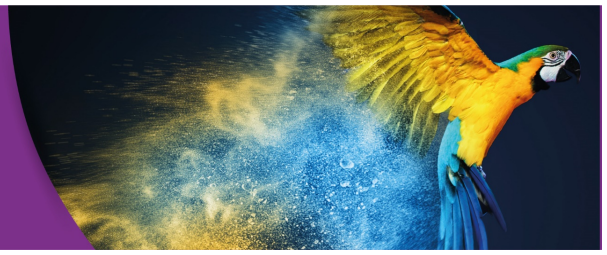


ASDC Dyeing Theory

4.2. Kinetics of Dyeing

4.2.1. Diffusion

Learning Objectives for this section

- How do we define and describe the concept of diffusion in terms of a dye/fibre system?

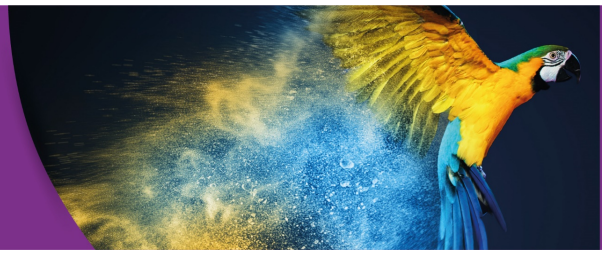
Diffusion

The preferred outcomes of aqueous dyeing are to obtain a dyed material that is of the desired colour, of the required depth of shade[1] and which displays the requisite level of *fastness*[2]; from a commercial point of view, the principal aim is that such dyeings are achieved in as short a processing time as possible. As commercial dyeing is *not* carried out to equilibrium, the *thermodynamics of dyeing* do not concern commercial dyeing processes. Instead, the *kinetics of dyeing* are used to study real dyeing processes, in order to determine the *rate* at which dyeing is achieved, with particular effort being placed on measuring the *rate of dye diffusion* within both the dyebath and fibre phases, which is commonly expressed in terms of the experimentally observed *diffusion coefficient* of the dye within the dyebath and/or fibre phases.

The kinetics of dyeing is the subject of several textbooks [e.g. (1, 2, 5-7, 93-99); see (11) for a summary of this large area.

[1] *the amount of dye applied to a substrate, expressed as percentage on mass of fibre, % omf; <2% omf = pale depth of shade, 2% omf = medium depth of shade, >2% omf = deep depth of shade:* 11. Burkinshaw SM. Physico-chemical aspects of textile coloration. Chichester: Wiley; 2016.

2 because dyed materials are routinely exposed to various agencies (eg domestic laundering, light, perspiration, etc.), dyed substrates commonly undergo a change in colour and/or depth of shade during use, owing to, for example, degradation of the dye and/or fibre, loss of dye from the dyeing (fading), adsorption of vagrant dye molecules from adjacent materials (staining); all dyed materials fade, but at different rates and extents, depending on the nature and extent of exposure;



Diffusion is the name given to the process by which all matter (in our case dye molecules) within a system (in our case a dyeing process), is transferred from a region of *higher concentration* to one of *lower concentration*. As such, diffusion proceeds *down* the *concentration gradient* from the region of higher to lower concentration because the *driving force* for this diffusional *mass transfer* process that involves *random motion* of individual molecules[3] is simply the *difference in concentration* between the two regions.

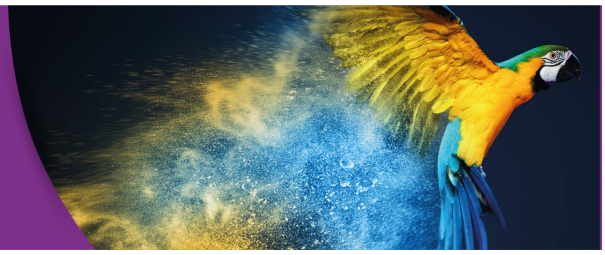
By way of brief explanation, prior to the start of an aqueous dyeing process, all of the dye molecules are present in the dyebath phase whilst the fibre phase contains no dye molecules. When dyeing is commenced, and the fibre and dyebath are brought together, a very high dye concentration gradient exists between the dye molecules in the dyebath and fibre phases which results in the dye molecules transferring spontaneously from the dyebath to the fibre and a very high rate of dyeing ensues. As the transfer of dye molecules from the dyebath phase to the fibre phase continues, so the concentration gradient between the two phases decreases gradually and, as a corollary, the driving force for dyeing also decreases gradually with the result that the rate of dyeing falls gradually, until either an equilibrium is established between the amounts of dye in the two phases, which will occur only in the case of an *infinite dyebath*[4], or, as is usually encountered in commercial immersion dyeing processes, all of the dye has transferred to the fibre (i.e. the dyebath phase no longer contains dye molecules) which occurs in the case of a *finite dyebath*[5].

This *diffusional mass transfer process*, in which dye molecules move from the dyebath phase to the fibre phase, because of the influence of a dye concentration gradient, should cease when there is no longer a dye concentration gradient between the two phases. Although theoretically, this will correspond to ~50% transfer (i.e. 50% exhaustion) of the dye to the fibre because the dye concentration gradient will be zero, in the case of commercial dyeing processes, 100% dye transfer is always achieved. The reason for this is that *diffusional mass*

[3] sometimes referred to as a *random walk*

[4] an infinite dyebath is *one in which the dyebath contains a sufficient amount of dye to enable dyeing to occur from a constant concentration of dye at the fibre surface throughout the course of dyeing*: 11. Burkinshaw SM. Physico-chemical aspects of textile coloration. Chichester: Wiley; 2016.

[5] a finite dyebath *contains a limited amount of dye and therefore, the amount of dye in both the dyebath and the fibre surface continuously decrease during dyeing until equilibrium is achieved between the amount of dye in the dyebath and the fibre surface*: 11. ibid.



transfer is not the *sole driving force* behind the transfer of dye molecules from the dyebath to the fibre, but, instead, *dye-fibre substantivity* provides a fundamentally crucial supporting role (17).

This can be explained in terms of a simple, three-stage process that represents the transfer of dye molecules from the dyebath phase to the fibre phase (i.e. the process of dyeing) depicted in Figure 17:

(i) dye molecules, in either *solution* or *dispersion,* transfer through the aqueous *dyebath phase* to the water-filled amorphous regions within the *fibre phase*;
(ii) dissolved dye molecules diffuse within water-filled amorphous regions of the *fibre phase*;
(iii) dissolved dye molecules interact with appropriate *sites* or *regions* within the macromolecular chains at the surface of the fibre and become *adsorbed*.

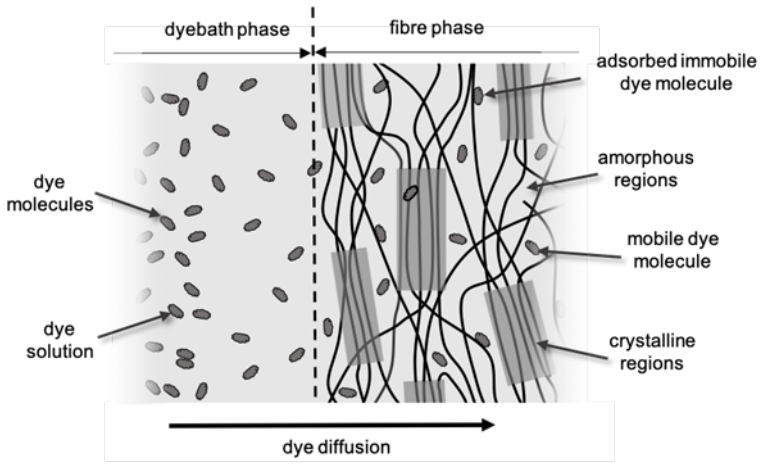
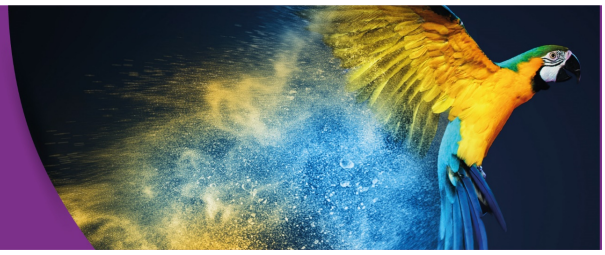


Figure 17 simplified representation of three-stage dyeing process (dye and fibre molecules not to scale)

When a diffusing, dissolved dye molecule has interacted with appropriate *sites* or *regions* within the macromolecular chains at the surface of the fibre by means of some combination of intermolecular force (e.g. van der Waals, H-bonding, ion-dipole, etc.) and become *adsorbed*, the dye molecule is immobilised and therefore is no longer a component of the aqueous dyebath phase (Figure 17). Thus, even though the overall dye concentration gradient within the dyebath phase has decreased because of the (successful) transfer of the dye molecule to the fibre on which it is now adsorbed and immobile, a net *positive* dye



concentration gradient will now exist in the dyebath phase because the presence of the adsorbed dye molecules within the solid fibre phase does not contribute to the *effective dye concentration* within the dyebath phase. So long as mobile dye molecules within the dyebath phase, then a dye concentration gradient will always exist between the dyebath and fibre phases that will drive the diffusional mass transfer process. It follows that this situation will persist until the dyebath phase no longer contains dye molecules, which, theoretically, will arise when all of the dye has transferred to the fibre and become adsorbed (and immobile).