19. *Studies in Adsorption. Part XIII.* Anomalous (Endothermic) Effects of Adsorption on Inorganic Solids.*

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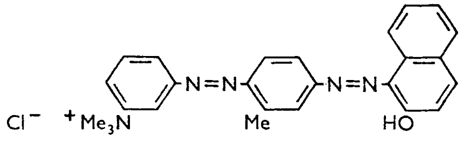
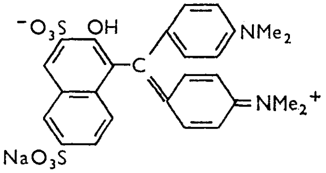
The adsorption of two dyes from water on to inorganic surfaces is found to be apparently endothermic, saturation adsorption rising with temperature. Both dyes are associated in aqueous solution. From a dissociating solvent (methanol) the adsorption is normal, the amount sorbed falling with rise in temperature. The anomalous adsorption from water is considered to be the result of partial dissociation at the substrate surface.

Adsorption of dye as micelles appears to occur even from methanol, and it is suggested that association takes place at the moment of adsorption.



Janus Red B (C.I. 26,115)



Lissamine Green BN (C.I. 44,090)

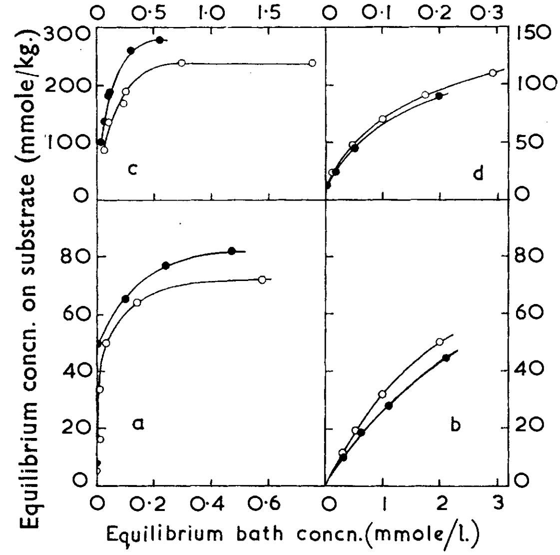


FIG. 1. *Solution adsorption isotherms.*

(a) *Janus Red B* (C.I. 26,115) *on silica* (*specific surface area* 0·108 × 10⁵ cm.²/g.) *from water, at* (○) 30°, (●) 50°.

(b) *As* (a), *from methanol, at* (○) 16°, (●) 37° (*silica, specific surface area* 0·062 × 10⁵ cm.²/g.).

(c) *Lissamine Green BN* (C.I. 44,090) *on chromatographic alumina* (ref. 1*b*; *specific surface area* 5 × 10⁵ cm.²/g.) *at* (○) 20°, (●) 42°.

(d) *As* (c), *from methanol, at* (○) 19·5°, (●) 36·5°.

Apparent heats of adsorption, calc. from the curves, are: (a) +5·8 ± 1·4; (b) −2·4 ± 0·5; (c) +6·0 ± 2·6; (d) −1·7 ± 0·6 kcal./mole.

ADSORPTION from solution is usually, like vapour-phase adsorption, exothermic, so that a rise in temperature causes a decrease in saturation adsorption. In a few cases change in temperature produces no change in adsorption, but so far all such cases are apparently ion-exchange adsorption, usually on organic surfaces.[1] Little is known of systems showing a reversed temperature effect, *i.e.*, where rise in temperature increases the saturation adsorption: previously recorded cases include the adsorption of (i) two azo-dyes (C.I. 14,600, anionic; C.I. 26,115, cationic) from water by silica; (ii) butanol from its mixtures

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* Part XII, *J.*, 1961, 58.

[1] See, *e.g.*, (*a*) Allingham, Cullen, Giles, Jain, and Woods, *J. Appl. Chem.*, 1958, **8**, 108; (*b*) Cummings, Garven, Giles, Rahman, Sneddon, and Stewart, *J.*, 1959, 535; (*c*) Giles, Mehta, Rahman, and Stewart, *J. Appl. Chem.*, 1959, **9**, 457 [Fig. 5 (left), for *f*, *g* read *g*, *f*; Fig. 6, C_F scale for (XIV) is 0—50 units].

with water by charcoal;[2] (iii) succinic acid from water or ethanol, by charcoal;[3] and (iv) long-chain sulphate esters by wool.[4] Bikerman[3] attributes this behaviour to a negative temperature coefficient of the solubility of the solute or to a steep simultaneous decrease of the real adsorption of the solvent.

Cause of the Anomaly.—In the present work we have examined the adsorption of several dyes by inorganic solids. Some results are shown in Fig. 1. In the two cases in which adsorption rises with temperature there is good evidence that the dyes are highly aggregated in solution; thus the solutions do not obey Beer's law and show marked light-scatter. Further, when a dissociating solvent is used (methanol) the adsorption is normal, falling with rise in temperature. The apparent endothermic nature of these systems is therefore a result of the aggregation of the solutes in solution, as shown in the energy-level diagrams (Fig. 2). In these cases it appears that the solute is partly dissociated on adsorption.

Nature of Association on Substrate.—Two facts indicate that the adsorbed layer of both dyes (even in methanol) consists of aggregated particles, and is not a true unimolecular layer: (*a*) the shape of the isotherms (*L*2, ref. 5),* and (*b*) the high " coverage factor " (*i.e.*, the amount of dye adsorbed to fill a " monolayer " divided by the amount calculated for a unimolecular layer) which is *ca.* 30 for the red dye at 16° and *ca.* 2 for the green dye at 19·5°.

FIG. 2 (*a*). *Energy-level diagram for normal* (*exothermic*) *adsorption of dye on solid surface.*

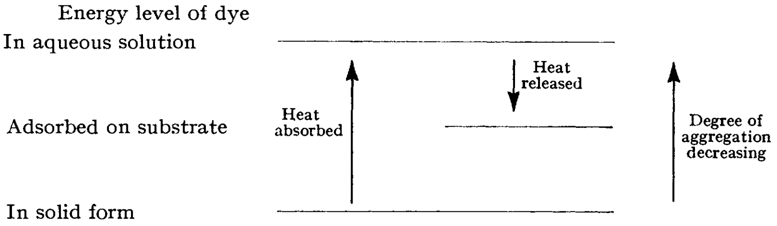
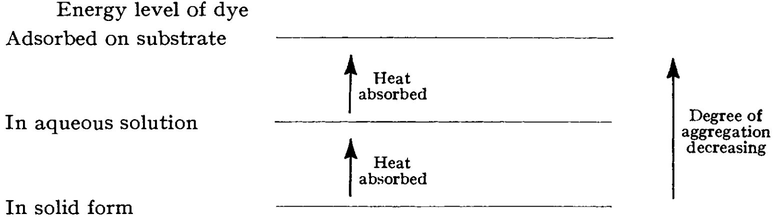


FIG. 2 (*b*). *Energy-level diagram for anomalous* (*endothermic*) *adsorption of colloidal dye on solid surface.*



It is especially interesting that aggregates can apparently be adsorbed under conditions (high temperature in disaggregating solvents) in which the dyes must be molecularly dispersed. This is consistent with the view already expressed that aromatic solutes in water are associated at a solid surface during adsorption, either immediately before or at the moment of attachment to the surface. Even highly sulphonated dyes, the most likely to be molecularly dispersed in water, appear to behave thus.[6,7]

* In a unimolecular layer, both dyes would be oriented end-on to the surface and so would be expected to give the *S* isotherm (for reasons see ref. 5).

[2] Bartell, Thomas, and Fu, *J. Phys. Chem.*, 1951, **55**, 1456.

[3] 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.

[4] Aickin, *J. Soc. Dyers Colourists*, 1944, **60**, 60.

[5] Giles, MacEwan, Nakhwa, and Smith, *J.*, 1960, 3973.

[6] Baxter, Giles, and Rahman, *Textile Res. J*, in the press.

[7] (*a*) Campbell and Giles, *J. Soc. Dyers and Colourists*, 1958, **74**, 164; (*b*) Campbell, Cathcart, Giles, and Rahman, *Trans. Faraday Soc.*, 1959, **55**, 1631.

Orange I.—This dye also gives anomalous isotherms on silica,[1a] but adsorption from aqueous pyridine or methanol is also anomalous. These unexpected results were found to be due to slow decolorisation of the dye solutions at high temperature, presumably owing to hydrolysis of the azo-group. The red and the green dye were not decolorised in this way.

Experimental.—The methods have been described.[1] The dyes were commercial products recrystallised three times from 1 : 1 v/v ethanol–water, which gave constant molar extinctions. The state of aggregation of the dyes in solution was detected qualitatively by nephelometric measurement (EEL instrument). Molecularly dispersed solutions, in *e.g.*, methanol or pyridine, gave zero readings.

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