Adsorption at Organic Surfaces. Part I. Adsorption of Organic Compounds by Polyamide and Protein Fibres from Aqueous and Nonaqueous Solutions.

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The adsorption of a range of aliphatic and aromatic non-ionic compounds, on nylon and wool, from a variety of solvents has been investigated. Water has also been used as a solute in certain organic solvents.

In aqueous solution all the water-soluble compounds used have unrestricted access to the non-crystalline regions of the fibres, by virtue of the swelling action of the solvent, and the adsorption is probably due to hydrogen bonds. In non-aqueous solution the fibres are unswollen and the molecules of solutes which are non-solvents for the fibre may be adsorbed only in certain circumstances, which are (a) that they are within certain limiting dimensions, viz., approximately those of the n-butanol molecule and the anthracene molecule in the aliphatic and aromatic series respectively; and either (b) that they contain a free hydroxy-group or an extended conjugate system; or (c) that the solvent in which they are dissolved is itself unable to penetrate the fibre. The evidence suggests that from non-aqueous solution hydroxy-compounds are adsorbed by the formation of O · · · · H · · · · O hydrogen bonds, probably with the enolic forms of amide or peptide groups of the fibre, whereas with non-hydroxylic compounds physical adsorption occurs.

Estimates of the internal surface area of the wool fibre between 2×10^5 and $>70 \times 10^5$ sq. cm. per g. are obtained, according to the nature of the solute adsorbed.

In recent years there have been many investigations of the processes of adsorption of strong electrolytes, particularly of mineral acids and acid wool dyes, by polyamide and protein fibres from aqueous solution (see, e. g., Vickerstaff, " The Physical Chemistry of Dyeing," Edinburgh, Oliver and Boyd, 2nd. Edn., Ltd., 1954). Adsorption of these substances is attributed to the formation of electrovalent salt linkages with the free amino-groups of the fibre. Some combination with ionised imino-groups of the main molecular chains of the fibre has also been detected in nylon (O'Briain and Peters, J. Soc. Dyers Col., 1953, 69, 435) and suggested as a possibility with protein fibres (with which experimental difficulties arise in working at the necessarily very low values of pH) (Steinhardt, Fugitt, and Harris, J. Res. Nat. Bur. Stand., 1941, 26, 293). The formation of electrovalent linkages does not, however, account for all the known facts, which point to other forces' being involved in adsorption by the fibres mentioned.

The maximum amount of a strong acid, mineral or organic (including the free acids of many dyes), adsorbed by wool is about 900 m.equiv./kg. and is more or less independent of the nature of the anion. There are good grounds for supposing that this amount of acid is combined by electrovalent salt linkage with the basic groups in the fibre. Acids are similarly bound by salt linkage to other proteins, e.g., silk and gelatin, and to nylon also. Yet while the maximum adsorbtion value remains nearly constant, the affinity does not. This rises with increasing size of the anion, i.e., the larger the anion, the lower the degree of acidity required to induce maximum adsorbtion. This rise in affinity appears to have no relation to the dissociation constant of the acid (Steinhardt et al., loc. cit.) and must apparently be due to non-ionic attractive forces acting between the substrate and the anion, but its exact nature has remained undetermined. The only possible types of force would appear to be either purely physical, or specific and polar in nature, hydrogen bonding being probably by far the most important of the latter type. The operation of such bonding was in fact suggested by Steinhardt et al., whereas Meggy (J. Soc. Dyers Col., 1950, 66, 510) and Vickerstaff (ibid., 1953, 69, 279) have drawn attention to the possible importance of van der Waals attraction.

There is an almost linear relation between affinity for wool and either the length of an attached alkyl chain or the total molecular weight in certain azo-dyes (Vickerstaff, *op. cit.*; *loc. cit.*), which certainly suggests the operation of physical forces between dye and fibre. Hydrogen bonding, however, would seem to be responsible for the swelling action of phenol on nylon (for which it is a solvent) and wool; and also for the greatly increased adsorption by wool of weak organic acids, *e.g.*, acetic or chloroacetic acid, compared with hydrochloric acid (Steinhardt, Fugitt, and Harris, *J. Res. Nat. Bur. Stand.*, 1940, **25**, 219; 1943, **30**, 123; Speakman and Stott, *Trans. Faraday Soc.*, 1935, **31**, 1425), since the molecules of these substances must be too small to exhibit sufficient van der Waals attraction to account for the observed effects. Hydrogen bonding is probably also responsible for the adsorption of water by these fibres, at least in the initial stages, but the mechanism of bonding of water by wool, and indeed by proteins in general is still a subject of discussion (see review by McLaren and Rowen, *J. Polymer Sci.*, 1951, **7**, 289).

The present paper describes some preliminary adsorption experiments designed to detect the operation of the attractive forces just discussed, using a technique of application of certain simple non-polar and polar solutes to nylon and wool, in water and various dry solvents. Phenol and certain alcohols were amongst the solutes used. The action of these materials upon wool, under somewhat different conditions from those used here, has been studied by other investigators, whose conclusions are summarised below. The other solutes studied do not appear to have received much attention in this type of work, nor do organic solvents appear to have been used in adsorption studies on such fibres.*

The action of phenol on protein fibres has been described by a number of investigators. Barr and Speakman (*J. Textile Inst.*, 1944, **35**, T 77) found that wool fibres undergo a pronounced lateral swelling and a small contraction in length when treated with phenol, either molten or in concentrated aqueous solutions; the effect being reversible, the original dimensions are restored by water washing. Elöd and Zahn (*Melliand Textilber.*, 1948, **29**, 17) also have disclosed the effects of certain treatments upon the supercontraction of wool in solutions of phenol (and also of sodium hydroxide, sodium hydrogen sulphite, and formamide). Zahn (*Z. Naturforsch.*, 1947, 2b, 286; cf. *Chem. Abs.*, 1948, **42**, 5678) also treated wool and horse-hair at room temperature with aqueous solutions of phenol (1—7%), catechol, resorcinol, quinol, *o*- and *p*-nitrophenol, and salicylic acid, and measured the fibre shortening, or the stretch before breaking, and the effect of the treatments on the elastic modulus. Consideration of X-ray patterns and physical properties, *e.g.*, swelling, anisotropy, and double refraction, showed that the primary valencies (peptide links and cystine bonds) were unaffected, hydrogen bonds only being broken. Pakshver, Mankash, and Kukonkova (*Tekstil. Prom.*, 1951, June, **11**, 15; through *J. Soc. Dyers Col.*, 1951, **67**, 473) determined length changes of undrawn, partly drawn, and fully drawn nylon yarns in 2—4·5% aqueous phenol solutions, and explained the observed reduction in the extension, with increase in draft, as due to compacting of fibre structure, which reduces diffusion of solute into the fibre.

Speakman (*J. Soc. Dyers Col.*, 1933, **49**, 180) measured the pore size of dry wool by treatment with aliphatic alcohols in pure liquid form, or as binary mixtures, and estimated it as *ca.* 6 Å because only alcohols with molecules smaller than *n*-butanol were found to be capable of influencing its mechanical properties. King (*Trans. Faraday Soc.*, 1947, **43**, 552), after making vapour-phase adsorption experiments with wool, suggested that this apparent absence of penetration of the fibre by *n*-butanol may have been due merely to a very slow rate of penetration, but the present work (see p. 4384) seems to confirm Speakman's interpretation.

DISCUSSION

In order that the present results may be correctly interpreted, it is necessary first to discuss the possible dependence of the adsorption process upon a number of conditions.

* *Note added in Proof.*—Since this paper was submitted Forward (*J. Textile Inst.*, 1954, **45**, T 559) has reported investigations on the swelling behaviour of nylon in solutions of phenol in various non-aqueous solvents.

Influences upon Adsorption.—Amongst the factors likely to influence adsorption are the following : (*a*) the crystallinity of the fibre and the size of its intermolecular pores; (*b*) the chemical architecture of the solute molecules, since this will determine the intensity of their van der Waals attraction for the fibre; (*c*) the mutual hydrogen-bonding affinity of individual groups in solute and fibre; (*d*) cross-links normally present in the fibre, and the flexibility of its molecular chain; (*e*) the nature of the solvent; (*f*) the presence or absence of a resistant " skin " or cuticle on the fibre surface. These factors will now be discussed individually.

(*a*) *Fibre structure.* Very little precise information is available upon the degree of crystallinity and pore size of the present fibres (see, *e.g.*, Vickerstaff, *op. cit.*); Speakman (*loc. cit.*) found that the pore size of wool increased from *ca.* 6 Å in the dry state to *ca.* 40 Å when wet; and the extent of lateral swelling in water, which is determined by both the size of the amorphous regions and the number of polar groups therein (fewer in nylon than silk or wool), is 5, 18, and 16% for nylon, silk, and wool respectively (Meredith, in " Fibre Science," ed. Preston, Manchester, The Textile Institute, 2nd edn., 1953).

(*b*) *Physical attraction.* Competition by the great excess of solvent is likely to prevent measurable adsorption, by van der Waals attraction, of small solute molecules which cannot form hydrogen bonds, but this attraction may become significant in the case of some large molecules. There is evidence that it is operative in the adsorption of anionic compounds on wool (see p. 4376) and cellulose (Allingham, Giles, and Neustädter, *Discuss. Faraday Soc.*, 1954, **16**, 92).

(*c*) *Hydrogen-bonding affinities.* Table 1 gives approximate data for the abundance of some of the principal hydrogen-bonding and cross-linking groups in the fibres under discussion. Any of these (except the sulphur-containing groups) could interact with hydrogen-bonding groups in solutes of the type used in this work, but the peptide group is the most important, being the most abundant.

TABLE 1. *Approximate content (m.equiv./kg.) of principal polar groups in fibres.*

Groups	Nylon [1]	Silk [2,3,4]	Wool [2,4]
Acid	90	290	2080
Basic	100	200	2430*
Hydroxyl (alcoholic)	—	1590	1520
„ (phenolic)	—	730	260
Sulphur-containing (principally cystine) (×0·5)	—	—	1130
Peptide (–CO·NH–)	8850	11,840	8620

* This includes primary and secondary amino-groups in the side chains. The most recent figure for the primary (side-chain and terminal) amino-groups is 852 m.equiv./kg. (Corfield and Robson, quoted by Horner, *Discuss. Faraday Soc.*, 1954, **16**, 113).

[1] Vickerstaff, *op. cit.* [2] Haurowitz, " Chemistry and Biology of Proteins," Academic Press, N.Y., 1950. [3] Howitt in " Fibre Science," see (*a*), above. [4] Traill, *J. Soc. Dyers Col.*, 1951, **67**, 257.

It would of course be desirable to know the values of the free energy of formation of hydrogen bonds under the present conditions, but very little information is available upon this subject. Flett has determined thermodynamic data for the formation of some hydrogen bonds, by infra-red spectrophotometry, but in one solvent only, carbon tetrachloride. Some of his data for free energy are summarised in Table 2. In the absence of precise information we must assume that these bonds will have affinities of similar relative magnitude in the solvents used in the present work; thus an $O \cdots H \cdots O$ bond probably has a higher free energy than a $N \cdots H \cdots O$ bond between similar compounds. Presumably a $N \cdots H \cdots N$ bond has a still lower value, though no data are available. The bonds formed by phenol are the strongest of any of those examined by Flett.

(*d*) *Cross-linkages.* The nature of the principal hydrogen-bond cross-linkages in a fibre is important in determining its ability to adsorb any given solute. If these are stronger than those which might be formed between fibre and solute, the latter will probably not be adsorbed by a hydrogen-bonding mechanism. The principal hydrogen bond cross-links in protein fibres are those between peptide groups, and in nylon those between amide groups, and their strength will largely determine the adsorptive properties

of the fibres. It is usually assumed that these links are of $-N-H \cdots O=C<$ type in the crystalline regions of polypeptides and proteins (see, *e.g.*, Bath and Ellis, *J. Phys. Chem.*, 1941, **45**, 204; Robinson and Ambrose, *Trans. Faraday Soc.*, 1952, **48**, 854). There is evidence, however, that the peptide group is planar, the C–N bond having partial double-bond character (Pauling, Corey, and Branson, *Proc. Nat. Acad. Sci.*, 1951, **37**, 205;

TABLE 2. *Free energy of formation* $[-\Delta G$ (60°), *kcal./mole*] *of intermolecular hydrogen bonds (in* CCl_4) *(after Flett*, J. Soc. Dyers Col., 1952, **68,** 59).

Solutes and type of bond.

$N \cdots H \cdots O$		$O \cdots H \cdots O$	
Diphenylamine + dioxan	0·70	Dioxan + phenol	1·36
Benzyl alcohol + azobenzene	0·69	Benzyl acetate + phenol	2·12
Benzo-*p*-toluidide + dioxan	1·02	Benzyl alcohol + dimethylformamide	2·23
Acetonitrile + phenol	1·66	Phenol + dimethylformamide	3·23
Diphenylamine + dimethylformamide	1·92		
Benzo-*p*-toluidide + dimethylformamide	2·75		

Pauling and Corey, *ibid.*, pp. 235, 241, 251, 256, 261, 272, 282; Robinson and Ambrose, *loc. cit.*), which implies that the group is partially enolic, and hence the inter-chain peptide bonds and perhaps the bonds in nylon also are partially of $O \cdots HO$ character. Such inter-chain bonds in crystalline regions of the fibres are unlikely to be influenced by water, which does not readily penetrate these parts and they should, therefore, resemble those formed between model compounds in dry solvents. Buswell, Rodebush, and Roy (*J. Amer. Chem. Soc.*, 1938, **60**, 2444) by infra-red spectrophotometry, obtained evidence of considerable association and enolisation of monosubstituted amides, *e.g.*, *N*-ethylacetamide, in carbon tetrachloride. It has, in fact, been observed (Arshid and Giles, unpublished work) that the enol form of simple alkylamides appears to be the more stable form in non-aqueous solution. An additional fact pointing to the existence of $O \cdots HO$ inter-chain bonds in nylon is that only the very strongest hydrogen-bond disruptive reagents (*e.g.*, phenol or formic acid) dissolve this fibre. If all the inter-chain bonds were of $NH \cdots O$ type weaker reagents capable of forming $OH \cdots O$ bonds (*e.g.*, water or alcohols) might also dissolve it.

(*e*) *The nature of the solvent.* Several specific effects may depend upon the nature of the solvent, *e.g.*: (i) inactivation of potential bonding groups in substrate or solute; (ii) disturbance of the keto–enol equilibrium in the peptide links (this may only apply to the non-crystalline regions of the fibre, the crystalline regions being inaccessible to the solvents used); (iii) ionisation—amino- and carboxyl groups are ionised by water, thus their mutual hydrogen bonds are broken and the resultant solvation of the ions by solvent molecules causes swelling of the fibre structure. Hence from an ionising solvent, especially water, larger solute molecules may be adsorbed than from a non-ionising solvent.
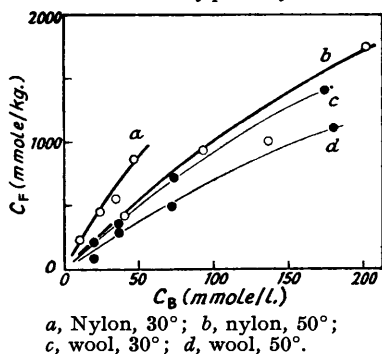
(*f*) *The wool fibre cuticle.* It has now been established by electron-microscopy that wool has an outer cuticle which is highly resistant chemically and retards the entry of liquids except where it is broken by mechanical action (Gralén, *J. Soc. Dyers Col.*, 1950, **66**, 465). This is likely to affect rates of adsorption by wool, rather than equilibrium values. It may also influence the nature of adsorption from organic solvents, *e.g.*, that of azobenzene (see p. 4386).

Interpretation of Present Results.—The results are summarised in Table 3 and some of the quantitative data are shown in Figs. 1—9. Interpretations follow.

Adsorption from aqueous solution. The pores of the present fibres in water are quite large enough to admit all normal dye molecules, and since the water-soluble solutes used here have molecules smaller than most dyes, there can be no mechanical restriction to their actual entry into the interior of the fibre. The extent of their adsorption must therefore be entirely determined by the balance of forces of attraction between solute, water, and the molecular chains of the fibres. These forces must be principally those due to hydrogen bonding, because the small size of the solute molecules used here in water will reduce the magnitude of their van der Waals attraction for the fibre. This attraction in any case cannot be very readily identified in the adsorption of solutes from water,

because their solubility in water will arise from the presence of either a hydrogen-bonding or an ionising group and the chemical effects due to these will tend to mask any purely physical attraction. These general remarks in favour of a hydrogen-bond mechanism can be reinforced by the following more specific arguments in the case of the adsorption of

FIG. 2. *Isotherms of phenol on wool from organic solvents.*

FIG. 1. *Isotherms of phenol from water.*

a, Nylon, 30°; b, nylon, 50°;
c, wool, 30°; d, wool, 50°.

For C_B and C_F see footnotes to Table 3.

a, Ethanol, 40°; b, ethanol, 50°;
c, isooctane, 30°.

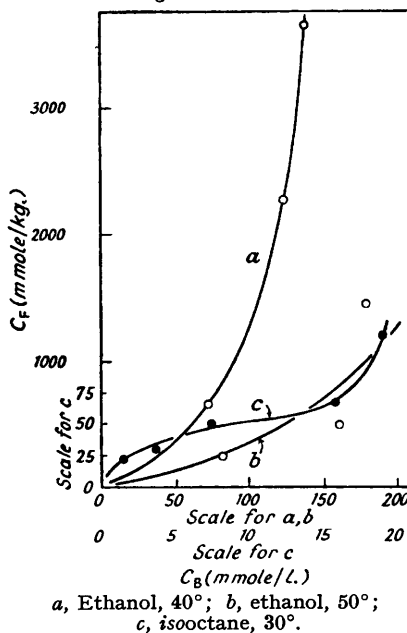FIG. 3. *Isotherms of* p-*nitrophenol from benzene at 60°.*
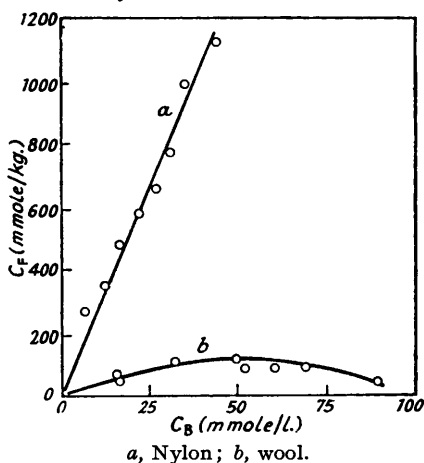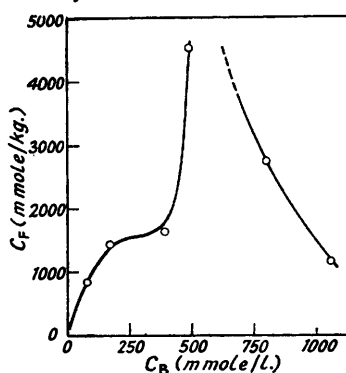
FIG. 4. *Isotherm of benzene on wool from* n-*butanol at 50°.*

a, Nylon; b, wool.

particular solutes (cf. Zahn, *loc. cit.*); (i) Physical attraction alone cannot explain the adsorption, *e.g.*, of aniline, or phenol (Fig. 1), otherwise pyridine, a molecule of similar size, would be adsorbed. Phenol has, in fact, much higher affinity for nylon from water than has benzoic acid, even though its solubility in water is higher at 25° (*ca.* 87 g./l. and 3·45 g./l. respectively). No very detailed work was done to determine the relative degrees of adsorption, but it was observed that the molar ratio of phenol to benzoic acid

TABLE 3.

Compound *	Solvent †	Substrate ‡	Temp.	Time, hr.§	Result ‖	C_B	C_F
Acetone	B	N, W	30°	100	NS		
	D	N, W	30	100	NS		
	C	N, W	30	100	NS		
	W	N, W	30	100	NS	. . See Fig. 9	
p-Aminoazobenzene	B	W	30, 50	50	S		
Aniline	B	W	50	45	NS		
	C	W	50	45	NS		
Anthracene	B	W	35	60	S	{ 10 21	38 38
		N	35	60	S	10	38
Azobenzene	B	aN, N, W, aW	25, 60	100, 25	S	. . See Fig. 7	
	mC	W	50	25	NS		
	C	W	60	12	S	25	49
Azoxybenzene	B	N, Wd	60	24	NS		
	C	Wd	60	24	NS		
Benzene	Bu	N, W, Wa	30, 50	72, 24	S	. . See Fig. 4	
	M	W	60	12	NS		
Phenylazo-1-naphthol	B	W	60	50	NS		
Phenylazo-2-naphthol	B	N, N69, W, Wd	60	50	NS		
	BE (1 : 1)	N, W	25	35	NS		
	C	Wd	60	15	NS		
* Phenylazo-m-toluidine	T	W, N	50, 60	48	NS		
Benzoic acid	W	acN, N	25, 40	15	S		
Benzophenone	C	Wd	60	15	NS		
	H	N, W	40	30	NS		
	T	N, W	40	30	NS		
Benzoquinone	D	N, W	35, 60	20	(decomp.)		
Bisphenylazobenzene	B	N, W	50	50	NS		
n-Butanol	B	N, W	50, 30	50, 75	NS		
Catechol	W	N	40	48	S	{ 100 220	130 230
		S	40	48	S	{ 100 220	120 220
		W	40	48	S	{ 100 220	120 180
Diethylamine	C	W, N	50	48	(decomp.)(?)		
	W	W, N	50	48	NS		
p-Dimethylamino-azobenzene	B	N, W	60	25	S	. . See Fig. 9	
	C	Wd	60	25	S		
Diphenyl	B	N, W	60	60	NS		
p′-Dodecylphenylazo-p-cresol	B, C	N, N69, Wd	60	25	NS		
Hæmatoxylin	El	W	30	50	NS(?)		
	W	N, S, W	30, 60	70, 25	S		
2-Hydroxyanthra-quinone	Bu	N, W	50	25	NS		
	D	W	50	25	NS		
	El	W	50	50	NS		
* o-Hydroxyazobenzene	B	W	30, 50	100, 70	S	0·16	19
p-Hydroxyazobenzene	B	N, N69, W, Wa	60	25	NS		
	C	Wd	60	25	NS		
	ElW (1 : 1)	Wd	60	25	NS		
Methanol	B	N, W	30	70	S	. . See Fig. 6	
* Methyl 2-naphthyl ketone	B	N, W	40	30	NS		
1-Naphthol	B	N, W	50	70	NS		
2-Naphthol	B	N	50	70	NS		
		W	56	70	S	26	72

TABLE 3. (*Continued.*)

Compound *	Solvent †	Substrate ‡	Temp.	Time, hr.§	Result ||	C_B	C_F
o-Nitrophenol	B	N	25, 40, 60	70—25	S		
		N69, Wd	25, 40, 60	70—25	NS		
	C	Wd	40	25	NS		
	D	N, W	45	70	NS		
	E	N, W	25	70	NS		
	El	Wd	40	70	NS		
	EG	N, W	60	25	NS		
p-Nitrophenol	B	W	40	96	S	70	166
	B	N, W	60, b. p.	96, 25	S . . See Fig. 3		
	E	W	40	96	S	65	360
	E	W	b. p.	6	S		
	O	W	b. p.	6	NS		
Phenol	El	W	30, 40, 50	70, 50	S} . . See Fig. 2		
	O	W	30, 50	70, 50	S}		
	W	acN, N, W	30, 50	70, 50	S . . See Fig. 1		
* Phenylhydrazine	B	W	50	50	NS		
Pyridine	B	N, W	50, 60	35, 20	NS		
	W	N, W	50, 60	35, 20	NS		
Quinol	W	N	40	45	S	{ 60, 130	700, 1500
		S	40	45	S	{ 60, 130	700, 1500
		W	40	45	S	{ 100, 175	1000, 1500
Resorcinol	W	N	40	45	S	{ 100, 200	1400, 1800
		S	40	45	S	{ 100, 250	1200, 1500
		W	40	45	S	{ 100, 250	1200, 1500
Stilbene	B	N, W	60	25	S . . See Fig. 8		
2 : 3 : 4-Trihydroxy-benzophenone	B	W	50	25	NS		
	Bu	W	50	50	NS		
	D	W	50	50	NS		
	El	W	50	50	NS		
Water	BEl (4 : 1)	W	50	20	S		
	Bu	W	30, 50, 60	90, 50, 25	S . . See Fig. 5		
	iBu	W	50	20	S		
	D	W	50	20	S		
	El	W	50	20	S		
	M	W	25	70	S		
	iP	W	50	20	S		
	nP	W	50	20	S		
	nPl	W	50	20	S		

* Compounds marked with an asterisk were tested at not more than two concentrations at each temperature. Others were tested in a full series of 6 or more concentrations.

† A = acetone; B = benzene; iBu = *iso*butanol; Bu = *n*-butanol; C = carbon tetrachloride; mC = *m*-cresol; D = dioxan; E = diethyl ether; El = ethanol; EG = ethylene glycol; M = methanol; O = *iso*octane; nPl = *n*-pentanol; iP = *iso*propanol; nP = *n*-propanol; T = toluene; W = water.

‡ N = nylon; aN = alkali-treated nylon; acN = acetylated nylon; N69 = "69 nylon"; S = silk; W = wool; aW = alkali-treated wool; Wd = "specially dried" wool.

§ Two or more figures refer to the respective temp. in col. 4.

\|\| S = adsorbed, NS = not adsorbed, C_B = equilibrium concentration in bath (mmoles/l.), C_F = equilibrium concentration in fibre (mmoles/kg.).

present on the fibre at equilibrium at 25° with a bath of 1·2 g./l. concentration is of the order of 10 : 1. Acetylation of the fibre was found not to alter the affinity for phenol, but to reduce considerably that for benzoic acid, which therefore must be adsorbed partly by an acid–base reaction with free amino-groups. (ii) Both phenol and hæmatoxylin have been shown (Arshid and Giles, unpublished work) to form hydrogen-bond complexes with alkylamide groups in aqueous solution, and they should therefore be able to do the

same with such groups in these fibres in water. (iii) The order of affinity for the fibres, as determined by the maximum adsorption, appears to be phenol > benzoic acid > aniline, which agrees with the hydrogen-bond affinity data (Table 2). (iv) The apparent heats of adsorption of phenol by nylon and wool from water are about —4·5 and —4·0 kcal./mole, respectively; these are of the expected order of magnitude for the formation of one
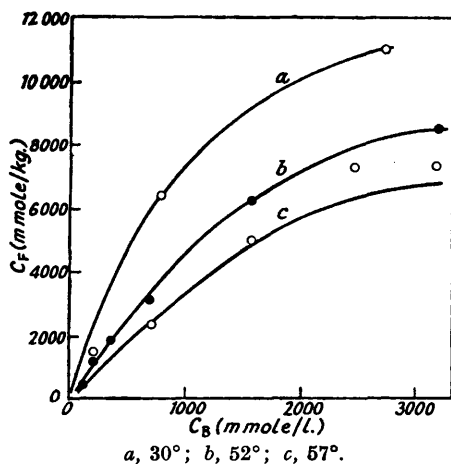

FIG. 5. *Isotherms of water on wool from n-butanol.*

a, 30°; *b*, 52°; *c*, 57°.

FIG. 6. *Isotherms of methanol from benzene.*

a, Nylon, 50°; *b*, wool, 30°; *c*, wool, 50°.
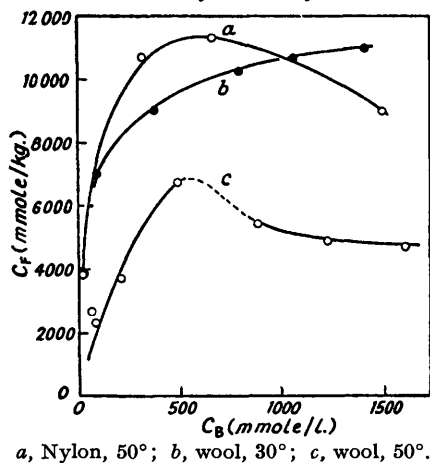
FIG. 7. *Isotherms of azobenzene from benzene.*

a, Alkali-treated wool, 50°; *b*, wool, 30°; *c*, wool, 50°; *d*, alkali-treated nylon, 50°; *e*, untreated nylon, 50°.
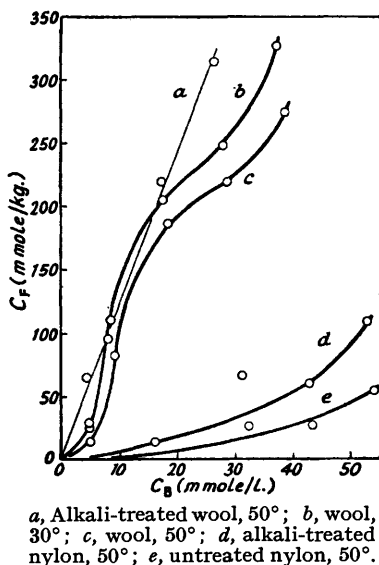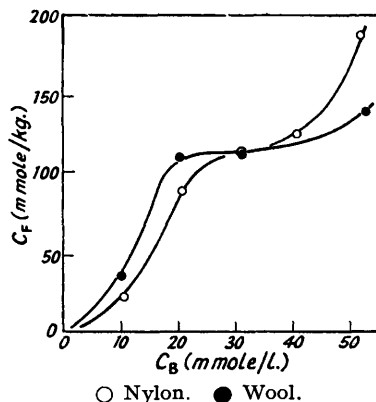

FIG. 8. *Isotherms of stilbene from benzene at* 60°.

O Nylon. ● Wool.

hydrogen bond by adsorption from aqueous solution. The corresponding figure for adsorption of phenol, from water, on γ-Al$_2$O$_3$, almost certainly a hydrogen-bond reaction, is —4 to —4·5 kcal./mole (Giles, Mehta, Stewart, and Subramanian, preceding paper). (v) Phenol is found to be entirely unadsorbed by nylon from alkaline solutions, but it is readily adsorbed from neutral or acid solution and change in pH value on the acid side has little effect on the amount adsorbed; Marsden and Urquhart (*J. Textile Inst.*, 1942, **33**, T 105) observed a similar effect with cellulose acetate. Only the neutral phenol

molecule, and not the phenoxide ion, can therefore be adsorbed by these substrates. (vi) There is much evidence (see, *e.g.*, Gustavson, *J. Polymer Sci.*, 1954, **12**, 317) that hydrogen bonds are formed between the phenolic groups of vegetable tannins in water and peptide groups of adjacent protein chains.

The non-adsorption of acetone and pyridine from water may be attributed to the protective action of the solvent. [The keto-group in aliphatic ketones appears not to form hydrogen-bond complexes in water (Arshid and Giles, unpublished work).] Alternatively, it might mean that the active sites are donor atoms, *e.g.*, nitrogen in the enolic form of the peptide group. Adsorption of hydrogen-bond acceptors would then occur without disruption of the inter-chain bonds. This does not, however, seem likely.

Adsorption from non-aqueous solution. Non-hydroxylic solvents do not swell these fibres, since they neither take part in hydrogen bonding nor promote ionisation of any groups. The adsorption from such solvents of solutes of the types used in this work will therefore be much more dependent than adsorption from water on (*a*) the molecular size of the solute, since this in all cases is close to the pore size of the unswollen fibres, and (*b*) the hydrogen-bond affinity of the solute, because in the absence of a swelling solvent the solute itself should be capable of breaking inter-chain bonds in the fibre if it is to be adsorbed by hydrogen bonds. In fact, it is likely for the reasons already given that the inter-chain bonds will be broken only by hydroxylic compounds. This does in fact occur, and almost all hydroxylic compounds are adsorbed (see, *e.g.*, Figs. 2, 3, 5, 6).

Phenols. Phenol itself is readily adsorbed by nylon or wool from non-aqueous solution (Fig. 2); * it is clearly able to disrupt the inter-chain bonds between –CO·NH– groups, because if the solution is sufficiently concentrated (*e.g.*, 20% in benzene), nylon is entirely dissolved. Practical difficulties prevented the full examination of its adsorption from non-aqueous solutions; its light-adsorption band lies in the lower ultra-violet region, in which most of the possible solvents also absorb, whereas in, *e.g.*, *iso*octane, which has low ultra-violet absorption, it has low solubility. *p*-Nitrophenol, however, can more readily be determined absorptiometrically and its adsorption was studied from benzene solution. It is adsorbed by wool (though the affinity is lower than that of phenol), and to a very high degree by nylon (Fig. 3), on which no sign of any limiting adsorption is observed even in solutions as concentrated as *ca.* 10 g./l. (approaching saturation).

1-Naphthol and *p*-hydroxyazobenzene, however, are not adsorbed by these fibres and 2-naphthol is adsorbed to only a small extent. In an attempt to interpret these observations, molecular-weight determinations of these compounds (in benzene) were made. The results (Fig. 10) show that *p*-hydroxyazobenzene is considerably associated; clearly, the mutual affinity of the phenolic groups in this solute is greater than their affinity for any of the potential hydrogen-bonding groups in the substrate. 1-Naphthol is solvated by the solvent, which circumstance, together with the size of its molecule, may account for its non-adsorption. 2-Naphthol, though apparently unassociated, is adsorbed to only a small extent. The reason for this has not been further examined, but it may simply be due to the resistance offered by the fibre to the penetration of the bulky aromatic nucleus.†

Alcohols and water. Methanol is readily adsorbed by nylon or wool from benzene solution, and shows a high degree of penetration (Fig. 6 and see also below). Hydrogen bonding must be responsible for its affinity for these fibres.

The adsorption of water from a number of solvents was also studied. A consideration of the results (Table 4, Fig. 5) suggests that the affinity may be determined by a balance between the tendency of the solvent on the one hand to prevent adsorption, by solvation, and on the other to promote it by swelling the fibre. Full isotherms were determined with *n*-butanol as solvent (Fig. 5). In this system the solvent cannot enter the fibre; only solute molecules escaping from solution can do so, and these may be considered to be in the vapour phase.

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* Non-adsorption of phenol from *iso*octane (2 : 2 : 4-trimethylpentane) at its b. p. is attributed to the high negative apparent heat of sorption, which so reduces the affinity at that temperature that the amount removed from solution is not measurable.

† Nylon dissolves in molten 1- or 2-naphthol.

TABLE 4. *Adsorption of water by wool * from various solvents.*

Solvent	Equilibrium adsorption, mmoles/kg.	Solvent	Equilibrium adsorption, mmoles/kg.
Methanol	Nil †	isoPropanol	$0\cdot6 \times 10^4$
Ethanol	Nil †	isoButanol	$1\cdot4 \times 10^4$
n-Propanol	$1\cdot3 \times 10^4$	Benzene–ethanol (4 : 1)	$2\cdot9 \times 10^4$
n-Butanol	$1\cdot1 \times 10^4$	Dioxan	$1\cdot1 \times 10^4$
n-Pentanol	$1\cdot8 \times 10^4$		

Conditions : Initial concn. 275 mmoles/l.; 50°, 18 hr.
* Normally dried. † Negative adsorption was actually observed, *i.e.*, traces of water appeared to be extracted from the fibre.

Benzene as solute. It was proposed to apply many of the non-hydroxylic compounds to wool from solution in benzene, and tests were therefore made to determine whether benzene itself is specifically attracted by the fibre, by using it as a *solute*. Methanol and *n*-butanol were chosen as the solvents and adsorption was found to occur from the latter (Fig. 4), but not from the former. *n*-Butanol cannot penetrate the dry fibre; methanol can; it is thus clear that the benzene molecule by itself can also penetrate and that it has appreciable attraction for the fibre, provided there is no competition by the solvent. The attraction must be solely physical. Attention was next turned to a number of other non-hydroxylic compounds.

Other non-hydroxylic compounds. The adsorption of these substances seems to be determined solely by van der Waals attraction between fibre and solute, and hydrogen bonds do not appear to be formed. It is difficult to demonstrate unequivocally that this is so, but a number of facts point to this conclusion. For instance, (*a*) the smaller molecules, *e.g.*, acetone, aniline, phenylhydrazine, and pyridine, are unadsorbed from solvents able to enter the fibre, though they are themselves small enough to penetrate it, and in many cases they would be expected to be quite capable of forming intermolecular hydrogen bonds; (*b*) when the conjugate system of the solute molecule is extended, affinity for the fibre increases—anthracene, azobenzene (Fig. 7), *p*-aminoazobenzene (Fig. 9), *o*-hydroxyazobenzene, *o*-nitrophenol (on nylon, but not on wool), and stilbene (Fig. 8) are adsorbed, whereas compounds with molecules of similar shape and size, but without a fully extended conjugate chain, *e.g.*, benzophenone, diphenyl, and 2 : 3 : 4-trihydroxybenzophenone, are not. The adsorption of *o*-nitrophenol only from benzene by nylon, all other tests (see Table 3) giving negative results, is difficult to explain, but in the absence of other information it may be attributed to a combination of pore-size and solvent effects together with the more pronounced hydrophobic nature of nylon. Molecular-weight determinations (Fig. 10) show evidence of solvation; association occurs only at high concentrations, and then only slightly.

The non-adsorption by either nylon or wool of azoxybenzene, phenylazo-2-naphthol, phenylazo-*m*-toluidine, bisphenylazobenzene, dimethylaminoazobenzene, dodecylphenylazo-*p*-cresol, 2-hydroxyanthraquinone, methyl 2-naphthyl ketone, and (perhaps) *o*-nitrophenol (by wool) must be attributed to the fact that their molecules are either of the wrong shape or are too large to enter the pores of the fibre. Anthracene must be approaching the limiting size for entry, for its adsorption is only measurable in the more dilute solutions.

Apart from these general observations, a number of other interesting facts are revealed by the results, and merit brief discussion, as follows.

Pore size of fibres. This work confirms Speakman's observation that the pores of dry wool are too small to allow *n*-butanol molecules to pass. They appear, however, to offer no obstruction to benzene. The penetrability of an alkyl chain is thus determined by its cross-section when in the crumpled, rather than the extended, form. Dry nylon must have pores very slightly larger than those of wool; the penetrability of the two fibres for most solutes appears to be similar, yet *o*-nitrophenol enters the one fibre but not the other (see, however, the remarks above).

Influence of certain solvents upon adsorption. The following observations on solvent effects may be noted : (*a*) *p*-Nitrophenol has considerably higher affinity for wool from ethanol than from benzene (Table 3), even though its solubility is higher in the former

solvent : the cause must be a small swelling action of ethanol, due either to its hydrogen-bonding or to slight ionising properties. (*b*) Azobenzene is unadsorbed by wool from *m*-cresol, owing either to high solubility or to blockage of the molecular chains of the fibre by attached solvent molecules. (*c*) When nylon was immersed in a cold alcoholic solution (0·16 g./l.) of phenylazo-2-naphthol, which was then diluted with 4 parts of water, *i.e.*, nearly sufficient to cause precipitation, the solute was adsorbed by the fibre (to the extent of *ca.* 10 mmoles/kg.), and could not be washed out by fresh alcohol. It is believed that the water, by swelling the fibre and simultaneously reducing the affinity of the solvent for the azo-compound, enables van der Waals attraction between fibre and solute to become effective.

Isotherms with maxima. Several of the isotherms, *e.g.*, those for benzene in *n*-butanol (Fig. 4), and for *p*-aminoazobenzene (Fig. 9), methanol (at 50°; Fig. 6), and *p*-nitrophenol (on wool) (Fig. 3) all in benzene, exhibit the very unusual feature of a maximum, beyond
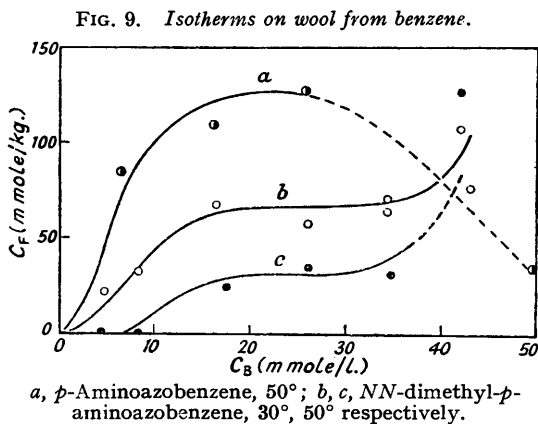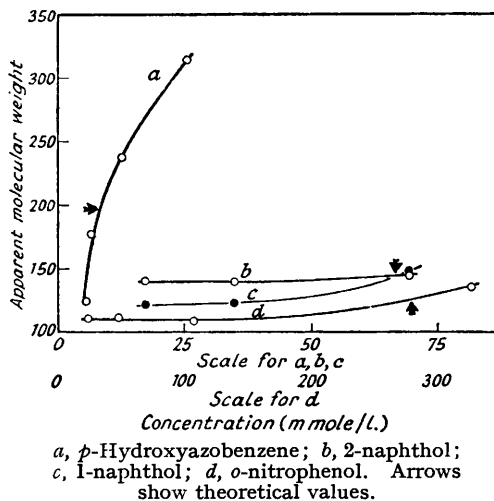

FIG. 9. *Isotherms on wool from benzene.*

a, *p*-Aminoazobenzene, 50°; *b, c*, NN-dimethyl-*p*-aminoazobenzene, 30°, 50° respectively.

FIG. 10. *Apparent molecular weights in benzene.*

a, *p*-Hydroxyazobenzene; *b*, 2-naphthol; *c*, 1-naphthol; *d*, o-nitrophenol. Arrows show theoretical values.

which an increase in solution concentration leads to a decrease of amount of solute sorbed. The cause is clearly some competing process, the most likely being association of the solute in the external phase.

Measurements of total surface area. In Table 5 the values for the apparent total internal surface area of wool are shown, calculated from the isotherms for the respective solutes, on the assumption that a monolayer is represented either by the first " knee "

TABLE 5. *Total surface area measurements (wool).*

Adsorbent (and solvent *)	Temp.	Approx. area × 10⁻⁵ (cm.²/g.)	Adsorbent (and solvent) *	Temp.	Approx. area × 10⁻⁵ (cm.²/g.)
Nitrogen	−195°	0·096 †	Water vapour	25°	20·6 †
p-Dimethylaminoazobenzene (B)	30	2	Benzene (Bu)	50	20
p-Nitrophenol (B)	60	2·5	Methanol (B)	30	25
p-Aminoazobenzene (B)	50	5	Water (Bu)	30	55
Azobenzene (B)	30	9	Phenol (El)	40	>70

* B = Benzene, Bu = *n*-butanol, El = ethanol. † Rowen and Blaine, *Ind. Eng. Chem.*, 1947, **39**, 1659.

of the curve or by the maximum, where one occurs. These values are seen to be in reasonable agreement with Rowen and Blaine's estimate made from water-vapour adsorption measurement. The following arbitrary assumptions were used as a basis for the present estimations : (i) that the molecules of benzene, methanol, and the phenols are oriented at right angles to the molecular chains of the fibre, and those of water and the azobenzene compounds parallel thereto; (ii) that only two-thirds of the surface is available to the

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hydroxylic compounds (*i.e.*, in each CHR·CO·NH unit only the CO·NH part is covered). It is interesting that the surface area available to a hydroxylic compound (methanol) which is a non-solvent for the fibre, is approximately the same for nylon as for wool. When the hydroxylic compound is a solvent for the fibre (*e.g.*, the phenols with nylon) the apparent area of course increases indefinitely with rise in concentration of the bath.

The apparent heat of adsorption. Quite large differences occur between the apparent heat of adsorption of many of the compounds examined, even though their real heats of adsorption may be expected not to differ much. Examples are given in Table 6. The data seem to demonstrate a connection between the heat change on adsorption and the nature of association between solute and solvent. Similar effects are observed in adsorption on γ-alumina (Giles, Mehta, Stewart, and Subramanian, *loc. cit.*). As the change of entropy on adsorption falls, the apparent heat of sorption becomes more positive. It has a high negative value when the solute is aromatic and the solvent aliphatic, or *vice versa*; in these circumstances the difference between the shape and the size of the two types of molecule, and the consequent low mutual physical attraction, will ensure a highly random distribution of solute and solvent molecules. When both solute and solvent are aromatic, however, the strong mutual physical attraction of their hydrocarbon nuclei will ensure a more ordered association in solution and consequently there will be a smaller entropy change when a solute molecule is removed from solvent to substrate.

Peculiarities in azobenzene adsorption. The affinity of azobenzene for wool is much higher than for nylon when the last traces of moisture are removed by drying the *solution* itself; but when *solvent* and fibre only are dried, the affinity for wool falls considerably, whereas the affinity for nylon rises a little, so that both fibres then adsorb the solute to a similar extent. It is difficult to account for this observation except perhaps as follows. The van der Waals attraction which the fibres offer to the solute is that of the main molecular chains. Traces of water adsorbed at the −CO·NH− groups therein will reduce adsorption by wool, by interference with the adlineation of the solute molecules to the chains. Nylon has much fewer hydrophilic groups and the effect of water addition will be different; it may even act in the opposite sense, because by breaking some inter-chain bonds between −CO·NH− groups it may expose relatively much larger areas of hydrophobic surface.

TABLE 6. *Apparent heats of adsorption* (ΔH_a, kcal./mole).

Solute	Solvent	Fibre	Temp. range	C_F *	ΔH_a † (approx.)
Azobenzene	Benzene	Wool	30—50°	50	−3
				150	−2·5
				200	−2·5
Phenol	Water	Wool	30—50	500	−4
				1000	−4
Phenol	Water	Nylon	30—50	500	−4·5
p-Dimethylaminoazobenzene ...	Benzene	Wool	30—50	20	(−8·5) ?
Phenol	Ethanol	Wool	40—50	500	(−14) ?
Methanol	Benzene	Wool	30—50	6000	(−17) ?

* C_F = Equilibrium concentration on the fibre (mmoles/kg.).
† The convention followed here is that a negative value for ΔH_a represents an exothermic adsorption process.

Wool treated with alcoholic potassium hydroxide, which according to Lindberg (*Textile Res. J.*, 1953, **23**, 67, 225, 573) increases the polarity of the epicuticle without affecting the internal structure of the fibre, shows a slightly greater affinity for azobenzene (Fig. 7), attributable to a reduction of the affinity of the solvent. Nylon similarly treated, however, shows a rather more pronounced increase in affinity than wool; since this fibre has no epicuticle, the change may be due to some attack on the internal fibre structure.

Non-sorption by an " odd " polyamide. An " odd " distribution of amide groups in a polyamide produces, amongst other effects, a reduction in m. p., compared with corresponding " even " polymers; *e.g.*, pentamethyleneadipamide (" 56 nylon ") has a lower m. p. (223°) than hexamethyleneadipamide (" 66 nylon ") (265°) (Reynolds, in " Fibre Science," see above). If the main molecular chains are parallel, every amide group in

" even " polyamides can cross-link with another in an adjacent chain, but only alternate amide groups can do so in " odd " polyamides, and it has sometimes been suggested that the lowered m. p. of the " odd " polymers is due to this inability of one-half of the total amide groups to engage in hydrogen bonding. If so, the free amide groups should confer the ability to adsorb donor compounds from non-aqueous solvents. Accordingly, experiments were made in which o-nitrophenol and three azo-compounds were applied to an " odd " polyamide (" 69 nylon "), but in no case was any adsorption noted. This suggests that amide groups are not present in an unbonded state, and thus that their mutual hydrogen-bond attraction is sufficient to ensure that each group associates with its nearest neighbour, even in the " odd " polyamides. This would involve a slight disorientation of part of the hydrocarbon chain, to which the lowered m. p. must be due.

Conclusions.—The main conclusions of this investigation may be related to the points detailed on p. 4377 as follows :

(*a*) *Pore-size.* The average pore size of dry wool, estimated by Speakman as *ca.* 6 Å is confirmed and thus only solutes whose molecules are not larger than those of *n*-pentanol in the aliphatic series and anthracene or certain simple azobenzene derivatives in the aromatic series can penetrate the intermolecular pores of the unswollen fibre from non-aqueous solution. The pore size of dry nylon appears to be comparable with that of wool.

(*b*) *Molecular structure of solute.* Purely physical attraction seems to hold non-hydroxylic solutes to the fibres in absence of water. This attraction appears to be more critically dependent than is hydrogen-bond affinity on the length of the conjugate chain in the solute molecule and it sets a lower limit to the molecular size, below which adsorption from a penetrating solvent is inappreciable. For wool this limit is at about the size of the azobenzene molecule, and for nylon it appears to be near that of o-nitrophenol.

(*c*), (*d*) *Hydrogen bonding affinity, and cross-linkages in fibres.* The adsorption results suggest that the inter-chain hydrogen bonds in both nylon and wool in absence of water may be largely of $O \cdots H \cdots O$ type; this is shown to be in conformity with recent views on the nature of the peptide linkage in proteins. Such bonds can be broken, and replaced by intermolecular bonds with the solute, only when the latter is a hydroxylic compound, and hydrogen bonds are thus formed only with such solutes. Previous workers (see above) have also found that phenols and related bodies break inter-chain hydrogen bonds in wool.

(*e*) *Nature of solvent.* The swelling power or penetrability of the solvent is important in determining the extent of adsorption of the solute; *e.g.*, if the solvent has a high affinity and can enter the fibre, it may by competition prevent the adsorption of a low-affinity solute dissolved in it, but if the solvent cannot penetrate the fibre, such a solute may then be adsorbed. On the other hand, the adsorption of a solute of high affinity may be promoted by an increase in the swelling power of the solvent, presumably because this releases new adsorption sites in the fibre.

A somewhat similar reason may account for the ability of non-hydroxylic compounds with small molecules to adsorb from aqueous solution, when they do not do so from non-aqueous solution. The opening up of large additional internal regions of the fibre by the great swelling power of water may expose sufficient sites for the adsorption of such compounds to become measurable.

(*f*) *Wool cuticle.* The only evidence of the presence of the wool cuticle which has been obtained in this work is a slight change in the adsorptive properties of the fibre after alkaline treatment.

The process of adsorption of a penetrating solute from solution in a non-penetrating solvent resembles a vapour-phase reaction. This seems to open up the possibiltiy of studying vapour-phase adsorption by fibres by a new method, which is both simpler and more rapid than the conventional one.

Implications regarding adsorption of dyes. Nothing precise is known of the physical forces of attraction between the molecules of the present fibres and large unsulphonated aromatic residues. It is clear, however, from this work that such forces are powerful enough to operate even when solute and substrate molecules are rather widely separated,

i.e., when they are in presence of excess of a solvent, *viz.*, benzene, which, being itself strongly attracted both to the fibre and to the solute molecule, may remain sandwiched between them. Moreover, physical attraction appears to be able to hold sulphonated dye molecules in water to the molecular chains of cellulose in similar circumstances, *i.e.*, when a layer of solvent molecules is interposed between them (Allingham, Giles, and Neustädter, *loc. cit.*), and thus it may be equally as effective with other fibres.

A sulphonated dye requires to have a lengthy planar molecule in order to exhibit sufficient affinity for cellulose to show useful substantivity (Vickerstaff, *op. cit.*). This requirement is no doubt a result of the rigid planar structure of the cellulose molecule, since otherwise the dye molecule could not adlineate itself sufficiently closely thereto for physical attraction to be significant. The molecules of protein fibres and of nylon, however, are much more flexible than those of cellulose and can therefore accommodate themselves more readily to dye molecules of varying shapes and sizes. Thus there is no evidence (Vickerstaff, *loc. cit.*) that any particular molecular features other than molecular weight and ionic charge influence the affinity of sulphonated dyes for wool. It therefore seems highly probable that the affinity of sulphonated dye anions for wool (or nylon) is at least partly determined by physical attraction. Whether hydrogen bonds also contribute to the affinity is, however, still undecided, for the following reasons.

On the one hand, it appears that *unsulphonated* compounds containing the groups, *e.g.*, hydroxy, amino, etc., which are also present in most sulphonated dyes can form hydrogen bonds with the fibres when applied from water. There is also a little evidence (Allingham *et al.*, *loc. cit.*) that such groups even when present in *sulphonated* dyes dissolved in water can unite by hydrogen bonding with a solid substrate (a condensed monolayer). Vickerstaff (*loc. cit.*) also believes that hydrogen bonding is at least to some extent effective between such dyes and wool, because " if it were not so, all dyes of the same degree of sulphonation should vary in wash fastness in direct proportion to their molecular area." On the other hand, Derbyshire and Marshall (*Discuss. Faraday Soc.*, 1954, **16**, 140), by calorimetric studies, obtained evidence that naphthalene-orange G (Colour Index No. 151), a typical sulphonated wool dye, does not form a hydrogen bond with amino-acids (used as models of protein fibres) in water. A similar conclusion was reached by Jain (personal communication) in studies of the hydrogen bonding of sulphonated dyes with alcohols in water. It appears that the sulphonated molecules in solution may be too strongly solvated by water for weak hydrogen-bonding agents, which are also dissolved, to approach the potential reacting centres. The apparent inconsistency of some of these facts has not yet been resolved.

EXPERIMENTAL

Reagents.—All solutes were either commercial products of analytical quality or purified laboratory specimens. Benzene, ether, and toluene were stored over sodium, the ethanol was commercial " absolute " material (*ca.* 99%), the dioxan and methanol were of the completely anhydrous " specially dried " quality (B.D.H.) used for Karl Fischer analyses; the remaining alcohols were of analytical-reagent quality, and distilled water was used for the aqueous solutions.

Phenylazo-*m*-toluidine (orange leaflets, m. p. 73°, from *iso*octane) was prepared in the normal manner from aniline and *m*-toluidine. Bisphenylazobenzene, prepared from *p*-aminoazobenzene and nitrosobenzene (Mills, *J.*, 1895, **67**, 925), formed orange crystals, m. p. 168°, from glacial acetic acid. *o*-Hydroxyazobenzene was separated in very small yield (*ca.* 1%) by steam-distillation from a sample of *p*-hydroxyazobenzene (Bacovesu, *Ber.*, 1909, **42**, 2938).

Methyl 2-naphthyl ketone was prepared from resublimed naphthalene and freshly distilled acetyl chloride by Friedel–Crafts synthesis in nitrobenzene. The solvent was removed by steam-distillation; the product, recrystallised from glacial acetic acid, formed white crystals, m. p. 54°.

Azobenzene, aminoazobenzene, and other non-hydroxylic solutes gave inconsistent results unless the *solutions*, and not the solvents alone, were dried over sodium. Evidently traces of water adsorbed on the reagents in the solid state interfere with adsorbtion by the fibres. Solutions of hydroxylic compounds could not be dried in this way because they reacted or formed adsorption complexes with the drying agents; the solid solutes were therefore oven-

dried at 110° for up to 7 days before use. In addition, all the non-aqueous solutions which were not sodium-dried were made up freshly before each experiment, otherwise inconsistent results were liable to be recorded, again probably owing to the adsorption of traces of atmospheric moisture on standing.

Fibres.—These were first purified as follows and then stored in well-stoppered bottles : nylon (15 fil., 45 den. drawn yarn and undrawn monofil), by scouring in 0·5% solution of a non-ionic detergent (Lissapol N) (Imperial Chemical Industries Limited) with addition of a little ammonia, at 60° for 15 min., followed by thorough rinsing in distilled water; silk (raw domestic), by treatment in 3% soap solution at the b. p. for 1 hr., then again in 1% soap solution at the b. p. for 30 min., followed by rinsing and drying; before use, traces of yellowish solvent-soluble colouring matter were extracted (Soxhlet) from the fibre by toluene; wool, root ends (1·5—2 in.) of a Lincoln fleece were lightly scoured as for nylon, then extracted (Soxhlet) for 24 hr. with ether or methylene dichloride (which is more effective than ether in removing waxes), then steeped overnight in distilled water. Before use, all fibres except those " specially dried " were conditioned in air at room temperature for 24 hr., weighed in the air-dry state, then oven-dried at 100—110° for 12—18 hr. and immediately introduced into the adsorption liquors. The quoted weights are those in the air-dry state.

69 Nylon. This was received in the form of lumps of a very hard white resin, m. p. 197—199°. It was dissolved in phenol, precipitated in water, washed overnight in running water to remove adsorbed phenol, rinsed in distilled water, dried at 110°, then conditioned at room temperature before use.

" *Specially-dried* " *fibres.* Some samples of nylon and wool (indicated in Table 3) were dried more completely than usual by steeping for successive 12-hr. periods in absolute ethanol, " specially dried " methanol, and dry ether, followed by oven-drying at 100—110° for 4 hr. They were then immediately placed in the adsorption tubes.

Acetylation of nylon. Peters's method was used (*J. Soc. Dyers Col.*, 1945, **61**, 95). Drawn nylon yarn (15 g.) was treated with acetic anhydride (90 g.) in dry benzene (270 c.c.) at 75° for 48 hr. After being rinsed with benzene, then with acetone, and finally with water, the yarn was dried and conditioned. Peters found that this treatment almost fully acetylated the fibre.

Adsorption Tests.—0·2—0·5 G. of fibre and 5—15 c.c. of 0·1—10 g. per l. solutions were placed in closed tubes, ground-glass stoppers being used for aqueous solutions, and complete sealing of the glass for those in organic solvents. The tubes were placed in a thermostat and mechanically agitated, end-over-end, at *ca.* 35 cycles per min. The fibre was packed into a separate, inner, open-ended, perforated glass tube, which falls to-and-fro during the agitation cycle, out of phase with the main container, so that liquor is caused to pulsate in and out of the fibre through the perforated walls. This simple device overcomes the difficulty, otherwise experienced, of a mass of loose fibre blocking the adsorption tube and preventing adequate agitation and contact with the solution.

Where positive adsorption was observed, the time required to reach equilibrium was determined by rate measurements at the appropriate temperature.

Methods of Analysis.—Most of the aromatic compounds, and acetone, were determined absorptiometrically in either a Hilger Spekker absorptiometer or a Unicam SP500 Photo-electric Spectrophotometer. The use as solvent of *iso*octane, which has low ultra-violet absorption, enabled a number of colourless compounds, *e.g.*, phenol or pyridine, to be analysed thus. Volumetric methods were used for benzoic acid, (aqueous) phenol (bromate–bromide; Koppeschaar, *Z. anal. Chem.*, 1876, **15**, 233), dihydric and trihydric phenols (potassium permanganate; Pence, *J. Ind. Eng. Chem.*, 1913, **5**, 218), and water. For the last, Karl Fischer (direct) titration in a Townson and Mercer (B.D.H.) pattern apparatus was employed.

Some aromatic and aliphatic compounds whose analysis might otherwise have been difficult, *e.g.*, methanol or butanol in benzene, and pyridine in water, were determined by refractometric measurement of the solutions on a Zeiss–Pulfrich refractometer. A correction, if necessary, was applied for any slight change in refractive index of the pure solvent kept in contact with a sample of fibre, in a blank experiment run simultaneously, and attributed to traces of impurity or decomposition products from the fibre extracted in the prolonged adsorption procedure. As an additional precaution, the fibres used in such experiments were extracted (Soxhlet) for several hours before the experiment with the solvent to be used for the adsorption tests.

Examination of azobenzene solutions. Spectroscopic examination of the azobenzene solutions was made before and after the adsorption tests, in comparison with solutions of azoxybenzene, in

order to determine whether the apparent reduction in concentration of the former might be due simply to a loss in optical density caused by a catalytic oxidation * to the azoxy-compound, and not to adsorption by the fibre.   In view of the identical position of the azoxybenzene peak and one of the peaks of azobenzene (in the spectral range examined, both compounds have an absorption peak at 3300 Å; azobenzene, but not azoxybenzene, has one at 4400 Å), it was not possible to obtain decisive evidence, but the results gave no indication that azoxy-benzene was present after the tests.

Thermodynamic Data.—The apparent heat of adsorption, *i.e.*, the resultant value of the heat generated by formation of the bond between solute and substrate and that generated by removal of solute from solution, was calculated in the usual manner by the Clausius–Clapeyron equation, from the value of the solute concentration in the liquid in equilibrium with a given concentration in the substrate at two temperatures.

Molecular-weight Determinations.—These were made by the Beckmann f. p. method in the special quality benzene (B.D.H.) supplied for the purpose.