Wetting layers in electrolyte solutions

R.F. Kayser

To cite this version:


HAL Id: jpa-00210769
https://hal.archives-ouvertes.fr/jpa-00210769
Submitted on 1 Jan 1988

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Wetting layers in electrolyte solutions

R. F. Kayser

Thermophysics Division, National Bureau of Standards, Gaithersburg, MD 20899, U.S.A.

(Reçu le 13 octobre 1987, révisé le 17 décembre 1987, accepté le 18 décembre 1987)

Résumé. — Lorsqu'un mélange de liquide non polaire et de liquide polaire est mis en contact avec un substrat chimiquement ionisable, il peut y avoir formation d'une couche mouillante contenant essentiellement la phase polaire. On considère ici l'effet sur cette couche mouillante d'un sel ajouté. Dans la limite des faibles concentrations en sel, l'épaisseur d'équilibre se réduit à un résultat obtenu précédemment. Dans la limite des fortes concentrations en sel, l'épaisseur se réduit à une longueur d'écran de Debye multipliée par une fonction de deux paramètres sans dimensions.

Abstract. — When a predominantly nonpolar mixture is in contact with a chemically ionizable substrate, thick wetting layers of a predominantly polar phase can form on the substrate. This paper considers the effects of added salt on such layers. In the limit of low salt concentrations, the equilibrium thickness reduces to a result previously derived by the author. In the limit of high salt concentrations, the thickness reduces to a Debye screening length times a known function of two dimensionless parameters.

1. Introduction.

Figure 1 shows two partially miscible phases of a binary liquid mixture coexisting in a gravitational field at a height $L$ above a solid substrate. When phase $\beta$ wets the solid, a thin layer of phase $\beta$ can intrude between phase $\alpha$ and the solid. The equilibrium thickness of such a layer is determined by a competition between the forces responsible for wetting and the gravitational field tending to destabilize the layer [1].

Dzyaloshinskii, Lifshitz, and Pitaevskii [2] (DLP) have shown that dispersion forces can stabilize relatively thick layers of phase $\beta$, layers whose equilibrium thickness, $d$, is much larger than the correlation length, $\xi$, in either fluid phase. In the limit of thin films, DLP obtain

$$2Wd^{-3} = \Delta \rho g L,$$  \hspace{1cm} (1)

Where $W$ is a generalized Hamaker constant and $\Delta \rho = \rho_\alpha - \rho_\beta$ is the mass density difference between phases $\alpha$ and $\beta$. A typical value of $2W/\Delta \rho$ is $10^{-24}$ m$^5$ s$^{-2}$, which implies that dispersion forces can stabilize wetting layers that are tens of nanometers thick for $L$ on the order of 1 cm. This paper considers only layers for which $d \gg \xi$ and $L \gg d$.

In addition to dispersion forces, Kayser [3] has shown that electrostatic forces can sometimes stabilize thick wetting layers of phase $\beta$. This mechanism can predominate when phase $\beta$ is predominantly polar, phase $\alpha$ is predominantly nonpolar, and the substrate is ionizable.

This paper considers the effects of added salt on wetting layers stabilized by electrostatic forces. It further generalizes Langmuir's formula [4], which was originally derived for water layers on glass in contact with slightly undersaturated water vapor. The analysis is closely related to that involved in calculations of the forces between identical plates immersed in aqueous electrolyte solutions [5]. The force depends on the concentration of ions at the
midplane compared to bulk, and the fluid between either of the plates and the midplane is then a model for a wetting layer.

There are two principal differences between this work and previous work. First, the emphasis is on wetting and phase separation in binary liquid mixtures. One can not apply previous results based on force calculations because these assume that the concentration of ions outside of the wetting layer is zero. In the mixtures considered here, ions can « leak out » of the wetting layer into an adjoining fluid which need not have a greatly different chemical composition. Second, the emphasis is on the wetting layer thickness in an external field (controlled by L), not on the forces between interfaces or plates. Thus, one can derive an explicit expression for the equilibrium wetting layer thickness as a function of external field, even though the corresponding expression for force as a function of separation does not exist. The new expression is germane to experiments ongoing at Cornell [6].

Section 2 describes the physical situation and gives the final results for the equilibrium wetting layer thickness with added salt, Section 3 contains the mathematical details, and Section IV discusses generalizations and relevant experimental situations.

2. Physical picture and results.

When water at room temperature is in equilibrium with its vapor one centimeter below a glass plate, water layers 150 nanometers thick form on the plate [7]. Our understanding of such layers traces back to a calculation by Langmuir [4]. When in contact with a layer of water, glass becomes electrically charged (e.g., hydroxyl groups on the surface of the glass dissociate). The concentration of dissolved counterions (e.g., solvated protons) decreases from a large value at the glass surface to a low value at the edge of the water layer. The latter concentration decreases as the layer thickness increases. Because the counterions lower the vapor pressure of the layer, the layer adjusts its thickness until the vapor pressure of the layer equals the pressure of the vapor immediately outside.

This section generalizes these ideas to the situation in figure 1. The model assumes that phase β can induce a charge density on the surface of the solid, that the resulting counterions are relatively insoluble in phase α, and that the charge density is sufficiently high that dispersion forces are negligible. The model also considers, for the first time, the effects of added salt. When the equilibrium concentration of salt in phase β becomes sufficiently large, screening should reduce the effective charge on the solid surface, leading to a reduction in the equilibrium thickness of the wetting layer. Any mixture of polar and nonpolar molecules that separates into a dense nonpolar phase (α) and a less dense polar phase (β) that wets an ionizable substrate would be an example of a system likely to meet these criteria.

In figure 1, let z denote the distance above the solid, with the gravitational field g acting downward. Assume that the solid has a surface charge density Σ and that the associated counterions have a valence z (unsigned). Assume that the added salt is a z-z electrolyte with concentration n in bulk phase β and concentration fn, f ≪ 1, in bulk phase α. Assume that the partition coefficient for the counterions is also f. Let β−1 denote Boltzmann’s constant times the absolute temperature, −e the electron charge, εβ (εα) the static dielectric constant of phase β (α), and ε0 the permittivity of free space. All equations use SI units throughout.

The final expression for the equilibrium wetting layer thickness, derived in section 3, is

\[
d = D \left( 1 + \kappa^2 \right)^{-1/2} \left[ F \left( \tan^{-1} \left( D/\ell \right) \right) m - F \left( \tan^{-1} Y/m \right) \right],
\]

where \( F(\psi|m) \) is an elliptic integral of the first kind [8],

\[
F(\psi|m) = \int_0^\psi d\theta \left( 1 - m \sin^2 \theta \right)^{-1/2},
\]

and

\[
D = \left[ 2 \varepsilon_\beta \varepsilon_0 / (\beta^2 z^2 e^2 \Delta \rho \, g L) \right]^{1/2}
\]

\[
\kappa^2 = 2 \beta z e \varepsilon_0 / (\varepsilon_\beta \varepsilon_0)
\]

\[
\ell = 2 \varepsilon_\beta \varepsilon_0 / (\beta z e |\Sigma|)
\]

\[
m = \kappa^2 D^2 / (1 + \kappa^2 D^2)
\]

\[
Y = \left[ (f \varepsilon_\alpha / \varepsilon_\beta) / (1 - f \varepsilon_\alpha / \varepsilon_\beta) \right]^{1/2}.
\]

Of the lengths D, κ, and \( \pi D/2 \) is the wetting layer thickness in the Langmuir model (see below), \( \kappa^{-1} \) is the Debye screening length in bulk phase β, and \( \ell \) is the distance from a surface with charge density Σ at which the potential energy of a charge is \( \beta^{-1} \). Of the dimensionless quantities m and Y, m is a measure of the importance of the effects of added salt, and Y is a measure of the relative extent to which ions are soluble in phases α and β.

Equation (2) admits several simple limiting cases. Consider first the case of low salt concentration, \( m \ll 1 \), where the effects of added salt are negligible. Because \( F(\psi|m) \) approaches ψ for small m, d becomes [3]

\[
d = D \left[ \tan^{-1} \left( D/\ell \right) - \tan^{-1} Y \right] = D \tan^{-1} \left[ (D - Y \ell) / (D Y + \ell) \right].
\]

In the limit of high charge density, D is much larger than \( \ell \), and this simplifies to

\[
d = D \tan^{-1} \left( 1/Y \right).
\]
With the additional assumption that $Y$ is small, this becomes

$$d = \pi D/2,$$

which is the Langmuir result for the wetting layer thickness. Thus, equation (3) extends the Langmuir result to the case of arbitrary surface charge density, and it includes the possibility that the counterions are soluble in phase $\alpha$, i.e., that they can « leak out » of phase $\beta$. Note that $d$ is independent of $\Sigma$ and varies as $L^{-1/2}$ when $\Sigma$ is sufficiently large, in contrast to the $L^{-1/3}$ dependence for nonretarded dispersion forces (see Eq. (1)). When $\Sigma$ is not large, the dependence of $d$ on $L$ is more complicated and $d$ depends explicitly on $\Sigma$ (see Sect. 4).

Now consider the case of high salt concentration, $m \approx 1$. Because $F(\psi|m)$ approaches $\ln [\sec \psi + \tan \psi]$ when $m$ approaches unity, $d$ becomes

$$d = \kappa^{-1} \left\{ \ln [X + (1 + X^2)^{1/2}] - \ln [Y + (1 + Y^2)^{1/2}] \right\}. \quad (4)$$

where $X = D/\ell$. When $D \gg \ell$ and $Y \ll 1$, this reduces to

$$d = \kappa^{-1} \ln [2D/\ell].$$

In these results, $d$ is proportional to the Debye screening length, $\kappa^{-1}$, and varies as $\ln L$. The dependence on $\kappa^{-1}$ is what one would expect. If a wetting layer had a thickness much greater than $\kappa^{-1}$, the concentration of ions outside of the double layer (of thickness $\kappa^{-1}$) would be exponentially small, much smaller than the concentration that would pertain in the absence of added salt. Therefore, the thickness of the layer would have to decrease to a thickness on the order of the Debye screening length.

### 3. Derivation.

This section contains the derivation of equation (2), the principal result for the equilibrium wetting layer thickness in figure 1. The analysis is classical, but it is tricky to obtain an expression for $d$ in closed form.

Assume that the charge density of the solid surface is $\Sigma$, that the concentration of added salt in bulk phase $\beta$ (phase $\beta$ near $z = L$) is $n$, and that that in bulk phase $\alpha$ is $fn$, where $f \leq 1$. Denote the concentration of positive ions in phase $\beta$ at position $z$ by $n^+(z)$, with similar definitions for $n^+(z)$, $n^+(z)$, and $n^+(z)$; all ions have valence $z$. Denote the electric potential at position $z$ by $\varphi(z)$. Poisson's equation relates the potential to the local charge density:

$$- \epsilon_\beta \epsilon_0 \varphi''(z) = ze \left( n^+(z) - n^-\right), \quad 0 \leq z < d$$

$$- \epsilon_\alpha \epsilon_0 \varphi''(z) = ze \left( n^+(z) - n^-\right), \quad d < z.$$

There is no need to consider the potential for $z = \sigma(L)$, and one can take $z$ in phase $\alpha$ to infinity. This region contributes a correction to equation (2) that is at most of relative order $d^2/L^2$.

The electric potential must satisfy the usual boundary conditions at the interfaces and at infinity:

$$- \epsilon_\beta \epsilon_0 \varphi'(0) = \Sigma,$n

$$\varphi(d^-) = \varphi(d^+),$$

$$\epsilon_\beta \varphi'(d^-) = \epsilon_\alpha \varphi'(d^+),$$

$$\varphi'(z) \to 0 \quad \text{as} \quad z \to \infty,$n

$$\varphi(z) \to 0 \quad \text{as} \quad z \to \infty.$n

In addition to the electrostatic equations, assume that the ion number densities obey Boltzmann distributions,

$$n^+_\beta (z) = n^-\left( d \right) \exp \left\{ - \beta ze \left[ \varphi(z) - \varphi(d) \right] \right\}, \quad 0 \leq z < d$$

$$n^-\left( z \right) = n^-\left( d \right) \exp \left\{ + \beta ze \left[ \varphi(z) - \varphi(d) \right] \right\}, \quad 0 \leq z < d$$

$$n^+_\alpha (z) = n^+_\alpha (d) \exp \left\{ - \beta ze \left[ \varphi(z) - \varphi(d) \right] \right\}, \quad d < z$$

$$n^-\left( z \right) = n^-\left( d \right) \exp \left\{ + \beta ze \left[ \varphi(z) - \varphi(d) \right] \right\}, \quad d < z,$n

and satisfy the following boundary conditions:

$$n^+_\beta (d)/n^-\left( d \right) = f,$n$$

$$n^-\left( d \right)/n^-\left( d \right) = f,$n

$$n^+_\alpha (z), n^-\left( z \right) \to fn \text{ as } z \to \infty.$n

The conditions at $z = d$ assume that the counterions and ions of the same charge from the added salt have equal partition coefficients, which is consistent with the use of Boltzmann distributions.

Combination of the above equations leads to the usual nonlinear Poisson-Boltzmann equations:

$$- \epsilon_\beta \epsilon_0 \varphi''(z) = -2 ze \sinh \left[ \beta ze \varphi(z) \right], \quad 0 \leq z < d$$

$$- \epsilon_\alpha \epsilon_0 \varphi''(z) = -2 ze fn \sinh \left[ \beta ze \varphi(z) \right], \quad d < z.$n

Multiplication by $\varphi'(z)$ and integration yields

$$[\varphi'(z)]^2 = \left\{ 4 n / \left( \beta \epsilon_\beta \epsilon_0 \right) \right\} \times$$

$$\times \left\{ \cosh \left[ \beta ze \varphi(z) \right] - 1 - C \right\}, \quad 0 \leq z < d \quad (5)$$
\[
\varphi'(z)^2 = \left[ 4 \frac{f n}{(\beta \varepsilon_a \varepsilon_0)} \{ \cosh \{ \beta \varepsilon \varphi(z) \} - 1 \} \right],
\]
where the integration constant \( C (\neq 0) \) is given by
\[
C = (1 - f \varepsilon_a / \varepsilon_\beta) [n_\beta^+ (d) + n_\beta^- (d) - 2n] / (2n) .
\]  
Note that \( \varphi(d) \) and \( \varphi(0) \) can be written
\[
\beta \varepsilon \varphi(d) = \text{sgn}(\Sigma) \cosh^{-1} \left[ 1 + C + CY^2 \right], \\
\beta \varepsilon \varphi(0) = \text{sgn}(\Sigma) \cosh^{-1} \left[ 1 + C + 2 \kappa^{-2} \ell^{-2} \right],
\]  
where \( \kappa, \ell \), and \( Y \) are defined in section 2.

One can derive an equation for \( C \) by rearranging equation (5) and integrating from \( z = 0 \) to \( z = d \):
\[
2^{1/2} \kappa d = \int_{\rho \varepsilon(0)}^{\beta \varepsilon(d)} dy \left[ \cosh(y) - 1 - C \right]^{-1/2} .
\]  
Although it is not possible to solve this explicitly for \( C \), the following considerations reveal that only certain features of the full solution are needed to derive equation (2). A free-energy formulation leads to results identical to those that follow [9]. First consider the situation in figure 1 without gravity. The pressures in the \( \beta \) layer and in phase \( \alpha \) are then constant but unequal. The pressure in the \( \beta \) layer over that in phase \( \alpha \) is
\[
The first term is the difference between the ideal gas pressures of the ions at \( x = d \), over and above what the pressures would be if the ion concentrations had their bulk values. The second term is the contribution to the pressure from the discontinuity in the zz component of the Maxwell stress tensor. With continuity of \( \varepsilon \varepsilon'(z) \) at \( z = d \), equations (6) and (7) imply that \( \Pi \) and \( C \) are simply related:
\[
\Pi = 2 nC / \beta .
\]  
Now consider the effects of gravity on the pressures in the \( \alpha \) and \( \beta \) phases at \( z = d \). The pressure in the \( \alpha \) phase becomes \( p_0 + \rho_0 gL \), while that in the \( \beta \) layer becomes \( p_0 + \Pi + \rho_\beta gL \), where \( p_0 \) is the pressure at the upper \( \alpha - \beta \) interface. The equality of these two pressures determines the equilibrium value of \( d \):
\[
\Pi = \Delta \rho g L ,
\]  
where \( \Delta \rho = \rho_\alpha - \rho_\beta \). \( C \) is therefore given by
\[
C = \beta \Delta \rho g L / (2n) = 2 / (\kappa^2 D^2) ,
\]  
where \( D \) is defined in section 2.

With this result for \( C \), equation (9) is an explicit expression for the equilibrium wetting layer thickness. With the change of variable \( \theta = \tan^{-1} \left\{ \left[ \cosh(y) - 1 - C \right]^{1/2} / C^{1/2} \right\} \), one can derive
\[
\int_{\rho}^{\theta_1} d\theta \left[ 1 - m \sin^2 \theta \right]^{-1/2} ,
\]  
where \( m = 2 / (2 + C) \)

and
\[
\theta_1 = \tan^{-1} \left\{ \left[ \cosh(y_1) - 1 - C \right]^{1/2} / C^{1/2} \right\} .
\]  

With equations (7) and (8), this leads directly to equation (2).

4. Conclusion.

The goal of this paper has been to extend the theory of wetting layers stabilized against gravity by ionic forces. The principal result is equation (2), which gives the equilibrium thickness of a wetting layer on a charged substrate in an electrolyte solution.

A number of generalizations of equation (2) are immediately possible. Combination of equations (1), (10), and (11) gives an equilibrium condition that includes the effects of both dispersion and ionic forces:
\[
2 nC / \beta + 2 W / d^3 = \Delta \rho g L .
\]  

Equation (2) is valid in this more general case when \( \Delta \rho g L \) in the definition of \( D \) is replaced by \( \Delta \rho g L - 2 W / d^3 \). To describe wetting layers off coexistence [1], one need only replace \( \Delta \rho g L \) by \( \Delta \mu \), the difference between the chemical potential of the fluid and its value on the coexistence curve.

The preceding analysis assumes that the charge density on the surface of the solid is a known constant, but it generally depends on the potential at the surface and on the nature of the added electrolyte [10]. With \( \Sigma < 0 \) for definiteness, equation (8) implies that \( \Sigma \) and \( n_\beta^+ (0) = n \exp \left\{ - \beta \varepsilon \varphi(0) \right\} \) are related by
\[
D^{-2} \ell^{-2} = (\kappa^2 n) \left[ n_\beta^+ (0) - n \right]^2 / [4 n_\beta^- (0)] ,
\]  
where \( \ell^{-1} \) is proportional to \( \Sigma \) (see Sect. 2). The simplest way to proceed is to assume that the charge density of the completely charged surface is \( \Sigma_0 \), and that adsorption of cations reduces this (in magnitude) to the value \( \Sigma \). Denoting the equilibrium constant for the surface adsorption reaction by \( K \), one can eliminate \( n_\beta^+ (0) \) in equation (12) using
\[
n_\beta^- (0) = K (\Sigma_0 - \Sigma) / \Sigma .
\]
The resulting expression relates \( \Sigma \) to \( L \) and \( n \) when \( \Sigma_0 \) and \( K \) are known. Remarkably, one can determine \( \Sigma \) independently from these considerations (which do not involve \( d \) explicitly) and then use the result in equation (2). A myriad of limiting cases is possible.

As mentioned in section 2, any mixture of polar and nonpolar molecules that separates into a dense nonpolar phase (\( \alpha \)) and a less dense polar phase (\( \beta \)) that wets an ionizable substrate is an example of a system to which equation (2) would apply. With the change \( g \rightarrow -g \), it also describes the situation of a dense polar phase in equilibrium with a less dense nonpolar phase when the dense polar phase wets an ionizable substrate immersed in the less dense nonpolar phase. In either case, the polar phase could be mostly water, the nonpolar phase could be mostly oil, and the substrate could be glass.

Partially miscible mixtures of nitromethane (polar) and carbon disulfide (nonpolar) in contact with glass provide a realization of the situation in figure 1. Experiments indicate that thick wetting layers of a less dense nitromethane-rich phase (\( \beta \)) intrude between a denser carbon disulfide-rich phase (\( \alpha \)) and the glass [11]. However, calculations indicate that dispersion forces oppose wetting by phase \( \beta : W \) in equation (1) is negative [12]. Because wetting layers in a gravitational field require favorable long-range forces to exist, it is plausible that ionic forces stabilize the thick layers that are observed [3]. Experiments to confirm this and to study the effects of added salt are underway [6].

Acknowledgments.
The author is grateful to the NASA Microgravity Sciences Program for partial support under Contract H-27954-B.

References


