786. *Studies in Adsorption. Part XI.* A System of Classification of Solution Adsorption Isotherms, and its Use in Diagnosis of Adsorption Mechanisms and in Measurement of Specific Surface Areas of Solids.*

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Isotherms for adsorption of organic solutes are divided into four main classes, according to the nature of slope of the initial portion of the curve, and thereafter into sub-groups. The significance of their features is discussed.

The main classes are: (i) *S* Curves, indicative of vertical orientation of adsorbed molecules at the surface. (ii) *L* Curves, the normal or " Langmuir " isotherms, usually indicative of molecules adsorbed flat on the surface, or, sometimes, of vertically oriented adsorbed ions with particularly strong intermolecular attraction. (iii) *H* Curves (" high affinity ") (commencing at a positive value on the " concentration in solid " axis), often given by solutes adsorbed as ionic micelles, and by high-affinity ions exchanging with low-affinity ions. (iv) *C* Curves (" constant partition "), linear curves, given by solutes which penetrate into the solid more readily than does the solvent.

The sub-groups of these classes are arranged according to the shape of the parts of the curves farther from the origin, and the significance of plateaux and changes of slope are described. Thus, if the adsorbed solute molecules in the monolayer are so oriented that the new surface they present to the solution has low attraction for more solute molecules, the curve has a long plateau; if they are oriented so that the new surface has high attraction for more solute, the curve rises steadily and has no plateau.

The choice of solutes for reliable measurement of specific surface areas is very restricted. It is suggested that *p*-nitrophenol may be one of the best compounds for this purpose.

THIS is a study of the relation between solute adsorption mechanisms at solid surfaces and the types of adsorption isotherm obtained. It describes a system of classification of all solution adsorption isotherms, and suggests how their form can be used to diagnose the adsorption mechanism, to obtain information regarding the physical nature of the solute and the substrate surface, and to measure the specific surface area of the substrate. The last-mentioned has hitherto been the principal use of solution adsorption isotherms, but it has been hampered by lack of information on the detailed meaning of the curves.

Possibly the first attempt at a general classification of adsorption isotherms was that made in 1922 by Ostwald and de Izaguirre,[1] who described two of the curves included in

* Part I, *J.*, 1954, 4360; previous papers in this series were divided into two series, for inorganic and organic substrates respectively. Parts I—V, organic series, are considered as Parts VI—X in the present series. Thus, Part X is *J. Soc. Dyers Colourists*, 1958, **74**, 846 (ref. 12*a*).

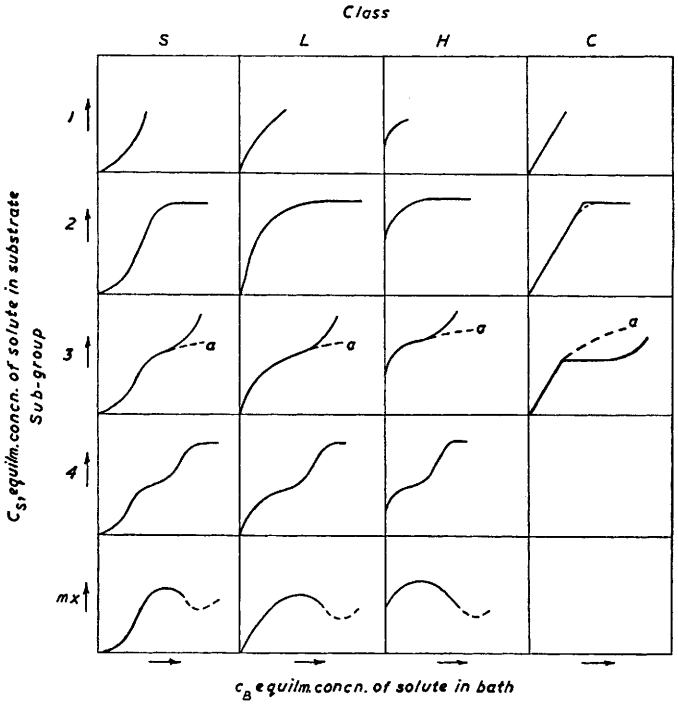
[1] Ostwald and de Izaguirre, *Kolloid-Z.*, 1922, **30**, 279.

the present system and a number of others, having marked maxima found only in adsorptions from binary solutions over wide concentration ranges (cf. Fig. 1, footnote). Brunauer [2] later defined five types of isotherm that are observed in vapour-phase adsorption (cf. Fig. 1, footnote). An outline of the present system of classification has already been given; [3] but the conclusions then drawn and the classification have been modified and developed as a result of later investigations, and are given here in more detail and with experimental evidence.

Classification System.—The present system divides all isotherms into four main classes according to the initial slope, and sub-groups are described for each class, based on the shapes of the upper parts of the curves. The four main classes (Fig. 1) are named the *S*, *L* (*i.e.*, "Langmuir" type), *H* ("high affinity"), and *C* ("constant partition") isotherms, and the variations in each class are divided into sub-groups.

The *L* curves are the best known; indeed the *L*2 curve occurs in probably the majority of cases of adsorption from dilute solution and few cases of the other types appear to have been previously recorded.

FIG. 1. *System of isotherm classification.*



Ostwald and de Izaguirre's two types of curve for adsorption from dilute solution are classified as *L*2 and *C*1 here, and their several other curves for adsorption from concentrated liquid binary mixtures would come under the present sub-group *mx*, with one exception (*C*1, with *negative* slope).

Brunauer's five types of vapour-phase (physical) adsorption isotherm (ref. 2, p. 150) are defined as *H*2, *L*3, *S*1, *L*4, and *S*2 under the present system.

The present nomenclature is slightly different from that originally given.[3]

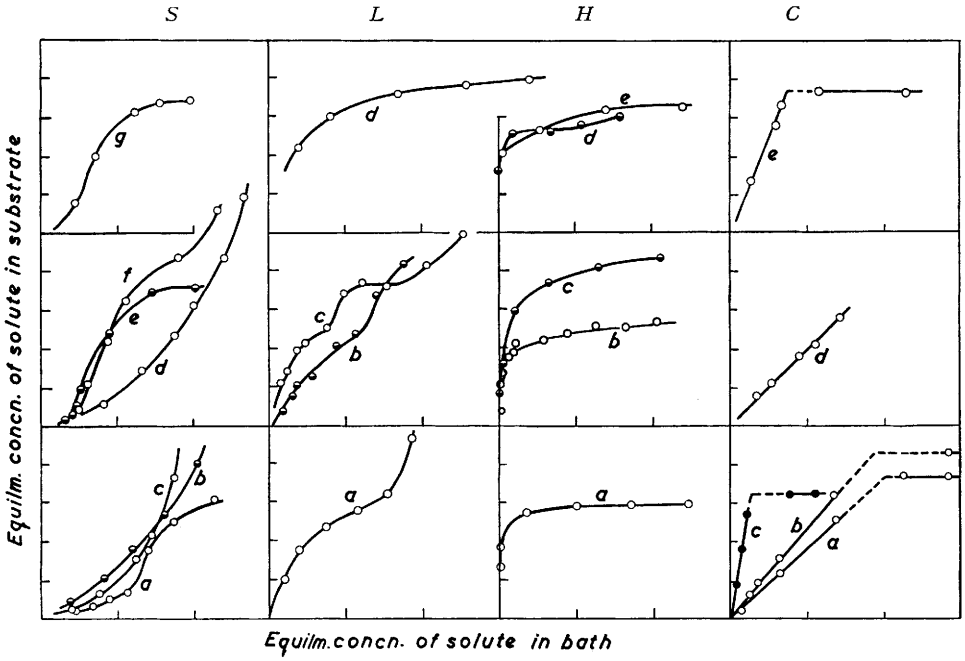
The system can be readily adapted to describe curves with additional variations not shown above, *e.g.*, the isotherm for phenol adsorption on graphite (Fig. 2*LC*) has two inflections followed by a further rise and would here be defined as *L*5 and curves with two successive maxima (see Table 1) as *mxmx*.

Systems are listed in Table 1 according to the isotherm type obtained and some isotherms are shown in Figs. 2—8. The features of the curves and their probable causes

[2] Brunauer, "The Adsorption of Gases and Vapours," Oxford Univ. Press, London, 1944, p. 150.

[3] Giles and MacEwan, *Proc. 2nd Internat. Congr. Surface Activity*, 1957, **3**, 457; Giles, *Discuss. Faraday Soc.*, 1954, **16**, 112.

FIG. 2. *Examples of adsorption isotherms of the four classes.*



Curve and ref.	System	Scales (box limits) Horizontal (mmole/l.)	Vertical (mmole/kg.)
	S *Curves*		
a [12a]	Naphthalenesulphonic acid, Na salt, on cellulose (water); 50°	0—60	0—50
b	Phenol on n-octadecyl alcohol crystals (water); 29°	0—300	0—2500
c	As *b*, but from 10% w/v aqueous Na_2SO_4 solution	0—300	0—10^4
d	Phenol on wool (water); 18°	0—15	0—100
e [5]	Phenol on alumina (water); 58°	0—120	0—500
f	2,4-Dinitrophenol on wool (water); 59°	0—0·30	0—100
g [9]	Azo-dye (C.I. 15,620) on anodic alumina film (water); 50°	0—6	0—500
	L *Curves*		
a [14]	Anthracene-1-sulphonic acid on graphite (water); 20°	0—30	0—25
b	Quinol on wool (water); 18°	0—30	0—100
c [14]	Phenol on graphite (water); 18·5°	0—60	0—25
d [5]	Resorcinol on alumina; 58°	0—60	0—125
	H *Curves*		
a [5]	Sulphanilic acid → R-acid azo-dye on alumina (water); 49° and 60°	0—3	0—100
b [22]	Metal–unsulphonated ligand (1,2) dye on stretched nylon (water)	0—1·2	0—100
c [22]	Metal–unsulphonated ligand (1,2) dye on unstretched nylon (water)	0—1·2	0—100
d [14]	Methyl Violet (C.I. 42,555) on graphite (water)	0—0·3	0—12·5
e [16]	Janus Red B (C.I. 26,115) on silica (water); 50°	0—0·6	0—125
	C *Curves*		
a	Water on wool (n-butanol); 57°	0—3330	0—10^4
b	As *a*, 52°	0—3330	0—10^4
c	As *a*, 19°	0—2400	0—2 × 10^4
d	Phenol on cellulose triacetate (2,2,4-trimethylpentane); 29°	0—6	0—500
e [30c]	Disperse dye (C.I. 11,110) on cellulose diacetate (adsorbed from starch paste)	0—3 *	0—25 *

* Units: mg./g.

TABLE 1. *Classified list of systems* (for abbreviations, etc., see p. 3978).

Solute	Solvent *	Substrate	Isotherm	Ref.†
	S *Curves*			
Anthraquinone dye, monosulphonated	H_2O	SiO_2	*S*1 (see Fig. 7*a*)	
trans-Azobenzene	C_6H_6	N	*S*1(?)	4
cis-Azobenzene	EW80	Al_2O_3	*S*1	5
Benzyl alcohol	H_2O	Wl	*S*1	6
Dyes:				
Azo-monosulphate ester	H_2O	Al_2O_3(an)	*S*1	7
Cyanine (non-planar)	H_2O	AgX	*S*1, *S*2	8
Monosulphonated	H_2O	Al_2O_3(an)	*S*1	9
Hæmatein	H_2O	Wl	*S*1 (see Fig. 3)	10
Hæmatoxylin	H_2O	Cll	*S*1 ‡	10
2-Hydroxybiphenyl	H_2O	Cll	*S*1	11
2-Naphthol-6-sulphonic acid	EW50	Cll	*S*1	12*a*
m-, *p*-Nitrophenol	H_2O	S	*S*1	6
2,4-Dinitrophenol	H_2O	Al_2O_3(an)	*S*1	7
Phenol	H_2O	N	*S*1(?)	4
Phenol	H_2O	CeOH, StOH	*S*1 (see Fig. 2*Sb*, *c*)	2*a*
Phenol	H_2O, E	Wl	*S*1 (see Fig. 2*Sd*)	4
Phenol, *p*-cresol, *m*- and *p*-fluorophenol	H_2O	Pg	*S*1(?)	6
Phenol derivatives (monosubstituted): *m*-, *p*-Ac; *m*-, *p*-Br; *m*-$HO_2C{\cdot}CH_2$; *p*-Cl; *p*-Et; *m*-, *p*-F; *p*-iodo-, *m*-, *p*-Me; *m*-, *p*-MeO; *m*-, *p*-$Me{\cdot}SO_2$	H_2O	Wl	*S*1	6
Polynuclear aromatic hydrocarbons	X	Al_2O_3	*S*1, *S*2	13
p-Aminoazobenzene	H_2O	Cll	*S*3	
Benzenesulphonic acid	H_2O	C(gr)	*S*2	14
Cellobiose	H_2O	Al_2O_3(HCl)	*S*2	5
Dodecylammonium chloride	H_2O (pH 2·9)	Al_2O_3	*S*2	15
Dyes:				
Anthraquinone, unsymmetrically sulphonated; $C_{12}H_{25}$ substituent (C.I. No. 62,075)	H_2O	SiO_2	*S*2	
Azo (unsymmetrically) disulphonated	H_2O	Al_2O_3(an)	*S*2(?)	9
Azo (unsymmetrically) disulphonated; $C_{12}H_{25}$ substituent	H_2O	Al_2O_3(HCl)	*S*2	5
Monosulphonated, various	H_2O	Al_2O_3(an)	*S*2 (cf. Fig. 2*Sg*)	9
Monosulphonated (C.I. 15,510)	H_2O	SiO_2	*S*2 §	16
p-$HO{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_4{\cdot}SO_3H$-*p*	H_2O (pH 3·5)	Ch	*S*2	12*a*
MeOH	C_6H_6	Cll	*S*2 (Fig. 5*a*)	12*a*
2-$C_{10}H_7{\cdot}SO_3H$ and Na salt	H_2O	Cll	*S*2 (see Fig. 2*Sa*)	12*a*
2-Naphthol-6-sulphonic acid	H_2O	Cll	*S*2	12*a*
Nitrobenzene	C_6H_6	Al_2O_3	*S*2	5
p-Nitrophenol	H_2O	SiO_2	*S*2 (see Fig. 4*a*)	
Phenol	H_2O	Al_2O_3	*S*2 (see Fig. 2*Se*)	5
Phenol	H_2O, iso-O	Ch	*S*2	12*a*
Di- and tri-sulphonated aromatic compounds	H_2O	C(gr)	*S*2	14
Azobenzene	C_6H_6	Wl	*S*3	4
Azo-dye, monosulphonated (C.I. 15,510)	H_2O	Al_2O_3(an)	*S*3	9
$C_6H_5{\cdot}N{:}N{\cdot}C_6H_4{\cdot}NMe_2$-*p*	C_6H_6	Wl	*S*3	4
MeOH	C_6H_6	Ch	*S*3(?)	12*a*
p-Nitrophenol	H_2O	Wl	*S*3	
2,4-Dinitrophenol	H_2O	Wl	*S*3 (see Fig. 2*Sf*)	4
Quaternary ammonium surface-active agents	H_2O	cll, oxy-cll	*S*3, *Smx*	17
Stilbene	C_6H_6	N,Wl	*S*3	4
Benzene	Bu^nOH	Wl	*S*3 (see Fig. 5*d*)	4
Sodium dodecyltoluenesulphonate	H_2O	Al_2O_3(an)	*Smx*	7
	L *Curves*			
$C_6H_5{\cdot}N{:}N{\cdot}C_6H_4{\cdot}NH_2$-*p*,HCl	H_2O	SiO_2	*L*1	16
Benzidine hydrochloride	H_2O	Cll	*L*1	11
Dyes:				
Azo, non-ionic	C_6H_6,MeOH	CA	*L*1	18
	BuOAc	CA	*L*1(?)	18
Bis-azo-, disulphonated (C.I. 24,895)	H_2O (NaCl)	Cll	*L*1	19
3-Hydroxydiphenylamine	H_2O	Cll	*L*1	11
MeOH	C_6H_6	CTA	*L*1 (See Fig. 8*c*)	
Resorcinol	H_2O	Ch	*L*1(?)	12*a*
Alkyl sulphate esters (Na salts)	H_2O	Al_2O_3(an)	*L*2	7
4-Aminoazobenzene	D	Al_2O_3	*L*2	5
Ammonium ion	H_2O	cat X	*L*2	20
(*cis*?)-Diphenylazobenzene	EW80	Al_2O_3	*L*2	5

[cont. on p. 3977]

TABLE 1. (*Continued.*)

Solute	Solvent *	Substrate	Isotherm	Ref.†
		L *Curves.* (*continued*)		
4,4′-Diaminodiphenylmethane	H_2O	Cll	*L*2	11
2,2′-Dihydroxybiphenyl	H_2O	Cll	*L*2(?)	11
Dyes:				
Anthraquinone, *sym.*-disulphonated (C.I. 63,010)	H_2O (pH 1·35)	N,S,Wl	*L*2	21
Anthraquinone, *sym.*-disulphonated (C.I. 63,010)	H_2O	SiO_2	*L*2 (see Fig. 7*b*)	
Anthraquinone, disulphate ester (C.I. 70,601)	H_2O (pH 9)	Cll, Ch	*L*2	12*a*
Azo, monosulphonated	H_2O	Cll	*L*2	12*a*
	H_2O	SiO_2	*L*2	16
Azo, *sym.*-disulphonated (C.I. 16,045)	H_2O	CA	*L*2	
Azo, *sym.*-disulphonated	H_2O	Al_2O_3(an)	*L*2	9
Azo, *asym.*-disulphonated	H_2O	Cll	*L*2	12*a*
Azo, trisulphonated (sulphanilic acid → R-acid)	H_2O (pH 2·9)	Wl	*L*2	
Azo, trisulphonated	H_2O	Al_2O_3(an)	*L*2	9
Disazo-, disulphonated (C.I. 22,120)	H_2O	Ch	*L*2	12*a*
Disazo-, tetrasulphonated (C.I. 24,410)	H_2O	Al_2O_3(an)	*L*2	9
Disazo-, tetrasulphonated (C.I. 24,410)	H_2O	Ch	*L*2	12*a*
Triphenylmethane, *asym.*-disulphonated (C.I. 42,045)	H_2O (pH 2·2)	Wl	*L*2	21
Azo, unsulphonated, 1,2-metal ligand	H_2O	S,Wl	*L*2	22
Glucose	H_2O	C(gr)	*L*2	14
p-HO·C_6H_4·N:N·C_6H_4·SO_3H-*p*	H_2O	Cll	*L*2 (?)	12*a*
MeOH	C_6H_6	d Cll	*L*2 (see Fig. 5*c*)	
Phenol	H_2O	aq. P (C.I. 59,700, 69,025)	*L*2	
Phenol	H_2O	C(ch)	*L*2	23
Phenylazo-2-naphthol	iso-O	C(gr)	*L*2	12*a*
Phenylazo-2-naphthylamine	D	Al_2O_3	*L*2(?)	5
Proflavine	H_2O	DNA	*L*2	24*a*
Resorcinol	H_2O	Al_2O_3	*L*2 (see Fig. 2*Ld*)	5
Sucrose	H_2O	C(gr)	*L*2	14
Terephthaldehyde	C_6H_6	Al_2O_3	*L*2	5
n-Aliphatic acids ($>C_4$)	H_2O	C	*L*3	23
n-Aliphatic alcohols ($>3_3$)	H_2O	C	*L*3	23
Anthracene-1-sulphonic acid	H_2O	C(gr)	*L*3 (see Fig. 2*La*)	14
Anthraquinone-2,7-disulphonic acid	H_2O (pH 9)	Wl	*L*3	
Dyes:				
Anthraquinone, disulphonated	H_2O (pH 1·0)	Wl	*L*3	
Azo, monosulphonated (C.I. 15,510)	H_2O (pH 2·8)	Wl	*L*3*a*	
Azo, disulphonated	H_2O	Wl	*L*3	
Merocyanine	H_2O	AgX (emul.)	*L*3*a* (see Fig. 6)	8*b*
Hæmatoxylin	H_2O	N,Wl	*L*3 (see Fig. 3)	10
Naphthalene-2-sulphonic acid	H_2O (pH 9)	Wl	*L*3	
p-Nitrophenol	C_6H_6	Al_2O_3	*L*3 (see Fig. 4*b*)	
Phenol	iso-O	Wl	*L*3	4
Dodecylammonium chloride	H_2O (pH 6·3)	Al_2O_3	*L*4	15
Phenylazo-2-naphthol	C_6H_6	C(gr)	*L*4	14
Quinol	H_2O	Wl	*L*4 (see Fig. 2*Lb*)	
Phenol	H_2O	C(gr)	*L*5 (see Fig. 2*Lc*)	14
Methanol	C_6H_6	N,Wl	*Lmx*	4
p-Nitrophenol	C_6H_6	Wl	*Lmx*	4
Na alkyl sulphates	H_2O	Wl	*Lmx*	24*b*
Na alkyl sulphates	H_2O	C	*L*4*mx*	24*e*
Na alkylaryl sulphates	H_2O	Cll	*L*4*mx*	24*c*, *d*
Na palmitate	H_2O	Wl	*L*4*mxmx*	24*c*
		H *Curves*		
Fatty acids	C_6H_6	Ni, Pt	H ‖	25
Alkylammonium ions ($>C_4$)	H_2O	cat X	*H*2	20
2,4-Diacetoxyazobenzene	C_6H_6	Al_2O_3	*H*2(?)	5
Dyes:				
Anthraquinone, *asym.*- disulphonated $C_{12}H_{25}$ substituent (C.I. 62,075)	H_2O (pH 1·7)	Wl	*H*2	21
Azo, mono-, di-, tri-sulphonated	H_2O	Al_2O_3 (HCl)	*H*2 (cf. Fig. 2*Ha*)	5
Azo, 1,2-metal unsulphonated ligand	H_2O	N	*H*1, *H*2, *H*4 (cf. Fig. 2*Hb*, *c*)	22

[cont. on p. 3978]

TABLE 1. (*Continued.*)

Solute	Solvent *	Substrate	Isotherm	Ref.†
	H *Curves* (*continued*)			
Dyes (*continued*):				
Basic (various)	H_2O	SiO_2	*H*2, *H*3 (cf. Fig. 2*He*)	16
Cyanine (planar)	H_2O	Ag X (emul.)	*H*2	8
Octadecylammonium ion	H_2O	an X	*H*2	20
Stearic acid	C_6H_6	Ag, Ni, Pt (pdr.)	*H*2	26
Stearic acid	C_6H_6	$NaNO_3$	*H*2	26*b*
Dyes:				
Azo-, monosulphonated	H_2O	C(gr)	*H*3	14
Azo-, disulphonated ($C_{12}H_{25}$ substituent), trisulphonated	H_2O	Al_2O_3(an)	*H*3	9
Bisazo-, disulphonated (C.I. 24,140) ¶	H_2O (pH 2·4)	Ch	*H*3*a*	12*a*
Basic (various)	H_2O	C(gr)	*H*3 (cf. Fig. 2*Hd*)	14
Poly(vinyl acetate) derivatives	Al. solv.	Fe(pdr)	*H*3	27
Sulphuric acid	H_2O	Wl	*H*3	28
Alkylammonium ions (C_{10}, C_{12})	H_2O	an X	*H*4	20
Dodecylammonium chloride	H_2O (pH 6)	Al_2O_3	*H*4	15
Dodecyl sulphate ion	H_2O	an X	*H*4	20
Dodecyl sulphate, Na salt	H_2O	Al_2O_3(an)	*H*4	7
Dodecyl sulphate, Na salt	H_2O	$BaSO_4$	*H*4	15
p-Nitrophenol	H_2O	C(gr)	*H*5(?)	14
	C *Curves*			
Azobenzene	C_6H_6	W (al. tr.) **	*C*1	4
Azo-dye (non-ionic)	CCl_4	CA	*C*1	18
Azo-dye, monosulphonated (C.I. 15,510)	H_2O	CA	*C*1	
Benzene	n-C_7H_{16}	Wl	*C*1	
Benzoic acid	H_2O	T	*C*1	29*a*
p-Nitrophenol	C_6H_6	N	*C*1	4
p-Nitrophenol, *p*-bromophenol	H_2O	Pg	*C*1	6
Phenol	H_2O	CTA	*C*1 (see Fig. 8*b*)	
Phenol	iso-O	CTA	*C*1 (see Fig. 2*Cd*)	
Phenol	H_2O	S	*C*1(?)	6
Phenol	H_2O	T	*C*1	29*a*
Phenol, *p*-cresol, and monohalogeno-phenols	H_2O	Ppa	*C*1	6
Quinol	H_2O	CTA	*C*1	
Aromatic hydrocarbons (naphthalene, toluene, xylene)	aq. (disp)	T	*C*2	29*a*
Me salicylate	H_2O	T	*C*2 (see p. 3985)	29*b*
Non-ionic disperse dyes (anthraquinone and azo-classes)	H_2O	CA, CTA, T	*C*2 (cf. Fig. 2*Ce*)	30
Biphenyl	aq. (disp)	T	*C*3	29*a*
Water	Bu^nOH	W	*C*2 (see Fig. 2*Ca*—*c*)	4
Hæmatoxylin	H_2O	CTA	*C*3(?)	10
Biphenyl	aq. (disp)	T	*C*3*a*	29*a*
Aliphatic alcohols	H_2O	Wl	*S*1	45
Phenylazobenzene cpds. (non-ionic)	H_2O	Wl	*C*1	46
HCl	H_2O + MeOH	Wl	*L*2	47
HCl	H_2O + dioxan	Wl	*L*2	47

* Solvents, etc.: aq. (disp), aqueous dispersion; al. solv., aliphatic solvents; Bu^nOH, butan-1-ol; D, dioxan; E, ethanol: EW50, ethanol–water (1 : 1 v/v); EW80, ethanol–water (4 : 1 v/v); iso-O, 2,2,4-trimethylpentane; X = xylene.

Substrates: al. tr., alkali treated; an, anodic film; an X, anion exchange resin; AqP, anthraquinone derivative pigment (water-insoluble); AzP, azo-derivative pigment (water-insoluble); CA, sec.-cellulose acetate; C, varieties of carbon; C(ch), charcoal; C(gr), graphite; cat X, cation exchange resin; CeOH, n-heptadecyl alcohol; Ch, chitin; Cll, cellulose; d Cll, intensively dried cellulose; CTA, cellulose triacetate; oxy-cll, oxycellulose; Pg, polyglycine; Ppa, polyphenylalanine; N, Nylon; S, silk; StOH, n-octadecyl alcohol; T, Terylene polyester fibre; Wl, wool.

† Where no reference is given, the tests have been made here specifically for the present investigation.

‡ Probably oriented as in Fig. 11.

§ This dye is probably in the quinonehydrazone form, the reactive group towards SiO_2 being >NH.

‖ See note on p. 3983.

¶ Fig. 5*a*, ref. 12*a*, shows this and not the named dye.

** The treatment presumably reduces the permeability of the fibre to solvent.

will now be discussed. For more detailed experimental evidence earlier papers from this laboratory may be consulted.

Discussion

Initial Slope.—This depends on the rate of change of site availability with increase in solute adsorbed. As more solute is taken up, there is usually progressively less chance that a bombarding solute molecule will find a suitable site on which it can be adsorbed; *i.e.*, to cause adsorption of a given additional amount of solute, the external solution concentration must be raised by ever-increasing amounts. This applies to the normal *L* curves and to the later stages of the *S* and *H* curves. In the initial part of the *S* curves, however, the opposite condition applies, and the more solute there is already adsorbed, the easier it is for additional amounts to become fixed (cf. Fig. 9). This implies a side-by-side association between adsorbed molecules, helping to hold them to the surface. This has been called " co-operative adsorption " (ref. 8, and see p. 3984). In the *C* curves the availability of sites remains constant at all concentrations up to saturation.

The probable causes of these effects will now be described and illustrated.

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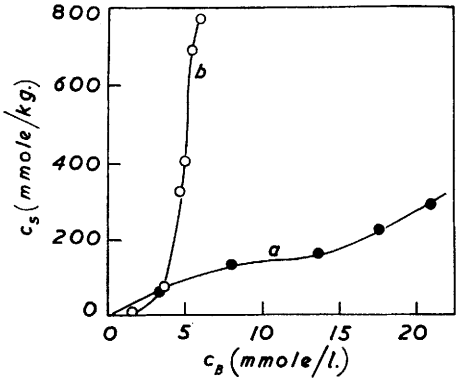
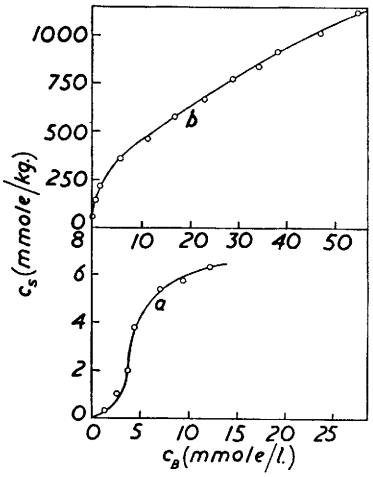
[46] Bird and Firth, *loc. cit.*, p. 735.
[47] Larose and Donovan, *loc. cit.*, p. 699.

FIG. 3. *Adsorption isotherms on wool from aqueous solution at* 60°.



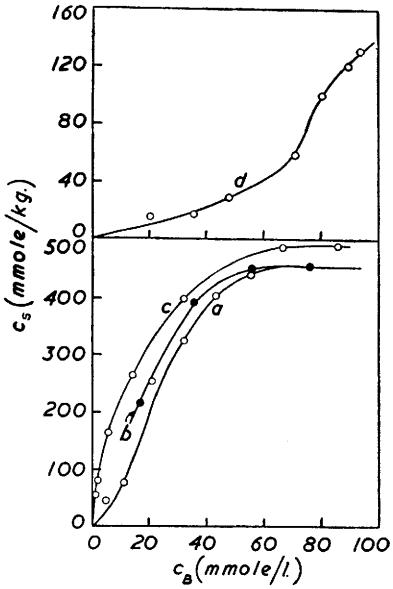
(*a*) *Hæmatoxylin.* (*b*) *Hæmatein* (pH 1·7, *under* CO_2)

FIG. 4. *Adsorption isotherms of* p-*nitrophenol on inorganic substrates.*



(*a*) *On powdered silica from water, at* 15°.
(*b*) *On chromatographic alumina* (*Grade I*) *from benzene, at* 20°.

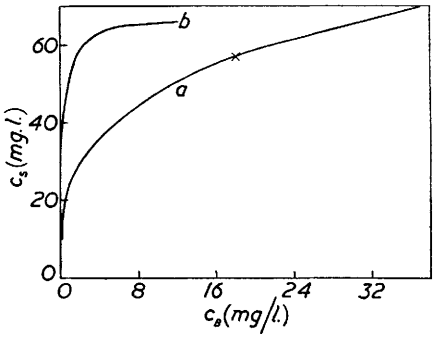
FIG. 5. *Adsorption isotherms of organic liquid solutes on organic substrates.*



(*a*), (*b*), (*c*), *Methanol in benzene on normally dried* (*a*) *and intensively dried* (*b*, *c*) *cellulose* (*viscose rayon*) *at* 50°, 23°, 19°, *respectively.* (*d*) *Benzene in butan*-1-*ol on wool at* 50°.

Note: c_s *scale in Fig.* 4, *ref.* 4, *should read* " mmole/kg. × 10."

FIG. 6. *Adsorption isotherms of cyanine dyes on silver halide emulsion.*[8b]



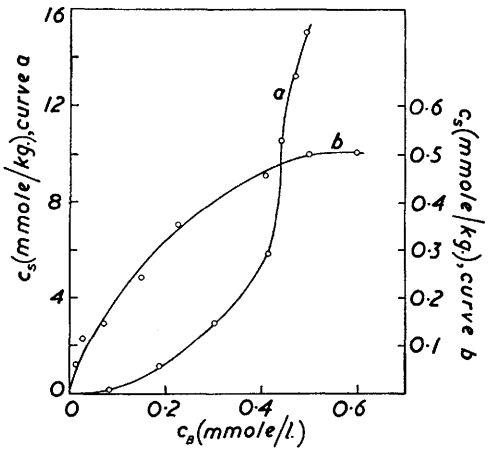
(*a*) *Non-ionic merocyanine dye*; " *Point B* " (*see p.* 3986) (*completion of monolayer*) *is marked* ×. (*b*) *Cationic cyanine dye.*

The S *Curve*

The initial direction of curvature shows, as just explained, that adsorption becomes easier as concentration rises. In practice, the *S* curve usually appears when three

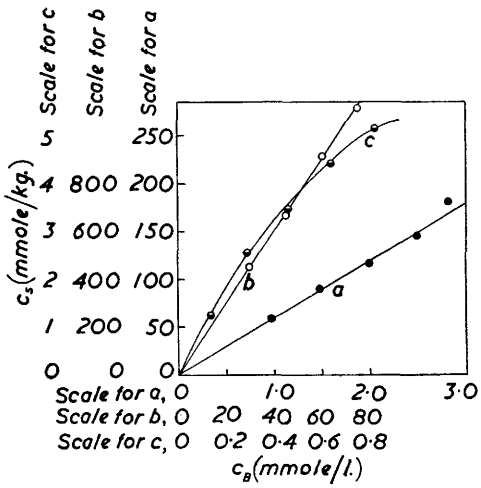
conditions are fulfilled: the solute molecule (*a*) is monofunctional, (*b*) has moderate intermolecular attraction, causing it to pack vertically in regular array in the adsorbed layer, and (*c*) meets strong competition, for substrate sites, from molecules of the solvent or of another adsorbed species. Thus, monohydric phenols usually give *S* curves, especially when adsorbed on a polar substrate, *e.g.*, alumina, from a polar solvent such as water or ethanol, but not from a non-polar solvent such as benzene or 2,2,4-trimethylpentane (cf. Fig. 4) which does not compete for the adsorption sites. So also do aqueous systems

FIG. 7. *Isotherms for sulphonated aminoanthraquinone dyes adsorbed by hydrogen bonding on powdered silica.*



(*a*) *Monofunctional* (1-*amino*) *dye* (III). (*b*) *Bifunctional* (1,5-*diamino*) *dye* (IV).

FIG. 8. *Adsorption isotherms of organic solutes on cellulose triacetate.*



(*a*) *Phenol in* 2,2,4-*trimethylpentane at* 59°. (*b*) *Phenol in water at* 58°. (*c*) *Methanol in benzene at* 23·5°.

Both c scales are in molar units.

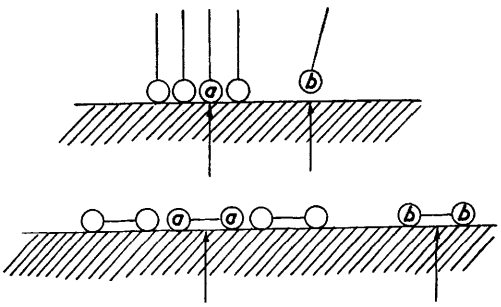
of non-planar cyanine dyes on silver halide, and surface-active quaternary ammonium salts on cellulose, and many monosulphonated dyes on anodic alumina. This isotherm thus apparently indicates a tendency for large adsorbed molecules to associate rather than to remain as isolated units (cf. Fig. 9 and the discussion under *H* curves, p. 3983).

Monofunctionality.—The definition of "monofunctional" in this context is that the solute molecule has a fairly large hydrophobic residue ($>C_5$) and a marked localisation of

FIG. 9. *Schematic illustration of conditions favouring production of* S *and* L *isotherms.*

Top: *Monofunctional polar solute on polar substrate in polar solvent. A solute molecule is more stable adsorbed at a, adjacent to other already adsorbed molecules, than in isolation at b. Result*: S *isotherm.*

Bottom: *A bifunctional solute molecule is equally stable when adsorbed at a as at b. Result*: L *isotherm.*

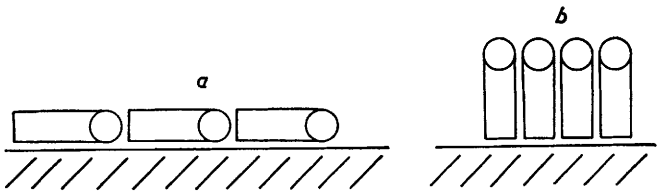


the forces of attraction for the substrate over a short section of its periphery, and that it is adsorbed as a single unit and not in the form of a micelle.* Thus, phenol is monofunctional in its attraction towards a polar substrate, *e.g.*, alumina, because the attraction

* Phenol adsorbed on chitin from pH 9 buffer solution seems not to give an *S* curve (ref. 12*a*, Fig. 3, but the critical initial part of the curve is not determined). This might be evidence of some adsorption of mixed phenol–phenoxide ion micelles.

arises from its hydroxy-group, but it is initially not monofunctional towards either graphite (Figs. 2, 10) or powdered water-insoluble vat dyes with large planar assemblages of aromatic nuclei. With these it does not give an *S* isotherm, because its attraction for the substrate lies probably in non-polar forces operating over the whole phenol nucleus. Aromatic sulphonic acids appear to be monofunctional towards graphite in water, probably because the very high attraction of the sulphonate group for water draws this group as far as possible into the water phase, and thus only the opposite unsulphonated end of the nucleus is in contact with the graphite (cf. Fig. 11).

FIG. 10. *Schematic representation of probable orientation of phenol molecules adsorbed on a graphite surface, from water.*



(*a*) *At low concentration.* (*b*) *At high concentration.*

Specific surface-area measurements confirm the view that the molecules of monofunctional solutes are adsorbed edge-on or end-on to the substrate surface. In this way the strong intermolecular forces between their hydrophobic residues can exert their maximum effect: hence the isotherm is initially convex to the horizontal axis (see Fig. 9).

It might be thought from the above definition that all surface-active substances, being, as they are, monofunctional under the above definition, would give *S* isotherms, but in practice this is not so. Possible reasons are they are that adsorbed as ionic micelles, or that their intermolecular attraction is very high; this is discussed below. Sometimes high salt concentration promotes *S*-curve formation [24c] with surface-active solutes; perhaps conditions (*b*) and (*c*) apply.

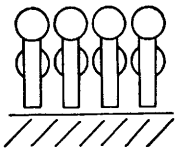
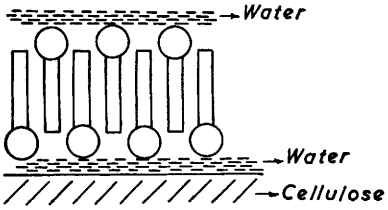


FIG. 11. *Schematic representation of probable orientation of the first adsorbed layer of a disulphonated azo-dye* (C.I. 16,045), *on graphite, from water.* [*The sulphonate groups* (*circles*) *stand as far away as possible from the hydrophobic surface. A second layer may then be adsorbed with reversed orientation, but separated by water. The isotherm is* S4 (*ref.* 14, Fig. 3, *h*, *i*). *The molecules are shown here edge-on.*]

As a working hypothesis we may say that whenever an *S* curve is obtained with any aromatic solute, or an aliphatic solute with more than about five carbon atoms, the adsorbed molecules are oriented perpendicularly to the surface. The converse is not always true: not all systems with perpendicularly oriented adsorbed molecules give *S* curves, especially some with strong solute intermolecular attractions.

FIG. 12. *Schematic representation of the probable orientation of the adsorbed layer of an aromatic monosulphonic acid* (e.g., *anthracene-*1*-sulphonic acid*) *on cellulose in water.* (*This arrangement ensures that sulphonic groups are presented both to the external solution and to the firmly-bound layer of water at the cellulose surface.* S *isotherms are obtained.*)



Adsorptions on Cellulose.—Molecules of monosulphonates of naphthalene and anthracene adsorbed on cellulose give *S* isotherms. This implies a more marked tendency to pack face-to-face vertically at the cellulose–water surface * than to lie flat on the cellulose

* Probably with their long axes parallel to the cellulose molecules. Examination under the microscope of single cellulose (ramie) fibres containing adsorbed anthracenesulphonic acid and Congo Red, severally, in polarised light, showed similar effects.

molecule. In so doing, sulphonate groups are exposed along the top and bottom of the layer of adsorbed molecules, as shown in Fig. 12. These substances have low affinity for cellulose, because of their short molecular length (the apparent affinity rises linearly with the logarithm of the molecular length [12a]). Larger molecules, *e.g.*, bisazo-dyes, having higher affinity for cellulose, lie partly flat on the cellulose–water complex and do not give *S* curves.

Methanol adsorbed from benzene on normally dried cellulose (or chitin) gives *S* isotherms, probably as a result of competition for hydrogen-bonding sites by traces of firmly bound water not removed from the cellulose in normal drying. Competition is reduced and adsorption promoted by methanol associating on adsorption: hence the form of the *S*-curve. When the material is intensively dried, competition from water is eliminated, and the curve has the normal *L* shape (Fig. 5).

The L *Curve*

Here the initial curvature shows that as more sites in the substrate are filled it becomes increasingly difficult for a bombarding solute molecule to find a vacant site available. This implies either that the adsorbed solute molecule is not vertically oriented (on the argument used for the *S* curve, cf. Fig. 9) or that there is no strong competition from the solvent.

The types of system which give this curve do in fact fulfil these conditions (cf. Table 1). Thus they have one of the following characteristics: (i) the adsorbed molecules are most likely to be adsorbed flat, *e.g.*, resorcinol and terephthaldehyde on alumina, or (ii) if adsorbed end-on, they suffer little solvent competition; examples of (ii) are (*a*) systems with highly polar solute and substrate, *e.g.*, phenol and alumina, and a non-polar solvent, *e.g.*, benzene or 2,2,4-trimethylpentane, and (*b*) systems in which monofunctional ionic substances with very strong intermolecular attraction, *e.g.*, long paraffin-chain sulphate esters, are adsorbed from water by ion–ion attraction.* It is possible that in these cases (systems *b*) the adsorbed ions may have become associated into very large clusters just before adsortion takes place. (See also the comments on cyanine dyes under *H* curves, below.)

The H *Curve*

This is a special case of the *L* curve, in which the solute has such high affinity that in dilute solutions it is completely adsorbed, or at least there is no measurable amount remaining in solution. The initial part of the isotherm is therefore vertical. The adsorbed species are often large units, *i.e.*, ionic micelles or polymeric molecules, but sometimes they are apparently single ions which exchange with others of much lower affinity for the surface, *e.g.*, sulphonated dye ions which exchange with chloride ions on alumina,[5] and cyanine dye cations adsorbed by ion–ion attraction on silver halides (see below). In the most extreme form, the curve is a horizontal line running into the vertical axis. This was found for chemisorption of fatty acids on Raney nickel.[25]

Cyanine Dyes.—A particularly interesting case is that of the cyanine-sensitising dyes adsorbed on " emulsions " of silver halide in gelatin. West *et al.*[8] found that many of these systems give *H* isotherms; spectroscopic tests show that the adsorbed dye is associated, usually in the " J-aggregate " form (long assemblages of stacked planar dye molecules each separated by a water molecule), and that all dye molecules are oriented edge-on to the silver halide surface. Some of these dyes, however, give the *S* curve, often with a sharp discontinuous change from the convex to the concave portion (relative to the

* It now seems likely that the *L* curve obtained for adsorption of Orange I (sulphanilic acid → 1-naphthol) from water on anodic alumina [9] is attributable to end-on orientation with strong intermolecular forces, especially hydrogen bonds between adjacent hydroxy-groups, which reduce competition from the solvent. If the orientation were at first flat, and later end-on, as suggested earlier,[31] a two-step (*L*4) curve would have been expected. The isomeric dye Orange II (sulphanilic acid → 2-naphthol) also stands end-on, but gives the *S* curve; its intermolecular association in the adsorbed layer is probably weaker than that of Orange I, because of the absence of the *p*-hydroxy-group.

[31] Giles, in " Hydrogen Bonding," Pergamon Press, London, 1959, p. 449.

horizontal axis). Beyond the inflection the curve is of the normal *L* form. Spectroscopic tests in these cases show that the inflection represents the concentration at which the J-aggregates begin to be taken up (called by these authors the onset of " co-operative adsorption "). At lower concentrations the dye must be oriented edge-on at the surface in small clusters of associated dye ions, according to the hypothesis developed above, since the *S* curve is obtained. When large aggregates are adsorbed the curve is always normal in shape, even though the individual ions in the aggregate are oriented edge-on. It therefore seems possible that the aggregates may be formed just before adsorption. Increase in the gelatin concentration in the emulsion also favours the formation of the *S* curve, presumably by making J-aggregate formation more difficult.

The C *Curve*

This is characterised by the constant partition of solute between solution and substrate, right up to the maximum possible adsorption, where an abrupt change to a horizontal plateau occurs.* This is the type of curve obtained for the partition of a solute between two immiscible solvents, and many authors consequently have used the term " solid solution " for adsorption processes which give it, but it is doubtful if the term is quite appropriate, though it is admittedly difficult to coin a more expressive one; " adsorption without solvent " may be suggested, for reasons given below.

The conditions favouring the *C* curve appear to be (*a*) a porous substrate with flexible molecules and regions of differing degrees of crystallinity, and a solute with (*b*) higher affinity for the substrate than the solvent has, and with (*c*) better penetrating power, by virtue of condition (*b*) and of molecular geometry, into the crystalline regions of the substrate.

Fundamentally, the linearity shows that the number of sites for adsorption remains constant; *i.e.*, as more solute is adsorbed more sites must be created. Such a situation could arise where the solute has a higher attraction for the substrate molecules than the solvent itself has. The solute could then break inter-substrate bonds more readily than the solvent could, and if its molecular dimensions were suitable, could penetrate into the

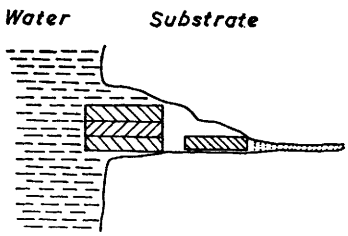


FIG. 13. *Schematic representation of conditions favouring the* C *isotherm.* [*Adsorbed molecules of a low-solubility solute* (e.g., *a non-ionic disperse dye*) *in water, entering a hydrophobic substrate beyond the region swollen by water.*]

structure of the substrate in regions not already penetrated by the solvent. This action has been compared[3] with the opening of a Zip fastener, the fastenings representing the intermolecular bonds of the substrate, and the slider the first molecule or group of molecules of solute to penetrate; this opens up the structure and allows more solute molecules to enter (cf. Fig. 13). The action stops abruptly when more highly crystalline regions of the substrate are reached. In fact the isotherms usually do suddenly change direction to give the horizontal plateau. Thus a linear isotherm indicates that the solute is penetrating regions inaccessible to the solvent.

Partition of a solute of limited solubility between two immiscible solvents is a special case of this behaviour; neither solvent penetrates between the molecules of the other but the solute penetrates both solvents.

* The lowest part of the *L* curve is, of course, sometimes virtually linear, and some almost linear curves which are borderline cases, intermediate between *S* and *L* types, are occasionally found.

This isotherm has now been found to occur in at least four types of system,* though it has hitherto been known for only one [(i) below]. The four systems are:

(i) Non- or mono-ionic aromatic solutes on hydrophobic polymers, *e.g.*, cellulose acetate or poly(ethylene terephthalate), from an " inert " liquid, *i.e.*, one which does not readily swell the substrate, and may also be an indifferent solvent for the adsorbing solute. Systems under this description are the non-ionic (" disperse ") dyes applied from fine aqueous dispersions (Table 1; Fig. 2,*Ce*) or from carbon tetrachloride, and colourless aromatic substances (" carriers ") used in aqueous solution or dispersion to assist the penetration of this type of dye into polyester fibres.[29] (These substances are in fact found, by physical tests, to be capable of penetrating into the crystalline regions of the fibre.[29b])

When the solute molecule has two widely spaced, strongly ionic (sulphonate) groups, *e.g.*, dye C.I. 16,045 (see Table 1), it has reduced affinity for the polymer,[30e] does not penetrate crystalline regions, and does not give the *C* curve.

(ii) Benzene in n-heptane and water as a solute in butan-1-ol adsorbed by dry wool fibre (Fig. 2*Ca*, *b*). This solvent (butanol) does not penetrate dry wool readily, if at all (cf. ref. 10).

(iii) Certain amino-acids and peptides, in water, on silica dust.[3] The mechanism here is rather obscure. Probably it involves hydrogen-bonding of the amino-groups with silica in regions of the amorphous layer around the silica particles which are less readily penetrated by water.

(iv) Phenols, in water, on synthetic polypeptides (Table 1). The same solutes on wool give *S* curves. Presumably the highly crystalline structure of the synthetic products makes them less readily penetrable by water.

Abnormalities.—We are aware of only three examples of the *C*3 curves: Adsorption of biphenyl by poly(ethylene terephthalate) (Terylene) fibre from hot aqueous dispersion [29a] appears to give the *C*3*a* isotherm.† The upper part of this curve must represent very deep penetration of the crystalline regions of the fibre, which appears to proceed without limit.[29a,b] Some disperse dyes, especially of the anthraquinone class, give *C*3*a* isotherms, the upper portion rising more steeply if a second dye is present which has the effect of promoting adsorption of the one measured. Part of this steady increase in adsorption beyond the inflection is attributable to building-up of adsorbed dye on the outer surface of the fibres. [Some *L*3*a* isotherms were obtained with systems of type (i) (above) by Bird and Manchester [30a] (cf. ref. 32) using cellulose acetate fibre. They traced the cause to the presence of large dye particles in the dispersions used.] The third example (hæmatoxylin) is doubtful, because there are insufficient experimental points to establish the shape at high concentrations.

The organic substances (" carriers "), used to aid the penetration of disperse dyes into polyester fibres, normally give adsorption isotherms of type *C*.[29a] Rochas and Courmont,[29b] however, obtained curves for several of these substances, in which an initial *S* portion changes abruptly to a flat plateau. These unusual curves are probably not true adsorption isotherms; on account of the method of analysis used (weighing of centrifuged fibres

* *Note added in proof.*—A new type of *C* isotherm system has recently been described,[46] *viz.*, non-ionic phenylazobenzene derivatives adsorbed by wool from water. It seems probable that because of their weak hydrogen-bonding properties (cf. refs. 4, 22*b*, 48) and steric effects, these solute molecules cannot form a stable attachment to the fibre in the presence of water, but they can do so by hydrogen-bond and non-polar forces in some of the more crystalline regions which are not penetrated by water. The system is thus essentially similar to other *C* systems. In wool there are, however, few crystalline regions [49] (10—15% inaccessible to D_2O), so that these solutes are adsorbed to a very limited extent (saturation adsorption is one-tenth of that in cellulose acetate [46]).

4-Aminoazobenzene, tested here on cellulose, gives the *S* isotherm. In this substrate the conditions are different: the cellulose molecule is planar, and can adsorb planar aromatic solute molecules from water by non-hydrogen-bonding forces,[12a] either oriented flat or edge-on (as probably in this case, of. Fig. 12), in water-penetrated regions.

† Rochas and Courmont [29b] say their curve for this system was " linear," but do not give details.

[32] Vickerstaff, " The Physical Chemistry of Dyeing," Oliver and Boyd, Ltd., Edinburgh, 2nd edn., 1954. [48] Cameron, Giles, and MacEwan, *J.*, 1958, 1224. [49] Burley, Nichols, and Speakman, *J. Textile Inst.*, 1955, **46**, T427.

after treatment in " carrier " solutions, allowance being made for the entrained water), the amount of solute returned as adsorbed will include some held in solution in the mechanically held liquid. In fact, when excess of solute was removed by rinsing in acetone, that remaining gave a normal *C* isotherm.

Unlike water, benzene from butan-1-ol on wool does not give a *C* curve. Here the solvent has the higher affinity (by hydrogen-bonding), because of its large molecule, but normally penetrates wool only with great difficulty. It is completely miscible with benzene and probably penetrates better from the mixture than alone. The *S* curve (Fig. 5*d*) indicates end-on orientation of adsorbed benzene.

Additional Characteristics

(i) *Indications of the Monolayer.*—Nearly all sufficiently complete curves have either a plateau or an inflection (" knee "). Those that do not (Sub-group 1) are clearly incomplete: saturation of the surface has not been reached, probably because of experimental difficulties. The plateau, or the beginning of the linear portion above the " knee " (Brunauer's " Point B ", ref. 2, p. 287) must represent " first degree saturation " of the surface, *i.e.*, the condition in which all possible sites in the original surface are filled and further adsorption can take place only on new surfaces. For convenience, this degree of coverage may be called the formation of a complete " monolayer," but this does not necessarily imply that it is a close-packed layer of single molecules or ions, as in a compressed monolayer on water. It may be so in some cases, and when it is, specific surface-area determinations can readily be made. Generally, however, the layer may (*a*) contain solvent as well as solute molecules,* or (*b*) consist only of isolated clusters of solute molecules adsorbed on the most active sites, or (*c*) consist of ionic micelles, either packed closely or well separated.

(ii) *Solvent in the Monolayer.*—Adsorption tests with *p*-nitrophenol give some indication of the likelihood of the presence of solvent in an adsorbed monolayer. Table 2 shows

TABLE 2. *Adsorption of* p-*nitrophenol by chromatographic alumina* (*Grade* I), *at* 20°.

Solvent	Benzene	Water
Isotherm class	*L*3*a*	*S*2
Monolayer adsorption:		
mmole/kg.	425	260
estimated from	" Point B "	plateau
Assumed cross-section of adsorbed molecule (Å^2)	15	25
Specific surface area (cm.^{2}/g. $\times$ 10^{-5})	3·93	3·90

that estimates of specific surface area of alumina made by using two solvents agree well if it is assumed that the adsorbed monolayer is a condensed one and does not contain benzene, but does contain water, when these solvents are used. The values of (*a*) 15 Å^2 and (*b*) 25 Å^2 for the cross-sectional areas of *p*-nitrophenol agree with estimates from models assuming end-on orientation, with respectively (*a*) close-packing and (*b*) packing with one water molecule sandwiched between each pair of phenolic groups (cf. the value of 24 Å^2 for *p*-alkylphenols in condensed monolayers on water [34]).

We therefore suggest, as a working hypothesis, that (*i*) no solvent is present in adsorbed monolayers on solids of opposite degree of polarity to the solvent, *i.e.*, monolayers on polar solids in non-polar liquids, and probably also not in monolayers on non-polar solids in polar liquids; and (*ii*) a molecule adsorbed from water occupies the same cross-sectional area on a solid polar surface as it would do in a condensed monolayer, at zero compression, on water.

* Fu, Hansen, and Bartell [23a] found that " monolayers " of butyric acid adsorbed on carbon from water contained solvent (cf. also ref. 33*b*).

[33] (*a*) See, *e.g.*, Kipling and Tester, *J.*, 1952, 4123; Blackburn and Kipling, *J.*, 1954, 3819; 1955, 1493; Kipling and Peakall, *J.*, 1956, 4828; Jones and Mill, *J.*, 1957, 213; (*b*) Bikerman, " Surface Chemistry, Theory and Applications," Academic Press Inc., New York, 2nd edn., 1958, Chap. IV.

[34] Adam, *Proc. Roy. Soc.*, 1923, *A*, **103**, 676.

(iii) *Adsorption of Isolated Clusters of Molecules, and of Ionic Micelles. Differences in Monolayer Capacity.*—In some systems, *e.g.*, polynuclear aromatic hydrocarbons adsorbed from xylene on alumina (cf. Table 1), certain basic dyes on crystalline quartz,[16] and anionic dyes on silica dust (Fig. 7), the amount of solute taken up at the " monolayer " stage is much less than the surface capacity estimated by other methods. In these cases adsorption probably takes place only on a few highly active sites. Indeed, the adsorption of basic dyes under different conditions is a good example of the variation of " monolayer " capacity which can occur. Thus the cationic azo-dye Janus Red B (C.I. 26,115), which is very colloidal in solution, is adsorbed on finely ground amorphous silica (at 40°) in about 18 times the amount theoretically required to form a condensed monolayer.[16] It is probably adsorbed as large ionic micelles. On coarser silica and on crystalline quartz, however, it is adsorbed in rather less than the theoretical monolayer capacity.[16] (The amorphous " disturbed " outer layer developed on silica by mechanical grinding is known to have higher adsorptive powers than the normal crystalline surface.[35])

In all adsorptions of large organic molecules, in fact, there is the possibility that association of the adsorbed ions or molecules may occur, because at the adsorbing surface they are brought close together. Association may thus occur just before or just after the moment of adsorption (cf. the discussion on the *H* curve, p. 3984). Association of dyes in the adsorbed state has indeed been detected by a variety of indirect means [36] and by a direct method, with use of electron micrography.[37] By this method a number of (water-soluble, sulphonated) direct cotton dyes are seen to be present in cellulose as dense clusters of minute particles or microcrystals (size >40 Å). There is as yet no certain evidence of the stage at which these aggregates are formed, but there are some indications of their formation during adsorption.[36]

(iv) *Significance of Plateau Length or " Point B " Slope Change.*—In practice the precision of the value of the " monolayer " capacity determined from the curve varies widely. At one extreme there are curves with a long flat plateau (*e.g.*, Fig. 2*Ha*), and, at the other, those with only a very small change of slope at " Point B." Indeed, in some cases the position of this point is not very clear (cf. Fig. 2*Lb*); these can be considered special cases in which the plateau is very short.

The significance of a long plateau must be that a high energy barrier has to be overcome before additional adsorption can occur on new sites, after the surface has been saturated to the first degree. The solute has high affinity for the solvent, but low affinity for the layer of solute molecules already adsorbed. It is perhaps significant that adsorptions of ionic micelles give curves with long plateau; in these cases the surface of the solid, when covered, will tend to repel other micelles holding the same charge.

A short plateau must mean that the adsorbed solute molecules expose a surface which has nearly the same affinity for more solute as the original surface had. Consider the isotherms of *p*-nitrophenol adsorbed on alumina from water and from benzene respectively. The first (*S*2) has a well-marked plateau, the second (Fig. 4*b*) has the *L*3*a* form, without plateau. The calculations of specific surface area, just discussed, indicate that the " monolayer " probably contains solvent in the first case, but not in the second. We assume, therefore, that all phenol molecules adsorbed from water are attached to the alumina by the $-O \cdots HO-$ bond, and therefore the outer surface they expose after adsorption consists largely of benzene nuclei and has less affinity for molecules of phenol from solution than the original surface has. The nitrophenol molecules adsorbed from benzene, however, appear to be close-packed, and the surface they expose after adsorption has almost as high affinity for additional phenol molecules as the original surface has. Further, the isotherm beyond " Point B " rises steadily without inflection to a level representing

[35] Gibb and Ritchie, *J. Appl. Chem.*, 1954, **4**, 483.
[36] Campbell, Cathcart, Giles, and Rahman, *Trans. Faraday Soc.*, 1959, **55**, 1631, and reference quoted therein.
[37] Weissbein and Coven, *Textile Res. J.*, 1960, **30**, 58, 62.

adsorption several layers deep. These facts could be explained by assuming that the adsorbed phenol molecules have their hydroxy-groups alternately facing up and down, *i.e.*, in contact with the external solvent and with the alumina. The adsorbed layer then has an exposed surface with a high concentration of hydroxy-groups, which have high affinity for more phenol molecules. If the molecules in each subsequent layer are oriented as they are in the first, the affinity of the outer surface for an additional layer of phenol will remain almost constant, no matter how many layers are already present. This could account for the long and nearly constant slope of the isotherm.

Further interesting examples of plateau variations are given by two isotherms [8b] for cyanine dyes adsorbed on silver halide (Fig. 6). The cationic dye, adsorbed edge-on to the surface by strong ion–ion attraction, gives almost a flat plateau. The ionic centres in the dye molecule are held to the silver halide, and thus when the monolayer is complete it presents to the solution a new surface composed entirely of the hydrophobic upper edges of the dye molecules, which has less attraction for bombarding dye cations than the original silver halide surface had. Thus a second layer builds up with difficulty. The non-ionic merocyanine dye, however, is adsorbed flat, and the covered surface therefore readily accepts another layer of dye molecules, which stack flat on top of those already there. The curve therefore rises steadily.

The length of the plateau in the cases of certain cyanine dyes adsorbed on silver halide in gelatin emulsion was found by West *et al.*[8] to depend upon the length of time the emulsion and the dye solution had been in contact before analysis. After only a short period a long flat plateau appeared in the curve; with increasing time of contact this became shorter and less pronounced. The gelatin probably has some complicating influence.

(v) *Second Rise and Second Plateau.*—These (cf. sub-groups **3** and **4**) are attributed to the development of a fresh surface on which adsorption can occur, the second plateau (sub-group **4**) representing the complete saturation of the new surface, though this stage is not always realisable, and the curve then appears as in sub-group **3**.

The fresh surface may be: (*a*) the exposed parts of the layer already present (*e.g.*, basic dyes adsorbed from water as ionic micelles, on graphite, curve *H*3*a*, cf. Fig. 2*Hd*); this will be the case, of course, only if there is room for a second layer (*e.g.*, Fu, Hansen, and Bartell [23a] obtained curves with a second rise for phenol adsorption on several types of highly porous carbon, but on sugar charcoal, which had very small pores, only a single plateau was obtained); or (*b*) new, probably more crystalline regions of the substrate structure into which the solute begins to penetrate, *e.g.*, aromatic sulphonic acids on chitin,[12a] which is highly crystalline, and certain sulphonated dyes on (chromic acid) anodic film on aluminium (*L*3) where the penetration is so complete that the substrate eventually crumbles away when excess dye is present; or (*c*) part of the original surface.

Thus, under (*c*) a proportion of the original surface may be uncovered by re-orientation of the molecules already adsorbed. This may apply to the adsorption of phenol (from water) by graphite (*L*5) (Fig. 2*Lc*), where the appropriate measurements are consistent with complete coverage in flat orientation at the first plateau, and complete coverage in vertical orientation at the second. A similar phenomenon was noted by Daniel [26a] in the adsorption of fatty acids on metal powders. Alternatively, the second plateau may, apparently, in many cases represent a second condensed monolayer formed on top of the first; examples are certain monosulphonated aromatic compounds on graphite, from water (curve *S*4), and some cyanine dyes on silver halide (*L*4).

Curves of groups **3** and **4** are given by many solutes on wool fibres, but the evidence is not yet sufficient to assign a cause. Here the possibility of adsorption on different types of site successively must be considered.

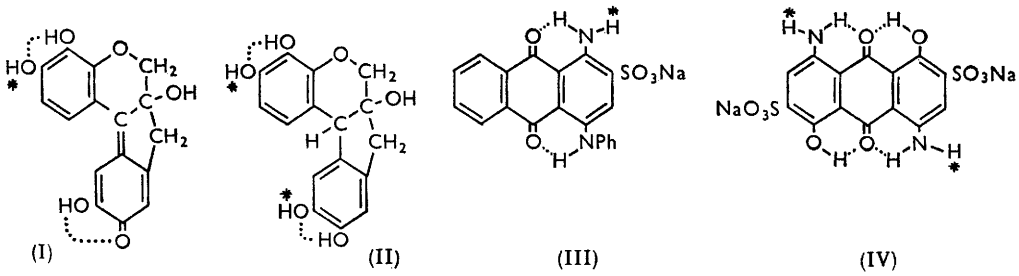
It is observed that adsorption of ionic micelles seldom produces a rise in the isotherm beyond the first plateau. Possibly the mutual repulsion of the charged layer and micelles in solution, already mentioned, prevents this.

(vi) *Maxima.*—Occasionally a fall in slope occurs after the first inflection, *i.e.*, the isotherm has a maximum (sub-group *mx*). This is probably due to association of the solute in solution, *i.e.*, with increase in concentration the solute–solute attraction begins to increase more rapidly than the substrate–solute attraction. Examples are adsorption of *p*-aminoazobenzene and of *p*-nitrophenol on wool from benzene, anionic detergents on wool, methanol on Nylon, and quaternary ammonium surface-active agents on cellulose,[17] where the maximum occurs at solution concentrations a little higher than the critical micelle concentration. Often there is a minimum after the first maximum, and the curve thereafter rises again; sometimes still more complex curves, with successive maxima (*mxmx*), occur.[24c]

Adsorption of Binary Liquid Mixtures.—Many studies have been made of adsorption of pairs of miscible liquids (say A and B) by solid surfaces.[33] Normally, measurements are made over the whole range of possible mixtures, lying between pure A and pure B. At each end of the range, of course, the isotherm represents the adsorption of one solute from a dilute solution in the other, and so the end portions of the curves can be divided into the present classes. With increase in the proportion of one component of the mixture the isotherm reaches a maximum and then descends as in the *mx* sub-group defined here.

Changes in Isotherm Shape with Change in Adsorption.—Variables. Sometimes a small change in some variable can change the isotherm class. Adsorptions of phenols are an interesting example (Figs. 2 and 4; Table 1). Phenol gives: *S* curves from polar solvents on polar substrates (alumina, silica, wool fibre); *L* curves on graphite from water or on polar substrates from non-polar solvents (*e.g.*, alumina, from benzene); and a *C* curve on cellulose triacetate from 2,2,4-trimethylpentane or water (both of which have low swelling power for this polymer). The reasons for these variations will be apparent from the discussion above.

Particularly useful examples to consider are those of the difference between (*a*) hæmatein (I) and hæmatoxylin (II), its leuco-derivative, on fibres, and (*b*) certain anthraquinone dyes (III, IV) on silica.



* Probable hydrogen-bonding centres.

From water, (I) on polar fibres and (III) on silica give *S* curves, but (II) and (IV) give *L* curves on the respective substrates (Figs. 3, 7). This suggests that (I) and (III) are close-packed vertically in the monolayer and (II) and (IV) are adsorbed flat.

Tests of (I) and (II) with the Langmuir–Adam film balance support this suggestion (Fig. 14). When tested under films of methoxymethylnylon, (II) acts as a cross-linking agent, decreasing the area of the film and making it more rigid. Attempts to spread (II) itself (on hydrochloric acid) showed that it does not form a film. Both these effects are consistent with a flat orientation of the molecule at the water surface. (I), however, has a similar effect on the film to that of a surface-active dye, making the film more soluble (*i.e.*, more compressible); (I) can also be spread alone (on strong acid solution) to form a stable condensed monolayer with a zero-compression area of 60 Å^2, very close to that estimated from models for vertical close-packing. This monolayer is fairly compressible, because the molecule is non-planar and therefore cannot pack very tightly.

In (I) the active centres at opposite ends of the molecule are different and have different degrees of affinity for water or for the solid surface. Probably the pair of *o*-hydroxy-groups is the most active and therefore the one most likely to dissolve in the monolayer on water, or to attach to a solid polar surface; the hydroxy-group *ortho* to the quinone group will probably chelate therewith and thus be inactivated and rendered less water-soluble [(I) is much less soluble in water than (II)].

In (III) and (IV) the >NH groups presumably form hydrogen bonds with the silica surface. These dyes are anionic and the silica is negatively charged in water. Thus there is a potential barrier to be overcome before adsorption occurs (this is confirmed by the very low rate of adsorption). The *S* curve given by (III) is not, however, attributable to

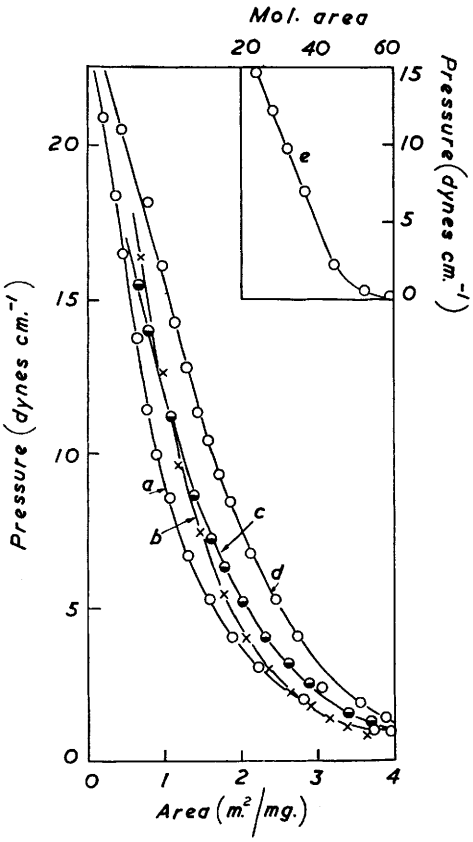


FIG. 14. *Force–area curves for methoxymethylnylon films and hæmatein films.*

(*a*) *Methoxymethylnylon on* 10^{-3}M-*hæmatoxylin*, pH 1·60. (*b*) *As a*, pH 3·30 *buffer solution*; *control*. (*c*) *As b, on* 10^{-3}M-*hæmatein solution, at* pH 3·30. (*d*) *As a, on* pH 1·60 *buffer solution*; *control*. (*e*) *Hæmatein on* 2M-HCl.

low affinity due to the potential barrier (cf. inorganic adsorptions, see below); if it were, (IV) would give an *S* curve also.

A surface-active cationic solute [7] dodecylammonium chloride, adsorbed on alumina [5] from aqueous solutions, has recently been reported to give differently shaped isotherms according to the pH value of the solution. From weak acid solution *L* curves are obtained —doubtless micellar adsorption of cationic micelles is occurring. From strong acid solution *S* curves are obtained; and the amount adsorbed is reduced below the " monolayer " capacity; perhaps end-on adsorption of individual ions occurs.

We have not encountered any evidence that change of temperature causes changes in the class of the adsorption isotherm, though of course the position of the isotherm is usually altered.

Determination of Specific Surface Area.—Dyes in aqueous solution have often been used

to estimate by adsorption the specific surface areas of finely divided solids. The method is simple, and is probably reliable if only comparative values of different samples of the same material are required, but it is less reliable for absolute values, mainly because dyes are apparently in many cases adsorbed as ionic micelles and the true extent of coverage of the surface is then indeterminate.

In the light of the present work, measurements of specific surface area should be most reliable when made with a solute which (i) is highly polar, to ensure strong attachment to the whole surface of polar solids; (ii) has hydrophobic properties to enable it to be adsorbed by non-polar solids; (iii) has a small molecule which is preferably planar and likely to be adsorbed as a vertically oriented close-packed monolayer, thus ensuring precision in cross-sectional area estimation (it thus follows that *S* curves are more likely to give reliable data than other types of curve); (iv) is not highly surface-active, to ensure that three-dimensional micelles are not formed at the solid surface; (v) is coloured, for ease of analysis; (vi) has good solubility in water, for convenience, but is also soluble in non-polar solvents when required for use with water-soluble solids.

These are exacting requirements and it is unlikely that any one substance will be found to satisfy them for all substrates. One compound, however, appears to satisfy them reasonably well, for a variety of materials. This is *p*-nitrophenol, and in results obtained so far it has given promising results. It is, however, unsuitable for use with some polar organic polymers, *e.g.*, Nylon, for which it is an effective swelling agent. For these materials methanol in benzene can be used, analysis being by refractometry.

Note on adsorption of inorganic solutes. Samuelson [38] described the relation between the ion-exchange affinities of inorganic ions on resins and their exchange isotherms, which are of *S*, *C*, or *L* class when the entering ion has respectively lower, similar, or higher affinity than the one removed. Some metal ions when adsorbed from salt solutions by cation-exchange resins [39] and (apparently) calcium hydroxide adsorbed on silica [40] give *H* isotherms. These are probably the result of covalent bond formation (to the substrate).

Corrections.—Some isotherms in previous papers from this laboratory are incorrectly shown. Thus, the curves in Fig. 1 (ref. 4) (cf. Fig. 2*Sd* here), Fig. 4 (ref. 4) (cf. Fig. 5*d* here), and Fig. 9 (ref. 16) (cf. Fig. 4*a* here) were incorrectly extrapolated to the origin: they are now found to be *S* curves. The curves of Fig. 5 in ref. 4 (and probably also Fig. 2*e*,*f* in ref. 10) should be drawn as *C* curves; *C* curves, in fact, fit the experimental points of the first-mentioned curve better than those originally shown; see Fig. 2*Ca-c* here, in which the same experimental points are used, and a new experiment by a different operator is included in confirmation.

Experimental

Most of the isotherms illustrated were determined in this laboratory, by the methods described earlier (refs. 4, 5, 7, 9, 10, 12, 14, 16). Hæmatoxylin and hæmatein were purified samples, and were spread from aqueous solution; methoxymethylnylon (Imperial Chemical Industries Limited, 40% methoxymethyl substitution in the amide group of Nylon 66) was spread from 0·01% solution in dry methanol; hæmatoxylin was dissolved in water containing a little sodium dithionite (hydrosulphite) to retard oxidation by air. The fibre samples of viscose rayon (Fig. 5) and wool (Fig. 5) were intensively dried by heating at 105° for 48 hr.

The viscose rayon sample used for the experiment of Fig. 5*a* (also the chitin for that of Fig. 1, ref. 12*a*) was dried at 100° for 4 hr. after being refluxed with dry benzene.

Appendix

Use of Isotherms for Solute Affinity Measurement.—Isotherms are often used for evaluating affinities of solutes for substrates and so correlating the affinities with structural features in the

[38] Samuelson, "Ion Exchangers in Analytical Chemistry," John Wiley and Sons Inc., New York, 1953.
[39] Boyd, *J. Amer. Chem. Soc.*, 1947, **69**, 2818.
[40] Greenberg, *J. Phys. Chem.*, 1956, **60**, 325.

solute molecules. In theory the determination of the affinity is simple, requiring only a knowledge of the activities of the solute in the solution and the substrate phases, but difficulties arise in practice in determining the activity in the substrate.

First, the *extent* of the substrate phase, *i.e.*, the true area or volume of the adsorbing surface layer, is hard to define; and secondly, the adsorbed solute is not ideal, and is often present as aggregates or micelles (see p. 3987). Nevertheless, at least three methods of affinity determination have been proposed:

(*a*) Use of the term $\theta/(1 - \theta)$ to express solute activity in the solid, where θ is the proportion of available sites occupied. This was proposed by Gilbert and Rideal [41] in calculating the affinity of simple mineral acids for wool fibres, and later by Vickerstaff [32] for acid dyes on wool. The assumption is made that there is no interaction between the adsorbed ions, but this is very unlikely with large ions.

(*b*) Use of the hypothesis that the adsorbed solute is dissolved in a specific volume of the solvent in the surface layer, which is more closely associated with the substrate than is the main body of solvent. The value of the volume term used is determined empirically. This method was used by Peters and Vickerstaff [42] for dyes on cellulose. It does give rational results which enable useful correlations to be made between affinity and solute molecular structure,[12a,14] but the real significance of the " volume term " is uncertain.

(*c*) Use of the method of Bartell *et al.*,[43] based on measurement of the initial angle of the isotherm: $-\Delta\mu^\circ = -\boldsymbol{R}T \ln K$, where K is the equilibrium constant. The isotherm must be replotted with ordinates expressed as weight of solute per unit volume of adsorbed layer, involving again the estimation of the layer volume or thickness. Further, the value of K is given by the slope of a line drawn through the origin, tangential to the initial slope of the isotherm. Considerable variation in estimates for the slope is possible since this portion of the isotherm is the least accurate. For H isotherms the slope is infinite; for S isotherms it is zero. Also, in general, no account is taken of the total amount of solute adsorbed.

Kinetic treatment. In Langmuir's formula [44] the rate at which molecules bombard the surface is assumed to be directly proportional to the pressure (or concentration, of a solution). This assumption gives the equation of the $L1$, $L2$, $H1$, and $H2$ curves. Here we assume that in some cases the rate is proportional to some other function of the pressure or concentration, and show that this can explain other forms of curve. A further assumption, necessary in applying the Langmuir concept to solution adsorption, which we make in common with earlier authors, is that in adsorption from dilute solution the action of the solvent molecules is solely to reduce the energy of the surface, by competition with the solute. (Heit *et al.*[18] show by a thermodynamic argument that, if it is assumed that both dye and solvent are adsorbed at the same set of sites, each in accordance with the classical Langmuir equation, then the solution adsorption isotherm should fit this equation.)

In the classical Langmuir treatment, the amount adsorbed, $y = k_1k_2p/(1 + k_1p)$, where p is the pressure (concentration in the present cases) and k_1 and k_2 are constants for the given system, k_1 is proportional to α/γ, where α is the proportion of bombarding molecules which adhere to the surface and γ is the rate of evaporation from a completely covered surface. Thus the classical formula assumes α/γ to be a constant, characteristic of the system. We assume that it is not generally a constant, but is a function of the concentration (or pressure).

Thus if $k_1 = f(p)$, then

$$\frac{dy}{dp} = k_2 \frac{\left(k_1 + p\dfrac{dk_1}{dp}\right)}{(1 + k_1p)^2}$$

Special Cases.—(i) *The* S2 *curve* (*see Fig.* 1). When (1) $y = 0$, $p = 0$ and $dy/dp = 0$; (2) $y = k_2$, $p = \infty$ and $dy/dp = 0$; therefore $k_1 = 0$ at $p = 0$, and k_1 must be a function of p to a positive power if dy/dp is to be zero at $p = 0$; *i.e.*, $k_1 = p^\alpha$ where $\alpha > 0$.

(ii) *The* H2 *curve* (*see Fig.* 1). When (1) $p = 0$, $y = 0$ and $dy/dp = \infty$; (2) $p = \infty$, $y = k_2$ and $dy/dp = 0$. To satisfy $dy/dp = \infty$ at $p = 0$, k_1 must a function of p to a negative power,

[41] Gilbert and Rideal, *Proc. Roy. Soc.*, 1944, *A*, **182**, 335.
[42] Peters and Vickerstaff, *Proc. Roy. Soc.*, 1948, *A*, **192**, 292.
[43] Bartell, Thomas, and Fu, *J. Phys. Colloid Chem.*, 1951, **55**, 1456.
[44] Langmuir, *J. Amer. Chem. Soc.*, 1916, **38**, 2221.

and to satisfy $y = 0$ at $p = 0$ the power must lie between 0 and -1; *i.e.*, $k_1 = p^{-\beta}$ where $0 < \beta < 1$.

(iii) *The* C2 *curve* (*see Fig.* 1). Here $y = ap$, where a is a constant. Hence $k_1k_2p/(1 + k_1p) = ap$; wherefore $k_1 = a/(k_2 - ap)$. This means that k_1 is infinite at $p = k_2/a$, and that if p is greater than k_2/a the sign of k_1 would change from positive to negative, which is impossible, because the components of k_1 (α and γ) are both positive. When $k_1 = \infty$ the rate of evaporation is zero. It follows that when the concentration a/k_2 is reached the value of y will remain fixed and the curve will change abruptly to the horizontal.

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