Supplementary Information for:

Solvation Effects in Liquid-Phase Esterification Reactions Catalyzed by Hydrogen-form Ion Exchange Resins

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S1. Thiele Modulus Calculations

Assessing internal mass transport limitations in solid-catalyzed reactions presents significant challenges. The Thiele Modulus is a theoretically rigorous tool for this purpose. However, practical use of the Thiele Modulus is difficult because the calculation requires the intrinsic rate constant, which can be measured in the absence of transport limitations, and the effective diffusivity, which must be estimated. This difficulty is often circumvented by use of the Weisz-Prater number, which substitutes the observed reaction rate for the intrinsic rate constant, although the effective diffusivity is still required.[1]

In an alternative approach, the Thiele Modulus can be calculated directly, without needing either the intrinsic rate constant or effective diffusivity. The approach involves measuring the reaction rate using samples of the same catalyst with distinct pellet sizes; a ratio of the effectiveness factors for these cases leads to a system of equations with the two Thiele Moduli as the only unknown quantities. We begin with the the Thiele Modulus, Φ:

$$\Phi = R_P \sqrt{\frac{k}{D_{eff}}} \tag{1}$$

where R_P is the pellet radius, k is the intrinsic first-order rate constant, and D_{eff} is the effective diffusivity. For a spherical particle, the Thiele Modulus can be used to estimate an effectiveness factor, η, that corresponds to the ratio of the observed rate, r_{obs}, to the maximum (*i.e.*, intrinsic) rate, r_{max}:

$$\eta = \frac{r_{obs}}{r_{max}} = \frac{3}{\Phi}\left[\frac{1}{\tanh(\Phi)} - \frac{1}{\Phi}\right] \tag{2}$$

As shown by Froment and Bischoff, while the form of the Thiele Modulus in Equation 1 corresponds to a first-order reaction, the values of the effectiveness factor are not strongly influenced by changes in Thiele Modulus for reaction orders ranging from 0.1 to 3.[2] Similarly, the effectiveness factor given in Equation 2 corresponds to spherical particles, but as Levenspiel shows, the particle geometry does not significantly impact the value of the effectiveness factor for a given Thiele Modulus.[3] Thus, the use of these simpler equations is justified here.

If rates are measured using two catalyst samples of identical material at different pellet sizes (and at identical reaction conditions), then one can take the ratios of the effectiveness factors and Thiele Moduli, leading to a system of equations where the unknowns are the two Thiele Moduli. The effective diffusivity and intrinsic rate constant, both being independent of particle size, cancel from the analysis.

$$\frac{\eta_1}{\eta_2} = \frac{r_{obs1}/r_{max}}{r_{obs2}/r_{max}} = \frac{\frac{3}{\Phi_1}\left[\frac{1}{\tanh(\Phi_1)} - \frac{1}{\Phi_1}\right]}{\frac{3}{\Phi_2}\left[\frac{1}{\tanh(\Phi_2)} - \frac{1}{\Phi_2}\right]} \tag{3a}$$

$$\frac{\Phi_1}{\Phi_2} = \frac{R_{P1}\sqrt{\frac{k}{D_{eff}}}}{R_{P2}\sqrt{\frac{k}{D_{eff}}}} = \frac{R_{P1}}{R_{P2}} \tag{3b}$$

Notably, for this analysis, it is important that at least one of the pellet sizes used for reaction be large enough to exhibit an effectiveness factor below unity, otherwise the system of equations has no solution. Similarly, it is important that the pellet sizes be of sufficiently different radii that distinct effectiveness factors can be measured within the confines of experimental uncertainty.

References:

1. M. A. Vannice, *Kinetics of Catalytic Reactions*, Springer, New York, NY, 2005.
2. G. F. Froment and K. B. Bischoff, *Chemical Reactor Analysis and Design*, John Wiley & Sons, New York, NY, 1979.
3. O. Levenspiel, *Chemical Reaction Engineering*, John Wiley and Sons, Inc., New York, 3rd edn., 1999.