again the polymer itself in an attempt to clarify the picture of such pigment migration. The following points are worth considering:

(1) Is there a change in diffusion behaviour at the glass-transition temperature?
(2) Dissolved pigments may have a plasticising effect and lower the crystallinity and the glass-transition temperature. Plasticisers are known to exude—why not pigments?
(3) It is claimed that particles migrate, e.g. in titanium dioxide chalking. What sort of free volumes are necessary if such effects are real?

The answer to the first question has been shown to be positive for polyester and there is no reason to believe it should be different for other polymer systems. The extent of the plasticising effect of certain pigments on certain polymers is known, and the change in diffusion might be expected to be less sharp in some pigment–plasticiser systems. With respect to the movement of particles inside a polymer matrix, *Figure 9* is a reproduction of a relation between free volume and diameter of diffusant calculated by Kumins and Rotemann (*15*). It is immediately obvious that the diffusion of particles differs fundamentally from this, and that the movement of titanium dioxide or similar particles from the interior to the outside of plasticised polymer systems has nothing to do with diffusion, but is best explained as migration in a plasticiser flux out of the polymer system; one might even say that the particles are squeezed out of the plastic as the polymer system loses plasticiser.

Finally, there is an analogous situation in textiles, where the dyeing of polyolefins with disperse dyes always leads to poor fastness (*16*). Here dyeing at elevated temperatures produces a supersaturated solution of disperse dye in the polyolefin, which at room temperature exhibits the 'blooming' characteristics so well known in the pigment and plastics industry.

* * *

I thank Dr K. Hoffmann and Dr K. Merkle for technical discussions and Mr H. Weber for carrying out the practical work.

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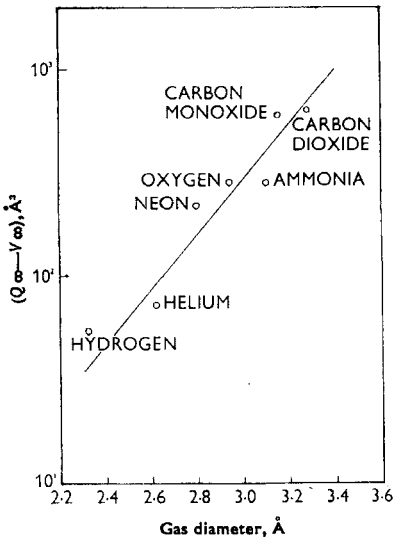

Figure 9—Plot of log free volume against gas diameter

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Adsorption of Cationic Dyes by Acrylic Films
I—Sorption Isotherms

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Sorption isotherms have been determined for five basic dyes on films prepared from an acrylic polymer. The results can be explained by an ion-exchange mechanism over 80% of the concentration range, or by a simple ion-distribution mechanism over the whole of the range. Addition of sodium ions reduces the dye uptake in accordance with the suggested mechanism. Isotherms of a dye mixture have shown that competition occurs, and the 'ion selectivity' constants calculated from these results agree well with those derived using the dyes singly.

Introduction

The dyeing of acrylic fibres by basic dyes is notable because, in the initial stages of dyeing, the rate at which dye is taken up is the same regardless of the concentration of dye in the liquor (*1*, *2*). This observation leads to the conclusion that the dye has a high substantivity and 'strikes' rapidly on to the fibre, subsequent diffusion into the fibre being relatively slow. It would seem, therefore, that the fibre surface is saturated in the initial stage and hence the adsorption properties will play a significant role in determining the subsequent diffusion process. In admixture, the surface will be shared by the dyes present in the bath and hence the adsorption properties of the dye will largely determine compatibility. The work reported in this paper is concerned with the mechanism of adsorption of basic dyes and their behaviour under equilibrium conditions when applied in mixtures.

The maximum extents to which basic dyes are sorbed by acrylic fibres have been shown in several instances to be approximately equivalent to the number of acidic groups in the fibre (*2*, *3*). In many acrylic fibres, these acid groups are 'strong' in character, being sulpho or sulphate groups attached (mainly) to the ends of the chains and which arise from the redox initiator used in polymerisation. In general, the dyeing process has been regarded as one in which the ions associated with the acid groups are exchanged for dye ions (*1*). Assuming the former ions to be hydrogen, the process may be written schematically as:

$$\text{Fibre-SO}_3\text{H} + \text{D}^+ \rightleftarrows \text{Fibre-SO}_3\text{D} + \text{H}^+$$

The equilibrium may be described by an exchange constant K_H^D, where

$$K_H^D = \frac{D_F\,[H_S]}{H_F\,[D_S]} \qquad \ldots(1)$$

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D_F and H_F refer to the quantities of dye and hydrogen ions in the fibre in g moles per kilogram of fibre and $[D_S]$ and $[H_S]$ are the corresponding concentrations of dye and hydrogen ions in solution. For this simplified model, activity coefficients have been set equal to unity in both the fibre and the external phases; the general validity of this assumption is questionable, but it may be accepted as an initial working hypothesis. The concentrations employed in dyeing are very small, and the activity coefficients of ions in an ion-exchange resin (styrene–divinylbenzene type) at similar concentration levels are not far from unity (*4*).

If we assume that $D_F+H_F=S_1$, the total number of acid groups in the fibre, then Eqn 1 may be written as a Langmuir isotherm, i.e.

$$\frac{D_F}{S_1-D_F}=\frac{K_H^D}{[H_S]}D_S, \text{ or } \frac{D_F}{D_S}=\frac{K_H^D}{[H_S]}(S_1-D_F) \quad \ldots.(2)$$
$$=K_L D_S \qquad =K_L(S_1-D_F)$$

Rosenbaum has extended this type of analysis to include the effects of additional competing cations such as the sodium ion (*1a*). The ion-exchange processes are considered to be subject to the condition:

$$D_F+Na_F+H_F=S_1 \quad \ldots.(3)$$

and an additional exchange coefficient K_{Na}^D may be written for the equilibrium:

$$\text{Fibre-SO}_3\text{Na}+D^+ \rightleftharpoons \text{Fibre-SO}_3D+Na^+ \quad \ldots.(4)$$

i.e.

$$K_{Na}^D=\frac{D_F\,[Na_S]}{Na_F\,[D_S]} \quad \ldots.(5)$$

The corresponding sorption isotherms are obtained by combining Eqn 3 with either Eqn 1 or Eqn 5. If Eqn 5 is chosen, for example, we have the isotherm:

$$\frac{D_F}{(S_1-H_F-D_F)}=\frac{K_{Na}^D}{Na_S}D_S \quad \ldots.(6)$$

Rosenbaum observed experimental deviations from the predictions of Eqn 6 and from those of the related isotherm

$$\frac{D_F}{(S_1-Na_F-D_F)}=\frac{K_H^D}{H_S}D_S \quad \ldots.(7)$$

These deviations were attributed to electrostatic interactions and to the weakly acidic character of the acidic groups in his experimental copolymer (*1a*). A re-analysis of these results suggests that at least some of the deviations observed were caused by the failure to take account of the anions sorbed by the acrylic copolymer (*5*).

More recently, however, many of the features of sorption isotherms have been deduced by a general approach in which the distribution of all the ions present is taken into account (*6*); in this, the simple assumption is made that the sorption of any ion i may be described by a distribution equation of the type:

$$C_i^f=K_i\lambda_i^{z}\,C_i^s \quad \ldots.(8)$$

where C_i^f is the concentration of ion i in the fibre (f) and C_i^s is its concentration in solution; z_i is the charge on ion i (including sign) and λ is a Donnan distribution coefficient. K_i is the 'chemical' distribution coefficient for the ion.

For example, in the present notation

$$D_F=K_D\lambda D_S \quad \ldots.(9)$$
$$H_F=K_H\lambda H_S \quad \ldots.(10)$$
$$Na_F=K_{Na}\lambda Na_S \quad \ldots.(11)$$

The distribution equations for ions bearing charges of the same electrical sign can always be combined in a purely formal way to define appropriate exchange coefficients, e.g.

$$\frac{K_D}{K_H}=\frac{D_F}{[D_S]}\frac{[H_S]}{H_F}=K_H^D \quad \ldots.(12)$$

but there is no need to assume corresponding ion-exchange mechanisms, such as that implied by Eqn 3 (*5*).

The conditions of electrical neutrality are employed to deduce the theoretical sorption isotherms and so the analysis applies to any type of dyeing system.

Eqn 3 for example would become

$$D_F+Na_F+H_F=C^-+X_F+OH_F \quad \ldots.(13)$$

where C^- is the concentration of acidic groups that are actually ionised. The concentrations, X_F and OH_F, of the inorganic and hydroxyl ions have now been included in the analysis. Since

$$X_F=K_X(1/\lambda)X_S \quad \ldots.(14)$$

and

$$OH_F=K_{OH}(1/\lambda)OH_S \quad \ldots.(15)$$

in these general terms, the isotherms contain the five coefficients K_D, K_H, K_{Na}, K_X and K_{OH}. The sorption isotherm therefore becomes

$$\frac{D_F}{(C^-+X_F+OH_F)-H_F-D_F}=\frac{K_{Na}^D}{Na_S}D_S \quad \ldots.(16)$$

The simple assumption that $K_X=K_{OH}=K$, say, when combined with the electrical-neutrality condition for the aqueous phase, i.e.

$$D_S+Na_S+H_S=X_S+OH_S \quad \ldots.(17)$$

and the use of Eqn 9, 14 and 15, gives

$$(X_F+OH_F)=KK_D\left(\frac{D_S}{D_F}\right)(D_S+Na_S+H_S) \quad \ldots.(18)$$

The anion concentrations that can provide a mechanism for 'overdyeing', or for deviations from Eqn 6, will become increasingly important as the concentration levels in the system increase, and these effects should be most pronounced with dyes of high 'affinity' (i.e. those with high K_D values).

Numerical computations for model systems have shown these effects clearly (*5–7*). A dye sorption in excess of S_1 is possible and shows up as a 'tail' when Eqn 2 is plotted. When K_D is high, significant deviations from Eqn 6 can occur even at dye concentrations D_F that are less than S_1.

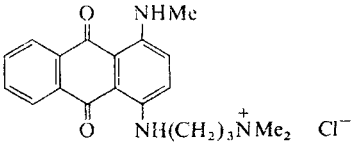
Despite these complexities, systems do exist for which Eqn 2 provides at least a formally satisfactory account of the results. Unfortunately, the interpretation of the parameter values is subject to controversy, so that the use of these simple equations is essentially empirical.

The work presented here is concerned with the analysis of adsorption isotherms of cationic dyes on films made from an acrylic polymer in order to show the extent to which Eqn 2 is obeyed for five dyes and to provide background information for analysis of the diffusion properties of these dyes to be discussed in a subsequent paper.

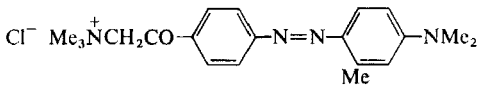
Experimental

DYES

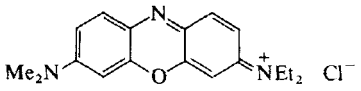
The following dyes were selected because they have above average stability in hot aqueous dyebaths:



(I; C.I. Basic Blue 22)



(II; C.I. Basic Red 14)



(III; an oxazine dye)

$C_{19}H_{26}N_8SO_8$ (mol. wt 506) (IV; C.I. Basic Red 24)

$C_{20}H_{40}N_6SO_6$ (mol. wt 492) (V; C.I. Basic Violet 19)

Dye III was obtained as a zinc double salt, from which the zinc was removed by precipitation with hydrogen sulphide. Dyes I, III, IV and V were purified by recrystallisation from absolute ethanol until the extinction coefficient became constant. Dye II was purified by dissolution in absolute ethanol followed by precipitation with dry diethyl ether until a constant extinction coefficient was obtained.

The purity of the dyes was checked by elemental analysis. Chromatographic techniques were used to ensure that coloured isomers were absent.

ACRYLONITRILE POLYMER FILM

A copolymer of acrylonitrile and vinyl acetate (ca 7% by wt of vinyl acetate) was supplied by the Chemstrand Corpn (now Monsanto Co.). Titration of the polymer in dimethylformamide solution was carried out electrometrically against tetramethylammonium hydroxide in methanol, using platinum as the standard electrode and glass as the other. The titration curve showed the presence of 35·1 milli-equiv. of strongly acidic groups per kilogram. Before titration, the polymer was transformed to the hydrogen form by dissolution in dimethylformamide, followed by precipitation with hydrochloric acid and washing in de-ionised water.

Films were cast from the polymer as follows. A solution of the copolymer (20 g) in dimethyl sulphoxide (85 ml) was prepared at 20°C and cast on to a glass plate to an original thickness not greater than 0·25 mm. The solvent was evaporated in an air oven at 60–65°C over 16 h, followed by a second period of at least 24 h at 80–85°C; the resulting films contained less than 1% of residual solvent. Before dyeing, the films were immersed in de-ionised water at 95–98°C for 2 h, the water being changed every 30 min; this procedure was designed to remove solvent and stabilise the film. A check made by differential infrared spectroscopy showed that the amount of solvent remaining was very small. The films used for sorption studies were ca 5 μm thick.

DYEING

Samples of the films (ca 50 mg) were attached to small glass sinkers and placed in Quickfit test-tubes (100-ml capacity) containing dye solution (50 ml) brought to pH 3·4 at room temperature by the addition of acetic acid (1 ml/l); the tubes were sealed with glass stoppers carrying Teflon sleeves. The tubes were immersed in a thermostat bath regulated to ±0·02 degC and agitated gently for at least 48 h, care being taken to ensure level dyeing.

After dyeing, the films were quickly removed, rinsed in cold water, blotted and dried *in vacuo* over phosphorus pentoxide. The dyebaths were cooled, the volume was measured to ensure that no loss had occurred owing to evaporation, and the pH and dye concentrations were measured in the usual way.

The dye content of the films was determined colorimetrically after dissolution in dimethyl sulphoxide, with the aid of a Unicam SP 600 spectrophotometer.

Results and Discussion

The isotherms plotted for the single dyes are shown in *Figures 1–5*. The graphs are linear over the major portion of the isotherm, as predicted by Eqn 2. These results differ from those of Rosenbaum, who found a sigmoidal shape, which he attributed to a variation of K_H^D with concentration arising from electrostatic effects. Extrapolation of the straight-line portion to the abscissa gives apparent saturation values. These are listed in Table 1, together with the apparent values of the constants K_H^D. The apparent saturation values are remarkable for their consistency, being $26–28 \times 10^{-3}$ equiv. per kg. The magnitude of these figures, however, does not agree with the number of acidic end-groups determined from titration of the polymer in solution ($35·1 \times 10^{-3}$ equiv./kg), and hence should strictly be regarded as an empirical parameter of the system.

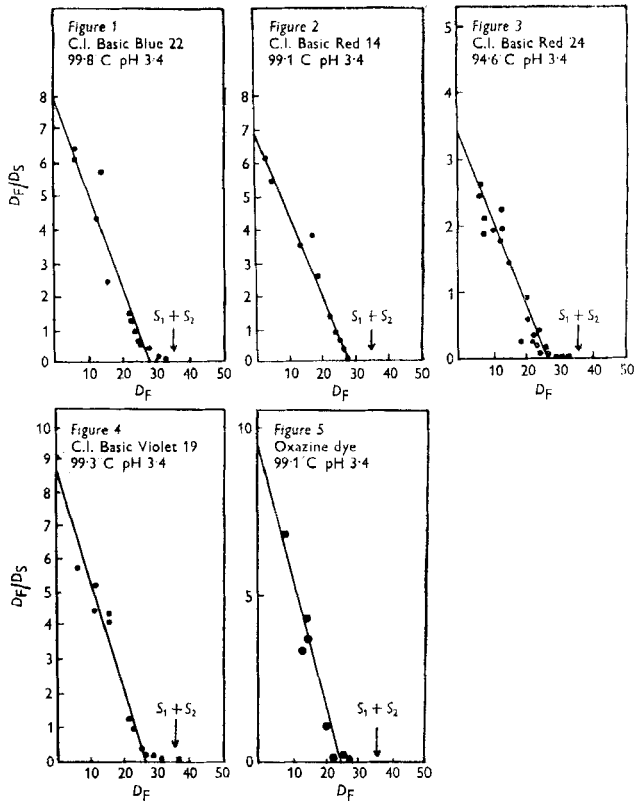


Figure 1–5—Langmuir plots of adsorption isotherms (D_F in m mole/kg)

TABLE 1

Sorption of Cationic Dyes by Films of an Acrylic Copolymer—Parameters for Eqn 1

Dye	Temp. (°C)	$10^{-4}K_LS_1$	10^3S_1	$10^{-6}K_L$	K_H^{D*}	In admixture K_H^{D*}
C.I. Basic Blue 22	99·8	0·81	28	0·29	115	(With C.I. Basic Red 14) 187
C.I. Basic Red 14	99·1	6·90	28	2·50	995	(With C.I. Basic Blue 22) 1152
C.I. Basic Red 24	94·6	3·40	27	1·30	518	
C.I. Basic Violet 19	99·3	8·50	26	3·30	1312	
Oxazine dye	99·1	9·50	26	3·70	1472	

*For D_F, D_S, S_1 in units of equiv./kg. Isotherms measured at 99·2°C.

However, the plots show the additional feature that dye can be sorbed in excess of this apparent saturation value and in some instances in an amount equal to the total quantity of strong acid groups in the fibre. The extrapolated values of the curves have been designated S_1 and the total content of strongly acidic groups

in the fibre S_1+S_2. It is important to note that the amount of dye sorbed rarely exceeds S_1+S_2, since this suggests that the 'anion effects' discussed above will not be a serious factor in the present experiments in which acetic acid was the only additional electrolyte, unless the acidic groups are incompletely ionised. Since the quantity of sulpho groups is about 80% of the total strongly acidic groups (*8*), corresponding to 28·0 m equiv./kg, it is possible that dyeing is associated with two kinds of ionic groups in the fibre, namely the sulpho groups and sulphuric acid end-groups, the latter in quantity corresponding to S_2. If this were so, the isotherm might be described empirically as follows:

$$D_F=\frac{K_{L_1}S_1D_S}{1+K_{L_1}D_S}+\frac{K_{L_2}S_2D_S}{1+K_{L_2}D_S} \quad \ldots.(19)$$

Eqn 19 has been shown to fit the results. For C.I. Basic Red 24, for example, $K_{L_1}=1\cdot3\times10^6$, $K_{L_2}=4\times10^3$, $S_1=27\times10^{-3}$ and $S_2=8\cdot6\times10^{-3}$ equiv./kg. However, the isotherms show that an amount of dye equivalent to S_1+S_2 is not always taken up. The dye sorption rarely exceeds this value, but sometimes falls substantially below it, even for high concentrations of dye in solution (*Figures 2 and 5*). Thus, although the correspondence with the Langmuir isotherm over the major part of the range would appear justified, the second term in Eqn 19 is debatable.

A second set of 'sites' corresponding to the saturation value S_2 would have to be associated with a much lower substantivity of the dye for the fibre than appears to be the case for the dye sorption influenced by the sulpho groups. As far as the apparent saturation value S_1 is concerned, it is tempting to suggest that its magnitude (approx. 80% of total acid groups as measured by titration) corresponds to the content of sulpho groups, the sulphate groups being inaccessible or hydrolysing to hydroxyl groups during the protracted dyeing periods used in this work to achieve equilibrium. Although no evidence of hydrolysis is presented here, this appears to be a possible explanation.

Alternatively, the acidic groups may be incompletely ionised at the experimental pH value of 3·4 and the apparent saturation value S_1 may correspond to those acidic groups that are both accessible and ionised at this pH. In this case, the additional sorption 'tail' would be attributable to the 'anion effects' and would have the characteristics usually attributed to an additional 'solution mechanism' with dyes of lower substantivity (*5, 7*). The K_H^D values are so high that K_D is undoubtedly large. The anion term given in Eqn 18 could therefore become important as (C_D^f/C_D^s) reaches low values, even though the total cation concentration $(C_H^s+C_D^s)$ is not large.

In this situation it is not surprising that Eqn 20 gives a good empirical fit to the results. This type of equation is often used to describe sorption by a dual sorption mechanism which involves both 'adsorption at fixed sites' and 'solution in the fibre':

$$D_F=\frac{K_{L_1}S_1D_S}{1+K_{L_1}D_S}+K_3D_S \quad \ldots.(20)$$

For C.I. Basic Red 24, $K_3=17\cdot3$.

The importance of S_1 is demonstrated by an isotherm in which mixtures of dyes are used. In the presence of a second dye, Eqn 2 becomes

$$K_H^{D_1}=\frac{D_{F_1}[H_S]}{H_F[D_{S_1}]} \text{ or } \frac{D_{F_1}}{[D_{S_1}]}=\frac{K_H^{D_1}}{[H_S]}(S_1-D_{F_1}-D_{F_2}) \quad \ldots.(21)$$

with a corresponding equation with 1 replaced by 2. In this work, an isotherm has been determined in which dyebaths of C.I. Basic Blue 22 and C.I. Basic Red 14 were prepared with an initial concentration ratio of 1·045:1 but with increasing total dye concentration. The results for each dye give good straight lines that extrapolate to values of S_1 equal to 29·0 and 28·2 m equiv./kg respectively, suggesting that competition for the limited number of 'sites' in the fibre is important (*Figure 6*). The values of the constants given by the slopes of the lines are shown in Table 2 and semi-quantitatively confirm the picture. An alternative way of treating the results is to divide Eqn 21 for each dye to give

$$\frac{D_{F_1}[D_{S_2}]}{[D_{S_1}]D_{F_2}}=\frac{K_H^{D_1}}{K_H^{D_2}}=\frac{K_{D_1}}{K_{D_2}} \quad \ldots.(22)$$

These results are shown in Table 2, where a fair degree of constancy can be observed. The ratio of the constants is 5·4, as compared with 8·6 for the corresponding figure for the single dyes. At this stage, this agreement is adequate.

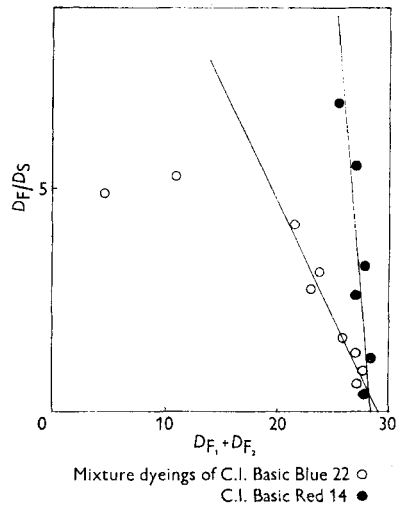


Figure 6—Langmuir plots of adsorption isotherms (D_F in m mole/kg)

TABLE 2 (*9*)

Competitive Sorption of C.I. Basic Red 14 (1) and C.I. Basic Blue 22 (2) at 99·2°C and pH 3·4

$10^3D_{F_1}$	$10^3D_{S_1}$	D_{F_1}/D_{S_1}	$10^3D_{F_2}$	$10^3D_{S_2}$	D_{F_2}/D_{S_2}	$K_H^{D_1}/K_H^{D_2}=\frac{K_{D_1}}{K_{D_2}}$
2·92	0·05	58,400	1·83	0·37	4900	11·9
6·63	0·175	37,900	4·68	0·89	5260	7·2
11·7	0·6	19,500	9·63	2·35	4100	4·8
13·4	0·9	14,900	10·3	3·36	3060	4·9
12·7	0·85	14,940	10·5	3·79	2770	5·4
14·5	2·1	6900	11·4	7·17	1590	4·3
15·5	2·84	5460	11·4	9·15	1250	4·4
15·5	4·78	3240	12·1	14·8	820	4·0
16·5	6·37	2590	10·9	18·3	600	4·3
14·6	11·7	1250	13·4	33·5	400	3·1
Average						5·4

Another test of the ion-exchange picture has been made by Rosenbaum (*1a*), namely the effect of additions of simple salts to the system. In the presence of sodium ions, the amount of dye sorbed is often reduced and equations for ion interchange may be written on the basis of Eqn 6 or 7 in the form

$$\frac{S_1-D_F}{D_F}=\frac{1}{[D_S]}(K_D^{Na}[Na]_S+K_D^H[H]_S) \quad \ldots.(23)$$

Only a limited investigation of the effect of salt was carried out (*Figure 7*). From the slope and the intercept of the initial portion of the graph, K_{Na}^D and K_H^D are estimated to be 5060 and 334. Unfortunately, since the experiments were carried out at high concentrations of dye in the regions of the 'toe' of the isotherm, they can be taken only as approximations. However, to explain the deviations from linearity according to Eqn 16 an additional term should be added to Eqn 23 to include anion effects, i.e. (*5*):

$$\frac{S_1-D_F}{D_F}=\frac{1}{D_S}(K_D^{Na}[Na]_S+K_D^H[H]_S)-K_DK_I\left(\frac{D_S}{D_F}\right)^2(Na_S+H_S+D_S) \quad \ldots(24)$$

Estimates of K_D and K_I from the adsorption at the highest salt concentration are 138 and $2\cdot7\times10^{-2}$. The line calculated using Eqn 24 is shown in *Figure 7*.

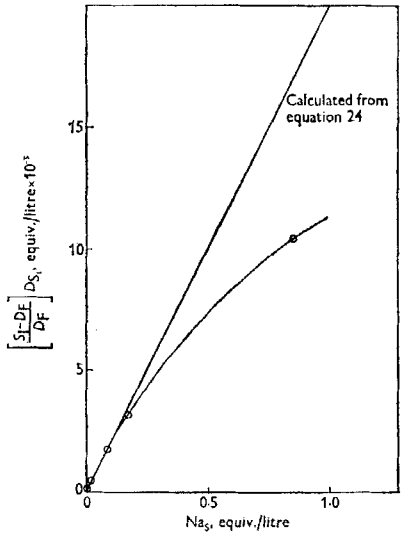


Figure 7—Effect of salt on dye sorption

Conclusions

From the foregoing it is clear that, to a first approximation, Eqn 2 is a good representation of the adsorption behaviour. Closer analysis shows deviations from this simple ion-exchange picture at the higher concentration end of the isotherm, as indicated by the 'tails' on the isotherms, a possibility not allowed for in Eqn 2. Three explanations of this have been suggested; two of these (Eqn 19 and 20) can be related to sorption mechanisms which have no supporting evidence. The third possibility, contained in Eqn 8–18, on the other hand offers a rational explanation of the shape of the isotherms and has been shown to apply to substrates other than the one discussed here.

* * *

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(*MS. received 20 December 1971*)

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Publications Sponsored by the Basic Dyes on Acrylic Fibres Committee—II

Compatibility Test for Combinations of Basic Dyes in the Dyeing of Acrylic Fibres

(New Test Proposed by the Society of Dyers and Colourists)

1. Purpose and Scope

1.1 In the dyeing of acrylic fibres with basic dyes, the classical parameters, e.g. the time of half-dyeing, of individual dyes do not give a true indication of their dyeing behaviour in admixture with other basic dyes.

Since basic dyes show virtually no migration in acrylic fibres, under normal dyeing conditions, compatibility is of major importance in selecting dye combinations with optimum level-dyeing behaviour. In this sense a compatible combination of basic dyes is one in which the individual components exhaust at similar rates, giving a build-up of colour that is constant in hue throughout the dyeing process.

1.2 The test is intended to determine the behaviour of a basic dye in relation to its compatibility when applied to acrylic fibres in the presence of other basic dyes.

2. Principle

2.1 Compatibility is assessed against one of two defined 1–5 scales, a yellow scale and a blue scale. The assessment should be made using the scale showing the greatest difference in hue from that of the dye under test.

The compatibility value of the dye is assessed by determining its dyeing behaviour in combination with each of the standard dyes in the relevant scale.

The dyes recommended as standards have been chosen because they form a series in which

(*a*) successive steps in each of the two scales represent equal changes in visual effect and

(*b*) corresponding standard dyes from each scale are compatible (see note 7.3).