111. *Adsorption at Inorganic Surfaces. Part IV.* Mechanism of Adsorption of Organic Solutes by Chromatographic Alumina.*

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Organic solutes are adsorbed by chromatographic alumina mainly by hydrogen-bond formation, ion exchange, and chelation. In non-ionic compounds proton-donor groups (*e.g.*, –OH, $-NH_2$, and some activated $\geqslant$CH groups) have the highest affinity, and proton-acceptor groups are adsorbed weakly, probably by bonding with the small content of aluminium hydroxide in the substrate. Sulphonated azo-dyes are readily adsorbed by acid-treated alumina; the reaction has a very small temperature coefficient and is probably mainly ion-exchange. Trisulphonate ions may be orientated flat as a monodisperse layer, but mono- and di-sulphonates appear to be adsorbed partly as anionic micelles. Adsorption is complete in less than 5 min. in the cold; the kinetics are consistent with the rate-controlling factor's being exchange of dye anions for inorganic anions across a thin liquid boundary film around the alumina particles. There is no evidence of any adsorption in internal pores. Solvents, *e.g.*, ethanol or water, with hydrogen-bond affinity for solute or substrate, or those with van der Waals attraction for the solute, reduce affinity by competition.

THIS paper describes an investigation into the mechanism by which chromatographic alumina adsorbs organic non-ionic and ionic solutes. The substrate, prepared by low-temperature (<700°) dehydration of alumina trihydrate, is a mixture of γ-alumina and a little alumina monohydrate (Al_2O_3,H_2O) with some sodium carbonate. High-temperature ignition (>900°) completes the dehydration and produces the less active α-alumina.[1] The adsorbing power of the technical material is often classified by the rate of travel of azobenzene and certain of its simple derivatives in non-aqueous solution down a column under standardised conditions.[2,3] Grade I represents highest and Grade III lowest activity (*i.e.*, most rapid passage of solute); Grade III can be prepared from Grades I and II by adding a little water.

When water is the solvent the reaction of the alumina—whether acid or alkaline—considerably affects its adsorptive powers; bases are adsorbed better on alkaline than on acid alumina and acids show the opposite behaviour.[3,4]

Relation between Structure and Adsorption Effects.—(i) *Non-ionic solutes.* Much information is available upon the relative order in which organic solutes separate on the alumina column.[1,5] Strong adsorption (slow passage) is favoured generally by high polarity, by an increase in the number of polar substituents or of aromatic nuclei, and by the absence of internal chelation (*i.e.*, with such groups as amino-, hydroxy-, or thiol in anthraquinone or azo-compounds).[3,6,7,8] Configuration also influences adsorption (*cis*- but not *trans*-azobenzene is adsorbed from light petroleum [9]). A solute may undergo catalytic change (*e.g.*, deacetylation) on an alumina column, or it may isomerise. Thus, several compounds which are colourless in cold benzene become highly coloured when adsorbed on alumina

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* Part III, *J. Appl. Chem.*, 1958, **8**, 416.

[1] Cassidy, "Fundamentals of Chromatography. Technique of Organic Chemistry, Vol. X," Interscience Publishers, Inc., New York, N.Y., 1957.

[2] Brockmann and Schodder, *Ber.*, 1941, **74**, *B*, 73.

[3] Brockmann, *Discuss. Faraday Soc.*, 1949, **7**, 58.

[4] Hesse and Sauter, *Naturwiss.*, 1947, **34**, 250, 251, 277.

[5] *E.g.*, Strain, "Chromatographic Adsorption Analysis," Interscience Publishers Inc., New York, N.Y., 1942.

[6] Hoyer, *Kolloid-Z.*, 1951, **121**, 121.

[7] Rao, Shah, and Venkataraman, *Proc. Indian Acad. Sci.*, 1951, **34**, *A*, 355.

[8] Williams, "An Introduction to Chromatography," Blackie and Son Ltd., London, 1946.

[9] Hillson and Birnbaum, *Trans. Faraday Soc.*, 1952, **48**, 478.

(*e.g.*, 1 : 3-dioxoindanes enolise, and *spiro*pyrans become heteropolar, in both cases with development of colour [10]).

Basu [11] recently suggested that adsorption of organic compounds on alumina is a form of molecular complex formation, and that the process is facilitated by (*a*) a high electron affinity of one component and (*b*) a low ionisation potential of the other. On the assumption that the energy of the top filled orbital of a conjugated organic molecule calculated by the LCAO method gives a rough estimate of (*b*), the position on the column of two series of compounds, *viz.*, five condensed-ring aromatic hydrocarbons and four αω-diphenylpolyenes, in both cases agrees with this hypothesis.

(ii) *Ionic solutes.* Investigations on adsorption of ionic solutes have been concerned mainly with dyes. Several authors [12–17] have studied qualitatively the effect of substitution in anionic dye molecules upon their ease of adsorption from water by alumina or aluminium hydroxide. Roosens,[18] who comprehensively surveyed previous work, defined the following general rules for adsorption of sulphonated azo-dyes: the greater the number of azo-groups, the stronger the adsorption; an amino- or a hydroxy-group is more effective when in the 2-position in the naphthalene nucleus (as second component) than in the 1-position; *o*-hydroxyazo-dyes are adsorbed more strongly than *p*-hydroxyazo-dyes; dyes containing a thio- or a hydroxyl group are more strongly absorbed than dyes free from those groups; the longer the wavelength at which the compounds adsorb light, the higher is the adsorption zone, in general, in the column; the greater the molecular weight, the stronger the adsorption; halogen substituents promote adsorption; and the more double bonds in the molecule, the stronger the adsorption. Also, the strength of adsorpton in the column increases with the number of sulphonate or of vinyl groups in the dye; [13] adsorption is weakened by a sulphonate group in the 8-position in phenylazo-2-naphthol dyes or *ortho*- to the central carbon atom in naphthyldiphenylmethane dyes; [15] the presence of phosphate ion in solution reduces adsorption of a sulphonated dye on hydrated alumina; [17] and there is some parallelism between adsorption and substantivity for cotton or rate of diffusion through gelatin.[13] Amongst sulphonated intermediates, 3-hydroxynaphthalene-1-sulphonic acid is adsorbed more strongly than 4-hydroxynaphthalene-1-sulphonic acid.[13]

Adsorption of inorganic ions. Several suggestions have been made to account for adsorption of inorganic ions by technical alumina. Chromatographic alumina normally is alkaline and contains sodium ions which exchange with cations in solution,[19] though even pure alumina adsorbs cations to some extent,[20] probably initially by an aluminium–hydrogen ion exchange.[21] Alumina can, in fact, function as an amphoteric ion-exchanger, *e.g.*, with cuprous chloride, but its normal sodium ion content makes it more effective in cation exchange.[22] Adsorption affinity rises with polarisability of the adsorbed ion or of groups co-ordinated with it.[21, 23]

Anions are readily adsorbed on alumina pre-treated with hydrochloric acid. Wieland [24] explains this as an anion-exchange with the chloride ions taken up from the acid.

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[10] Schönberg and Asker, *Science*, 1951, **113**, 56; Schönberg, Mustafa, and Asker, *J. Amer. Chem. Soc.*, 1951, **73**, 2876; 1952, **74**, 5640; 1953, **75**, 4645.

[11] Basu, *Chem. and Ind.*, 1956, 764.

[12] Mutch, *Quart. J. Pharm. Pharmacol.*, 1946, **19**, 490.

[13] Ruggli and Jensen, *Helv. Chim. Acta*, 1935, **18**, 624; 1936, **19**, 64.

[14] Ruiz, *Ind. parfum.*, 1946, **1**, 187; *Chem. Abs.*, 1948, **42**, 5675.

[15] Ruiz, Chovin, and Moureau, *Bull. Soc. chim. France*, 1946, **13**, 592.

[16] Weiser and Porter, *J. Phys. Chem.*, 1927, **31**, 1704.

[17] White and Gordon, *ibid.*, 1928, **32**, 380.

[18] Roosens, *Ind. Chim. Belg.*, 1952, **17**, 211, 339.

[19] Schwab and Jockers, *Naturwiss.*, 1937, **25**, 44.

[20] Fricke and Neugebauer, *ibid.*, 1950, **37**, 427.

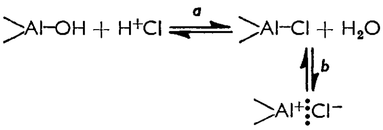
[21] Sacconi, *Discuss. Faraday Soc.*, 1949, **7**, 173.

[22] Jacobs and Tompkins, *Trans. Faraday Soc.*, 1945, **41**, 388, 395, 400.

[23] Venturello and Agliardi, *Chimica e Industria*, 1944, **26**, 72.

[24] Wieland, *Z. physiol. Chem.*, 1942, **273**, 24.

Source of zeta-potential. O'Connor, Johansen, and Buchanan[25] studied the electrokinetic properties of corundum (natural alumina) before and after various mechanical and heat treatments and treatments with solutions of acids, alkalis, and salts. Normally the zeta-potential in water is positive, which these authors attribute to the presence of a layer of $Al(OH)_3$ formed from chemically bound water, and resistant to very high temperatures: this releases hydroxyl ions into the diffuse layer and the oxide then has a surface of positively charged aluminium atoms. Pre-ignition at above 1000° gives a material (α-Al_2O_3) with negative zeta-potential in water, probably owing to a layer of the weakly acidic AlO·OH. Treatment with hydrochloric acid appeared to produce a surface consisting of covalently bound and ionised chloride:



$$\begin{array}{ccc} >\text{Al–OH} + \text{H}^{+}\text{Cl} & \overset{a}{\rightleftharpoons} & >\text{Al–Cl} + \text{H}_2\text{O} \\ & & \big\updownarrow b \\ & & >\text{Al}^{+}\vdots\text{Cl}^{-} \end{array}$$

Reaction (*b*) (formation of ionised chloride) is favoured by increase in acid concentration.

EXPERIMENTAL

Preparation of Substrate.—The substrate was mainly from a single sample of chromatographic alumina (Type H, Savory and Moore), but a few tests were made on another, coarser, sample. In its original state the former was alkaline (20 c.c. of distilled water shaken with 1 g. of powder at room temperature had pH 9·5). It adsorbed cationic dyes but not anionic ones, unless previously acidified. Consequently all the material used was before use washed twice with hydrochloric acid (100 g. in 200 c.c. of 2N-acid) and then rinsed several times with water. It was then over-dried at 150° for several days, and stored in a desiccator ($CaCl_2$); 20 c.c. of distilled water shaken with 1 g. of treated powder at room temperature had pH 4·4; activity: Grade II.

	Type H	Coarse powder
Loss on ignition	6·5	5·9
Sieve grading (%) +100	0·6	8·8
−100, +150	67·0	57·7
−150, +200	18·1	25·5
−200	14·3	8·0
pH of 5% w/v solution	8·7	9·2
Activity	I—II	II
Temp. of activation:		
normal	600°	—
max.	700°	—
Specific surface area, cm.^{2} g.$^{-1}$ (approx.) (phenol adsorption calc. from Fig. 1)	$5·0 \times 10^5$	$0·5 \times 10^5$
(air-permeability test)	$0·027 \times 10^5$	$0·004 \times 10^5$
(microscopical counts)	$0·035 \times 10^5$	$0·15 \times 10^5$

Characteristics of the substrates are tabulated. Air-permeability tests and microscopical counts gave specific surface areas less by factors of *ca.* 100 and 10, respectively, than those given by phenol adsorption. The discrepancies between the various area values could be explained by assuming (*a*) that the H-type powder has a much rougher surface than the other, and perhaps a higher content of extremely fine particles (note the fine sieve gradings), (*b*) that in the air-permeability test fine particles tend to lodge in cracks in the rough surface of coarse ones (especially of type H), and (*c*) that loss on ignition represents water molecules located inside the crystal rather than those adsorbed at the outer surface.

The solutes and solvents were purified normally, and water was distilled; benzene and 2 : 2 : 4-trimethylpentane were dried over sodium. The azo-dyes were mainly obtained from commercial sources, except (VI), (VII), and (X), which were laboratory preparations. The 1-acetamido-8-hydroxynaphthalene-3 : 6-disulphonic acid for (VI) and (VII) was prepared as described by Fierz-David and Blangey.[26] The dyes were purified to >95% ($TiCl_3$ analysis) by

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[25] O'Connor, Johansen, and Buchanan, *Trans. Faraday Soc.*, 1956, **52**, 229.

[26] Fierz-David and Blangey, " Fundamental Processes of Dye Chemistry," Interscience Publishers Inc., New York, N.Y., 1949.

salting-out from aqueous solution with sodium chloride, followed by recrystallisation from aqueous ethanol.

Adsorption Procedure.—0·1 g. samples of alumina and 5 c.c. of test solution in sealed glass tubes were tumbled at 35 r.p.m. in a thermostat.[27] Equilibrium is attained rapidly. The solutions were analysed after 10—15 minutes' agitation, the tubes being first left to stand vertically in the thermostat until the powder settled, and the solution then decanted through filter paper. Amounts of solute adsorbed were calculated from analyses of solutions before and after treatment.

In rate measurements it was possible to obtain reproducible results for times down to 10 sec. by using mechanical agitation, if the solution had previously reached temperature equilibrium in the thermostat. Variation in volume of the aqueous dye solutions from 2·5 to 20 c.c. did not affect the isotherms. No dissolved alumina was detected (by Aluminon) after shaking 0·1 g. of powder (H) with 5 c.c. of distilled water for up to 24 hr. at 18°. (The isotherms for adsorption on *anodic* alumina vary considerably with the liquid : solid ratio used, attributed to etching by the solution, the film oxide being very slightly soluble in water.[28])

Analysis.—Cellobiose and sucrose were determined by refractometry on a Pulfrich (Bellinghan and Stanley) instrument, in sodium light. All other solutes were determined absorptiometrically on a Hilger Spekker or a Unicam S.P. 500 or S.P. 600 instrument. The lowest measurable adsorption is *ca.* 0·01 mmole/kg. of Al_2O_3.

RESULTS AND DISCUSSION

Results are summarised in Tables 1 and 2 and Figs. 1—5.

Evidence for Hydrogen-bond Adsorption of Non-ionic Solutes.—Evidence from this and earlier work that hydrogen-bonding is the principal force responsible for adsorption of non-ionic solutes can be summarised thus: (*a*) The anodic film on aluminium adsorbs non-ionic solutes mainly by hydrogen bonds.[29] This film is chemically very similar to the present substrate. (*b*) The adsorption of simple non-ionic anthraquinones and azo-compounds on alumina columns (judged by speed of travel) is weaker when any amino-, hydroxy-, etc., groups they contain are internally chelated, than when they are free.[6] (*c*) The behaviour towards non-ionic compounds of the alumina powder here used is very similar to that of the anodic film, *i.e.*, proton donors are readily adsorbed and proton acceptors adsorbed weakly or not at all. (It is assumed that acetyl and aldehyde groups act as proton donors.[30]) (*d*) The evidence of isotherm shapes agrees with that given by

TABLE 1. *Behaviour of non-ionic solutes towards chromatographic alumina.*

Solute	Solvent *	Reaction †	Solute	Solvent *	Reaction †
trans-Azobenzene	B, AE	N	Phenylazo-2-naphthylamine	D	A
cis-Azobenzene	AE, P	A[9]	2 : 4-Diacetoxyazobenzene	B	A
Bis(phenylazo)benzene	B, AE,	N	Phenol	W	A
(*trans*?)	BE, BB		Resorcinol	W	A
,, ,,	O	A	Sucrose	W	N
Bis(phenylazo)benzene (*cis*?)	AE	A	*m*-Nitroaniline	AE′	A
Cellobiose	W	A	*p*-Nitroaniline	AE′	A
Chlorobenzene	B	N	Nitrobenzene	AE′	S
4-Aminoazobenzene	D	A	,,	B	N
2 : 4-Dihydroxyazobenzene	E	A	Terephthalaldehyde	B	A

Conditions: Solutions *ca.* 0·001—0·01M; temp. 20—60°; time, 5—30 min.

* B, Benzene; AE, ethanol–water (4 : 1 v/v); AE′, ethanol–water (1 : 1 v/v); BE. benzene-ethane-1 : 2-diol; BB, benzene–butane-1 : 4-diol; O, 2 : 2 : 4-trimethylpentane; D, dioxan; E, ethanol; P, light petroleum; W, water.

† A, adsorbed; N, not adsorbed; S, slightly adsorbed.

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[27] (*a*) Allingham, Cullen, Giles, Jain, and Woods, *J. Appl. Chem.*, 1958, **8**, 108; in this paper, the analysis of the MSC fine silica powder used should be: SiO_2, 96·5; Al_2O_3, 2·5; Fe_2O_3, CaO, MgO, alkali, etc. 1%. Also in Table I, first footnote, and Figs. 2, 6, and 7, *y*-axes, units should read mmole/kg.; (*b*) Galbraith, Giles, Halliday, Hassan, McAllister, Macaulay, and Macmillan, *ibid.*, 1958, **8**, 416.

[28] Stewart, Ph.D. thesis, Glasgow, 1957, 481.

[29] Giles, Mehta, Stewart, and Subramanian, *J.*, 1954, 4360.

[30] Arshid, Giles, and Jain, *J.*, 1956, 559, 1272.

TABLE 2. *Adsorption of sulphonated azo-dyes on chromatographic alumina.*

Dye	Max. ads. (mmole/kg.)	Cross-sectional area of anion (Å²) *					$-\Delta\mu$ (kcal./mole)	$-\Delta S$ (cal./mole/deg.) (50°)	$-\Delta E_A$ (kcal./mole)
		Found Dev. (%) (*a*) †	Calc.			Found Dev. (%) (*b*) †			
			End-on	Edge-on	Flat				
				Monosulphonates					
(I)	166	−13	*50*	80	150	−57	8·3 ± 0·5	25·5 ± 1·5	—
(II)	175	−8	*50*	75	150	−48	12·3 ± 0·5	38 ± 1·5	9·2
				Disulphonates					
(III)	104	−18	65	*80*	190	−57	21·0 ± 1·5	65 ± 4·5	13·0
(IV)	100	−20	60	*80*	190	−63	20·0 ± 0·5	62 ± 1·5	12·5
(V)	80	−36	60	*85*	195	−92 (+18, flat)	19·0 ± 0·5	58·5 ± 1·5	—
(VI)	132	+6	60	*85*	220	−15	17·0 ± 0·2	52·5 ± 0·5	—
(VII)	124	0	60	*85*	250	−24	18·0 ± 0·2	56 ± 0·5	—
(VIII)	106	−15	*65*	140	375	−89	19·3 ± 0·2	60 ± 0·5	3·2
(IX)	62	−50	55	*110*	235	−92	19·8 ± 0·2	61 ± 0·5	3·9
				Trisulphonates					
(X)	58	−8	65	85	*225*	0	31·0 ± 1·5	96 ± 4·5	1·4
(XI)	68	+8	55	80	*190*	0	26·5 ± 0·5	82 ± 1·5	—

* Area of smallest enclosing rectangle, measured by Catalin (Stuart-type) molecular models (no allowance for interlocking); most probable (monodisperse) orientation in italics.

† Deviation from theoretical values (*a*) for micellar adsorption, a mean value of 63 mmole/kg. being assumed for trisulphonates, equivalent to 125 and 190 mmole/kg. for di- and mono-sulphonates; (*b*) for orientated monodisperse adsorption (total surface coverage), values for trisulphonate dye X being assumed to represent a complete monolayer.

The amounts of *monodisperse* adsorbed anions should be inversely proportional to their appropriate cross-sectional areas, but the amounts of *micellar* adsorbed anions should be inversely proportional to their basicity, on the assumption that each sulphonate group is exchanged with one chloride ion, of which there is a limited supply.

other hydrogen-bond adsorptions.[31] Thus where there are two polar groups of similar affinity [*e.g.*, bis(phenylazo)benzene, resorcinol, terephthalaldehyde] the isotherm has the normal (L) shape, but where one group has much stronger hydrogen-bond affinity than any other in the molecule (*e.g.*, *cis*-azobenzene, cellobiose, phenol, nitroaniline) the curve is S-shaped. This appears to confirm that the main source of affinity is in the polar groups.

Hydrogen-bonding through $\geqslant$CH *Groups*.—The adsorption of cellobiose, 2 : 4-diacetoxyazobenzene, and terephthalaldehyde is attributed to $\geqslant$CH · · · bonding. Aldehyde and ester groups in solutes in aqueous or non-aqueous solutions can act as proton donors towards oxygen atoms in other solutes.[30] Some confirmation that this is the nature of the adsorption here is given by the difference in behaviour of cellobiose and sucrose. In water, cellobiose behaves monofunctionally as the open-chain aldehyde, and sucrose is unreactive towards other hydrogen-bonding solutes, because the hydroxy- and oxo-groups are protected by the solvent.[30] Similar behaviour is observed here in their reactions towards alumina, *i.e.*, cellobiose appears to be adsorbed as a monofunctional compound, giving as it does an S-shaped isotherm, and sucrose is not adsorbed.

There is of course the possibility that catalytic decomposition of these solutes in contact with alumina may occur, giving strongly adsorbed hydroxylic compounds; no evidence of decomposition could be obtained however by spectroscopy of solutions of 2 : 4-diacetoxyazobenzene before and after treatment with alumina, adsorption tests with cellobiose with acid and alkaline alumina (both appeared similarly effective), or pH measurement on distilled water shaken in air with a solution of terephthalaldehyde in benzene; there was no reduction in pH. No acid is therefore formed by air oxidation in *absence* of alumina. (Detection of oxidation on the column itself was not attempted.)

Proton-accepting Groups and Solvent Effects.—The hydroxide content of the powder is no doubt responsible for its slightly higher affinity for amino-, azo-, and nitro-groups than

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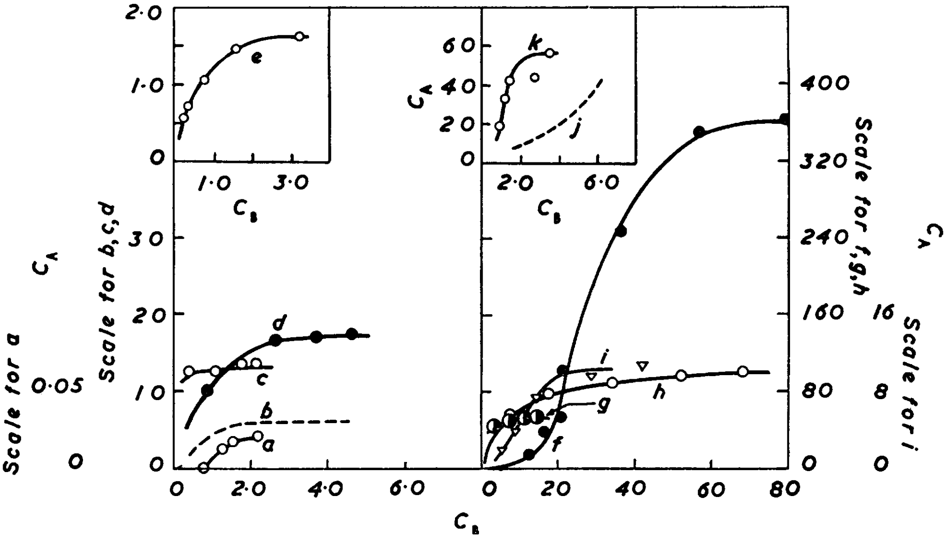
[31] Cf. Giles and MacEwan, Second Internat. Cong. Surface Activity, London, 1957, **3**, 457.

the anodic film (cf. Part I [29]). Even so, the affinity of these groups is low and subject to competition by the solvent; *e.g.*, *trans*-bis(phenylazo)benzene is adsorbed from 2 : 2 : 4-trimethylpentane, but not from benzene, where association will occur between the aromatic nuclei of solute and solvent, or from ethanol with which hydrogen-bonding can occur.

The greater ease of adsorption of *cis*- than *trans*-azobenzene * must be a steric effect, due to the more ready approach to the alumina surface of the *cis*-azo-group.

Sulphonated Azo-dyes.—The dyes were all sodium salts: (I) sulphanilic acid→2-naphthol (Orange II, C.I. 15510), (II) 4-aminonaphthalene-1-sulphonic acid→2-naphthol (C.I.15620), (III) 1-naphthylamine→2-hydroxynaphthalene-3 : 6-disulphonic acid (C.I. 16180), (IV) 4-aminonaphthalene-1-sulphonic acid→6-hydroxynaphthalene-2-sulphonic acid (C.I. 16045), (V) aniline→1-acetamido-8-hydroxynaphthalene-3 : 6-disulphonic acid (C.I. 18050), (VI) *p*-*n*-butylaniline→1-acetamido-8-hydroxynaphthalene-3 : 6-disulphonic acid, (VII) *p*-*n*-dodecylaniline→1-acetamido-8-hydroxynaphthalene-3 : 6-disulphonic acid, (VIII) phenol←*O*-ethyl ether of *o*-tolidine→2-aminonaphthalene-3 : 6-disulphonic acid (C.I. 23605), (IX) 4-(4-amino-*m*-tolylazo)toluene-3-sulphonic and→crocein acid (C.I. 27165), (X) sulphanilic acid→2-hydroxynaphthalene-3 : 6-disulphonic acid, (XI) 4-aminonaphthalene-1-sulphonic acid→7-hydroxynaphthalene-1 : 3-disulphonic acid (C.I. 16255).

FIG. 1. *Adsorption isotherms of non-ionic solutes on chromatographic alumina.*



a,* Nitrobenzene in ethanol–water (1 : 1 v/v), 20°.
b, *cis*-Bis(phenylazo)benzene in ethanol–water (4 : 1 v/v), 30°.
c, 2 : 4-Diacetoxyazobenzene in benzene, 44°.
d, 4-Aminoazobenzene in dioxan, 58°.
e,* Terephthalaldehyde in benzene, 20°.
f, Phenol in water, 58°.
g, Phenylazo-2-naphthylamine in dioxan, 58°.
h, Resorcinol in water, 58°.
i,* 4-Nitroaniline in ethanol–water (1 : 1 v/v), 20°.
j, *cis*-Azobenzene in ethanol–water (4 : 1 v/v), 30°.
k, Cellobiose in water, 53°.

C_A is the equilibrium concentration on the alumina (mmole/kg.) and C_B that in the bath (mmole/l.).
* Coarser alumina; all others chromatographic alumina.

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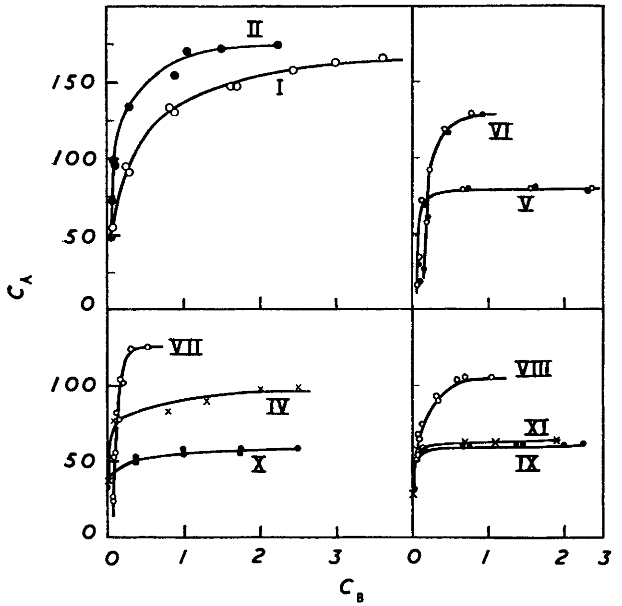
* The isotherms for the two azobenzenes are shown without experimental points (Fig. 1). The solutions were exposed to light, to effect isomerisation to *cis*-forms, before adsorption, but some *trans*-isomers may have remained unchanged. The *x*-axis scale therefore refers to the combined total of both isomers.

Adsorption is very rapid, and the isotherms have well-defined plateaux with apparently no subsequent rise (Fig. 2). This suggests that a monolayer is formed on the outer surface of the alumina particles, with no penetration of the internal structure. The isotherms for different temperatures are identical, *i.e.*, the apparent heats of adsorption are all very low (<*ca.* 0·25 kcal./mole) (Fig. 2), consistent with ion-exchange adsorption. The shapes of the isotherms indicate that the anions have much higher affinity for the substrate than has the solvent (water).[31] *

Orientation of Adsorbed Dye Anions.—As stated, the shapes of the isotherms indicate that the adsorbed dye anions form a monolayer, and this could be composed either of mono-disperse anions, each oriented with all sulphonate groups as close as possible to the surface, or of anionic micelles (cf. the cationic micellar adsorption of basic dyes by silica [27b]). On first principles it can be postulated that dyes capable of packing with large areas of aromatic nuclei in close association, *i.e.*, the mono- and some di-sulphonates, will form some micelles, whereas trisulphonates will orientate as single anions flat on the surface. The data (Table 2) are however not adequate to prove this hypothesis, though they appear to be in reasonable agreement with it; they indicate also that the acetamido-group in dye (V) may assist a flat orientation by hydrogen-bonding. (This is the only unalkylated dye used here containing a proton-donating group.) It seems probable from the quantitative data that all ionic compounds form some monodisperse orientated monolayer, but with decreasing charge on the molecule relative to its molecular weight there is an increasing tendency for the adsorbed layer to contain micelles. Differences in the amounts of the dyes adsorbed may be accounted for by differences in their anions' ability to pack in the monolayer.

FIG. 2. *Adsorption isotherms of sulphonated azo-dyes from water on chromatographic alumina.*



Temperatures: I, 33°, 60°; II, 33°; IV, 26°; V, 50°, 60°; VI, 51°, 61°; VII, 50°, 60°; VIII, 49°, 61°; IX, 49°, 61°; X, 49°, 60°; IX, 26°. For clarity the points for individual temperatures are not differentiated in several cases. Roman numerals refer to dyes.

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* The initial portion of the isotherm for the dye with the long paraffin chain (VII) differs from that of its homologue (V) in being slightly convex to the x-axis (the scale of Fig. 2 is too small to show this); a similar difference between (V) and (VII) is observed on wool, on which adsorption is also by ion-exchange.

Dye Affinities.—The dyes (Na_zD) can be placed in an order of adsorption affinity and entropy by applying the expression $-\Delta\mu^\circ = -\boldsymbol{R}T \ln [Na]_s^z[D]_s$, where $[Na]_s^z[D]_s$ is the dye activity in a solution at equilibrium with alumina containing dye at half its maximum adsorption. This expression is derived from the affinity equation for ion-exchange adsorption of acids and dyes by protein fibres (cf., *e.g.*, ref. 32) though it is not certain that if adsorption is micellar the values so obtained (Table 2) are true thermodynamic free energies.

The data show that additive " partial affinity " values can be assigned to sulphonate groups according to their orientation, *e.g.*, 12·0 ± 2·5, 6·8 ± 0·7, and 6·5 ± 1·0 for positions 3, 6, and 8 in the coupling component, and 12 ± 0·5 for position 4 or 4″ in the first component [except dye (I)]. The rise in apparent entropy with increased sulphonation must be attributed to increased configurational entropy.[33]

Rate Measurements.—Rate curves determined for several dyes over a range of temperature (Fig. 3) show that, as expected the adsorption rate rises with temperature. The kinetics of ion-exchange adsorption by small particles, assumed spherical, have been studied by Boyd *et al.*[34] and Kressman and Kitchener,[35] using the Nernst static diffusion theory. A similar treatment is used here, it being assumed that adsorption involves transport of an ion from the bulk of the solution up to the boundary of a liquid film surrounding each particle, where anion exchange occurs at constant ionic concentration.

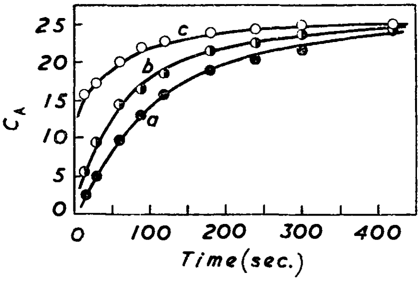

FIG. 3. *Rate curves for adsorption of dye* (II) (0·2 *g./l.*) *on chromatographic alumina.*

a, 9°; *b*, 14°; *c*, 25°.

If the rate of adsorption is controlled by diffusion through the liquid boundary layer, the plot of log $[(1 - Q_t)/Q_\infty]$ against t should be linear, with a gradient proportional to the diffusion coefficient in this layer. (Q_t and Q_∞ are the quantities of anions exchanged after time t and at equilibrium.) Plots of this type for five dyes (Fig. 4) are linear over nearly the whole range of time and temperature. There are exceptions where the early stages of adsorption (20—60 sec.) give points deviating from linearity in a direction corresponding with values of Q_t lower than required by theory, *i.e.*, the initial rate of diffusion of chloride ion outward, and dye anion inward, is too low.

The very high rate of attainment of equilibrium adsorption on the powder indicates fairly clearly that no diffusion into internal pores occurs. In confirmation, rate measurements were tested by an expression developed for internal diffusion in an adsorbent particle [34, 36-38] whereby a plot of Q_t/Q_∞ against $t^{\frac{1}{2}}$ should be linear. Kressman and Kitchener [35] find that this rule holds up to $Q_t/Q_\infty = 0{\cdot}8$ in some cases, but in general it can only be expected to hold for lower values. A plot of Q_t/Q_∞ against $t^{\frac{1}{2}}$ for one dye is given

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[32] (*a*) Gilbert and Rideal, *Proc. Roy. Soc.*, 1944, *A*, **182**, 335; (*b*) Vickerstaff, " The Physical Chemistry of Dyeing," Oliver and Boyd Ltd., London and Edinburgh, 2nd edn., 1954.

[33] Everett, *Proc.*, 1957, 38.

[34] Boyd, Schubert, and Adamson, *J. Amer. Chem. Soc.*, 1947, **69**, 2818; Boyd, Adamson, and Myers, *ibid.*, p. 2836.

[35] Kressman and Kitchener, *Discuss. Faraday Soc.*, 1949, **7**, 90.

[36] Carslaw and Jaeger, " Conduction of Heat in Solids," Oxford Univ. Press, London, 1947.

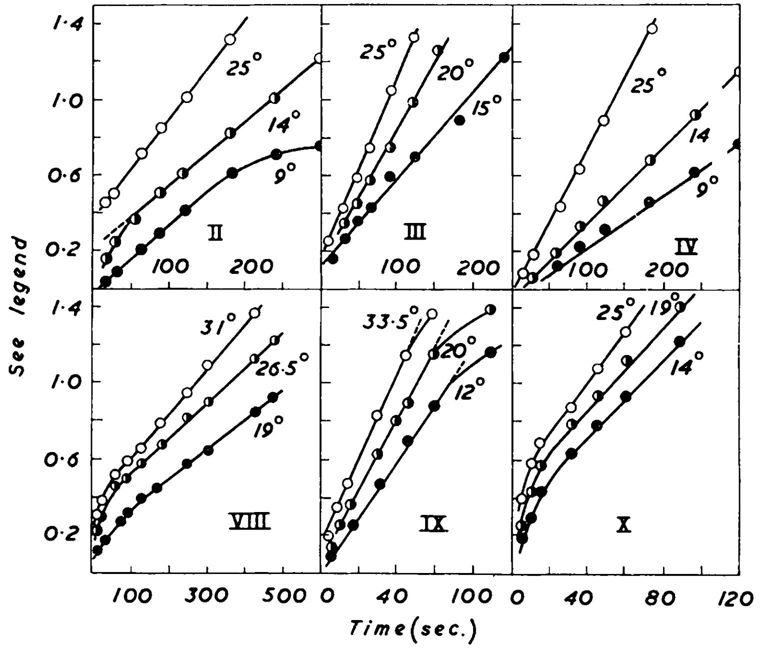
[37] Paterson, *Proc. Phys. Soc.*, 1947, **59**, 50.

[38] Barrer, *Trans. Faraday Soc.*, 1949, **45**, 358.

in Fig. 5 and this plot shows that the agreement with theory for internal diffusion is less satisfactory than for the boundary-layer diffusion for the same dye (Fig. 4).

Activation Energy.—Plots of the values of the diffusion coefficient (calculated from the gradients of plots in Fig. 4) against the reciprocal of the absolute temperature are linear, and from the slopes of these lines the activation energies in the last column of Table 2 were calculated. The data are insufficient for any certain generalisation to be made, and clearly the relation between structure and activation energy is complex, but it appears that dyes with aromatic residues of similar shape, and the same number of ionic groups, tend to have similar activation energies.

FIG. 4.—*Rate of adsorption of azo-dyes by chromatographic alumina plotted on liquid boundary film hypothesis.*



Vertical axis: $\log [(1 - Q_t)/Q_\infty]$.

Cationic Compounds.—The alkaline oxide adsorbs basic dyes. No quantitative work was carried out on this type of adsorption, but there appears no reason to doubt that the mechanism is one of cation exchange. Basic dyes will probably be adsorbed as cationic micelles, as they are by silica powder.[27a]

Chelating Dyes.—These are adsorbed with production of the colour of the aluminium chelate (scarlet with alizarin or sulphonated alizarin) so that, as in the case of the anodic film, adsorption must take place by direct formation of lakes with aluminium atoms in the alumina crystal lattice.

Conclusions.—Adsorption mechanism of non-polar solutes. Polynuclear aromatic hydrocarbons generally separate on the alumina column according to the number of their aromatic nuclei; [5,8] those containing the most nuclei are the less readily eluted. Two reasons can be suggested for this: (*a*) that a polar complex is formed between the alumina and the π-electrons of the hydrocarbon; (this resembles the mechanism suggested by Basu [11]), and (*b*) the rate of travel of the solute down the column is determined by the rate of transfer of solute to the eluting solvent from the initial solvent holding the solute at the top of the column (a partition-chromatography effect).

Adsorption mechanism of polar and ionic solutes. The adsorption of most organic solutes, from water or non-aqueous solution, can be accounted for by the general principles revealed here. The main source of affinity of a non-ionic solute for alumina appears to be hydrogen-bonding through proton-donor groups in the solute. Proton-acceptor groups have low affinity, and probably form hydrogen-bonds with the hydroxide content of the substrate. Aldehyde and ester groups may act as proton-donors. The recorded observations (p. 535) on the relative order of separation of solutes on alumina columns can be explained on these hypotheses. Steric effects may occur in certain cases (*cis*-azobenzene is better adsorbed than the *trans*-isomer). The influence of the solvent is very important. Thus proton-donor solvents, such as ethanol or water, may reduce the affinity of a solute for alumina by being adsorbed preferentially themselves and so favour elution. Solvents which associate with the solute, either by hydrogen-bonding (*e.g.*, ethanol or water with polar solutes), or by van der Waals forces (*e.g.*, aromatic solvents with aromatic solutes), compete with the alumina for the solute and so favour elution. Proton-donor solvents will also compete with the solute for the substrate, *i.e.*, they will tend to deactivate the substrate by being adsorbed on sites on the alumina to the exclusion of the solute.

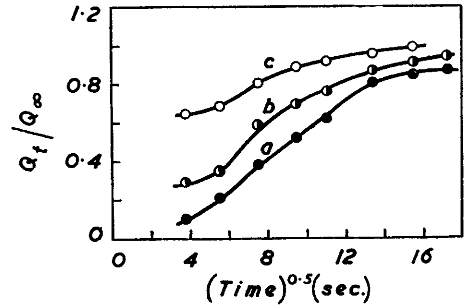


FIG. 5.—*Rate of adsorption of dye* (II) *plotted according to the pore penetration hypothesis.*
a, 9°; *b*, 14°; *c*, 25°.

The reported more effective adsorption of *o*-aminoazo- or *o*-hydroxyazo-compounds than of their *para*-isomers is probably due to chelation with aluminium of the first-mentioned classes.

Adsorption mechanism of anionic solutes. The reaction of hydrochloric acid-treated oxide with anions is probably mainly exchange of chloride ions for the adsorbed anions, but some covalent bonding may also occur. Alumina which has been given other pretreatments (*e.g.*, anodic film [29]) may have a greater tendency to adsorb anions by covalent bonding. This will be discussed elsewhere.

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