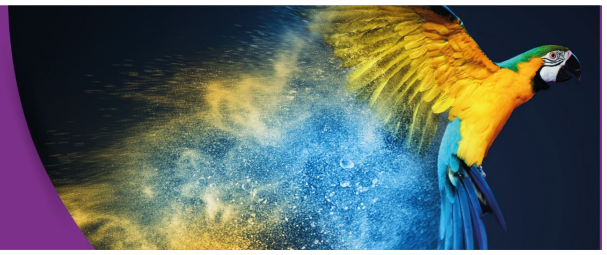


4. ASDC Dyeing Theory

4.1 Thermodynamics of Dyeing

4.1.2. Adsorption Equilibrium Isotherms

Learning Objectives for this section

- How do we define Adsorption Equilibrium Isotherms in relation to the dyeing process?
- What are the three more important Adsorption Equilibrium Isotherms observed in dyeing?
- Which dye/fibre systems behave according to any given adsorption mechanism?

Adsorption Equilibrium Isotherms

Experimentally observed *adsorption equilibrium isotherms*[1] generally correspond to one of six types (Figure 2) of which the first five (types I to V in Figure 2) were proposed by *Brunauer, Deming, Deming* and *Teller* in their landmark 1940 publication[2] (19), the sixth type (type VI in Figure 2) having been more recently introduced as part of the IUPAC system of classification of adsorption isotherms (20).

[1] including those observed for the sorption of dyes onto textile fibres
[2] often referred to as the *BDDT classification*

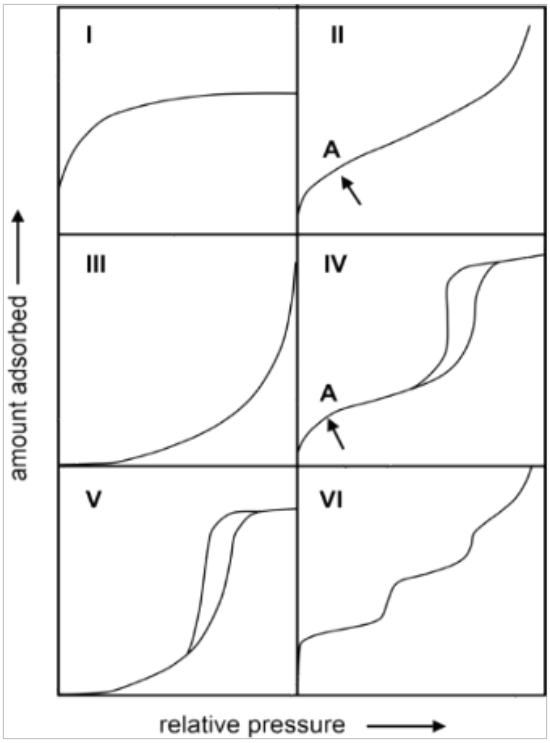
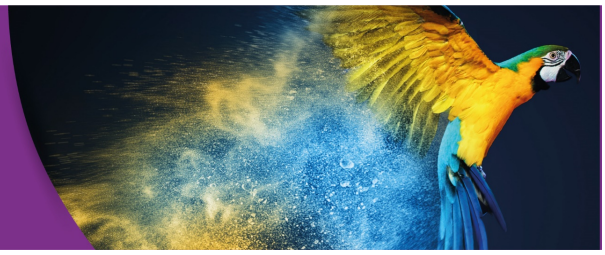


Figure 2 Six types of adsorption isotherm according to IUPAC (20); the amount of adsorbate adsorbed is plotted as a function of relative pressure, P/P_o[3]; **A** represents the start of an almost linear section of the isotherm (20)

Adsorption equilibrium is a *thermodynamic equilibrium* in which the molecules adsorbed at the fibre surface are in equilibrium with the non-adsorbed molecules in the dyebath, as a function of concentration, provided the temperature is constant; in this case, the extent of adsorption achieved, a, will be a particular function, f, of the adsorbate concentration, c as expressed by the simple relationship $a = f(c)$. A wide variety of equilibrium adsorption isotherm *models* have been devised which seek to mathematically describe the curves obtained in such equilibrium adsorption plots (such as those shown in Figure 2), each of which describes a particular *function*, f, that relates the extent of adsorption achieved, a, to adsorbate concentration, c. The use of such models can provide an insight into the adsorption mechanism in operation as well as the characteristics of the adsorbing surface.

The majority of adsorption models were originally developed for gas or vapour adsorption and subsequently applied to the phenomenon of solute adsorption. The models are often

[3] where P is the adsorbate equilibrium pressure and P_o the saturation vapour pressure of the adsorbate



classified according to the number of *parameters*[4] that have to be determined from the experimentally obtained data; generally, whilst the quality of data fitting increases with increasing number of parameters, so the complexity of the equations increases[5] [eg *single parameter model*: Henry (1803); *two parameter models*: Hill (1910), Langmuir (1918), Freundlich (1906), Dubinin-Radushkevich (1971), Temkin (1940); *three parameter models*: Sips (1948), Koble-Corrigan (1952), Redlich-Peterson (1959), Toth (1971), Kahn (1997); *four parameter models*: Marczewski and Jaroniec (1983); *five parameter models*: Fritz and Schlünder (1974)]. As two parameter models can be *linearised*, the fit of a particular adsorption model to experimental data can be estimated using *linear* or *non-linear regression*: as non-linear regression involves minimising the error distribution observed between the experimental data and the predicted isotherm model, several mathematical error functions can be employed (eg *hybrid fractional error function* (HYBRID), *Marquardt's % standard deviation* (MPSD), *non-linear chi-square test* (χ^2), *average relative error* (ARE), *sum of absolute errors* (EABS), etc.) of which the most widely used is the *coefficient of determination*, r^2.

Adsorption equilibrium isotherms observed in dyeing

The extent of adsorption of a particular dye on a given textile fibre that is achieved when the equilibrium state has been reached (in which the processes of dye adsorption and dye desorption are equal), is determined experimentally

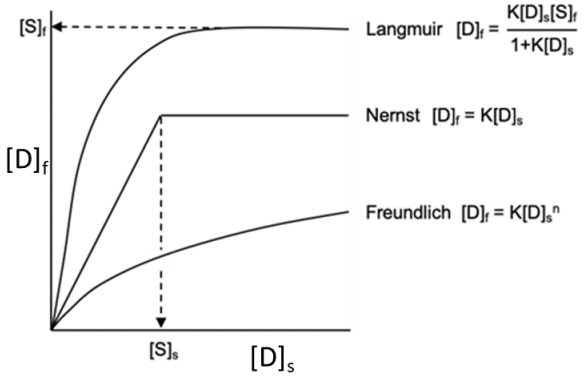
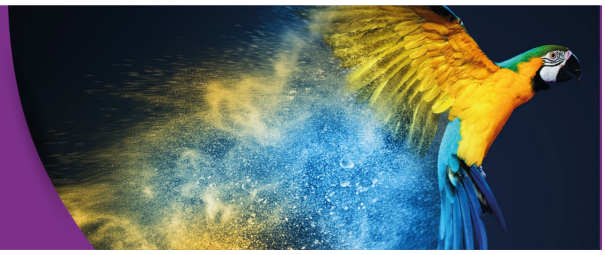


Figure 3 general form of dye adsorption equilibrium isotherms

[4] also referred to as *fitting parameters*

[5] in essence, many of the models are extensions of the Langmuir or Freundlich isotherm equations



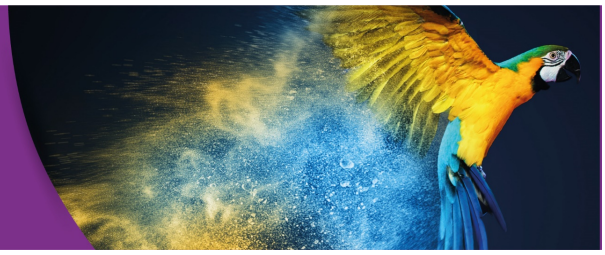
When the experimentally obtained values of $[D]_f$ are plotted versus the corresponding experimentally determined values of $[D]_s$, an *equilibrium adsorption isotherm* is secured, which describes the relationship between the amount of dye adsorbed up by the fibre, $[D]_f$, and the amount of dye in the external dyebath, $[D]_s$, at *constant temperature*. Adsorption isotherms obtained for dye/fibre systems are generally considered to correspond to one of three main types namely *Nernst* (*Henry)*, *Langmuir* and *Freundlich* (Figure 3) though bimodal mechanisms of adsorption often apply to dyeing systems (eg *Nernst-Langmuir*, etc) [see (11)].

Nernst isotherm (aka Partition isotherm)

The adsorption mechanism described by this isotherm denotes that a *linear relationship* exists between $[D]_f$ and $[D]_s$, as defined by Equation 3, where *K* is the *distribution coefficient* or *partition coefficient*. The start of the horizontal line in Figure 3 represents the *saturation value*, S_s, of the dye in solution, which corresponds to the maximum aqueous solubility of the dye.

$$[D]_f = K[D]_s \qquad 3$$

This isotherm is typically obtained for the adsorption of disperse dyes on PET and other types of hydrophobic fibre, as exemplified by the results of the pioneering 1954 study by Schuler and Remington (21), which revealed that *rectilinear*, *Nernst* (aka partition) adsorption isotherms were obtained in the case of disperse dyes on PET and other types of fibre, that took the form of line (a) shown in Figure 4, findings that were subsequently confirmed for several types of fibre [eg PA (22-24), PP (25), PET (23, 26, 27), CA (28-31) and CTA (30); see (11) for a summary].



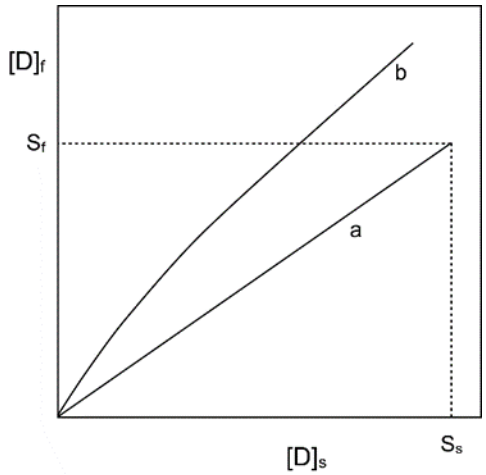


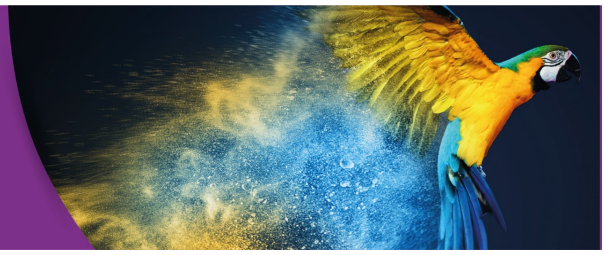
Figure 4 general forms of (a) rectilinear and (b) curvilinear adsorption isotherms obtained for disperse dyes on PET and other types of fibre

The linearity of the adsorption isotherms obtained for PET fibres (Figure 4a) was assumed (21) to imply that the dye was *monomolecularly dispersed* in both the dyebath and fibre phases. Furthermore, the linearity of the adsorption isotherm indicated (21) that dyeing proceeded by a mechanism that involved *dye solution in the fibre*, which was analogous to Kartarschoff's 1925 observations regarding the dyeing of CA fibres (32), that solid disperse dye was adsorbed onto the surface of the substrate and the dye was retained by means of a *solid solution process*.

Such linear adsorption isotherms can be described using Equation 3a, which is a simple extension of Equation 2, where S_f and S_s are the saturation values of the dye in the fibre phase and solution phase.

$$K = \frac{[D]_f}{[D]_s} = \frac{S_f}{S_s} \qquad 3a$$

Equation 3a denotes that there is a linear partition of the dye between the dyebath and fibre phases, under equilibrium conditions; the higher the value of K then the greater is the partition of the dye in favour of the fibre phase (ie $[D]_f > [D]_s$) and, therefore, the greater is the extent of dye uptake onto the substrate. As line (a) in Figure 4 shows, dye adsorption varies in a linear fashion up to the point at which both the dyebath and fibre phases achieve *saturation*, this being denoted by S_s and S_f, respectively.

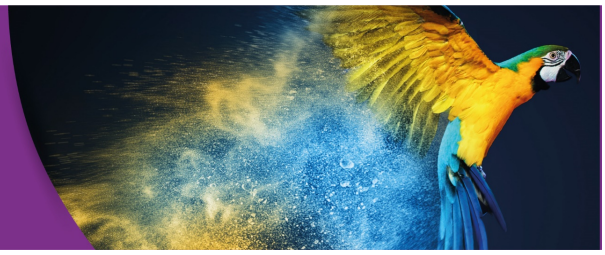


According to Kartarschoff's theory of dye adsorption, whereby the hydrophobic dye dissolves in the solid fibre by means of a solid solution mechanism, then the cessation of the linear adsorption plot shown in Figure 4a can be attributed to the fibre having become saturated with dye and, therefore, the extent of dye uptake depends on the *saturation value of the dye in the fibre*, S_f, rather than the *saturation value of the dye in the aqueous solution* (ie dyebath), S_s. However, in sharp contrast, an alternative theory, proposed by Clavel and Stanisz (33, 34) in the early 1920's, suggested that dyeing proceeds by adsorption of the low solubility disperse dye onto the substrate from an *aqueous dyebath solution*, according to which, the point at which equilibrium dye adsorption ceases (Figure 4a) can be attributed to the aqueous dyebath having become saturated with dye, from which it follows that the extent of dye uptake depends on the saturation value of the dye in the aqueous solution, S_s.

However, the two parameters, S_s and S_f, are quite different in terms of the information they provide regarding the possible mechanism of disperse dye adsorption; a brief discussion seems appropriate.

If the point at which equilibrium dye adsorption ceases (Figure 4a) is due to the dye solution (i.e. dyebath phase) having become saturated with dye, then a relationship should exist between the solubility of a particular disperse dye in the dyebath, S_s, and the solubility of the dye in a fibre, S_f. This was indeed observed by Bird and Harris[6] (35) for several types of AQ, azo and dinitroarylamine disperse dyes on CA fibres at 80°C, insofar as high values of S_f were generally achieved at higher values of S_s, which implies that the aqueous solubility of the dye is important from the viewpoint of dye adsorption. Furthermore, the solubility of the various AQ, azo and nitrodiarylamine disperse dyes was considerably greater in the CA substrate than in water ay 80°C, by an average factor of between ~500 and ~1500 (35). This pronounced differential solubility of the disperse dyes in the aqueous dyebath and fibre phases is of fundamental importance in terms of the mechanism of their adsorption, insofar as, according to Equation 3a, $K = S_f/S_s$, the much higher solubility of the dyes in the hydrophobic fibre phase, S_f, than in the aqueous solution phase, S_s, (i.e. dyebath), means that the partition coefficient, K, of the dyes will be intrinsically very high because the hydrophobic dyes inherently prefer the (hydrophobic) fibre phase to the aqueous dyebath phase. Indeed, the ratio S_f/S_s provides a measure of the differential solubility of the dyes in the fibre and solution phases and, as such, the ratio expresses the relative hydrophobicity/hydrophilicity of the dyes; from Equation 3a, it follows that the partition coefficient, K, of the various AQ, azo and

[6] this paper formed one part of several pioneering studies published by Bird *et al* which sought to determine the mechanism of adsorption of disperse dyes on CA fibres



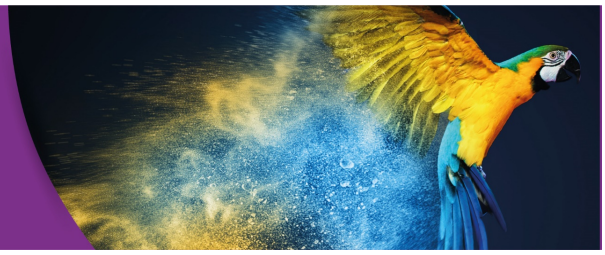
dinitroarylamine disperse dyes on CA fibres at 80°C, should increase as the ratio S_f/S_s increases, as was indeed observed (35).

These findings suggest that the aqueous solubility of the disperse dye, as reflected in terms of its aqueous solubility in the dyebath phase, S_s, under the dyeing conditions used, is the principal factor that determines the extent of dye uptake achieved for a particular fibre, as discussed below.

If, in contrast, the cessation of dye uptake in Figure 4a was due to the fibre having become saturated with dye, S_f, then a *specific-site* adsorption mechanism would apply, according to which, maximum dye uptake, expressed in terms of fibre saturation, S_f, would correspond to the adsorbed dye molecules having occupied all of the *limited number* of sites available in the fibre. Such a notion that PET and other types of fibre may contain a limited number of specific sites at which disperse dye molecules interact gains support from the findings that *curvilinear adsorption isotherms*, which take the generic form of curve (b) in Figure 4, have been obtained for disperse dyes on various fibre types of fibre, as exemplified by PET (36-38), CA (29, 39, 40), PA (41, 42) PTT (37, 43), such deviation from the previously discussed linear adsorption isotherms depicted by line (a) in Figure 4, correlating well with an IUPAC type 1 (Figure 2) or Langmuir-type adsorption model that is indicative of the presence of specific sites within the substrate.

From the foregoing it is apparent that the precise nature of the interactions between disperse dyes and PET and other types of fibre has not been fully elucidated, as is the case with many other dye/fibre systems (11).

Nonetheless, it is widely held that despite the characteristically low aqueous solubility of disperse dyes, the accepted mechanism by which the dyes are adsorbed on PET fibres (as well as CA, CTA, etc.) depends upon their dissolution in the aqueous dyebath [see (11)]. In essence, at the start of dyeing, the majority of the dye is present in the dyebath as *particles* (ie aggregates of dye molecules) which form an aqueous *dye dispersion*; also present in the dyebath is a very small amount of *dissolved* dye molecules that comprise a very dilute *aqueous dye solution*. Thus, the initial dyebath contains both *dye particles* that reside within a bulk *dye dis*persion, as well as dissolved *dye molec*ules that constitute a small, but nevertheless very important, dilute *dye solution*. Dissolved dye molecules move from the dilute aqueous dye solution to the fibre surface, are adsorbed and then diffuse within the amorphous regions. Dye molecules are then released from the aqueous dye dispersion into the dyebath and



dissolve, thereby replenishing the small aqueous dye solution with dissolved dye molecules, which can transfer to the fibre surface and become adsorbed. This process of dye molecules from the bulk dispersion dissolving and forming an aqueous dye solution from which dye adsorption occurs, continues until either the dyebath contains no more dye (ie is exhausted) or the fibre is saturated with dye.

It follows, therefore, that the characteristically small aqueous solubility of disperse dyes is of crucial importance in terms of the manner by which the dyes are adsorbed onto PET (and all other types of fibre).

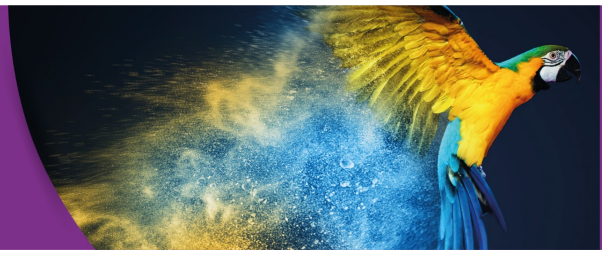
Langmuir isotherm

According to this adsorption mechanism, which accords with an IUPAC type-a adsorption model (Figure 2), dye uptake occurs at a *finite number* of *equivalent, specific sites* within the fibre, there being *no interaction* between the sites or the dye molecules that occupy the sites; once a site has been occupied by a dye molecule, the site is *incapable of further adsorption*. When all adsorption sites have been occupied, the fibre is *saturated*, the extent of this being referred to as the *fibre saturation value*, S_f. The most widely employed form of the equation that fits the curved Langmuir line displayed in Figure 3 is Equation 4 from which Equation 5 can be derived by inversion.

$$[D]_f = \frac{K[D]_s S_f}{1+K[D]_s} \qquad 4$$

$$\frac{1}{[D]_f} = \frac{1}{K[D]_s[S]_f} + \frac{1}{[S]_f} \qquad 5$$

According to Equation 5, if $1/[D]_f$, (dye adsorbed) is plotted as a function of $1/[D]_s$ (dye in solution) , the ensuing straight line has a slope of $1/K[S]_f$ and intercepts at $1/[S]_f$ (Figure 5); such a *reciprocal plot* is used to obtain the fibre saturation value, $[S]_f$, which can be used in Equation 5. Alternatively, a plot of $[D]_f/[D]_s$ as a function of $[D]_f$ provides a straight line that intercepts the $[D]_f$ axis at $[S]_f$ (Figure 5).



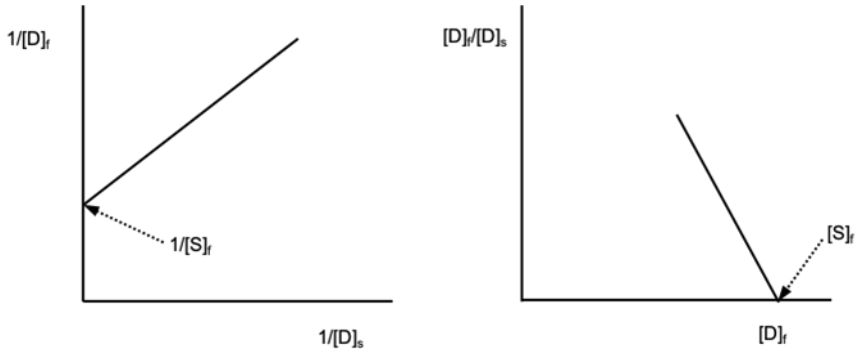


Figure 5 alternative Langmuir plots

At low amounts of dye, when $[D]_f << [S]_f$, the Langmuir isotherm resembles the Nernst isotherm so that Equation 6 applies.

$$\frac{[D]_f}{[D]_s} \approx k[S]_s \qquad 6$$

The Langmuir isotherm is typically obtained for the adsorption of anionic dyes (eg non-metallised acid dyes) on wool, silk and PA fibres, as well as basic dyes on PAN fibres, as exemplified by the results presented in Figure 6.

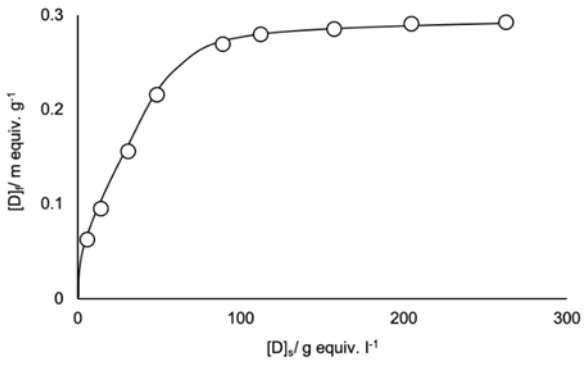
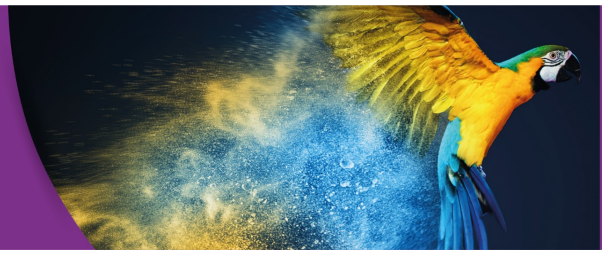


Figure 6 adsorption isotherm obtained for C.I. Acid Blue 138 on PA 66 at pH 6.1 at 85°C (44); drawn using data from (44)



However, wool is highly susceptible to *hydrolysis* when exposed to hot aqueous conditions, such as those employed in typical dyeing processes. Consequently, during equilibrium dye adsorption experiments, which necessitate treating the thermally-sensitive fibre for extended periods at high temperature in aqueous dyebaths, both the chemical and physical structure of the fibre change markedly, with the result that the nature of the dyebath components also change as a function of time due to the dissolution of various oligomeric and monomeric fractions from the substrate. Nonetheless, practical equilibrium dye adsorption isotherms for wool have been undertaken (even, surprisingly, in more recent times [e.g. (45-47)]), the results of which must be treated with caution owing to the marked levels of hydrolytic degradation which the substrate will invariably have incurred.

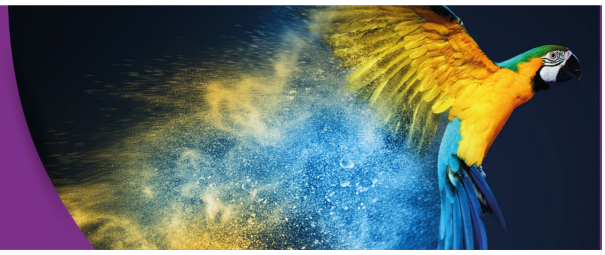
In order to circumvent the inherent experimental difficulties involved in undertaking anionic dye adsorption equilibrium isotherms using wool, the mechanism of adsorption of dye anions on the substrate is *mathematically modelled* on the basis of the adsorption of simple acids (e.g. HCl, H_2SO_4) and alkalis (e.g. NaOH, KOH), in the form of experimentally obtained *titration curves* [e.g. (2, 48-54)]. This particular approach, which is discussed in section 2.6.2, is assumed to apply in the cases of silk and other natural protein fibres, insofar as the mechanism of anionic dye adsorption is assumed to parallel that of wool. Furthermore, even though PA fibres display considerably greater hydrolytic and thermal resilience than either wool or silk fibres, and equilibrium dye adsorption isotherms can be obtained using PA substrates, such as that presented in Figure 6, unfortunately, the (entirely) theoretical models of dye adsorption derived for wool are considered to apply to synthetic polyamide fibres.

Freundlich Isotherm

The adsorption mechanism described by this isotherm (see the curved Freundlich line in Figure 3) takes the form of Equation 7 where *n* is a constant. Taking logarithms of both sides of Equation 7 provides the linear equation, Equation 8, which is used to confirm adherence of experimental adsorption equilibrium isotherm results to the Freundlich adsorption mechanism, since a plot of log $[D]_f$ vs log $[D]_s$ (Figure 7), provides a straight line of slope *n* in Equation 8.

$$[D]_f = K[D]_s^n \qquad 7$$

$$\log[D]_f = \log K + n \log[D]_s \qquad 8$$



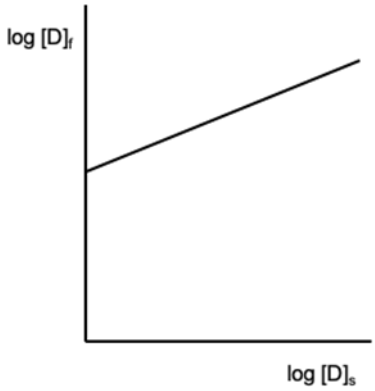


Figure 7 Freundlich log-log plot

This type of isotherm describes the adsorption of, for example, direct dyes and reactive dyes[7] on cotton and other cellulosic fibres in the presence of added inorganic electrolyte (NaCl or Na_2SO_4), as exemplified by the results presented in Figure 8, which were obtained by Willis *et al* (55) as part of a detailed and elegant series of investigations into the mechanism of adsorption of direct dyes on cellulosic substrates.

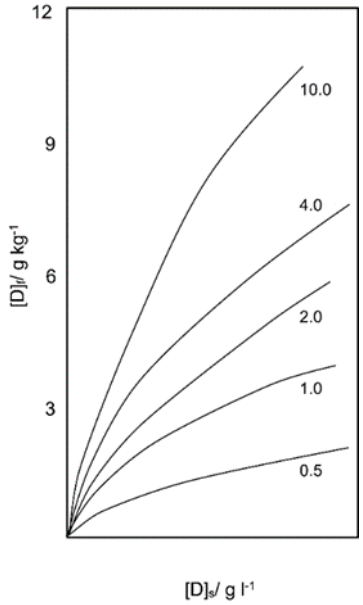
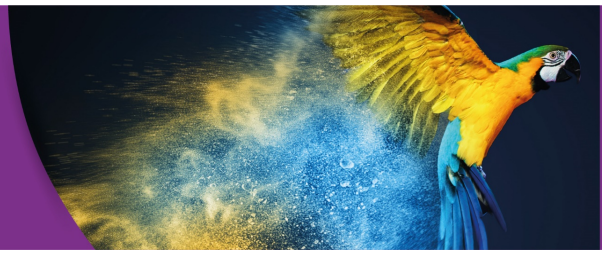


Figure 8 adsorption isotherms obtained for C.I. Direct Yellow 12 on CV sheet at 97.5°C in the presence of different amounts of added NaCl/g l^{-1} (shown by numbers on curves); drawn using data from (55)

[7] prior to the formation of covalent bonds between the dye and fibre



The characteristic sigmoidal-shaped curves (Figure 8) are indicative of *monolayer-multilayer adsorption* at non-specific sites within the cellulosic substrate, insofar as, in the initial stages of dye adsorption, *monolayers* of adsorbed dye ions are established and the subsequent formation of *multilayers* of adsorbed dye molecules at non-specific sites in the fibre is characteristic of *dye aggregation* within the substrate (11, 56). Such *dye self-association* and the concomitant formation of multilayers of adsorbed dye molecules can be considered to be a corollary of the marked tendency of the characteristically, long, planar, direct dye molecules to self-associate in solution via π-π interactions between adjacent dye molecules, which is promoted in the presence of added inorganic electrolyte due to suppression of dye solubility (11, 56).

However, equilibrium direct dye adsorption on cellulosic substrates has been observed to correlate with a Langmuir-type model [(2, 7, 11)], according to which, the cellulosic fibre would contain a limited number of specific sites at which the direct dye molecules interact and dye uptake results in monolayer formation. Clearly, such a mechanism represents a major departure from a Freundlich-type model, insofar as, whilst the latter model describes adsorption onto *heterogeneous* surfaces in which the adsorption sites vary in terms of their interaction with the dye molecules, a Langmuir-type model assumes an *homogeneous* surface that contains a finite number of identical sites that are equivalent in terms of their interaction with adsorbing dye and there is negligible interaction between adsorbed molecules.

From the viewpoint of a Freundlich-type adsorption mechanism, as depicted by the curves displayed in Figure 8, it seems likely that the sites within the cellulosic substrate at which the adsorbing direct dye molecules will interact will be hydroxyl groups, bearing in mind the proliferation of -OH groups in cellulose (11). Such sites can also be assumed as the most likely participant in terms of dye-fibre interaction from the perspective of a Langmuir-type adsorption process, although in this case, the limitation of specific sites within the substrate implies some form of pronounced selectivity of the participating -OH groups; however, the precise nature of such site-selectivity is unclear.

From the foregoing brief discussion, it is apparent that the precise nature of the manner by which anionic dyes are adsorbed onto cellulosic substrates in the presence of added inorganic electrolyte, and become adsorbed onto the substrate, remains a matter of debate.