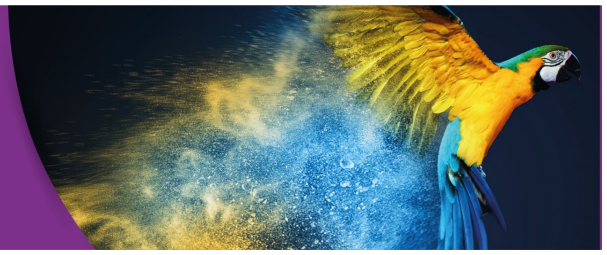


4. ASDC Dyeing Theory

4.1 Thermodynamics of Dyeing

4.1.1 Substantivity and Adsorption

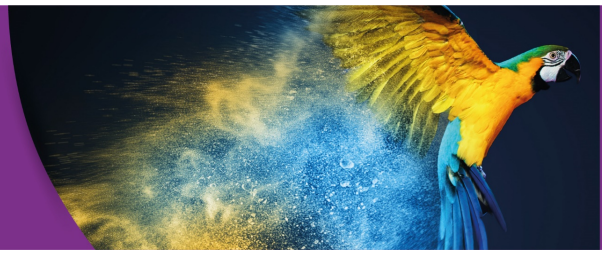
Introduction

Although thermodynamics originated in the C19th as a means of understanding and advancing mechanical *heat engines*[1] convert heat into mechanical power, it has subsequently been extended to many areas of science and engineering, including, of relevance to dyeing processes, *chemical reactions*, which are the focus of the large and complex field of *chemical thermodynamics*, which seeks to describe the feasibility of a given reaction in terms of its spontaneity. Introductory accounts of chemical thermodynamics are available [e.g. References (11-14)]. From the viewpoint of the thermodynamics of dyeing, detailed accounts are available [e.g. References (1, 2, 11, 15, 16)].

Chemical thermodynamics concerns the relationship between heat and work in chemical reactions, as well as changes of state within systems that are in or near to equilibrium. In this context, the thermodynamics of dyeing processes determines the relative distribution of a dye between the dyebath phase and the fibre phase when the dyeing system is at equilibrium, under which conditions, no further increase in dye adsorption onto the fibre can occur, irrespective of the time of dyeing involved (i.e. when the processes of dye adsorption onto the substrate and dye desorption from the substrate, are equal).

When equilibrium dye adsorption has been achieved, the amount of dye present in the fibre relative to the amount of fibre, $[D]_f$ equals the amount of dye in solution (i.e. the external dyebath) relative to the amount of solution, $[D]_s$, as represented by Equation 1. In this case, the partition of the dye between the fibre phase and the solution phase is described by Equation 2 where K is the equilibrium partition coefficient (adsorption equilibrium constant).

[1] ie steam engines



$$[D]s \rightleftharpoons [D]f \qquad 1$$

$$K = \frac{[D]_f}{[D]_s} \qquad 2$$

K is the distribution coefficient as it describes the distribution of the dye between the dyebath, s and fibre, f, phases at equilibrium; as K increases so the distribution of the dye favours the fibre phase (i.e. $[D]_f > [D]_s$) and, therefore, the greater is the extent of dye uptake onto the substrate.

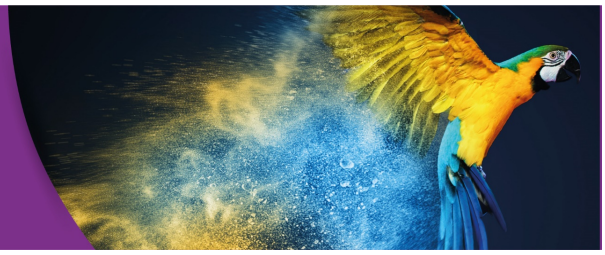
From this equilibrium dye partition, the feasibility of the dyeing process, or rather, the spontaneity of the transfer of dye molecules from the dyebath phase to the fibre phase, can be quantified in terms of the magnitude of the ensuing change in chemical potential, $\Delta\mu^{\ominus}$, of the dye molecules. This will be covered later within this course. Thus, the thermodynamics of dyeing seeks to establish a quantitative measure of the propensity of the dye to transfer from the dyebath phase to the fibre phase and, thereby, determine the mechanism by which dye adsorption occurs.

As thermodynamics does not relate to rates of change, the thermodynamics of dyeing does not concern the rate at which dyeing occurs, as previously mentioned. Instead, the kinetics of dyeing seek to establish the rate at which dyeing proceeds and, therefore, is concerned with the rate at which dyes diffuse in both the dyebath and fibre phases as a function of time of dyeing; the kinetics of dyeing does not require the dyeing system to be at equilibrium.

Substantivity

Equation 2 describes the tendency of a dye molecule to move from the aqueous dyebath to the fibre under particular equilibrium dyeing conditions (pH, temperature, liquor ratio, etc.) and, therefore, reflects the inherent attraction between the dye molecule and the fibre, which is referred to as dye-fibre substantivity (11). The term substantivity describes the intrinsic, essential, physical and chemical characteristics of the dye and the fibre which combine, synergistically, when the two phases are brought together, so as, to encourage the dye molecules to move from the aqueous dyebath to the solid fibre (17).

Dye-fibre substantivity has both mechanical and physico-chemical origins (11) in that it involves physical interactions between dye molecules within the aqueous dyebath and the

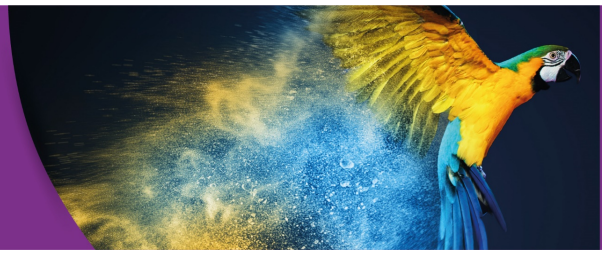


water-swollen substrate, as well as various physical forces of interaction (e.g. H-bonding, van der Waals forces, etc.) operating between the dye and fibre molecules. As such, the level of substantivity displayed by a given dye towards a particular fibre can be readily controlled by the dyer, through manipulation of both physical parameters (e.g. rate and extent of dyebath-fibre exchange, etc.) and the nature and extent of the dye-fibre forces of interaction (e.g. pH, temperature, etc.). Because of the multi-faceted nature of the physical and chemical characteristics of dyes and fibres that contribute to dye-fibre substantivity, it follows that the level of substantivity displayed by a given dye towards a particular fibre will, more likely than not, be different for other types of fibre; in a similar vein, different dyes will display different substantivity towards the same fibre. From this brief discussion, it is evident that dye-fibre substantivity is a fundamentally important, but highly complex and mostly unresolved parameter, of aqueous immersion dyeing processes; for a more detailed discussion see (17).

In terms of the distribution of dye depicted by Equation 2, high dye-fibre substantivity means that the dye displays a high tendency to move from the dyebath phase to the fibre phase, so that K in Equation 2 will therefore be high, which results in the preferential adsorption of the dye onto the fibre. In contrast, when dyeing is carried out under conditions of low dye-fibre substantivity, the dye displays an inherent low tendency to transfer from the aqueous dyebath phase to the fibre phase, so that K in Equation 2 will be low.

Adsorption

Adsorption refers to the accumulation of solute molecules at an interface (e.g. solid/liquid, liquid/liquid) and occurs as a result of forces of interaction operating between the adsorbate (i.e. a dye molecule) and the adsorbent surface (i.e. a textile fibre surface) (11). Commonly, solid adsorbent surfaces, such as those within textile fibres, comprise sites that are able to interact with solutes in an adjacent aqueous phase (e.g. a dyebath) because both the adsorbate molecules and adsorbent sites possess a particular combination of electronic and spatial characteristics (e.g. $-S(=O)_2O^-$, $-O^{\delta-}\cdot\cdot H^{\delta+}$, π-π systems, etc.). As such, surface sites possess different energies and, therefore, adsorbent surfaces are physically and chemically heterogeneous; in a similar vein, adsorbate molecules will display particular types and levels of interaction energies depending on, for instance, the nature of the component polar groups, relative hydrophobicity/hydrophilicity, etc. Thus, the particular nature of an adsorption process is a function of the intrinsic characteristics of the adsorbate molecules and those of the adsorbent sites, as well as the nature of the adsorbate/adsorbent interactions. It follows, therefore, that adsorption processes are markedly influenced by the properties of the liquid phase (e.g. pH, temperature, ionic strength, etc.) as this will influence the electronic charge, solubility, etc. of the adsorbate molecules as well as the polarity, extent of ionisation, etc. of



the adsorbate sites. Thus, dye-fibre substantivity is greatly influenced by the particular dyebath conditions (pH, temperature, etc.) that operate.

When viewed from the perspective of aqueous immersion dyeing, the adsorption process by which dye molecules are adsorbed onto a textile surface reflects the mechanical and physico-chemical origins of substantivity insofar as, the mechanical movement of dye molecules within a hydrated, water-swollen fibre enables the dye molecules to approach surface sites close enough to permit the operation of both short-range interactions (between molecules) and long-range interactions (between macroscopic particles or surfaces).

Thus, when the level of substantivity displayed by a particular dye towards a given fibre surface is manipulated during aqueous dyeing by controlling both the physical and chemical nature of the dyeing process (e.g. pH, temperature, level of fibre-dyebath interchange, liquor ratio, etc.), so the nature of the process by which the adsorption of the dye on the fibre surface proceeds, is manipulated.

Two major types of adsorption phenomena are relevant to dyeing systems:

(i) Physical adsorption (aka physisorption): in which the forces involved are intermolecular forces (van der Waals forces) of the same kind as those responsible for the imperfection of real gases and the condensation vapours, and which do not involve a significant change in the electronic orbital patterns of the species involved (18); van der Waals forces can be augmented by several types of electrostatic force (e.g. ion-ion, ion-dipole, H-bonds, etc.), the relative contribution of each type of force varying for different adsorbate/adsorbent systems; such interactions between the adsorbate and adsorbent are intrinsically very weak;

(ii) Chemical Adsorption (aka chemisorption): which results from chemical bond formation (strong interaction) between the adsorbent and the adsorbate in a monolayer on the surface (18); chemisorption is characterised by specificity in terms of the binding forces and the surface sites involved as well as the forces of interaction involved; such interactions between the adsorbate and adsorbent are inherently very strong and involve partial electron sharing.