Under diffusion limitations, the rate per unit volume is usually expressed in terms of the effectiveness factor as follows:

$$r_s = \eta \frac{V_m''[\mathrm{S}_s]}{K_m + [\mathrm{S}_s]} \tag{3.59}$$

The *effectiveness factor* is defined as the ratio of the reaction rate with diffusion limitation (or diffusion rate) to the reaction rate with no diffusion limitation. The value of the effectiveness factor is a measure of the extent of diffusion limitation. For $\eta < 1$, the conversion is diffusion limited, whereas for $\eta \approx 1$ values, conversion is limited by the reaction rate and diffusion limitations are negligible. The factor is a function of ϕ and β as depicted in Figure 3.20.

For a zero-order reaction rate ($\beta \to 0$), $\eta \approx 1$ for a large range of Thiele modulus values such as $1 < \phi < 100$. For a first-order reaction rate ($\beta \to \infty$), $\eta = (\phi,\beta)$ and η is approximated to the following equation for high values of ϕ.

$$\eta = \frac{3}{\phi}\left[\frac{1}{\tanh\phi} - \frac{1}{\phi}\right] \tag{3.60}$$

When internal diffusion limits the enzymatic reaction rate, the rate-constant $V_{m,\mathrm{app}}$ and $K_{m,\mathrm{app}}$ values are not true intrinsic rate constants, but apparent values. To obtain true intrinsic rate constants in immobilized enzymes, diffusion resistances should be eliminated by using small particle sizes, a high degree of turbulence around the particles, and high substrate concentrations.

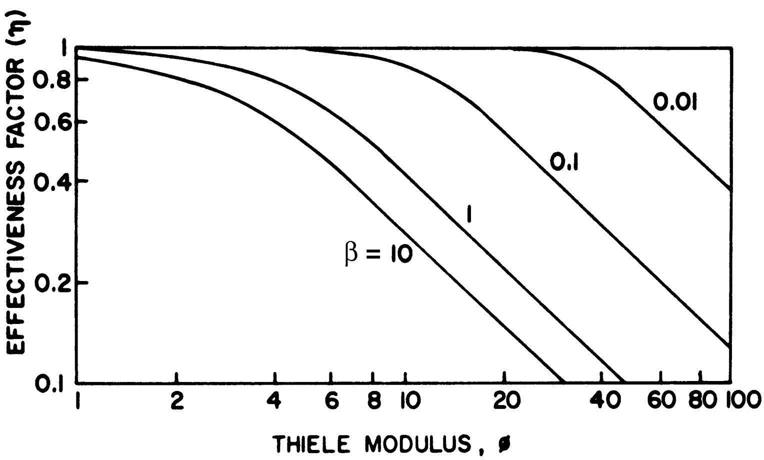

Figure 3.20. Theoretical relationship between the effectiveness factor η and first-order Thiele modulus, ϕ, for a spherical porous immobilized particle for various values of β, where β is the dimensionless Michaelis constant. (With permission, from D. I. C. Wang et al., *Fermentation and Enzyme Technology*, John Wiley & Sons, Inc., New York, 1979, p. 329.)