3.4.2. Diffusional Limitations in Immobilized Enzyme Systems

Diffusional resistances may be observed at different levels in immobilized enzymes. These resistances vary depending on the nature of the support material (porous, nonporous), hydrodynamical conditions surrounding the support material, and distribution of the enzyme inside or on the surface of the support material. Whether diffusion resistance has a significant effect on the rate of enzymatic reaction rate depends on the relative rate of the reaction rate and diffusion rate, which is characterized by the Damköhler number (Da).

$$\text{Da} = \frac{\text{maximum rate of reaction}}{\text{maximum rate of diffusion}} = \frac{V_{m'}}{k_L[S_b]} \tag{3.52}$$

where $[S_b]$ is substrate concentration in bulk liquid (g/cm^3) and k_L is the mass-transfer coefficient (cm/s).

The rate of enzymatic conversion may be limited by diffusion of the substrate or reaction, depending on the value of the Damköhler number. If Da >> 1, the diffusion rate is limiting. For Da << 1, the reaction rate is limiting, and for Da ≈ 1, the diffusion and reaction resistances are comparable. Diffusion and enzymatic reactions may be simultaneous, with enzymes entrapped in a solid matrix, or may be two consecutive phenomena for adsorbed enzymes.

3.4.2.1. Diffusion effects in surface-bound enzymes on nonporous support materials. Assume a situation where enzymes are bound and evenly distributed on the surface of a nonporous support material, all enzyme molecules are equally active, and substrate diffuses through a thin liquid film surrounding the support surface to reach the reactive surfaces, as depicted in Fig. 3.17. Assume further that the process of immobilization has not altered the protein structure, and the intrinsic kinetic parameters (V_m, K_m) are unaltered.

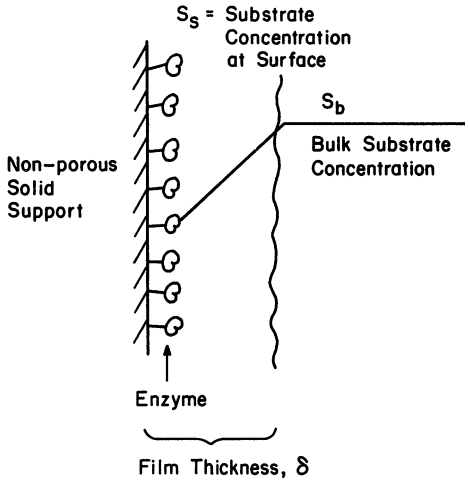

Figure 3.17. Substrate concentration profile in a liquid film around adsorbed enzymes.