864. *Researches on Monolayers. Part VI.* A Study of Reactions in Surface Films of Acetates and Ketones, and their Relation to Adsorption by Cellulose Acetate.*

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Monolayers of cetyl acetate, cellulose triacetate, methyl stearyl ketone, and ethyl stearyl ketone have been spread on water and aqueous solutions of a variety of aliphatic and aromatic compounds; a mixed film of cellulose triacetate with a non-ionic " disperse " dye for cellulose acetate has also been examined. The molecular area and compressibility data show that in presence of water the ketone group has much weaker hydrogen-bonding power than the acetate group, and the films of the ketones are consequently expanded much less by all the solutes than the acetate films are. Highly ionised compounds, including sulphonated dyes, cause considerable expansion of the cellulose triacetate films, even though they have no affinity for the same material in bulk.

The results are used to interpret the mechanism of adsorption of solutes by cellulose acetates.

Previous papers in this series [1,2] have described various types of hydrogen-bonding reactions between monolayer molecules on water and solutes in the water beneath. The results in one case [2] were used to interpret the mechanism of adsorption of solutes by cellulose and cellulose acetate. The present investigation is an attempt to use reactions in monolayers in a more detailed manner to throw light on the mechanism of adsorption of solutes by cellulose acetates.

The substances spread as monolayers were cellulose triacetate, cetyl acetate, ethyl

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[1] Giles and Neustädter, *J.*, 1952, 3806.
[2] Allingham, Giles, and Neustädter, *Discuss. Faraday Soc.*, 1954, **16**, 92.

stearyl ketone, methyl stearyl ketone, etc.   The second and third have almost identical molecular area and compressibility as films (cf. Table 1), and their alkyl chains are nearly equal in length, but their polar groups differ in hydrogen-bonding properties.   Thus they

TABLE 1. *Molecular areas, compressibilities, etc., of monolayers of acetates and ketones.*

Substrate (aq. soln.) Water	Cetyl acetate *a* *			*b* †	Ethyl stearyl ketone *a*			*b*
	24	40	21	0·4	25	29	24	0·5
Group I								
0·1M-Ethylene glycol	30	53	25	0·6	—	—	—	—
0·1M-Mesaconic acid	28	53	24	0·5	—	—	—	—
4·5M-Urea	45	75	35	1·4	29	—	25	0·67
0·1M-Ethyl methyl ketone	—	—	—	—	—	—	—	—
Group II								
0·1M-Benzenesulphonic acid	27	55	21	0·5	—	—	—	—
0·1M-Benzoqúinone	27	55	21	0·5	—	—	—	—
0·1M-Phenol	60	90	47	3·0	—	—	—	—
0·1M-Pyridine	27	47	24	0·45	—	—	—	—
0·1M-Quinol	62	75	50	1·7	32	55	27	1·0
0·1M-Sucrose	25	—	18	0·5	—	—	—	—
Group III								
0·01M-Acid magenta	—	—	—	—	—	—	—	—
0·00025M-Pinacyanol	83	110	72	1·7	34	45	30	0·82
0·025M-2 : 2'-Dipyridyl	59	76	54	1·8	—	—	—	—
0·01M-Sulphato-ester dye	—	—	—	—	30	50	23	1·05
0·01M-Anthraquinone-2-sulphonic acid	—	—	—	—	—	—	—	—
Dispersol fast crimson B (mixed film)	—	—	—	—	—	—	—	—

Substrate (aq. soln.) Water	Methyl stearyl ketone *a*			*b*	Cellulose triacetate *a*			*b*
	21	26	20	0·2	37	60	34	0·4
Group I								
0·1M-Ethylene glycol	—	—	—	—	—	—	—	—
0·1M-Mesaconic acid	23	32	23	0·4	—	—	—	—
4·5M-Urea	—	—	—	—	70	87	63	1·15
0·1M-Ethyl methyl ketone	—	—	—	—	41	54	34	0·71
Group II								
0·1M-Benzenesulphonic acid	—	—	—	—	—	—	—	—
0·1M-Benzoquinone	—	—	—	—	—	—	—	—
0·1M-Phenol	—	—	—	—	—	—	—	—
0·1M-Pyridine	—	—	—	—	—	—	—	—
0·1M-Quinol	30	44	27	0·5	42	64	45	0·56
Group III								
0·01M-Acid magenta	—	—	—	—	77	70	95	1·0
0·00025M-Pinacyanol	32	44	28	0·45	60	87	55	0·75
0·025M-2 : 2'-Dipyridyl	36	68	28	0·9	48	—	—	—
0·01M-Sulphato-ester dye	—	—	—	—	65	90	55	1·4
0·01M-Anthraquinone-2-sulphonic acid	—	—	—	—	40	54	35	0·54
Dispersol fast crimson B (mixed film)	—	—	—	—	37	60	34	0·4

* The three figures under *a* show, in order: Molecular area (Å²) at zero compression, at commencement of development of measurable surface pressure, and at lowest point of upper linear part of force–area curve.

† Film compressibility, *b*, is expressed as slope of upper section of force–area curve (units: Å²/dynes/cm.).

should have almost identical non-polar attraction, but different polar attraction for solutes introduced into the water phase, and any differences between their films in penetrability or expansion by the solute will thus be attributable to differences in the polar attraction of the keto- and the acetyl group.   Polar attaction by the keto-group is in fact likely to be

very low, because ketones do not appear to form hydrogen-bond complexes with other solutes in water,[3] whereas acetates do.[4]

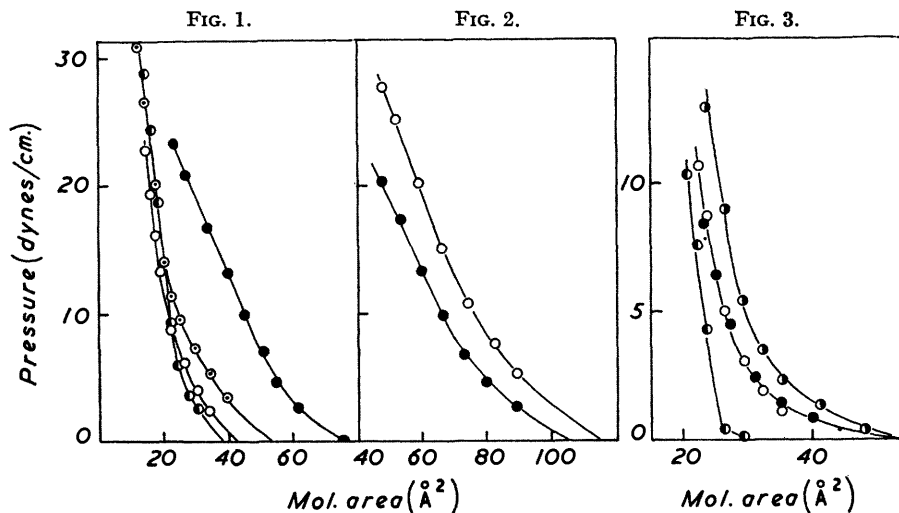The solutes used are water-soluble compounds of varied molecular sizes and shapes.

FIG. 1.   FIG. 2.   FIG. 3.

FIG. 1.   *Cetyl acetate on various substrates*: ◯, 0·1M-Sucrose; ◐, 0·1M-pyridine; ⊙, 0·1M-benzo-quinone; ●, 0·1M-quinol.

FIG. 2.   *Cetyl acetate on dye solutions*: ◯, 0·01M-Acid magenta; ●, 0·00025M-pinacyanol.

FIG. 3.   *Ethyl stearyl ketone on various substrates*: ◐, Water; ●, 0·1M-quinol; ◑, 0·002M-pina-cyanol; ◯, 4·5M-urea.

FIG. 4.   FIG. 5.
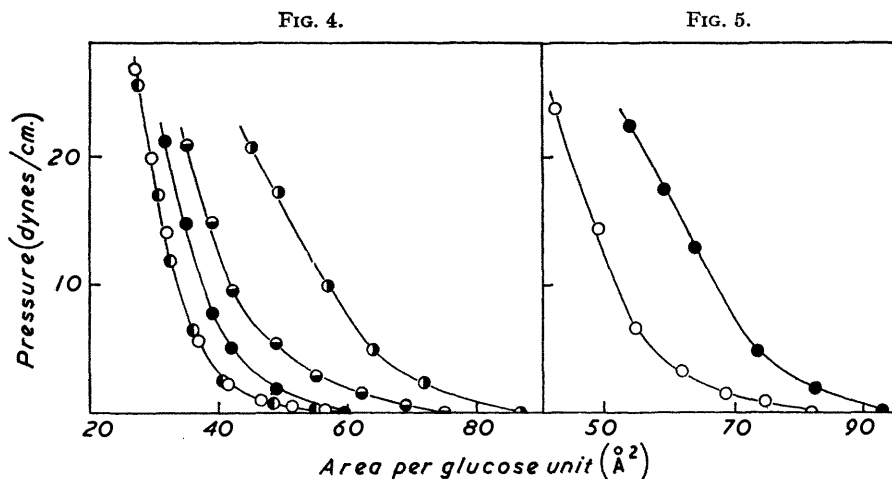
FIG. 4.   *Cellulose triacetate on various substrates*: ◯, Water; ●, 0·1M-quinol; ◑, 4·5M-urea; ◓, 0·025M-2 : 2'-dipyridyl; ◐, dispersol fast crimson B (mixed film).

FIG. 5.   *Cellulose triacetate on various substrates*: ◯, 0·0002M-Pinacyanol; ●, 0·01M-acid magenta.

The results are summarised in Tables 1 and 2 and in the Figures.   The normal molecular area and compressibility data are given, together with other parameters sufficient to characterise the curves (Tables 1 and 2).

[3] Arshid, Giles, and Jain, *J.*, 1956, 559.
[4] *Idem, J.*, 1956, 1272.

TABLE 2. *Molecular areas, compressibilities, etc., of monolayers on tannic acid solutions*

Substrate	Cellulose triacetate				Cetylaniline			
	a *			*b* †	*a*			*b*
Water	45	61	42	0·5	25	32	25	0·6
Tannic acid	45	60	42	0·6	29	(37)	26	0·3
Concn. of tannic acid (mg./l.)		15				44		

Substrate	Cetyl acetate				*N*-Methylstearamide				Stearyl alcohol			
	a			*b*	*a*			*b*	*a*			*b*
Water	23	40	21	0·4	27	38	24	0·3	22	23	20	0·01
Tannic acid	28	(100)	24	0·7	31	65	24	0·4	26	31	25	0·4
Concn. of tannic acid (mg./l.)		44				46				46		

* † See footnotes, Table I.

RESULTS AND DISCUSSION

The solutes are conveniently classified according to the size of the hydrophobic residue in their molecules, and accordingly the results may be interpreted as follows:

Solutes with small molecules. There can be little non-polar attraction of these molecules, for the monolayers and their expansion effects must be almost entirely due to hydrogen-bond cross-linking. The ketone films are almost unaffected by them but both acetate films are expanded, so that the prediction of higher polar attraction in water by the acetate group than by the keto-group is confirmed.

The increase in both molecular area and compressibility of the acetate films on urea is particularly marked. Smaller effects are observed with ethylene glycol and mesaconic acid than with urea, which may be due to their small molecular size, allowing them to penetrate the film without much disturbance of packing. Neither, *e.g.*, high water solubility nor association in solution could account for the small effect of mesaconic acid: its solubility in water is only 2·7 g./100 c.c. at 18° (cf. phenol: 6·7 g./100 c.c. at 16°) and a determination of molecular weight showed that it is not associated in water; it should thus be free to form intermolecular bonds. Adsorption tests showed that ethylene glycol in aqueous solution appears to have no affinity for powdered cellulose triacetate.

On water, cellulose triacetate polymer chains are incompletely separated and do not form a true monolayer; *e.g.*, the apparent area per glucosidic residue, 37 Å², is only about half the theoretical value.[5] The chains are probably present as micellar bundles, but these are disaggregated by powerful hydrogen-bonding agents, *e.g.*, urea. (There must, of course, be a considerable attraction for water itself to enable the films to spread on water.)
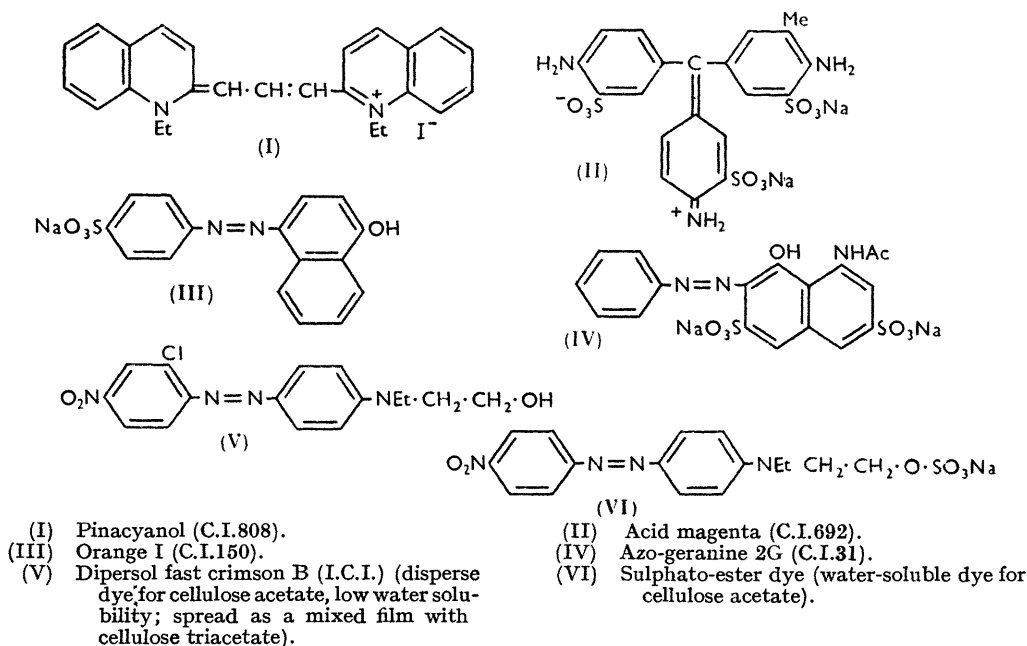
Solutes with medium-sized molecules. Phenol and quinol have considerable effect on acetate films, presumably by hydrogen bonding with the head groups therein; quinol no doubt acts as a cross-linking agent, as it does for some films of azo-compounds.[1] Phenol appears to raise the solubility of the film considerably, since the large effect on the compressibility and the magnitude of the increase in area are much more than can be accounted for by 1 : 1-attachment to the acetate groups in a rigid monolayer.

The small effects of benzenesulphonic acid, benzoquinone, pyridine, and sucrose are due to weak hydrogen-bonding power; and the very small effect on the cellulose triacetate film produced by ethyl methyl ketone, which is regarded as non-hydrogen bonding in water, shows that the triacetate has little ability to adsorb water-soluble solutes by other than hydrogen-bond forces.

Solutes with large molecules. The annexed dyes were amongst the compounds used. The ionic compounds expand the ketone films, presumably by non-polar association

[5] Borgin and Johnston, *Trans. Faraday Soc.*, 1953, **49**, 956.

between their hydrophobic residues and the alkyl chains of the ketone. Cetyl acetate, however, is affected considerably more than the ketones, clearly by a combination of polar and non-polar forces. The triacetate film is less expanded by the solutes with large molecules than is the cetyl acetate film, because of its smaller proportion of hydrophobic residue, and a comparison of effects produced by these solutes upon the several films shows that non-polar association probably plays little part in adsorption at the triacetate film.

(I)   Pinacyanol (C.I.808).
(III) Orange I (C.I.150).
(V)   Dipersol fast crimson B (I.C.I.) (disperse dye for cellulose acetate, low water solubility; spread as a mixed film with cellulose triacetate).

(II)   Acid magenta (C.I.692).
(IV) Azo-geranine 2G (C.I.31).
(VI) Sulphato-ester dye (water-soluble dye for cellulose acetate).

The non-ionic disperse dye, which has a high affinity for cellulose acetate in bulk, when spread as a mixed film with cellulose triacetate produces no noticeable effect on the area or compressibility. Presumably it is adsorbed beneath the film, with its aromatic nuclei lying horizontally, in juxtaposition with the glucosidic rings.* Harding and Adam [6] noticed that the surface pressure of cellulose triacetate films on water is not appreciably altered by picric acid in the aqueous layer, but the surface potential is markedly lowered. They believed that the acid or its anion is adsorbed below the film.

Action of Tannic Acid.—Solutions of tannic acid were examined as substrates because the hydrogen-bonding properties of this compound with surface films have been the subject of thorough study by other authors by various means (see, *e.g.*, ref. 7). Protein films are made less compressible by tannic acid, which is adsorbed beneath the film and condenses together a number of protein chain molecules in a horizontal raft-like structure.[7] The present results (Table 2 and Fig. 6) demonstrate a somewhat different effect. The films of the monomeric compounds are slightly expanded at high pressures by tannic acid, and very considerably expanded at low pressures; they are made considerably more compressible in all cases except cetylaniline. It is suggested that at low pressures gaseous films of the hydrogen-bond complex of tannic acid with film monomer are formed, but with increasing pressure the film molecules tend to condense into the orientation normally

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* The dye alone forms a condensed film on water with a molecular area of *ca.* 34 Å², which agrees closely with the value (32 Å²) estimated from models for vertical orientation on the OH group. Pressure steadily falls owing to the slow dissolution of the dye in water.

[6] Harding and Adam, *Trans. Faraday Soc.*, 1933, **29**, 837.
[7] Ellis and Pankhurst, *Discuss. Faraday Soc.*, 1954, **16**, 170.

taken up on water alone, with the tannic acid molecules bonded beneath the film. Thus the upper part of the π–A curves for films on water or tannic acid solution tend to coincide, showing that the acid has then become entirely forced out from the film into the under-lying solution.

The film of cetylaniline is made *less* compressible by tannic acid, perhaps because of some form of association between the aromatic nuclei of the film and of the solute.

Cellulose triacetate on tannic acid behaves rather like the monomeric aliphatic compounds, but only if urea is also present in the solution, whereby its micelles are broken up; otherwise there is actually no significant effect on the film. Presumably, in this case the

FIG. 6.

(Left) *Cetylaniline films on*: ●, Water; ○, tannic acid (44 mg./l.).

(Right) *Stearyl* (n-*octadecyl*) *alcohol films on*: ●, Water; ○, tannic acid (44 mg./l.)
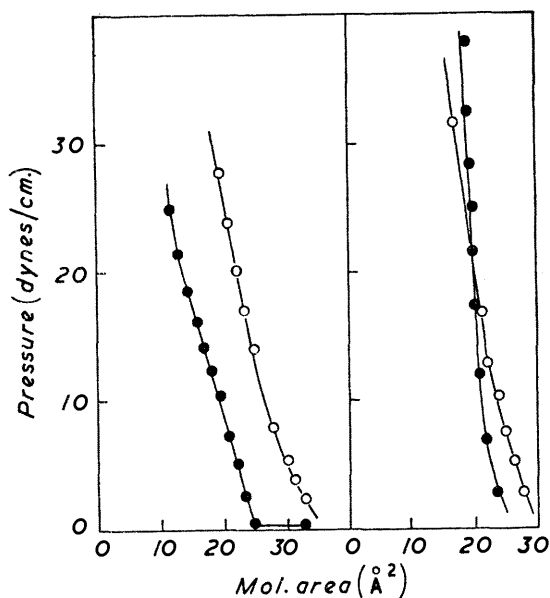
tannic acid molecules are attached entirely beneath the cellulose triacetate micelles and, being much smaller than the latter, do not interfere with their compression or orientation.

Action of Non-ionic and Ionic Dyes upon Monolayers.—The above results show that a solute with a planar molecule and multiple points of attachment for hydrogen bonds around its periphery, as tannic acid has, does not necessarily cause much change in the area or compressibility of films of aliphatic compounds, including acetates, even though it is capable of forming bonds with the film molecules. Therefore the insignificant change in cellulose triacetate films when the highly substantive disperse dye is added is not incon-sistent with a dye–acetate hydrogen-bonded attachment. The presence of sulphate ester, sulphonate, or other ionic groups in the dye, however, appears to prevent this " raft " type of attachment of dye beneath cellulose acetate, and considerable expansion occurs. This must be due to the effect of solvated water around the ionic groups, which prevents the necessary close approach of the two reacting molecules over their whole areas. In-stead, the solute molecules penetrate the film *between* the individual chains in such a manner that individual acetate groups can become attached to hydrogen-bonding centres in the solute molecule and the ionic groups remain in the water below. This hypothesis helps to explain some of the phenomena of adsorption by cellulose acetates, as described below.

Adsorption Properties of Cellulose Acetates.—The adsorption properties of cellulose acetates for aromatic substances in aqueous solutions may briefly be described as follows:

(i) Most non-ionic polar compounds, *e.g.*, phenols and " disperse " dyes, are readily adsorbed by secondary cellulose acetate or cellulose triacetate. Exceptions to this rule

are very water-soluble substances with rather weak hydrogen-bonding groups, *e.g.*, aliphatic alcohols and pyridine. The disperse dyes are mostly azo- or anthraquinone derivatives containing a number of polar groups, *e.g.*, OH, NH_2, etc., but no ionic groups. Though they are almost insoluble in water, dyeing takes place through their extremely weak saturated solutions diffusing into the body of the polymer.[8,9]

(ii) The presence of any ionisable group in a dye almost entirely removes its affinity for cellulose triacetate, but not necessarily for the secondary acetate. Thus dyes with the sulphate ester group have high affinity for the latter. Even the highly ionised sulphonate group does not entirely destroy affinity for secondary acetate for this adsorbs monosulphonated dyes appreciably, but not disulphonated ones. Probably similar rules apply to the cationic groups in basic dyes, but information is not available on this point.

*Mechanism of Adsorption by Cellulose Acetates.**—Tests by the refractive-index method [10] (with some confirmation by infrared spectrophotometry [4,11]) used with solutions of binary mixtures of model compounds indicate that hydroxy-groups in dyes are bonded to the ether-oxygen atom of the acetate group in cellulose acetates,[10] and nitrogen atoms in dyes, to the methyl group, which is activated by the adjacent carbonyl double bond.[4,11] Both of these bonds are weak (except with powerful hydrogen-bonding agents, *e.g.*, phenol or urea) and the adsorption phenomena described above may be explained as follows in the light of the present results.

Cellulose acetates are hydrophobic and are little swollen in water. Any water-soluble solutes with hydrogen-bonding groups will penetrate into the amorphous, water-swollen region of the triacetate polymer in bulk and be adsorbed by hydrogen bonds, but the amorphous region is a very small proportion of the whole. Ionic dyes do this, but they do not penetrate the regions inaccessible to water; consequently their total adsorption is not practically significant (the adsorption of, *e.g.*, sulphato-ester dyes can readily be measured, though they do not appreciably colour the substrate).

In order to register any significant amount of adsorption a solute must penetrate some of the more ordered regions of the polymer not normally swollen by water. To do this each penetrating solute molecule must break simultaneously several interchain acetate–acetate bonds and replace them by dye–acetate bonds (hydrogen bonds and perhaps some van der Waals association). This it can probably do only if its own bonding groups are in at least two fairly widely spaced positions in the molecule, and no ionic groups are present to interfere in the manner referred to above. The penetration in this way of regions not normally swollen by water has some resemblance to solid solution, which for long was regarded as the mechanism of adsorption by cellulose acetate.[9]

The less highly ordered secondary acetate is more readily penetrated, and ionic compounds are as stated in many cases significantly adsorbed.

EXPERIMENTAL

Apparatus.—The unimolecular film balance used is a modification of Allan and Alexander's recent design.[12] The float is made of Duralumin, and the head is of brass and is pivoted on agate knife edges and planes; this allows it to be removed more readily than when spring-control is used. Allan and Alexander's instrument was designed for use at much lower surface pressures than those employed here, and the sensitivity of the present apparatus was accordingly reduced (to 0·1 dyne per cm.) by the use of a heavier beam. The ends of the beam were sealed to the trough by fine Polythene monofilament (0·005 in. Courlene X3, Courtaulds Ltd.).

The trough itself (10 × 25 cm. internal dimensions) was constructed from a single block of

* For summaries of hypotheses of the nature of the cellulose acetate–dye bond, see refs. 4, 9, and 11.

[8] Bird, Manchester, and Harris, *Discuss. Faraday Soc.*, 1954, **16**, 85.

[9] Vickerstaff, "The Physical Chemistry of Dyeing," Oliver and Boyd, Ltd., Edinburgh, 2nd edn., 1954.

[10] Arshid, Giles, McLure, Ogilvie, and Rose, *J.*, 1955, 67.

[11] Campbell, Cathcart, and Giles, unpublished work.

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

Polythene, bolted to a brass plate for rigidity, and the movable barrier was also made of Polythene. This material has proved rather more convenient in use than glass, because the need for constant waxing of the surface is avoided except with some solutions of particularly low surface tension. The whole instrument is screened by an aluminium case, the barriers being mechanically controlled from outside. All measurements were made at room temperature. The ends of the bolts within the trough were wax coated.

Reagents.—*Methyl stearyl ketone.* Agaric acid (10 g.) and sulphuric acid (d 1·84) (100 c.c.) were heated on a water-bath for 1 hr., then cooled in ice, and mixed with 2 l. of water, and the mixture was extracted with ether. The ether extract was shaken with aqueous potassium carbonate solution, then filtered, and the ether removed. The residue was dissolved in ethanol, decolorised by charcoal, and recrystallised several times from ethanol, forming colourless plates, m. p. 56°.

Ethyl stearyl ketone. This was prepared by Gilman and Nelson's method.[13] Powdered cadmium chloride (0·16 mole) was stirred gradually into an ice-cooled ether solution of methylmagnesium bromide [prepared from magnesium (0·35 mole) and ethyl bromide (0·3 mole)] and stirring was continued for 30 min. Stearoyl chloride was then added gradually, at first in ether (0·05 mole in 40 c.c.) and then undiluted (0·16 mole). Stirring was continued for 1 hr. in the cold and then for 2 hr. on the boiling-water bath. Crushed ice was then carefully added, followed by water and sufficient sulphuric acid to dissolve the white precipitate formed. The ether layer was washed with alkali and then with water, and evaporated. The white solid residue was heated with concentrated aqueous sodium hydroxide solution, cooled, and separated by filtration; it was finally redissolved in ether, which was washed with water. The residue after evaporation of the ether was recrystallised twice from ethanol; it had m. p. 53°.

The preparation of cetyl acetate has already been described.[2] The samples of cellulose triacetate used for the experiments summarised in Table 1 (and Figs. 4 and 5) and Table 2 had Ac, 58 and 62·5%, respectively. Both were spread from chloroform solution. The other reagents were pure laboratory or commercial products; distilled water was used for the aqueous phase. The sulphonated dyes were recrystallised from water to 91—98% purity ($TiCl_3$ analysis): remaining impurites are likely to be sodium chloride or bound water.

Solute Concentration.—As in the previous work, the solutes were used mostly at the highest practicable concentration, in aqueous solution, in some cases approaching saturation. It seems likely that under these conditions a very high proportion of active monolayer headgroups will be attached by polar bonds to solute molecules. Tests made with cetyl acetate films on phenol solutions of increasing concentration show that above 0·05M no further film expansion occurs with increase in solute concentration.

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[13] Gilman and Nelson, *Rec. Trav. chim.,* 1936, **55**, 518.