

**858.** *Mechanism of Adsorption of Cationic Dyes by Alumina, and a Note on Heat Changes in Solution Adsorption.\**

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A range of cationic dyes has been applied to (alkaline) chromatographic alumina powder. The nature of the adsorption has been interpreted from the shape of the adsorption isotherms, the ease of desorption, the effect of temperature on the equilibrium, and the "coverage factor," *i.e.*, the factor by which the maximum adsorption exceeds the theoretical value for a monolayer of flatwise close-packed molecules. In most cases adsorption occurs by ion exchange of ionic micelles of dye, giving coverage factors  $>$  unity and the dye is completely desorbable by water alone. Rhodamine 6GB, which has hydrogen-donor groups, is adsorbed edgewise in a vertically close-packed monolayer, and is not completely desorbed by water; it thus appears to be held to the surface by hydrogen bonds; another hydrogen-bonding solute, *p*-nitrophenol, is also not completely desorbable. The triphenylmethane dyes show anomalous effects with rise in temperature: the amount adsorbed increases considerably. As the temperature approaches *b. p.* a marked change in adsorption occurs: adsorption of monodisperse dye molecules, oriented edge-on, appears to replace adsorption of ionic dye micelles.

The heat change in solution adsorption in general is discussed. This can be exothermic, temperature-independent ("athermic"), or endothermic, and it is shown that the sign and magnitude of the change can depend upon the nature of association of the solute on adsorption.

ADSORPTION on alumina is of obvious importance in the study of chromatographic mechanisms. In previous Papers in this series we described investigations of the adsorption of polar non-ionic,<sup>1</sup> anionic,<sup>1</sup> and hydrocarbon<sup>2</sup> solutes by kinetic and thermodynamic methods. Various types of hydrogen bond, covalent bond, and ion-exchange mechanisms were identified, and various heat changes described; the rate-controlling process in adsorption of anionic solutes was shown to be diffusion across a thin liquid film at the particle surface.<sup>1</sup> Cationic solutes were not examined, but it was suggested that they are probably adsorbed by ion exchange. The present Paper describes an investigation of the adsorption of cationic dyes by alumina, and a discussion of the causes of variation in heats of solution adsorption in general. The constitution and ionising properties of the chromatographic powder have been described.<sup>1</sup>

\* Part XX in the series "Studies in Adsorption," Part XIX, Giles and Tolia, *J. Appl. Chem.*, 1964, **14**, 186.

<sup>1</sup> Cummings, Garven, Giles, Rahman, Sneddon, and Stewart, *J.*, 1959, 535; in Fig. 4 and p. 542, l. 13 (up) the expression should read " $\log(1 - Q_i/Q_\infty)$ ."

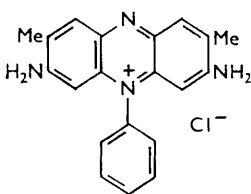
<sup>2</sup> Giles and McKay, *J.*, 1961, 58.

## EXPERIMENTAL

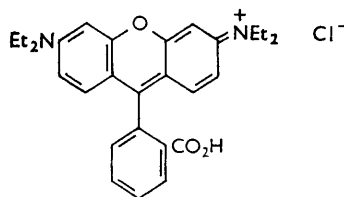
*Dyes.*—Dyes were obtained as diluent-free ("batch") samples (except 52015) from the manufacturers, and were recrystallised from hydrochloric acid (concentrated acid diluted 10:1 with water), and dried at low temperature (first at 40–50° in air and then in a vacuum desiccator cold over potassium hydroxide, overnight). The elemental analyses show that the samples contained 85–95% of pure dye and traces of sodium (presumably as chloride); the remainder was assumed to be water, with some hydrochloric acid. The analytical data agree well with this assumption, except for Methylene Blue, and even this could be explained by the presence of a homologue, equivalent to an additional  $C_2H_4$  group (see below). (It seems unlikely that the traces of acid likely to accompany the dyes in the tests can have any significant effect on the adsorptions. A test made by shaking a dye (Safranin) solution, alumina, and twice the maximum amount of hydrochloric acid which could thus be introduced, revealed only a relatively small pH change in the liquid—6.9 to 5.6.)

Malachite Green (C.I. 4200) and Victoria Blue BN (C.I. 44045) were also purified but could not be used because of precipitation by the alkalinity of the alumina. A commercial "batch" sample of Rhodamine 6GB (C.I. 45160) (purity *ca.* 90%) was also used without purification. One-dimensional paper chromatography with a solvent mixture of benzyl alcohol, dimethylformamide, ethylmethyl ketone, and water (cf. ref. 3) showed no evidence of coloured impurities in the purified dyes. Tests by thin-layer chromatography were also made with two dyes on silica gel from chloroform; each showed less than 2% of other organic material. There was no evidence of coloured impurities in either dye, but the Methylene Blue BP sample appeared to consist of material with perhaps two anions. It is difficult to explain this; the analytical data suggest the presence of an additional  $-CH_2$  or  $-C_2H_4$  group, which may indicate the presence of an organic anion.

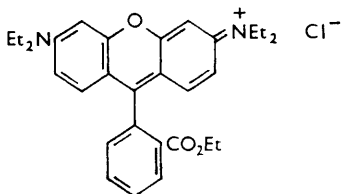
The dyes whose structures are relevant to the following discussion are:



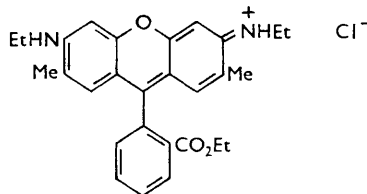
Safranin T



Rhodamine B



Rhodamine 3B



Rhodamine 6GB

*Dye Analyses.*—C.I. 42510 (Magenta P). Found: C, 61.8; H, 6.4; Na, 0.08. Calc. for  $C_{20}H_{20}N_3Cl \cdot 2H_2O \cdot 0.5HCl$ : C, 61.5; H, 6.3%.

C.I. 42555 (Crystal Violet). Found: C, 66.4; H, 7.6; Na, 0.24. Calc. for  $C_{25}H_{30}N_3Cl \cdot 1.5H_2O \cdot 0.5HCl \cdot 0.05NaCl$ : C, 66.2; H, 7.4; Na, 0.26%, corresponding to 89.8% purity;  $TiCl_3$  analysis gave purity 88%.

C.I. 42595 (Victoria Pure Blue BO). Found: C, 72.4; H, 7.3; N, 7.8 (Na, 0.31). Calc. for  $C_{33}H_{40}N_3Cl \cdot HCl$ : C, 72.2; H, 7.5; N, 7.7%.

C.I. 42600 (Ethyl Violet). Found: C, 69.4; H, 7.9; N, 7.8. Calc. for  $C_{31}H_{42}N_3Cl \cdot 1.1HCl$ : C, 69.6; H, 8.1; N, 7.9%.

<sup>3</sup> Brown, *J. Soc. Dyers and Colourists*, 1960, **76**, 536.

C.I. 45170 (Rhodamine B). Found: C, 67.0; H, 6.1; N, 5.5; Cl, 8.1 (Na, nil). Calc. for  $C_{28}H_{31}O_3N_2Cl \cdot 0.65H_2O \cdot 0.12HCl$ : C, 67.9; H, 6.55; N, 5.7; Cl, 8.1%.

C.I. 45175 (Rhodamine 3B). Found: C, 65.9; H, 6.6; N, 5.0. Calc. for  $C_{30}H_{35}O_3N_2Cl \cdot HCl$ : C, 66.5; H, 6.6; N, 5.2%.

C.I. 50240 (Safranin T). Found: C, 59.3; H, 6.5; N, 14.2; Na, 0.21. Calc. for  $C_{20}H_{19}N_3Cl \cdot 3H_2O$ : C, 59.4; H, 6.2; N, 13.9%.

C.I. 52015 (Methylene Blue BP). Found: C, 51.1; H, 7.2; Cl, 13.4; Na, 0.12. Calc. for  $C_{16}H_{18}N_3SCl \cdot CH_2 \cdot 2.5H_2O \cdot 0.5HCl$ : C, 51.0; H, 6.4; Cl, 13.4. Calc. for  $C_{16}H_{18}N_3SCl \cdot C_2H_4 \cdot 3H_2O \cdot 0.5HCl$ : C, 51.2; H, 6.8; Cl, 13.1%.

Carbon, hydrogen, and nitrogen in the dye samples were determined by combustion, chloride ion by electrometric titration, and sodium by flame photometry. Analyses of dye solutions were made by a Unicam S.P. 600 spectrophotometer.

Dye solutions were freshly prepared, because tests of Beer's law (on C.I. 45160, 45170) showed that the degree of aggregation rose on keeping.

*Substrate and Adsorption Procedure.*—The substrate, chromatographic alumina (May and Baker, except where stated otherwise), had a specific surface area of  $4.8 \text{ m}^2 \cdot \text{g}^{-1}$ , measured by adsorption of the anionic anthraquinone dye, C.I. 62055, as described elsewhere,<sup>4</sup> or  $5.0 \text{ m}^2 \cdot \text{g}^{-1}$ , measured by adsorption of *p*-nitrophenol from water.

The adsorption procedure already described<sup>1</sup> was used, 0.05 g. samples of alumina being tumbled in 10 c.c. portions of dye solution in a thermostat tank, except for Magenta when tested at b. p.; the latter was shaken by hand in tubes under air condensers. For the Rhodamine dyes 0.1 g. of alumina in 10 c.c. solution was used, to increase the sensitivity. Adsorptions were complete in only a few minutes, even in the cold.

*Desorption Procedure.*—First an adsorption isotherm was obtained in the usual way, then the solution of initial strength corresponding to one particular point on the isotherm (usually on the plateau) and the appropriate weight of powder were placed in a Quickfit test-tube (B. 14), cut to fit the (M.S.E.) centrifuge, and tumbled as before to obtain adsorption. When adsorption was complete the tube was centrifuged and 5 c.c. of the supernatant liquor was removed for spectrophotometric comparison with a set of standard solutions; 5 c.c. of water was now added to the tube and tumbling resumed. The removal of solution and addition of water was repeated several times, and all the solutions were analysed, after dilution if necessary.

All glassware was rinsed before use in a cationic agent (cetyltrimethylammonium bromide, Lissolamine A, from ICI) (CTAB) to prevent the adsorption of dyes by the apparatus.

The cross-sectional areas of the dye molecules were estimated from Catalin (Stuart) models.

The spectral absorption curves of Safranin were determined at several temperatures in sealed cells made from small-bore glass tubing, by using the special cell-heating device described by Grant *et al.*<sup>5</sup> The cell was heated by a constant voltage rectifier (Farnell Transistorised Power Supply, type P.S.O.) set at a predetermined voltage and current.

## RESULTS AND DISCUSSION

*Nature of the Adsorption.*—Adsorption and desorption isotherms are shown in Figs. 1 and 2. All the dyes tested are readily adsorbed by alumina in the alkaline state, but not when it is acidified. They are also desorbable by water. Adsorption of dyes without hydrogen-donor groups is completely reversible: the dye is entirely removed by water. This is evident in qualitative tests, but some quantitative tests (Fig. 2) were made. Desorption of the two hydrogen-donor compounds tested (Rhodamine 6GB and *p*-nitrophenol, is not completely reversible (Fig. 2a, d); the bond to the surface must here be partly covalent. Also one dye is readily replaced by another, or by CTAB.

These facts suggest that cationic solutes are adsorbed by ion exchange with cations (mainly sodium) in the alumina surface (cf. ref. 6); any hydrogen-donor groups in the solute molecule may also form bonds with alumina oxygen atoms.

More detailed information is given by "coverage factors" and the isotherm shapes.

<sup>4</sup> Giles and Nakhwa, *J. Appl. Chem.*, 1962, **12**, 266.

<sup>5</sup> Grant, Glanville, and Strachan, *Spectrochim. Acta*, 1958, **12**, 109.

<sup>6</sup> Schwab and Jockers, *Naturwiss.*, 1937, **25**, 427.

The coverage factor <sup>7</sup> (c.f.) is the factor by which the adsorption exceeds the value for coverage of the surface with close-packed dye colour ions, oriented flatwise in a monolayer. [The adsorption used in this calculation is that of the first plateau or "Point B" (ref. 8,

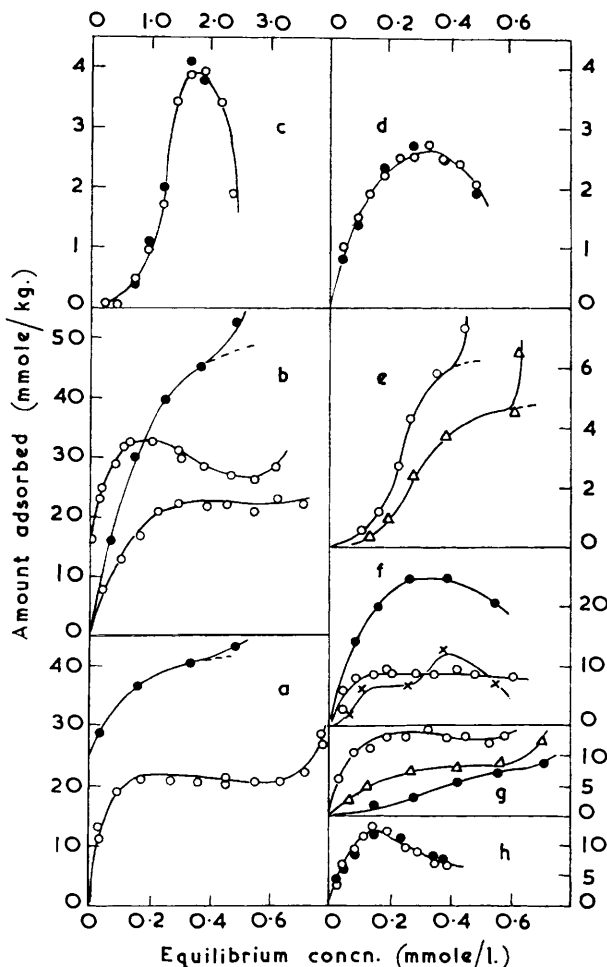


FIG. 1. Adsorption isotherms of cationic dyes from water on chromatographic alumina.

a, C.I. 42600; b, 42555 (bottom curve), 42595 (top curves); c, 45170; d, 45165; e, 45160; f, 42510; g, 50240; h, 52015.

○, 20°; △, 40.5°; ●, 60°; ×, 100°.

at p. 287) in the isotherm, or at the maximum if the curve has one, e.g., Fig. 1b, f, h.] A factor of unity or less is assumed to represent in most cases adsorption in a monolayer of monodisperse dye, and one significantly greater than unity is assumed to represent adsorption in multi-layers or more probably in a monolayer of ionic micelles. The factor for dyes other than the Rhodamines, which are discussed below, is seen (Table) to rise regularly at each temperature with molecular weight of the dye. An increase in c.f. with

<sup>7</sup> Allingham, Cullen, Giles, Jain, and Woods, *J. Appl. Chem.*, 1958, **8**, 108. (On p. 112, l. 11, the peaks are at 6670 and 6100 Å, respectively, and in the order given.)

<sup>8</sup> Brunauer, "The Adsorption of Gases and Vapours," Oxford Univ. Press, London, 1944, p. 287.

Adsorption data for cationic dyes (in order of cationic weight) on chromatographic alumina.

Dye (C.I. No.)	Temp. (°c.)	Maximum adsorption (mmole/kg.)	Molecular area (Å <sup>2</sup> )	Coverage factor *	Cationic weight	Apparent heat of adsorption
42,510	20	9.0	170	1.9	302	pos.
	60	25.0		5.3		
	100	6.5				
52,015	20	13.0	120	1.95	310 †	zero
	60	13.0		1.95		
50,240	20	13.0	150	2.4	315	neg.
	40.5	10.0		1.9		
	60	9.0		90		
42,555	20	21.5	225	6.0	372	
45,170	20	3.9	124	0.65 ‡	443	zero
	60	3.9		0.65 ‡		
42,600	20	20.5	270	6.9	456	pos.
	60	42.0		14.2		
45,175	20	2.7	220	0.7	471	zero
	60	2.7		0.7		
45,160	20	6.2	125	1.0	471	neg.
	40.5	4.5		0.7		
	20	33.0		11.0		
60	48.0	16.2				

\* The coverage factor (c.f.), is the apparent specific surface area (s.s.a.) assuming dye to be adsorbed flatwise in a monolayer, divided by the "true" s.s.a. (see Experimental section). † Assuming the molecule has an additional C<sub>2</sub>H<sub>5</sub> group (see Experimental section). ‡ Assuming the molecule stands edge-on to the surface; all other c.f. values are calculated from flat orientation areas.

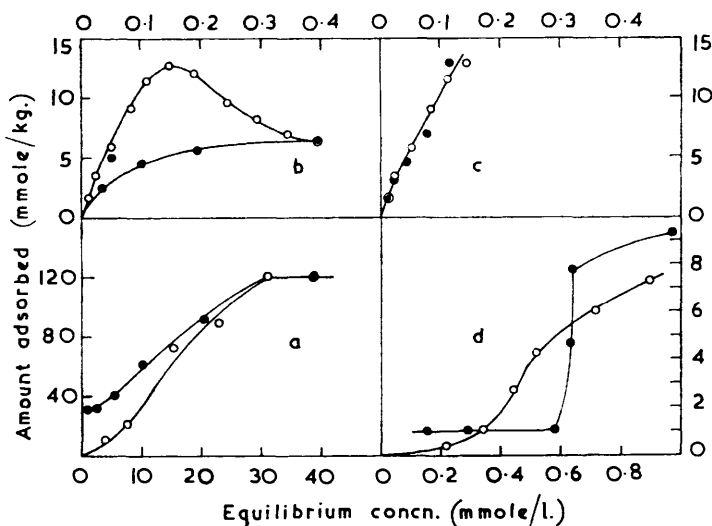


Fig. 2. Desorption isotherms of cationic dyes and *p*-nitrophenol on chromatographic alumina (○, adsorption; ●, desorption). a, *p*-nitrophenol (for this test alone, B.D.H. alumina was used); b, c, C.I. 52015; d, 45160.

In (2b) the desorption curve cannot follow the adsorption curve through the maximum because the total amount of adsorbed dye at the starting point is clearly less than would be present at the maximum; when the desorption is commenced with a sample representing the maximum in the curve, however (2c), this situation does not occur, and the curves coincide. The results together show that all the adsorbed dye is desorbable. In (2d) the adsorption and desorption tests were made with different samples of alumina, but it is clear that some dye is not desorbable.

molecular weight occurs in other adsorption systems, and it will be discussed in more detail in a later Paper.

Three of the dyes when chromatographed from water on an alumina column, and eluted with water, separated in order of c.f.; Victoria Pure Blue BO (c.f. 11) was held most firmly, Safranin T (c.f. 2.4) less so, and Methylene Blue BP (c.f. 1.95) least firmly. It would appear, from an examination of the effect of temperature, discussed below, that some of these dyes might separate best on the column at high temperature.

Three of the four classes into which solution adsorption isotherms can be divided<sup>9</sup> are represented here: the S-curve (Fig. 1c, e, g; Fig. 2a, d), the L-curve (Fig. 1a, b, d, f, g, h; Fig. 2b, c) and the H-curve (Fig. 1a, b). From the coverage factors (Table 2) it appears that these three classes represent the following forms of adsorption; S-curve, edge-on (monodisperse); L-curve, flatwise (monodisperse) or a monolayer of small ionic micelles; H-curve, a monolayer of large ionic micelles. These interpretations agree with facts given earlier in a general classification of isotherms.<sup>9</sup> The maxima in some curves are assumed to indicate association of the dye in solution.

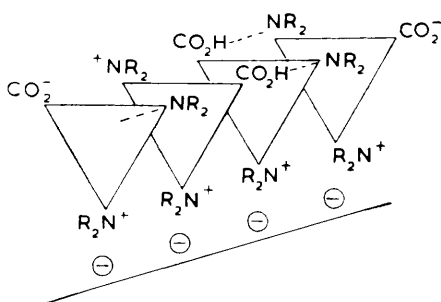


FIG. 3. Sketch showing suggested orientation of Rhodamine B molecules at the negatively-charged alumina surface.

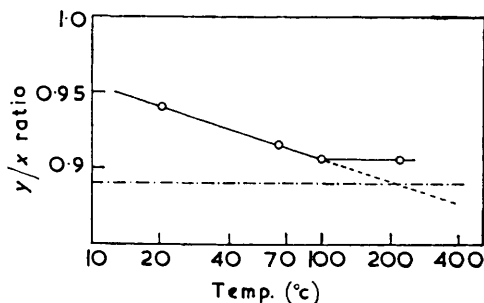


FIG. 4. Relation between  $y/x$  spectral-band extinction ratio and temperature for aqueous solutions ( $3 \times 10^{-5}M$ ) of Safranin T. The horizontal line represents the value in cold ethanol solution ( $3 \times 10^{-5}M$ ).

*Peculiar Behaviour of the Rhodamines.*—The Rhodamine dyes show some interesting adsorption features. Marks B and 6GB are unlike any of the other dyes (except Safranin T at  $60^\circ$ , discussed below); both appear to give edgewise adsorption (Fig. 1c, e) (coverage factors near unity; note also the isotherm, which has a shape often characteristic of edgewise orientation). With Mark 6GB this seems to be due to stabilisation of the mono-disperse monolayer by partial hydrogen-bonding between the  $>NH$  groups and the alumina surface. Supporting evidence is given by the desorption test—the dye is not completely desorbed by water (Fig. 2d)—and by the temperature effect, discussed below. Mark B, however, is completely desorbed; it is probably not hydrogen-bonded to the surface. The mono-disperse monolayer may perhaps be stabilised by intermolecular bonding between the  $NR_2$  group in one molecule and the  $-COOH$  in the next; this leaves one  $NR_2$  group free to form the ion-ion bond with the surface. The intermolecular bonding here could be both ion-ion ( $\bar{C}OO^- \cdots \bar{N}R_2$ ) and hydrogen bond ( $-COOH \cdots NR_2$ ), because resonance distributes the positive charge between the two  $-NR_2$  groups. This hypothesis, illustrated by Fig. 3, was confirmed by tests with Rhodamine 3B, which unlike B and 6GB has neither a hydrogen donor nor an anionic group. It should not therefore orient edgewise, and it might be expected not to give the S-isotherm. In fact it gives the normal (L) type of isotherm (Fig. 1d); the low coverage factor of 0.7 may be the result of its low basicity and the absence of hydrogen-bonding groups; it was completely desorbable.

<sup>9</sup> Giles, McEwan, Nakwa, and Smith, *J.*, 1960, 3973.

*Temperature Effects with Magenta and Safranin.*—Unlike the other dyes tested, these two show a change of isotherm shape (*i.e.*, from L to S) when the temperature is raised considerably (Fig. 1f, g). This seems to be due to a change in the adsorbed species, which up to a certain temperature (which varies with the dye—between 40 and 60° for Safranin, 60 and 100° for Magenta) is an ionic micelle (see *c.f.* values in Table) and above this is a monodisperse molecule, probably adsorbed edge-on. When the Safranin molecule is adsorbed edge-on, it must carry the positive charge (see Table) partly on the unsubstituted nitrogen atom, which can come into contact with the surface. The dye is completely desorbed by water, so that apparently no hydrogen bonds are formed with the surface by the amino-groups.

Since Safranin seems to be adsorbed in monodisperse form at 60° it was thought that it might be entirely monodisperse in solution also at that temperature. Aggregation or disaggregation of dye can be conveniently examined qualitatively<sup>10</sup> by measuring the ratio of extinctions at the peaks of the  $y$  and  $x$  wavebands,<sup>11</sup> representing, respectively, aggregate and monomer. The lower the  $y/x$  band-extinction ratio, the lower the degree of aggregation. A test of the  $y/x$  spectral-band ratios<sup>11</sup> of this dye in solution over a range of temperatures up to b. p. and beyond, shows that they are in each case higher than in cold ethanol (in which the dye is probably fully dissociated) (Fig. 5); the plot of  $y/x$  ratio against log. temperature is linear for water solutions (Fig. 4) and by extrapolation a temperature of 210° would appear to be necessary before the  $y/x$  ratio in water falls to the value in ethanol. A test actually made at that temperature, however, in a sealed tube under pressure, gave the same value as at 100°, though there was a considerable fall in extinction, due probably to decomposition of dye, so that the test may not be conclusive.

The marked change in coverage factor of these two dyes as the temperature is raised is attributed to instability of adsorbed aggregates at the higher temperature, *i.e.*, the forces holding individual dye molecules to the substrate become stronger than those causing dye molecules to associate together as micelles *at the surface*.

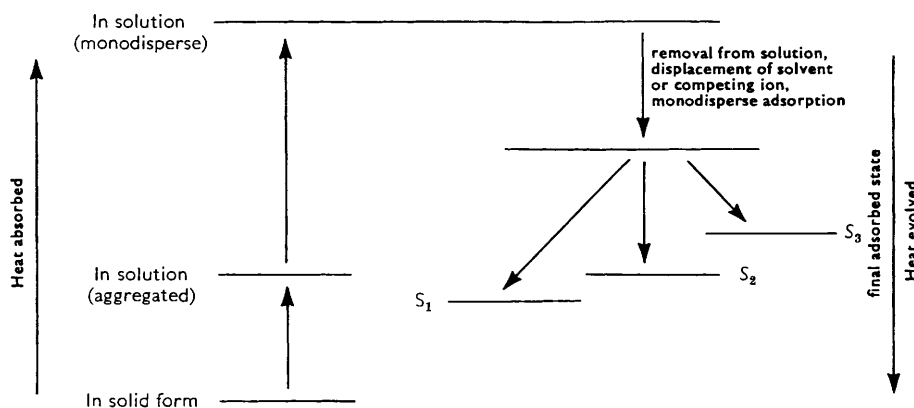


FIG. 5. Energy-level diagram for solution adsorption, showing effect of heat changes due to solute association after adsorption.  $S_1$ ,  $S_2$ , and  $S_3$  represent different degrees of such association.

*Note on the Nature of Heat Changes in Solution Adsorption.*

The results in the preceding section show that with rise in temperature the adsorptions are affected in all three possible ways, *viz.* (i) reduced, with Safranin T (as just discussed) and with the hydrogen-bonding dye, Rhodamine 6GB (Fig. 1e), as with other hydrogen-bonding solutes;<sup>1</sup> (ii) unaffected (Rhodamines B, 3B, Methylene Blue; Fig. 1c, d, h) as

<sup>10</sup> Giles, Rahman, and Smith, *J.*, 1961, 1209.

<sup>11</sup> Lewis and Calvin, *Chem. Rev.*, 1939, 25, 273.

with many other ion-exchange systems;<sup>1</sup> and (iii) raised (Ethyl Violet, Victoria Pure Blue BO, Magenta; Fig. 1a, b, f).

We consider the wider significance of these variations. On basic thermodynamic principles, all true adsorption steps are necessarily exothermic, because they involve decrease of entropy and are spontaneous. Accordingly, all simple vapour-phase adsorptions on clean surfaces are exothermic. Most solution adsorptions are also exothermic, but in a few anomalous cases, some of which are described above, they are either endothermic or temperature-independent (*athermic* \*).

In vapour-phase adsorption the magnitude of the heat change gives useful information on the nature of the adsorption: heat values up to *ca.*  $-10$  kcal./mole represent physical adsorption and value higher by one or two orders of magnitude represent adsorption by covalent bonds (chemisorption).<sup>8</sup> In solution adsorption, the true heat of adsorption is obscured by heat changes in the several successive steps of transference of solute from solution to the solid phase, and the "apparent heat" values actually obtained can give little information on the mechanisms. Majury<sup>12</sup> has examined quantitatively the successive heat changes in solution adsorption of some aromatic amines by cellulose acetates, but otherwise the subject has received little attention. Some examples of the three types of heat change observed are as follows:

*Negative* (exothermic, decreasing with temperature rise): hydrogen-bond adsorption of solutes with small molecules on several organic polymers from aqueous or non-aqueous solution; †<sup>13</sup> organic acids and anionic dyes from water on cellulose,<sup>14-16</sup> and on wool;<sup>15b,17,18</sup> non-ionic (disperse) dyes from water on cellulose acetate.<sup>19</sup> The measured heats are usually in the range  $-0.3$  to  $-7$  kcal. mole<sup>-1</sup>, though some direct dyes on cellulose give values between  $-10$  and  $-30$  kcal. mole<sup>-1</sup>.

*Zero* (*athermic*—unaffected by temperature): cation-exchange adsorption on several resins;<sup>20</sup> ion exchange of several anionic and cationic dyes on inorganic substrates.<sup>21</sup>

*Positive* (endothermic, increasing with temperature): some aliphatic compounds of low mol. wt., from aqueous media, on charcoal;<sup>22,23</sup> some detergents from water on wool;<sup>24</sup> some ion-exchange adsorptions of dyes from water on inorganic substrates.<sup>25</sup> The measured heats are usually in the range  $-1$  to  $-10$  kcal. mole<sup>-1</sup>. Bikerman<sup>22</sup> has suggested that the cause of this effect in some low-molecular-weight organic solutes may be a high negative temperature-coefficient for the solute dissolution, or a high degree of simultaneous desorption of solvent. With most high-molecular-weight ionic organic solutes, however, as in the present work, the cause can be ascribed to association effects.

In many other cases the amount of dye adsorbed at a non-porous surface greatly exceeds

\* We are indebted to Dr. J. J. Kipling and also to a referee for suggesting this term.

† There is a little evidence that the numerical value of the apparent heat is greater the more unlike the solvent and solute, *e.g.*, for adsorption of a given aromatic solute it is greater in an aliphatic solvent than in an aromatic solvent, owing to entropy effects.<sup>13</sup>

<sup>12</sup> Majury, *J. Soc. Dyers and Colourists*, 1954, **70**, 442.

<sup>13</sup> Chipalkatti, Giles, and Vallance, *J.*, 1954, 4375.

<sup>14</sup> Giles and Hassan, *J. Soc. Dyers and Colourists*, 1958, **74**, 846.

<sup>15</sup> (a) Marshall and Peters, *J. Soc. Dyers and Colourists*, 1947, **63**, 446; (b) Vickerstaff, "The Physical Chemistry of Dyeing," Oliver and Boyd, Ltd., Edinburgh, 2nd edn., 1954.

<sup>16</sup> Daruwalla and D'Silva, *Textile Res. J.*, 1963, **33**, 40.

<sup>17</sup> (a) Derbyshire and Marshall, *Discuss. Faraday Soc.*, 1954, **16**, 140; (b) Derbyshire, *Trans. Faraday Soc.*, 1955, **51**, 909; (c) Speakman and Stott, *ibid.*, 1935, **31**, 1425; 1938, **34**, 1203.

<sup>18</sup> Steinhardt, Fugitt, and Harris, *J. Res. Nat. Bur. Stand.*, 1940, **25**, 519; 1941, **26**, 293.

<sup>19</sup> Bird and Harris, *J. Soc. Dyers and Colourists*, 1957, **73**, 199.

<sup>20</sup> Boyd *et al.*; Magistad *et al.*; Patton and Ferguson; Vanselow, quoted by Walton, in "Ion Exchange," ed. Nachod, New York, Academic Press Inc., 1949, p. 20.

<sup>21</sup> (a) Galbraith, Giles, Halliday, Hassan, McAllister, Macaulay, and Maxmillan, *J. Appl. Chem.*, 1958, **8**, 416; (b) Cummings, Garven, Giles, Rahman, Sneddon, and Stewart, *J.*, 1959, 535.

<sup>22</sup> Bikerman, "Surface Chemistry, Theory and Applications," Academic Press Inc., New York, 2nd edn., 1958, p. 294; cf. Heyne and Polanyi, *Z. phys. Chem.*, 1928, **132**, 284.

<sup>23</sup> Bartell, Thomas, and Fu, *J. Phys. Chem.*, 1951, **55**, 1456.

<sup>24</sup> Aickin, *J. Soc. Dyers and Colourists*, 1944, **60**, 60.

<sup>25</sup> Giles, Greczek, and Nakhwa, *J.*, 1961, 93.



the monolayer capacity,<sup>21a,25,26</sup> so that the dye must be adsorbed either in multilayers or in a monolayer of aggregates or micelles, and in the endothermic systems it is even more highly aggregated on the solid at high than at low temperatures. Yet in aqueous solution the opposite is found, at least with all dyes so far examined: rise in temperature shifts the equilibrium towards the monodisperse state (see above, and refs. 15*b*, 26). Therefore in such cases the association of adsorbed solutes into ionic micelles must occur at the solid surface, and after removal from solution. The mechanism of association in solution and after adsorption must therefore differ. This is understandable because in solution micelles are formed under the influence of solvation forces operating from all directions, but at the solid-liquid interface under strong forces mainly from one direction; therefore the structures of the resultant micelles or aggregates will very probably differ. Little is known, however, of the structure of dye micelles in solution and nothing of that of adsorbed micelles.

At low temperature there is some direct adsorption of aggregates from solution; this was confirmed by spectroscopic examination of solutions of two cationic dyes, which showed that the degree of aggregation in solution was lower immediately after adsorption than in a freshly-prepared solution of equal concentration.

These aggregation effects and the different sign of the heat change in different adsorptions can be explained qualitatively by the energy-level diagram in Fig. 5. This applies to any solution adsorption and is more comprehensive than that given in a previous Paper,<sup>25</sup> which included some quantitative data on endothermic adsorption. It does not include the cause suggested by Bikerman and just referred to; this would require some sections of the Figure to be inverted.

By this diagram we can explain the known facts that adsorption of small monodisperse molecules with a low state of aggregation both in solution and on the substrate is almost always exothermic, but adsorption of solutes which have a strong tendency to aggregate is either exothermic, athermic, or endothermic. The variations with aggregated solutes arise from slight changes in the relative magnitude of the energy changes required to break down the aggregates in solution and to re-form them on the substrate.

In Fig. 5, if the energy level of the aggregate in solution is  $S_1$ , the adsorption is apparently exothermic, but if  $S_2$  or  $S_3$  then adsorption is, respectively, athermic or endothermic. Exothermic adsorptions are thus likely to occur with solutes having low aggregation in solution and high aggregation on the substrate; highly soluble dyes often give exothermic adsorptions for this reason. An example is the adsorption of the sodium salt of sulphonated, uncomplexed alizarin from water, on alumina<sup>27</sup> in which the species actually adsorbed is the (2 : 1) alizarin-aluminium complex, whose molecular weight is more than twice that of the original solute and so it is probably more highly aggregated. The marked endothermic nature of the adsorption of triphenylmethane dyes by alumina revealed in the present work can be explained as the result of a high degree of aggregation both in solution and on the substrate.

We thank Professor P. D. Ritchie for his interest, Allied Colloids Ltd. for a sample of Ethyl Violet, Imperial Chemical Industries Limited, Dyestuffs Division, for other samples, Dr. E. V. Truter for the thin-layer chromatographic tests, the D.S.I.R. for a Scholarship (to R. B. McK.), and Dr. W. Good for discussions.

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[Received, October 12th, 1963.]

<sup>26</sup> (a) Rabinovitch and Epstein, *J. Amer. Chem. Soc.*, 1941, **63**, 69; (b) Alexander and Stacey, *Proc. Roy. Soc.*, 1952, *A*, **212**, 274.

<sup>27</sup> Giles and Datye, *Trans. Inst. Metal Finishing*, 1963, **40**, 113.