Adsorption at Inorganic Surfaces. Part I. An Investigation into the Mechanism of Adsorption of Organic Compounds by the Anodic Film on Aluminium.

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The adsorption of organic compounds by chromic acid anodised films on aluminium has been studied. In water the film is positively charged and anionic compounds are adsorbed, but not cationic compounds. Non-ionic compounds of suitable structure may also be adsorbed from aqueous or non-aqueous solution. The film consists of substantially pure γ-alumina and the following adsorption mechanisms are shown to operate in aqueous solution : (a) salt formation between the metal of the film and certain sulphonated compounds, (b) ion-exchange at the surface with some sulphate esters, (c) hydrogen-bond formation between the oxygen of the film and the hydrogen atom of phenolic groups, (d) chelation between the metal of the film and suitable pairs of *ortho*-substituents in the solute; and in non-aqueous solution : (e) hydrogen-bond formation with phenols and amines, and (f) a " bridge-bonding " mechanism by which some donor solutes can be adsorbed ; in this a bifunctional hydrogen-bonding compound, *e.g.*, quinol, is attached by one of its substituent groups to the film and by the other to the donor compound, *e.g.*, azobenzene.

Except by mechanism (f) donor compounds are not adsorbed. The protective action of the solvent can also prevent adsorption of many solutes, such as some sulphonates from water, and amines from benzene or water.

ANODIC oxide films on aluminium are readily prepared in uniform and consistent quality. Moreover, as the present paper describes, they exhibit a wide variety of attractive forces in their adsorption properties, so that they are a suitable subject with which to study some aspects of the adsorption of organic compounds at inorganic surfaces.

Nature of Anodic Films on Aluminium.—The production of hard, protective oxide films on aluminium by anodic treatment in acid solution, and their coloration by dyeing to give deep and fast shades, was disclosed by Bengough and Stuart (B.P. 223,994—5) in 1923. Both processes are now extensively employed on a technical scale. In practice, solutions of sulphuric acid (Gower and Stafford O'Brien and Partners, Ltd., B.P. 290,901), oxalic acid (Zaidan Hojin, Rikagaku, and Kenkyujo, B.P. 226,536), or chromium trioxide (Bengough and Stuart, *loc. cit.*) are normally used as electrolytes in the anodising process. These solutions have a partial solvent action on the film, which gives the outer layers an open structure and allows the electrolyte to remain in contact with an inner, more compact layer, which probably controls the electrical properties. The film can be built up to any desired thickness, even to the point of almost complete disappearance of the base metal, but the rate of growth reaches a maximum and then decreases, owing to the competing solvent action of the electrolyte. A thin compact oxide layer is formed first at the metal surface, then, as electrolysis proceeds, Al^{3+} ions diffuse outwards through this layer, under the influence of the applied electric field, and some of them unite with O^{2-} ions at the liquid–solid boundary to form alumina. In sulphuric acid solution the remainder form a soluble salt with the electrolyte and diffuse away into the solution. The outer layers of the film appear to be penetrated by evenly distributed tube-like pores, forming 5—15% of the total surface area. The porosity may be increased, at the expense of the hardness of the film, by raising the temperature of the electrolyte.

Although the physical properties of the film vary considerably according to the nature of the electrolyte and conditions of electrolysis, its chemical composition remains the same. This is essentially amorphous or very finely crystalline γ-alumina. Impurities from the metal or the electrolyte may be present; thus films from sulphuric acid baths contain about 13% of basic sulphates, some monohydrate (Al_2O_3,H_2O), and some loosely

held water. The film formed in chromic acid is the purest and is almost entirely γ-alumina (s.g. *ca.* 2·7) with only *ca.* 0·1% of impurity (as Cr). Some partial hydration of the oxide may take place during electrolysis but the present work gives no evidence of this. The degree of crystallinity appears to increase with rise in temperature of the electrolyte. Dry heating above 100° drives off any loosely held water, but does not decrease the adsorptive powers; treatment with steam or with water above 80°, however, causes the film to lose its adsorptive powers entirely. This effect, known as " sealing," is caused by blocking of the pores through the formation of a thin layer of α-alumina monohydrate (boehmite) containing an additional molecule of lattice water. Dry heating above 100° subsequent to sealing removes water and reconverts a proportion of the monohydrate into γ-alumina. The adsorptive capacity of the film is thus partially restored. Heating to temperatures up to 650° does not appreciably alter the film, but at *ca.* 900° the internal structure changes entirely, and α-alumina is produced (Pullen, *Metal Ind.*, 1939, **54**, 327; also personal communication; Jenny and Lewis, " Anodic Oxidation of Aluminium and its Alloys," London, Charles Griffin and Co. Ltd., 1940; see also, *e.g.*, Burwell and May, Pittsburgh Intern. Conf. on Surface Reactions, 1948, 10, through *Chem. Abs.*, 1948, **42**, 7222; Edwards and Keller, *Trans. Electrochem. Soc.*, 1941, 79, Preprint through *Chem. Abs.*, 1941, **35**, 1705).

Excellent general accounts of the preparation and properties of these films are given in two recent monographs : (*a*) The Aluminium Development Association, Inform. Bull. No. 14 " Anodic Oxidation of Aluminium and its Alloys," London, 1949, which includes comprehensive literature and patent references; and (*b*) Hübner, " Aluminium—Surface Treatment and Colouring," Ciba Review No. 92, Basle, Ciba Ltd., June, 1952.

In contrast with the large amount of investigation devoted to the nature of anodic films, virtually no serious attention seems to have been given to the investigation of their adsorption properties; Gill (*J. Electrodepositors' Tech. Soc.*, 1946, **21**, 235), in a general account of the methods of dyeing the material, suggested that lake formation occurs with dyes which form aluminium chelate complexes, and physical adsorption with those which do not, and Haller (*Kolloid Z.*, 1943, **105**, 147) has suggested that the degree of dispersion of both the dye and the grains of oxide in the film have some influence on adsorption. Further, comparatively little study appears to have been made of the detailed chemical mechanism of adsorption of dyes and simple aromatic compounds by the various other forms of solid or hydrated alumina, though this is such an important factor in various technical processes, including chromatography. Ruggli and Jensen (*Helv. Chim. Acta*, 1935, **18**, 624; 1936, **19**, 64) made a variety of chromatographic tests by which they determined the qualitative influence of structural characteristics of dyes, *e.g.*, the position and number of azo-, vinyl, or sulphonic acid groups upon their ease of adsorption on alumina columns; and several other investigators (Mutch, *Quart. J. Pharm.*, 1946, **19**, 490; Weiser and Porter, *J. Phys. Chem.*, 1927, **31**, 1704; White and Gordon, *ibid.*, 1928, **32**, 380; Ruiz, *Ind. parfum.*, 1946, **1**, 187, through *Chem. Abs.*, 1948, **42**, 5675; Hesse and Sauter, *Naturwiss.*, 1947, **34**, 250) have examined the adsorption of acid and basic dyes by various forms of aluminium oxide; and Hoyer (*Kolloid Z.*, 1951, **121**, 121) observed the reduced strength of adsorption by alumina of amino- or hydroxy-compounds when these are involved in intramolecular chelate ring systems.

The aim in the present research has been to determine the nature of the forces operating in the adsorption of organic solutes on the anodic films, the actual solutes used being so chosen that the action of each of the possible types of attractive force, *i.e.*, physical (van der Waals attraction, electrostatic attraction) or chemical (chelation, hydrogen-bond formation, salt formation) could be demonstrated. The substances used have been mainly simple aromatic compounds, but a few aliphatic or more complex aromatic compounds have been included where necessary. A subsequent communication will describe a more detailed study of the adsorption of dyes by the film.

The procedure followed was to anodise aluminium foil in chromic acid solution, and then to treat it with the selected solutes under a variety of conditions of concentration, temperature, time, and nature of solvent, the extent of adsorption of some solutes being determined by quantitative analysis of the solutions before and after the test.

TABLE 1. *Summary of results of adsorption tests.**

Positive adsorption.	Solvent †	Initial bath concn. (g./l.)	Temp.	Time (hr.)	C_F ‡ (mmole/kg.)	Remarks
Amino-compounds.						
4-Aminoazobenzene	D	—	—	—	—	Qual.
Phenylazo-1-naphthylamine	B, C	—	—	—	—	Fig. 3
	ElW	0·1	15°	72	*ca.* 20	
Phenylazo-,,2-naphthylamine,,	C	—	—	—	—	Fig. 3
Magenta (C.I. 677)	D	—	—	—	—	Qual.
Anionic compounds.						
Azobenzene-4-sulphonic acid	W	—	40	24	{275, 440, 550, 550	
Na dodecyltoluenesulphonate	W	—	—	—	—	Fig. 8
Hæmatein (C.I. 1246), water-soluble Cr-complex **	W	—	—	—	—	Qual.
Naphthalene-2-sulphonic acid	W	1—10	40	24	*ca.* 100	
2-Nitronaphthalene-4 : 8-disulphonic acid	W	0·05—0·2	40, 60	48	max. *ca.* 50	
Sulphonated azo-dyes, *e.g.*, Orange I, II, Tartrazine (C.I. 150, 151, 640, respectively)	W	—	—	—	—	Fig. 7
Sulphonated triphenylmethane dyes, *e.g.*, Acid Green M conc., Erioglaucine, Acid Magenta, Lissamine Green V (C.I. 669, 671, 692, 735, respectively)	W	0·1—0·3	40, 55	40	—	Qual.
Na tetradecyl sulphate	W	—	—	—	—	Fig. 5
Na oleyl sulphate	W	—	—	—	—	Fig. 5
Hydroxy-compounds.						
Phenylazo-2 : 4-dihydroxyquinoline (Dispersol yellow 3G §)	P	—	—	—	—	Qual.
Phenylazo-1-naphthol	B	—	—	—	—	Fig. 4
2 : 4-Dinitrophenol	W	—	—	—	—	
p-Nitrophenylazo-*N*-ethyl-*N*-2-hydroxy-ethylaniline (Dispersol Fast Scarlet B §)	P, D	—	—	—	—	Qual.
2-Chlorophenylazo-*N*-ethyl-*N*-2-hydroxy-ethyl-4-nitroaniline (Dispersol Fast Crimson B §)	P	—	—	—	—	Qual.
Phenol	W	—	—	—	—	Fig. 4
Quinol	W	0·1	40	24	230	
Resorcinol	W	0·1	40	24	50	
Lake-forming compounds.						
Catechol	W	0·1	40	24	300	
Alizarin	ElW, W	—	—	—	—	Fig. 1
Na 1 : 4-diaminoanthraquinone-2-sulphonate	W	—	—	—	—	Qual.
Hæmatein	W	—	—	—	—	,,
1 : 4 : 5 : 8-Tetra-aminoanthraquinone (Duranol Brilliant Blue CB §)	D, S	—	—	—	—	,,
Solway Blue B (C.I. 1054) and other water-soluble mordant dyes	W	0·5	60	1	—	cf. Fig. 2
No adsorption.						
Amino-compounds.						
2-Aminoanthraquinone	T	0·1	40	48	—	
4-Aminoazobenzene	B	0·2	24, 48	24	—	
p-Anisidine	W	10	40	24	—	
Aniline	W	10	40	24	—	
Phenylazo-2-naphthylamine	B	0·2	20	48	—	
m-Nitroaniline	W	10	40	20	—	
p-Nitroaniline	ElW	2	40	20	—	
,,	B	2	40	20	—	
,,	W	0·02—1	40	4	*ca.* 1·5 ¶	
2 : 4-Dinitroaniline	B, W	0·05—0·15	50	48	—	
2-Naphthylamine	ElW, B, El, T	0·1—10·0	40	20	—	
Anionic compounds.						
Benzenesulphonic acid	W	0·4	40	48	—	
Na benzenesulphonate	W	0·4	40	48	—	

TABLE 1. *(Continued.)*

No adsorption.	Solvent †	Initial bath concn. (g./l.)	Temp.	Time (hr.)	C_F ‡ (mmole/kg.)	Remarks
Donor compounds.						
Anthraquinone	T	1·0	40	48	—	
Azobenzene	B	0·1	40, 60	48	—	
Phenylazo-2-naphthol	B	0·1—2·0	40, 60	48, 24	—	
3-Methoxybenzanthrone (Duranol Brilliant Yellow 6G)	T	0·2	40	48	—	
Naphthylazo-2-naphthol	B	0·1	40—60	48, 24	—	
1 : 2-Naphthaquinone	B	0·1	40	48	—	
Nitrobenzene	B	5·0	40	48	—	
p-Nitrophenylazodiphenylamine (Dispersol Fast Orange A §)	P	—	—	—	—	Qual.
o-Nitrophenol	W	0·05—1·0	40, 60	48, 24	—	
Cationic Compounds.—						
Azo-compounds.						
Bismarck Brown (C.I. 20)	W	1·0	40	4	—	Qual.
Janus Red B (C.I. 266)	W	1·0	40	4	—	Qual.
Phenolic compounds.						
Hæmatein, water-soluble Al-complex **	W	—	—	—	—	Qual.
*iso*Hæmatein sulphate	W	—	—	—	—	Qual.
2-4'-Hydroxystyrylbenzothiazole ethiodide	W	*ca.* 0·1	20	48	—	Soln. dec.
2-4'-Hydroxystyrylquinoline methiodide	W	*ca.* 0·1	20	48	—	Soln. dec.
Triphenylmethane compounds, etc.						
Malachite Green (C.I. 657)	W	1·0	40	4	—	Qual.
Methyl Violet 2B (C.I. 680)	W	1·0	40	4	—	,,
Methylene Blue B (C.I. 922)	W	1·0	40	4	—	,,
Rhodamine B (C.I. 749)	W	1·0	40	4	—	,,
Results uncertain owing to suspected decomposition.						
Na anthracene-1-carboxylate	W	0·02—0·1	60	24	—	
Anthracenesulphonic acid	W	0·5—2·0	60	24	—	
Azobenzene	D, El	0·1	25, 50	48, 24	—	
Phenylazo-2-naphthylamine	D	0·15—0·6	40, 55	44	—	
Dimethyl terephthalate	O	0·05—0·2	45, 60	24	—	
2 : 4-Dinitroanisole	C	0·1—0·5	30, 50	72, 24	—	
Glycerol triacetate	W	0·05—0·25	54, 60	24	—	
2-Methoxynaphthalene	El	0·5	50	12	—	
2-Acetoxynaphthalene	tyB	0·1	50, 60	24	—	
2-Naphthylamine	B, El, ElW	0·5	40	3	—	
2-Naphthylamine-4-sulphonic acid	W	0·2	40	24	—	
2-Naphthylamine	B, El, ElW, T	0·1—2·5	40	24	—	
p-Nitrophenol	W	0·3—1·5	50, 60	24	—	
*iso*Octane	B, N	0·04—0·2	50, 60	24	—	

* C.I., Colour Index No.; Qual. = Qualitative; Dec. = Decolorised.
† Solvents : B, benzene; tyB, *tert.*-butanol; C, carbon tetrachloride; D, dioxan; El, ethanol; N, nitrobenzene; O, *iso*octane; P, aqueous dispersion; S, " Cellosolve "; T, toluene; W, water; ElW, aqueous ethanol.
‡ C_F, Equilibrium concentration in film. Values of C_B, the equilibrium concentration in the bath, for azobenzene-4-sulphonic acid : 0·35, 0·65, 1·50, 1·84, mmole/l., were determined.
¶ From 0·02 g./l. of solution. Not measurable from more concentrated solutions.
§ Knight, *J. Soc. Dyers Col.*, 1950, **66**, 169.
** Arshid, Connelly, Desai, Fulton, Giles, and Kefalas, *J. Soc. Dyers Col.*, 1954, **70**, 402.

RESULTS AND DISCUSSION

A summary of the experiments is given in Table 1 and some of the quantitative data are shown in Figs. 1—8. In some cases baths of a range of initial concentrations were employed, so that full isotherms could be plotted from the results. In addition these experiments were repeated at two temperatures, so that the apparent heat of adsorption could be calculated. In other cases only one or two bath concentrations were used in order

to obtain a semi-quantitative measure of the adsorption, and in yet other cases the adsorption was judged only qualitatively, by observation of the colour of the treated film. Where the change in composition of the solutions during the test is so small as to be within the limits of experimental error the compound is considered to be unadsorbed. No precise figure can be given for the lowest detectable amount of adsorption, on account of the different sensitivities of the analytical methods, but it may be considered to be roughly between 1 and 5 mmole of solute per kg. of film.

Evidence for Lake Formation.—Qualitative evidence that lakes are formed by aluminium
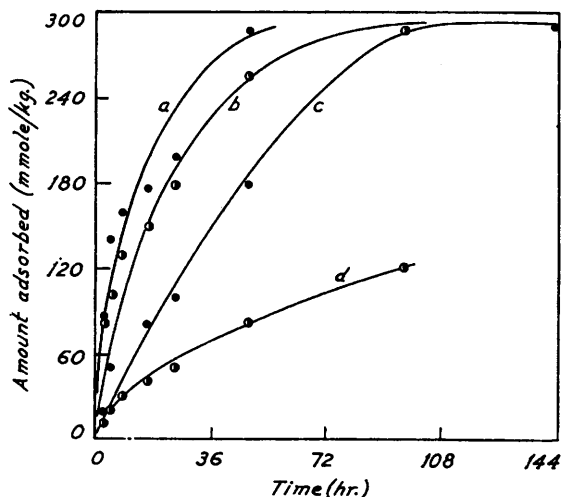
FIG. 1. *Rate of adsorption of alizarin by the anodic film on aluminium.*

a, 80°; *b*, 60°; *c*, 40°; *d*, 25°.

Initial concn., 1·0 g./l.

FIG. 2. *Rate of adsorption of Solway Blue BN by the anodic film on aluminium.*

a, 60°; *b*, 40°; *c*, 25°.

Initial concn., 0·4 g./l.
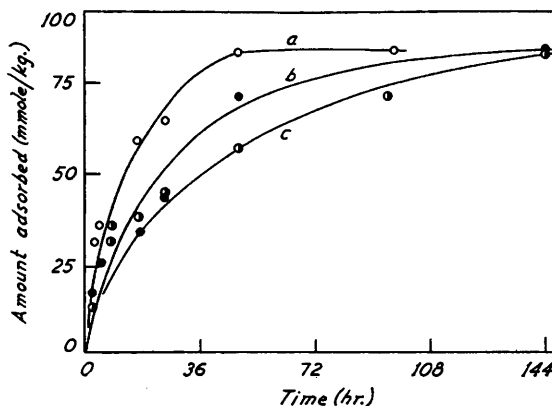
in the film, with suitable compounds, was obtained by the application of catechol, which gives a dull green colour (cf. the colours of aluminium–catechol complexes reported by Weinland and Denzel, *Ber.*, 1914, **47**, 737), and of a number of mordant dyes. Certain dyes of this class were chosen, which show pronounced colour changes when applied to wool mordanted with aluminium salts. These were then applied to the film from aqueous or aqueous-alcoholic solution. In each case the film was coloured to a shade resembling that of the mordanted and dyed wool, *e.g.*, blue with Eriochrome Azurol B or Eriochrome Cyanine R, scarlet with alizarin, violet with hæmatein (Colour Index Nos. 720, 722, 1027, 1246, respectively), violet with Solochrome Blue B, and pink with Solochrome Violet R.

Quantitative evidence of lake formation was provided by the adsorption-rate curves of 1 : 2-dihydroxyanthraquinone (alizarin) (Fig. 1) and sodium 1 : 5-diamino-4 : 8-dihydroxyanthraquinone-3 : 7-disulphonate (Solway Blue B, C.I. 1054) (Fig. 2), which

appear to demonstrate that the equilibrium adsorption values are independent of temperature. The adsorption process therefore involves the irreversible formation of very stable chelate complexes with the metal of the film. In confirmation of this, it was found that when the dyed films were subjected to prolonged treatment with water at the temperature used for adsorption, no colour was removed, whereas some colour does bleed off under these conditions when the film is coloured with non-chelating dyes.

FIG. 3. *Adsorption isotherms of phenyl-azonaphthylamines on the anodic film on aluminium.*

a, 1-derivative, 49° (24 hr.).
b,   „   58°   „
c, 2-derivative, 36° (72 hr.).
d,   „   50° (24 hr.).
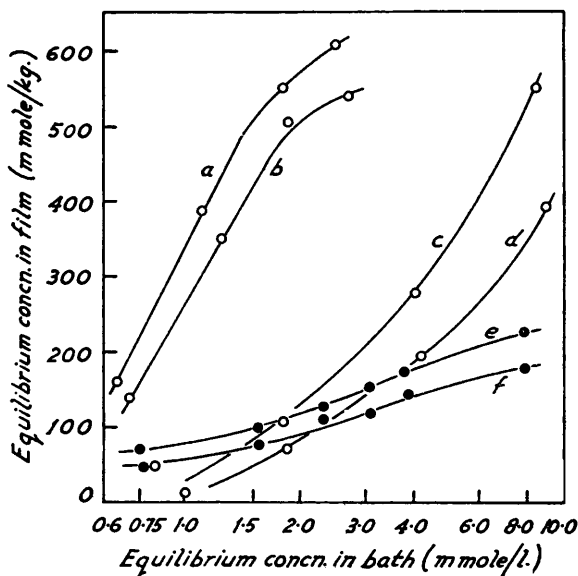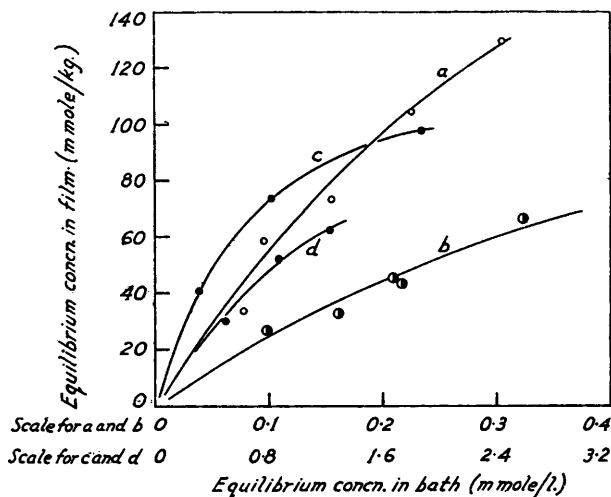
FIG. 4. *Adsorption isotherms of phenols on the anodic film on aluminium.*

a, 2 : 4-Dinitrophenol in water,   50° (24 hr.).
b,   „   „   60°   „
c, Phenol   „   „ 40° (48 hr.).
d,   „   „   60° (24 hr.).
e, Phenylazo-1-naphthol in benzene 40° (48 hr.).
f,   „   „   60° (24 hr.).

Abscissa values are plotted on a logarithmic scale.

When dry solutions of alizarin in benzene or ethanol were used, lake formation commenced only after the addition of phenol or water respectively. The reason for this behaviour was not investigated.

Evidence for Hydrogen Bonding.—An examination of the data in Table 1 shows that amongst the non-ionic compounds only those with a hydrogen atom free to form inter-molecular bonds, *i.e.*, hydroxy- and (some) amino-compounds, are adsorbed. All donor compounds, including intramolecularly chelated hydroxy-compounds, *e.g.*, *o*-nitrophenol

or phenylazo-2-naphthol, are not adsorbed, but phenylazo-1-naphthylamine, which is internally chelated but still retains a free active hydrogen atom, is adsorbed (from certain solvents). These facts seem to be clear evidence that hydrogen bonds are responsible for the adsorption of amino- and hydroxy-compounds.

There are some indications (Arshid and Giles, unpublished work) that a number of intermolecular hydrogen-bond complexes formed between organic molecules in solution are more stable when the solvent is carbon tetrachloride or dioxan than when it is benzene or water. This observation prompted the examination of carbon tetrachloride and dioxan as solvents, after earlier experiments had failed to reveal measurable adsorption of some amines from benzene or water. Carbon tetrachloride and dioxan were in fact found to promote positive adsorption; the non-adsorption of amines from benzene or water must therefore be attributed to protection of the amino-group by the solvent.

By comparing the isotherms of the two aminoazo-compounds, phenylazo-1-naphthylamine and its 2-isomer (Fig. 3) it will be observed that the amount present in the film in equilibrium with any given concentration in solution is higher, and hence the affinity is higher, for the 1- than for the 2-isomer. Now the latter can form only one hydrogen bond, but the 1-compound has two free active hydrogen atoms and its higher affinity suggests that both of these can form bonds simultaneously with the oxide film.

The lower equilibrium adsorption values of both the aminoazo-compounds compared with those of hydroxy-compounds (Fig. 4) and the ease with which adsorption of amines, but not that of hydroxy-compounds, can be prevented by certain solvents are alike evidence that the $N \cdots H \cdots O$ bond formed in adsorption has lower free energy than the $O \cdots H \cdots O$ bond. In agreement with this, Flett (*J. Soc. Dyers Col.*, 1952, **68**, 59) found that the free energy of formation of many intermolecular $N \cdots H \cdots O$ bonds (in carbon tetrachloride solution) is lower than that of corresponding $O \cdots H \cdots O$ bonds.

In spite of all precautions, a number of individual tests in these experiments with aminoazo-compounds returned very erratic and non-reproducible results. This may be due to catalytic action (see Experimental section). Some changes were in fact observed in the absorption spectra of the solutions in these cases, but we cannot explain the erratic nature of the effect. The experiments were however repeated many times and the curves shown (Fig. 3) each refer to a single experiment in which no erratic results occurred, and in which spectroscopic examination showed no evidence of chemical change in the solute.
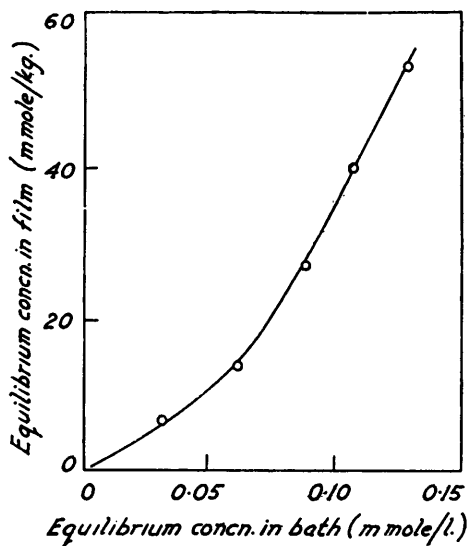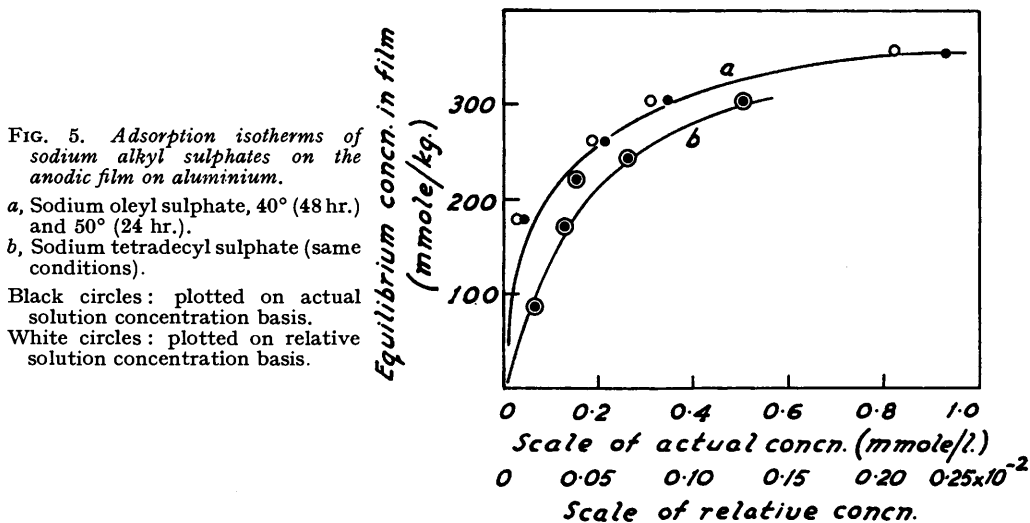
A number of examples of intermolecular hydrogen bonds involving hydrogen attached to carbon are known, and attempts were made to discover if adsorption on anodic films could take place by this means. No direct evidence was obtained, because all the compounds which it was thought might exhibit this form of attachment appeared to be considerably decomposed by catalytic action in the tests, though this in itself does suggest that some form of close association of these solutes and the film must occur. The compounds in question included 2-acetoxynaphthalene, dimethyl terephthalate, glycerol triacetate, and 2 : 4-dinitroanisole.

The Surface Charge and its Effect on Adsorption.—By prolonged electrolysis the aluminium anode can be completely oxidised, leaving a wafer of brittle alumina. Material obtained in this way was dispersed in water by grinding and examined by electrophoresis. It had a positive electrokinetic potential. It is therefore expected that anions will be attracted to the surface in water, and cations repelled. In general, this is found to be so. The potential is progressively reduced, and eventually reversed, by addition of increasing concentrations of sodium chloride, an isoelectric point being observed at a concentration of *ca.* 0·09% of the salt.

Cationic Compounds.—Qualitative tests with aqueous solutions of representative basic dyes of the azo-, thiazine, and triphenylmethane classes (see Table 1) gave no significant evidence of adsorption, except in the presence of sufficient sodium chloride or trisodium phosphate to reverse the surface charge. Films which have been coloured by adsorption of magenta from dioxan solution are washed clear by thorough rinsing in water, no doubt because of the simultaneous formation of cations of the colouring matter and development of the positive surface charge on the film.

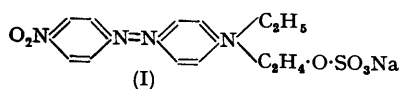Tests were made to determine whether the presence of a free hydroxy-group in a cationic

compound would promote adsorption. Four suitable compounds were examined : *iso*-hæmatein sulphate, the aluminium lake of hæmatoxylin (both of these compounds contain one pair of free *o*-hydroxy-groups) and two cyanine dyes, 2-4'-hydroxystyrylbenzothiazole ethiodide and 2-4'-hydroxystyrylquinoline methiodide. The first two of these compounds are not adsorbed from water and the affinity of their hydroxy-groups is therefore insufficient to overcome the electrostatic repulsive forces. No conclusion could be reached regarding the cyanine dyes, because their solutions were decolorised by the film.

FIG. 5. *Adsorption isotherms of sodium alkyl sulphates on the anodic film on aluminium.*

a, Sodium oleyl sulphate, 40° (48 hr.) and 50° (24 hr.).
b, Sodium tetradecyl sulphate (same conditions).

Black circles : plotted on actual solution concentration basis.
White circles : plotted on relative solution concentration basis.

FIG. 6. *Adsorption isotherm of a sulphated azo-compound on the anodic film on aluminium at 37° (48 hr.) and 50° (24 hr.).*

The same range of initial bath concentrations was used at each temperature and the respective amounts adsorbed were in each case identical. The experimental points in Figs. 5 and 6 therefore each represent results at the two temperatures.

Basic dyes can be fixed in the film if it is pre-treated with an anionic compound to act as a mordant, *e.g.*, tannic acid, or H-acid (1-amino-8-naphthol-3 : 6-disulphonic acid) ; adsorption is then remarkably rapid and is complete in a few minutes.

Anionic Compounds : Sulphate Esters.—Two aliphatic anionic compounds, sodium oleyl and tetradecyl sulphates, were readily adsorbed. Surprisingly, neither exhibits a measurable temperature coefficient (Fig. 5). This may be evidence of a process of purely

physical adsorption, *i.e.*, ion-exchange, representing a transfer of solute ions from association with water in the liquid phase to association with water molecules held at the solid surface, no chemical valency bonds being formed or broken. Adsorption of cationic dyes from water by certain negatively charged surfaces (graphite, silica) has been found similarly to have a negligible temperature coefficient (Cullen, Macaulay, Theses, Glasgow, 1951). Patton and Ferguson (*Canad. J. Res.*, 1937, **15**, B, 103), and Rothmund and Kornfeld (*Z. anorg. Chem.*, 1918, **103**, 129; 1919, **108**, 215) have pointed out that temperature has little or no effect on base-exchange equilibria between ions of the same valency. Very low temperature coefficients have been observed also in cation-exchange on resins by Boyd *et al.*, Magistad *et al.*, Patton and Ferguson, and Vanselow (quoted by Walton, in "Ion Exchange," ed. Nachod, New York, Academic Press Inc., 1949, p. 20). Steinhardt, Fugitt, and Harris (*J. Res. Nat. Bur. Stand.*, 1940, **25**, 219; 1943, **30**, 123) found a very low value for the heat of adsorption of monochloroacetic acid on wool at low temperatures (0·3—0·4 kcal./mole). They supposed that this was due to replacement of a solvated molecule of water in the fibre by another of acid, held only slightly more strongly.

$$O_2N\underset{}{\overbrace{}}N{=}N\underset{}{\overbrace{}}N\underset{C_2H_4 \cdot O \cdot SO_3Na}{\overset{C_2H_5}{<}}$$

(I)

In confirmation that the sulphate ester group itself is responsible for the observed effect, and not the surface-active nature of the alkyl sulphates, an azo-dye (I) containing the group when applied to the film showed virtually no temperature coefficient (Fig. 6) and it must presumably be adsorbed by ion-exchange. A physical process of this type should be readily reversible, and indeed prolonged treatment with water at the temperature of adsorption desorbed the alkyl sulphates from the film, whereas Solway Blue B, which is chemically bonded, was not thus removed.

We therefore conclude that sulphate esters in general are adsorbed by the anodic film by a physical process of anion exchange, *i.e.*, they are not adsorbed on to specific sites in the oxide and no chemical reaction is involved.

Sodium oleyl sulphate apparently has a higher affinity for the film than has the tetra-decyl compound when the isotherms are plotted in the normal way, but this does not allow for the differences in water solubility of the two compounds. If this allowance is made by plotting as abscissae *relative* concentration values (*i.e.*, actual concentration/concentration at saturation point) it is seen (Fig. 5) that the oleyl compound has also the higher real affinity. This may be attributable to the differences in inter-molecular cohesion between the solute molecules in the adsorbed layer: the oleyl compound has the longer chain and will consequently have a greater tendency to form a condensed monolayer. Alternatively the unsaturated linkage in the oleyl chain itself may confer higher affinity for adsorbed water at the surface; it is, of course, well known that such linkages in long alkyl chains in monolayers confer higher affinity for the aqueous subphase (cf. Adam, "The Physics and Chemistry of Surfaces," Oxford Univ. Press, 3rd edn., 1941).

Anionic Compounds : Sulphonic Acids and Sulphonates.—Attention was next directed to sulphonated compounds, the simplest aromatic sulphonic acids being first examined. Benzenesulphonic acid and its sodium salt showed no measurable adsorption, and naphthalene-2-sulphonic acid was adsorbed to a very small extent. Virtually all sulphonated dyes, however, colour the film strongly, even those which contain no other group capable of combining with the substrate, *e.g.*, certain sulphonated aminotriphenyl-methane and *o*-hydroxyazo-compounds (Table 1). The attraction here must clearly be attributed to the sulphonic acid groups, and the non-adsorption of the simpler sulphonic acids must therefore be due to their high water solubility, which reduces the affinity for the substrate. (The sulphate esters described above have much lower water solubility). Attempts to promote adsorption of the sulphonic acids by reducing their solubility by the use of ethanol–water mixtures as solvents were unsuccessful and attention was therefore turned to aromatic sulphonates in which water solubility is reduced by "loading" with substituent groups unlikely themselves to take part directly in the adsorption process. Four types of compounds were chosen, containing as loading groups : (*a*) an additional condensed benzene ring; (*b*) a phenylazo-group; (*c*) an *o*-hydroxyphenylazo-system, in

which the hydrogen of the hydroxy-group is involved in a chelate ring; and (*d*) a long alkyl chain; also one compound with two of these loading groups present simultaneously.

Anthracenesulphonic acid and 2-nitronaphthalene-4 : 8-disulphonic acid were used as examples of type (*a*) but the results in some cases were believed to be complicated by catalytic oxidation and the use of these compounds was not pursued. Azobenzene-4-sulphonic acid represented type (*b*). It was measurably adsorbed and the adsorption showed a significant temperature coefficient, but in view of the possibility of oxidation,

FIG. 7. *Adsorption isotherms of sodium phenylazo-2-naphthol-3 : 6-disulphonate on the anodic film on aluminium.*

a, 40° (72 hr.); b, 52° (24 hr.).
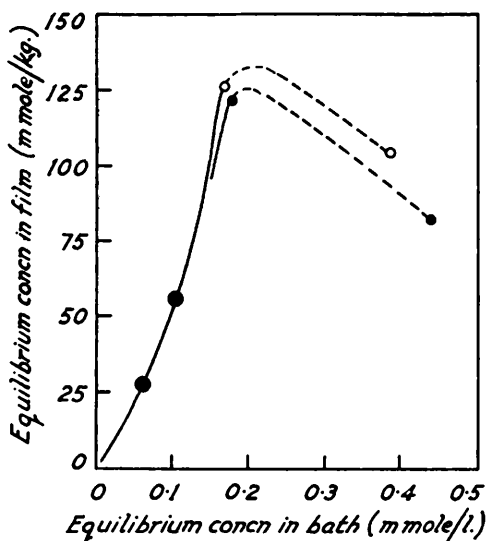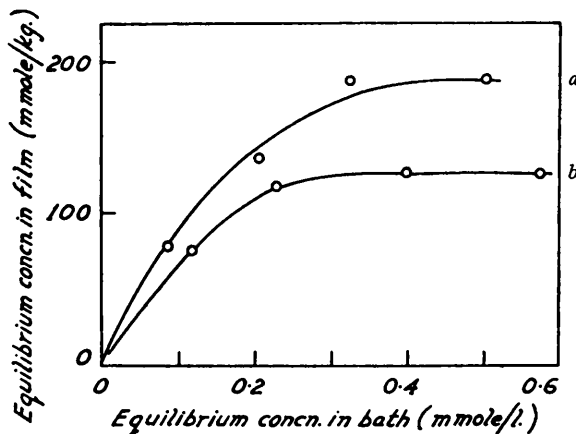
FIG. 8. *Adsorption isotherms of sodium dodecyltoluenesulphonate on the anodic film on aluminium.*
White circles : 37° (48 hr.).
Black circles : 50° (24 hr.).

as with azobenzene itself (see p. 4373), attention was directed more particularly to types (*c*) and (*d*).

Phenylazo-2-naphthol-3 : 6-disulphonic acid (C.I. 28) was used to represent class (*c*). This also showed considerable adsorption and a measurable temperature coefficient (Fig. 7; Table 2). Further details of the behaviour of this and related compounds will be given in a subsequent paper, but it is clear that the mechanism of adsorption of a sulphonic acid group by the film must differ fundamentally from that of a sulphate ester group. The heat change observed must, in fact, represent a chemical reaction, probably the formation of a salt between the acid group and aluminium.

The following observations also provide evidence in favour of the suggested salt

formation between the film and sulphonic acid groups : (*a*) traces of aluminium were detected (by Solochrome Cyanine R ; C.I. 722) in a solution of naphthalene-2-sulphonic acid (*ca.* 0·1 g./l.) which had been agitated for 24 hr. at 60° with a portion of anodised film, and then twice filtered. Evidently some aluminium salt of the sulphonic acid is dissolved out into the water (a solution of sodium oleyl sulphate which had been similarly treated

TABLE 2. *Apparent heats of adsorption on the anodic film.*

Solute	Solvent *	Temp. range	C_F (mmole/kg.)	ΔH (— kcal./mole)
Phenylazo-1-naphthol	B	40—60°	100—150	4·5—5
Sodium phenylazo-2-naphthol-3 : 6-disulphonate	W	40—52	50—100	7—8
Phenylazo-1-naphthylamine	C	39—58	20—60	21·5—22·5
Phenylazo-2-naphthylamine	C	36—50	20—60	10—10·5
2 : 4-Dinitrophenol	W	50—60	200—400	4·5—5·0
Phenol	W	40—60	100—400	4—4·5

* See footnote to Table I.
The adsorptions are exothermic and the sign convention is that ΔH is negative.
In Fig. 3 the isotherms are plotted on logarithmic abscissæ for ease of comparison of the ΔH values.

contained no aluminium, as would be expected if it is adsorbed only by ion exchange) ; (*b*) sulphuric acid combines with the film, because appreciable quantities of aluminium sulphate are present in films anodised in this acid (Pullen, personal communication).

Sodium dodecyltoluenesulphonate was used as representative of a compound of type (*d*). This is strongly adsorbed. At low concentrations it shows no measurable temperature coefficient, but at the higher concentrations a small difference in adsorption at two temperatures was observed (Fig. 8) together with a fall in adsorption with increase in bath concentration, which may be due to increasing association in solution. The compound was not precisely characterised, but it was certainly sulphonated in the nucleus. The surface-active properties of this compound appear in some manner to prevent salt formation by the sulphonic acid group, so that only ion-exchange adsorption can take place. Anionic micelles are perhaps involved in this case, and their surrounding layer of solvated water molecules may reduce the affinity between sulphonate groups and aluminium in the same way that benzenesulphonic acid is prevented from becoming attached to the film when dissolved in water. This behaviour is not characteristic of all higher alkyl sulphonates, because it is not shown, *e.g.*, by *p*-dodecylphenylazo-2-naphthol-3 : 6-disulphonic acid, which contains weighting groups of both types (*c*) and (*d*). This will be discussed in a subsequent paper.

Van der Waals Attraction.—There is no evidence that non-ionic compounds without hydrogen-bond acceptor groups are adsorbed. Their adsorption could occur only through van der Waals attraction, and in the concentrations used, the solvent itself being in great excess and subject to similar attraction, probably offers too much competition for the substrate.

One specific test was made in which *iso*octane was applied from benzene solution. It was hoped that this flexible hydrocarbon molecule might be capable of accommodation to the contours of the substrate better than the rigid molecule of the solvent and so the effect of competition might be reduced, but the results were inconclusive owing to apparent catalytic decomposition of the solute, though this may of course be the result of an initial adsorption process.

The Nature of the Isotherms and the Apparent Heats of Adsorption.—The isotherms for adsorption from organic solutes are all of the normal type (Brunauer type I) ; those for adsorption from water appear to be sometimes of type I and sometimes of types III or V. This matter will be discussed more fully in a subsequent paper, but it may be remarked here that the shape appears to be determined largely by the relative affinity of the solvent and solute for the surface. Thus in the case of a hydrogen-bonding compound in an organic solvent the affinity of the solute is greater than that of the solvent, but in the case of some anions in water it is less than that of the solvent and this is reflected in the shape of the isotherm.

The apparent heats of adsorption, calculated from the isotherms by the Clausius–Clapeyron equation, are shown in Table 2. Surprisingly they are almost constant in each case over the whole measurable range of the isotherms, within the experimental error.

The magnitude of the apparent heat of adsorption is not a direct indication of the number of bonds formed between adsorbent and adsorbate, in consequence of its being the algebraic sum of heat changes taking place in two successive processes, (*a*) the removal of solute from association with solvent and (*b*) the attachment of solute to substrate. It can, however, be used for comparative purposes in conditions where only one variable is altered; thus the values for the adsorption of phenol from aqueous solution on various substrates are: for cellulose triacetate $-2\cdot5$ kcal./mole (Cameron, personal communication), for nylon and wool -4 to $-4\cdot5$ kcal./mole (Chipalkatti, Giles, and Vallance, following paper), and for anodised aluminium -4 to $-4\cdot5$ kcal./mole. The closeness of these figures supports the hypothesis that hydrogen bonding is the principal adsorption force in each case.

An interesting point is that the apparent heat of adsorption on a given substrate appears to increase numerically with an increasing dissimilarity of structure between the solute and solvent. Thus phenylazo-1-naphthol in an aromatic solvent (benzene) gives a low numerical value, $-4\cdot5$ to -5 kcal./mole, but the very similar phenylazo-1- and -2-naphthylamine in an aliphatic solvent (carbon tetrachloride) give much higher values (about -10 and -22 kcal./mole respectively). Parallel phenomena in adsorption on nylon and wool have been attributed to entropy effects (Chipalkatti *et al.*, *loc. cit.*). Thus, if both solvent and solute are aromatic strong intermolecular forces will ensure close and ordered association of their respective nuclei. Consequently when the solute molecule is transferred from the solvent to an ordered layer at the substrate surface the entropy change is less than when the solute is aromatic and the solvent aliphatic; for in those circumstances the dissimilarity in the size and shape of the two types of molecules will lead to a much less ordered solvent–solute association and hence to a more pronounced increase in order on adsorption. On this argument, the relatively low values of the apparent heat of adsorption of the phenols point to an ordered association of water molecules and phenol molecules in solution.

Adsorption Promoted by Cross-linking Agents.—In consequence of the detection of several examples of hydrogen-bond cross-linkage of organic donor compounds in solution or in monolayers on water, by bifunctional solutes, *e.g.*, water or quinol (Giles, Rose, and Vallance, *J.*, 1952, 3799; Allingham, Giles, and Neustädter, *Discuss. Faraday Soc.*, 1954, **16**, 92), tests were made to discover whether a similar type of " bridge " linkage can " key " donor solutes to the anodic film. A number of these compounds, principally azo-compounds, were applied from non-aqueous solvents in presence of a little water, resorcinol, or quinol. In view of the possible catalytic oxidation special precautions were taken to exclude air from the test-tubes and in some cases films anodised in sulphuric acid were used to avoid the presence of traces of chromium. Many of the solutions were examined spectrographically before and after the tests, but no firm evidence was obtained of

TABLE 3. *Effect of " bridging " compounds on adsorption from benzene.*

Solute	Adjuvant	Initial concn. (g./l.) Solute	Adjuvant	Temp.	Time (hr.)	C_F (mmole/kg.)
p-Aminoazobenzene	—	0·15	—	25°, 50°	48, 24	0
,, ...	Quinol	,,	0·5	40	24	30
Azobenzene	—	0·2	—	25, 50	48, 24	0
,, ...	Quinol	,,	0·5	25, 50, 55	48, 24, 24	110, 80, 60
p-Nitrophenylazo-2-naphthol ...	—	0·05	—	60	72	0
,, ,, ...	Resorcinol	0·05	0·5	,,	,,	20

decomposition, except in some solutions of azobenzene in aqueous ethanol, though several of the results obtained were erratic and non-reproducible. In a number of cases, however, there were indications that the presence of the adjuvant can promote adsorption of donor compounds. A few typical results are summarised in Table 3. The action of water in these cases may not of course be to form a cross-linkage, but rather to form some aluminium hydroxide in the film, which may then unite directly with the donor solute.

In control tests in which phenol was used as adjuvant to the solutions in place of quinol no evidence of adsorption of donor compounds was obtained. Phenol could not of course act as a bridging compound.

EXPERIMENTAL

Materials.—Reagents and solvents were purified commercial or laboratory samples, except for a few dyes used in qualitative tests, which were of ordinary commercial quality. Sulphonated azo-dyes were purified by passage through columns of anionic and cationic exchange resins in series, the resultant free acid being subsequently neutralised with sodium hydrogen carbonate. Janus Red B (C.I. 266) was purified by recrystallisation from water; the sulphate ester dye from aqueous ethanol, after being salted out with sodium chloride; and the water-insoluble cellulose acetate ("Dispersol" and "Duranol") dyes by (Soxhlet) extraction with benzene. Pure sodium oleyl sulphate was obtained by continuous extraction of the commercial detergent (Lissapol C; Imperial Chemical Industries Limited) with ethanol. The sample of sodium tetradecyl sulphate (96·5%) was kindly supplied by Dr. M. A. T. Rogers. Non-aqueous solvents were completely dried. The "specially dried" quality of dioxan (B.D.H.), as supplied for Karl Fischer titrations, was used.

The aluminium foil (0·002 in.) was of 99·99% purity, though trials with material of normal commercial purity which may contain up to 1% of impurities, chiefly iron and silicon (Pullen, personal communication), did not give noticeably different results.

Azobenzene-4-sulphonic acid. Azobenzene (1 mol.) was heated at 130° for 15 min. with 20% oleum (5 mol.). The mixture was then cooled in ice and carefully drowned in twice its volume of ice and water. The crystalline precipitate was filtered off, washed with the minimum amount of cold water, and dried at 100°. It formed orange plates, m. p. 127°.

Sodium dodecyltoluenesulphonate. A sample was kindly supplied by Dr. M. A. T. Rogers and Imperial Chemical Industries Limited, Dyestuffs Division, as a brown greasy paste, purity 73·5% (by titration against cetyltrimethylammonium bromide); moisture content, 11%; the remaining impurities were stated to be probably other homologues and/or sodium sulphate.

Anthracenesulphonic acid. A commercial sample of anthraquinone-1-sulphonic acid was recrystallised several times from water, and then reduced by zinc dust and acetic acid.

Determination of Solubility of Sodium Alkyl Sulphates.—Excess of sodium tetradecyl or oleyl sulphate was shaken with 10 c.c. of distilled water at 45° (*i.e.*, a temperature intermediate between those used for the adsorption measurements) for 2 hr. The mixture was then rapidly filtered and the filtrate cooled and analysed (bromophenol-blue). Solubilities of 425 and 450 mmole/l. respectively were recorded.

Preparation of Substrate, and Adsorption Procedure.—The anodising cell was a 2-l. glass beaker immersed in a thermostat tank. The anode was a strip of aluminium foil (8 × 2 in.), the cathode a strip of lead (8 × 2 × 1/16 in.), and the electrolyte 3% aqueous chromium trioxide (analytical reagent quality). The electrodes, extending 1 in. above the liquid surface, and connected through a variable resistance to a direct current supply, were maintained at a fixed distance apart by a skeleton frame of "Perspex." The electrolyte was agitated by a slow-speed stirrer placed between the electrodes, ensuring constancy of film weight over all parts of the anode within ±0·5%.

Before treatment, the metal foil was cut to shape, smoothed flat on a hard surface and cleaned of grease with cotton wool moistened with carbon tetrachloride. The electrolyte was heated to 45° before use and maintained at 45° ± 1° throughout the treatment. The voltage was adjusted to 45, which ensured a current density of *ca.* 6 amp./sq. ft. of anode. Electrolysis was continued for 1 hr. with unmodulated direct current, providing a film about 6 μ thick, representing about 20% conversion of metal into oxide. With rectified alternating current the time of electrolysis must be nearly doubled to obtain equal conversion. For accurate work the electrolyte was renewed for each portion of foil.

In special cases where sulphuric acid-treated film was required, a 20% (w/v) solution of sulphuric acid was used at 25° ± 2°, at 12 v.

After removal from the electrolyte, the anode was well rinsed in distilled water, dried at 130—140° for 1 hr., stored in a desiccator, and used within 24 hr. Tests with a typical sulphonated azo-dye showed that the film began to lose its adsorptive powers after this period of storage; this is believed to be due to changes in the lattice structure of the alumina affecting the pore size (Pullen, personal communication).

For use the treated material was cut into strips ¼—½ in. wide, each piece being weighed

before use. The amount of film was determined by weighing each piece after its use in the adsorption test, and after boiling in a stripping solution containing phosphoric acid (85%; 35 c.c.), chromium trioxide (20 g.), distilled water (to 1 litre) (Edwards, *Amer. Soc. Test. Mat.,* Preprint 19, June 1940, 14; through *Brit. Abs.,* 1941, BI, 37); then rinsing and drying at 110°. The process was repeated to constant weight, though usually one 5-min. treatment was sufficient. The film was removed, but the metal remained intact.

For the adsorption tests the weight of liquor was varied from about 100 to 500 times that of the film used, according to the affinity of the solute, the aqueous solutions being placed in ground-glass or rubber-stoppered test-tubes, and the organic solvent solutions in completely sealed glass tubes. The tubes were mechanically shaken at 35 or 20 r.p.m. in a thermostat. The experiments with lake-forming dyes were made under conditions of less vigorous (hand) agitation, so that the rate of adsorption was lower than it would be with regular mechanical agitation (cf. Rideal, *Discuss. Faraday Soc.,* 1954, **16**, 9).

The amount of solute adsorbed was in all the quantitative tests determined by analysis of the solutions before and after treatment, the final liquors being filtered to remove traces of abraded alumina. It was impracticable to determine the amount of solute adsorbed in the film other than by this difference method, because no satisfactory procedure for the removal of adsorbed material from the film could be found. Very concentrated solutions cannot therefore be reliably employed because of the relatively small concentration changes. In practice, however, this limitation is unimportant.

Determination of sign of charge on film. Electrolysis was continued until anodisation was complete (*ca.* 4 hr. with direct current). At this point the metal had disappeared and the current fell suddenly almost to zero. The film had become a brittle sheet of alumina, but isolated specks of free metal remained and made the film difficult to grind. They were removed by careful treatment with hydrochloric acid, after which the oxide was thoroughly rinsed in distilled water until free from acid, and then ground with water in a mortar to a fine white suspension. The charge was determined by introducing this suspension, diluted to 1 g./100 c.c., into a standard electrophoresis U-tube, carefully adding more water, and applying 250 v (d.c.). The suspension moved towards the negative pole. Addition of sodium chloride in increasing quantities steadily reduced the rate of flow to zero and then reversed it and caused it to increase in the opposite direction, the isoelectric point occurring in solutions of about 0·09% sodium chloride content.

Analyses.—The following methods of determining the concentration of the solutes were employed. Amines, naphthalene derivatives, nitro-compounds : photoelectric absorptiometry with a tungsten or mercury vapour lamp. Free sulphonic acids : direct or electrometric titration, or photoelectric absorptiometry, as appropriate. Phenol : volumetric analysis by the potassium bromate–bromide method (Koppeschaar, *Z. anal. Chem.,* 1876, **15**, 233; cf. *J.,* 1877, *i,* 746). Catechol, resorcinol, and quinol : volumetric analysis with potassium permanganate by Pence's method (*J. Ind. Eng. Chem.,* 1913, **5**, 218). Sodium alkyl sulphates and dodecyltoluenesulphonic acid : titration against pure cetyltrimethylammonium bromide, using chloroform and bromophenol-blue indicator (Barr, Oliver, and Stubbings, *J. Soc. Chem. Ind.,* 1948, **67**, 45). *iso*Octane : by absorptiometry at 2800 Å.

Sodium benzenesulphonate was first converted into the free acid by passage in aqueous solution through a column of an ion-exchange resin ("H⁺ cycle"); this material, uniformly packed in a long separating funnel, provided with a swan-neck at the exit end, was first washed with 100-c.c. portions of boiled distilled water, which were then titrated against 0·01N-sodium hydroxide until two successive portions gave an equal titre. This was taken as the blank reading and subtracted from the actual titre. Portions (25 c.c.) of the sodium salt solutions were passed through the column, followed by three successive 25-c.c. portions of distilled water, and the whole was titrated with 0·01N-sodium hydroxide. A similar method was used by Futterknecht (*Teintex,* 1949, **14**, 191) for the analysis of sodium sulphate in dye-baths, this being otherwise difficult to determine.

The purity of dye samples was determined by the acid–dichromate oxidation method (Arshid, Desai, Giles, and McLintock, *J. Soc. Dyers Col.,* 1953, **69**, 11).

Spectroscopic measurements were made with a Unicam S.P.500 Spectrophotometer and absorptiometric determinations with the same apparatus or with a Hilger Spekker photoelectric absorptiometer.

Catalytic action and film loosening. Erratic and non-reproducible results noticed in a number of the adsorption tests are attributed to the anodic film promoting catalytic decomposition of some solutes. Feachem and Swallow (*J.,* 1948, 267) find that γ-alumina is the catalytically active

species and that the materials usually employed as catalysts, prepared by dehydration of boehmite, AlO(OH), owe their activity to the presence of this species. Alumina is, of course, well known as a catalyst in organic reactions at high temperatures, and some observations on its ability to decompose substances on the chromatographic column are on record. The following observations were made in the present tests, though no systematic work has been carried out to confirm them. Decomposition occurs with some amino-, azo-, and triphenyl-methane compounds and appears to take place most readily in hydroxylic solvents. Water, aqueous ethanol, dry ethanol, dry dioxan, and dry benzene appear to form a descending series in effectiveness, and indeed only 1-naphthylamine, a very readily oxidisable substance, was noted as being particularly affected in dry benzene; this occurred at considerable dilution, perhaps partly by air oxidation. The action in nearly all cases was shown by an increased optical density of the solutions, though some triphenylmethane dyes, *e.g.*, Acid Green M conc. (C.I. **669**), Acid Magenta (C.I. **692**), and the two cyanine dyes, were irreversibly and completely decolorised. The facts seem consistent with oxidation of the affected azo-compounds, resulting possibly in the introduction of hydroxy-groups into the solute molecule; the oxidised product may then itself be adsorbed by the film. In one case (anthracene-2-carboxylic acid) a pressure of gas was generated sufficient to burst the sealed tubes.

Another difficulty sometimes encountered is loosening of the film, which flakes off from the surface or can be readily removed by rubbing with the finger. This also seems erratic in its occurrence, and the exact conditions favouring it have not been identified. It has not been noticed to occur in non-aqueous solutions, but high temperature, severe agitation, increasing numbers of sulphonic acid groups in the molecule, and the presence of inorganic salts (Pullen, personal communication) all appear to favour film disintegration, but not consistently.

Traces of the oxide film sometimes become detached by abrasion and remain suspended as very fine particles in the solvent (whether aqueous or non-aqueous). Suspensions of the oxide in carbon tetrachloride have an absorption peak at 3450 Å, consequently when ultra-violet radiation was used for determination of solutes after adsorption the liquids were filtered or centrifuged before analysis, and the absorptiometric measurements of solute concentration were made wherever possible in the visible region.

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