

pathway of small molecules. This assumption is valid if the polymer chains' self-diffusion is much smaller than that of the diffusants. This concept was first introduced by Fricke in 1924 (Fricke 1924) and later various forms of it were developed. In general, for all obstruction effect models, the diffusion coefficient,  $D$ , of small molecules diffusing through a network swollen with a swelling agent is expressed as a function of that network's swelling ratio,  $q$ , and the diffusion coefficient of the same small molecules in the pure swelling agent,  $D_o$ :

$$\frac{D}{D_o} = F(q) \quad 34$$

For a swollen network equilibrated in the swelling agent  $q = Q_{eq}$ . Now, the  $F(Q_{eq})$  function in Equation 34 determines how equilibrium swelling ratio of a network — which is controlled by the network parameters— affects the diffusion process. For simplified Maxwell-Fricke model (Pickup and Blum 1989),  $F(Q_{eq})$  is:

$$F(Q_{eq}) = \frac{\Psi Q_{eq}}{\Psi Q_{eq} + 1} \quad 35$$

where  $\Psi$  is a shape factor for the diffusing molecules (ranging from 1.5 for rods to 2 for spheres). In the Mackie-Meares approach (Mackie and Meares 1955), which is based on a simple cubic lattice model, the  $F(Q_{eq})$  function becomes:

$$F(Q_{eq}) = \left[ \frac{1 - Q_{eq}^{-1}}{1 + Q_{eq}^{-1}} \right]^2 \quad 36$$

In both Equations 35 and 36, the effect of diffusant size on the reduced diffusion coefficient has been neglected. Other models such as Ogston (Ogston et al. 1973), however, account for the size of diffusant by incorporating the hydrodynamic radius of the diffusing agent into the  $F(Q_{eq})$  function. Another approach to define the diffusion coefficient in a swollen network is based *the hydrodynamic* theories, where the interactions between the solute, the solvent and the polymer chains are taken into account. Regardless of what model is used to determine the diffusion coefficient, however, the swelling ratio of the network always plays the central role. Therefore, any factor(s) that affect the equilibrium swelling ratio will have a direct impact on the diffusion process.

## Hydrogel Toughness

Finally, the effect of network parameters on toughness is considered. Many applications for hydrogels require a reasonable degree of mechanical robustness to operate without failure when exposed to external stresses. Mechanical failure often occurs by a fracture process where a macroscopic sized crack propagates through the material causing it to separate into two or more fragments. The resistance to crack propagation through a material is the definition of a material's toughness and is quantified as the energy needed to propagate the crack by a given increase in area. Until recently, synthetic hydrogels have been considered to be very brittle materials with toughness values (or 'fracture energies') as low as 1–10 Jm<sup>-2</sup>. Newly discovered strategies to toughen