Determination of the Intrinsic Acid−Base Dissociation Constant and Site Density of Ionizable Surface Groups by Capillary Rise Measurements

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A theoretical description is presented for the equilibrium capillary height (h_{eq}) of a solution between parallel, flat, solid surfaces which contain ionizable groups. The h_{eq} is related to the change in gravitational potential energy, the intrinsic wettability of the un-ionized surface, and the free energy of formation of the ionizable surface in aqueous solution. The theoretical approach takes into account both the electrostatic free energy of charging the surface and the change in the free energy associated with the acid−base reactions of the surface sites. It is shown that the dependence of h_{eq} on pH depends on the number of ionizable surface sites per unit area, the intrinsic acid−base dissociation constant (K_a^i) of the surface sites, and the background electrolyte. The negative free energy change which accompanies the acid−base reactions dominates over the positive electrostatic free energy of charging the surface. Consequently, the overall free energy of ionization is negative, and an ionized surface is more wettable than an un-ionized surface. The theoretical description is applied to experimental values of h_{eq} as a function of pH, measured between two heptylamine plasma polymer surfaces in the presence of 1 mM NaCl. The theoretical fit to the data indicates that the plasma polymer surface contains *ca.* 10^{17} amines/m^2 and the pK_a^i of the amine groups is *ca.* 5. The surface site density is in reasonable accord with values obtained by both derivatization techniques and contact angle measurements. The pK_a^i is consistent with a low effective dielectric constant for the polymer−water interface.

Introduction

The wettability of surfaces may be characterized using contact angle or capillary rise measurements. The former method requires solid surfaces which are smooth, flat, and impervious to the probe solutions. Capillarity techniques, on the other hand, can be applied to powders and fibers as well as flat sheet samples.

For a surface that contains ionizable groups, the macroscopic solid/vapor/solution contact angle varies when measured using drops with different pH values. Changes in the wettability of a surface with the pH of the probe solution can thus be used to obtain information on acid−base equilibria of surface groups. This method was applied by Holmes-Farley *et al.* to determine the apparent pK_a of carboxylic acid groups on polymer surfaces.[1,2] More recently we have presented a quantitative theory describing the variation of contact angles on ionizable surfaces with the degree of ionization.[3] The theory enables determination not only of the intrinsic pK_a value of ionizable surface groups but also of their surface density. Such quantitative characterization of surface charge and its pH dependence can be used, for instance, to further our understanding of the role of electrostatic effects in the adsorption of proteins onto biomaterials and membrane surfaces.

The "contact angle titration" method described above can only be carried out conveniently when the un-ionized surface is not very hydrophilic. We have therefore developed an alternative method based on capillary rise, which can be applied to surfaces of arbitrary wettability. The method relates variations in the equilibrium capillary height, measured with probe solutions of various pH, to the free energy of ionization of surface chemical groups. A simple experimental method thus enables determination of the intrinsic pK_a and surface density of the ionizable groups.

The approach is illustrated using experimental data measured on a surface containing amine groups, prepared by the plasma deposition of a thin polymeric coating onto glass. The coating was obtained by the activation of *n*-heptylamine vapor in a radiofrequency gas plasma (glow discharge).[4] A plasma-deposited polymeric coating was particularly suitable for this investigation as plasma polymers can be very thin and smooth. Moreover, their surface layers typically possess much less segmental mobility than the surface layers of conventional polymers[5] and thus are unable to undergo significant media-induced reorientation motions on the time scale of the present experiments. Such motions would complicate interpretation as they alter the surface density of chemical groups. The variation of capillarity with pH could be modeled by treating the plasma film as an ionizable surface, and the best-fit values of the pK_a and surface density of the amine groups agree well with the results of previous contact angle titration studies.

Experimental Section

The general plasma deposition procedure and the custom-built plasma apparatus have been described elsewhere.[6,7] Briefly, the reactor chamber (volume = 7600 cm^3) contained two vertical

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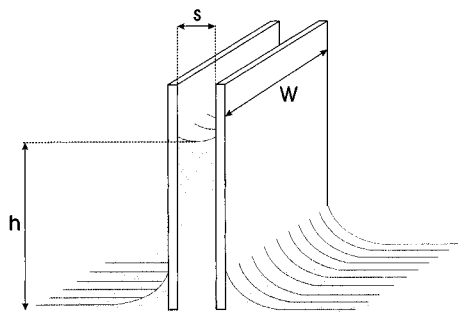
Figure 1. Schematic diagram of the apparatus used in the capillarity measurements.

copper electrodes of dimensions 90×18 mm placed in an upright glass cylinder. The electrodes were separated by 16 mm. A glass microscope slide was attached to each electrode using small pieces of double sided sticky tape. Plastic and glass fittings defined a controlled path for the flow of incoming vapor, passing from the gas inlet through the interelectrode space. The pressure in the reactor was adjusted via a throttle valve in the monomer feed line. The plasma discharge was powered by a commercial generator (HPG-2) operating at variable frequency in the range 125–375 kHz. Typical conditions for the deposition of heptylamine plasma polymer were frequency = 225 kHz, power = 10 W, pressure = 0.38 Torr, and treatment time = 30 s.

The above plasma treatment conditions were chosen so that the coating contained amine groups. Moreover, the coating was sufficiently thick so that the substrate (glass) properties were completely masked. Under these conditions, the wetting of the flat plates was controlled by the properties of the coating and the solution.

The plasma polymer coated glass slides were used for capillarity measurements within 1–2 days of fabrication, in order to avoid complications which arise from the slow oxidation of amines to amides.[8] The separation between the two surfaces was controlled using a 25 μm thick spacer composed of fluorinated ethylene propylene (FEP; DuPont, Type 100A). The pH of a 1 mM NaCl solution was adjusted using small volumes of HCl. The distance that each solution moved up between the coated glass slides was measured to the nearest millimeter.

Theory

The equilibrium theory of capillary rise between two identical, ionizable surfaces may be conveniently derived in two steps. In the first step, we use a measurement at the point of zero charge (pzc) to parameterize the capillary force due to un-ionized groups (by relating it to the negative of the gravitational force). We then combine this empirical force term with the forces predicted by electrical double layer and chemical reaction theory.

Capillarity at the Point of Zero Charge (pzc). Consider two flat plate surfaces of width W separated by a distance s (Figure 1). When the lower edge of the sandwich is in contact with the surface of a solution, liquid will move up to a height h between the plates ($h = 0$ is defined as the surface of the reservoir solution). The total change in the free energy of the system (ΔF^{tot}) is given by

$$\Delta F^{\text{tot}}(h) = \Delta F^{\text{grav}}(h) + \Delta F^{\text{pzc}}(h) \quad (1)$$

The gravitational term may be expressed as

$$\Delta F^{\text{grav}}(h) = 0.5\, W s \rho g h^2 \quad (2)$$

where ρ is the density of the solution and g is the

(8) Gengenbach, T. R.; Vasic, Z. R.; Chatelier, R. C.; Griesser, H. J. *Surf. Interface Anal.*, in press.

acceleration due to gravity. The term ΔF^{pzc} represents the change in free energy which accompanies the interaction of the solution with the un-ionized groups on the solid surface.

$$\Delta F^{\text{pzc}}(h) = 2\, Wh(\gamma_{\text{SL}}^{\text{pzc}} - \gamma_{\text{SV}}^{\text{pzc}}) \quad (3)$$

where $\gamma_{\text{SL}}^{\text{pzc}}$ and $\gamma_{\text{SV}}^{\text{pzc}}$ represent the surface tension of the solid–liquid and solid–vapor interfaces, respectively, at the point of zero charge. If $h > 0$, then the gravitational term (ΔF^{grav}) is positive and the ΔF^{pzc} term is negative. It is difficult to measure $\Delta F^{\text{pzc}}(h)$ directly; therefore we use the equilibrium height of the solution on the un-ionized surface to determine $\Delta F^{\text{pzc}}(h)$. At equilibrium

$$\frac{\text{d}}{\text{d}h} \Delta F^{\text{tot}}(h) = 0 \quad (4)$$

i.e., the total driving force acting on the solution is zero. At equilibrium, eqs 1, 2, and 4 can be combined to yield

$$2\, W(\gamma_{\text{SL}}^{\text{pzc}} - \gamma_{\text{SV}}^{\text{pzc}}) = -Ws\rho g h_{\text{pzc}} \quad (5)$$

where h_{pzc} is the equilibrium height of the solution at the point of zero charge (i.e., when the groups on the surface are un-ionized).

Note that the driving force due to the interaction of the solution with the un-ionized groups on the surface is not a function of height. It is therefore possible to parameterize this term at the point of zero charge, and then use the same value to represent this component of the force at any value of pH.

Capillarity at Arbitrary pH. Consider now the capillary rise of a solution of arbitrary pH between two ionizable surfaces. When the pH is such that the surfaces become charged, there will be a diffuse double layer in the solution. The change in free energy when the liquid rises a height h between the two surfaces will now contain terms in addition to those given by eq 1. These additional terms are associated with the change in electrical (ΔF^{elec}) and chemical (ΔF^{chem}) free energy when the ionizable surface comes into contact with the solution at a given pH. The total change in the free energy of the system now reads

$$\Delta F^{\text{tot}}(h,\text{pH}) = \Delta F^{\text{grav}}(h) + \Delta F^{\text{pzc}}(h) + \Delta F^{\text{elec}}(h,\text{pH}) + \Delta F^{\text{chem}}(h,\text{pH}) \quad (6)$$

Expressions for the change in free energy of an ionizable surface due to electrostatic (ΔF^{elec}) and chemical reaction (ΔF^{chem}) terms have been given previously.[3] The change in electrical free energy associated with charging up the ionizable groups is obtained from the Gouy–Chapman theory of the diffuse double layer

$$\Delta F^{\text{elec}}(h,\text{pH}) = 2\, Wh \left[\sigma_0 \psi_0 - \epsilon_0 \epsilon \kappa \left(\frac{2kT}{e} \right)^2 \left\{ \cosh\left(\frac{e\psi_0}{2kT} \right) - 1 \right\} \right] \quad (7)$$

where ψ_0 is the electrical potential of the solid–liquid surface, σ_0 is the surface charge density, k is Boltzmann's constant, T is the absolute temperature, e is the elementary electrostatic charge, ϵ_0 is the permittivity of free space, ϵ is the dielectric constant of water, and κ is the Debye reciprocal length (in units of m^{-1}). The factor 2 preceding the W arises because both plates in Figure 1 are covered

with the ionizable surface. For a 1:1 electrolyte in water at 298 K, κ may be calculated from the equation[9]

$$\kappa = \frac{\sqrt{c}}{3.04 \times 10^{-10}} \tag{8}$$

where c is the molar concentration of electrolyte.

When the ionizable groups are monobasic (e.g., amines), and we assume a mass-action model to describe the protonation of the surface groups, then the change in chemical free energy associated with protonating the groups may be expressed as

$$\Delta F^{\text{chem}}(h,\text{pH}) = 2\,WhkTN_s\{(1-\alpha)\ln(1-\alpha) + \alpha\ln\alpha + \alpha\ln(K_a^{\,i}/[\text{H}^+])\} \tag{9}$$

where N_s is the surface density of ionizable groups, $K_a^{\,i}$ is the intrinsic dissociation constant of the charged (protonated) monobasic groups, and α is the fraction of groups which are protonated

$$\alpha = \sigma_0/eN_s \tag{10}$$

The equilibrium height, h_{eq}, is found by setting the total driving force to zero

$$\frac{\text{d}}{\text{d}h}\Delta F^{\text{tot}}(h,\text{pH}) = 0 \qquad \text{at} \quad h = h_{eq} \tag{11}$$

Combining eqs. (2 and 5−11), and after some rearrangement, we obtain the final expression for the equilibrium capillary height (h_{eq}) as a function of pH

$$h_{eq}(\text{pH}) - h_{pzc} = \frac{2}{\rho gs}\left[\sigma_0\psi_0 - \epsilon_0\epsilon\kappa\left(\frac{2kT}{e}\right)^2\left\{\cosh\left(\frac{e\psi_0}{2kT}\right)-1\right\}\right] - \frac{2kTN_s}{\rho gs}\{(1-\alpha)\ln(1-\alpha) + \alpha\ln\alpha + \alpha\ln(K_a^{\,i}/[\text{H}^+])\} \tag{12}$$

Note that eq 12 is only relevant to capillarity between flat parallel plates. When nonideal geometries are used, such as a powder or fibers packed between parallel plates, the factor ($2W$) in eqs 7 and 9 must be replaced by the area of ionizable surface per unit height (A). Moreover, the mass of water which rises up between the parallel plates must be adjusted to take account of the volume excluded by the powder or fibers. The expression for h_{eq} as a function of pH may then be written

$$h_{eq}(\text{pH}) - h_{pzc} = \frac{A}{Ws\rho g(1-f)}\left[\sigma_0\psi_0 - \epsilon_0\epsilon\kappa\left(\frac{2kT}{e}\right)^2\left\{\cosh\left(\frac{e\psi_0}{2kT}\right)-1\right\}\right] - \frac{AkTN_s}{Ws\rho g(1-f)}\{(1-\alpha)\ln(1-\alpha) + \alpha\ln\alpha + \alpha\ln(K_a^{\,i}/[\text{H}^+])\} \tag{13}$$

where f is the volume fraction occupied by the solids. Note the restriction that eq 13 makes use of electrical double layer theory pertaining to flat surfaces and is therefore applicable to powders or fibers with *thin* double layers.

Computational Methods. Iterative numerical methods are used to calculate the equilibrium capillary height

at a given pH. By balancing the diffuse layer potential with the potential developed by the surface groups, we obtain the equation for determining the equilibrium surface charge density σ_0

$$2\sinh^{-1}\left\{\frac{e\sigma_0}{2kT\epsilon_0\epsilon\kappa}\right\} - \ln\left[\frac{[\text{H}^+]}{K_a^{\,i}}\left\{\frac{eN_s}{\sigma_0}-1\right\}\right] = 0 \tag{14}$$

Thus given values of $K_a^{\,i}$, N_s, and [H$^+$], eq 14 can be solved numerically to yield σ_0. The value of σ_0 was inserted into the Gouy−Chapman expression[10]

$$\psi_0 = \frac{2kT}{e}\sinh^{-1}\left\{\frac{e\sigma_0}{2kT\epsilon_0\epsilon\kappa}\right\} \tag{15}$$

to yield the surface potential ψ_0, and the degree of ionization α was obtained from eq 10. The value of h_{pzc} was estimated from the limiting value of h at high pH where the monobasic surface groups are neutral, and then h_{eq} was calculated by using eq 12.

The following values and SI units were used for the variables in the calculations: $kT = 4.1162 \times 10^{-21}$ J/molecule, $e = 1.6021 \times 10^{-19}$ C/charge, $\epsilon = 80$, $\epsilon_0 = 8.85 \times 10^{-12}$ C/(V·m), and $\rho = 1$ g/mL. The N_s, σ_0, and ψ_0 terms were expressed in units of molecules/m^2, C/m^2 and V, respectively. All distances (W, h, s) were expressed in meters.

Monoacidic Groups at Surfaces. By a similar line of reasoning, the analogous equation for h_{eq} between parallel plates when the surfaces contain monoacidic groups (e.g., carboxyls) is

$$h_{eq}(\text{pH}) - h_{pzc} = \frac{2}{\rho gs}\left[\sigma_0\psi_0 - \epsilon_0\epsilon\kappa\left(\frac{2kT}{e}\right)^2\left\{\cosh\left(\frac{e\psi_0}{2kT}\right)-1\right\}\right] - \frac{2kTN_s}{\rho gs}\{(1-\alpha)\ln(1-\alpha) + \alpha\ln\alpha + \alpha\ln([\text{H}^+]/K_a^{\,i})\} \tag{16}$$

and the equation for finding σ_0 is

$$2\sinh^{-1}\left\{\frac{e\sigma_0}{2kT\epsilon_0\epsilon\kappa}\right\} - \ln\left[\frac{K_a^{\,i}}{[\text{H}^+]}\left\{\frac{eN_s}{\sigma_0}-1\right\}\right] = 0 \tag{17}$$

Results and Discussion

It is difficult to visualize the behavior of the equilibrium capillary height for various surface and solution conditions from an inspection of the equations alone. We therefore present some model curves of $h_{eq} - h_{pzc}$ as a function of pH under several different conditions in order to illustrate the theory. The properties of the surface and the solution have been varied systematically, using realistic values of p$K_a^{\,i}$, N_s, and the concentration of a 1:1 electrolyte. The model curves are presented in terms of $h_{eq} - h_{pzc}$, since this term is independent of the inherent wettability of the constituent surface groups.

Figure 2 shows $h_{eq} - h_{pzc}$ versus pH when N_s is fixed at 10^{17} monobasic surface sites/m^2 and p$K_a^{\,i}$ is varied between 4 and 10. Note that the curves do not plateau at low values of pH where the sites are almost completely ionized. This is because the chemical potential of the protons in solution increases as the pH is decreased, and therefore the reduction in free energy upon binding also increases as the pH is decreased. The linear relationship between $\Delta F^{\text{chem}}(\text{pH})$ and pH in the limit where almost all

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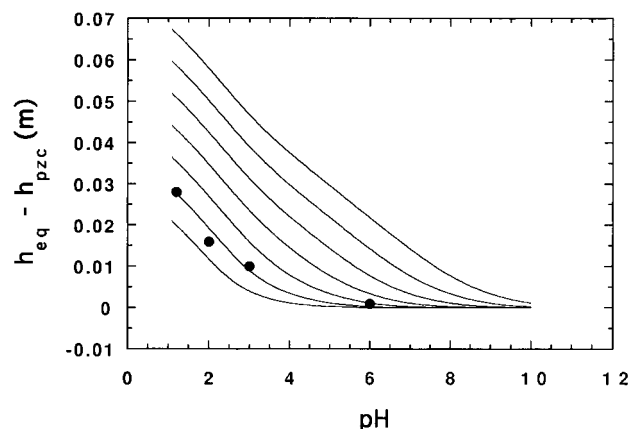
Figure 2. Plot of $h_{eq} - h_{pzc}$ versus pH at various values of $pK_a{}^i$. In the simulations, the value of N_s is fixed at 10^{17} monobasic surface groups/m^2 and the background 1:1 electrolyte concentration at 1 mM. From left to right, values of $pK_a{}^i$ increase from 4 to 10 in integer increments (solid lines). Also shown are the measured equilibrium capillary heights between heptylamine plasma polymer surfaces as a function of the pH of 1 mM aqueous NaCl solutions (filled circles).
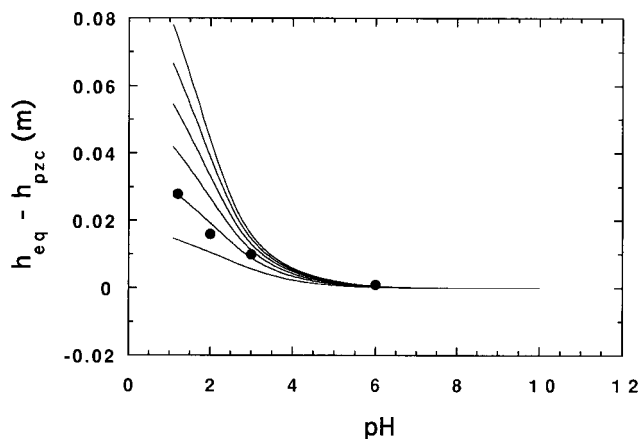

Figure 3. Plot of $h_{eq} - h_{pzc}$ versus pH at various values of N_s. In the simulations, the $pK_a{}^i$ value is fixed at 5 and the background 1:1 electrolyte concentration at 1 mM. From bottom to top, values of N_s are (0.5, 1, 1.5, 2, 2.5, and 3) × 10^{17} monobasic surface groups/m^2, respectively (solid lines). Also shown are the measured equilibrium capillary heights between heptylamine plasma polymer surfaces as a function of the pH of 1 mM aqueous NaCl solutions (filled circles).

sites are ionized results in the linear dependence of h_{eq} on pH at low values of the pH.

Figure 3 shows $h_{eq} - h_{pzc}$ versus pH when $pK_a{}^i$ is fixed at 5 and N_s is varied between 0.5 and 3 × 10^{17} monobasic sites/m^2. At low surface site densities there is only a small pH-dependent change in h_{eq}. As the surface site density increases, the surface becomes more wettable at low pH due to the larger change in ΔF^{them}(pH).

The valency and concentration of the background electrolyte are other important factor controlling the h_{eq} versus pH profile. Figure 4 shows $h_{eq} - h_{pzc}$ versus pH when $pK_a{}^i$ and N_s are fixed and the concentration of 1:1 electrolyte is varied between 1 and 100 mM.

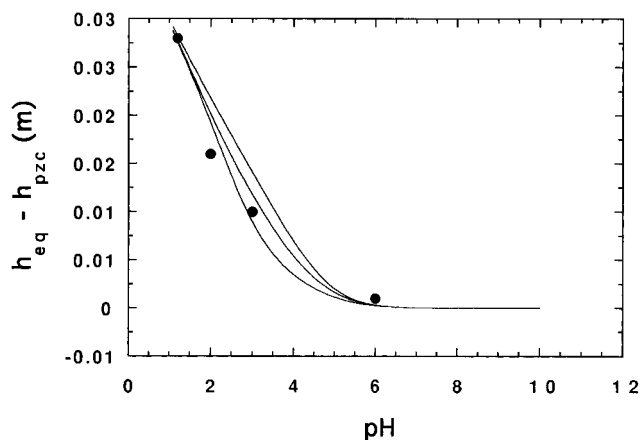Also included in Figures 2–4 are some data measured using flat glass plates coated with heptylamine plasma

Figure 4. Plot of $h_{eq} - h_{pzc}$ versus pH at various concentrations of background 1:1 electrolyte. In the simulations, the value of $pK_a{}^i$ is fixed at 5 and N_s at 10^{17} monobasic surface groups/m^2. From left to right, 1:1 electrolyte concentrations are 1, 10, and 100 mM, respectively (solid lines). Also shown are the measured equilibrium capillary heights between heptylamine plasma polymer surfaces as a function of the pH of 1 mM aqueous NaCl solutions (filled circles).

polymer. The data are well described by the theory. The best-fit value of N_s is 10^{17} amines/m^2, which is close to the lower end of the values obtained by derivatizing the amine surface sites with fluorescein isothiocyanate.[4] The best-fit value of N_s derived from capillarity data also compares favorably with N_s values inferred from contact angle titrations ((3.3–3.8) × 10^{17} amines/m^2).[3] The best fit value of $pK_a{}^i$ is 5, which also agrees well with contact angle titrations (5.5–6.3).[3]

Note that this $pK_a{}^i$ value is very different from the pK_a value for monomeric heptylamine solubilized in aqueous solution ($pK_a{}^w \sim 10.7$). However, the amine groups are located at the interface between an aqueous phase and a relatively hydrophobic, hydrocarbon-rich polymeric material. The low dielectric constant of the latter is responsible for the reduced stability of the charged groups compared with the situation when the same groups are fully surrounded by an aqueous medium. Therefore, the $pK_a{}^i$ of surface amine groups is expected to be much lower than the pK_a of the monomeric amine in a high dielectric medium such as water.

Conclusions

We have presented a theoretical approach to model the equilibrium capillary height of electrolyte solutions between ionizable surfaces on flat plates as a function of pH. The theory was illustrated by simulating h_{eq} versus pH using various values for the surface density of ionizable groups, the intrinsic acid–base dissociation constant, and the concentration of background 1:1 electrolyte. The theory was used to fit experimental h_{eq} versus pH curves for a heptylamine plasma polymer surface. Reasonable best-fit values were obtained for the surface density and the intrinsic pK_a of the ionizable groups.