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Condensation of monovalent and divalent metal ions on a Langmuir monolayer

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A system that consists of a monolayer spread on a solution containing a monovalent and a divalent ion is investigated. The solution of the Poisson-Boltzmann-Stern equation for this system indicates that the metal ions segregating to the surface can be found in two distinct states. Divalent ions are chemically condensed on the monolayer, while monovalent ions are electrically attracted to it. We derive simple expressions for the charge left on the surfactant monolayer and the amount of metal ions condensed on the monolayer. These formulas reproduce very accurately (to within *pro milles*) the values obtained using the nonlinear Grahame equation and eliminate the need to solve that equation. That permits a simple identification of the state of the surfactant monolayer and we propose a universal condensation chart that characterizes the state of the surfactant. We further derive a chemical equilibrium equation for the surface components that has considerable range of validity. This equation requires a knowledge of the bulk concentrations only, and thus allows in many cases the identification of the state of the monolayer, avoiding the need to solve the full nonlinear Poisson-Boltzmann equation. All existing experimental results on Langmuir systems are in good agreement with the one-dimensional Poisson-Boltzmann-Stern model with no adjustable parameters. Several of these fits are presented in this work and are also mapped on the condensation chart. Our calculations point to some characteristic differences between the monovalent and the divalent ions that explain why it is possible to build Langmuir-Blodgett multilayers from divalent compensated surfactants but not from monovalent ones.

I. INTRODUCTION

Surfactant monolayers on liquid and solid substrates have been the subject of experimental investigations for almost a century now. They received renewed attention with the advent of tools that could measure *in vitro* the in-plane structure that the surfactant chains acquire on a molecular scale.[1–4] Langmuir monolayer molecules consist of a hydrophobic chain that keeps them afloat on a liquid aqueous surface and a hydrophilic polar head that interacts with the components of the aqueous solution. The balance of the two interactions creates an organized single layer on the surface of the liquid. It has been known for several decades now that these surfactants can be withdrawn from the liquid-air interface and be deposited on a solid substrate to create layered composite materials.[5–7] Interest in these materials has been aroused by the application possibilities vested in using these controllable monolayers for electronic and optical components on the atomic scale[8] [see a review article 8(b) by Agarwal].

One structural aspect of these monolayers—the segregation of metal ions from the liquid bulk to the liquid-surface—monolayer interface and the eventual condensation of the metal ion on the monolayer—has been experimentally studied extensively over several decades.[9–29] Metal ions in the subphase solution are known to play a central role in the modification of the characteristics of the Langmuir monolayer spread on liquid subphase. The surface pressure-area diagrams show a characteristic tendency to be stiffer upon the addition of minute quantities of divalent ion to the subphase solution. The minimal area per surfactant molecule is smaller and the electric potential of the surfactant changes. Monolayers of surfactant withdrawn from the liquid were shown to incorporate the metal ion in their three-dimensional (3D) structure in very specific positions.[4,5] The presence of the metal ion at the surface was also verified using radio tracer techniques directly on the surface of the liquid and recently the x-ray near-total external fluorescence (NTEF) technique was employed to obtain an absolute value of the amount of metal ion segregating to the liquid surface.[4] The experiments revealed that the amount of metal ion next to the surface is dependent on the nature of the ion, the concentration of the metal ion, and the hydrogen ion in the subphase. Earlier attempts to explain the metal ion segregation to the liquid surface, induced by the surfactant monolayer, were phenomenological in nature and invoked the notion of mixture between dissociated and condensed surfactant species with some adjustable interchange energy parameter.[9–11] These parametric models assumed that the concentration of the solute ions at the interface is equal to that in the bulk and thus ignored the electrical attraction of the cations to the surfactant and did not distinguish between condensed ions and those that are only electrically attracted. A physical description of the problem was introduced based on the electrochemical double layer concept.[30–33] After spreading on the surface of the water, the surfactant partially dissociates and becomes negatively charged in the process. The metal ions in the subphase solution and the hydrogen ions are electrically attracted to the surface and their concentration in the vicinity of the surface is greatly enhanced. The higher concentration of the positive ions at the surfactant surface causes a larger degree of condensation of the proton or the metal ion on the monolayer. This in turn reduces the negative charge on the monolayer and by that, the concentration of the cations next to it. An equilibrium is then reached between the ions attracted to the interface and those chemically condensed on it. This system can be described in terms of the Poisson-Boltzmann-Stern (PBS) equation. The Poisson-Boltzmann (PB) equation deals with two competing processes occurring in an electrically polarized system. Generally speaking, some of the charges in the system under investigation are fixed in space and provide the electrostatic boundary conditions for the system. The rest of the charged particles are free to move under the influence of the electric field of the system until they reach a static distribution in space. The distribution in space of the free charged particles can be derived by solving the Poisson-Boltzmann equation subject to the assumptions inherent in the Poisson-Boltzmann equation. The electrical interaction, described by the Poisson equation, tends to bring together charges of opposite signs and thereby minimizes the total energy of the system. In the absence of other mechanisms opposite charges would have of course collapsed on each other and thereby the system would have ceased to be polarized. For an ensemble at a temperature of the same order of magnitude as the electric interaction, the attraction is counterbalanced by the entropy of the system which obtains a minimum when the charged particles are evenly distributed in the system. The equilibrium that the system reaches as the result of the two opposing interactions results in a Boltzmann distribution of the distances between the positive and the negative particles and with a finite distribution distance. The Poisson-Boltzmann equation was applied extensively since its first introduction by Gouy,[34] Chapman,[35] and more than 75 years ago in disciplines as diverse as plasma physics and electrochemistry. The spherical PBE was the starting point in the theory of Debye and Hückel for the screening of strong electrolytes in solutions.[36] The cylindrical PBE was first employed by Katchalsky and collaborators in their polyelectrolyte theory.[37] The subject of this work, the one-dimensional Cartesian Poisson-Boltzmann (PB) sometimes referred to as the Guoy-Ghapman equation, was extensively used in the last two decades to describe the electrochemical nature of membranes of vesicles made of lipids and related materials significant to biophysical research.[38] The general Cartesian Poisson-Boltzmann equations are collected in the Appendix. The PB equations for a solution mixture of 1:1 and 1:2 electrolytes can be found in the membrane vesicle literature of the last decade or so. In Sec. II A we collect those equations that are relevant to the Langmuir monolayer system. The approximations involved in the PB equation and the validity of the application of the PB equation to our systems are discussed in Sec. II B. These equations require numerical solutions, however. We derive simple approximate formulas for the electrochemical quantities of a Langmuir monolayer relevant to our system for (i) monovalent ions (Sec. III A). (ii) a mixture of two monovalent ions (Sec. III B). (iii) divalent ions (Sec. III C), and (iv) a mixture of monovalent and divalent ions (Sec. III D). The accuracy of these formulas is tested against the numeric solution of the PB equation. We compare in Sec. IV the experimental values obtained for the amount of monovalent and divalent ion segregating to the Langmuir monolayer to the theoretical predictions using the equations of Sec. III. In Sec. V we review earlier models used to explain the metal ion segregation to Langmuir monolayers (Sec. V A), comment about the condensation state of the monolayers (Sec. V B), compare it to the state of a hypothetical 3D solution of the monolayer material (Sec. V C), and comment about the general qualities of the monovalent and divalent systems (Sec. V D) and the transition region between a monovalent and divalent dominated system (Sec. V E). The conclusions are presented in Sec. V F.

II. POISSON-BOLTZMANN-STERN EQUATION OF A SYSTEM WITH MONOVALENT AND DIVALENT COUNTER IONS IN SOLUTION

The Poisson-Boltzmann-Stern (PBS) equations were very successful in describing the electrochemical state of vesicle membranes.[38] That model was, however, rarely applied to resolve the Langmuir monolayer structure. A large body of experiments on Langmuir monolayers was published without a convincing theory to explain the metal segregation to the monolayer (see Sec. V A). As of now we are aware of only one recent study where the Poisson-Boltzmann equation was used to analyze a Langmuir monolayer system with only a *monovalent* metal ion solution.[33] Since Langmuir systems generally involve a divalent ion in the solution, it was of great interest to apply the Poisson-Boltzmann equation for a mixture of monovalent and divalent solution near a flat partially dissociated interface.[39] Not only do the equations for a divalent ion take a different form than in the monovalent case but also the effect of the divalent ion on the properties of the surfactant is remarkably different. These formulas are our starting point and are used in the rest of the work. They can be found in the vesicle membrane literature of the last decade or so and are presented for completeness in Sec. II A in the context of a Langmuir monolayer.

A. Electrochemical description of our system

We consider a system made out of a surfactant fatty acid monolayer, indicated schematically by LH, where L stands for the amphiphilic carbohydrate chain and H is the proton in the carboxylic group. Each surfactant molecule occupies area A of the liquid surface. The monolayer is partially dissociated as a result of interaction with a subphase aqueous solution. If the surfactant monolayer were to be completely dissociated, then it would carry one electron unit of charge $q=-1$ on each chain and the surface charge would originally be $\sigma=1/A$ in electron units. The subphase solution contains monovalent and divalent cations N^+ and M^{2+} and their counterpart monovalent anions. The charge left on the surfactant chains L^- upon dissociation is offset by the condensation[40] of the divalent and the monovalent ions according to the reactions

$$L^- + \mathrm{H}^+ \Longrightarrow L\mathrm{H}\ , \tag{1a}$$

$$L^- + M^{2+} \Longrightarrow (LM)^+\ , \tag{1b}$$

$$L^- + N^+ \Longrightarrow LN\ . \tag{1c}$$

The condensation ratios of the divalent ion, the monovalent ion, and the proton on the chains to the dissociated chains are determined by the chemical equilibriums

$$\begin{aligned} X_M &= \frac{\Phi^s_{LM^+}}{\Phi^s_{L^-}} = K_M \Phi^s_{M^{2+}}\ , \\ X_N &= \frac{\Phi^s_{LN}}{\Phi^s_{L^-}} = K_N \Phi^s_{N^+}\ , \\ X_\mathrm{H} &= \frac{\Phi^s_{L\mathrm{H}}}{\Phi^s_{L^-}} = K_\mathrm{H} \Phi^s_{\mathrm{H}^+} \end{aligned} \tag{2}$$

with the chemical equilibrium constants K_H, K_M, and K_N for these three reactions. $\Phi^s_{A_i}$ is the concentration of component A_i at the surface.

In these equations the concentrations of the components at the surface are different from those found in the bulk and are yet unknown. The sum of the surface concentrations of the different surface species is equal to the monolayer concentration $\Phi^s_{L^0}=\Phi^s_{LM^+}+\Phi^s_{LN}+\Phi^s_{L\mathrm{H}}+\Phi^s_{L^-}$. The fraction of the monolayer that is condensed with hydrogen to make the LH species is given then using Eq. (2) by

$$\Gamma_{L\mathrm{H}} = \frac{\Phi^s_{L\mathrm{H}}}{\Phi^s_{L^0}} = \frac{X_\mathrm{H}}{1+X_\mathrm{H}+X_M+X_N}\ . \tag{3a}$$

Similarly,

$$\Gamma_{LN} = \frac{\Phi^s_{LN}}{\Phi^s_{L^0}} = \frac{X_N}{1+X_\mathrm{H}+X_M+X_N}\ , \tag{3b}$$

$$\Gamma_{LM^+} = \frac{\Phi^s_{LM^+}}{\Phi^s_{L^0}} = \frac{X_M}{1+X_\mathrm{H}+X_M+X_N}\ , \tag{3c}$$

and the fraction of the dissociated chains is given by

$$\Gamma_{L^-} = \frac{\Phi^s_{L^-}}{\Phi^s_{L^0}} = \frac{1}{1+X_\mathrm{H}+X_M+X_N}\ . \tag{3d}$$

The sum of the fractal condensations is

$$\Gamma_{L\mathrm{H}}+\Gamma_{LN}+\Gamma_{LM^+}+\Gamma_{L^-}=1\ . \tag{4}$$

In Eq. (2) the divalent ion is considered to bind to the negative surfactant ion and to form only 1:1 complexes $(LM)^+$. We found that fits to the experimental condensation curves such as those shown in Sec. III do not require condensation with two surfactants to a single divalent metal ion and the equilibrium constant for such process would be negligibly small. The structure of fatty acid soaps reveals that the divalent metal ion (in Ca stearate) orients itself almost colinearly with two neighboring carbohydrate chains. The carbohydrate chains are oriented antiparallel to each other, facing the metal ion with their carboxylic groups. This conformation cannot be realized when the two chains are parallel to each other, as in a surfactant spread on solution. This could be the reason for not having a significant amount of 2:1 complexes in surfactant systems. Researchers studying the membrane vesicle systems arrived independently to the same conclusion. They found that for their systems (phosphatedylserine as membrane material, the monovalent sodium ion and divalent nickel, manganese, calcium, magnesium, cobalt, barium, and strontium), the inclusion of 2:1 complexes did not contribute to agreement with the experimental measured electric potential.[41] If such complexes were to be significant, then the dependence of the ζ potential on the concentrations of the monovalent and divalent ions would have been different than observed. This is because of an additional term in the equilibrium equation proportional to the square of the concentration of the dissociated surfactant $[L^-]^2$. They have also found that a reversal of potential and charge occurs when a sufficient amount of divalent ion was added to the solution,[42] as expected when the number of the 1:1 complexes $[(LM)^+]$ is larger than that of the dissociated membrane molecules $[L^-]$ [see Eq. (8) below]. This concentration is generally higher by orders of magnitude from that used in surfactant Langmuir systems. That might explain why such a reversal of potential was not reported yet in Langmuir systems. The average charge per surfactant chain in electron units q includes a negative contribution originating with the dissociated fatty acid chain $[L^-]$ and a positive charge contribution originating with the $[LM^+]$ species condensed on the monolayer. This feature is special to a divalent counterion and is the origin of the different behavior of this monolayer to that spread on a monovalent solution. Using Eq. (3) one obtains an explicit form of Eq. (A6) in the Appendix:

$$\begin{aligned} q=\sigma A &= \Gamma_{LM^+}-\Gamma_{L^-} = 2\Gamma_{LM^+}+\Gamma_{L\mathrm{H}}+\Gamma_{LN}-1 \\ &= \frac{X_M-1}{1+X_\mathrm{H}+X_M+X_N}\ . \end{aligned} \tag{5}$$

The divalent contribution X_m appears both in the nominator and the denominator while the monovalent contributions X_N and X_H appear only in the denominator in the last equation.[43] This turns out to be the origin of the stronger condensation of the divalent ions and allows us the derivation of the equilibrium condition for a monolayer spread on a solution with both monovalent and divalent ions.

The surface charge invokes redistribution of the free ion concentrations $\Phi_{A_i}(z)$ in the subphase. The concentrations of the counterions at a distance z from the interface are

$$\begin{aligned}\Phi_{\mathrm{H}^+}(z)&=P(z)\Phi^b_{\mathrm{H}^+}\ ,\\ \Phi_{N^+}(z)&=P(z)\Phi^b_{N^+}\ ,\\ \Phi_{M^{2+}}(z)&=P^2(z)\Phi^b_{M^{2+}}\ .\end{aligned}\tag{6}$$

Here

$$P(z)=\exp[e\Psi(z)/T]\tag{7}$$

is the Boltzmann concentration enhancement factor of a positive monovalent ion at a distance z from the solution surface, and $\Phi^b_{A_i}$ is the bulk concentration of ion i. The total charge density

$$\rho(z)=\rho^{(1)}+\rho^{(2)}\tag{8}$$

at a distance z from the interface is the sum of the contributions from the monovalent and the divalent ion charge densities

$$\begin{aligned}\rho^{(1)}&=e(\Phi^b_{\mathrm{H}^+}+\Phi^b_{N^+})[P(z)-1/P(z)]\ ,\\ \rho^{(2)}&=2e\Phi^b_{M^{2+}}[P^2(z)-1/P(z)]\ .\end{aligned}\tag{9}$$

Equation (9) includes the excess charge due to the cation and also the depletion of the negative monovalent anion charge near the liquid surface.

Equation (8) is substituted in (A3) and yields after integration

$$E(z)=\frac{4\pi e}{\epsilon}\frac{Q(z)}{A}\ ,\tag{10}$$

where

$$\frac{Q(z)}{A}=\sigma(z)=-\left[\frac{[P(z)-1]^2}{P(z)R_0}\{\Phi^b_{\mathrm{H}^+}+\Phi^b_{N^+}+\Phi^b_{M^{2+}}[P(z)+2]\}\right]^{1/2}\ .\tag{11}$$

The integration constant was determined by the condition that the electric field inside the liquid far from the interface vanish, i.e., $E(z\to\infty)\to 0$. Here $R_0=2\pi e^2/T\epsilon\approx 4.37\times 10^{-7}$ cm for water at room temperature. Similar expressions were given in the literature for the charge density of a mixture of a monovalent and divalent ion in interacting cellular surfaces[44] and for charged phospholipid membranes.[45]

Comparing q from the condensation expression Eq. (5) with (10) with $z=0$ yields our Grahame equation

$$\left[\frac{P_0-1}{P_0}\right]\left[U_{\mathrm{H}}X_{\mathrm{H}}+U_NX_N+U_MX_M\left[\frac{P_0+2}{P_0}\right]\right]^{1/2}=\frac{1-X_M}{1+X_{\mathrm{H}}+X_M+X_N}\ ,\tag{12}$$

where $U_{\mathrm{H}}=A^2/(R_0K_{\mathrm{H}})$, and U_N and U_M are similarly defined with N or M substituted accordingly in the last expression. Substituting X_i from (2) and using (6), a polynomial equation of the seventh order in the enhancement factor $P(z=0)=P_0$ is obtained. A simple conclusion can be drawn from that equation in the limit where condensation is not allowed and at low bulk counter-ion concentrations. These conditions are met when the surfactant monolayer would be completely dissociated with $K_{\mathrm{H}}=K_N=K_M=0$ and at large concentration enhancements $P_0\gg 1$. Then $X_i=0$, but $U_iX_i=R_0/A^2=R_0\sigma^2$ and Eq. (12) for a single ion (either divalent or monovalent) takes the form

$$\Phi^s_i=R_0\sigma^2=\Phi^b_i\exp(e\Psi_0 z/T)\tag{13}$$

or

$$\Psi_0=\frac{T\ln 10}{ez}\log_{10}\left[\frac{R_0\sigma^2}{\Phi^b_i}\right]\ .\tag{14}$$

At room temperature $T\ln 10/e$ equals about 60 mV and therefore that would also be the slope of the potential as a function of the logarithm of the bulk concentration of a monovalent ion (with $z=1$). For a divalent ion ($z=2$) the slope will be 30 mV accordingly.[38] In obtaining (14) we note that when no condensation is allowed, the charge on each surfactant monolayer is

$$q=-1\ e\ ,\tag{15}$$

and therefore the average charge density of the monolayer is equal to the inverse of the area per surfactant chain A. The 60-mV/decade slope is believed by some to originate with considerations more general than the Poisson-Boltzmann theory. In Sec. III we derive an equivalent relation in the highly condensed regime. There, of course, the residual charge on the surfactant is much smaller than 1e. The expressions for the monovalent and divalent ion are different than those in the uncondensed case that we consider here but the slopes are still 60 and 30 mV per decade of concentration of the monovalent and the divalent ions, respectively.

For a general system P_0 is calculated numerically from (12) and used to find all the other parameters of the surface. The condensation fractions $\Gamma_{L\mathrm{H}}$, Γ_{LN} and $\Gamma_{(LM)^+}$ are determined by substituting P_0 in Eq. (3) and using Eq. (6).

The concentration profile of the counterions for our system is obtained by substituting the charge density from (8) in (A5) and replacing variable $\Psi(z)$ by $P(z)$,

$$z+z_0'=-\frac{R_D}{2}\int\frac{dP}{(P-1)\{P[1+(P-1)C]\}^{1/2}}\ ,\tag{16}$$

where $R_D=(\Phi^bR_0)^{-1/2}$, $C=\Phi^b_{M^{2+}}/\Phi^b$, and $\Phi^b=3\Phi^b_{M^{2+}}+\Phi^b_{N^+}+\Phi^b_{\mathrm{H}^+}$. Upon direct integration of (16) we obtain

$$\frac{z}{R_D}=\ln\left[\frac{f(p)}{f(p_0)}\right],$$

where (17)

$$f(p)=\frac{p^{1/2}+(cp+1-c)^{1/2}}{(p-1)^{1/2}}.$$

We will use this equation in Secs. III A and III C to obtain the falloff radii for the concentration profiles of the monovalent and divalent ions next to the interface. Equation (17) yields after some algebraic manipulation an analytic expression for the concentration profile $P(z)$ of a mixture of monovalent and divalent ions at a distance z from a charged interface,

$$P(z)=\frac{R^2}{(R^2-1)}=\coth^2(\phi),$$

where

$$R=\left[1-\frac{c}{2}\right]\cosh\left[\frac{z+z_0'}{R_D}\right]-\frac{c}{2}\sinh\left[\frac{z+z_0'}{R_D}\right],$$

$$\phi=\operatorname{arccosh}(R). \tag{18}$$

z_0' is an integration constant determined by the boundary $P(z=0)\rightarrow P_0$. Using the hyperbolic sum formulas Eq. (18) can be rewritten as

$$R=(1-c)^{1/2}\cosh\left[\frac{z+z_0}{R_D}\right],$$

with $z_0=z_0'+r$ and $\coth(r/R_D)=(2-c)/c$.

Substituting this value for R in (16) we obtain[45]

$$P(z)=\frac{\cosh^2[(z+z_0)/R_D]}{\sinh^2[(z+z_0)/R_D]-c/(1-c)}. \tag{19}$$

The integration constant z_0 (different from z_0') is given by the boundary condition $P(z=0)\rightarrow P_0$ which, after some algebra, yields the result

$$\frac{z_0}{R_D}=\ln\frac{P_0^{1/2}+[(P_0-1)C+1]^{1/2}}{(P_0-1)^{1/2}(1-C)^{1/2}}.$$

Expression (19) yields a $\coth^2[(z+z_0/R_D]$ dependence for a monovalent ion, as can be evidenced by substituting $c=0$ ($\Phi^b_{M^{2+}}=0$) in (19). 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.[46]

Integration over the concentration profiles of the cations and anions in the solution, substituting (19) in (9), yields the charge excess of the monovalent and divalent ions near the surface. The excess charges on the ions attracted to the monolayer q' compensate the net negative charge on the partially condensed monolayer q and since the system is neutral as a whole it requires that $q=-q'$. This identity was used to check the accuracy of our numerical solution of Eq. (12). In all cases we obtained a convergence better than $0.001e>q+q'$.

We also obtained the condensation fractions $\Gamma_{[LM]}$, $\Gamma_{[LN]}$, and $\Gamma_{[LH]}$ of the M, N, and H ions condensed on the monolayer, the fractions of the M and H ions attracted electrically in the diffuse double layer $\Gamma_{[M]}$ and $\Gamma_{[\mathrm{H}]}$, and the electrical contribution to the surface pressure Π_e.

B. Applicability of the PBS equation for Langmuir monolayers

While the spherical PB equations requires the linearization of the concentration exponent, the one-dimensional Cartesian PBS equation is integrable analytically for any electric potential [Eq. (A3) in the Appendix]. The Cartesian PBS equation still requires a number of assumptions that seem at first to severely restrict its usefulness. These limitations received extensive attention. (i) It assumes that the charge on the liquid surface is distributed with a uniform density q/A and disregards the discrete nature of the charge q associated with each surfactant monolayer. (ii) It also assumes point charges for the counterions and co-ions in the solution. (iii) It further neglects the variation in the static dielectric constant near the interface as a result of the high concentration of the counterion near the interface.

It is therefore surprising that this simple model was successful in reproducing with remarkable accuracy experimental results on phospholipid vesicle membranes.[47(a)] The exponential dependence of the electrical potential on the bulk concentration of the counterion was verified to be about 60 mV per decade of monovalent counterions (see the discussion following Eq. (14) [Refs. 47(b)–49]) and so was the absolute value as predicted by the PBS equation. The potential in these experiments was either measured directly with an electrode above a spread monolayer (Ref. 50), or using electrophoretic mobility, ion conductance, or NMR (Ref. 51) and ESR (Ref. 52).

In a different set of experiments aimed at measuring the error introduced in the PB equation by assuming a fixed spatial dielectric constant the force between bilayers was measured as a function of the distance between the bilayer surfaces[53–58] and was found to agree with the Poisson-Boltzmann equation for distances larger than 20 Å. Smaller distances were dominated by the hydration force, and the applicability of the PB equation could not have been tested for them.

Models that take into account the discreteness of charge effect, such as the Nelson-McQuarrie model,[59] predict that the potential of membranes with equal but opposite charge densities would differ not only in sign but also in magnitude. NMR and fluorescent experiments[51] failed to find this asymmetry and the results agreed much better with the simple PB equation. Failure to observe the Esin-Markov deviation of the electric potential from the values expected from the PB equations further indicate that the discreteness of charge corrections seem to be not significant even when the distance between the charges is of the order of magnitude of the Debye length.

A simplistic argument suggests that since the ions are not static but have a thermic motion, each of the ions in solution experiences a "mean-field potential" originating with the charges on the interface and the rest of the ions in the solution. This time averaged potential would not carry the discreteness information. The averaged potential calculated from the Nelson-McQuarrie model[59] is indeed equal to the potential obtained from a system with its charge homogeneously spread at the interface.[60] This however cannot fully account for the validity of the PBS equation since the ion population expression requires the averaging over the exponents of the potential—the Boltzmann factors—and that average does not necessarily coincide with the exponent of the averaged potential. Recent work[61] based on a comprehensive theoretical work by Kjellander and Marcelja[62,63] seems to suggest that when the finite size of the ions in solution and their mobility together with the discrete ions at the interface are taken in account, then the system behaves very much like that expected from the simple Poisson-Boltzmann equation.

The approximations involved in taking the ions as point charges were further addressed by computer simulations,[64] by finite-size corrections to the PB equation,[65,66] by experiments where different size counterions were tested,[49] and also by changing the Debye length through changes in the concentration.[48] These studies indicate that the finite size can be disregarded for counterions smaller than the Debye length.[49]

A further possible source of error in the use of the static Poisson-Boltzmann equation is the disregard of the possible currents of chemical products in the z direction, perpendicular to the interface. In our system the condensation products $[LH]$, $[LM]$, and $[LN]$ are bound to the monolayer at the surface of the liquid. Therefore in a stationary system the current density of each surface product is $\mathbf{J}_{A_i}=0$. We also assumed for simplicity that the cations and anions in the solution are completely dissociated and therefore there is no "creation" or "annihilation" of their products in the bulk liquid. It is important to note, however, that even if such reactions were to be allowed, the concentration enhancement $P(z)$ of the various components of the components of a reaction at any distance z from the surface would have still satisfied the chemical equilibrium equation

$$\frac{\Phi_{A^+}(z)\Phi_{B^-}(z)}{\Phi_{[AB]}(z)}=\frac{P(z)\Phi^b_{A^+}[1/P(z)]\Phi^b_{B^-}}{\Phi^b_{[AB]}}$$

$$=\frac{\Phi^b_{A^+}\Phi^b_{B^-}}{\Phi^b_{[AB]}}=K_{[AB]}\ .$$

Thus the stationary concentration profile at the interface is not accompanied by currents of the chemical products (and the associated electrical currents). When concentration-dependent activities are required in the chemical equilibrium equations (generally at high concentrations), then the equilibrium equation is not satisfied simultaneously for every z, and steady currents might be significant.[67]

In conclusion, for systems where the surface charges are bound to the interface, as is the case for the Langmuir systems and for nonpolyvalent ions, there is mounting experimental data and theoretical work to suggest that the Poisson-Boltzmann equation has a range of validity far wider than that which one could have naively expected from the approximations leading to this equation.

III. THE POISSON-BOLTZMANN-STERN EQUATION FOR A LANGMUIR MONOLAYER

The Grahame equation for the classical Cartesian Poisson-Boltzmann equation for a solution of a mixture of divalent and monovalent counterions is of the third order in the electric potential exponent at the interface $\exp(e\Psi/T)$ and was solved analytically.[45] Equation (12) for the Poisson-Boltzmann-Stern system yields a seventh-order equation in the surface potential exponent and requires a numerical solution. We find, however, that when only one type of counterion exists in a dilute solution, either monovalent or divalent, the parameters of the charged Langmuir monolayer in the PBS equations can be approximated by simple closed-form expressions.

Consider the Grahame equation (12) in the dilute solution limit. This condition is equivalent (see below) to having a large enhancement factor P_0. In this limit Eq. (12) reduces to

$$\frac{1-X_M}{1+X_H+X_N+X_M}=-(X_H U_H+X_N U_N+X_M U_M)^{1/2}\ . \tag{20}$$

A. The monovalent case

The equations for the proton H and the monovalent ion N are identical. The difference in their effect on the monolayer originates from a difference of about five orders of magnitude in their equilibrium constants.

When the concentration of the monovalent ion N is high enough to dominate the system and when $P_0>1$ (20) takes the form

$$q=-\frac{1}{1+X_N}=-(U_N X_N)^{1/2}\ . \tag{21}$$

For $U_N<1$ the solution of (21) yields

$$X_N\approx U_N^{-1/3}-\tfrac{2}{3}>1\ . \tag{22}$$

Substituting X_N back in (21) and using (5) one obtains the net average charge per surfactant

$$q=\Gamma_{LN}-1\approx -U_N^{1/3}+\tfrac{1}{3}U_N^{2/3}\lesssim 0\ . \tag{23}$$

The last expression indicates that the charge on the surfactant monolayer for $U_N<1$ is small. The original charge on the monolayer is neutralized by condensation of the monovalent ions on the monolayer chains so that $\Gamma_{LN}\approx 1-U_N^{1/3}\lesssim 1$ and $\Gamma_{L^-}\approx U_N^{1/3}\gtrsim 0$. The concentration enhancement of the monovalent ion is

$$P_0^N\approx\frac{U_N^{-1/3}-\frac{2}{3}}{K_N\Phi^b_{N^+}} \tag{24}$$

in the high condensation limit $U_N\ll 1$. The surface concentration of the monovalent ion in this regime

$$\Phi^s_{N^+}=P_0^N\Phi^b_{N^+}=\frac{U_N^{-1/3}-\frac{2}{3}}{K_N} \tag{25}$$

is independent of the bulk concentration of the monovalent ion $\Phi^b_{N^+}$.

Numeric examples for the monovalent hydrogen and sodium counterions are given in Table I. The condensation parameter U for both is smaller than unity, although it is still about six orders of magnitude larger for the sodium ion. Consequently the surfactants in both systems are primarily condensed but the charge on the monovalent ion is not negligible ($-0.28e$). Note that the simple approximate equations developed in this section for the charge and the monovalent ion concentration in the condensed regime [Eqs. (23) and (25)] are in excellent agreement with the values obtained from the numeric solution of the seventh-order Grahame equation (12) for both ions. These values should be compared to those obtained from the conventional Poisson-Boltzmann equations (14) and (15) derived by Gouy[34] and Chapman.[35]

The surface concentration of the monovalent ion is independent of the bulk concentration in both regimes. Not surprisingly the surface concentration of the counterions is very high in the noncondensing regime, as is the surface potential.

In both the strong condensation regime and also the noncondensing regimes the surface potential Ψ_0 will change by about 59 mV per decade of bulk concentration change of the monovalent ion. This is due to the exponential dependence of the potential in both regimes on the monovalent ion bulk concentration $\Phi^b_{N^+}$ [compare Eqs. (14) and (24)]. Therefore the classic 59-mV per decade slope does not distinguish between the condensed and the dissociated state. The absolute value of the potential in the condensed regime is many times smaller than in the noncondensing regime (compare the values for the surface concentrations of the two cases in Table I).

The falloff radius r_N of the concentration profile for a monovalent ion attracted to the surface is defined as the distance from the interface at which the concentration enhancement $P^N(r_N)$ drops to half its value at the surface P^N_0. With $U_N < 1$ we obtain from Eq. (16) after expansion to second order in $U_N < 1$

$$\frac{r_N}{R_D} \approx (2^{1/2}-1)P_0^{-1/2} \approx 0.414 P_0^{-1/2} = 0.207\left[\frac{K_N A}{R_0^2}\right]^{1/3} , \qquad (26)$$

i.e., in the limit of total electrical neutralization, r_N is independent of the bulk concentration of the monovalent ion. r_N can be used to obtain a rough estimate of the total charge q' electrically attracted to the surface per one surfactant monolayer. Using Eqs. (24) and (26) we obtain

$$1 \gg q' = \alpha r_N A \Phi^s_{N^+} < U_N^{1/3} = q \ . \qquad (27)$$

α is of the order of unity and is introduced to compensate for the approximation in the integration. This result is consistent with the charge neutrality requirement for the whole system, i.e., the attracted charge q' would be equal in value and opposite in sign to the charge on the monolayer q. The possible high concentration of the monovalent ion at the surface [see Eq. (24)] is still consistent with the small total charge excess attracted to the surface since the excess radius r_N is very narrow. For hydrogen

TABLE I. Using the equilibrium constants K_i from Ref. 68 the condensation parameters $U = A^2/(K_m R_0)$ for a surfactant spread on a solution with dilute concentration of H^+, Cd, Ca, Ba, and Na are calculated for an area of 20 Å^2 per surfactant. These are the equilibrium constant values that we used in all our fits. Using these values the ion concentration near the surface was calculated by solving numerically the seventh-order Grahame equation (12), and using formulas (24) for the monovalent and (38) for the divalent ion. For comparison the values for the Poisson-Boltzmann equation without condensation are also given [Eq. (13)]. Next the charge per one surfactant chain Q is given using the Grahame equation and our formulas (23) and (36). For comparison the values for a system without condensation are also given [Eq. (13)]. From these values it is clear that (i) the monovalent and divalent ions are primarily condensed, with the divalent ions more so than the monovalent; (ii) the simple explicit expressions (23), (36), (24), and (38) provide very good approximations and a numerical solution of Eq. (18) is not required. The asterisk shows a value extrapolated from low-concentration data.

Ion	H^+	Cd^{2+}	Ca^{2+}	Ba^{2+}	Na^+
$\log_{10}K$ (Å^3/particle)	8.090	5.150	3.721	3.561	2.449*
$U(A=20$ Å$^2)$	7.44×10^{-8}	6.49×10^{-5}	1.74×10^{-3}	2.51×10^{-3}	3.25×10^{-2}
Φ^s(mol/l)					
Eq. (12)	0.0032	0.0116	0.292	0.415	14.88
Eq. (24)	0.0032				14.57
Eq. (38)		0.0116	0.290	0.411	
Eq. (13)	177	177	177	177	177
Q (electron)					
Eq. (12)	−0.0042	−0.0079	−0.040	−0.047	−0.284
Eq. (23)	−0.0042				−0.285
Eq. (36)		−0.0080	−0.040	−0.048	
Eq. (15)	−1	−1	−1	−1	−1

we obtain $r_{\mathrm{H}} \approx 25$ Å. This distance is considerably smaller than the Debye radius $R_D = (\Phi^b_{N^+} + R_0)^{-1/2}$ [see Eq. (16)] which for a neutral solution ($p\mathrm{H}=7$) yields $R_D \approx 2000$ Å. More importantly, the algebraic form of the Debye radius would not satisfy the charge neutrality of the system and the association[31,33] of R_D with the concentration falloff radius seems to be inaccurate.

B. Two different types of monovalent ions exist in the subphase solution

The case where both a monovalent ion and a proton coexist in the solution has practical implications as it is impossible to have a monovalent solute ion in aqueous solution without the presence of hydrogen ions. When the two monovalent ions N^+ and H^+ coexist in the subphase solution and are dilute enough so that $P_0 > 1$, Eq. (12) takes the form

$$q = -\frac{1}{q + X_I} = -(U_I X_I)^{1/2} \,, \tag{28}$$

where

$$\begin{aligned} X_I &= X_{\mathrm{H}} + X_N = (K_N \Phi^b_{N^+} + K_{\mathrm{H}} \Phi^b_{\mathrm{H}^+}) P_0 \,, \\ U_I &= A^2/(R_0 K_I) \,, \end{aligned} \tag{29}$$

and

$$K_I = K_{\mathrm{H}} \frac{\Phi^b_{\mathrm{H}^+}}{\Phi^b_{\mathrm{H}^+} + \Phi^b_{N^+}} + K_N \frac{\Phi^b_{N^+}}{\Phi^b_{\mathrm{H}^+} + \Phi^b_{N^+}} \,. \tag{30}$$

Equation (28) is of the same form as the equivalent expression for a single-type monovalent ion and we can generalize the results of Sec. III A to this case by substituting the single-ion quantities by their correspondent combined quantities defined by Eqs. (29) and (30). The combined chemical equilibrium constant K_I is a weighted average of the chemical equilibrium constants of the constituent ions multiplied by their fractional concentrations. The condensation condition $U_I < 1$ for this combined system maintains the same formal form as that of the individual components. The total charge is given by

$$q = \Gamma_{LN} + \Gamma_{L\mathrm{H}} - 1 \approx -U_1^{1/3} + \tfrac{1}{3} U_I^{2/3} \lesssim 0 \,. \tag{31}$$

The concentration enhancement for both types of ions is the same:

$$P^I_0 \approx \frac{U_I^{-1/3} - \frac{2}{3}}{K_I \Phi^b_{I_+}} \tag{32}$$

is the concentration enhancement in the total condensation limit $U_I \ll 1$.

The surface concentrations of each monovalent component is dependent on its relative bulk concentration

$$\begin{aligned} \Phi^s_{N^+} &= P^I_0 \Phi^b_{N^+} = \frac{U_I^{-1/3} - \frac{2}{3}}{K_I} \frac{\Phi^b_{N^+}}{\Phi^b_{I_+}} \,, \\ \Phi^s_{\mathrm{H}^+} &= P^I_0 \Phi^b_{\mathrm{H}^+} = \frac{U_I^{-1/3} - \frac{2}{3}}{K_I} \cdot \frac{\Phi^b_{\mathrm{H}^+}}{\Phi^b_{I_+}} \,. \end{aligned} \tag{33}$$

However, the total surface concentration of the two types of monovalent ions

$$\Phi^s_{I^+} = \Phi^s_{N^+} + \Phi^s_{\mathrm{H}^+} = \frac{U_I^{-1/3} - \frac{2}{3}}{K_I}$$

is independent of their bulk concentrations just as in the single monovalent case. The condensation fractions of the two ions are given by

$$\Gamma_{[LN]} = \frac{K_N \Phi^b_{N^+}}{K_I \Phi^b_{I_+}} (1 - U_I^{1/3}) \,,$$

$$\Gamma_{[L\mathrm{H}]} = \frac{K_{\mathrm{H}} \Phi^b_{\mathrm{H}^+}}{K_I \Phi^b_{I_+}} (1 - U_I^{1/3}) \,.$$

C. The divalent case

When the concentration of the divalent ion is high enough to dominate the system and when $P_0 > 1$, then Eq. (12) takes the form

$$q = \left[\frac{X_M - 1}{X_M + 1} \right] = -(U_M X_M)^{1/2} \,, \tag{34}$$

where $X_M = K_M \Phi^b_{M^{2+}} P_0^2$ and $U_M = A^2/R_0 K_M$. For practically all cases of interest for a divalent ion $U_M < 1$ using K_M from Table I, the solution of Eq. (34) then yields

$$X_M \approx 1 - 2U_M^{1/2} \lesssim 1 \tag{35}$$

and

$$q = 2\Gamma_{LM_+} - 1 = -U_M^{1/2} + U_M \lesssim 0 \tag{36}$$

[see Eq. (5)]. The absence of charge on the monolayer is achieved in the divalent ion case by having approximately half of the surfactant chains condensed with the $(LM)_+$ species carrying $+1e$ and the other half dissociated with the charge $-1e$ so that

$$\Gamma_{LM^+} = \tfrac{1}{2}(1 - U_M^{1/2}) \lesssim \tfrac{1}{2}, \quad \Gamma_{L^-} = \tfrac{1}{2}(1 + U_M^{1/2}) \gtrsim \tfrac{1}{2} \,. \tag{37}$$

The concentration enhancement of the divalent ion is

$$(P^M_0)^2_0 = \frac{1 - 2U_M^{1/2}}{K_M \Phi^b_{M^{2+}}} \tag{38}$$

in the limiting case when $U_M < 1$. The surface concentration of the divalent ion is

$$\Phi^s_{M^{2+}} = P_0^2 \Phi^b_{M^{2+}} = [1 - 2U_M^{1/2}]/K_M \,. \tag{39}$$

The expressions for the concentration enhancement, the uncompensated charge, and the surface concentration take different algebraic forms for the divalent ion as compared to the monovalent ion. However, in both cases the surface concentration is independent of the bulk concentration, and the condition $U < 1$ where the monolayer is almost completely charge free is identical for both. The surface concentration $\Phi^s_{M^{2+}}$ is only slightly dependent on the density of the monolayer. This is in contrast to the monovalent case where the surface concentration is proportional to $A^{-2/3}$. The different dependence originates with the two different compensation mechanisms for the two cases. In the monovalent ion case charge compensation occurs when almost all the surfactant monolayers are condensed and $X_{\mathrm{H}} \gg 1$. In the divalent ion case only half of the surfactant monolayers need to be condensed with the divalent ion for complete charge neutrality so that $X_M \approx 1$. Therefore the area per surfactant scales out in this approximation. In Table I we show the charge per surfactant and the surface potential for the divalent barium, calcium, and cadmium that we later use in our fits to experiments. Note that just as in the monovalent case the simple approximate expressions (36) and (39) developed in this section for the divalent strong condensing case gives values indistinguishable within the accuracy of the calculation, from those obtained by numerically solving the Grahame equation (12).

For the falloff radius r_M of the concentration profile of a divalent ion attracted to the surface, we take the distance from the interface at which the concentration enhancements $P^M(r_M)$ drops to half its value at the surface $P_M(0)=P_0^M$. When $U_M<1$, expanding Eq. (16) to second order in $U_M<1$ we obtain after somewhat lengthy algebra

$$\frac{r_M}{R_D} \approx \frac{(2^{1/2}-1)3^{1/2}}{2} P_0^{-1} \approx 0.358 P_0^{-1} = 0.179 \left[\frac{K_M}{R_0} \right]^{1/2} . \tag{40}$$

Here again, the algebraic form of r_M is different from the monovalent expression, but as in the monovalent case it is also independent of the bulk concentration of the divalent ion. r_M can be used to obtain a rough estimate of the total electrically attracted charge per one surfactant monolayer

$$1 \gg q' = \alpha r_M A \Phi^s_{M^{2+}} = U_M^{1/2} = -q \ . \tag{41}$$

α is of the order of unity and is introduced to compensate for the approximation involved in replacing r_m as the mean integration value over the concentration profile. This result is also consistent with the charge neutrality requirement for the whole system that is $q+q'=0$. For divalent cadmium we obtain a falloff radius $r_{\mathrm{Cd}} \approx 5.6$ Å.

D. The divalent and the monovalent ions coexist in the solution

In the following discussion we refer to index I as the subscript for a single monovalent ion, but the conclusions can be generalized in a straightforward way using the results of section III A for any number of monovalent ions. From the previous discussion we concluded that when both $U_I<1$ and $U_M<1$ then the monolayer is almost totally electrically neutralized and the residual charge q per single chain is much smaller than $1e$ [see Eqs. (23) and (36)]. The dissociated monolayer is neutralized with complete condensation when a monovalent ion is dominant in the solution but requires only half of the divalent ions for complete condensation. The enhancement factor $P(z=0)=P_0$ is given by Eqs. (32) and (38), respectively, when one of the ions is dominant in the solution. It will always take the smaller of the two values in the presence of both ions since by reaching this enhancement factor the total neutralization of the monolayer is achieved. This is demonstrated on the condensation diagram (Fig. 1). The axes of this diagram are $\log_{10}P_0^M$ and $\log_{10}P_0^I$. Contour lines of the enhancement factor $\log_{10}P_0$ calculated using Eq. (12) appear as straight parallel and perpendicular lines on this diagram. The inflection point of the contour lines occurs when the enhancement factors of the two ions are equal. Using (38) and (32) we obtain the equation for the locus of the inflection point to be a straight diagonal line that crosses the origin on the condensation diagram (heavy diagonal line on Fig. 1)

$$\log_{10}P_0^I - \log_{10}P_0^M = \tfrac{1}{2}\log_{10}(K_M\Phi^b_{M^{2+}}) - \log_{10}(K_I\Phi^b_{I_+}) - \tfrac{1}{3}\log_{10}U_I = 0 \ . \tag{42}$$

It divides the condensation diagram into a lower right triangle dominated by monovalent ion enhancement factor P_0^I and an upper left triangle dominated by the divalent metal ion enhancement factor $(P_0^M)^2$ given by Eqs. (32) and (38), respectively.

From Eqs. (3) and (6) we obtain the ratio between the condensation fractions of the two ions

$$\Theta_s = \frac{\Gamma_{LI}}{\Gamma_{LM}} = \frac{X_N}{X_M} \ .$$

It would be incorrect to use expressions (29) or (35) for X_N or X_M because they were obtained for a system with only one kind of counterion, either monovalent or divalent but not both. Using (2) for X_N and X_M and with (6) we obtain

$$\begin{aligned} \log_{10}\Theta_s &= \log_{10}(K_I\Phi^b_{I_+}) - \log_{10}(K_M\Phi^b_{M^{2+}}) - \log_{10}P_0 \\ &= 2\log_{10}P_0^M - \log_{10}P_0^I - \log_{10}P_0 \\ &\quad - \tfrac{1}{3}\log_{10}U_I \ . \end{aligned} \tag{43}$$

Note that P_0^M and P_0^I are free variables defined by the bulk concentrations of the monovalent and the divalent ions using Eqs. (24) and (38). $P_0(P_0^M,P_0^I)$, on the other hand, is the actual concentration enhancement of the system, which depends on P_0^M and P_0^I and can be determined using the condensation diagrams (Fig. 1) or the Grahame equation (12).

As in the enhancement factor diagram we can also divide the condensation diagram into an upper left triangle that corresponds to states with divalent ion condensation and lower right triangle that corresponds to states with monovalent ion condensation. However, the transition region between the divalent condensed and monovalent condensed monolayer states does not coincide with the transition region defined by the monovalent and divalent enhancement factors but is shifted horizontally into the divalent ion enhancement region by $\tfrac{1}{3}\log_{10}U_I$.

The horizontal transition width $\Delta\log_{10}P_0^I=\Delta\log_{10}\Theta$ between the monovalent and divalent condensation regimes can be estimated. The condition where there is only 10% monovalent condensation corresponds to $\Theta_{s2}=\Gamma_{LH}/\Gamma_{LM}=0.1/0.45=0.2$. The condition where the monovalent ion is 90% condensed corresponds to $\Theta_{s1}=\Gamma_{LH}/\Gamma_{LM}=0.90/0.05=18$. The condensation transition region between the monovalent and divalent condensation regimes $\Delta\log_{10}\Theta_s=\log_{10}\Theta_{s1}-\log_{10}\Theta_{s2}$ is therefore equal to $\Delta\log_{10}P_0^I=1.95$ as can also be seen on

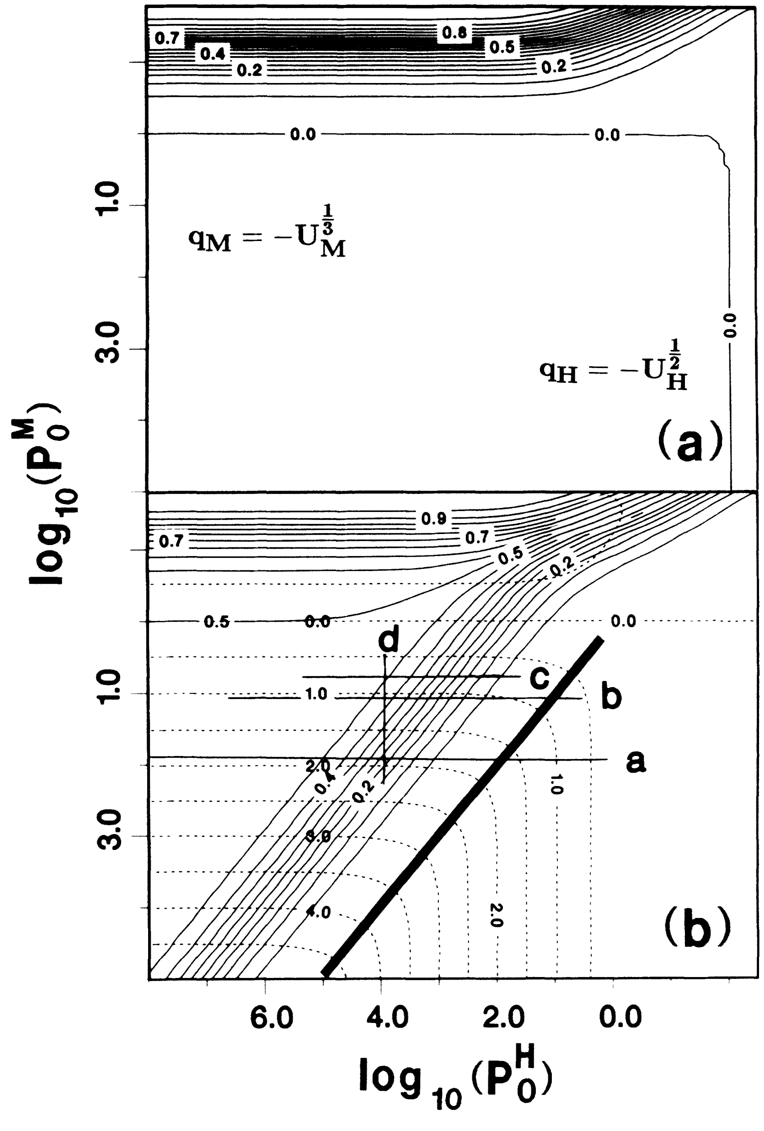

FIG. 1. Universal condensation charts for a surfactant monolayer spread on aqueous solution of a divalent salt. The coordinates are $\log_{10}(P_0^H)$ and $\log_{10}(P_0^M)$ where the enhancement factors for the monovalent and divalent ions P_0^H and $(P_0^M)^2$ are given by Eqs. (32) and (38). It is evident that for low-bulk divalent metal ion or proton concentrations $\Phi^b_{M^{2+}}$ and $\Phi^b_{H^+}$, the charge per surfactant molecule q is very small (a). In comparison a completely dissociated monolayer would yield a value of $q=-1(e)$. The straight dashed horizontal and vertical contour lines of $\log_{10}(P_0)$, where $P_0=\Phi^s_{H^+}/\Phi^b_{H^+}$ is the Boltzmann concentration enhancement factor, as shown in (b). The value of $\log_{10}(P_0)$ is calculated using Eq. (12) and *is equal* to that of the X and Y axes, demonstrating that the concentration at the surface is independent of the bulk concentrations, and is given by Eqs. (32) and (38). The inflection points in these contour curves indicate the conditions where the proton and divalent ions are equally dominant in determining P_0. The locus of these inflection points is indicated by a heavy diagonal line. The area to the right of this line describes systems whose enhancement factors are given by P_0^H. The area on the left of this line is of systems with the enhancement factor P_0^M. The fractional condensation of the metal ion Γ_{LM^+} is indicated by the solid diagonal contour lines. These lines lie in the region where the enhancement factor is given by the divalent ion enhancement $(P_0^M)^2$. This results from their different valency and thereby a different algebraic dependence of the compensation mechanism. The fact that the condensation transition region is governed by (P_0^M) allows us to obtain the surface equilibrium Eq. (46). The maximum metal ion condensation exceeds 0.5 ions per surfactant molecule at high metal ion concentrations for $P_0^M>1$. In this situation the monolayer is positively charged. This charge reversal is strictly a divalent ion effect. High hydrogen concentration (large P_0^H) can at most electrically neutralize the monolayer.

the condensation diagram (Fig. 1). Therefore, in a system with $-\frac{1}{3}\log_{10}U_1 > \frac{1}{2}\Delta\log_{10}\Theta_s \approx 1$, the condensation equation (43) takes an especially simple form. In this important case, which occurs when the monovalent ion is primarily hydrogen (pure aqueous divalent metal ion solution or such solution with only low additional concentration of monovalent ion), $P_0(P_0^M, P_0^I) = (P_0^M)^2$ in the transition region and can be substituted in (43)

$$\Theta_s = \frac{P_0^M}{U_I^{1/3} P_0^I} = \frac{K_I \Phi_{I_+}^b}{(K_M \Phi_{M^{2+}}^b)^{1/2}} . \tag{44}$$

Hence we find that the loci of fixed condensation fraction ratios Θ_s are straight diagonal lines on the universal condensation diagram with $\log_{10}P_0^M$ and $\log_{10}P_0^I$ as its coordinates (Fig. 1).

Since the monolayer is virtually completely condensed and therefore neutral we can derive a simple expression for the monovalent ion and the divalent metal condensation fractions per one surfactant molecule:

$$\Gamma_{LM} = \frac{1}{\Theta_s + 2}, \quad \Gamma_{LI} = \frac{\Theta_s}{\Theta_s + 2} . \tag{45}$$

Θ_s can take values between 0 and ∞, and the ranges of values that Γ_{LH} and Γ_{LM} can take are 0 to 1 and $\frac{1}{2}$ to 0, respectively, consistent with our condensation picture. Substituting Θ_s from Eq. (43) in Eq. (45) and using the equilibrium constants of Table I we quantitatively identify the composition of the surfactant monolayer and this constitutes one of the central results of our derivation. Equation (45) is valid for all the divalent ion monolayers for concentrations $\Phi_{M^{2+}}^b < 1/K_M$ (i.e., $P_0^M > 1$) and thus covers the range of concentrations of interest for Langmuir materials.

Equation (12) reveals a feature special to the divalent condensation at high divalent ion concentrations. When $K_M \Phi_{M^{2+}}^b > 1$ the charge condensed on the monolayer reverses its sign and becomes positive. This occurs with the condensation fraction $\Gamma_{LM^+} > \frac{1}{2}$ and $\Gamma_{L^-} < \frac{1}{2}$. The concentration enhancement P_0 becomes smaller than unity (see the upper third of the condensation diagram) in an attempt to deplete the concentration of the divalent ion $\Phi_{M^{2+}}^s = (P_0)^2 \Phi_{M^{2+}}^b$ so that the total charge condensed on the monolayer would be minimal. In the monovalent case a full ion condensation $\Gamma_{LH} = 1$ or $X_H \gg 1$ can at most drive q very close to zero [Eq. (21)] but cannot overcompensate the monolayer. This charge reversal is also clearly seen on the condensation diagram (Fig. 1), where for $P_0^M < 1$ the contours of condensed charge become positive while high hydrogen concentration (small P_0^H on the right portion of the condensation diagram) cannot reverse the charge on the surfactant to be positive. It is interesting to note that although the divalent and monovalent ions have different algebraic forms in the condensation equation, the condensation condition for both cases takes the same algebraic form $U_{A_i} = A^2/(R_0 K_{A_i}) < 1$.

IV. COMPARISON BETWEEN EXPERIMENT AND THEORY

The addition of metal ions to the subphase changes the properties of the monolayer. The effect of metal ions in the subphase solution on straight paraffinic acid surfactant was observed as changes in the π-A diagrams of these materials (see Refs. 15 and 18 for divalent ion effects and Ref. 19 for monovalent ion effects). Experiments aimed to measure quantitatively the segregation of metals ions to the monolayer-liquid-surface interface could be crudely divided into two groups. (i) Experiments that measure the amount of metal ions that segregate to the liquid surface using *in situ* radiotractor techniques[9–28] where soft characteristic radiation from a radioactive metal ion in the solution was collected and a model was used to relate this quantity to the total metal ion segregating to the surface. (ii) Determination of the amount of metal in the material collected from the liquid surface using chemical analysis, IR spectroscopy, photoelectron spectroscopy, or neutron activation analysis.[12] Recently Richardson and Roser[13] measured the reflectivity of Langmuir monolayers spread on water and extracted from the reflectivity profile the amount of metal ions attracted to the monolayer. The synchrotron NTEF technique was used recently to obtain a direct and absolute measurement of the amount of metal segregated to the monolayer.[4]

We compiled and digitized most of the experimental data known to us where quantitative accumulation of metal ions from the subphase was reported as a function of subphase pH or divalent and monovalent ion concentrations in the subphase. Several representative experimental results together with our model predictions using Eq. (12) (solid line) and the approximate Eq. (44) are presented here. It should be emphasized that there are no fitting parameters in this model. The calculated curves to all the above experiments were done using the equilibrium constants tabulated in Table I. Equilibrium constants for long chain fatty acids and their salts are scarce. However, for carbohydrate chains with the number of carbon atoms $n > 3$ the equilibrium constants are dependent primarily on the polar head ot the acid (Ref. 68). The change in the equilibrium constants as a function of chain length was negligible as compared to the accuracies of the measurements and we primarily used values given for butanoic and propanoic acid. These values should be compared to those measured and reported in the vesicle membrane literature. For the association constant of phosphatidylserine (PS) and calcium ion for example, the range of values reported in the literature covers five orders of magnitude, from 0.1 l/mol (165 Å^3/particle),[69,70] to 1×10^4 l/mol (165×10^4 Å^3/particle).[71] Careful analysis of the experimental techniques leading to these values[72] indicated that the low values were due to the assumption which was proved incorrect,[47,73,74] that monovalent ions do not bind to the membrane while the high values originate with the erraneous assumption that the divalent ion next to the interface is all bound and condensed on the membrane. When both assumptions are corrected, then the associa-

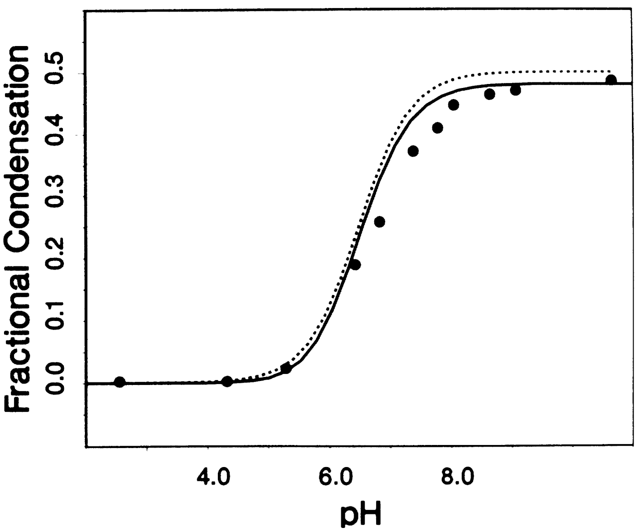

FIG. 2. Experimental fractional condensation of Ca on stearate acid as a function of proton concentration in the subphase solution (Ref. 9). The Ca concentration in the bulk is 1×10^{-4}. The solid line is calculated using our Eq. (12) with the equilibrium constants from Table I. The dashed line was obtained using the surface equilibrium Eq. (46) approximation.

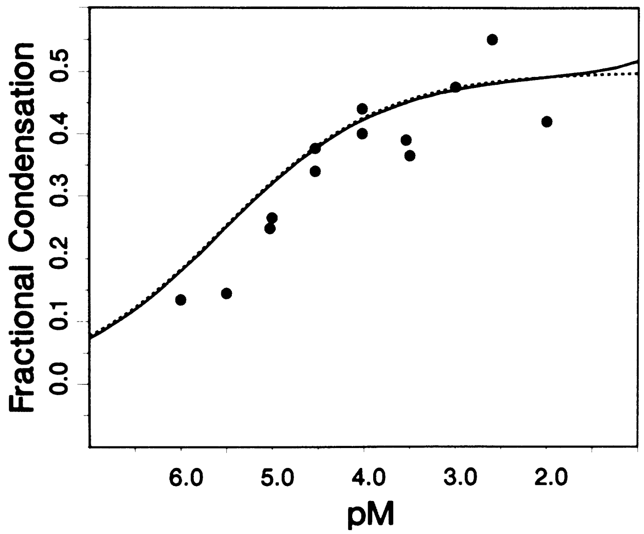

FIG. 4. Experimental fractional condensation of Cd, Γ_{LCd^+}, at pH = 8 on arachidic acid as a function of the Cd salt concentration in the liquid bulk (Ref. 12). The solid line is calculated using our Eq. (12) with K_{Cd} and K_H from Table I. The dashed line is calculated with the approximate equilibrium Eq. (46) and provides a good approximation.

tion value obtained for phosphatidylserine (PS) and the calcium ion is of the order of 10 mol/l and of phosphatidylserine (PS) and the sodium ion is of the order of 0.5 mol/l and is consistent with electrophoretic measurements.[72] These values are larger by a factor of 3 than those we used in Table I (3.2 and 0.17 mol/l for calcium and sodium, respectively). The difference can be attributed to the different surfactant (fatty acid and phosphatidylserine). In any case, since concentrations in the Langmuir systems typically vary over several decades and are generally observed on a logarithmic scale (such as pH), we consider the fact that the equilibrium constants are of the same order of magnitude to be supportive of

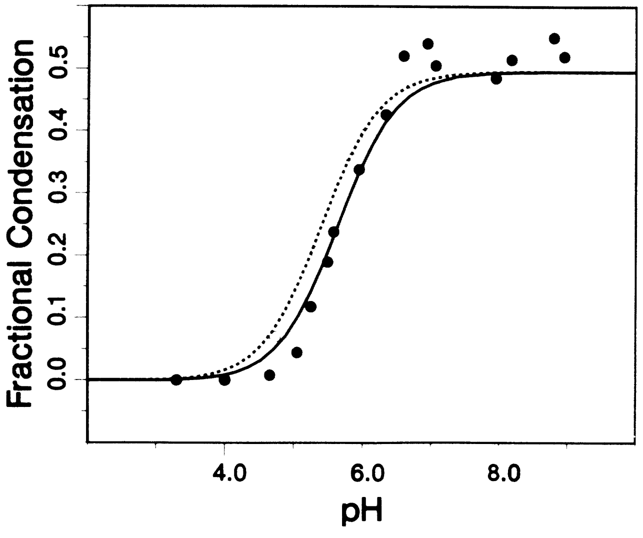

FIG. 3. Experimental fractional condensation of Cd on arachidic acid as a function of proton concentration in the subphase solution (Refs. 12 and 29). The Cd concentration was 10^{-4} mol/l (open circles) (Ref. 29) and 3×10^{-4} mol/l (solid circles) (Ref. 12). The solid and dashed lines are calculated using our Eq. (12) with $K_{Cd}=84.8$ and $K_H=7.40\times10^4$ mol/l from Table I. The approximate surface equilibrium Eq. (46) yielded curves indistinguishable from those obtained with (12).

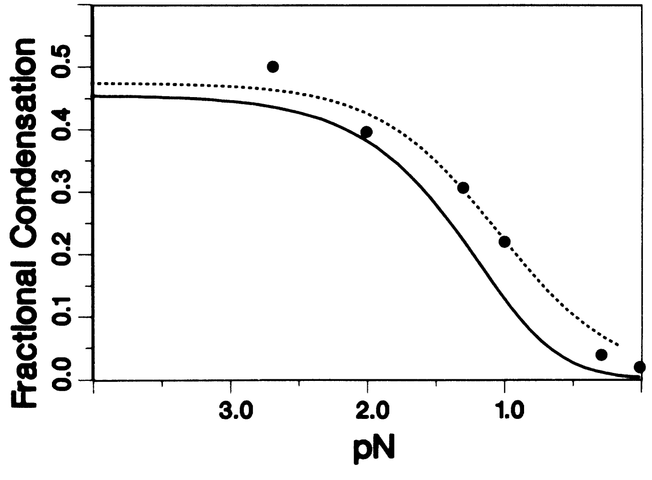

FIG. 5. Experimental fractional condensation of Ca ion on arachidic acid as a function of a Na ion concentration in the liquid bulk (Ref. 11). The Ca concentration in the subphase solution is 1.7×10^{-5} Mol/l and the pH of the subphase solution is 8. The solid line is calculated using Eq. (12) with the equilibrium constants from Table I. The dashed line is calculated with the approximate equilibrium equation (46). See Sec. V E for the discussion of the applicability of (46).

our approach.

The condensation fraction Γ_{LCa^+} of divalent Ca ions on a monolayer of stearic acid increases when the pH of the solution is raised (Fig. 2). When the divalent Cd ion concentration in the subphase solution is raised, then the onset of the CD metal substitution in a monolayer of arachidic acid occurs at lower pH (higher hydrogen concentration) (Fig. 3). This effect can also be evidenced when the amount of condensed divalent Cd metal is measured as a function of the metal concentration in the subphase (Fig. 4). The addition of a monovalent ion to the subphase solution charges the monolayer. The equilibrium coefficient for monovalent ions is typically one to two orders of magnitude smaller than that of the divalent ions and therefore U_N is larger than that for the divalent ion. More importantly, because of the different form of the condensation expressions (28) and (34) for the monovalent and the divalent ions the residual charge on the monolayer has a different power-law dependence on U_N as compared to U_M [see Eqs. (31) and (36)] which further favors the electrical attraction mechanism. For sodium $q = -U_N^{1/3} \approx -0.28$ for our example while for the divalent calcium $q = -U_M^{1/2} \approx -0.04$. The charging of the monolayer that occurs when the monovalent ion concentration is increased, was noted by Helm and collaborators (Ref. 33) in a system with a single monovalent ion in the subphase of a lipid monolayer. They assumed, however, that the chemical equilibrium constant of dissociation K_N of the monovalent ion from the lipid is zero and therefore their calculation predicted a completely dissociated monolayer. We analyzed a system that contains a monovalent Na and also divalent Ca ions in the subphase. Our calculations provide here also good agreement with experiments where the divalent ion and the monovalent ion compete in their segregation to the liquid surface (Fig. 5). In Fig. 6 we show the amounts of condensed divalent metal, monovalent metal, and hydrogen, as well as the amount of monovalent metal attracted electrically to the surface calculated as a function of the monovalent ion concentration in the subphase. The concentration excess of the monovalent ion which is relatively small when the divalent ion neutralizes the monolayer becomes substantially larger when the monolayer is compensated with the monovalent ion. This is in agreement with the finding that monovalent compensated surfactant ions carry significantly more charge than their divalent counterparts.

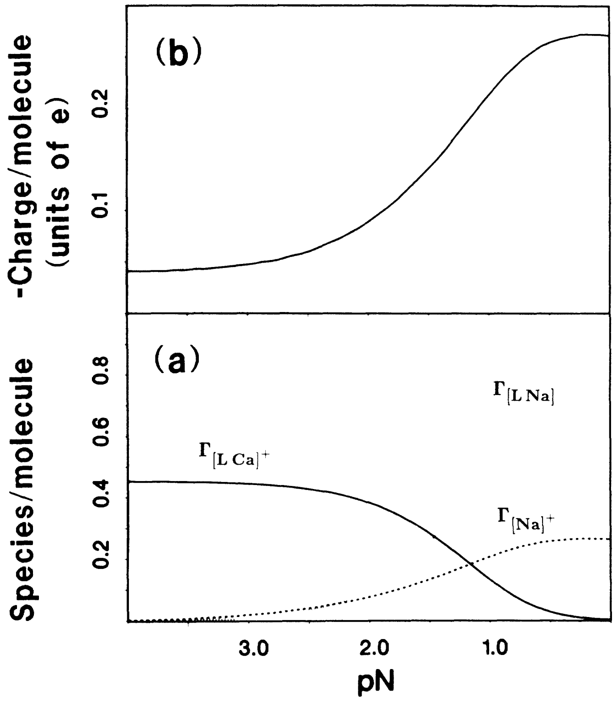

FIG. 6. Condensation (a) and accumulated charge (b) for the experimental conditions of Fig. 5 as a function of Na ion concentration $p\mathrm{N} = -\log_{10}\Phi^b_{\mathrm{Na}^+}$ in the subphase. The curves were calculated by solving the nonlinear Eq. (12). The equations of Sec. III provide a satisfactory approximation. At low Na-ion concentrations $\Phi^b_{\mathrm{Na}^+}$, the total charge on the monolayer is very small, $q = -0.04e/$(surfactant molecule) [Eq. (36)]. The divalent Ca ion is almost completely condensed on the monolayer in the form $[LM^+]$ with average fractional condensation $\Gamma_{LCa^+} \approx \frac{1}{2}(1+q) = 0.46$ [Eq. (37)], i.e., about every second surfactant molecule L is condensed with divalent Ca ion. The amount of Ca^{2+} ions electrically attracted to the surfactant for low Na concentrations $\Gamma_{\mathrm{Ca}^{2+}} = 0.04$ $e/$surfactant molecule is equal to the charge on the monolayer, is small, and is not indicated on the figure. The Ca concentration near the surface is, however, not negligible $\Phi^s_{\mathrm{Ca}^{2+}} = 0.29$ mol/l [Eq. (39)]. This concentration is required to have the Ca ions condense on the monolayer and neutralize it. When the bulk Na concentration $\Phi^b_{\mathrm{Na}^+}$ is raised, the surfactant monolayer is charged. Using (23) we obtain the charge on the monolayer to be $q = -0.28$ $e/$surfactant and the electrically attracted Na fraction to be $\Gamma_{\mathrm{Na}^+} = -q = 0.28/$(surfactant/molecule). The surface concentration of the Na ion $\Phi^b_{\mathrm{Na}^+} = 14.5$ mol/l is given by Eq. (25). Thus the monovalent ion exists in both states: condensed on the monolayer $[L\mathrm{Na}]$ and electrically attracted to the liquid monolayer interface Na^+.

V. DISCUSSION

A. Comparison with earlier models

In the past, attempts were made to understand experimental adsorption diagrams along the ideas of Langmuir for adsorption of gases on metals. This approach was suggested by Matsubara and his collaborators[9] and used by several researchers to interpret their adsorption data.[11-13] Their model considers the surfactant monolayer as a 2D lattice where each surfactant monomer is occupied by a condensed metal ion or a proton (the full condensation regime in our treatment $U_{\mathrm{H}} < 1$ and $U_M < 1$). They further suggest that the interaction between two neighboring surfactant monolayers would be strongly dependent on the type of ions condensed and their nearest neighbors and thus the energy difference ϵ between the two types of neighbors would require the modification of the equilibrium equations. This modification was implemented by having ϵ-dependent activities substituted in place of the bulk concentrations in the ordinary chemical equilibrium equations [such as Eq. (2) in this text]. From the fit of their model to experimental data they obtained a value for their phenomenological mixing parameter ϵ. The Langmuir-Bragg-type mixing model could describe gas adsorption on a 2D matrix. It is, however, inadequate for the description of the adsorption mechanism from electrolyte solution since it ignores the concentration variation of the constituent electrolyte ions $\Phi_{M^{2+}}$, Φ_{H^+}, and Φ_{N^+} near the surfactant charged interface due to the electrical attraction.[75] In reality our calculations show that the electrical attraction of the cations to the surface enhances the cation concentration *by several orders of magnitude* and is the primary effect that defines the adsorption-condensation characteristics. Matsubara *et al.* used bulk concentration values in their chemical equilibrium equation [similar to our Eq. (2)]. Therefore, his model required the introduction of an empirical parameter ϵ that had the effect of modifying the values of the concentrations and by substituting these empirical activities in place of concentrations in the chemical equilibrium equations. It is demonstrated here that the Poisson-Boltzmann solution captures the major features of the interaction of partially dissociated surfactant ions with the monovalent and divalent ions in the subphase solution. We were able to reproduce the main bulk of metal condensation data accumulated over some 40 years using the numerical solution of Eq. (12). No adjustable parameters were used and no new mechanisms had to be invoked in our model. We further showed that it is not necessary to resort to a numerical solution since for the ranges of interest for Langmuir systems simple analytical expressions provide a satisfactory approximation. The agreement between the experiments and the calculations presented here are also an indication that the interaction with neighboring-site ions are small enough to be ignored in evaluating the condensation state of the surfactant beyond the electrical interaction. Our calculation implicitly includes the change in the interaction within the surface charged monolayer by allowing the surfactant monolayer to acquire a *partially* neutralized state that is determined by solving equations (11) and (12) self-consistently.

B. The condensed and the attracted systems

Another result of our model is the realization that the metal ions in the proximity of the surfactant are always found in two distinct states: condensed on the monolayer and electrically attracted to it. One cannot exist without the other and the ratio between the two defines the dissociation level of the monolayer. The sum of the charges of the two $q'=q'_{\text{condensed}}+q'_{\text{attracted}}$ is equal (after normalization per one surfactant chain) to one electron charge $+e$ and thus maintains the neutrality of the system as a whole. The uncompensated charge left on the monolayer is $q=-e+q'_{\text{condensed}}$. This is the charge responsible for attracting the solute cations and for creating the concentration excess of the electrolyte ions in the subphase near the surfactant interface. This ion excess determines, through the chemical condenation equilibrium between the ions and the surfactant, the amount of charge that is actually condensed on the monolayer $q'_{\text{condensed}}$. We further find that surfactant systems can be divided into two groups: (i) systems that are condensation driven, and (ii) principally dissociated systems. Type (ii) monolayers primarily electrically attract the subphase ions but little chemical condensation takes place. This occurs in systems where the condensation energy cannot offset the electric energy stored in the excess electrolyte layer. We identified a simple criterion that identifies to which of the two a system belongs. Using equilibrium constants listed in the literature, we find that all the surfactant systems with a divalent metal ion and also, but to a lesser degree of completion, monovalent ion aqueous solutions of fatty acids satisfy the condensation conditions $U_{\mathrm{H}}<1$ and $U_M<1$ and belong to the first group.

C. Comparison between the condensed 2D surfactant systems and conventional 3D solution

The condensed systems of type (i) attempt to primarily minimize the free charge on the surfactant by having the positive ion condense on the monolayer and almost completely neutralize the negative monolayer charge. In order to do so, the monolayer controls the concentrations of the electrolyte ions near the surface Φ_i^s and brings them to a level that will satisfy a full chemical condensation. The surface concentration at which full condensation occurs depends on the chemical equilibrium constant of the surfactant-ion interaction and on the surface concentration of the monolayer, but is almost independent on the bulk subphase concentration (or any other bulk quantity). For this reason the surface concentration of these systems is (almost) completely independent of their bulk concentrations [Eqs. (33) and (39) in the text]. Therefore, even miniscule amounts of metal ion bulk impurities (10^{-11} mol/l in high-pH systems in some cases) result in substantial concentration near the surfactant and can dramatically alter the monolayer qualities. This buffering effect at the interface manifests itself in stabilizing the surface concentration and by neutralizing the charge on the monolayer. In Figs. 7 and 8 we compare the equilibrium condition obtained using our Poisson-Boltzmann equation (12) with the hypothetical system of "3D surfactant material" dissolved in the solution but with all other properties similar to the 2D monolayer system. In the 3D case the hydrogen condensation on the "3D surfactant" $\Phi_{[L\mathrm{H}]}^{3\mathrm{D}}$ is very small throughout the whole range of the divalent ion concentrations while the divalent ion concentration $\Phi_{[LM]}^{3\mathrm{D}}$ is negligible below $pM=4$ and then smoothly rises and obtains the maximum value 1 at about $pM=1.5$. Similarly the charge on the 3D surfactant is close to $-1e$ up to concentration of $pM=4$ and then rises smoothly and reaches the maximum value of $+1\ e$ by the time the metal is completely condensed on the monolayer. In our real 2D case, the electrochemical balance adjusts the concentrations of the different ions in the solution near the surfactant in order to minimize the charge on the monolayer. At low divalent ion concentrations the buffering effect of the sur-

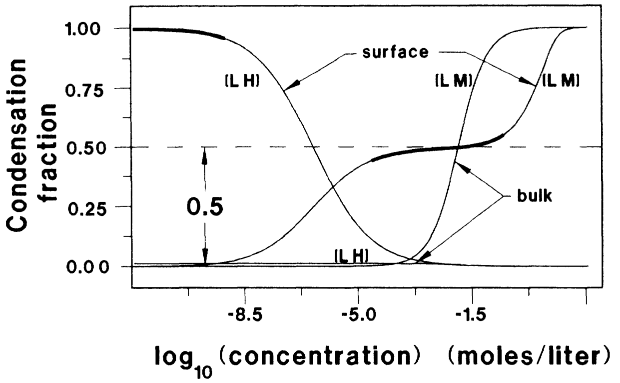

FIG. 7. Condensed divalent metal $[LM]$ and hydrogen $[L\mathrm{H}]$ for a surfactant monolayer spread on aqueous solution of divalent ion and the equivalent values that would have been obtained if the surfactant were to be dissolved in the solution. The buffering effect in the surfactant case stabilizes the values $[L\mathrm{H}]\approx 1$ and $[LM]\approx\frac{1}{2}$ required in order to electrically neutralize the charge on the surfactant. See the discussion in Sec. V.

factant monolayer, organized as a plane sheet on the liquid surface, manifests itself in raising the concentration of the hydrogen near the surface $\Phi^s_{\mathrm{H}^+}$ to a level that will maintain full condensation of the hydrogen on the surface ($\Gamma_{[L\mathrm{H}]}\lesssim 1$). When the bulk divalent ion concentration $\Phi^b_{M^{2+}}$ is raised, the concentrations of both ions at the surface $\Phi^s_{M^{2+}}$ and $\Phi^s_{\mathrm{H}^+}$ are adjusted so that the charge on the monolayer will still be negligible. At even higher divalent ion concentrations ($pM>5$) the concentration of the divalent ion at the surface $\Phi^s_{M^{2+}}$ obtains a value close to $1/K_M$ and stabilizes the condensation fraction of the divalent ion to be $\Gamma_{[LM]}\approx\frac{1}{2}$. At concentrations higher than $pM=0$ the monolayer cannot adjust the surface concentration efficiently any more, and the surface metal concentration $\Phi^s_{M^{2+}}$ rises. The monolayer is overcompensated by excessive divalent ion condensation and consequently is being charged (Fig. 8). The cation excess near the surface that is required for the complete neutralization seems at first to violate the charge neutrality of the system as a whole since the excess charge carried by the cations should be cancelled by the residual charge on the monolayer. The high surface concentration of the divalent cation is, however, achieved with only small total charge excess in the subphase solution. This is because the concentration profile of the dissolved cations is appropriately narrow [see Eqs. (27) and (41)]. The divalent ion concentration profile $P^2(z)$ would, with everything else similar, create a charge excess larger by the order of P_0 but also narrower as compared to that of the monovalent ion with concentration profile $P(z)$. This is consistent with our result that divalent ions have a considerably greater tendency to condense than monovalent ions and therefore the condensed monolayer carries a smaller net negative charge to compensate the charge on the ions attracted to the interface. However, a small residual charge on the surfactant is always necessary to provide the attraction for the ions in the subphase and even in condensed monolayers some charge is always left uncompensated for [Eqs. (23) and (36)]. When the system is monovalent ion condensed the net charge on the monolayer is larger than when this ion is absent from the solution. To neutralize the larger charge on the surfactant more net charge is also attracted to the surfactant. This effect is demonstrated in Fig. 6.

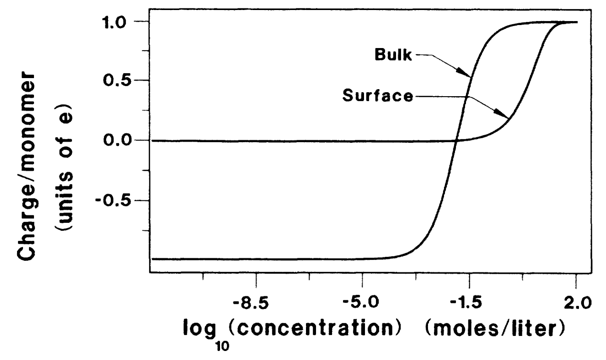

FIG. 8. The charge on the monolayer for the conditions of Fig. 7. In the hypothetical bulk condition the surfactant is first negatively charged and when the divalent ion concentration reaches a certain value it soon becomes positively charged. In the surfactant case the charge is neutralized for most of the concentration range of the divalent ion. For concentrations above $pM\approx 1$ the monolayer cannot control the concentration of the divalent ion near the surface and the monolayer gets to be positively charged.

D. General qualities of the monovalent and the divalent systems

By virtue of their almost complete neutrality the condensation driven condensed systems of type (i) lend themselves to a simple algebraic description. Their properties can be remapped into a condensation chart that would allow the determination of the state of the monolayer at specific concentrations of the different subphase ions. This same quality allowed us to give closed-form expressions to all the other relevant quantities of the monolayer such as residual charge on the monolayer, the falloff radius of the concentration profile, and the condensation fractions of the monovalent and divalent ions. It is important to note that these expressions take a different algebraic form for the monovalent and the divalent subphase ions. Also, the nature of the fully condensed state is completely different in the two systems. This difference may seem peculiar at first since the only difference between the two systems is the charge on the counterions, which could have suggested that the formulas for the two are scalable. It is therefore important to realize that the *ratio* between the charge on the dissociated surfactant molecule ($-e$) and the charge carried on a counterion $+e$ or $+2e$ is a characteristic quantity of the system and therefore the divalent or the monovalent ions constitute systems of different symmetry and are not independently scalable. Furthermore, Eqs. (28) and (34) contain only one characteristic parameter: either U_I or U_M, and neither of them contains bulk quantities. Therefore, the surface quantities—concentration, condensation, and charge—are completely independent of the bulk quantities for the pure divalent and monovalent systems and are not the result of the approximations used in solving Eqs. (28) and (34). Also, the "contact value theorem" of about 60-mV change in the potential per decade of monovalent ion concentration will be still valid in the condensed regime, as it is for the noncondensed Poisson-Boltzmann regime, but with a different coefficient [compare Eq. (13) with Eqs. (25) and (39)].

This is no more true when the subphase contains a mixture of divalent and monovalent ions. Then, even in the regime treated in this work the surface qualities are also dependent on the bulk concentrations. Equation (20) can be solved only after the substitution of P_0 in X_N and X_M. This leaves the bulk concentrations to be parameters that define the concentration enhancement.

E. The transition region between the monovalent and the divalent region

We have shown in Sec. III D that the condensation transition region is shifted by $\log_{10}(U_I^{-1/3})$ into the divalent dominant enhancement factor, i.e., into the region where the concentration enhancement factor is given by the divalent expression (38). It was also shown that the transition region halfwidth is $\Delta(\log_{10}P_0^I)/2 \approx 1.00$. Therefore, for systems with both monovalent and divalent components, and when U_0^I of the monovalent ions mixture given by Eqs. (29) and (30) is smaller than 10^{-3}, the condensation transition region will occur wholly in the region where the enhancement factor is given by Eq. (38). This celebrated result permits us to substitute the enhancement factor given by (38) in the surface equilibrium condition (43) and to derive a simple closed-form relation that describes the transition region surface state of the surfactant monolayer using bulk concentrations. We copy Eq. (44) here:

$$\Theta_s = \left[\frac{\Gamma_{LI}}{\Gamma_{LM}} \right]_s = \frac{K_I \Phi^b_{I^+}}{(K_M \Phi^b_{M^{2+}})^{1/2}} \; . \tag{46}$$

This expression should be compared with the 3D bulk solution equilibrium condition of the same materials

$$\Theta_b = \left[\frac{\Gamma_{LI}}{\Gamma_{LM}} \right]_b = \frac{K_I \Phi^b_{I^+}}{K_M \Phi^b_{M^{2+}}} \; . \tag{47}$$

Θ_b is different from Θ_s in the exponential dependence of Θ on the concentration and equilibrium constants of the divalent ion. The numerical results are also markedly different. Using Eq. (43) we obtain $\Theta_s = 0.93$ for an aqueous solution of 1×10^{-3} mol of Mn ion and $p\mathrm{H}=6$. It indicates that the surfactant is condensed with almost equal amounts of hydrogen and Mn ions. Using the bulk equilibrium expression would yield $\Theta_b = 11.7$ and that would have suggested that the surfactant is primarily hydrogen condensed. The condition $U_0^I < 1\times10^{-3}$ required for Eq. (43) to correctly approximate the transition region between the divalent and the monovalent condensed monolayer is stricter than the condition $U_0^I < 1$ required for the approximations for a monolayer constituted entirely of monovalent or divalent ions (Secs. III A, III B, and III C). It is still applicable to most of the Langmuir systems of interest. For a monolayer spread on a pure divalent solution and area of 20 Å^2/chain, $U_{\mathrm{H}} = 7.44\times10^{-8}$ and the system clearly satisfies this requirement. Thus, Eq. (43) describes adequately all the systems composed of divalent ions in pure water. We have used Eq. (46) to model the fractional condensations given in Figs. 2–5. They provide very good approximations to Eq. (12) for Figs. 2–4. The surface equilibrium equation approximation (46) deviates from the exact solution of Eq. (12) for the case where high concentration of sodium ion is added to the aqueous divalent solution. Sodium at the experimental conditions for Fig. 5 yields $U_{\mathrm{Na}} = 3.25\times10^{-2}$. From Eq. (30) for a mixture of two monovalent ions we obtain

$$\frac{1}{U_I} = \frac{1}{U_{\mathrm{Na}}} \frac{\Phi^b_{\mathrm{Na}}}{\Phi^b_I} + \frac{1}{U_{\mathrm{H}}} \frac{\Phi^b_{\mathrm{H}}}{\Phi^b_I} \; .$$

Using the last expression we find that a solution of Na ions in water would satisfy the requirement $U_0^I < 1\times10^{-3}$ if its concentration Φ^b_{Na} in the solution would be smaller than $1.28\times10^4\times\Phi^b_{\mathrm{H}}$. For a solution of pH 6, Eq. (43) can thus be useful up to Na^+ concentrations of ≈ 0.01 (mol/l). Accordingly the curve obtained using Eqs. (46) and (45) (dashed line on Fig. 5) shows a growing deviation from the solid line calculated using Eq. (12) for concentration values $\Phi^b_{\mathrm{Na}} > 0.01$ moles (below $p\mathrm{Na}=2.0$). Such a concentration is, however, rarely used in Langmuir monolayers.

F. Conclusion

We demonstrated that the Cartesian one-dimensional Poisson-Boltzmann-Stern formalism (the Gouy-Chapman-Stern equation) yields a surprisingly accurate quantitative description for the monovalent and divalent alkali-metal ion segregating from a dilute aqueous solution to a Langmuir monolayer spread on the surface of the solution. This we did by comparing experimental values of metal ions segregated next to the liquid surface to those values obtained from the PBS equation using the conventional equilibrium constants found in literature. The calculations presented here capture remarkably well the major features of the metal substituted monolayer. This is in view of the simplifications introduced in the assumption that the charge is uniformly distributed on the surface of the liquid following the Gouy-Chapman model.[34,35] We cannot, however, reproduce with this assumption the phase transitions predicted from kinks in the Π-A diagrams. Such transitions would require a discrete surfactant model and inclusion of the cooperative interaction that drives the transition.

We have also identified universal parameters that define the extent and nature of the metal ion condensation on the monolayer. They permit one to predict the state of a monolayer. A simple equilibrium equation for the monolayer condensation reaction has also been derived. Only *bulk* concentrations of the ions enter into this equation. The use of the universal parameters and the equilibrium equation eliminates the need for a numeric need to solve the Grahame equation numerically and suggests additional physical insight into the problem. Finally, our calculations may provide a clue to the origin of the in-plane structure of Langmuir-Blodgett (LB) monolayers.

(i) 50% of the surfactant molecules on a divalent ion solution are metal condensed and carry a positive charge. The other 50% are dissociated and carry a negative charge. It is therefore expected that the distance between two similar molecules would be different than that between two molecules with opposite charges. The smallest unit cell in this case would be orthorhombic rather than the triangular closed pack. In this structure each surfactant molecule would have four nearest neighbors of the opposite charge and two next-nearest neighbors of the same charge. This orthorhombic structure is indeed the symmetry that LB multilayers and monolayers acquire on a solid substrate.

(ii) Multilayers could be produced from many fatty acids and from their divalent ion soaps. It is considered impossible to build monovalent soap Langmuir-Blodgett multilayers. Our calculations indicate that monolayers compensated by monovalent ions are charged while the acid surfactant and the divalent substituted monolayers are neutralized. We suggest that the negatively charged monovalent monolayers are electrically attracted to the liquid and therefore are not likely to be withdrawn intact to a solid substrate.

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APPENDIX: THE POISSON-BOLTZMANN EQUATION

An idealized Poisson-Boltzmann system consists of a flat plane interface charged with a fixed surface charge density σ. We assume the interface to lie in the x-y plane (i.e., $z=0$). The semi-infinite volume with $z>0$ is electrically natural as a whole but contains positive and negative charged ions free to move in that volume. The electric potential $\Psi(z)$ originating with the surface charge σ and the charge distribution $\rho(\Psi(z))$ has to satisfy the Poisson equation

$$\frac{\partial^2\Psi(z)}{\partial z^2}=-\frac{4\pi}{\epsilon}\rho(\Psi(z)) \tag{A1}$$

with the given Neuman boundary condition of surface charge σ on the interface.

The charge density $\rho(z)$ is a function of the concentrations $\Phi_i(\Psi(z))$ of the different counterions and co-ions A_i in the solution at a distance z from the interface

$$\rho(z)=\rho((\Phi_i(\Psi(z)))) \ . \tag{A2}$$

In Eqs. (A1) and (A2) $\Psi(z)$ is the electric potential at a distance z from an interface. The distinctive signature of the PBE is the dependence of the charge density ρ on the distance from the interface *only through the electric potential.* This allows for a simple integration of (A1) resulting in

$$E(z)=-\frac{\partial\Psi}{\partial z}=\left[\frac{8\pi}{\epsilon}\int_{\Psi=0}^{\Psi(z)}\rho(\Psi')d\Psi'\right]^{1/2} . \tag{A3}$$

The potential at the interface $\Psi(z=0)=\Psi_0$ is obtained from the boundary condition

$$E(z=0)=\frac{4\pi}{\epsilon_0}\sigma=\left[\frac{8\pi}{\epsilon}\int_{\Psi=0}^{\Psi_0}\rho(\Psi')d\Psi'\right]^{1/2} , \tag{A4}$$

the last being known as the Grahame equation.[76] σ is the surface charge density of the system at the interface.

The electric potential profile is obtained by second integration of (A3):

$$z+z_0=\int\frac{d\Psi}{\left[\frac{8\pi}{\epsilon}\int_{\Psi=0}^{\Psi(z)}\rho(\Psi')d\Psi'\right]^{1/2}} . \tag{A5}$$

z_0 is an integration constant defined by substituting the electric potential Ψ_0 at the interface ($z=0$) obtained by solving the boundary Grahame equation (A4).

In the classical Poisson-Boltzmann equation σ has a fixed given value. It was first suggested by Stern that the charged static ions at the interface responsible for the charge density σ could react with the counter ions in the solution next to the interface (responsible for the charge density ρ) and thus reduce the net surface charge at the interface.[77] In such model the net surface charge σ depends on the concentration of the different counter ions at the interface $[\Phi_i^s(\Psi_0)]=[\Phi_i(z=0)]$ so that

$$\sigma=\sigma[\Phi_i^s(\Psi_0)] \ . \tag{A6}$$

An electrochemical system is defined by substituting an explicit form for $\rho(\Psi(z))$ in Eqs. (A3) and (A4) and for the net charge density $\sigma(\Psi_0)$ in Eq. (A6).

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