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:

\[
h = \frac{2\gamma}{\rho gr}
\]  
(2.1)
where $\gamma$ is the surface tension of the liquid, $\rho$ 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:

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

where $\theta$ 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:

$$F(\text{down}) = \pi r^2 \rho gh$$

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

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

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.
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. 2.2](image1.png) Calculated capillary rise h (in mm) for various glass tubing radii r (in mm)

![Fig. 2.3](image2.png) 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 mm. Redrawn from Nguyen et al. [3] with the permission of Elsevier
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

<table>
<thead>
<tr>
<th>Radius ( r ) (μm)</th>
<th>Surface tension ( \gamma ) (mN/m)</th>
<th>Calculated capillary rise ( h ) (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>72.8</td>
<td>5.0</td>
</tr>
<tr>
<td>30</td>
<td>72.8</td>
<td>0.50</td>
</tr>
<tr>
<td>30</td>
<td>36</td>
<td>0.24</td>
</tr>
</tbody>
</table>
Young and Laplace Equation

The pressure difference $\Delta p$ across a spherical bubble of a fluid is given by the Young and Laplace equation:

$$\Delta p = 2\gamma / r$$  \hspace{1cm} (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:

$$\Delta G = \gamma dA - \Delta p dV$$ \hspace{1cm} (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 $A = 4\pi r^2$, $dA = 8\pi rdr$. With $V = (4/3)\pi r^3$, $dV = 4\pi^2 r^2 dr$. 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](image)

**Fig. 2.5** A curved surface defined by two different radii of curvature. Adapted from Ref. [1], p. 9
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 \( r_2 = \infty \). Thus,

\[
\Delta p = \gamma \left( \frac{1}{r_1} + \frac{1}{r_2} \right)
\]

if the two glass plates are separated by a 0.5 mm thin layer of water, then \( \Delta p \) is calculated to be \( \Delta p = 146 \) 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: Force = \( \Delta p \times (\text{Wetted area of plates}) \).

**Application to Poultice Corrosion**

Poultice 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, poultice corrosion is not a separate form of corrosion but shares many
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:

\[
\Delta G = \gamma_{wo} + \gamma_{mw} - \gamma_{mo}
\]  

(2.9)

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

\[
\gamma_{mo} > \gamma_{wo} + \gamma_{mw}
\]  

(2.10)
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 $\gamma_{wo}$ or $\gamma_{mw}$ 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 Wilmhelmy 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

Surface Chemistry of Aqueous Corrosion Processes
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