

Chapter 2

Capillarity and Corrosion

Introduction

The surface of a liquid or solid exhibits the property of surface tension because molecules at the surface of the liquid or solid have fewer neighbors than those in the bulk. This situation leads to a net force perpendicular to the surface plane toward the interior of the liquid (or solid). In the case of solids, the property is called its surface free energy and may depend on the orientation of the solid surface.

The surface tension of water at 20 °C is 72.8 mN/m (millinewtons/m). The following units are equivalent:

$$72.8 \text{ dynes/cm} = 72.8 \text{ erg/cm}^2 = 72.8 \text{ mN/m} = 72.8 \text{ mJ/m}^2$$

Some values of surface tension for various liquids are given in Table 2.1 [1, 2].

Capillarity

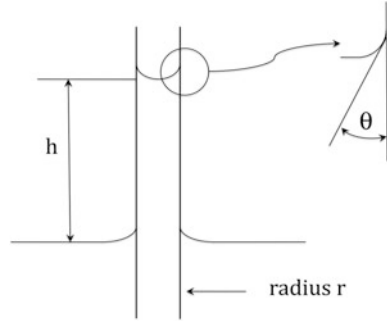
When a small-diameter glass tube is immersed in a liquid, the liquid will rise in the capillary tubing, as shown in Fig. 2.1. (If the liquid is mercury there will be a depression rather than a rise in the capillary column, but we will be dealing with only aqueous fluids here.) The height of the capillary rise (h) is given by:

$$h = \frac{2\gamma}{\rho g r} \quad (2.1)$$

Table 2.1 Some surface tension values in mN/m at 20 °C [2]

Water	72.94
Methylene iodide	67.00
Dimethyl sulfoxide	43.54
Benzene	28.88
Methanol	22.50
Perfluoroheptane	13.19

Fig. 2.1 Capillary rise of water in a small-diameter glass tube



where γ is the surface tension of the liquid, ρ is the density of the wetting liquid, g is the acceleration due to gravity, and r is the radius of the capillary.

This equation arises as follows. The force upward in the capillary liquid is:

$$F(\text{up}) = \gamma(2\pi r) \cos \theta \quad (2.2)$$

where θ is the contact angle and is usually zero (see Fig. 2.1).

The downward force is due to the weight of the liquid and is given by:

$$F(\text{down}) = \pi r^2 \rho g h \quad (2.3)$$

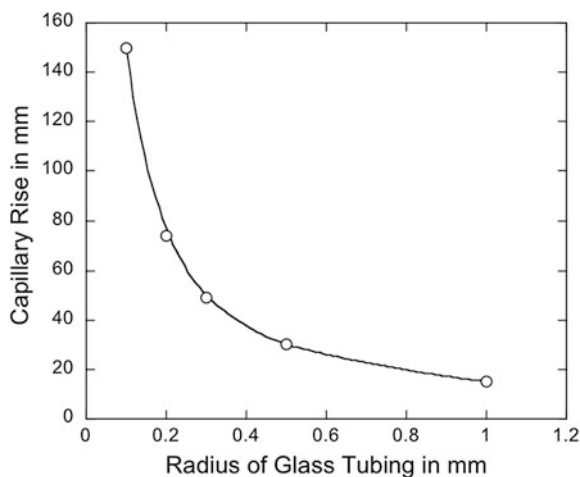
At equilibrium, the force up and the force down are equal:

$$F(\text{up}) = F(\text{down}) \quad (2.4)$$

This gives Eq. (2.1).

Figure 2.2 shows some calculated values of the capillary rise h for various capillary radii r . The smaller the capillary radius, the higher the capillary rise.

Fig. 2.2 Calculated capillary rise h (in mm) for various glass tubing radii r (in mm)



Application to Organic Coatings

It is well-known that organic coatings do not form perfect barriers to corrosion, but instead they are semi-permeable membranes into which water, oxygen, and chloride ions can pass. Nguyen et al. [3] have detected the presence of molecular water in organic coatings on silicon using Fourier transform infrared-multiple internal reflection. Their results showing the accumulation of water at the organic coating/metal interface are given in Fig. 2.3. Consider an organic coating which is 500 μm

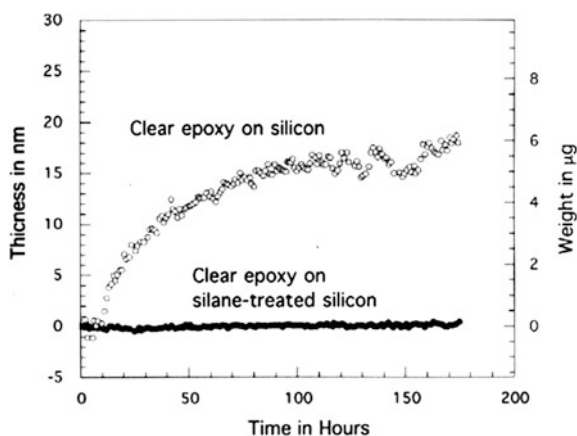
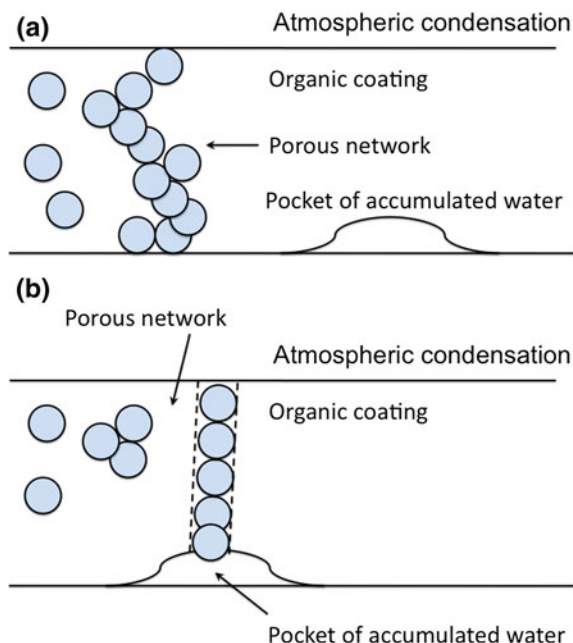


Fig. 2.3 Thickness and amount of water at the coating/substrate interface for clear epoxy coatings on silicon and silane-treated silicon. The epoxy coating thickness was 130–140 μm . Redrawn from Nguyen et al. [3] with the permission of Elsevier

Fig. 2.4 **a** Schematic drawing of an irregularly shaped capillary path in an organic coating. **b** Capillary rise in a porous organic coating



thick (0.5 mm) and having an array of pores which align to give an irregularly shaped capillary path through the organic coating, as shown in Fig. 2.4.

If the accumulated liquid water at the base of the organic coating encounters the porous path in the coating, it will be possible for liquid water at the base of the coating to undergo capillary rise. For an effective pore radius of 3 μm , the height of capillary rise is calculated from Eq. (2.1) to be $h = 5.0$ m. This means that the capillary height far exceeds the thickness of the organic coating. See Table 2.2.

If the effective pore radius is 30 μm , the calculated height of capillary rise is 0.50 m. We can then consider that some of the organic matter from the coating can leach out into solution, so that the surface tension of the liquid phase will decrease, say to half its value for pure water, 36 mN/m. In that case, the calculated height of capillary rise is still substantial at 0.24 m and exceeds the thickness of the organic coating. Thus, the aqueous solution in the pores connects the internal electrolyte within the network of pores to the external electrolyte, which may be a thin film of water condensed from the atmosphere. This serves to promote degradation of the organic coating and underfilm corrosion.

Table 2.2 Calculated capillary rise in an organic coating

Radius r (μm)	Surface tension γ (mN/m)	Calculated capillary rise h (m)
3	72.8	5.0
30	72.8	0.50
30	36	0.24

Young and Laplace Equation

The pressure difference Δp across a spherical bubble of a fluid is given by the Young and Laplace equation:

$$\Delta p = 2\gamma/r \quad (2.5)$$

where r is the radius of the spherical bubble. This equation arises by considering the free energy change involved when a spherical bubble expands from radius r to radius $r + dr$. The free energy change is:

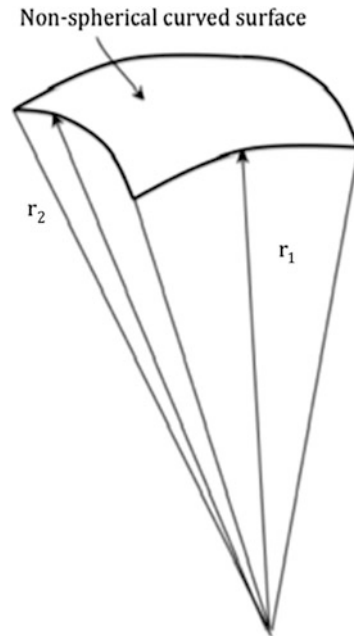
$$\Delta G = \gamma dA - \Delta p dV \quad (2.6)$$

where A is the area of the bubble and V is its volume.

The minus sign in Eq. (2.6) is required because work is done by the system. With $A = 4\pi r^2$, $dA = 8\pi r dr$. With $V = (4/3)\pi r^3$, $dV = 4\pi r^2 dr$. Substitution of these simple expressions for dA and dV into Eq. (2.6) with $\Delta G = 0$ at equilibrium gives the result in Eq. (2.5).

If the curved surface is not spherical but instead has two principal radii of curvature r_1 and r_2 as in Fig. 2.5, then the term $1/r$ in Eq. (2.5) is replaced by the term $(1/r_1 + 1/r_2)$, and the Young and Laplace equation becomes:

Fig. 2.5 A curved surface defined by two different radii of curvature. Adapted from Ref. [1], p. 9



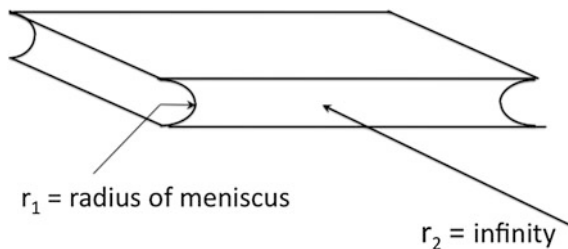


Fig. 2.6 The force required to separate two flat glass plates (separated by a thin film of liquid) can be calculated from the Young and Laplace equation

$$\Delta p = \gamma \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \quad (2.7)$$

The derivation of this equation has been given by Adam [1] and Adamson [2]. When $r_1 = r_2 = r$, Eq. (2.7) reduces to Eq. (2.5).

Force Between Glass Plates

The Young and Laplace equation can be used to calculate the pressure required to separate two flat glass plates which are held together by a thin film of water (or of an aqueous solution). See Fig. 2.6. Here r_1 is given by the radius of curvature of the meniscus and $r_2 = \text{infinity}$. Thus,

$$\Delta p = \gamma \left(\frac{1}{r_1} \right) \quad (2.8)$$

if the two glass plates are separated by a 0.5 mm thin layer of water, then Δp is calculated to be $\Delta p = 146 \text{ Pa}$. Note that the calculated pressure difference depends only on the surface tension of the wetting liquid and on the geometry of the system. The material properties of the solids are not involved in the calculation. The force between the two glass plates is then: $\text{Force} = \Delta p \times (\text{Wetted area of plates})$.

Application to Poultrice Corrosion

Poultrice corrosion is the name given collectively to corrosion that results from the accumulation of dirt, dust, corrosion products, and other forms of debris.

When this happens, a highly corrosive condition can be created. Strictly speaking, poultrice corrosion is not a separate form of corrosion but shares many

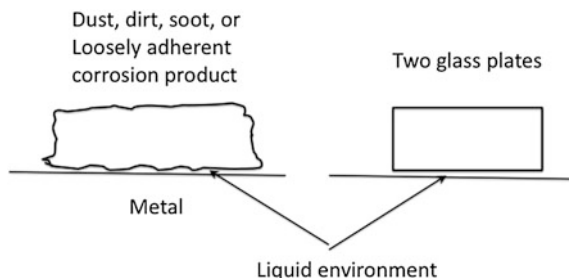


Fig. 2.7 Separation of two glass plates is a model for removing foreign objects from a metal surface

common features with crevice corrosion, which has been discussed in more detail elsewhere by the author [4].

The Young and Laplace equation in the form of Eq. (2.8) can be used to calculate the pressure required to remove a piece of debris from a surface, as shown in Fig. 2.7. This is because the material properties of the solids are not involved in the calculation. Knowing this required pressure, we can assess which cleaning methods will provide sufficient energy to surpass the adhesive force keeping the debris particle connected to the metal surface.

Accumulated dirt, dust, corrosion products, and other forms of debris often are contaminated with oil.

Then, the principles of detergency can be applied. See Fig. 2.8 which is adapted from Adamson [2] and shows an oil-contaminated particle before and after detachment. The change in free energy for detachment is:

$$\Delta G = \gamma_{wo} + \gamma_{mw} - \gamma_{mo} \quad (2.9)$$

where the subscripts refer in turn to the following interfaces: water/oil-contaminated particle, metal/water, and metal/oil-contaminate particle. For the process to be spontaneous we need $\Delta G < 0$. This leads to:

$$\gamma_{mo} > \gamma_{wo} + \gamma_{mw} \quad (2.10)$$

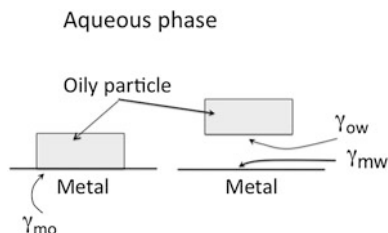


Fig. 2.8 Surface free energy relationships in the detachment of an oily particle from a metal surface. Adapted from Adamson [2] with the kind permission of John Wiley

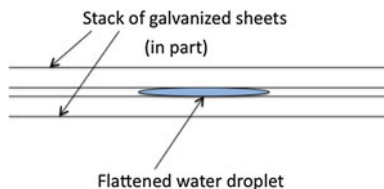


Fig. 2.9 Schematic diagram of a “wet pack” used to test the white rusting (wet storage stain) of galvanized sheets

Equation (2.10) is the condition which describes the effect of detergents on the detachment of oily dirt or oily debris from a metal surface. Detergents which can reduce γ_{wo} or γ_{mw} will serve to make the inequality in Eq. (2.10) hold. Thus, useful detergents are those which can adsorb both at the oily particle/water interface and at the metal/water interface.

Interfacial tensions can be measured with a Wilhelmy balance in which the force is measured to immerse a thin plate into a two-liquid system. Details are given elsewhere for measurements for the chromium/hexadecane/aqueous solution interfaces [5].

Application to White Rusting

Stacked sheets of galvanized steel can undergo a phenomenon called white rusting (wet storage stain). Here the spaces between adjacent metal sheets act like capillaries for the ingress of water. A differential oxygen cell is set up between metal under the outside of the flattened water droplet (the cathode) and metal in contact with the interior of the water droplet (the anode) [4]. White rusting can be minimized by the use of post-galvanized chemical surface treatments, vapor phase inhibitors, and by storage in a low humidity environment.

The effect of various surface treatments on white rusting can be tested by the use of “wet packs” of galvanized steel. Here small water droplets are deliberately placed between stacked sheets for later visual inspection, as shown schematically in Fig. 2.9.

References

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