THEORY

2.1   MECHANISM OF DISPERSE DYE TRANSFER AND DYEING (20,22)

When   a   disperse   dye   is   added to the dyebath for
dyeing   a   hydrophobic   fibre,   usually the dye is in excess
of   its   solubility   limit so that the dye is present in the
dyebath   in   three   states, namely dissolved dye, dye in the
micelles,   and   solid   dye   (or   insoluble dye but finely
dispersed), the   relative   amounts, being   determined by the
solubility   of   the dye in water at that temperature, can be
written   diagrammatically   as   being in equilibrium as shown
below (22).

$$\text{Dye}_{\text{solid}} \rightleftharpoons \text{Dye}_{\text{in micelle}} \rightleftharpoons \text{Dye}_{\text{dissolved}}$$
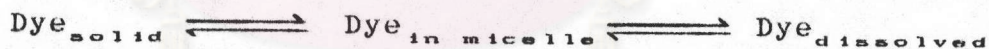
When   the   fibre   is   entered   into   the   dyebath, the
dissolved   dye   slips   molecule   by molecule into the narrow
pores   present   in   the   fibre   structure   and gets attached
there by   certain forces. As a result, the concentration of
the   dissolved   dye   in   the   dyebath decreases and more and
more   dispersed   dye   particles   break   up   to be in micelle
form,   and   eventually absorbed by the fibre. The dye in the
micelle   therefore, may be considered to act as a reservoir,
which   replenishes   the   dyebath,   when   it   is   depleted by

dyeing. Since the dyeing occurs via the soluble dye, it is to be expected that the ease of dyeing bears some relation to the solubility; in general terms, lower solubility results in a lower rate of adsorption but the reverse may not necessarily be true since the rate of diffusion into the fibre will become the controlling factor and there appears to be no advantage in increasing the solubility above 10 mg/l.

Since disperse dye has limited solubility in water, i.e., since it has an essentially hydrophobic nature, there is an inherent tendency in the dissolved dye to leave the aqueous phase, and a hydrophobic fibre when present in the dyebath readily accept the dye molecules similar to the manner in which the dye is extracted by a suitable solvent.

The rate of dyeing hydrophobic fibres with disperse dyes depends on the temperature of the dyebath and the type of the dispersing agent used. The dispersing agents assist the particle size reduction of the dye and increase the solubility of the dye in water (Table 2.1) (20). With an increase in temperature also the solubility increases (Table 2.2) (22). Therefore, the solubilising effect of the dispersing agent at higher temperatures is less marked. As a direct consequence of the solubilising action of the dispersing agent, the adsorption of large particles of the dye onto the fibre surface is effectively prevented. This, in turn, facilitates the production of level dyeing.

Table 2.1 Solubilities of three disperse dyes at 25 °C in
water and two 0.5 % solutions of dispersing
agents (20)

Dyes	solubility (mg/l)		
	water	sodium oleyl-p-anisidine sulphonate	sodium oleate
4-nitro-4'-aminoazobenzene	9.5	60	26
4-nitro-4'-phenyl-aminoazobenzene	0.5	46	17
1,4-diaminoanthraquinone	17.0	57	34

Table 2.2 Solubilities of some disperse dyes (22)

Dye	solubility in water (mg/l)	
	25°C	80°C
Azobenzene	5	
4-Aminoazobenzene	32	330
4-N-Ethyl-N-(β-hydroxyethyl)-4'-nitroazobenzene	0.3	7
4-N-Di(β-hydroxyethyl)-4'-nitroazobenzene	0.4	18
2-Aminonapthalene azobenzene	<0.2	1.9
1-Aminoanthraquinone	0.4	9
1-Amino-4-hydroxy-anthraquinone	0.2	7.5
1-N-Methylamino-4-N-phenyl-aminoanthraquinone	<0.2	<0.2
1-N-Methylamino-4-hydroxy-5-N-methylamino-8-hydroxy anthraquinone	<0.2	<0.2

In the initial stages of dyeing, the adsorption of the dissolved dye by the fibre surface results in the build up of a higher concentration of the dye in the surface layer of the fibre. Along with further adsorption, another process starts, in which the adsorbed dye diffuses from the fibre surface into the fibre structure towards the centre. This diffusion process continues until the fibre is uniformly dyed, provided sufficient time is given.

Thus dyeing may be considered as a process of dye transfer from a liquid solvent (water) to a solid organic solvent (fibre) and the dyeing is considered to take place in the following simultaneous steps:

(1) the convective transfer of dye from the bulk of the liquor to the fibre surface,

(2) adsorption of the dissolved dye from the solution onto the fibre surface, and

(3) diffusion of the adsorbed dye from the fibre surface into the interior of the fibre towards the centre.

The first step depends on the dispersability and solubility of the dye, further aided by the presence of dispersing agents in the dyebath and rise in temperature, and it is not influenced by the fibre characteristics. The second step, being generally considered to occur instantaneously so that the dye in the liquid adjacent to the surface is in equilibrium with that adsorbed on the fibre surface itself, is influenced by the concentration (or solubility) of the dye in the fibre and that in the dyebath of which their ratio is determined as partition coefficient (defined by the former divided by the latter). The diffusion rate into the fibre (third step) is very much lower than that through the liquid and hence it may be taken to be the rate-determining step in dyeing.

When equilibrium dyeing is reached, the following subsidiary equilibria are established.

(1) Dye dispersed in the bath $\rightleftharpoons$ Dye dissolved in the bath

(2)   Dye dissolved in the bath $\rightleftharpoons$ Dye adsorbed on the fibre

(3)   Dye adsorbed on the fibre $\rightleftharpoons$ Dye diffused in the fibre

If the aqueous solubility of the dye and the diffusion of the dye in the fibre which are the two important factors governing the dyeing process are affected, the rate of dyeing, the percentage exhaustion of the dyebath and the level dyeing characteristics of the dye are also affected.

2.2   ADSORPTION ISOTHERMS (24)

Adsorption isotherms are the curves obtained by plotting the dye adsorbed by the fibre, $[D_f]$, against the concentration of the dye in solution, $[D_s]$, at constant temperature. The curves fall, essentially, into three categories, each characteristic of a different phenomenon which may be involved in dyeing.

1. Nernst Isotherm
2. Langmuir Isotherm
3. Freundlich Isotherm

1.   Nernst Isotherm is the simplest of three which considers the partition of a solute between two immiscible solvents. In this case $[D_f]/[D_s] = K$, where K is the partition coefficient. This equilibrium is often referred to as the Nernst distribution. When $[D_f]$ is plotted against $[D_s]$ at constant temperature the curve is a

straight line which terminates at the point when both the fibre and the dyebath are saturated (Figure 2.1). There are slight deviations from the linearity of the curve, particularly as the solutions become more concentrated or large dye particles which have lower solubility are present in the dyebath. This isotherm is essentially found in the case of the application of disperse dyes in aqueous suspension for dyeing,
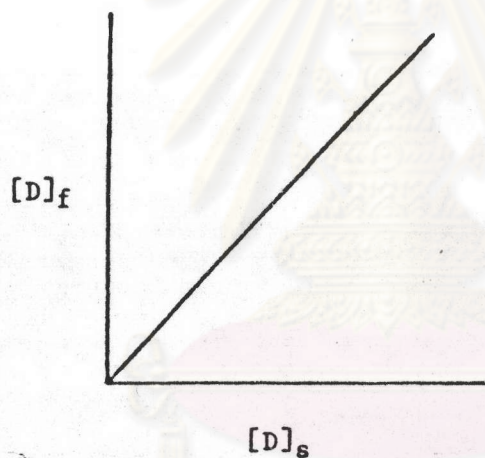

Figure 2.1   Nernst isotherm (24)

2.   Langmuir isotherm is obtained where there are a definite number of sites within the fibre which can enter into combination with the dye, Na_zD, the state of affairs which exists with the protein fibres. If it is assumed that the cations present in solution are independently adsorbed by the carboxyl groups, and the

anions by the amino groups, then

$$-\Delta\mu^\circ = RT \ln[\theta_D/(1-\theta_D)][\theta_{Na}/(1-\theta_{Na})]^z - RT \ln[Na]_s^z[D]_s \quad (2.1)$$

when, in this case, Na is the cation. If it is assumed that the fibre contains an equal number of positive and negative sites, and the dye is derived from a monobasic acid, the equation (2.1) becomes

$$-\Delta\mu^\circ = 2RT \ln[\theta/(1-\theta)] - 2RT \ln[D]_s \quad (2.2)$$

where θ is the fraction of sites in the fibre which are occupied. In this case when $[D_s]$ is plotted against $[D_f]$ the curve becomes parallel with the $[D_s]$ axis when all the sites are occupied as shown in Figure 2.2.
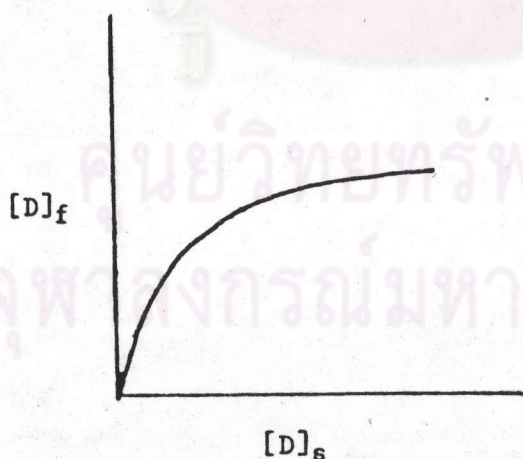

Figure 2.2   Langmuir isotherm (24)

3.   Freundlich isotherm is applicable to the adsorption of direct and vat dyes by cellulosic fibres. In this case the attachment is not at specific sites so that there is no stoichiometric limiting factor. If attachment is brought about by hydrogen bonds and physical forces the limitation is the available surface within the pores. The adsorption is rapid at first because the sites are easily accessible but becomes slower as the dye molecules have to seek out the more remote points of attachment. The $[D_f]/[D_s]$ curve, therefore, is not a straight line nor does it reach a point at which it becomes parallel with the horizontal axis, as shown in Figure 2.3.
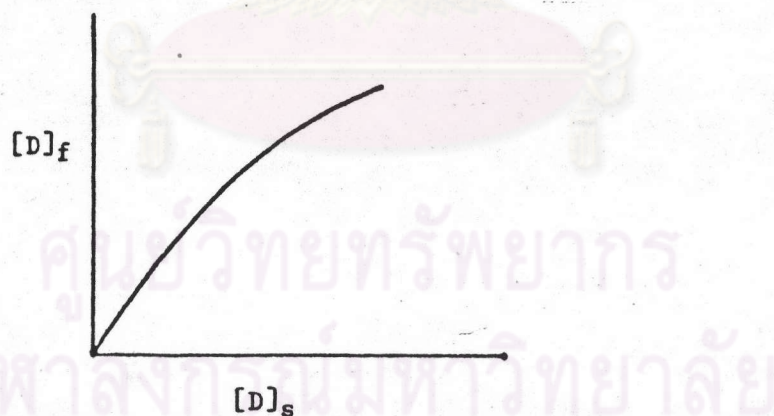
Figure 2.3   Freundlich isotherm (24)

2.3 KINETICS OF DYEING OF DISPERSE DYES

2.3.1 RATES OF DYEING

The rate of dyeing with disperse dyes or the speed of dye uptake can be explained by many terms, but the preferably one is by the term of time of half-dyeing ($t_{1/2}$) which is defined as the time at which half of the equilibrium adsorbed dye amount is uptaken by the fibre (Figure 2.4). Changes in concentration of dye in the bath do not modify the rate of dyeing. Additions of dispersing agents modify both the equilibrium dye uptake and the rate of dyeing (Table 2.3) (22). A reduction in exhaustion occurs as the dispersing agent concentration increases; the times of half-dyeing show an increase in rate with the rather insoluble Duranol Blue 2G but a
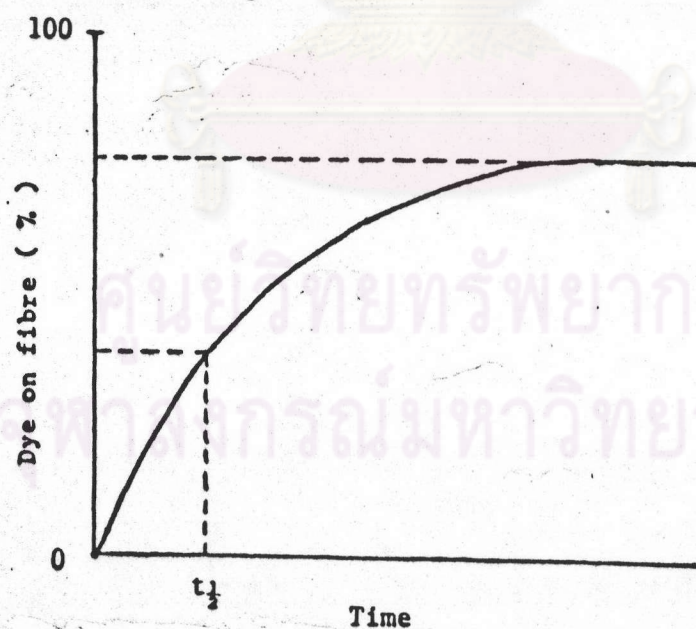

Figure 2.4 Time of half-dyeing (22)

decrease with the more soluble Dispersol Fast Scarlet B and Serisol Fast Red 2RD. In the former case, the increase in rate is considered to arise from the increase in the rate of solubilisation of the dye particles; with the latter being relatively easy to dissolve, the dispersing agent reduces the effective dye concentration in solution as a result of the increase in micelles present, thereby reducing the diffusion rate.

Table 2.3   Effect of increasing amounts of Lissapol LS on dyeing secondary cellulose acetate at 80 °C (22)

Lissapol LS (g/l)	Duranol Blue 2G		Dispersol Fast Scarlet B		Serisol Fast Red 2RD	
	$t_{1/2}$ (min)	%Exhaustion	$t_{1/2}$ (min)	%Exhaustion	$t_{1/2}$ (min)	%Exhaustion
1	45	92	4.5	90	4	74
5	20	78				
9.3*					14	50
15*			7	50.5		
20	12	51				

* Sufficient to give approx. 50 % exhaustion at equilibrium.

2.3.2 <u>DIFFUSION</u> (22,24,25)

At the beginning of the dyeing process, the dye is distributed non-uniformly through the substrate with a high concentration at the surface and a zero concentration inside. A concentration gradient is therefore set up which causes the dye to transfer itself from the higher to the lower regions of concentration. This behaviour is described in terms of Fick's Law which states that the flux of dye (g or g-moles/unit area/ unit time) is proportional to the gradient of concentration and can be expressed by the equation

$$dQ/dt \; = \; J \; = \; -D(\partial C/\partial X) \qquad (2.3)$$

where dQ/dt is the quantity of material crossing unit area during the time interval dt and is equal to the flux J, D is the diffusion coefficient and C is the concentration at any point distance X from the surface, namely the amount of material crossing unit area in unit time under unit concentration gradient.

D is essentially a measure of the speed with which the dye molecules move under the action of unit force and has the dimensions $(length)^2/time$, and also of the permeability of the fibre. The smaller the dye molecule the more readily will it diffuse, and the more porous the fine structure of the fibre the easier will be the passage of the molecules of the dye.

In eqn. (2.3), the force responsible for the flux, namely concentration gradient, has been taken as "ideal"; a more correct assignment is given by the gradient of chemical potential, i.e.

$$J = -D^\circ C(\partial\mu/\partial X) \tag{2.4}$$

where D° is the relevant diffusion coefficient. Substituting for the chemical potential μ (i.e. $\mu = \mu^\circ +$ RT ln a) gives.

$$J = -RTD^\circ C(\partial\ln a/\partial X) \tag{2.5}$$

If ln a is written as $C\gamma$ where γ is the activity coefficient, eqn. (2.5) becomes

$$J = -RTD^\circ(1+(\partial\ln \gamma/\partial\ln C))(\partial C/\partial X) \tag{2.6}$$

The effect of introducing the non-ideal behavior into eqn. (2.4) is to emphasise the fact that the measured D depends on the thermodynamic properties. With the disperse dyes, as judged by the equilibrium data which indicate apparent "ideal" behaviour, it is to be expected that γ may be equated to unity and hence diffusion follows essentially eqn. (2.3) with D replaced by RTD°.

2.4 EFFECTS OF TEMPERATURE (20,22,24,25)

In common with most processes, a rise in temperature increases the rate at which the dye is adsorbed (Figure

2.5). The effects of temperature changes are normally expressed in terms of the activation energy of the process. The changes in diffusion coefficient (D) are then described by eqn. (2.7)

$$D = D_o e^{-\Delta E/RT} \qquad (2.7)$$

where ΔE is the activation energy, i.e. the difference in energy between activated molecules and the remainder of those in solution, D_o is a constant independent of temperature, R is the gas constant and T is the absolute temperature. ΔE is found from the slope of the graph of ln D versus 1/T.

The activation energy is a reflection of the way in which the diffusion coefficient changes with temperature. It may, however, be regarded as the energy which the dye molecule must acquire in order to be able to move and could be regarded as a measure of a barrier to movement of dye.

The effect of dyeing temperature on the dyeing of a hydrophobic fibre with various disperse dyes are not identical. The dyeing behaviour of some of the rapid diffusing type of disperse dyes, shown in Figure 2.6, describes the effect of dyeing temperature on the exhaustion of the dyebath for three rapid-diffusing and one slow-diffusing disperse dye. The amount of the dyes on the fibre is expressed as a percentage of the dye originally present in the dyebath.
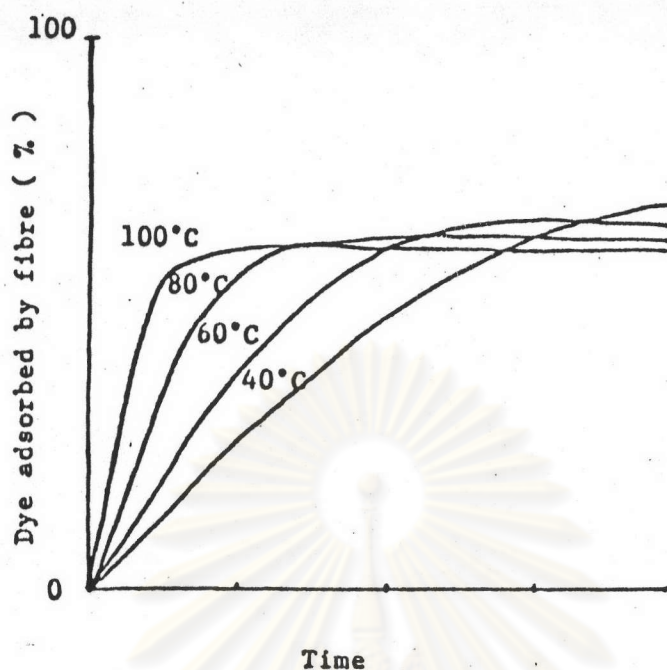
Figure 2.5   Effect   of   temperature   on the dyeing rate and
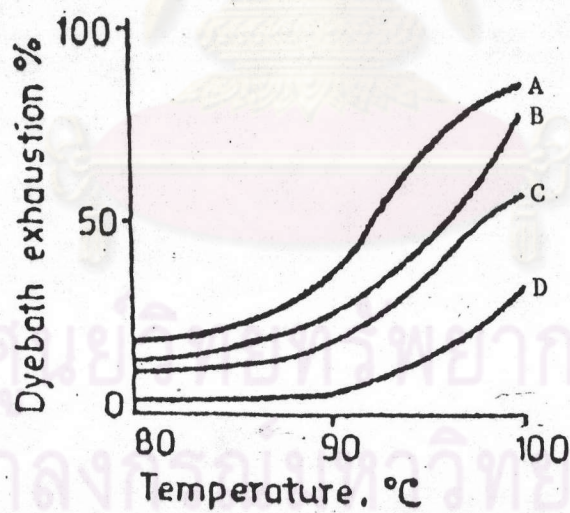equilibrium (22)

Figure 2.6   Effect   of   dyeing temperature on the exhaustion
of   dyebath   for   some disperse dyes (A) Duranol
Red 2B (B) Dispersol   East   Orange G (C) Duranol
Blue   GN   and   (D) Dispersol Fast Scarlet B (20)

It is seen from the steep slopes of the curves (Figure 2.6) obtained that above 85 °C even a slight increase in temperature increases the dyebath exhaustion considerably.

2.5 CARRIER DYEING (6,20,22,23,26-28)

2.5.1 Theory of Carrier Dyeing

Many theories have been advanced to explain the mechanism of carrier dyeing. One of these is based on the ability of carriers to solubilize disperse dyes. This theory is untenable because many organic solvents solubilize the dyes and yet do not exhibit carrier properties. Another one proposes that the carrier produces fiber swelling and allowing penetration. Another theory suggests that the carrier coats the individual fibres, forming a layer through which the dye transfers to the fibre. Still another suggests that the carrier loosens the binding forces holding the polymer chains together, thus providing suitable spaces for the dye molecules. Although there are many theories offering understanding of this subject, no universal agreement exists on the mechanism of carrier dyeing (23). But it is probably a combination of all these factors that is suitable in explaining (28).

The characteristic of carriers is the fact that for carrier action they must be adsorbed by fibres. It has been observed that the effectiveness of carriers is a function of the molar concentration in the fibre.

2.5.2 Rate Increases on Carrier Addition

The increase in magnitude in the dye uptake brought about by carriers may be shown by the changes in dyebath exhaustion and rate of dyeing (Figure 2.7) (20). It is seen from Figure 2.7 that Tumescal D (a carrier based on diphenyl) can offer increasing the dyebath exhaustion from 48 % to 80 % at 100 °C and from 11 % to 63 % at 85 °C by using 8 % Tumescal D during a dyeing time of 60 min.
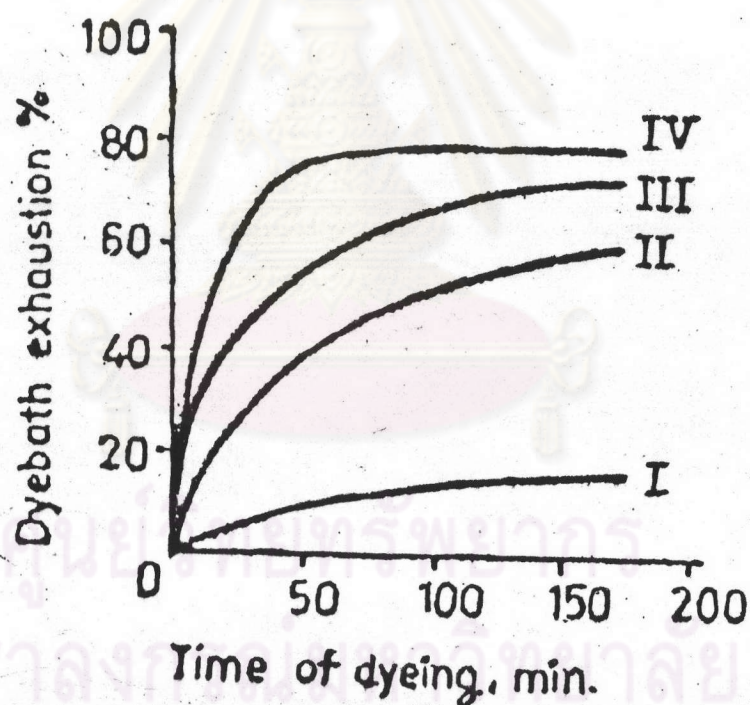

Figure 2.7 Effect of carrier on the rate of dyeing Dispersol Fast Scarlet B (I) no carrier, at 85°C; (II) no carrier, at 100 °C; (III) 8 % carrier, at 85 °C; (IV) 8 % carrier, at 100 °C (20)

2.5.3 Effect of Carrier Concentration (22)

Since carrier promotes the dye uptake and rate of dyeing, but the amount of using is not proportional to the required outlets. It is significant that the dye uptake increases and then decreases as the carrier concentration is increased (Figure 2.8) (22). The optimum concentration would seem to correspond to the amount of carrier necessary to saturate the system and any in excess of this will cause a reduction in dye uptake.
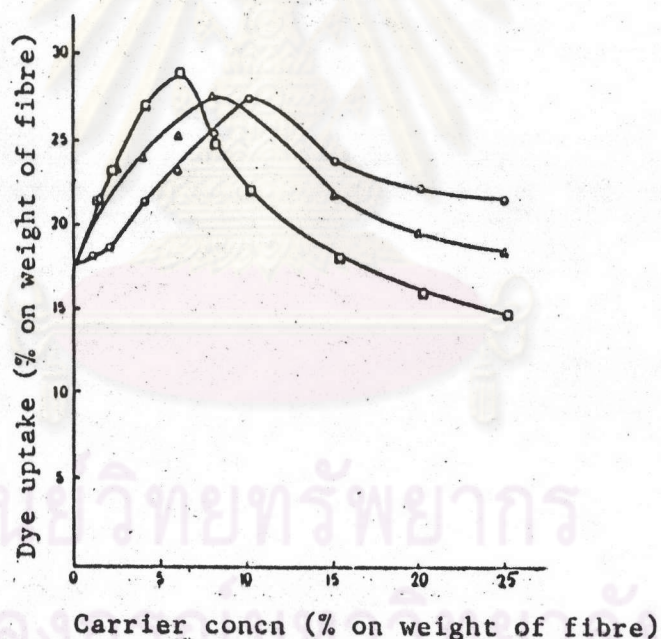

Figure 2.8 Effect of carrier concentration on the uptake of Amacel Fast Blue AGF Conc. at 100 °C. □ , Biphenyl; ○ , phenyl salicylate; △ , o-phenylphenol. (22)