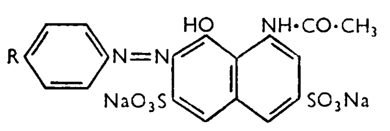
612. *Studies in Monolayers. Part V.* Formation of Monolayers by Sulphonated Azo-dyes on Water and Aqueous Solutions.*

By A. Cameron and C. H. Giles.

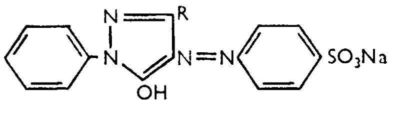
Research on the monolayer-forming properties, on water and inorganic acid and salt solutions, of water-soluble sulphonated azo-dyes is reported. Cetyltrimethylammonium bromide or inorganic salts aid in forming condensed monolayers, but on pure water even dyes with long alkyl chains spread incompletely.

Few investigations of the behaviour of dyes in monolayers on water have been reported. In previous papers the film-forming properties of unsulphonated surface-active dyes, *e.g.*, phenylazonaphthol compounds with substituted long alkyl chains, on water, acids, alkalis, and solutions of a variety of organic solutes have been described, and also the properties of mixed films of dyes and models for fibres.[1] Dyes containing long alkyl chains, and therefore having potential surface-activity, are technically important.

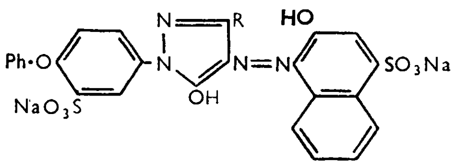
The effect of inorganic ions upon monolayers of dyes has not apparently been studied, but several investigators have examined [2] the reactions of metal ions with monolayers of long-chain fatty acids, and their reactions with sulphated compounds have also been recorded.[3] On neutral or alkaline solutions these monolayers occupy a smaller area than on acids, because of dissociation and partial solution. Solidification of the monolayer occurs only in presence of complexes of metal ions which stabilise it by hydrogen bonding; Ba^{2+} and Ca^{2+} produce no condensing effect because the salts they form are partially soluble.



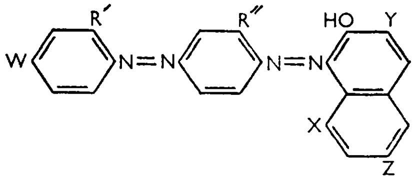
(I) R = H; (II) R = n-C_4H_9; (III) R = n-$C_{12}H_{25}$.



(IV) R = CH_3; (V) R = $C_{17}H_{35}$.



(VI) R = CH_3; (VII) R = $C_{17}H_{35}$.



(VIII) W, X, R′, R″ = H; Y, Z = SO_3Na.
(IX) W, X = SO_3Na; R′, R″ = CH_3; Y, Z = H.

We have used the sulphonated azo-dyes (I—IX), most of which can be spread as monolayers on water from solutions in benzene–ethanol–water. When inorganic salts and acid solutions are used as substrates, or a cationic agent is added to the dye solution before spreading, all the dyes form films which in suitable conditions reach or approach the state of true condensed monolayers.

The characteristics of the films are shown in the Tables and typical force–area curves, etc., in Figs. 1 and 2. In Table 1 the areas occupied in the films at zero compression are compared with theoretical values measured from models. The models indicate that the

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* Part IV, Allingham, Giles, and Neustädter, *Discuss. Faraday Soc.*, 1954, **16**, 292.

[1] Allingham, Giles, and Neustädter, *Discuss. Faraday Soc.*, 1954, **16**, 292.

[2] *E.g.* (*a*) Adam, *Proc. Roy. Soc.*, 1921, *A*, **99**, 336; (*b*) Langmuir and Schaefer, *J. Amer. Chem. Soc.*, 1936, **58**, 284; (*c*) Sasaki and Matsuura, *Bull. Chem. Soc. Japan*, 1951, **24**, 274; (*d*) Wolstenholme and Schulman, *Trans. Faraday Soc.*, 1950, **46**, 475; (*e*) *idem, ibid.*, 1951, **47**, 788; (*f*) Havenga, *Rec. Trav. chim.*, 1952, **71**, 73; (*g*) Webb and Danielli, *Nature*, 1940, **146**, 197.

[3] Thomas and Schulman, *Trans. Faraday Soc.*, 1954, **50**, 1131.

aromatic portions of all the dye molecules are planar, and the theoretical values given are calculated on this basis. They are given to the nearest 5 Å, and represent the smallest rectangle enclosing the projection of the model, no allowance being made for solvated water molecules around the sulphonate groups. The value for the cross-sectional area of the cetyltrimethylammonium ion measured in this way is about 31 Å^2, the same as the experimental value quoted by Schulman [4] but rather less than Pankhurst's [5] calculated value.

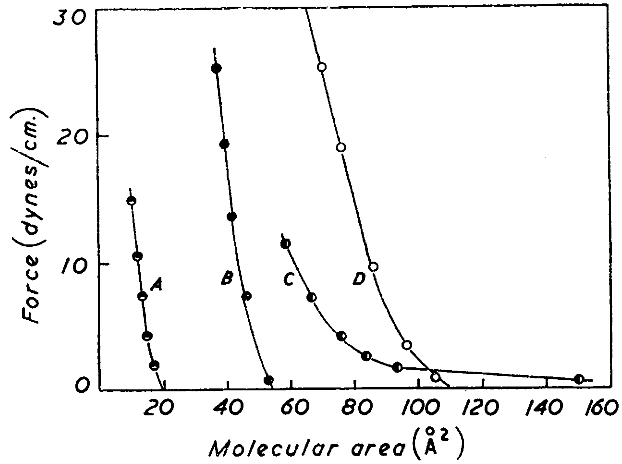

FIG. 1. *Force–area curves for sulphonated azo-dyes with alkyl side-chains.*

Dyes: *A*, (III) on distilled water; *B*, (III) on 0·2M-BaCl$_2$; *C*, (VI) on 4M-NaCl; *D*, (VII) on 3M-NaCl.

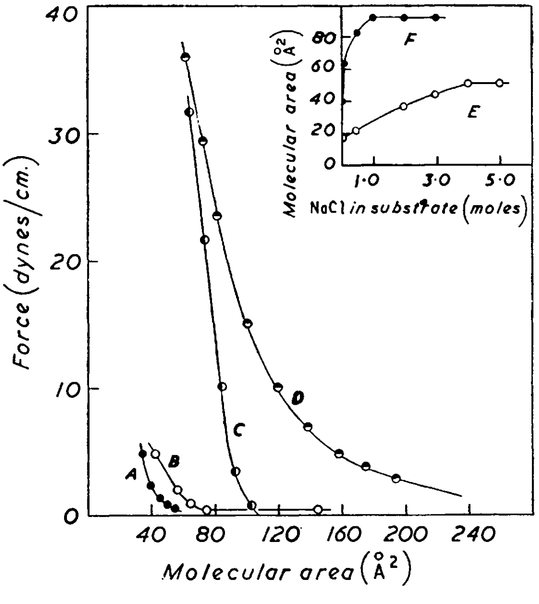

FIG. 2. *Force–area curves for sulphonated azo-dyes and (inset) the effect of sodium chloride on molecular areas of surface-active dyes at zero compression.*

Dyes: *A*, (IX) on 4M-NaCl; *B*, (VIII) on 4M-NaCl; *C*, (I) + cetyltrimethylammonium bromide on distilled water; *D*, (I) + cetyltrimethylammonium bromide on 4N-NaCl; *E*, (III); *F*, (VII).

Sulphonated Dyes spread on Pure Water.—The long-chain (C$_{17}$) monosulphonated dye (V) forms a condensed film on water, but the molecular area is only about 20% of the theoretical. (The long-chain sulphate esters on water occupy more than this proportion of their theoretical areas.[3]) The disulphonated long-chain (C$_{12}$ and C$_{17}$) dyes (III) and (VII) also give condensed films, but their areas are still lower (*ca.* 25% of the theoretical). The shorter-chain dyes (I), (II), (IV), and (VI) do not give films on pure water.

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[4] Schulman, in discussion following ref. 5.

[5] Pankhurst, *Discuss. Faraday Soc.*, 1949, **6**, 52.

Sodium Chloride Solutions as Substrate.—Sodium ions reduce the solubility of all these dyes by the common-ion effect, and tend to improve the film-forming properties. The dyes with the smallest molecules [(I), (II)] still do not form films, however, even on salt solutions concentrated enough to precipitate them completely. Presumably under these conditions the dyes exist as floating aggregates. Those with medium-sized molecules and well-spaced hydrophilic groups, but no alkyl chains [(IV), (VI), (VIII), (IX)] tend to form gaseous films, with a force of *ca.* 0·5 dyne/cm. at very large areas on 4M-salt solution. The long-chain dyes form condensed films approaching the theoretical molecular areas on concentrated salt solutions.

TABLE 1. *Molecular areas* (Å) *and compressibilities* (Å^2 *dynes*$^{-1}$ *cm.*$^{-1}$) *of sulphonated azo-dyes.**

				Molarity of salt solution in substrate ‡							
Dye	CTAB (mol.) †	Area (calc.)	H$_2$O	0·1 *0·0002*	0·5 *0·005*	1·0 *0·02*	2·0	3·0	4·0	5·0	*0·2*
(I)	2	125	92(0·95) 108, 86						119(1·6) 280, 98		
(III)	—	65	17(0·46) 20, 17		27(0·40) 44, 20		39(0·40) 60, 32	46(0·50) 66, 40	53(0·40) 72, 44	53(0·40) 72, 44	*47(0·35)* *54, 42*
(IV)	—	80	×						57(2·2) 150, 46		
(IV)	1	110	52(0·80) 88, 46						74(0·70) 140, 60		
(V)	—	80	22(0·42) 29, 19					72(0·90) 85, 58			*65(0·90)* *77, 54*
(VI)	—	120	×						79(2·0) 150, 67		
(VI)	2	180	98(1·2) 148, 84						166(2·5) 256, 148		
(VII)	—	120	40(0·50) 46, 38	61(0·70) 82, 56	82(0·80) 98, 72	92(0·90) 106, 86	92(0·90) 106, 86	92(0·90) 108, 82			
(VII)	—	120	40(0·50) 46, 38	*53(0·7)* *60, 46*	*67(0·7)* *74, 62*	*84(0·8)* *94, 78*					*84(0·80)* *94, 78*
(VII)	2	180	134(1·7) 148, 114				143(1·6) 162, 113		143(1·6) 162, 113		*143(1·6)* *162, 113*
(VIII)	—	65	×						61(4·0) 150, 50		
(VIII)	2	130							148(1·8) 280, 110		
(IX)	—	120	×						42(2·5) 150, 36		
(IX)	2	180	116(1·2) 160, 96						158(2·0) 255, 136		

* The compressibility, in parentheses, follows the area at zero compression. The last two figures in each entry are the area at commencement of development of measurable surface pressure and that at the lowest point of the linear portion of the force–area curve.

† Cetyltrimethylammonium bromide. ‡ Roman numerals, NaCl; italics, BaCl$_2$.

× No film formed.

TABLE 2. *Effect of change of* pH *on monolayers of dye* (VII).

Substrate	pH	Apparent molecular area *	Compressibility †	Substrate	pH	Apparent molecular area *	Compressibility †
Buffer	4·2, 3·1	49, 60, 44	0·56	5×10^{-4}M-BaCl$_2$	10·1, 8·1, 7·2, 6·6	57, 62, 51	0·80
	2·1	53, 73, 45	0·69				
	1·6	75, 107, 60	1·13	10^{-3}M-CuCl$_2$ ...	6·1	53, 64, 50	0·63
0·1N-HCl ...	1·2	90, 119, 76	1·00		5·2	48, 64, 44	0·55
1·0N-HCl ...	0·4	90, 119, 76	1·00		4·4	36, 46, 33	0·40
					3·1	45, 54, 39	1·20

* In Å^2, at zero compression, first measurable pressure, and lowest point of force–area curve, respectively.

† From force–area curve (Å^2 dyne^{-1} cm.$^{-1}$).

The films of dyes (IV) and (VI) are not very stable, and collapse at fairly low surface pressures (11 and 12 dynes/cm. respectively); their areas at zero compression (by extrapolation) are only slightly less than those of their respective long-chain homologues, so that the orientation must be similar. This appears to be more or less perpendicular to the water surface, with the sulphonate group or groups in the lowest possible position, except for (IV) and (V) where the hydrophilic nature of the hydroxyazo-chelate ring causes the molecule to stand with both this ring and the sulphonate group level with the surface (cf. the similar effect of the hydroxyazo-group in unsulphonated azo-dyes[6a]).

The Effect of Change of pH.—One long-chain dye (VII) was spread on a series of acid solutions of decreasing pH. Rise of acidity reduces solubility by suppressing ionisation of the sulphonate groups, and causes an increase in film area, until at pH 1·2 complete spreading of the dye appears to be attained. The film on acid is slightly more compressible than that on salt solutions, perhaps because of the smaller size of the ionic head-group in the acid form.

The agreement of the molecular areas found for each dye with those estimated from models, without allowance for any water atmosphere round the sulphonate groups, suggests that the water held between these groups is largely forced out when the films are compressed. This is confirmed by the small decrease in molecular areas (*ca.* 8 $Å^2$) when the bivalent barium ion replaces sodium as the cation. Any water cross-bonded to adjacent pairs of azo-groups (as in the unsulphonated azo-dyes [1a]) could be accommodated between the dye molecules, because the sulphonate groups are thicker than the aromatic nuclei.

Barium Chloride Solutions as Substrates.—Complete spreading is obtained with much more dilute solutions of this salt than of sodium chloride, because of the much lower solubility of the barium salts of the dyes, but the maximum molecular areas obtained at a given pH are slightly less than those on sodium chloride, by almost the same amount in each case; the film compressibility is not altered. The effect is similar to that of barium on, *e.g.*, stearic acid.[2c] The sulphonate groups are apparently therefore linked intermolecularly in pairs by the bivalent barium ion, and the decrease in area is attributable to the absence of the water atmosphere between the two sodium ions.

Change of pH, both inside and outside the range in which basic barium ions are formed, did not alter the monolayers of dye (VII) spread on barium chloride. The insolubilising effect of barium on this dye must therefore be due to simple salting-out rather than to cross-bonding.

Cupric Chloride Films as Substrates.—Copper and other metal salts have been used to form condensed monolayers of partially soluble or incompletely spreading surface-active substances; thus films of myristic acid or long-chain sulphates are changed from liquid-expanded to solid types in presence of basic complex copper carbonate ions.[2d, 3] The dye (VII) was therefore spread on 10^{-3}M-cupric chloride solutions saturated with carbon dioxide at pH values between 3·1 and 6·1. Very incompressible films are formed between pH 4·4 and 6·1, the area of the film increasing with pH but being always less than the theoretical. Apparently a cross-linked network of dye anions and complex copper carbonate ions is formed, which is fairly soluble in water. At pH 3·1 the compressibility is similar to that on acidic sodium chloride, and the complex copper–dye network is probably absent.

Mixed Films with Cationic Agent.—When the dyes are mixed with equivalent quantities of cetyltrimethylammonium bromide all of them spread on pure water. The apparent molecular areas are somewhat less than those calculated for a completely condensed film in which each sulphonate group is associated with one molecule of the cationic agent, so that partial solution of the dye–cationic agent complex must be taking place. On sodium chloride solutions, however, the mixed films give molecular areas much nearer the theoretical. The mixed films are usually much more compressible when the dye has no long alkyl chain than when it has a C_{12} or C_{17} chain, and evidently the alkyl chain prevents the dye from being forced down into the water under pressure.

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[6] Giles and Neustädter, (*a*) *J.*, 1951, 918; (*b*) *J.*, 1952, 1864; (*c*) *J.*, 1952, 3806.

EXPERIMENTAL

The dyes were purified specimens, some prepared by us; distilled water was used, and inorganic materials were of Analytical Reagent quality. All experiments were made at room temperature. Cetyltrimethylammonium bromide was 99% pure.

The design of the film balance used is developed from one described by Allan and Alexander.[7] The trough and movable barrier are machined from solid blocks of Polythene and bolted to a heavy brass plate to ensure rigidity. The only paraffin-wax coating required is a small amount covering the countersunk bolt heads. The floating barrier is made of Teflon (polytetrafluoroethylene) attached by fine Polythene threads to the trough and suspended from the balance head; this swings on agate knife-edges, and carries the usual mirror for the optical lever system. The whole apparatus is enclosed in a metal case and the controls are operated from outside.

All the dyes, alone or mixed with cetyltrimethylammonium bromide, were spread from solutions in water–ethanol–benzene (1 : 2 : 2, v/v).

Stuart-type atomic models (Catalin Ltd.) were used to measure molecular dimensions.

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[7] Allan and Alexander, *Trans. Faraday Soc.*, 1954, **50**, 863.