements were observed for NaCl, and the distance measured between the paired ions is $\sim 0.72$ nm, consequently the ion-pair radius is $0.36$ nm, and because the periodicity of the NaCl crystal is $0.56$ nm, which is twice the separation of NaCl in the crystalline lattice, the ions are at the distance of closest approach. For KCl, a similar
arrangement of ion pairs was obtained, and the measured separation for these ion pairs is 0.85 nm, resulting in an ion-pair radius of 0.42 nm; the ionic separation in the KCl crystal is 0.62 nm (the ion-pair radius is 0.31 nm). Then, the ions in the KCl ion pair are also at the distance of the closest approach.

Now, let us compare the measured dimensions of the ion pairs with the Bjerrum cutoff distance \( q \) calculated for the experimental configuration used in this work. We have measured the interfacial dielectric permittivity at the HOPG surface and have observed a variable time-dependent dielectric permittivity profile. The calculated interfacial dielectric permittivity profile at the HOPG/water region shows values starting at \( \varepsilon_r \approx 4 \) at the HOPG surface, which then increases to \( \varepsilon_r \approx 11 \) at a distance of \( \sim 50 \) nm from the surface. Therefore, we used these values in the Bjerrum cutoff distance, which is given by

\[
q = \frac{e^2}{2 \times 4 \pi \varepsilon_0 k_B T} \text{, where } k_B \text{ is the Boltzmann constant, } T \text{ is the thermodynamic (Kelvin) temperature and } \varepsilon_r, \varepsilon_0 = \varepsilon \text{ is the dielectric permittivity. Bjerrum suggested that all oppositely charged pairs of ions at a distance smaller or equal to } q \text{ should be considered as associated ion pairs. For } \varepsilon, \approx 80 \text{, the calculated value of } q \text{ is 0.348 nm, which is smaller than the measured radius for the KCl and } \text{NaCl pairs, consequently there is no ion-pair formation in the KCl and } \text{NaCl solution in bulk water. For the measured interfacial dielectric permittivity values, initially for } \varepsilon, \approx 4 \text{, the value of } q \text{ is calculated to be 6.96 nm, and for } \varepsilon, \approx 11 \text{ } q \text{ is 2.53 nm. The measured value of the ion-pair size then satisfies the criterion that the ion-pair radius } R = (r^+ + r^-) \text{ is smaller than the Bjerrum length } q. \]

Figure 17. Model arrangement of an ion-pair deposit on HOPG immersed in 1 M KCl solution. The vertical profile image of the force corresponds to a part of the profile shown in Figure 7 (span \( \approx 0-4 \) nm). The vertical yellow columns indicate measured arrangement of the ion-pair distribution, the small circle indicates the C atoms of the HOPG surface distribution and the large circles indicate the position of the ion pairs in the arrangement. Two periodicities are observed, 1.47 nm for the large separation and 1.09 nm for the small separation. This arrangement indicated the formation of pairs of ion pairs. The separation distance of two ion pairs (diameter of the ion pair) is 0.82 nm.

Figure 18. Same as that shown in Figure 17 corresponding to the image shown in Figure 8 scanned at a velocity of 500 nm/s. The modeled profile interval is 4-8.5 nm and the separation distance for the ion pairs is 0.82 nm, which is equal to the ion-pair diameter.

Figure 19. Same as that shown in Figure 17 corresponding to the image shown in Figure 9 scanned at a velocity of 600 nm/s. The modeled profile interval is 4-8.5 nm and the separation distance of the ion pairs is 0.82 nm in the horizontal direction and 0.73 in the vertical direction. The aggregation of pairs of ion pairs is clearly shown by the formation of columns of two ion pairs. The separation distance of two ion pairs (the diameter of the ion pair) is 0.82 nm.
Eigen and Tamm\(^{41,42}\) developed a multistage ion-association treatment for the interpretation of sound adsorption relaxation processes in electrolyte solutions. The sound waves cause alternate compression and expansion of the solution and the concentration of the ion pairs responds to the pressure changes with a relaxation time \(\tau\). To explain the time dependence, they assumed that a multistage ion-pair formation process takes place from solvated-separated ion pairs through solvent-shared ion pairs to contact ion pairs. In our experimental setup, the scanning movement causes alternative compression and expansion of the solution, and because the ion-pair concentration responds to pressure changes,\(^{41,42}\) we observed a multistage ion-pair aggregation process, resulting in distinct ion-pair configurations for distinct scanning speeds (see Figures 13–19).

2.5. Mechanism of Ion Pair Pattern Formation in Interfacial Regions. All these results consistently indicate that the patterns represent oriented arrangements of ion pairs attached on or near a HOPG surface. However, one may ask whether these patterns are attached on the hydrophobic surface from the beginning or generated during the scanning of the surface. Because identical scanning should result in identical patterns, as observed, we considered that the periodicity of the patterns is associated with the relative motion of the substrate/tip. A sharp tip is brought into contact with the ion-pair covered surface and a lateral force imposed by the substrate scanning displaces the ion pairs parallel to the surface along the scanning direction (the \(x\) direction). Figures 3–9 show the lateral force profiles measured upon scanning ion pairs adsorbed on a HOPG surface at room temperature. Then, during lateral sliding, for which the tip comes into contact with the edge of the ion pair, the cantilever deforms elastically, changing the lateral force. The lateral force increases until the tip can rise over the ion pairs. The ion-pair substrate forces are not the weak van der Waals force but are the force gradient associated with the variation of the interfacial permittivity. The ion-pair motion induced by the substrate displacement placed the ion pairs at the center of the HOPG structural hexagonal arrangement of C atoms. Because the ion pairs experience a weakly corrugated potential along the \(y\) axis, we were able to arrange ion pairs in a variety of patterns on a HOPG surface, see Figures 13–19. The long-range electrostatic force that keeps the partners of an ion pair together are nondirectional; however, at the surface, the spatial distribution of the interfacial dielectric permittivity has a large gradient in the normal direction to the surface, which fixes the ion pair to the surface. Therefore, scanning, that is, the relative motion of the tip-substrate generates a pattern with a periodicity in the scanning direction. This periodicity changes with the scanning speed, indicating a mechanism similar to that described by Eigen and Tamm\(^{41,42}\). Let us define a formation time as follows: because the arrangement was formed by the scanning of the substrate, there is a formation time involved which corresponds the time that is taken by the tip to go from one ion-pair column to the next (spatial periodicity). Ion pairs are not formed by the tip but only their arrangement, because we are observing a constructed structure, which is used to measure the ion-pair spatial period; we defined a formation time as the time that takes the tip to transit one ion-pair column to the next column. This formation time is a constant, independent of the scanning speed, as shown in Figure 20, but the formation time varies with the electrolyte.

![Figure 20](image_url)  
**Figure 20.** Formation time of the constructed structure defined as the size of the structure divided by the scanning speed. The NaCl and KCl arrangements are indicated by ▲ and □, respectively.

The separation of the ion pairs along the vertical direction (\(y\)-axis) is determined only by the pair—pair repulsion and by the substrate arrangement, because there is not a clear measured pattern in this direction. Images also show that NaCl forms aligned ion pairs and that KCl forms intercalated structure pairs. The image resolution is not sufficient to determine if ion triplets are formed by the long-range electrostatic forces induced by the spatially variable interfacial dielectric constant profile; however, the intercalation of ion pairs was observed.

3. CONCLUSIONS

To the best of our knowledge, this is the first time that real images of ion pairs in solutions have been reported. The fixing of ion pairs in an orderly manner allows the dimension of the ion pair to be measured. Here, we have combined ion—ion interactions with solid—liquid interface electric fields, so that intramolecular interactions in solution (which govern the formation of the ion pairs) and intermolecular forces (which govern the self-assembly of the ion pairs) at the solid—liquid interface are responsible for the formation of the observed structure.

AFM images of a substrate immersed in the electrolyte solution show a periodic arrangement of NaCl and KCl ion pairs adsorbed on a HOPG surface with lattice parameters of <1 nm. Induced ion-pair arrangements were observed in water electrolytes at room temperature. The intermolecular forces were measured by probing the dielectric permittivity at the interface, which showed values as low as \(\varepsilon \approx 3–11\). Therefore, we suggest that this distribution is responsible for the ion-pair formation mechanism at HOPG surfaces.

The presence of ion pairs on the surface is detected from AFM signal profiles. Under the shear stress induced by the substrate motion during the scanning action, ionic structures are restructured and the scanning-velocity-dependent profiles are measured. The fact that the ion-pair assembly on HOPG cannot be broken via AFM contact, scanning suggests the existence of binding interactions between a neutral ion pair and the interface plane because of the water/HOPG hydrophobic structure. These findings may be useful in understanding the stability of ion pairs formed within polyelectrolyte films,\(^{39}\) and have the potential to impact micro- and nanoscale device fabrication which is associated with this molecular assembly.
control and stability. Systematic control over the molecular spacing between ion pairs on surfaces has been a challenge. In this work, we show that ion-pair formation proceeds through a two-step process involving an initial pair formation on the interfacial region followed by the gradual reordering of ion-pair complexes into periodically ordered arrangements in the scanning directions.

The distance between ions in solution below which ions are to be considered paired is given by the Bjerrum cutoff distance $q$. The crystalline ion-pair size $(r^+ + r^-)$ is measured to be 0.37 nm for NaCl and 0.41 nm for KCl, and the distance $q$ is 0.34 nm for bulk water with $\varepsilon \approx 80$, which is smaller than the distance measured for ion-pair separation; consequently, no KCl or NaCl ion pairs are observed in bulk water. The corresponding values of $q$ for the measured interfacial permittivity values in our experimental setup are $q = 7$ nm for $\varepsilon_x = 4$ and $q = 2.53$ nm for $\varepsilon_x = 11$; therefore, KCl and NaCl ion-pair formation is possible in the probed interfacial region. We have observed the formation of tight ion pairs in both KCl and NaCl solutions, and ion-pair-measured sizes satisfy the two criteria reported by Marcus and Heft in their theoretical considerations.

4. EXPERIMENTAL SECTION

Ion-pair detection is a difficult task because direct methods do not exist to measure the presence of such species in solutions. Only indirect methods such as the variation of mass not associated with charge variation in quartz microbalance measurements are available. Here, by using a hydrophobic matrix of the carbon atom HOPG surface, we deposited ion pairs at the interfacial region forming a regular observable structure.

The atomic force microscope is adequate equipment available for scanning surfaces in liquids, with a few angstroms of spatial resolution in the scanned plane and 0.01 nm in the normal direction, so we used AFM to scan the HOPG substrates in water electrolytes and image the adsorbed structure on this surface. An atomic force microscope (model TMX2000, TopoMetrix, CA, USA) equipped with a silicon nitride $(\text{Si}_3\text{N}_4)$ tip (model MSCT-AUHW, Microlevers, Vecco, CA, USA) with a spring constant of approximately 0.03 N/m was used to scan over the HOPG surfaces in aqueous electrolyte solutions. The radius of curvature of these AFM tips was approximately 5 nm. The sample surface maps consisted of $300 \times 300$ grid points. The best signal-to-noise ratio was obtained for a scan velocity of 200 nm/s for HOPG in air.

HOPG was cleaved with an adhesive tape in air, and then, the sample was immediately transferred to a chamber in which the atomic force microscope head was enclosed. Samples with a 1 $\times$ 1 cm$^2$ area, several tenths of a millimeter thick were used without any previous treatment. The AFM contact and lateral force images indicated that the surface was atomically flat. Freshly cleaved surfaces are free of contamination as shown by the contrast in the lateral force image.

A special cell was built for observations in liquid media. The cell was made from PTFE and moved in the $x$, $y$, and $z$ directions with respect to a stationary tip. The sample was fixed at the cell bottom. The laser beam does not cross the air–liquid interface, which is usually curved but enters and leaves the cell through a glass plate.

Water used in the cell was triple distilled and then passed through a commercial Milli-Q system (Milli-Q Plus quality, resistivity $\approx 15$ MΩ·cm) containing ion-exchange and charcoal stages. NaCl and KCl salts were obtained from Merck (PA 99.5%), and the stock solutions were prepared with standard techniques in fresh, triple distilled deionized Milli-Q water. The experiments were performed at a temperature of 25 °C. Images were registered with various scanning velocities and probing at least five different regions for each sample. Silicon wafers (100) with a resistivity of $10$ Ω·cm from Virginia Semiconductor, Inc. (VA, USA) and before use, $\sim 1 \times 1$ cm$^2$ pieces were then etched in a 50/50 HF solution for 15 min and then extensively rinsed with water.

AUTHOR INFORMATION

Corresponding Author
*E-mail: oteschke@ufiunicamp.br. Phone: 55 (19) 3521-4148Fax: 55 (19) 3521-5637.

ORCID
Omar Teschke: 0000-0002-1152-9319

Notes
The authors declare no competing financial interest.

REFERENCES

(1) Pandit, S. A.; Bostick, D.; Berkowitz, M. L. Mixed Bilayer Containing Dipalmitylophosphatidylcholine and Dipalmitylophosphatidylserine: Lipid Complexation, Ion Binding, and Electrostatics. *Biophys. J.* 2003, 85, 3120–3131.
(2) Cacace, M. G.; Landau, E. M.; Ramsden, J. J. The Hofmeister series: salt and solvent effects on interfacial phenomena. *Q. Rev. Biophys.* 1997, 30, 241–277.
(3) Roux, B.; Allen, T.; Bernèche, S.; Im, W. Theoretical and computational models of biological ion channels. *Q. Rev. Biophys.* 2004, 37, 15–103.
(4) Hu, J. H.; Shi, Q.; Davidovits, P.; Worsnop, D. R.; Zahniser, M. S.; Kolb, C. E. Reactive uptake of Cl2(g) and Br2(g) by aqueous surfaces as a function of Br− and I− ion concentration: The effect of chemical reaction at the interface. *J. Phys. Chem.* 1995, 99, 8768–8776.
(5) Finlayson-Pitts, B. J.; Hemminger, J. C. Physical chemistry of airborne sea salt particles and their components. *J. Phys. Chem. A* 2000, 104, 11463–11477.
(6) Knipping, E. M.; Lakin, M. J.; Foster, K. L.; Junwirth, P.; Tobias, D. J.; Gerber, R. B.; Dadhuk, D.; Finlayson-Pitts, B. J. Experiments and simulations of ion-enhanced interfacial chemistry on aqueous NaCl aerosols. *Science* 2000, 288, 301–306.
(7) Gibbs, J. W. The Collected Works of J. Willard Gibbs; Longmans: New York, 1928.
(8) Jungwirth, P.; Tobias, D. J. Specific ion effects at the air/water interface. *Chem. Rev.* 2006, 106, 1259–1281.
(9) Hey, M. J.; Shield, D. W.; Speight, J. M.; Will, M. C. Surface tensions of aqueous solutions of some 1:1 electrolytes. *J. Chem. Soc., Faraday Trans.* I 1981, 77, 123–128.
(10) Ishiyama, T.; Morita, A. Molecular Dynamics Study of Gas–Liquid Aqueous Sodium Halide Interfaces. I. Flexible and Polarizable Molecular Modeling and Interfacial Properties. *J. Phys. Chem. C* 2007, 111, 721–737.
(11) Minofar, B.; Vácha, R.; Wahab, A.; Mahiuddin, S.; Kunz, W.; Jungwirth, P. Propensity for the air/water interface and ion pairing in magnesium acetate vs magnesium nitrate solutions: Molecular dynamics simulations and surface tension measurements. *J. Phys. Chem. B* 2006, 110, 15939–15944.
(12) Garrett, B. C. CHEMISTRY: Ions at the Air/Water Interface. *Science* 2004, 303, 1146–1147.
(13) Minofar, B.; Vrba, L.; Mucha, M.; Jungwirth, P.; Yang, X.; Wang, X.-B.; Fu, Y.-J.; Wang, L.-S. Interior and Interfacial Aqueous Solvation of Benzene Dichloroacetate Diions and Their Methylation Analogues: A Combined Molecular Dynamics and Photoelectron Spectroscopy Study. *J. Phys. Chem. A* 2005, 109, 5042–5049.
(14) Minofar, B.; Mucha, M.; Jungwirth, P.; Yang, X.; Fu, Y.-J.; Wang, X.-B.; Wang, L.-S. Bulk versus Interfacial Aqueous Solvation of DiCarboxylate Dianions. J. Am. Chem. Soc. 2004, 126, 11691–11698.

(15) Picálek, J.; Minofar, B.; Kolafa, J.; Jungwirth, P. Aqueous solutions of ionic liquids: study of the solution/vapor interface using molecular dynamics simulations. Phys. Chem. Chem. Phys. 2008, 10, 5765–5775.

(16) Onsager, L.; Samaras, N. N. T. The Surface Tension of Debye-Hückel Electrolytes. J. Chem. Phys. 1934, 1, 528–536.

(17) Zangi, R.; Engberts, J. B. F. N. Physisorption of hydroxide ions from aqueous solution to a hydrophobic surface. J. Am. Chem. Soc. 2005, 127, 2272–2276.

(18) Arrhenius, S. A. Development on the theory of electrostatic dissociation. Nobel Lecture 1903, 45–58.

(19) Debye, P.; Huckel, E. De la theorie des electrolytes. I. Abaissement du point de congelation et phenomenes associés. Zeit. fur Phys. 1923, 24, 185–206.

(20) Bjerrum, N. Untersuchungen Uber Ionenassoziati. Mat. Fys. Medd., Kgl. Danske Videnskabernes Selskab; A. Fr. Host & Son, 1926; Vol. 7, pp 3–48.

(21) Kraus, C. A. The Ion-Pair Concept, Its Evolution and Some Applications. J. Phys. Chem. 1956, 60, 129–141.

(22) Freiser, H. Ion pair partition. Acta Pharm. Suec. 1972, 9, 609–611.

(23) Szwarc, M. Living polymers: a tool in studies of ions and ion-pairs. Science 1970, 170, 23–31.

(24) Atherton, N. M.; Weissman, S. I. Association Between Sodium and Naphthalene Ions. J. Am. Chem. Soc. 1961, 83, 1330–1334.

(25) Nagy, P. I.; Takacs-Novak, K. Theoretical and experimental study on ion-pair formation and partitioning of organic salts in octanol/water and dichloromethane/water systems. J. Am. Chem. Soc. 2000, 122, 6583–6593.

(26) Choi, M. M. F.; Douglas, A. D.; Murray, R. W. Ion-pair chromatographic separation of water-soluble gold monolayer-protected clusters. Anal. Chem. 2006, 78, 2779–2785.

(27) Wu, J.; Lee, H. K. Ion-pair dynamic liquid-phase micro-extraction combined with injection-port derivatization for the determination of long-chain fatty acids in water samples. J. Chromatogr. A 2006, 1133, 13–20.

(28) Kawamura, K.; Okuwaki, A.; Verheyen, T. V.; Perry, G. J. Separation of Aromatic Carboxylic Acids Using Quaternary Ammonium Salts on Reversed-Phase HPLC. 1. Separation Behavior of Aromatic Carboxylic Acids. Sep. Sci. Technol. 2006, 41, 379–390.

(29) Guerrero, D. Q.; Allemane, E.; Fessi, H.; Doelker, E. Applications of the ion-pair concept to hydrophilic substances with special emphasis on peptides. Pharm. Rev. 1997, 14, 119–127.

(30) Fang, L.; Numajiri, S.; Kobayashi, D.; Ueda, H.; Nakayama, K.; Miyamae, H.; Morimoto, Y. Physicochemical and crystallographic characterization of menamic acid complexes with alkanolamines. Pharm. Sci. 2004, 93, 144–154.

(31) Bordes, R.; Ribi, K.; Gonzalez-Perez, A.; Franceschi-Messant, S.; Perez, E.; Rico-Lattes, I. Novel polymerizable surfactants from 1:1 Mixtures of alkyloxyacetic acids and norbornene methylenamine. Langmuir 2007, 23, 7526–7530.

(32) Panda, A. K.; Plassmayer, F.; Petersen, N. O.; Nag, K.; Moulik, S. P. Physico-chemical studies on mixed oppositely charged surfactants: their uses in the preparation of surfactant ion selective membrane and monolayer behavior at the air water interface. Colloids Surf., A 2005, 264, 106–113.

(33) Panambur, G.; Zhang, Y.; Yesayan, A.; Galstian, T.; Bazuin, C. G.; Ritcey, A. M. Preparation and Characterization of Polyelectrolyte Complexed Langmuir–Blodgett Films Containing an NLO Chromophore. Langmuir 2004, 20, 3606–3615.

(34) Teschke, O.; de Souza, E. F. Water molecule clusters measured at water/air interfaces using atomic force microscopy. Phys. Chem. Chem. Phys. 2005, 7, 3856–3865.

(35) Teschke, O. Imaging ice-like structures formed on HOPG at room temperature. Langmuir 2010, 26, 16986–16990.

(36) Tsao, Y. H.; Evans, D. F.; Wennerstroem, H. Long-range attraction between a hydrophobic surface and a polar surface is stronger than that between two hydrophobic surfaces. Langmuir 1993, 9, 779–785.

(37) Teschke, O.; de Souza, E. F. Hydrophobic surfaces probed by Atomic Force Microscopy. Langmuir 2003, 19, 5357–5365.

(38) Sadek, H.; Fuous, R. M. Electrolyte-solvent interaction. IV. Tetrabutylammonium bromide in methanol-carbon tetrachloride and methanol-heptane mixtures. J. Am. Chem. Soc. 1954, 76, 5897–5901.

(39) Weinstein, S.; Clippinger, E.; Fainberg, A. H.; Robinson, G. C. Salt Effects and Ion-pairs in Solvolysis1. J. Am. Chem. Soc. 1954, 76, 2597–2598.

(40) Roberts, R. C.; Szwarc, M. The chemistry of the radical anion of tetraphenylethylene. J. Am. Chem. Soc. 1965, 87, 5542–5548.

(41) Eigen, M.; Tamm, K. Schallabsorption in elektrolytlösungen als folge chemischer relaxation I. Relaxationstheorie der mehrstufigen dissoziation. Z. Elektrochem. 1962, 66, 93–107.

(42) Eigen, M.; Tamm, K. Schallabsorption in elektrolytlösungen als folge chemischer Relaxation II. Meßergebnisse und relaxations mechanismen fur 2 − 2-wertige electrolyte. Z. Elektrochem. 1962, 66, 107–121.

(43) Azzaroni, O.; Moya, S.; Farhan, T.; Brown, A. A.; Huck, W. T. S. Switching the Properties of Polyelectrolyte Brushes via “Hydrophobic Collapse”. Macromolecules 2005, 38, 10192–10199.

(44) Chaki, N. K.; Vijayamohan, K. Self-assembled monolayers as a tunable platform for biosensor applications. Biosens. Bioelectron. 2002, 17, 1–12.

(45) Love, J. C.; Estroff, L. A.; Kriebel, J. K.; Nuzzo, R. G.; Whitesides, G. M. Self-assembled monolayers of thiocyanates on metals as a form of nanotechnology. Chem. Rev. 2005, 105, 1103–1170.

(46) Marcus, Y.; Heftel, G. Ion Pairing. Chem. Rev. 2005, 105, 10199–10210.