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ADSORPTION OF COUNTER IONS TO A STEARATE MONOLAYER SPREAD AT THE WATER-AIR INTERFACE: A SYNCHROTRON X-RAY STUDY*

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ABSTRACT

The Near Total External Fluorescence (NTEF) technique was used to measure *in-situ* the adsorption of a metal ion from a subphase solution to the liquid-air interface, induced by a surfactant monolayer on the interface. For a monolayer formed by spreading stearic acid (a surfactant material) 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 to be approximately 0.6 ± 0.2. SEXAFS experiments revealed local order of the Mn ions at the surface at the condensed phase but no order showed up in the expanded phase. We explain these finding using a self consistent Poisson-Boltzman calculation of a partially ionized monolayer. Our model also explains earlier reports of adsorption of metal ions to the liquid/monolayer interface.

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Introduction

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 a considerable attention since[2–7]. The monolayer, after spreading at the air/liquid interface is, partially dissociated as a result of the interaction with the subphase solution and becomes negatively charged in the process. The metal counter-ion in the subphase solution is electrically attracted to the charged interface and attempts to screen the monolayer at the liquid/gas interface. As a result a special type of an electrical double layer is formed[8]. The remarkable effect of the segregation of the counter ion to the interface and the change in the monolayer properties as a result of that provide a unique opportunity to examine the chemical double layer experimentally on the Angstrom scale. That is of central interest in understanding liquid/solid reactions and in particular the mediation of catalysts in chemical reactions. The better understanding of the structure of the electrical double layer at monolayers can also elucidate the role of similar membranes in biological cells [7] and the substitution of metal ions in the the process of multilayer buildup[9] Recent very stimulating x-ray diffraction from monolayers spread on the surface of liquids indicate that these monolayers can exhibit an in-plane long range order[10]. 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.

We report in this communication the first absolute measurement of the metal counter ion concentration at the interface using Synchrotron near total external fluorescence (NTEF) technique. We also present EXAFS results done from the liquid/gas interface that help explain the structure that the counter ions acquire. To the best of our knowledge this is also the first and only EXAFS experiment done so far from liquid surfaces.

An absolute measurement of the amount of metal ions segregating to the liquid/gas interface poses an experimental challenge. Earlier radiotracer techniques, allow for a measurement of the counterion directly on the surface of the liquid [6]. They demonstrated that the liquid/gas interface is rich with counter-ions (metal ions) but were not sufficiently accurate in obtaining absolute values for the absorption. They are also limited to only few suitable isotopes with adequate radiation. In a second class of experiments the surface of the liquid was skimmed and the collected monolayer material was analyzed for metal ions[2–5]. This process could yield absolute values for the concentrations for the metal ion in the collected monolayer but the collecting process disturbs the double layer equilibrium. More importantly we will show here that the metal ion at the liquid surface exists in two distinct states and this technique measures only that portion of the Mn ions that is condensed on the Langmuir monolayer.

The Near Total External Fluorescence (NTEF) technique introduced by one of us (JMB) and collaborators[11] allowed us to measure the metal concentration directly on the liquid surface using the natural Mn isotope. The NTEF technique is based on the fact that in the X-ray wavelength regime air is optically denser than an aquous solution. As a result, when X-rays are incident on an air-liquid interface from air, a critical angle α_c exists, below which total reflection takes place[12]. In the low angle region, where $\alpha < \alpha_c$ the X-ray intensity in the liquid decays exponentially in within couple of hundreds of Angstroms. For $\alpha > \alpha_c$ the regular absorption process takes over, and consequentially the penetration depth increases dramatically and for $\alpha >> \alpha_c$ it becomes proportional to α. The elements at the interface will be excited by the radiation and will fluoresce back in their respective natural energies. The total fluorescence intensity $I_m^f(\alpha)$ of element m will depend on the concentration dependence $\Phi_m(z)$ of this element as a function of the distance z from the surface.

$$I_m^f(\alpha) = \int \Phi_m(z)\, I(z,\alpha)\, dz. \tag{1}$$

The X-ray intensity distribution $I(z,\alpha)$ can be derived as a boundary problem of classical electrodynamics[14]. The intensity $I(z,\alpha)$ at depth z is a *functional* of the distribution of the dielectric constant of the interface at all other depths z' from the surface. The dielectric constant is in turn dependent on the concentration profiles of the different elements at the interface $\{\Phi'_n(z')\}$ and includes also the concentration profile of the element sought in the experiment $\Phi_m(z)$.

$$I(z,\alpha) = \mathcal{F}\{\Phi'_n(z')\} \tag{2}$$

For stratified media the calculation of the electric intensity $I(z,\alpha)$ amounts to the solution of a set of coupled Fresnel equations which is a well established albeit lengthy procedure. Substitution of (2) in (1) yields a closed form equation for the concentration profile $\Phi_m(z)$. When $I_m^f(\alpha)$ is measured with sufficient resolution in α it is possible in principle to obtain $\Phi_m(z)$ from (1).

Stearic acid was spread on the surface of a dilute aqueous solution containing 10^{-3} moles of $MnCl_2$ contained in a custom made Langmuir Blodgett trough[16]. The surface tension and the level of the liquid were monitored and computer controlled. This trough was made to fit into a Z-axiz diffractometer[15]. The synchrotron x-ray beam was tilted downward onto the liquid surface using an x-ray mirror and was computer controlled to an accuracy of 0.05 mrad. The primary x-ray beam excited the Mn ions in the solution. The resultant fluorescent K_α radiation was collected using a Li drifted Si detector placed normal to the liquid surface. At angles larger than the critical angle for the x-ray a Mn fluorescence signal was observed from a sample containing the dilute 10^{-3} moles of Mn ions (fig. 1A). The intensity of that signal dropped monotonically and was not observable at around the critical angle $\alpha_c \approx 0.13°$ consistent with the fact that the Mn ions were evenly distributed in the solution. When, at the same critical angle, a monolayer of pure stearic acid was spread on the surface of the solution a strong Mn signal was clearly observed. (Fig 1B). This 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. The fit (solid line) was done using 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 $\Gamma^{\circ}_{\mathrm{Mn}}$ and bulk concentration of $\Phi^{\circ}_{\mathrm{Mn}} = 1 \cdot 10^{-3}$ moles. The calculations were considerably simplified since the fall off length of The concentration profile $\Phi_{\mathrm{Mn}}(z)$ from the interface is shorter than the minimum penetration depth of the x-rays. The fluorescence signal is then primarily dependent on the total amount of the material $\Gamma^{\circ}_{\mathrm{Mn}} = \int \Phi_{\mathrm{Mn}}(z)\, dz$ at the interface. In our system, in addition to a narrow and high concentration profile of Mn ion at the interface there is also a background of a dilute Mn ion in the liquid bulk $\Phi_{\mathrm{Mn}}(z = \infty) = \Phi^{\circ}_{\mathrm{Mn}}$. The fit using (1) to our experimental data is dependent on the ratio $\Gamma^{\circ}_{\mathrm{Mn}}/\Phi^{\circ}_{\mathrm{Mn}}$. It determines the ratio between the peak intensity at the critical angle originating with the Mn surface excess and the slope at higher angles determined by the dilute bulk Mn concentration (fig1B). Since the concentration of the Mn ion in the solution is determined to high accuracy through the preparation of the solution 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 $\Gamma^{\circ}_{\mathrm{Mn}}$ and compare it to the number of the surfactant molecules using eqs. (1) and (2)[17]. We determine the number of Mn ions adsorbed to the surface to be a significant fraction of the number of the monolayer chains $\approx 0.6 \pm 0.2$. Experimental inaccuracies that are not inherent to the technique, result in a relatively large error bar that we plan to reduce in future experiments.

At this stage an EXAFS experiment was performed collecting the MnK_α 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 ($\approx 70\AA$)(Fig. 2A). The spectrum revealed structure only at distances smaller than $2.\AA$ consistent with $Mn-O$ distances. When the monolayer was compressed at this stage from about $33\AA^2$ per chain to about $20\AA^2$ per monolayer chain (see insert of fig. 2) a new peak appeared (Fig 2B) at about $4\AA$ after phase correction. These findings indicate 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. The ionized monolayer attracts the Mn^{++} and H^+ ions from the solution and repels the anions, OH^- and Cl^-. If this were to be the only process taking place at the surface then the excess metal ions would have created a diffuse layer next to the organic monolayer but would have not replicated the in-plane order of the monolayer chains. However 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 $K_{\rm Mn}$ and $K_{\rm H}$ respectively. The metal ions bound to the monolayer will replicate the in-plane order of the monolayer chains. The total charge on the monolayer will decrease with the chemical reaction also so will the electrical attraction of the metal ions to the diffuse double layer. An equilibrium will thus be reached between the fraction of the ions condensed on the monolayer $\Gamma_{[\rm L\,Mn]}$ and the concentration of the metal ions in the double layer near the interface $\Phi_{\rm Mn}(0)$. We further postulate that in the transfer process from the surface of the liquid to a solid substrate only that part of the metal ion that was condensed on the monolayer is also being transferred to the substrate. 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 processes described above in the presence of a divalent solute ion is required. Our approach is similar in principle to that used in the description of a monovalent ion solute[8] but departs from it considerably in its results. The right wing of the Poisson-Boltzman equation for a divalent solute ion M^{++}

$$\partial^2\Psi/\partial z^2 = -\frac{4\pi\rho}{\epsilon} = -\frac{4\pi e N_o}{\epsilon}\left[2\Phi^o_{\rm Mn}\left(P^2 - P^{-1}\right) + \Phi^o_{\rm H}\left(P - P^{-1}\right)\right] \qquad (3)$$

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 (3) is doubly integrable with the boundary Neiman condition for the surface charge σ on the monolayer. Here

$$\sigma = \frac{e}{A}\left(2\Gamma_{[\rm L\,Mn]} + \Gamma_{[\rm L\,H]} - 1\right) = \frac{e}{A}\left(2K_{[\rm L\,Mn]}\Phi^o_{\rm Mn}P^2(0) + K_{[\rm L\,H]}\Phi^o_{\rm H}P(0) - 1\right) \qquad (4)$$

is expressed in terms of the condensation fractions $\Gamma_{[\rm L\,Mn]}$ and $\Gamma_{[\rm L\,H]}$ of the $\left[L\,Mn^+\right]$ and the $[L\,H]$ species in the monolayer. Eq. (4) includes a positive charge contribution originating with the $\left[L\,Mn^+\right]$ species condensed on the monolayer. This feature is special to a divalent counter ion and is the reason for the different behavior of this monolayer as compared to that spread on a monovalent solution. From (3) and (4) we obtain an analytical expression for the concentration profile of the electrically attracted Mn ion in the double layer $P^2(z)$ next to the liquid surface[18] (fig. 3). We also obtain the condensation fractions $\Gamma_{[\rm L\,Mn]}$ and $\Gamma_{[\rm L\,H]}$ 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 $\Gamma_{[\rm Mn]}$ and $\Gamma_{[\rm H]}$ and the electrical contribution to the surface pressure Π_e. We were able to obtain very good fits to experimental data found in the literature[3] for the fraction $\Gamma_{[\rm L\,Mn]}$ of metal found in deposited monolayers as a function of the metal ion bulk concentraton and the PH of the soultion. These fits yielded the values for the equilibrium constants $K_{\rm L\,Mn} = 10^{2.0\pm0.4}$ and $K_{\rm L\,H} = 10^{4.0\pm0.5}$ for stearic acid. These values were in surprisingly good agreement with our measurements of the surface tension difference $\Delta\Pi = \Pi^e_{\mathrm{Mn}} - \Pi^e_H = 0.3 Dynes/Cm$ between an expanded monolayer on a solution with $1 \cdot 10^-3$ mole $MnCl_2$ to that spread on pure water. Similar values were reported in the literature for short chain acids and divalent ions[19]. The details of our calculations will be published elsewhere[18] and the primary results can be summarized as follows: (a) The divalent ion is strongly attracted to the surface. Its concentation is typically dozens to hundreds times higher than that of a dilute bulk. Using the equilibrium constants derived as explained above our model calculations predict that the concentration of the Mn ion at the interface averaged over $50\mathring{A}$ at the interface is around 0.3 mole/litre or is some 300 times higher than the bulk concentration. This compared to the experimental enhancement of around 420 which we obtained from the NTEF experiment. (b) The enhanced concentration of M^{2+} at the surface allows for its condensation on the monolayer and the creation of a positively charged species LM^+. (c) The LM^+ species offsets most of the negatively charged L^- and drastically reduces the net surface charge of the monolayer and therefore also reduces the concentration excess of the electrically attracted M^{++} ions to the surface. Our model suggests that the electrochemical balance struck between the LM^+ 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 90 % of the attracted Mn ions are chemically bonded to the monolayer i.e. $\Gamma_{[\mathrm{L\,Mn}]}/\Gamma^{\circ}_{\mathrm{Mn}} > 0.9$ (fig. 4). It is important therefore to realize that the Mn ions measured in our experiments are on the most part condensed on the monolayer with about 0.48 Mn ions per carbohydrate chain at both the expanded and also the condensed state. This value is very close to the maximum condensation possible $\Gamma_{[\mathrm{L\,Mn}]} = 0.5$ from electrochemical balance considerations. The in plane order of organic monolayer in the condensed phase is therefore replicated by the metal ions condensed on this monolayer as can indeed be evidenced from our EXAFS measurement. The absence of that order among the metal ions in the expanded phase indicates that the organic monolayer itself lacks the same local in-plane order. When a Langmuir monolayer is withdrawn from the liquid unto a solid substrate only that portion of the Mn ions that is condensed on the monolayer is also carried over with it. Experiments where the amount of metal ion is determined showed a wide variation of the metal ion in the monolayer as a function of molecular area as well as metal ion concentration in the liquid bulk consistent with our calculations.

In summary, the first NTEF experiments on the solution/monolayer interface show very strong segregation of divalent ions from a solution to the liquid surface. Surface EXAFS show that in the condensed phase the Mn ions acquire short range order consistent with that reported for the monolayer chain but this order was absent in the expanded phase. Our first principle divalent surface electrochmical model seems to capture the essential structural features of the liquid/monolayer interface. It predicts the Mn excess at the surface and the metal substitution in the monolayer. Using this model we were able to explain a host of earlier results where the metal content of a solid LB monolayers was investigated as well as our measurement of the depletion of the surface tension upon adding a divalent ion to the solution. Our model indicates 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 between the two favors strongly the state where the Mn is chemically bonded to the surfactant monolayer. The absence of the short range order in the expanded phase is therefore an indication that the monolayer itself does not seem to possess an order in that state. This conclusion is consistent with the loss of long range order as reported recently from x-ray diffraction from similar systems. 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.

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Figure captions:

Figure 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 a coupled Fresnel equations(see text). The peak at $\approx 0.13^\circ$ in (B) is a clear indication that the Mn ions are strongly segregated to the surface in the presence of a surface monolayer. Insert B: Schematics of the NTEF scattering instrument. For details see ref. 24.

Figure 2 Experimental SEXAFS fourier transform from the Mn excess at the liquid surface in the (A) expanded and (B) condensed phase (The states are incidated on the $\Pi - A$ diagram in the insert.) The peak at $\approx 4\AA$ (after phase correction) in the condensed phase indicates a $Mn - Mn$ short range order in the condensed phase that is missing in the expanded phase.

Figure 3 The condensation fraction $\Gamma_{[\mathrm{L\,Mn}]}$ (B), attraction fraction Γ_{Mn} (A) and the total $\Gamma^{\circ}_{\mathrm{Mn}}$ fraction of Mn ion at the monolayer/liquid interface (A+B), as a function of the metal equilibrium constant $K_{[L\,Mn]}$. The calculations shows that most of the excess Mn ion is condensed on the monolayer for our equilibrium constant. Insert: the calcualated normalized concentration profile for Mn at the diffuse double layer $\Phi_{\mathrm{Mn}}(z)\,/\Phi^{\circ}_{\mathrm{Mn}}$ (see text).

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17. The fluorescence equations include the contribution of the Mn ion concentration, yet unknown, to the refractive index of the thin double layer at the liquid surface. The details of the self consistent solution will be published elsewhere..

18. Our concentration profile expression reduces to $\coth^2(z/R)$ in the case when only monovalent ions are present. This is noteworthy since this is also the same functional concentration profile dependence obtained for a dissolved polymer which originates from a completely different Hamiltonian[11]. The details of the double layer Poisson Boltzman calculations for a divalent counter ion will be published separately..

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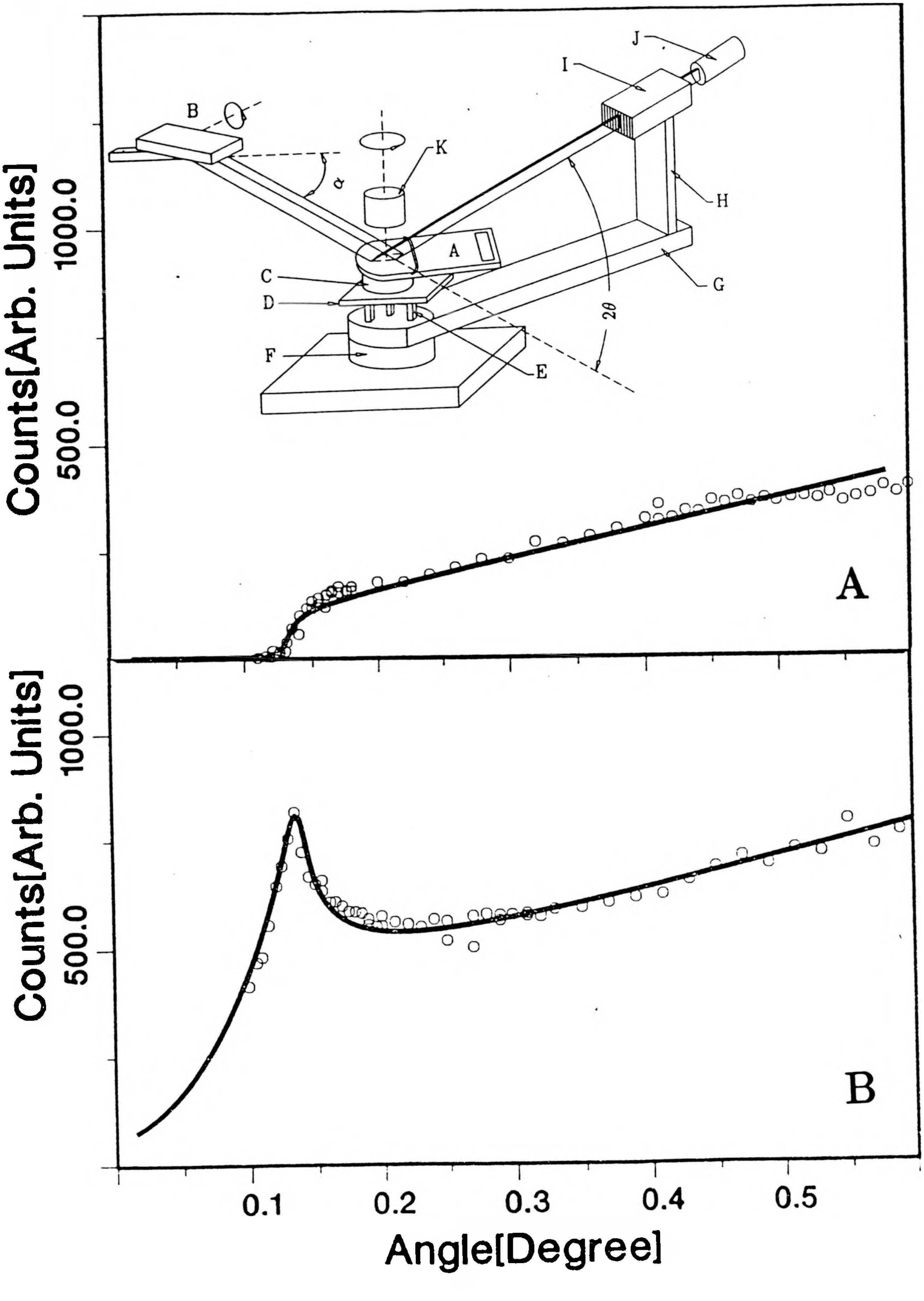

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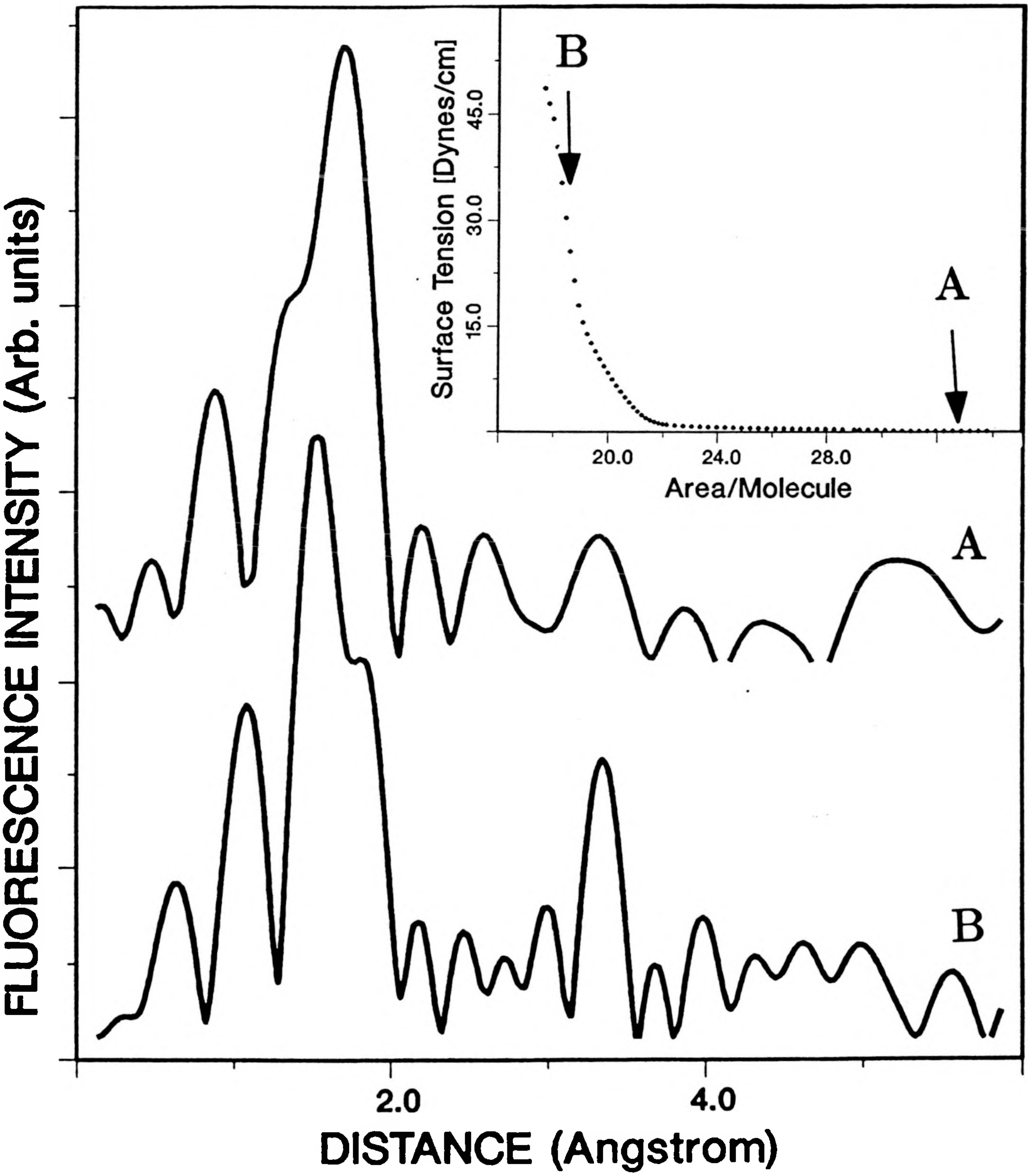
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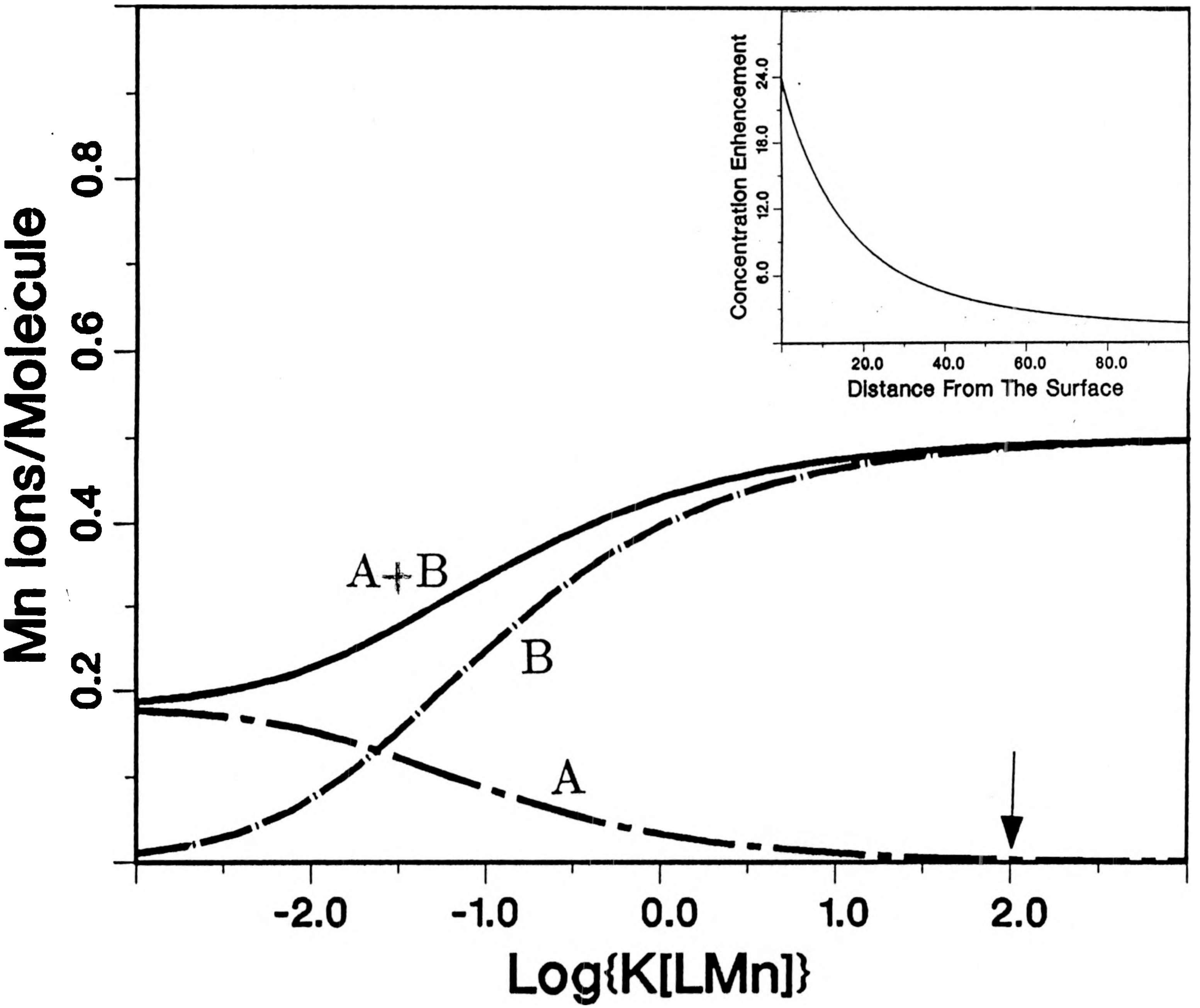
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