Effect of Surface Ionization on Wetting Layers

R. F. Kayser
Thermophysics Division, National Bureau of Standards, Gaithersburg, Maryland 20899

(Received 13 December 1985)

We generalize a surface ionization model due to Langmuir to liquid mixtures of polar and nonpolar components in contact with ionizable substrates. When a predominantly nonpolar mixture is near a miscibility gap, thick wetting layers of the conjugate polar phase form on the substrate. Such charged layers can be much thicker than similar wetting layers stabilized by dispersion forces. This model may explain the 0.4- to 0.6-μm-thick wetting layers formed in stirred mixtures of nitromethane and carbon disulfide in contact with glass.

PACS numbers: 68.15.+e, 68.45.Gd, 82.65.Fr, 87.20.Cn

In a beautiful paper in 1938, Langmuir[1] developed a model that is the basis for our present understanding of thick wetting layers of liquid water that form on glass in contact with slightly undersaturated water vapor. The model arose from a calculation of the forces between identically charged plates immersed in an electrolyte solution with Debye screening length large compared to the plate spacing. The results apply by analogy to a single plate of glass in contact with undersaturated water vapor in the case where chemical groups on the surface of the glass can dissociate. If hydroxyl groups dissociate (an element of our model), they leave the surface with a negative surface charge density. The associated counterions, in this case solvated protons, distribute themselves in a layer of liquid water at the surface in accordance with the Poisson-Boltzmann equation. The concentration of ions at the liquid-vapor surface of the water layer determines the equilibrium vapor pressure of the layer. As the layer thickens, this concentration decreases and the vapor pressure of the layer rises until it equals the ambient pressure of the undersaturated water vapor. I denote the thickness of the wetting layer by d and measure the undersaturation of the vapor by L, the height of the plate above the location of bulk coexistence of liquid and vapor water. The formula derived by Langmuir then takes the form

$$d=(kT/ze)(\pi^2\epsilon\epsilon_0/2\Delta\rho gL)^{1/2}, \tag{1}$$

where kT is Boltzmann's constant times the absolute temperature, z is the ionic valence, e is the electronic charge, ϵ is the dielectric constant of water, ϵ_0 is the permittivity of free space, $\Delta\rho$ is the mass density difference between liquid and vapor, and g is the gravitational acceleration. (I use SI units throughout.) A remarkable feature of the Langmuir formula is that it contains no adjustable parameters. With the values $T=300$ K, $\epsilon=80$, $z=1$, $g=9.8$ m$^2\cdot$s^{-1}, $\Delta\rho=1000$ kg$\cdot$m^{-3}, and $L=10^{-2}$ m, we find a typical equilibrium layer thickness of $d=0.15$ μm, a result which has been confirmed experimentally by Derjaguin and Churaev[2] and by Pashley and Kitchener.[3]

It is clear that the forces that give rise to wetting layers 0.15 μm thick must be very long ranged. That d varies as $L^{-1/2}$ shows that these forces are of even longer range than dispersion forces,[4] which would give the dependence $L^{-1/3}$ or $L^{-1/4}$, depending on whether or not retardation effects are taken into account. Indeed, the thickness of the water layer predicted[5] by the theory of dispersion forces without retardation is 4 nm for $L=10^{-2}$ m, only 3% of the thickness estimated above and observed experimentally! Many recent measurements of the thicknesses of wetting layers in binary liquid mixtures have in fact given thicknesses that cannot be explained by the theory of dispersion forces. My primary goal is to provide an alternative mechanism to dispersion forces, which, up to now, have been the focus of all the attention. While some of the observed thicknesses might be consequences of nonequilibrium effects,[6] I shall argue that in other cases the surface-ionization mechanism is dominant.

Let us consider the situation in Fig. 1, where two liquid phases of a binary mixture are in equilibrium at a height L above the substrate at the bottom. Let us assume that the lighter phase (β) consists mostly of a polar component, and the denser phase (α) mostly of a nonpolar component. Let us assume throughout that there is no added electrolyte and a sufficiently small

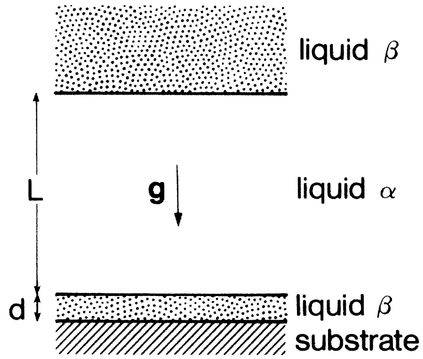

FIG. 1. A binary liquid mixture in contact with an ionizable substrate near a miscibility gap of the mixture. Wetting layers of phase β form when proximity to β favors ionization of the substrate.

concentration of electrolyte impurities to make the Debye screening length in the mixture much larger than the thickness of the wetting layer. For all practical purposes, the Debye length is infinite. Just as for the case of wetting layers of liquid water, we find that surface ionization of the substrate can lead to thick wetting layers of the β phase, much thicker than can be reconciled with the theory of dispersion forces. We also find that wetting layers can form even when dispersion forces attract the α phase in preference to the β phase. Later, I discuss some recent experiments[7] on nitromethane-carbon disulfide mixtures in contact with glass which might constitute an example of just such a case. A further possibility that emerges from the analysis is that wetting layers stabilized by surface ionization can disappear abruptly as the temperature is increased toward a consolute point. I note that this theory is the first for surface ionization in nonaqueous systems.

I now outline a derivation of a generalization of the Langmuir equation that is applicable to the situation in Fig. 1 and reduces to Eq. (1) in a limiting case. Let us assume that the charge density on the surface of the substrate has a value σ less than zero, and adopt a coordinate system in which x is measured upward from the substrate. The fluid side of the wetting layer is then located at $x=d$. Electrical neutrality of the system requires that

$$ze\int n(x)\,dx=-\sigma, \tag{2}$$

where $n(x)$ is the number density of counterions at height x above the substrate and z is their valence. The electric potential, $\phi(x)$, must be continuous and must satisfy Poisson's equation in both the β-like layer and in the macroscopic α phase outside. Let us assume that the α phase occupies the entire region $x>d$; this causes a negligible error in the potential when $L>>d$. Thus,

$$\begin{aligned}-\epsilon_\beta\epsilon_0\phi''(x)&=zen_\beta(x), \quad d>x\geqslant 0,\\ -\epsilon_\alpha\epsilon_0\phi''(x)&=zen_\alpha(x), \quad x>d,\end{aligned} \tag{3}$$

where the primes denote differentiation with respect to x. Let us assume that the counterion number densities are given by Boltzmann distributions,

$$\begin{aligned}n_\beta(x)&=n_\beta(d)\exp\{-ze[\phi(x)-\phi(d)]/kT\},\\ n_\alpha(x)&=n_\alpha(d)\exp\{-ze[\phi(x)-\phi(d)]/kT\}.\end{aligned} \tag{4}$$

Combining these with Eq. (3) we obtain the usual Poisson-Boltzmann equations for the potentials. The compositions of the α and β phases are assumed to be unaltered by the dissolution of counterions from the substrate surface. To complete the specification of the problem we need to specify the boundary conditions. In place of Eq. (2) I use

$$-\epsilon_\beta\epsilon_0\phi'(0)=\sigma. \tag{5}$$

I also require that $\phi'(x)$ vanish at infinity and that the x component of the electric displacement be continuous at $x=d$:

$$\epsilon_\beta\phi'(d-)=\epsilon_\alpha\phi'(d+). \tag{6}$$

Finally, let us specify the relative solubilities of the counterions in the α and β phases in local equilibrium at $x=d$. Simply write

$$n_\alpha(d)/n_\beta(d)=f, \tag{7}$$

where $0\leqslant f\leqslant 1$. If we set $f=0$ we recover the Langmuir model, which has vanishing electric field at the edge of the wetting layer and zero ion concentration outside. Nonzero values of f mean that ions can "leak" out of the β layer into the α phase, an effect that leads to a decrease in the thickness of the layer. After decreasing monotonically from a large value at the substrate surface, the counterion number density is discontinuous at $x=d$.

Two relations useful in solving for $\phi(x)$ and $n(x)$ are obtained by differentiation of Eq. (4) with respect to x, followed by use of Eqs. (3) and (4) and reintegration with respect to x:

$$\begin{aligned}n_\beta(x)&=n_\beta(0)-\left(\frac{\sigma^2}{2\epsilon_\beta\epsilon_0kT}\right)+\left(\frac{\epsilon_\beta\epsilon_0}{2kT}\right)[\phi'(x)]^2,\\ &\qquad\qquad d>x\geqslant 0,\\ n_\alpha(x)&=\left(\frac{\epsilon_\alpha\epsilon_0}{2kT}\right)[\phi'(x)]^2, \quad x>d.\end{aligned} \tag{8}$$

With these and Eqs. (6) and (7) we find

$$n_\beta(0)-(\sigma^2/2\epsilon_\beta\epsilon_0kT)=n_\beta(d)(1-f\epsilon_\alpha/\epsilon_\beta). \tag{9}$$

With this and Eqs. (3) and (8) one can derive

$$\begin{aligned}F''(x)&=-Z^2d^{-2}F(x), \quad d>x\geqslant 0,\\ F''(x)&=0, \quad x>d,\end{aligned} \tag{10}$$

where

$$F(x)=\exp[ze\phi(x)/2kT], \tag{11}$$

$$Z^2=d^2z^2e^2n_\beta(d)(1-f\epsilon_\alpha/\epsilon_\beta)/2\epsilon_\beta\epsilon_0kT. \tag{12}$$

These equations are easily solved and $n_\beta(d)$ and the constants of integration calculated from the boundary conditions. We find that $n_\beta(d)$ is determined by Eq. (12) and the transcendental equation

$$Z=\tan^{-1}[(X-Y)/(XY+1)], \tag{13}$$

where

$$X=(d/l)/Z, \tag{14}$$

$$l=2kT\epsilon_\beta\epsilon_0/ze|\sigma|, \tag{15}$$

$$Y=[(f\epsilon_\alpha/\epsilon_\beta)/(1-f\epsilon_\alpha/\epsilon_\beta)]^{1/2}. \tag{16}$$

The quantity l is a characteristic length.

I display the forms of $\phi'(x)$ and $n(x)$ for the case of a single fluid in contact with an ionizable substrate ($f=1, \epsilon_\beta = \epsilon_\alpha \equiv \epsilon$):

$$\phi'(x) = (2kT/ze)/(l+x), \tag{17}$$

$$n(x) = (2\epsilon\epsilon_0 kT/z^2e^2)/(l+x)^2. \tag{18}$$

These dependences illustrate the long-range nature of unscreened electrostatic interactions.

To calculate the equilibrium layer thickness let us first consider the configuration in Fig. 1 without gravity. The pressures in the β layer and in the α phase are then constant but unequal. By "pressure" I mean the xx component of the pressure tensor. The pressure in the β layer over that in the α phase is given by

$$\Pi = [n_\beta(d) - n_\alpha(d)]kT - \frac{\epsilon_0}{2}\{\epsilon_\beta[\phi'(d-)]^2 - \epsilon_\alpha[\phi'(d+)]^2\}. \tag{19}$$

The first term is the difference between the ideal-gas pressures of the counterions at $x=d$ and the second is the difference between the xx components of the Maxwell stress tensor. We can use Eqs. (8) and (9) to rewrite Π in the form

$$\Pi = n_\beta(d)(1 - f\epsilon_\alpha/\epsilon_\beta)kT. \tag{20}$$

Let us identify the constant pressure in the α phase with p_0, the pressure at the upper α-β interface. The constant pressure in the β layer is then $p_0 + \Pi$, and it is clear that in the absence of gravity the layer would be infinitely thick. Let us now consider the effects of gravity on the pressures in the α and β phases at $x=d$. The pressure in the α phase becomes $p_0 + \rho_\alpha gL$, while that in the β layer is given by $p_0 + \Pi + \rho_\beta gL$. Here ρ_α and ρ_β are the mass densities of the bulk α and β phases. The equilibrium layer thickness $d(L)$ is determined by requiring that these two pressures be equal. With Eqs. (12)–(16) we obtain our principal result:

$$d = D\tan^{-1}[(D - Yl)/(DY + l)], \tag{21}$$

where

$$D = (2kT/\pi ze)(\pi^2\epsilon_\beta\epsilon_0/2\Delta\rho gL)^{1/2}. \tag{22}$$

D is $2/\pi$ times the thickness in Eq. (1) and $\Delta\rho = \rho_\alpha - \rho_\beta$. Nonzero values of f (or, equivalently, Y) are important when the α and β phases are similar, as occurs near consolute points. Note that d will vanish if $D - Yl$ vanishes below a consolute point. The effects of dispersion forces can be included by addition of a term $-A/6\pi d^3$ to Π, where A is the Hamaker constant.[8]

For water layers on glass we can set $Y=0$ and $\epsilon_\beta = \epsilon$ in Eq. (21), and assume that $D \gg l$. This gives the Langmuir thickness, $d = \pi D/2$, which is therefore valid when either the layer thickness or the surface charge density is sufficiently large. To check the condition $D \gg l$, let us assume that the surface charge arises from dissociation of hydroxyl groups on the glass. The dissociation reaction and equilibrium constant are given by

$$\mathrm{OH_{surf}} \leftrightarrow \mathrm{O^-_{surf}} + \mathrm{H^+}, \tag{23}$$

$$K_{\mathrm{eq}} = [\mathrm{O^-_{surf}}][\mathrm{H^+}]/[\mathrm{OH_{surf}}], \tag{24}$$

where $[\mathrm{H^+}]$ is the molar concentration at the substrate surface. For $n(0) \gg n(d)$, Eq. (9) implies that $10^3 N_0[\mathrm{H^+}] = \Lambda^2\sigma_0^2/2\epsilon\epsilon_0 kT$, where N_0 is Avogadro's number. We have put $\sigma = \Lambda\sigma_0$, with Λ the fraction of hydroxyl groups dissociated and σ_0 the charge density on a completely ionized surface[9]: $\sigma_0 = -4.6e$ $\mathrm{nm}^{-2} = -0.74$ C m^{-2}. For $\Lambda \ll 1$ we can also write $[\mathrm{O^-_{surf}}]/[\mathrm{OH_{surf}}] = \Lambda/(1-\Lambda) \simeq \Lambda$. With these results Eq. (23) implies that

$$\Lambda = 10(2\epsilon\epsilon_0 N_0 kT K_{\mathrm{eq}}/\sigma_0^2)^{1/3}. \tag{25}$$

To estimate Λ we take[9] $-\log_{10}[K_{\mathrm{eq}}/(1\ \mathrm{mol\ dm^{-3}})] = 6.8$, $T = 300$ K, and $\epsilon = 80$. This gives $\Lambda = 0.0010$. Even in water the degree of dissociation is rather small. The length l in Eq. (15) now has the value 50 nm, and with the result $d = 0.15$ μm ($L = 10^{-2}$ m) one finds $D/l \simeq 2$. This simple dissociation model therefore gives a surface charge density not quite large enough to justify the Langmuir limit. The value of d calculated directly from Eq. (21) is 0.10 μm.

Wetting layers 0.4–0.6 μm thick have been observed in continuously stirred mixtures of nitromethane and carbon disulfide in contact with borosilicate glass.[7] The β phase in these mixtures is rich in nitromethane (the polar component), and the α phase is rich in carbon disulfide. The measurements of such thick layers cannot be reconciled with the theory of van der Waals forces in any case. Moreover, the Hamaker constant for the system "glass-β-α" must be negative for stable wetting layers of phase β (with the sign convention of Refs. 4 and 8), but calculations based on the Dzyaloshinskii-Lifshitz-Pitaevskii theory[4] show that it is positive: The preferred order of the phases is therefore "glass-α-β." I will argue that the very thick wetting layers are caused by the combined effects of surface ionization and continuous stirring. Only the measurements made at coexistence 3 K or more below the consolute point at $T_c = 335$ K are considered here.

The sign of the Hamaker constant was determined by evaluation of $F(d)$ in Eq. (4.13) of Ref. 4, where $F(d)d^3$ is a generalized Hamaker constant that includes retardation and nonadditivity of intermolecular forces. It was found that $F(d)$ was positive for all values of d. I plan to publish the details of these calculations elsewhere.[10] The Dzyaloshinskii-Lifshitz-Pitaevskii theory should apply to the thick films observed far from T_c because the observed thicknesses are much larger than the range of correlations in the mixture. The required inputs are the frequency-dependent dielectric constants of the glass, α, and β phases. I used the Clausius-Mosotti relation and data from the literature to construct Ninham-Parsegian representations with ultraviolet frequencies determined by Cauchy plots.[5] The sign of $F(d)$ was insensitive to large changes in the input frequencies. $F(d)$ also remained positive but increased in magnitude when lower-energy resonances were used. This primarily reflects the fact that the polarizabilities of phase α, phase β, and glass, respectively, are not ordered monotonically at zero frequency.

As noted above, the mixtures were subjected to continuous gentle stirring at the upper α-β interface (see Fig. 1). The stirring rates Ω were sufficiently slow ($\Omega \simeq 2\pi$ rad$\cdot$s^{-1}) that the interface waved but did not break up.[7] It has been shown in an idealized model[6] that stirring moves the effective plane of bulk two-phase coexistence (the upper α-β interface) closer to the wetting layer by a factor L/L_{eff}. L_{eff}, which is identified with the thickness of the diffusion boundary layer near the substrate surface, is given by

$$L_{\text{eff}} = D_\alpha^{1/3} \nu_\alpha^{1/6} \Omega^{-1/2}. \qquad (26)$$

D_α is the mutual diffusion coefficient in the α phase and ν_α is its kinematic viscosity. With $D_\alpha = 10^{-9}$ m$^2\cdot$s^{-1}, $\nu_\alpha = 10^{-6}$ m$^2\cdot$s^{-1}, and $\Omega = 2\pi$ rad$\cdot$s^{-1}, we obtain $L_{\text{eff}} = 40$ μm. Stirring can clearly lead to small effective values of L.

To apply the surface ionization model let us set $f = 0$ and estimate several properties at $T = 325.10$ K $[(T - T_c)/T_c = -0.03]$. With the mixture data of Greer *et al.*[11] and data for the pure components we find $\epsilon_\alpha = 3.2$, $\epsilon_\beta = 9.7$, $\Delta\rho = 100$ kg$\cdot$m^{-3}. To calculate Λ let us use

$$K_{\text{eq}}(\beta) = K_{\text{eq}} \exp[(E/kT)(\epsilon^{-1} - \epsilon_\beta^{-1})], \qquad (27)$$

where K_{eq} and ϵ have the values assumed earlier for water. E is the energy of an O—H bond. With $E \simeq N_0^{-1} 500$ kJ$\cdot$mol^{-1} we obtain $\Lambda = 1.9 \times 10^{-6}$. This degree of dissociation is $\frac{1}{500}$ that obtained for water and illustrates the extreme sensitivity of surface ionization to the dielectric constant of the neighboring fluid. For $\sigma_0 = -0.74$ C m^{-2} and $L = L_{\text{eff}} = 40$ μm we obtain $d = 0.9$ μm. This result shows that stirring combined with surface ionization can lead to very thick wetting layers. A nonzero value of f would reduce the estimate of d, but f at this temperature is very small because of the large difference between ϵ_α and ϵ_β. Without stirring we set $L = 10^{-2}$ m and obtain a wetting layer of thickness $d = 4.0$ nm. It is likely that van der Waals forces favoring the "glass-α-β" ordering of the phases would destabilize such a thin wetting layer. This suggests the possibility of a transition from wetting to nonwetting as the stirring rate is decreased.

We may note that the data of Wu, Schlossman, and Franck[7] imply that d varies as $(T - T_0)^{-1/4}$ with T as one approaches the α-β phase boundary at $T = T_0$. This behavior is consistent with a wetting layer stabilized by retarded van der Waals forces. I have not been able to reconcile this result, particularly the amplitude of the power law, with either the theory presented here or the theory of dispersion forces.

In conclusion, wetting layers stabilized by surface ionization can exhibit complex behavior as a function of temperature because of "leakage" (nonzero values of f) and because of the exponential dependence of Λ on ϵ_β. Added salt, variation of pH, and chemical alteration of the substrate surface can be used to control the surface ionization mechanism.

The author acknowledges useful discussions with Dr. M. R. Moldover and Professor C. Franck. This work has been supported in part by NASA under Contract No. H-27954-B.

---

[1] I. Langmuir, Science **88**, 430 (1938).

[2] B. V. Derjaguin and N. V. Churaev, J. Colloid Interface Sci. **49**, 249 (1974), and references therein.

[3] R. M. Pashley and J. A. Kitchener, J. Colloid Interface Sci. **71**, 491 (1979).

[4] I. E. Dzyaloshinskii, E. M. Lifshitz, and L. P. Pitaevskii, Adv. Phys. **10**, 165 (1961).

[5] D. B. Hough and L. R. White, Adv. Colloid Interface Sci. **14**, 3 (1980).

[6] R. F. Kayser, M. R. Moldover, and J. W. Schmidt, "What Controls the Thicknesses of Wetting Layers?," J. Chem. Soc. Faraday Trans. 2 (to be published).

[7] X. Wu, M. Schlossman, and C. Franck, Phys. Rev. B **33**, 402 (1986).

[8] J. N. Israelachvili, *Intermolecular and Surface Forces* (Academic, Orlando, 1985), Chap. 11.

[9] R. K. Iler, *The Chemistry of Silica* (Wiley, New York, 1979).

[10] R. F. Kayser, to be published.

[11] S. C. Greer, B. K. Das, A. Kumar, and E. S. R. Gopal, J. Chem. Phys. **79**, 4545 (1983).