

Sorption Kinetics for Diffusion Controlled Systems with a Strongly Concentration Dependent Diffusivity

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Systems in which the differential diffusivity increases strongly with concentration are quite common. Examples include the diffusion of critically sized sorbates with a highly favorable (Type 1) isotherm in microporous adsorbents such as zeolites or carbon molecular sieves, and the adsorption of favorably adsorbed species in macroporous adsorbent pellets, under conditions of macropore diffusion control.

For such systems the apparent or integral diffusivity, measured over a finite concentration step also increases with loading but the relationship between the integral and differential diffusivities is not straightforward and, when the diffusivity ratio (D_{∞}/D_0) is large, the apparent diffusivity may be far from the average diffusivity over the relevant concentration range. The familiar symmetry between adsorption and desorption, characteristic of constant diffusivity systems, is lost. Desorption becomes much slower than adsorption and the forms of the transient concentration profiles for adsorption and desorption become quite different. In the limit of a highly favorable isotherm the profile approaches the familiar shockwave form characteristic of irreversible adsorption and leading to “shrinking core” behavior.

These effects are analyzed in detail and the relationship between the effective and integral diffusivities is calculated for three common functional forms of concentration dependence. The form of the concentration profiles is illustrated by NMR imaging measurements.

Previously published experimental kinetic data for sorption of linear alkanes in NaCaA zeolite (~32.5% Ca exchange),^(1, 2) showing order of magnitude differences between the limiting transport diffusivity and self-diffusivity, are re-analyzed using the new model and it is shown that the self-diffusivity and limiting transport diffusivity are essentially the same.

- (1) R.M. Barrer and D.J. Clarke
Trans. Faraday Soc. **70**, 535-548 (1974)
- (2) A. Quig and L.V.C. Rees
Trans. Faraday Soc. **72**, 771-789 (1976)