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Observation of Ordered Structures in Counterion Layers near Wet Charged Surfaces: A Potential Mechanism for Charge Inversion

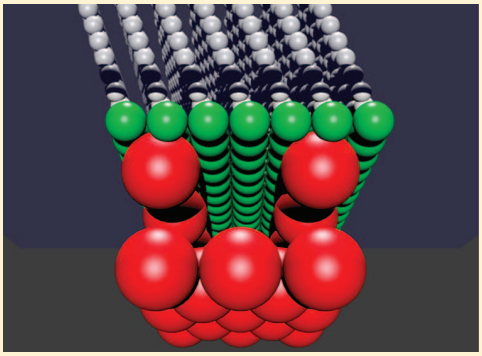
Mitchell Miller,[†] Miaoqi Chu,[†] Binhua Lin,[‡] Mati Meron,[‡] and Pulak Dutta*[,†]

[†]Department of Physics & Astronomy, Northwestern University, Evanston, Illinois 60208, United States

[‡]Center for Advanced Radiation Sources, University of Chicago, Chicago, Illinois 60637, United States

Supporting Information

ABSTRACT: Charged (e.g., colloidal) particles in aqueous solutions will sometimes behave as though their effective charge has reversed, rather than reduced, by the attracted counterions. This is counterintuitive because it increases the electrostatic energy, but it has been proposed that lateral ordering of the ions could lower the free energy and favor overcharging (charge inversion). Using X-ray diffraction, we have observed sharp diffraction peaks from incommensurate Er^{3+} counterion monolayers near charged surfaces formed by floating molecular monolayers. When the counterion lattice does not match the molecular surface lattice, this means that there is no specific attachment of ions, and thus the ionic lattice is formed due to interactions between charges in the counterlayer. Therefore, the existence of incommensurate ion lattices indicates that counterion ordering is a realistic mechanism. However, in this system our data rule out a well-known proposed "physical" mechanism—the Wigner liquid phase driven by Coulomb interactions.



INTRODUCTION

When a charged surface is in contact with an aqueous solution, counterions will naturally be attracted to the surface, and this will reduce the net effective surface charge.[1−3] One normally expects that the surface charge can at most be neutralized; its sign cannot be reversed because counterions are mobile, and any excess would be repelled. Yet charge inversion has been widely reported in e.g. colloids.[4] For example, if the colloidal particle charge is negative, in the presence of multivalent cations these particles will sometimes move under electric fields (electrophoresis) as though the effective (electrokinetic) charge is positive. This implies that the counterions that are close to and move with the charged surface add an excess of positive charge, and global charge balance is then achieved by negative charges further away that do not move with the colloidal particle. Such a charge distribution would seem to increase the electrostatic energy. The well-known mean-field predictions based on the Poisson−Boltzmann equation, such as those of Gouy,[5] and Chapman[6] and Stern,[7] all predict a nonoscillatory dependence of the ionic charge density on distance from the surface.

Mechanisms that compensate for the electrostatic energy cost of charge inversion have been proposed and debated for some years. Lyklema[4] has classified these ideas into "chemical" and "physical" theories. In the "chemical" picture, ions are thought to attach to the charged surfaces via hypothetical chemical bonds specific to the ion and surface involved ("specific adsorption"). In the "physical" picture, the ions nearest the surface reduce their free energy by forming a laterally ordered condensed phase. For macro-ions, there are also size considerations that are not discussed here; this paper focuses on monatomic cations.

The idea that dissolved ions can form laterally ordered interface phases even at room temperature is rather unexpected. There have been a number of theoretical analyses of the possible origins and effects of such ion−ion correlations.[8−11] In particular, Shklovskii and co-workers[12−14] have treated the layer of ions close to the surface as a one-component plasma: it is assumed that there are only Coulomb interactions between ions, with water acting merely as a structureless dielectric medium. Electrons are known to form liquid and solid phases driven purely by repulsive Coulomb forces; these are known as Wigner phases.[15] Unlike electrons, ions can be multiply charged, and as a result, such phases of polyvalent ions are predicted to form even at room temperature; for a review see ref 16. This is consistent with the fact that charge inversion effects are observed experimentally to increase with ionic charge and are never observed when only monovalent counterions are present.[4]

Several recent papers report phenomena consistent with the ordering hypothesis. Wernersson et al.[17] used electrochemical data for Mg^{2+} at the water−mercury interface to conclude that there is enrichment of ions close to the surface, attributed to ion−ion correlations since specific adsorption (chemical attachment) is negligible in this system. Laanait et al.[18] observed such enrichment using X-ray reflectivity at a liquid−

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liquid interface and were able to vary the effect by applying a variable voltage difference between the two liquids. Tan et al.[19] measured surface forces between mica plates separated by an aqueous solution of La^{3+} ions and attributed the observed adhesion and sticking to ion−ion correlation forces. None of these experiments, nor the many other studies reporting evidence for or against the ordering hypothesis, detect lateral ordering or the lack thereof directly, but only its predicted consequences. On the other hand, X-ray scattering experiments such as those reported here can directly detect positional order or lack thereof within the ionic layer adjacent to the charged surface (Stern layer).[7] Such observations are not subject to model-dependent interpretation.

Ordered structures of ions next to floating monolayers and mineral surfaces have been reported before, but those results are not germane to the question addressed here. In the presence of divalent ions such as Cd^{2+},[20] Pb^{2+},[21] Mn^{2+},[22,23] and Mg^{2+},[22,23] two-dimensional ordered structures form under floating monolayers, sometimes with more than ten X-ray diffraction peaks, and remarkably large unit cells of up to ∼1.4 nm^2 in area. An ionic lateral structure has also been seen, using atomic force microscopy, at a charged mineral surface.[24] However, all these unit cells were supercells of the molecular monolayer unit cells. Such commensurate structures are symptoms of specific adsorption: the inorganic lattice conforms to the molecular lattice because of interactions with the ordered molecules. Next to an ideal theoretical surface with a uniform charge (or its best experimental realization, a surface with a random distribution of charges), there will be no ordered lattice in these cases. In contrast, the data in the present paper show evidence of an incommensurate lattice in the presence of Er^{3+} ions, and this cannot be attributed to specific adsorption (chemical interactions).

EXPERIMENTAL SECTION

The charged surfaces we studied were formed by spreading amphiphilic monolayers with carboxylic acid and phosphate head groups on the surface of aqueous solutions (Figure 1). These floating monolayers (Langmuir films) form very dense ordered arrays of head groups. The subphases used were 10^{-4} M aqueous solutions of $Er^{3+}Cl^-_3$ or $Er^{3+}(NO_3)^-_3$; the pH was 5.8 and, in order to avoid introducing ionic impurities, was not modified further. Our X-ray results are not specific to 10^{-4} M Er^{3+}: we have seen the same features with three other lanthanides (Dy^{3+}, Tb^{3+}, and Yb^{3+}) and at other concentrations (10^{-3} and 10^{-2} M) under heneicosanoic acid monolayers (data not shown in this paper). These features are not observed when there are monovalent or divalent cations (or no added ions) in the subphase. Our results did not depend on whether the chloride or the nitrate salt was used. All data were collected at a temperature of 7.5 °C. We used grazing incidence synchrotron X-ray scattering (GIXD)[25] to probe the lateral packing of the molecules and the ions in these systems. In this scattering geometry, X-rays fall on the water surface at an angle of ∼0.2° to the horizontal plane and are scattered from the surface region without penetrating the bulk material.

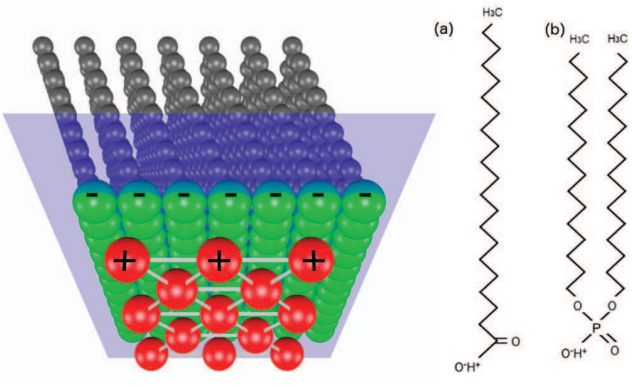

Figure 1. [left] Schematic diagram of the system studied. The shaded (blue) plane is the surface of the aqueous solution. The negatively charged (green) head groups are in contact with the solution and attract positive (red) counterions. [right] Structure of the lipid molecules used in this study. (a) Heneicosanoic acid, $CH_3(CH_2)_{19}COO^-H^+$; (b) dihexadecyl phosphate, $[CH_3(CH_2)_{15}O]_2POO^-H^+$. In both these molecules the hydrogen ion can dissociate, leaving a negatively charged surface in contact with the solution.

RESULTS AND DISCUSSION

We collected scattering intensity data as functions of the in-plane (Q_{xy}) and normal-to-plane (Q_z) components of the scattering vector Q. It is neither possible nor necessary to further distinguish the x- and y-components because the monolayers are powders in the plane, which means that all in-plane directions are identical.[25] The positions and widths of the peaks in the figures below are tabulated in the Supporting Information. The fact that the intensity distributions are vertical rods (Figure 2a) and not rings indicates that scattering originates from ultrathin horizontal layers. The width of the intensity distribution along the Q_z direction is inversely proportional to the thickness of the layer, and the width can thus be used to identify the type of layer from which the scattering originates.

When heneicosanoic acid monolayers are spread on 10^{-4} M $Er^{3+}Cl^-_3$ or $Er^{3+}(NO_3)^-_3$ solutions, 12 diffraction peaks can be identified in the GIXD data (Figure 2). We use the rod profiles (examples in Figure 2c) to identify three of the peaks (marked M in Figure 2b) as originating from the ∼2.5 nm thick molecular monolayer. These peaks correspond to an oblique two-dimensional molecular lattice with a = 0.495 nm, b = 0.413 nm, and γ = 111° (unit cell area 0.191 nm^2). The molecules are tilted, leading to some rods having a maximum intensity at Q_z > 0.

All remaining peaks have very broad intensity distributions along the rods, so that they are attributable to a much thinner layer (<0.5 nm). These peaks are seen only when there are erbium ions in the subphase. The upper limit is roughly consistent with the capillary roughness of the water surface (∼0.3 nm) combined with the size of an erbium ion (∼0.2 nm). In other words, the ordered layer is approximately one atom thick. Five of these peaks are commensurate with the molecular structure: they are marked "C" in Figure 2b. The fact that they can be indexed with half-integers means that both unit cell vectors are exactly doubled: the "C" lattice is oblique with a = 0.980 nm, b = 0.826 nm, and γ = 111° (unit cell area 0.763 nm^2).

Crucially, four diffraction peaks remain that cannot be indexed in terms of the molecular lattice. All these incommensurate peaks (labeled "I") can be attributed to a hexagonal lattice with a = 1.346 nm (unit cell area 1.812 nm^2). A hexagonal lattice cannot in general be commensurate with an oblique lattice; moreover, we used Epicalc software[26] to conduct an exhaustive but unsuccessful search for a lattice match. (See Supporting Information for more details.) This inorganic structure is not imposed by the arrangement of the

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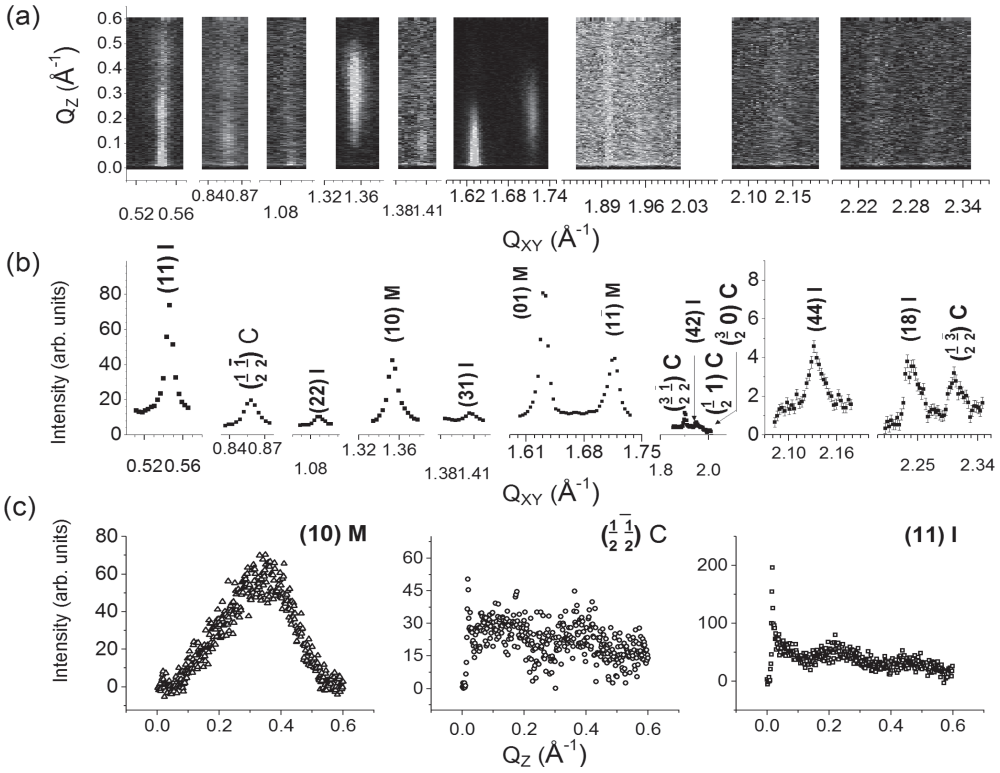

Figure 2. Grazing incidence X-ray diffraction data from a floating monolayer of heneicosanoic acid with erbium ions in the subphase. (a) Intensity contour in the Q_{xy}–Q_z plane, showing the "rods". (b) Background-subtracted scattering intensity as a function of Q_{xy} (integrated over the Q_z range of our data, 0–0.6 Å^{-1}). In the peak labels, M = molecular monolayer, C = commensurate ionic lattice, and I = incommensurate ionic lattice. (c) Q_z dependence of three representative peak intensities ("rod scans"), with background subtracted. The weak oscillations in the (11) I rod scan are discussed in the text and in the Supporting Information.

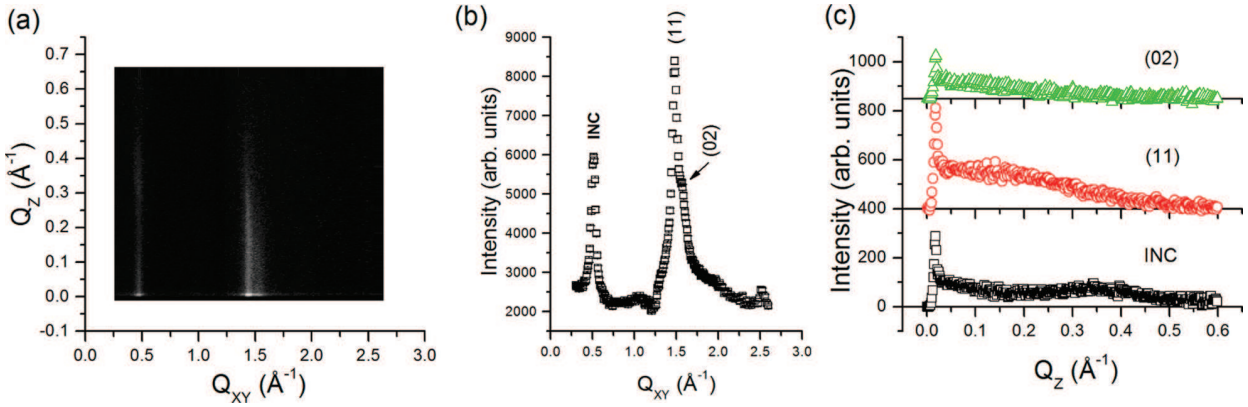

Figure 3. Grazing incidence X-ray diffraction data from a floating monolayer of dihexadecyl phosphate with erbium ions in the subphase. (a) Intensity contour in terms of the in-plane and out-of-plane components of the scattering vector Q. (b) Scattering intensity as a function of Q_{xy}, the in-plane component of Q (integrated over the Q_z range of our data, 0–0.6 Å^{-1}). (c) Q_z dependence of the three peak intensities ("rod scans"), with background subtracted. The (11) and (02) peaks are from the thicker molecular monolayer (~2.5 nm) while the peak labeled "INC" is from a monolayer lattice that forms only when erbium ions are present in the subphase.

floating molecules (substrate structure); rather, this lattice forms as a result of intralattice interactions.

The "I" rod scan in Figure 2 shows weak oscillations on top of its overall broad rod intensity distribution. This is a known effect of weak vertical modulations, "buckling", of the molecular monolayer.[22,23] The period of such modulations need not be commensurate with the molecular monolayer structure; incommensurate buckling has been observed in supported monolayers by refs 27 and 28. For more details, see the Supporting Information.

Our experiments do not tell us the relative positions of the commensurate and incommensurate ionic lattices. However, we speculate that the commensurate monolayer is directly next to the molecular monolayer, so that there is specific attachment, while the incommensurate monolayer is further away. If so, these might correspond to the so-called inner and outer Helmholtz planes.

An incommensurate inorganic structure is also seen under a dihexadecyl phosphate monolayer (Figure 3). We chose this molecule because phosphate surfactants have strong attraction

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to lanthanides and actinides in commercial liquid−liquid extraction. GIXD reveals three diffraction "rods", two of which are very close to each other. Using the intensity distribution along the "rods", we attribute the (11) and (02) peak rod profiles to the molecular monolayer. These peaks correspond to an orthorhombic molecular lattice with lattice vectors a = 0.459 nm and b = 0.844 nm (unit cell area 0.387 nm^2, two alkane chains per unit cell). The peak at lowest Q_{xy}, labeled "INC", has almost uniform intensity as a function of Q_z along the rod and must thus be attributed to an atomically thin hexagonal monolayer lattice with a = 1.420 nm (unit cell area 1.747 nm^2). It is seen only when there are erbium ions in the subphase. This structure is incommensurate with the charged surface (molecular film) structure.

CONCLUSIONS

It is not possible to detect charge inversion in the system studied, since the interface is static and there is no way to measure the electrokinetic charge. While it is possible to use anomalous X-ray scattering to measure the density distribution of erbium ions,[29] this would not determine the electrokinetic (attached) charge; it would not even measure the static charge distribution since H^+ and OH^- ions, which are essentially invisible to X-rays, also carry charge. However, charge accounting is not the goal of the present study. The main result of the present study is that lateral order can develop within real-world counterion layers near room temperature.

Is this ordered structure a condensed Wigner phase? For a system of point charges Ze in a dielectric medium of permittivity ε, ordering is determined[16] by the parameter $\Gamma \equiv Z^2e^2/(\varepsilon d k_B T)$, where d is the ion−ion distance. If $\Gamma > 1$, the system is strongly coupled and forms a correlated Wigner liquid. When $\Gamma > \sim 125$, there is a phase transition to a long-range-ordered Wigner crystal.[30] The value Z = 3 adds nearly an order of magnitude to the potential energy and thus to Γ compared to Z = 1 particles such as electrons, and in this situation there could be Wigner ordering even at room temperature. In our observations, if there is one Er^{3+} ion per monolayer unit cell, $d \cong 0.7$ nm and $\Gamma \cong 9$. For Γ to be large enough for long-range order, there would need to be >100 erbium ions in the <2 nm^2 area of one cell. Yet the lateral widths of the ionic peaks in Figure 2 are resolution-limited, which means that the correlation length is too large to measure (>50 nm). The ionic peak width in Figure 3 is somewhat larger than resolution but still indicates a correlation length of ∼10 nm. Such correlation lengths are inconsistent with liquid-like order. Thus, the Wigner picture is inapplicable to the observed ordered structures and is not the proposed "universal theory".[16]

Indeed, there is really no reason why the picture of point charges in a structureless dielectric medium should apply to ions in aqueous solutions. In reality water is not a uniform medium but consists of polar molecules as well as dissociated ions (H^+ and OH^-). It is known that metal ions are hydrated in bulk aqueous solutions; Er^{3+} forms aqua ions with ∼8 water molecules around each ion.[31] Aqua ions cannot be expected to behave as though they are point charges, but they could form ordered structures, for example via the use of water molecules or hydroxyl ions as bridging ligands. Such chemical mechanisms are more realistic than simple Coulomb interactions between point particles in a structureless dielectric medium.

In summary, our results make clear that well-ordered ionic structures do form at charged surfaces. Thus, the formation of an ordered monolayer phase is a realistic mechanism that may be invoked as an explanation for charge inversion, even if the Wigner liquid picture is not applicable.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.5b04058.

Diffraction peak position, widths, and indices; software search for commensurate relation between "M" and "I" peaks; further details regarding the weak oscillations in rod scan intensities (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail pdutta@northwestern.edu (P.D.).

Notes

The authors declare no competing financial interest.

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