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Surface Area of Hydrous Oxides by Dye Adsorption Method

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The adsorption behaviour of alizarin sulphonic acid, malachite green, methyl orange and methylene blue on hydrous oxide gels such as silicic acid, alumina and ferric oxide has been investigated. The surface areas of these gels have also been evaluated (1) from the monolayer capacity of the adsorbents, and (2) from the heat of immersion method. The results obtained by the two methods are comparable.

THE interaction of dyes with metal hydrous oxide sols and gels has been studied by a number of workers[1-6]. However, the effect of factors like shape and size of the dyestuff molecules, orientation on the surface of the adsorbent, *p*H, micellar structure of the dye, nature of the asdorbent, etc., has not been studied in depth. With this aim we have carried out investigations on the adsorption of dyes on a number of hydrous oxide gels. In order to assess the role of these factors in the adsorption phenomenon and also to determine the surface area of hydrous oxide gels, the adsorption of dyes such as alizarin sulphonic acid, malachite green, methyl orange and methylene blue on these gels has been studied and the results are presented in this paper.

Materials and Methods

Sodium salt of alizarin sulphonic acid, methyl orange, methylene blue and malachite green used in the investigations were of analar grades. The gels were prepared by the dialysis of the sols of silicic acid, alumina and ferric oxide prepared by the methods recommended by Hatschek[7], Weiser[8] and Krecke[9] respectively. Silicic acid gel was dried in an open furnace at 210° for 24 hr and the remaining two at 180° for 24 hr. The gels were passed through BS 100 sieve, and presoaked in Britton-Robinson buffer of *p*H 2·0 after drying.

Bausch & Lomb Spectronic-100 spectrophotometer was employed for the spectral measurements. The heats of immersion were measured by the method of Zettelmoyer *et al.*[10]. A small rise in temperature was registered with the help of a thermistor in conjunction with a suitable resistance bridge. The reproducibility of the heat of immersion values varied between ± 3 and 4%, depending upon the type of the gel used.

Procedure — The samples for adsorption measurements were prepared in the following manner: 100 mg of silicic acid gel + (i) varying amounts (0·6, 0·7, 0·8, 0·9 and 1·0 ml of $1{\cdot}5\times10^{-4}M$) of alizarin sulphonic acid; (ii) (1·0, 2·0, 3·0, 4·0 and 5·0 ml of $1{\cdot}96\times10^{-5}M$) of malachite green; (iii) (1·0, 2·0, 3·0, 4·0 and 5·0 ml of $4{\cdot}51\times10^{-5}M$) of methyl orange; (iv) (1·0, 2·0, 3·0, 4·0 and 5·0 ml of $3{\cdot}41\times10^{-5}M$) of methylene blue.

The total volume was made up to 10 ml by adding the requisite amount of B.R. buffer (5·0 ml) and water.

Similar sets were prepared by taking 100 mg each of ferric oxide and alumina gel.

The samples were agitated thoroughly for equilibration. After 24 hr, [dye] in equilibrium with adsorbent was measured spectrophotometrically and the amount of dye adsorbed was found from the difference in the optical density values. The adsorption isotherms were constructed from the amounts of dye adsorbed in the samples.

Results and Discussion

It is well known that a molecule having a high degree of polarizability in three directions can exhibit three bands, and in general, the wavelengths at the peaks are referred to as first, second and third bands in order of decreasing wavelengths. These dyes are characterized by oscillations in more than one direction. The surface areas corresponding to major orientation for the dyes sodium alizarin sulphonate, malachite green, methyl orange and methylene blue are 28·2, 49·0, 39·5 and 28·6 Å^2 respectively.

Any deviation from Beer's law is attributable to aggregation, and the degree of association between the dye molecules can be obtained by this assumption[11]. The concentration range selected in the present study was such that the dyes obeyed Beer's law and remained monomer in the concentration range under study.

Nature of isotherms — Giles *et al.*[12] have shown that the adsorption on inorganic oxides is either end-on as with polar molecules or flat-on as with dye stuffs, etc. These authors have shown that for a particular type of adsorption there is a need to determine specific effective cross-sectional area of the adsorbed molecules from which one can obtain different orientations of the adsorbed molecules from the shape

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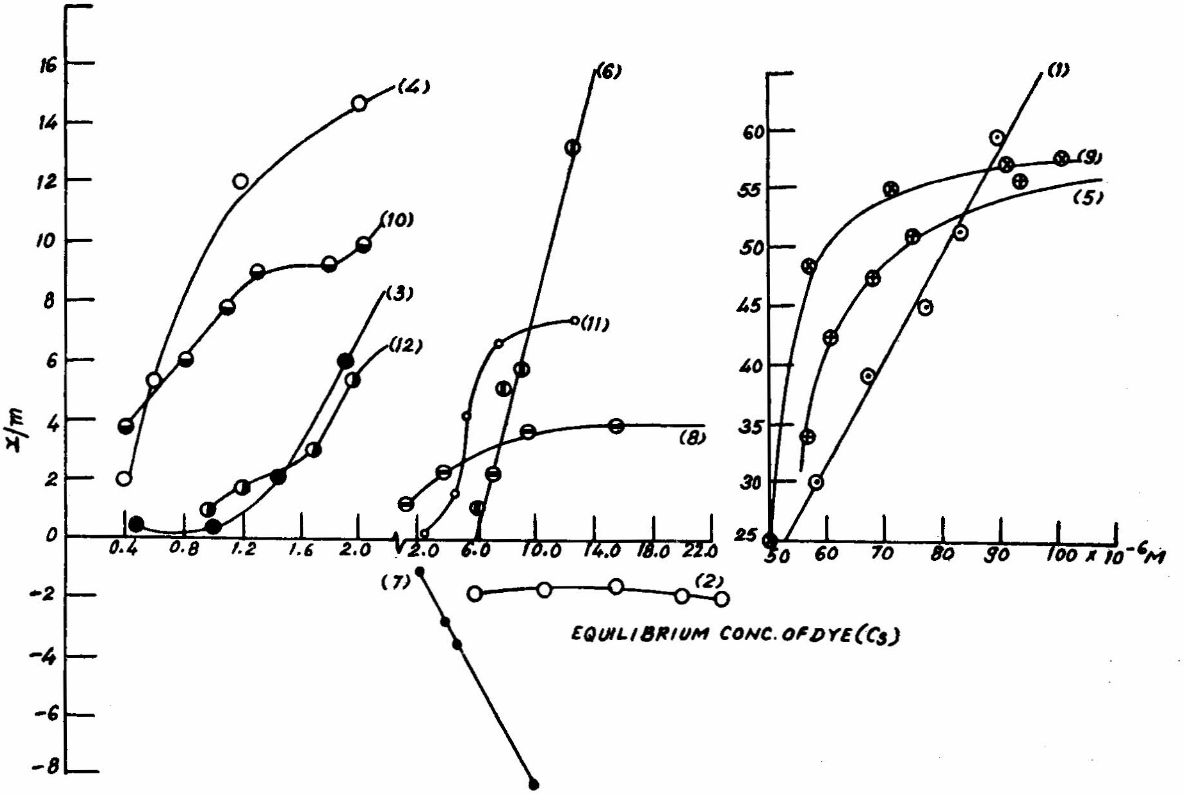

Fig. 1 — Plots of equilibrium concentrations of the dyes versus x/m [(1) Silica gel + alizarin sulphonic acid, (2) silica gel + methyl orange, (3) silica gel + malachite green, (4) silica gel + methylene blue, (5) ferric oxide gel + alizarin sulphonic acid, (6) ferric oxide gel + methyl orange, (7) ferric oxide gel + malachite green, (8) ferric oxide gel + methylene blue, (9) alumina gel + alizarin sulphonic acid, (10) alumina gel + methyl orange, (11) alumina gel + malachite green, and (12) alumina gel + methylene blue]

of the isotherm. In our case it was found that the adsorption of alizarin sulphonic acid on ferric oxide and alumina was flat-on (Fig. 1, curves 5 and 9) giving a normal shape isotherm (*L*2) (the terminology used here and thereafter is the same as recommended by Elworthy[13]). Similarly methylene blue gave *L*2 type isotherm (Fig. 1, curve 4) with silica gel and *L*1 type isotherm (Fig. 1, curve 8) with ferric oxide as per BET classification. The silica gel-alizarin sulphonic acid and ferric oxide-methyl orange systems result in a well established C1 constant partition like Henry's law range in adsorption of vapours, while alumina-methylene blue gave a second plateau (Fig. 1, curve 12) about twice the height of the first which is typical of *L*4 type isotherm. The second plateau probably represented a re-orientation of the adsorbed molecule to give end-on adsorption with increased concentration, thereafter, further layers may build up, as is shown by a further steep rise in the isotherm. The end-on adsorption from water gives the S2 isotherm which is intially convex to the concentration axis similar to that obtained in the case of adsorption of malachite green on both silica and alumina. The end-on adsorption from solvent gives another isotherm which is initially concave to the concentration axis and with a plateau resulting in a Langmuir type *Lmx* isotherm obtained for silica-methyl orange and ferric oxide-malachite green systems. The *Lmx* type of adsorption which is more precisely known

TABLE 1 — COMPARISON OF SURFACE AREA (S) OBTAINED BY ADSORPTION DATA AND HEAT OF IMMERSION METHOD

Adsorbent*	$\Delta H_i \times 10^6$ (ergs/g)	S (m^2/g) from Adsorption data	S (m^2/g) from Heat of immersion
	ALIZARIN SULPHONIC ACID		
(A)	1394	214	210
(B)	1018	281	267
(C)	936	243	252
	MALACHITE GREEN		
(A)	1376	211	203
(B)	958	265	264
(C)	900	234	230
	METHYL ORANGE		
(A)	1374	209	202
(B)	930	252	262
(C)	880	228	226
	METHYLENE BLUE		
(A)	1346	207	200
(B)	1000	276	261
(C)	825	213	210

*(A) = silicic acid gel-water, h^i = 650 ergs cm^{-2}.
(B) = ferric oxide gel-water, h^i = 362 ergs cm^{-2}.
(C) = alumina gel-water, h^i = 385 ergs cm^{-2}.

as negative adsorption, may be attributed to the increasing concentration of the solute whereby the solvent is adsorbed more and more. Based on the data of Ostwald and Izaguirre[14] a successful theory regarding this complex adsorption behaviour has been developed by Bartell and Sloan[15]. Our data fit well with this theory.

Surface area — The method[15] based on assumption that the adsorption was confined to a monolayer was used to calculate the surface area using Eq. (1).

$$n_1^s S_1 + n_2^s S_2 = S = \frac{X_{\text{mono}} N \times A}{M} \qquad \ldots(1)$$

where n_1^s and n_2^s are the number of moles of each components adsorbed, S_1 and S_2 are the area occupied by 1 mole each of the components. X_{mono} is the monolayer capacity in grams of solute per gram of solid, N and M are Avogadro's number and molecular weight respectively, A is the area occupied by one molecule of solute in a closely packed film on the surface of the solid, and S is the surface area. The values calculated by us are given in Table 1. The results have been verified from the heat of immersion measurement employing the relationship

$$\Delta H^i = h^i S \qquad \ldots(2)$$

where ΔH^i is the heat of immersion (in ergs) per gram of solid, and h^i is the standard heat of immersion per unit area of the solid in the given liquid.

The h^i values for the system silica acid gel-water[17], ferric oxide-water[18] and alumina oxide gel-water[19] have been reported to be 650, 362, 385 ergs cm^{-2} respectively. It may be noted that the values of S calculated by both the techniques compare favourably (Table 1). The maximum and minimum values obtained for alizarin sulphonic acid were 281 and 210 m^2 g^{-1} respectively which are not unexpected.

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