6.3 Kinetics of Dyeing

The primary objectives of commercial dyeing processes are to achieve uniform dyeings that display the desired level of fastness in as short a processing time as possible. Much attention therefore attends the development of dyeing recipes and process parameters that enable the consistent and reproducible uniform distribution of dye within a given textile material. As commercial dyeing is rarely carried out to equilibrium, considerable attention has focussed on understanding the kinetic aspects of dyeing processes with particular attention being placed on the rate at which dyes *diffuse* within the textile fibre, this being most commonly expressed in terms of the measured *diffusion coefficient* of the dye molecule within the fibre.

As mentioned, the aqueous dyeing process is heterogeneous insofar as it involves two phases, namely one phase that consists initially of the textile substrate and the other a dye solution in which the initially undyed fibre is immersed. Although the process of dyeing involves the transfer of dye from the external solution to the interior of the fibre, the nature of this transfer process is complex. In essence, the sorption of dyes onto textile fibres can be considered to comprise at least four sequential stages, of which the last is commonly considered as being the *rate-determining step* and is of particular relevance to this discussion:

(i) diffusion of the dye molecules through the external medium (usually water) to the fibre surface;
(ii) diffusion of the dye molecules through the *diffusional boundary layer* present at the fibre surface;
(iii) adsorption of the dye molecules onto the surface of the substrate;
(iv) diffusion of the dye molecules within the fibre interior.

In the cases of disperse dyes, sulphur dyes and vat dyes, the above four stages are preceded by an additional stage that involves dissolution of the dye. For vat dyes, sulphur dyes, mordant dyes and azoic colorants, a chemical reaction takes place after stage (iv) whilst, in the case of reactive dyes, a chemical reaction between the dye and fibre occurs after stage (iv).

In the context of the four stages of the dyeing process listed above, in principle, any one of these may influence or control the overall rate of dyeing. The first two of the four stages, namely diffusion of dye molecules through the dyebath to the fibre surface and thence through the *diffusional boundary layer that is* present at the fibre surface, are influenced by the hydrodynamic flow of the dye solution that carries the dye molecules and, therefore, by the extent of dyebath–fibre interchange, which is a function of, for example, dyebath circulation rate, textile construction and yarn shape. The more efficient the dyebath–fibre interchange, the less important are stages (i) and (ii), because the rate at which the dye molecules reach the fibre surface is more than sufficient to maintain the overall rate of dyeing. As relatively little is known about stage (iii) of the overall adsorption process, owing to experimental difficulties in determining dye adsorption directly at the surface, it is generally assumed that the adsorption of the dye molecules onto the

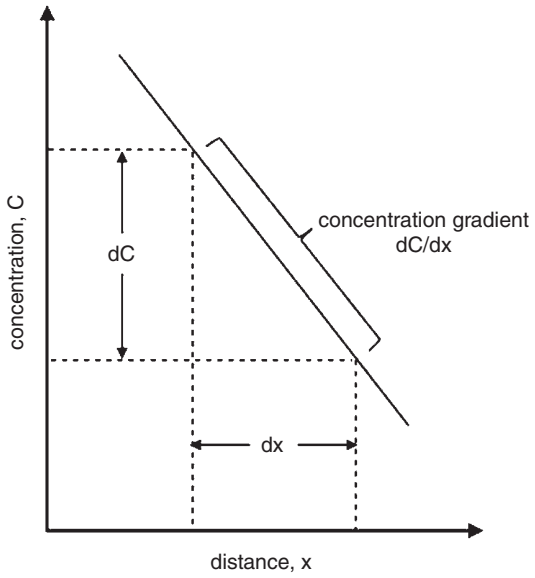

Figure 6.8 Representation of concentration gradient.

surface of the substrate occurs spontaneously and that an instantaneous equilibrium is established between the dye in solution and that adsorbed at the fibre surface [46]. The fourth and final stage of the dyeing process outlined, namely dye diffusion within the fibre interior, is considered by many workers to be the rate-controlling step of the overall dyeing process, especially in the case of conditions of efficient dye–fibre agitation; this aspect of the overall rate of dyeing, namely the measured *diffusion coefficient* of the dye molecule in the fibre, has received especial interest.

Several textbooks are of relevance to the kinetics of dyeing (e.g. [13, 42, 44, 47–49, 93–98]); in addition, a very large number of papers have been published on the subject.

6.3.1 Diffusion

All matter, irrespective of its nature (gaseous, liquid or solid), is in constant motion.[16] Because such motion involves collisions between the component molecules or particles, the movement of a given particle or molecule is *random*. However, the process by which matter, in our case dye molecules, is transferred within a system from a region of higher concentration to one of lower concentration (in our case from dyebath to fibre) is *diffusion*. Diffusion involves the random molecular motion of individual molecules[17] in which the driving force for this diffusional *mass transfer* process is the presence of a *concentration difference* between the two parts of the system.

For instance, the movement of dye molecules from the dyebath phase to the fibre phase that occurs during dyeing is driven by the *concentration gradient* between the two phases. Net transport of the *penetrant* (i.e. the dye molecule) is induced in the direction of decreasing concentration (i.e. dye diffusion occurs down the concentration gradient). The term *concentration gradient* describes the rate of change of (dye) concentration, C, as a function of distance, x, namely dC/dx (Figure 6.8); if the variation in concentration with distance (i.e. dC/dx) is linear, a *constant* concentration gradient arises.

Such diffusional transfer eventually results in equalisation of concentration and, therefore, of chemical potential throughout the system. Because two phases are involved in dyeing (dyebath and fibre), the chemical potential of the *diffusant* (i.e. the dye molecule) will be constant throughout the system only when dynamic equilibrium has been achieved, even though the concentration of the dye within each phase may differ markedly.

In the case of the diffusion of molecules (e.g. dye molecules in both solution and fibre), the movement of the molecules is referred to as *diffusivity* and is expressed in terms of the diffusion constant, D, of the molecule. As such, the diffusion constant reflects the mobility of the diffusing molecule within a particular environment (e.g. solution and fibre) and, therefore, varies according to nature of the environment. Thus, it follows that in a gas, diffusion processes are far more rapid (~0.1 $cm^2\ s^{-1}$) than in either liquids (~10^{-5} to 10^{-6} $cm^2\ s^{-1}$) or solids (~10^{-10} to 10^{-7} $cm^2\ s^{-1}$) [99]. Diffusion within polymers lies between that in liquids and solids [100]: for example, the diffusion coefficient of disperse dyes in PES at 130°C is ~10^{-10} $cm^2\ s^{-1}$ [101, 102]. Whilst diffusion in both gases and liquids can be predicted theoretically, in

[16] except of course at absolute zero.

[17] sometimes referred to as a *random walk*.

the case of solids, as diffusional rates display a much larger range (diffusion coefficients can differ $>10^{10}$) the estimation of diffusion is more difficult using theoretical models [103]. Diffusion in semi-crystalline polymers, such as textile fibres, is complex owing to issues relating to swelling, plasticisation, segmental chain mobility, crystallinity, porosity, etc. and no single mathematical model has been devised that is capable of describing the phenomenon owing to the varied and complex morphology and fine structure of fibres.

In the context of dyes and textile fibres, the rate of dyeing depends not only on such polymer properties but also on various fibre characteristics such as fibre linear density, fibre cross-sectional shape, fabric construction, and also as dye characteristics (e.g. solubility and affinity) as well as on several physico-chemical parameters, etc., as exemplified by temperature, pH, liquor ratio, electrolyte concentration, rate of fibre/dye solution interchange, etc. As so many factors influence dyeing rate, dyeing systems are studied on the basis of much simpler idealised situations carried out under precise experimental conditions. Indeed, the experimental determination of the diffusion coefficient of dyes within fibres is undertaken using especially stringent conditions (referred to as *boundary conditions*) demanded by the theoretical models employed. Unfortunately, such conditions often are not representative of those encountered in practical, industrial dyeing processes.

The diffusivity of low molar mass compounds within polymers is of interest in several areas of industry other than dyeing, such as drying, gas separation, packaging, coating, drug delivery and protective clothing. Consequently, the diffusion of low molar mass compounds other than dye molecules in polymers has been the subject of considerable scientific interest (e.g. [96, 98, 100, 104–108]).

6.3.2 Steady-State and Non-Steady-State Diffusion

Two types of diffusional process occur, namely *steady state* and *non-steady state*. In a steady-state diffusional system, the rate of flow of matter per unit area or *flux* occurs at a constant rate and, within this system, the concentration gradient is constant (i.e. dC/dx = constant) and there is no accumulation of matter at any point in the system (i.e. $dC/dt = 0$). In non-steady-state systems, the rate of diffusion is a function of time (i.e. $dC/dt \neq 0$) and, therefore, $dC/dx \neq 0$, as it varies with time. The two diffusional processes are described by *Fick's laws of diffusion*, the *first law* relating to both steady-state and non-steady state diffusion while the second law concerns only non-steady-state diffusion.

Theoretical studies assume that the overall rate of dyeing is determined by the rate of dye diffusion within the fibre.