260. *Studies in Hydrogen-bond Formation. Part V.* Complex-forming Properties of Esters, and their Relation to the Adsorption Properties of Cellulose Acetate and Other Polymers.*

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The complex-forming reactions of a variety of compounds containing the grouping CO·CH$_3$, in aqueous and non-aqueous solutions, have been investigated by measurements of dielectric constant, refractive index, and infrared absorption. Esters appear to act as monofunctional proton-donors. Diacetates are normally bifunctional proton-donors, but when the two acetate groups are vicinal they interact, probably by chelation through a Ch · · · hydrogen bond, and the compound is monofunctional. *N*-Acetylglucosamine appears to form bonds through the amino-group; its hydroxy-groups are also active in non-aqueous solvents but not in water.

The results are considered to be significant in the interpretation of the adsorption behaviour of cellulose acetate, chitin, and Terylene.

This investigation is principally a study of the hydrogen-bonding reactivity of esters, made with a view to determine the importance of this bonding in adsorption of solutes by chitin, cellulose acetate, and other polymeric esters; the technique has already been described.[1,2] Various acetates and *N*-acetylglucosamine have been used as models of cellulose acetate and chitin, respectively, and dimethyl terephthalate and ethylene glycol dibenzoate as models of polyethylene glycol terephthalate (Terylene). The results are shown in Table 1 and Figs. 1 and 2, and are discussed below.

Experimental

The general method has already been described;[1,2] in this work the Bellingham and Stanley (new model) Pulfrich refractometer was mainly employed, though some tests were made with the two instruments used for Part II.[2] The solvents and reagents were commercial or laboratory-prepared materials purified by standard methods.

It has been found that some systems give better results if the solutions are kept overnight before measurement, no doubt because the solutes have a low reaction or solution rate.

Catechol diacetate, prepared by mixing catechol and acetyl chloride in the cold, followed by addition of water, and recrystallisation from ethanol, formed needles, m. p. 63·5°.

3-Methoxybenzanthrone was a sample of Duranol Brilliant Yellow 6G (I.C.I.) recrystallised from benzene. (This was used as a typical cellulose acetate dye.)

Pentane-1 : 5-*diol diacetate.* Pentamethylene glycol was refluxed with excess of acetic anhydride and dry pyridine for 2 hr. The mixture was then washed successively with water, dilute acetic acid, and sodium carbonate solution. The oily layer was extracted with ether and redistilled, and the distillate kept over sodium to ensure removal of all traces of unesterified diol; the ester had b. p. 240°, f. p. 6°.

The glycerol triacetate used in the Rhodamine B test was also allowed to remain over sodium to remove unchanged alcohol.

Quinol diacetate was prepared by mixing quinol, acetic anhydride, and a few drops of sulphuric acid, in the cold. The product which separated recrystallised from ethanol as plates, m. p. 121°.

A Grubb-Parsons double-beam infrared spectrophotometer (sodium chloride prism) was used.

Infrared spectra. Catechol diacetate and quinol diacetate were examined as 1·5% CCl$_4$ solutions (0·8 mm. cells) and ethylene glycol diacetate and pentane-1 : 5-diol diacetate both as 1·5% CCl$_4$ solutions (0·8 mm. cells) and as pure liquids (0·025 mm.); Catechol diacetate and quinol diacetate both show a carbonyl peak at 1776 cm.$^{-1}$, while the former, but not the latter, has an additional peak at 1727 cm.$^{-1}$. There was no apparent difference between their CH$_3$

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* Parts III and IV, *J.*, 1956, 72, 559. In Part IV, the first line on p. 569, free acid *should read* on free acid.

[1] Part I, Giles, Rose, and Vallance, *J.*, 1952, 3799.

[2] Part II, Arshid, Giles, McLure, Ogilvie, and Rose, *J.*, 1955, 67.

symmetrical deformation bands at 1381 cm.$^{-1}$; a CH_3 symmetrical deformation band appears at 1439 cm.$^{-1}$ in quinol diacetate, while in catechol diacetate two peaks appear at 1443 cm.$^{-1}$ and 1468 cm.$^{-1}$. The C–O stretching peak at 1190 cm.$^{-1}$ (very broad) in quinol diacetate is shifted, and new peaks at 1205 and 1175 cm.$^{-1}$ appear instead.

No significant differences are apparent between the C=O bonds of ethylene glycol diacetate and pentane-1 : 5-diol diacetate; the centre of the broad C–O acetate band at 1070 cm.$^{-1}$ in the former is at 1050 cm.$^{-1}$ in the latter, and that of the C–O stretching band at 1247 cm.$^{-1}$ in the former shifts to 1258 cm.$^{-1}$ in the latter. In the CCl_4 solutions the CH_3 symmetrical deformation band at 1381 cm.$^{-1}$ occurs in both spectra, but a band at 1403 cm.$^{-1}$, probably also a CH_3 symmetrical deformation (cf. ref. 18) which occurs in the spectrum of pentane-1 : 5-diol diacetate, is not present in that of ethylene glycol diacetate. This change is not apparent in the spectra of the pure liquids because the absorption is too strong.

DISCUSSION

N-Acetylglucosamine (cf. Fig. 1).—This appears to be a monofunctional proton donor in water, probably through the acetyl group at the nitrogen atom or the carbon atom in the

FIG. 1. *Relation between refractive index (as instrument reading) and component ratio in solutions of binary systems.*

Top : *a*, Triethylamine; *b*, glycerol triacetate. Solvent, water.
Middle : *a*, Diisobutyl ketone; *b*, ethylene glycol diacetate. Solvent, dioxan.
Bottom : *a*, Diisobutyl ketone; *b*, pentane-1 : 5-diol diacetate. Solvent, toluene.
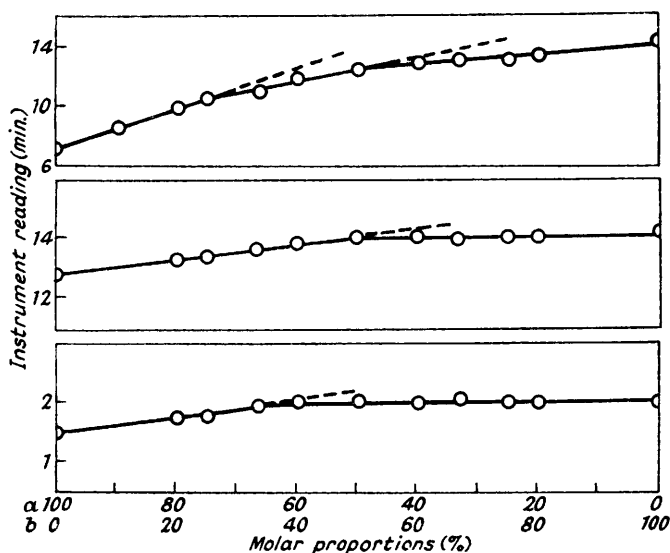
methyl residue, the hydroxy-groups being solvated and the molecule acting in the ring-form; * in ethylene glycol solutions 1 : 1 and 1 : 4 complexes are detected between this compound and alcohols or phenols, and in these cases three of the hydroxyl groups must also be reactive; the fourth is probably chelated, thus as in (*A*) (p. 1276). This type of chelate bond has been suggested by Darmon and Rudall [3] as existing (together with free >NH groups) in chitin, on the evidence of studies with polarised infrared and X-radiation.

Reactivity of Esters.—It is clear from the results shown in Table 1 that all the esters examined can interact with electron donors, *e.g.*, azobenzene, pyridine, or triethylamine, both in non-polar solvents and in water. It seems likely that this takes place through a –C–H · · · O or –C–H · · · N bridge facilitated by the enhanced lability of the carbon-hydrogen bond adjacent to a carbonyl group. The active C–H bond in some cases appears to be that attached α to the O–C=O group (*e.g.*, in ethylene glycol dibenzoate †) and in others α to the –C=O group (*e.g.*, in the acetates). For further examples, compare, respectively,

* Compare the inactivity of the hydroxy-groups in the ring forms of the carbohydrates in water (Part IV, *loc. cit.*).

† The existence of three examples of this type of complex is suggested also by molecular-weight determinations (Part II,[2] Figs. 8, 9, 10).

[3] Darmon and Rudall, *Discuss. Faraday Soc.*, 1950, **9**, 251.

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TABLE 1. *Results of complex-detection tests.*

Solutes a	b	Solvent *	Total molar concn.	Method(s) † and temp.	Mol. ratio ‡ of complex, a : b
Acetyl chloride	Acetone	C	0·2	n 19°	1 : 1
	Azobenzene	D	0·1	n 22	2 : 1
Benzyl acetate	Acetone	T	0·1	n 22·5	§
	Dioxan	T	0·1	n 22·5	§
	Pyridine	T	0·1	n 24	§
N-Acetyl-D-glucosamine	Methanol	W	0·25	n 19	1 : 1
		EG	0·1	n 18	1 : 1; (1 : 4)
	β-Naphthol	EG	0·05	n 18	(1 : 1); 1 : 4
	Phenol	EG	0·05	n 16, 18	1 : 1; 1 : 4
		W	0·25	n 18	1 : 1
	Triethylamine	W	0·25	n 20	1 : 1
	Quinol	W	0·25	n 20	2 : 1
2-Acetylpyridine	Acetone	T	0·1	n 21	(§)
	Triethylamine	T	0·1	n 21	1 : 1
3-Acetylpyridine	Acetone	T	0·1	n 21·5	§
	Pentyl alcohol	T	0·1	n 22	1 : 1
	Azobenzene	T	0·1	n 19·5	(§)
	Diisobutyl ketone	C	0·1	n 21	§
	Diethylamine	T	0·1	n 21	1 : 1
	Pyridine	T	0·1	n 19·5	(§)
	Triethylamine	T	0·1	n 21·5	§
Catechol diacetate	Acetone	D	0·1	n 21	§
	Diisobutyl ketone	C	0·05	n 21	1 : 1
		T	0·1	n 22·5	1 : 1; 1 : 2
	Triethylamine	C	0·05	n 20·5	1 : 1
		D	0·1	n 21	1 : 1
		T	0·1	n 22·5	(1 : 1)
Dimethyl terephthalate	Phenol	T	0·1	n 18	1 : 4
	Triethylamine	T	0·1	n 18	1 : 4
Ethylene glycol diacetate	Acetone	D	0·2	n 21	(1 : 1)
	Diisobutyl ketone	D	0·2	n 21	1 : 1
	Triethylamine	T	0·2	n 21	1 : 1
Ethylene glycol dibenzoate	Phenol	T	0·1	n 22	1 : 4
	Triethylamine	T	0·1	n 20	1 : 4
Ethyl acetate	Acetone	T	0·2	n 21	1 : 1
	Azobenzene	T	0·1	n 17, 21·9	4 : 1
	1-Naphthol-5-sulphonic acid (oxy-L-acid)	W	0·04	n 24	(1 : 1)
	o-Nitrophenol	P	0·1	n 20	(1 : 1)
		T	0·1	n 14	1 : 1
	p-Nitrophenol sulphuric ester	W	0·04	n 24	1 : 1
Ethyl trichloro-acetate	Acetone	T	0·2	n 20	1 : 1
	Azobenzene	C	0·2	n 20	1 : 1; 2 : 1
	Triethylamine	T	0·2	n 20	(1 : 1)
α-D-Glucose penta-acetate	Acetone	T	0·1	n 21	1 : 1; 1 : 3; 1 : 5
	Aniline	T	0·1	ε, n 20	(1 : 1)
	Anisole	T	0·1	ε, n 20	(1 : 1)
	Azobenzene	T	0·1	ε, n 20, 21	2 : 1; 1 : 1
	Benzoquinone	T	0·1	ε, n 20	(2 : 1)
	Diethylamine	T	0·1	ε, n 22	(1 : 1)
	o-Nitrophenol	D	0·1	n 20	1 : 1
	Phenol	D	0·1	n 20	1 : 1; 1 : 6
	Triethylamine	T	0·1	n 20, 21	1 : 1
		D	0·1	n 20	1 : 1; 1 : 6
Glycerol triacetate	Azobenzene	T	0·1	n 20·5	2 : 1
	Diisobutyl ketone	T	0·1	n 21	1 : 1; (1 : 2 or 1 : 3)
	Diethylamine	D	0·1	n 15	(1 : 3)
		T	0·1	n 12	1 : 1
	Dioxan	T	0·1	n 21·5	1 : 3
	2 : 2'-Dipyridyl	W	0·025	n 18·8	(2 : 1)
	4-Hydroxyazobenzene-4'-sulphonic acid	W	0·025	n 20·8	§
	1-Naphthol-5-sulphonic acid	W	0·05	n 21	(§)
	2-Naphthol-6-sulphonic acid	W	0·05	n 24	(§)
	o-Nitrophenol	T	0·1	n 21·5	1 : 1
	p-Nitrophenyl sulphuric ester	W	0·04	n 17·5, 23	1 : 1
	Pyridine	T	0·1	n 20·5	1 : 1
	Sulphanilic acid → 1-naphthol	W	0·01	n 22	(§)
	Triethylamine	W	0·2	n 20·8	1 : 1; 1 : 3

TABLE 1. *(Continued.)*

		Solution			
Solutes			Total molar concn.	Method(s) † and temp.	Mol. ratio ‡ of complex, a : b
a	b	Solvent *			
Methyl oxalate	Acetone	C	0·2	*n* 20·5	1 : 1; 1 : 2
	Phenol	D	0·05	*n* 16·5	1 : 2
	Triethylamine	C	0·2	*n* 20·5	1 : 1; 1 : 2
Pentane-1 : 5-diol diacetate	Di*iso*butyl ketone	T	0·1	*n* 21	1 : 2
	Triethylamine	T	0·1	*n* 21	1 : 2
*iso*Propyl acetate	Anisole	D	0·1	*n* 20	1 : 1
	Azobenzene	D	0·1	*n* 19	4 : 1
	Benzoquinone	T	0·2	ε, *n* 20	2 : 1
	3-Methoxybenzanthrone	D	0·01	*n* 20	(2 : 1)
	o-Nitrophenol	D	0·1	*n* 19	1 : 1
		T	0·1	*n* 20	1 : 1; (1 : 2)
	Phenol	T	0·2	ε, *n* 20	1 : 1
Quinol diacetate	Acetone	D	0·1	*n* 21	§
	Di*iso*butyl ketone	C	0·05	*n* 21	(1 : 1); 1 : 2
	Triethylamine	C	0·05	*n* 20·5	(1 : 2)
		D	0·1	*n* 21	1 : 2
Trichloroacetyl chloride	Acetone	C	0·1	*n* 22·5	1 : 1
	Azobenzene	D	0·1	*n* 22	(§)
	Di*iso*butyl ketone	T	0·1	*n* 21	(1 : 1 or 1 : 2)

* Solvents : B = benzene; C = carbon tetrachloride; D = dioxan; EG = ethylene glycol; P = light petroleum (b. p. 80—100°); T = toluene; W = water.
† ε = dielectric constant; *n* = refractive index.
‡ Data in parentheses denote uncertain indications.
§ No evidence of complex formation.

the greater ionisability of the hydrogen atom in the carboxyl group than that in the alcoholic group, and the activity of the methylene group in acetoacetic ester (see also Hughes [4]). The presence of labile hydrogen in some acetates is confirmed by the Rhodamine B test [5] which is positive with alcohol-free pentane-1 : 5-diol diacetate and with glycerol triacetate (though it is negative with ethyl acetate).

The trichloroacetyl chloride–acetone complex detected probably originates in dipole-dipole interaction, at the C=O bond, strongly activated by the trichloro-group. This is the first example of this type of non-hydrogen-bonded complex so far detected by the present means. With bases in non-aqueous solution, trichloroacetyl chloride gives copious precipitates of " Lewis salts."

Chelation in Esters.—If the acetate group is a proton-donor, then weak chelation might be expected between acetate groups in 1 : 2-positions, because a 7-membered chelate ring between them can be formulated. Accordingly, some polyacetylated compounds were examined, and it will be observed (Table 1, Fig. 1) that the compounds containing only two non-adjacent acetyl groups, *e.g.*, the diacetates of pentane-1 : 5-diol or quinol, are bifunctional, but those in which the groups are attached in 1 : 2-positions, *e.g.*, ethylene

TABLE 2. *Physical constants of diacetates of dihydric alcohols and phenols.*

Diacetate of	M. p.	B. p.	Diacetate of	M. p.	B. p.
Catechol	63·5°	—	Quinol	121°	—
Butane-1 : 2-diol	—	196—199°	Butane-1 : 3-diol	—	208°
Butane-2 : 3-diol	—	190(200)	Butane-1 : 4-diol	—	230
Pentane-1 : 2-diol	—	216—217 (219)	Pentane-1 : 5-diol	—	241
Hexane-2 : 3-diol	—	215—220	Hexane-1 : 6-diol	—	260
			Hexane-2 : 5-diol	—	225—230

glycol diacetate, penta-acetylglucose, and glycerol triacetate, can behave monofunctionally, which is consistent with interaction between the 1 : 2-groups. The values of the b. p.s or m. p.s of the recorded compounds of this type (Table 2) are also consistent with this

[4] Hughes, " Ionisation in Organic Chemistry," Roy. Inst. Chem. Lectures, 1955, No. 1.
[5] Lundgren and Binkley, *J. Polymer Sci.*, 1954, **14**, 139, cf. also ref. 6.

suggestion; the 1 : 2-compounds in each case having lower b. p.s or m. p.s than the corresponding ones with the substituent groups more widely separated (cf. the values for dialcohols and nitro-compounds given in Part IV [6]).

Certain differences in the infrared spectra of the two phenolic diacetates might be attributable to dipole–dipole interaction between the C=O groups, but this appears doubtful and a more likely interpretation is that some form of hydrogen bond is involved. There are differences between the spectra of the diacetates of ethylene glycol and of pentane-1 : 5-diol; these appear to indicate some weak disturbance of the –O– and CH_3 groups in the
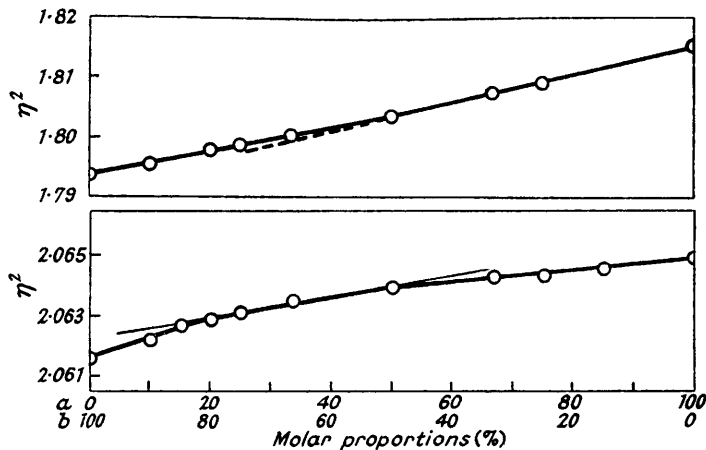
FIG. 2. *Relation between square of refractive index and component ratio in solutions of binary systems.*

Top : *a,* N-Acetyl-D-glucosamine; *b,* methanol. Solvent, water.
Bottom : *a,* N-Acetyl-D-glucosamine; *b,* methanol. Solvent, ethylene glycol.

ethylene glycol diacetate only, probably owing to hydrogen bonding; there is no evidence of any disturbance of the C=O bond. If a chelate ring involving a hydrogen bond is assumed to be present in ethylene glycol diacetate, it must be 7-membered, and of low energy : it can be broken by phenol, which seems to give a 3 : 1 complex with glycerol
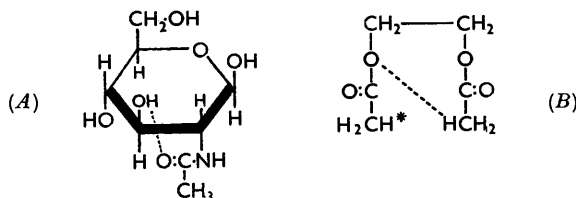
triacetate. This bond, it is suggested, may be formulated as in *(B)*. Thus the compound can behave as a monofunctional proton donor, one hydrogen atom (marked *) being available. Details of the infrared spectra are given in the Experimental Section.

Ketones.—No evidence is obtained that any symmetrical ketone can act as an electron acceptor; one isolated test with an unsymmetrical ketone, *viz.,* 2-acetylpyridine, suggests, however, that this compound might do so.

Mechanism of Adsorption of Solutes by Cellulose Acetate, by Chitin, and by Terylene.—
(i) *Cellulose acetate.** This material adsorbs many non-ionic polar compounds, *e.g.,* phenols and amines,[7] from water (dispersion or solution) or from non-aqueous solvents; some proton-acceptors, *e.g.,* azobenzene and certain derivatives, are also adsorbed; water-solubilisation by introduction of the sulphato-ester group into a dye molecule does not prevent adsorption, but the introduction of highly ionic groups, *e.g.,* sulphonate groups, usually does prevent it,[8] presumably because the attraction of the substrate is too weak

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* The commercial acetate, which is about one-third hydrolysed, has very similar adsorption behaviour to the fully esterified triacetate.

[6] Part IV, Arshid, Giles, and Jain, *J.,* 1956, 559.
[7] Marsden and Urquhart, *J. Textile Inst.,* 1942, **33**, T105.
[8] Vickerstaff, " The Physical Chemistry of Dyeing," Oliver and Boyd, Ltd., Edinburgh, 2nd Edn., 1954.

to overcome that of the water. It will be observed (Table 1) that ethyl acetate and glycerol triacetate form complexes in water with a sulphato-ester; and a sulphonic acid (oxy-L-acid) gives an uncertain indication of combination with ethyl acetate. The following specific adsorption mechanisms for cellulose acetate have been suggested : (*a*) Hydrogen-bonding by acceptance of a proton at the carbonyl oxygen atom of the acetyl group; [7, 8] this does not, however, account for adsorption of proton-acceptors. (*b*) Proton-donation by the methyl residues of the acetyl groups.[9] (*c*) Dipole–dipole interaction, not involving hydrogen, between the carbonyl group and the adsorbate molecule.[10] (*d*) Non-polar van der Waals attraction.[11] It seems very probable that adsorption of small solute molecules, *e.g.*, phenol, must be almost entirely due to polar forces, and recent work on cellulose triacetate monolayers [12] suggests that even the larger molecules may be adsorbed largely by polar forces. The present work seems to show that the hydrogen-bonding mechanism (*b*) is more likely than mechanism (*c*) to account for polar attraction. It may in fact be responsible for adsorption even of proton-donors, *e.g.*, phenol, because examination of the hydrogen-bonding properties of a wide variety of compounds has revealed no conclusive evidence that a carbonyl group can form intermolecular hydrogen-bonds in water.[6, 13] The –C–H $\cdots$ bond is weak, which is consistent with the general low affinity of solutes for cellulose acetate.

Moore and Russell [14] have used the dielectric-constant method [1] with binary solutions of some cellulose acetate solvents and of some models of this polymer. They detected complexes in hexane between benzyl acetate and chloroform or *m*-cresol, and (in dioxan) between cellobiose α-octa-acetate and aniline or *m*-cresol, but not between benzyl acetate and acetone, dioxan, or pyridine (all in hexane) or between cellobiose octa-acetate and acetone, chloroform, ethyl acetate, or pyridine (all in dioxan). In repetitions of some of these experiments by the present method (solvent : toluene) it is confirmed that benzyl acetate appears not to form a complex with acetone, dioxan, or pyridine.

(ii) *Chitin.* Chitin consists largely of poly-*N*-acetylglucosamine, and adsorption of non-ionic solutes thereon might take place through hydrogen-bonding at the hydroxy- or the acetamido-groups. The behaviour of *N*-acetylglucosamine suggests that in water the hydroxy-groups of chitin are solvent-protected and adsorption takes place by bonding at the acetamido-group. In organic solvents both types of group may be reactive. The results of adsorption experiments with chitin are not inconsistent with this deduction.[15, 16]

(iii) *Terylene.* It appears that models of this polymer can act as proton-donors, and a polar mechanism of this nature may therefore be at least partly responsible for adsorption of non-ionic compounds by Terylene (cf. Allingham *et al.*[9]), though for aromatic solutes non-polar attraction between aromatic nuclei in solute and substrate must also operate (cf. refs. 11 and 17).

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[9] Allingham, Giles, and Neustädter, *Discuss. Faraday Soc.*, 1954, **16**, 92.
[10] Majury, *J. Soc. Dyers Col.*, 1954, **70**, 442.
[11] Derbyshire and Peters, *ibid.*, 1955, **71**, 530.
[12] Cameron, personal communication.
[13] Part III, Arshid, Giles, Jain, and Hassan, *J.*, 1956, 72.
[14] Moore and Russell, *J. Appl. Chem.*, 1954, **4**, 369.
[15] Giles, Jain, and Hassan, *Chem. and Ind.*, 1955, 629.
[16] Hassan and Subramanian, personal communications.
[17] Giles, *Discuss. Faraday Soc.*, 1954, **16**, 248.
[18] Cf. Francis, *J. Chem. Phys.*, 1951, **19**, 942.