Adsorption of Counterions to a Stearate Monolayer Spread at the Water-Air Interface: A Synchrotron X-Ray Study

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(Received 14 July 1988)

The near-total-external–fluorescence technique was used to measure *in situ* the adsorption of a metal ion from a subphase solution to the liquid-air interface. For a monolayer formed by the spreading of stearic acid on a 10^{-3}-mole/l solution of $MnCl_2$, the ratio of Mn ions segregated to the interface to the number of stearate molecules on the surface was determined as 0.6 ± 0.2. Surface extended x-ray-absorption fine-structure experiments revealed local order of Mn ions at the surface at the condensed phase but no order showed in the expanded phase. We explain these findings using a self-consistent Poisson-Boltzmann calculation.

PACS numbers: 68.15.+e, 64.75.+g, 68.10.−m, 82.65.Fr

The electrical double layer is an established concept in surface chemistry. The surface charge at solid/liquid and gas/liquid interfaces induced by the difference between the chemical potentials of the two media rearranges the solute ions near the interface. The narrow layer within which the ion concentrations are determined by the surface is referred to as the electrical double layer. It plays a central role in reactions at the interface and, in particular, in the mediation of catalysts in chemical reactions. A special case of this double layer occurs at the liquid/monolayer interface. The adsorption of metal ions from a subphase solution to the liquid/air interface, induced by a surfactant monolayer, was first noticed by Blodgett[1] and attracted considerable attention.[2,3] After spreading at the air/liquid interface, the monolayer becomes partially dissociated as a result of the interaction with the subphase solution, and becomes negatively charged in the process. The metal counterion in the subphase solution is electrically attracted to the charged interface and forms a positively charged diffuse layer next to the liquid/gas interface.[4] The remarkable effect of segregation of the counterion to the interface and change in the monolayer properties as a result of that, provides a unique opportunity to examine the chemical double layer experimentally on the Angstrom scale. Difficulties involved in the study of the liquid/solid interface on the Angstrom scale make the study of the monolayer/liquid double layer especially advantageous. Recent stimulating x-ray diffraction experiments from surfactant monolayers spread on the surface of liquids indicate that these surfactants can acquire an in-plane long-range order.[5] It is ancillary to the characterization of the chemical double layer to establish to what extent the segregated metal ions mimic the long-range order of the monolayer.

An absolute measurement of the amount of metal ions segregating to the liquid/gas interface poses an experimental challenge. Earlier (i) radiotracer[2] and (ii) chemical analysis techniques[2] demonstrated that the liquid/gas interface is rich with metal counterions. They were limited, however, to either (i) only a few suitable isotopes and were not sufficiently accurate in obtaining absolute values for the adsorption, or (ii) required the withdrawal of the monolayer from the surface of the liquid which clearly disturbs the double-layer equilibrium. A recent reflectivity work also indicated that metal ions are attracted to the interface.[6]

We report in this Letter the first absolute measurement of the metal counterion concentration at the interface using the synchrotron near-total-external–fluorescence (NTEF) technique. We also present extended x-ray-absorption fine-structure (EXAFS) results done from the liquid/gas interface that help explain the structure that the counterions acquire. To the best of our knowledge, this is also the first and only EXAFS experiment done from liquid surfaces.

Stearic acid was spread on the surface of a dilute aqueous solution containing 10^{-3} mole/l of $MnCl_2$ contained in a custom-made Langmuir-Blodgett trough.[7] This trough was made to fit into a Z-axis diffractometer.[8] The synchrotron x-ray beam was tilted downward onto the liquid surface with an x-ray mirror and was computer controlled to an accuracy of 0.05 mrad. In the NTEF technique introduced by Bloch *et al.*,[9] the primary x-ray beam at the interface excited the Mn ions in the solution next to the interface. The resultant fluorescent Mn $K\alpha$ fluorescence radiation signal from a pure aqueous dilute solution of 10^{-3} mole/l of Mn ions [Fig. 1(a)] dropped monotonically with decreasing α and was not observable at around the critical angle

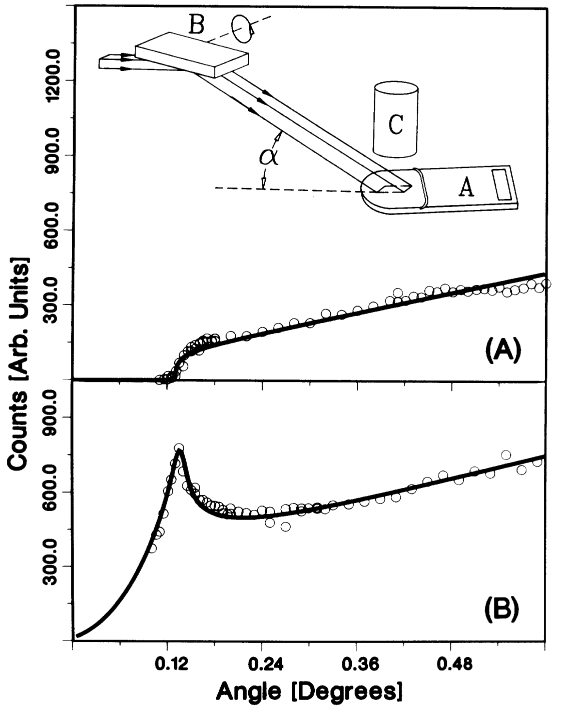

FIG. 1. Experimental NTEF Mn signal from the surface of (a) a dilute aqueous solution of $MnCl_2$; (b) same solution but with a monolayer of stearic acid spread on the interface. The solid line is a fit with the coupled Fresnel equations (see text). The peak at ≈0.13° in (b) is a clear indication that the Mn ions are strongly segregated to the surface in the presence of a surface monolayer. Inset B: Schematics of the NTEF scattering instrument. For details see Refs. 7 and 8.

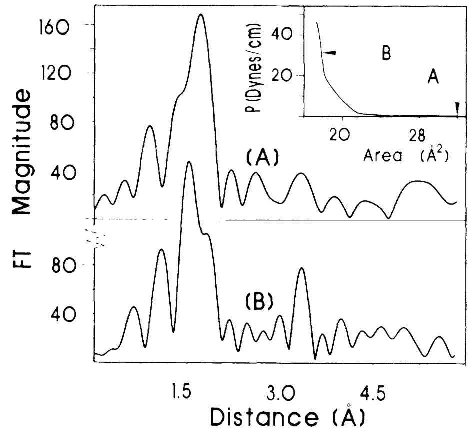

FIG. 2. Experimental surface EXAFS Fourier transform from the Mn excess at the liquid surface in the (a) expanded and (b) condensed phase. (The states are indicated on the pressure-area diagram in the inset.) The peak at ≈3.4 Å in the condensed phase (before phase-shift correction), corresponds to a Mn-Mn distance. After least-squares fitting of the data, we find a distance of 4.0±0.1 Å. This indicates short-range order in the condensed phase that is missing in the expanded phase.

$\alpha_c \approx 0.13°$. This is an indication that the Mn ions are evenly distributed in the solution and that the abrupt drop in signal at the critical angle α_c corresponds to the sudden decrease in the penetration depth. When, at the same critical angle, a monolayer of pure stearic acid was spread on the surface of the solution with an area of 32 Å per chain, a strong Mn signal was clearly observed [Fig. 1(b)]. At this angle the penetration depth of the primary beam is limited to only tens of angstroms and the Mn fluorescence peak is an unambiguous indication that the spread stearic monolayer caused a dramatic segregation of the metal ion from the liquid bulk to the liquid/gas interface. At angles higher than critical the dilute Mn concentration in the solution contributed an additional monotonic slope similar to that of the pure solution. The fit (solid line) was done by use of the coupled Fresnel equations formalism with a profile that includes a monolayer of stearic acid at the liquid surface and a thin layer of Mn ions with a surface density excess Γ^s_{Mn} and liquid bulk concentration of $\Phi^b_{\mathrm{MN}} = 1\times10^{-3}$ mole/l.[10,11] The fit to our experimental data yielded the ratio $\Gamma^s_{\mathrm{Mn}}/\Phi^b_{\mathrm{Mn}}$. Since the concentration of the Mn ion in the solution is determined to high accuracy and the number of the monolayer molecules is also predefined, we were able to obtain from a fit to the NTEF results an absolute value for the number of metal ions that were segregated to the liquid surface Γ^s_{Mn} and compare it to the number of the surfactant molecules. We determine the number of Mn ions adsorbed to the surface to be a significant fraction of the number of the monolayer chains ≈0.6±0.2. Experimental inaccuracies not inherent to the technique result in a relatively large error bar that we plan to reduce in future experiments.

At the same monolayer state (32 Å per chain) an EXAFS experiment was performed by our collecting the Mn *Kα* fluorescence as a function of energy. Since the angle of incidence was smaller than critical, the signal originated only from the Mn ions at a narrow strip at the surface (≈70 Å) [Fig. 2(a)]. The spectrum revealed structure only at distances smaller than 2 Å consistent with Mn-O distances. When the monolayer was compressed to about 20 $Å^2$ per monolayer chain (inset of Fig. 2), a new peak appeared [Fig. 2(b)] at about 4 Å after phase correction. This indicates that, although a substantial amount of Mn ions is attracted to the surface in the expanded phase, there is no evidence for in-plane order of the metal at this coverage.

In order to discuss our experimental results and to connect them with earlier investigations of metal ions found in *ex situ* chemical analysis of monolayers deposited on solids, a quantitative description of the partially dissociated surfactant spread at the surface of a subphase aqueous solution of a divalent ion was developed. Our approach is similar in principle to that used in the description of a monovalent ion solute[4] but departs from it considerably in its results. The ionized monolayer attracts the Mn^{++} and H^+ ions from the solution and the excess metal ions create a diffuse layer next to the organic monolayer. The high concentration of the metal ions in the diffuse double layer next to the interface makes it favorable for a large fraction of the ionized monolayer species L^- to react with the metal ions or the protons and to create L H and $L\ Mn^+$ species condensed on the monolayer, according to their equilibrium constants K_H and K_{Mn}. Those metal ions bound to the monolayer will replicate the in-plane order of the monolayer chains. The total charge on the monolayer σ decreases with the chemical reaction and equilibrium is reached between the fraction of the ions condensed on the monolayer $\Gamma_{[L\ Mn]}$ and the concentration of the metal ions in the double layer near the interface $\Phi_{Mn}(0)$. The right-hand side of our Poisson-Boltzmann equation,

$$\frac{\partial^2\Psi}{\partial z^2}=\frac{4\pi\rho}{\epsilon}=-\frac{4\pi e N_s}{\epsilon}\{2\Phi^b_{Mn}[P^2(z)-P^{-1}(z)]+\Phi^b_H[P(z)-P^{-1}(z)]\}\,, \tag{1}$$

includes the charge-density contributions of the divalent Mn^{++} ion as well as the monovalent proton. $\Psi(z)$ is the electric potential in the liquid at a distance z from the surface and $P(z)=\exp[e\Psi(z)/T]$. The transcendental equation (1) is doubly integrable with the boundary Neumann condition for the surface charge σ on the monolayer. Here

$$\sigma=\frac{e}{A}(2\Gamma_{[L\ Mn]}+\Gamma_{[L\ H]}-1)\frac{e}{A}[2K_{[L\ Mn]}\Phi^b_{Mn}P^2(0)+K_{[L\ H]}\Phi^b_H P(0)-1] \tag{2}$$

is expressed in terms of the condensation fractions $\Gamma_{[L\ Mn]}$ and $\Gamma_{[L\ H]}$ of the $[L\ Mn^+]$ and the $[L$ H] species in the monolayer. Equation (2) includes a positive charge contribution originating with the $[L\ Mn^+]$ species condensed on the monolayer. This feature is special to a divalent counter ion and is the origin for the different behavior of this monolayer as compared to the one spread on a monovalent solution. From (1) and (2) we obtain the condensation fractions $\Gamma_{[L\ Mn]}$ and $\Gamma_{[L\ H]}$ of the Mn and H ions condensed on the monolayer, the fractions of the Mn and H ions attracted electrically in the diffuse double layer $\Gamma_{[Mn]}$ and $\Gamma_{[H]}$, and the electrical contribution to the surface pressure Π_e. Using the equilibrium constants $K_{L\ Mn}=6.3\times10^4$ and $K_{L\ H}=7.4\times10^4$ l/mole reported in the literature for shorter chain acids and divalent soaps,[12] we obtained $\Delta\Pi=\Pi^e_{Mn}-\Pi^e_H=0.3$ dyn/cm for the surface-tension difference between an expanded monolayer on a solution with 1×10^{-3}-mole/l $MnCl_2$ to that spread on pure water. This is in agreement with our measurement $\Delta\Pi_{exp}=0.33\pm0.1$ dyne/cm. Using this model we were able to reproduce a host of earlier condensation curves reported over the last four decades[2,3] with no adjustable parameters as well as our measurement of the depletion of the surface tension upon addition of a divalent ion to the solution.[11] Details of our calculations will be published elsewhere[11] and the primary results are summarized here: (a) The divalent ion is strongly attracted to the surface. For our experimental conditions, our model calculations predict that the Mn ion concentration at the interface averaged over 50 Å is around 0.3 mole/l or some 300 times higher than the bulk concentration. This is compared to the experimental enhancement of around 420 which we obtained from the NTEF experiment. (b) The enhanced concentration of M^{++} at the surface allows for its condensation on the monolayer and the creation of a positively charged species $L\ M^+$. (c) Our model suggests that the Mn ion appears in two distinct states at the interface, but at our experimental conditions and for a divalent ion the electrochemical balance struck between the $L\ M^+$ ions condensed on the monolayers and those electrically attracted by the charged surface favors the state where the ions are condensed on the monolayer, and at our experimental conditions more than 95% of the attracted Mn ions are chemically bonded to the monolayer, i.e., $\Gamma_{[L\ Mn]}/\Gamma^e_{Mn}>0.95$. It is therefore important to realize that the Mn ions measured in our experiments are for the most part condensed on the monolayer with about 0.46 Mn ions per carbohydrate chain at both the expanded and also the condensed state. This value is very close to the limiting maximum condensation possible $\Gamma_{[L\ Mn]}=0.5$ derived from electrochemical balance considerations. The absence of the Mn-Mn short-range order in the expanded phase is therefore an indication that the monolayer itself does not seem to possess an order in the expanded phase. This conclusion is consistent with the loss of long-range order as reported recently from x-ray diffraction from similar systems. The characteristic Mn-Mn distance of $a'\approx4$ Å (after phase correction) at the condensed state suggests that the monolayer itself is ordered in this state. The metal ion is laterally displaced from the chain axis because the carboxylic polar head of the chain is tilted with respect to the chain axis in about 35° as a result of the bond direction in the first tetrahedral carbon next to the carboxylic group. The specific orthorhombic packing of these surfactant monolayers imposes the metal ion displacements to be almost orthogonal for two neighboring chains. Therefore, we expect the distances between the metal ions to be different from those between the carbohydrate chains. $a\approx4.6$ Å derived from the 18-$Å^2$ area per chain (inset of Fig. 2) and $a'=4.0$ Å would suggest that the metal ion displacement for a triangular lattice is in the neighborhood of $\Delta x\approx0.3$ Å. The Δx value is model dependent and more experimental work is required to determine its value. However, the absence of the characteristic distance among the metal ions in the expanded phase indicates that the organic monolayer itself lacks the same local in-plane order. It is planned to extend this first work to monovalent subphase ions, where our model predicts a significantly smaller condensation, and to study the competition of two different ions in segregating to the surface.

This work was partially supported by the U.S. Department of Energy, Office of Basic Energy Sciences- Materials Sciences, under Contract No. W-31-109-ENG-38. The experiments were done on beam line x18b of the National Synchrotron Light Source at Brookhaven Laboratory. One of us (J.M.B.) would like to acknowledge the hospitality of the National Synchrotron Light Source and the support of P. Eisenberger and S. Sinha without which this work would not have been completed.

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