114. *Studies in Hydrogen-bond Formation. Part IV.* The Hydrogen-bonding Properties of Water in Non-aqueous Solution and of Alcohols, Aldehydes, Carbohydrates, Ketones, Phenols, and Quinones in Aqueous and Non-aqueous Solutions.*

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By application of the refractive-index method of detecting complex formation in solution to over one hundred systems in various solvents the following conclusions are reached. The hydroxyl group in alcohols is monofunctional in hydrogen-bond formation and when present on vicinal carbon atoms in an aliphatic chain it forms weak five-membered chelate rings; consequently only one end-group in, *e.g.*, glycerol or mannitol, is normally available for intermolecular bonding. In aldehydes a variety of reactions demonstrate that the aldehyde group probably forms inter- and intra-molecular bonds through its hydrogen atom.

In aqueous solutions of carbohydrates the open-chain form of glucose or cellobiose, in presence of certain other solutes, such as pyridine or amines, is stabilised by hydrogen-bond interaction of the aldehyde group; the hydroxy-groups are inactive because of solvation by water, though they are active in ethylene glycol solution. In aqueous solutions the hydroxy-groups are less reactive in the ring than in the open-chain forms of the simple carbohydrates and in the ring forms they do not combine with other solutes, even phenol. The bearing of these facts on the adsorption behaviour of cellulose is discussed.

The keto-group of ketones behaves bifunctionally and the quinone oxygen atom of quinones monofunctionally; ketones do not however form intermolecular complexes in benzene, ether, or water solutions. In non-aqueous solvents water appears to act either bifunctionally, probably by cross-linking, or monofunctionally in forming hydrogen-bond complexes with second solutes.

IN Part II * the use of refractive-index measurements on solutions of binary mixtures of organic compounds to detect intermolecular or intramolecular complex-formation, principally of the hydrogen-bonding type, was described. The method has the advantage of being applicable to aqueous as well as to non-aqueous solutions. It was shown, both in theory and practice, that quite weak complexes can be readily detected, that the curves consist of virtually linear segments, intersecting at points corresponding to the molar ratio of the complex or complexes formed, and that forms of intermolecular association other than hydrogen-bonding can sometimes be detected. The nature of the bonds can, however, often be determined by inspection, when the complex-ratio is known.

The present investigation, in which it is assumed that most of the complexes detected are attributable to hydrogen bonds, was designed to determine the hydrogen-bonding properties of water itself, and of hydroxyl groups, especially in carbohydrates; aldehydes and ketones were included as a knowledge of their properties is necessary for the interpretation of those of the carbohydrates. Table 1 summarises the results and typical curves are shown in Figs. 1—8. A discussion and suggested interpretations of the results follow. Some of the tests which were duplicated by the previously reported dielectric-constant method [1] are indicated.

Alcohols.—The hydroxyl group appears to be normally monofunctional in the alcohols, one molecule of, for example, phenol combining with each such group in methanol (Fig. 2), ethanol, *n*-butanol, *n*-pentanol, ethylene glycol, glycerol, erythritol, or mannitol. In each of the polyhydric alcohols, however, an additional 1 : 1-complex is formed with phenol; and with methanol (Fig. 2), triethylamine, or water no other complex but that of 1 : 1 ratio is evident. The most reasonable interpretation of these observations seems to

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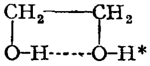
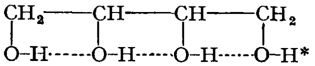
* Parts II and III, *J.*, 1955, 67; 1956, 72.

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

be that pairs of vicinal hydroxyl groups interact to form weak five-membered chelate rings, *e.g.*, in ethylene glycol or a carbohydrate chain :





This leaves in each polyhydric alcohol only one hydrogen atom (starred) free to form intermolecular bonds (in a suitable solvent) with a weak second solute such as methanol. Phenol, however, being a more powerful hydrogen-bonding agent, can disrupt these rings in some of the molecules and so unite with each hydroxyl group.

TABLE 1. (*For footnotes, see p.* 562.)

Solutes		Solution.			
a	*b*	Solv.*	Total mol. concn.	Method † and temp.	Mol. ratio of complex (*a* : *b*) ‡
Alcohols					
Methanol	Phenol	D	0·1	*n* 20°	1 : 1
		W	0·25	*n* 20	1 : 1
Ethanol	Water	D	0·1	ε, *n* 20	1 : 1
,,	Phenol	T	0·25	ε, *n* 19	1 : 1
		W	0·25	*n* 20	1 : 1
*iso*Butanol	Phenol	D	0·1	*n* 21	1 : 1
n-Pentanol	,,	D	0·1	*n* 21	1 : 1
Ethylene glycol	Methanol	D	0·1	*n* 20	1 : 1
,,	Phenol	D	0·1	*n* 19	1 : 1; 1 : 2
,,	Triethylamine	W	0·2	*n* 19·7	1 : 1
		W	0·25	*n* 20	1 : 1; (1 : 2)
Glycerol	Methanol	D	0·1	*n* 20	(1 : 1)
		W	0·25	*n* 20	§
,,	Phenol	W	0·25	*n* 20	1 : 1; 1 : 3
,,	Triethylamine	W	0·1	*n* 20	1 : 1
,,	Water	D	0·1	*n* 20	1 : 1
Erythritol	Methanol	W	0·25	*n* 21	§
,,	,,	Cs	0·05	*n* 18	1 : 1
,,	Phenol	W	0·25	*n* 19	1 : 1; 1 : 4
Mannitol	,,	W	0·25	*n* 19	1 : 6
,,	Water	EG	0·1	*n* 18	1 : 1
,,	Phenol	EG	0·1	*n* 22	(1 : 1); 1 : 6
Butane-1 : 4-diol	Methanol	D	0·1	*n* 15·5	§
,,	Phenol	D	0·1	*n* 16·5	§
Pentane-1 : 5-diol	Methanol	D	0·1	*n* 18	1 : 2
,,	Triethylamine	W	0·2	*n* 19·7	1 : 2
Aldehydes					
Acetaldehyde	Azobenzene	T	0·1	*n* 20	2 : 1
,,	Diethylamine	W	0·25	*n* 20	1 : 1
,,	Ethanol	W	0·25	*n* 20	§ **
,,	Phenol	W	0·25	*n* 20	(§)
Formaldehyde	Phenol	W	0·2	*n* 20	§
,,	Triethylamine	W	0·2	*n* 20	1 : 1
m-Nitrobenzaldehyde	Phenol	T	0·2	*n* 21	1 : 1; 1 : 3
,,	Pyridine	T	0·1	*n* 21	1 : 1
,,	Triethylamine	T	0·2	*n* 21	1 : 1
o-Nitrobenzaldehyde	Phenol	T	0·1	*n* 19	1 : 2
,,	Pyridine	T	0·1	*n* 21	§
,,	Triethylamine	T	0·1	*n* 19	§
Propionaldehyde	Diethylamine	B	0·2	*n* 15	1 : 1; (1 : 2)
,,	Dimethylformamide	C	0·2	*n* 18	1 : 1
,,	,,	W	0·2	*n* 18	1 : 1
,,	Ethanol	C	0·2	*n* 17·5	1 : 1
,,	,,	W	0·2	*n* 17·5	(§)
,,	Phenol	C	0·1	*n* 17	(1 : 1)
,,	,,	EG	0·2	*n* 18	1 : 1
,,	,,	W	0·2	*n* 17·5	§
,,	Pyridine	D	0·2	m.w.	1 : 1
,,	,,	W	0·2	*n* 17·5	1 : 1
,,	Triethylamine	W	0·2	*n* 17·5	1 : 1
Terephthalaldehyde	Triethylamine	T	0·2	*n* 18	1 : 2
,,	,,	W	0·1	*n* 17	1 : 2

TABLE 1. (*Continued.*)

Solutes		Solution.			
a	*b*	Solv.*	Total mol. concn.	Method † and temp.	Mol. ratio of complex (*a* : *b*) ‡
Carbohydrates					
D-Cellobiose	Aniline	W	0·25	*n* 16°	1 : 1
,,	Azobenzene-4-sulphonic acid	W	0·1	*n* 22	(2 : 1)
,,	Diethylamine	W	0·25	*n* 19	(1 : 1)
,,	Dimethylformamide	W	0·25	*n* 15	1 : 1
,,	Pyridine	W	0·1	*n* 18	1 : 1
,,	Quinol	W	0·25	*n* 16	(§)
,,	Triethylamine	W	0·25	*n* 15	(1 : 1)
D-Fructose	Ethanol	W	0·25	*n* 20	(§)
,,	Phenol	W	0·25	*n* 21	(§)
,,	Triethylamine	W	0·25	*n* 20	(§)
D-Glucose	Acetamide	W	0·25	*n* 22	1 : 1
,,	Aniline	W	0·25	*n* 18	2 : 1
,,	Azobenzene-4-sulphonic acid	W	0·1	*n* 19	(2 : 1)
,,	Diethylamine	W	0·25	*n* 19	1 : 1
,,	Dimethylformamide	W	0·25	*n* 18	1 : 1
,,	Ethanol	W	0·25	*n* 20	§
,,	Methanol	W	0·25	*n* 20	§
,,	*p*-Nitrophenol	W	0·10	*n* 18	1 : 1
,,	Phenol	W	0·25	*n* 20, 35; m.w.	§
,,	,,	Buffer pH 8·4	0·2	*n* 17·5	§
,,	,,	EG	0·1	*n* 20	1 : 6
,,	Pyridine	W	0·25	*n* 19	(1 : 1)
,,	Triethylamine	W	0·25	*n* 20	1 : 1
,,	Quinol	W	0·25	*n* 17	§
,,	Urea	W	0·2	*n* 15	§
,,	,,	W	2·0	*n* 16	§
,,	Water	EG	0·1	*n* 14	1 : 6; (2 : 1)
Sucrose	Triethylamine	W	0·25	*n* 20	§
2 : 3 : 4 : 6-Tetra-*O*-methylglucopyranose	Water	D	0·05	*n* 20	2 : 1; 1 : 2
Solutions of ternary mixtures					
D-Glucose (1 mol.) Pyridine (1 mol.)	Phenol	W	0·1	*n* 19	1 : 6
		W	0·2	m.w.	1 : 6
D-Glucose (1 mol.) Triethylamine (1 mol.)	,,	W	0·1	*n* 13	1 : 1; 1 : 6
Ketones					
Acetone	Aniline	B	0·3	ε	§
,,	Diethylamine	B	0·2	ε	§
,,	Phenol	E	0·25	*n* 20	§
,,	,,	W	0·1	*n* 20	§
,,	Methanol	C	0·25	*n* 20	(1 : 2)
	,,	D	0·05	*n* 17	1 : 2
,,	Propionaldehyde	T	0·2	*n* 20	1 : 1
,,	Triethylamine	W	0·25	*n* 21	§
,,	Quinol	E	0·25	*n* 18	§
Benzophenone	Phenol	B	0·25	*n* 18	§ ¶
Di*iso*butyl ketone	Phenol	D	0·25	ε, *n* 20	1 : 2
Quinones					
2 : 3-Benz-9-anthrone	*N*-*n*-Butylpropionamide	D	0·01	*n* 20	1 : 2
,,	Phenol	D	0·01	*n* 20	1 : 1 ‖
Benzoquinone	Anisole	D	0·1	*n* 20	1 : 2
,,	*N*-*n*-Butylpropionamide	T	0·2	ε, *n* 20	1 : 4 ‖
,,	Phenol	T	0·25	ε, *n* 19	(1 : 2)
Phenols					
Catechol	Methanol	D	0·1	*n* 15·5	1 : 1
,,	Phenol	D	0·2	*n* 16	(1 : 1; 1 : 2)
Pyrogallol	Phenol	W	0·25	*n* 20	(1 : 1); 1 : 3
Quinol	Methanol	D	0·1	*n* 20	(1 : 2)
,,	Phenol	W	0·25	*n* 19	1 : 2

TABLE 1. (*Continued.*)

Solutes		Solution.			
a	*b*	Solv.*	Total mol. concn.	Method † and temp.	Mol. ratio of complex (*a* : *b*) ‡
Water					
Water	Acetone	D	0·2	n 20°	1 : 1; 2 : 1
,,	Aniline	D	0·25	ε, n 20	(2 : 1)
,,	Aniline → 2-naphthol	D	0·1	ε, n 20	1 : 2
,,	Azobenzene	D	0·1	ε, n 20	1 : 1; 2 : 1
,,	Benzophenone	D	0·2	ε, n 20	(1 : 2)
				n 17	1 : 2
,,	*N*-*n*-Butylpropionamide	D	0·2	ε, n 20	1 : 2 ‖
,,	Di*iso*butyl ketone	D	0·1	ε, n 20	1 : 1
				n 17	1 : 1 ‖
,,	Phenol	D	0·2	n 20	1 : 1; 1 : 2
,,	Propionaldehyde	EG	0·2	n 17	1 : 1
,,	Styrene	D	0·2	n 20	1 : 2 ‖

* *Solvents* : B = benzene; C = carbon tetrachloride; Cs = "Cellosolve" (2-ethoxyethanol); D = dioxan; E = diethyl ether; El = ethanol; EG = ethylene glycol; T = toluene; W = water.
† *Methods* : ε = dielectric constant; n = refractive index; m.w. = apparent mol. wt.
‡ Data in parentheses denote uncertain indications.
§ No evidence of complex formation.
‖ These curves show particularly pronounced change of slope.
¶ Results by dielectric-constant method reported in Part I.[1]
** In Part II (*J.*, 1955, 67) Table 1, column 3, lines 1 and 2, *for* W *read* C.

Bastiansen [2] detected this form of intramolecular bond in ethylene glycol and glycerol by the electron-diffraction sector method, and pointed out that published heats of combustion confirm its presence, being for these compounds, respectively, 5·4 and 10·3 kcal./mole lower than required by theory, *i.e.*, less by about the values for one and two hydrogen bonds, respectively.

Further confirmation of the existence of this bond was obtained by the examination of a diol in which the pairs of alcoholic groups are too widely separated to react intramolecularly. Thus, in pentane-1 : 5-diol (Fig. 2) both groups are free to react intermolecularly and a 1 : 2-complex is formed with methanol. Butane-1 : 4-diol did not appear to form intermolecular complexes; possibly a seven-membered ring is present, but even this would not explain the complete unreactivity.

A similar intramolecular bond to that in the polyhydric alcohols has been detected between the *ortho*-hydroxyl groups in catechol by infrared spectroscopic examination of its carbon tetrachloride solution; [3] in the present work its existence is evident in the 1 : 1-complex formed between catechol and phenol, though the inflexions of the curves are not very clear.

TABLE 2. *Physical constants of certain chelated and unchelated compounds.*

Chelated	M. p.	B. p.	Unchelated	M. p.	B. p.
Alcohols and phenols					
Catechol	104°		Quinol	169°	
Butane-1 : 2-diol	—	191°	Butane-1 : 3-diol	—	203°
Butane-2 : 3-diol	—	183	Pentane-1 : 4-diol	—	219
Pentane-2 : 3-diol	188	—	Pentane-1 : 5-diol	—	238
			Pentane-2 : 4-diol	—	197
Nitro-compounds					
o-Nitrophenol	44	—	*p*-Nitrophenol	114	—
o-Nitrobenzoic acid	144	—	*p*-Nitrobenzoic acid	241	—
o-Nitrobenzaldehyde	44	—	*p*-Nitrobenzaldehyde	106	—

The m. p.s or b. p.s of certain diols (Table 2) also give evidence of chelation, the compounds with vicinal groups having lower values than the corresponding isomers with more widely separated groups. This is also evident with catechol and quinol.

Aldehydes.—The aldehyde group is monofunctional towards all the second solutes used, except ethanol or phenol in water, where the solvent prevents interaction; both aldehyde

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[2] Bastiansen, *Acta Chem. Scand.*, 1949, **3**, 415.
[3] Wulf, Liddel, and Hendricks, *J. Amer. Chem. Soc.*, 1936, **58**, 2287.

groups are reactive in the only dialdehyde tested (terephthalaldehyde, Fig. 4). There seems no doubt of the reality of the complexes formed with hydrogen-acceptors (pyridine, triethylamine), both by reason of the variety of reactions in which they are evident (including those of the carbohydrate mixtures discussed on p. 567) and the evidence given by molecular-weight experiments (Figs. 3 and 8). The most likely interpretation of the results is that the interaction is by bonding with the hydrogen atom of the aldehyde group,* which is activated by the carbonyl oxygen. The bond is thus somewhat similar to that in the hydrogen cyanide crystal : [4]

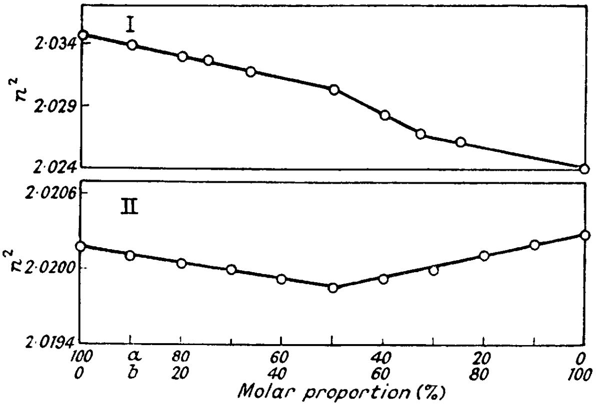


FIG. 1. *Relation between the square of the refractive index and the component ratio in solutions of binary mixtures containing water.*

I : *a*, Azobenzene ; *b*, water. Solvent : dioxan.

II : *a*, Di*iso*butyl ketone ; *b*, water. Solvent : dioxan.

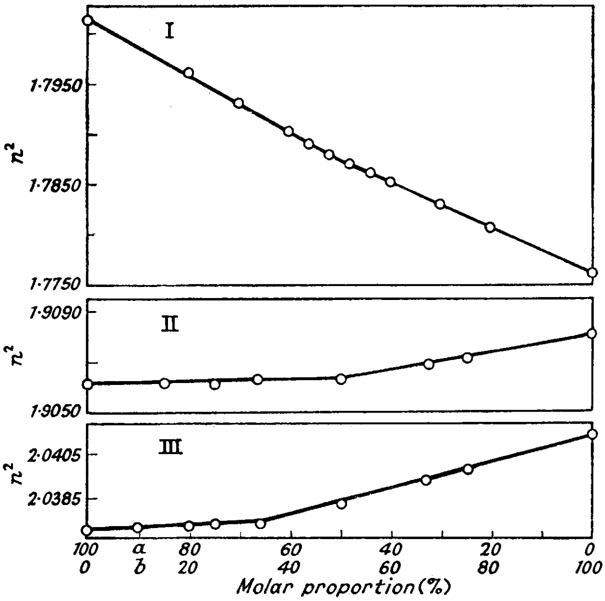
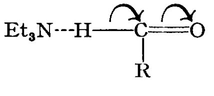


FIG. 2. *Relation between the square of the refractive index and the component ratio in solutions of binary mixtures containing methanol.*

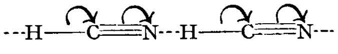
I : *a*, Phenol ; *b*, methanol. Solvent : water.

II : *a*, Methanol ; *b*, erythritol. Solvent : 2-ethoxyethanol.

III : *a*, Methanol ; *b*, pentane-1 : 5-diol. Solvent : dioxan.



$Et_3N{-}{-}H{-}\underset{R}{\underset{|}{C}}{=}O$



$--H-C{\equiv}N--H-C{\equiv}N--$

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* The reactions cannot be attributed to the presence of carboxylic acid formed by oxidation of the aldehyde by air, because of the infrared evidence (see Experimental section) that acid is not formed appreciably in presence of the hydrogen acceptor.

[4] Pauling, " The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, New York, 1944, 2nd edn., pp. 294—295.

Dipole-interaction effects produced by hyperconjugation of the attached alkyl group [5] cannot be responsible for these complexes because formaldehyde behaves like its higher homologues. The nature of the complexes formed by phenol or pyridine with nitrobenzaldehydes (Fig. 5) (cf. those between phenol and nitrophenols or nitrobenzene [6]) seems to indicate that the hydrogen atom of the aldehyde group can form intra- as well as inter-molecular bonds. Lundgren and Binkley,[7] using Rhodamine B (Colour Index No. 749) as a hydrogen-donor indicator (colourless in a hydrocarbon, becoming red in

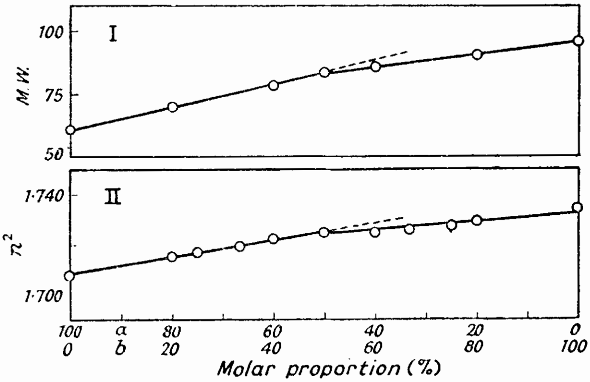
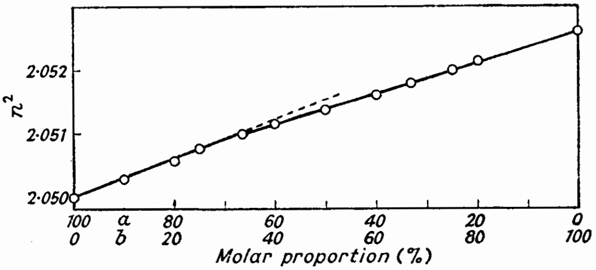


FIG. 3. *Relation between the molar ratio, square of the refractive index, and apparent molecular weight in solutions of binary mixtures containing propionaldehyde.*

a, Propionaldehyde; *b*, pyridine. Solvent: I, dioxan; II, water.

FIG. 4. *Relation between molar ratio and the square of the refractive index in solutions of binary mixtures containing a dialdehyde.*

a, Triethylamine; *b*, terephthalaldehyde. Solvent: dioxan.



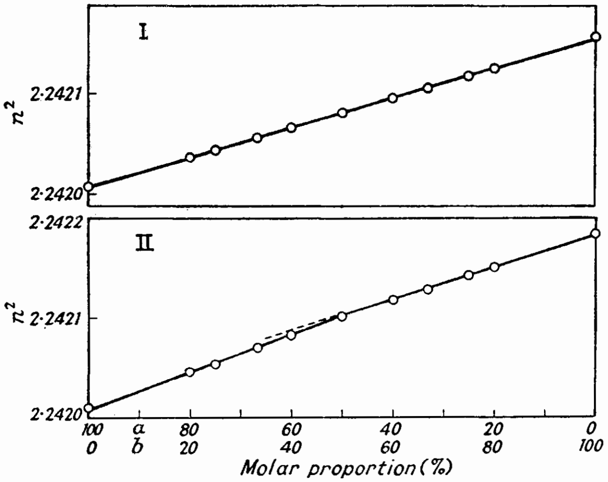


FIG. 5. *Relation between molar ratio and the square of the refractive indexes in solutions of binary mixtures containing nitrobenzaldehydes.*

I: *a*, Pyridine; *b*, *o*-nitrobenzaldehyde. Solvent: toluene.

II: *a*, Pyridine; *b*, *m*-nitrobenzaldehyde. Solvent: toluene.

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[5] Coulson, " Valence," Clarendon Press, Oxford, 1952, p. 311.

[6] Part II, Arshid, Giles, McLure, Ogilvie, and Rose, *J.*, 1955, 67; Part III, Arshid, Giles, Jain, and Hassan, *J.*, 1956, 72.

[7] Lundgren and Binkley, *J. Polymer Sci.*, 1954, **14**, 139.

presence of a hydrogen donor, *e.g.*, water or phenol), noticed that *o*-nitrobenzaldehyde exhibits little activity towards the dye, compared with the activity of the *meta*-isomer, and they attributed the difference to chelation in the *ortho*-compound. In the present work propionaldehyde in dry toluene gave a positive reaction with the dye (even after being kept over sodium hydrogen carbonate to remove traces of carboxylic acid).

The chelate ring in *o*-nitrobenzoic acid and *o*-nitrophenol gives these compounds a m. p. much lower than that of their unchelated *para*-isomers; the lower m. p. of *o*-nitrobenzaldehyde than of the *meta*-isomer may thus likewise be due to chelation.

The results of some infrared spectroscopic measurements on various mixtures containing aldehydes are described in the Experimental section, but unfortunately give no conclusive evidence for or against the present hypothesis that the aldehydic hydrogen atom is active in hydrogen bonding.

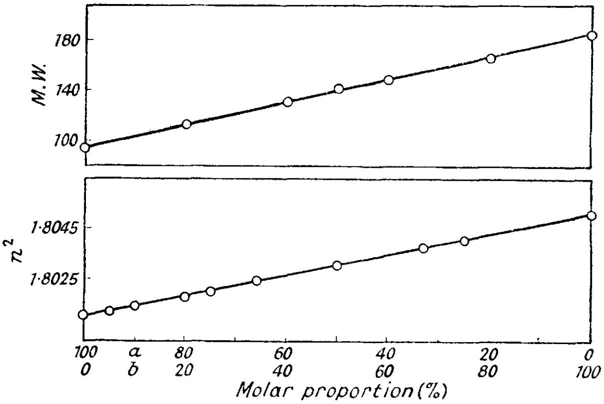

FIG. 6. *Relation between molar ratio, square of refractive index at* 20°, *and apparent molecular weight of solutions of binary mixtures*

a, Phenol; *b*, glucose. Solvent: water.

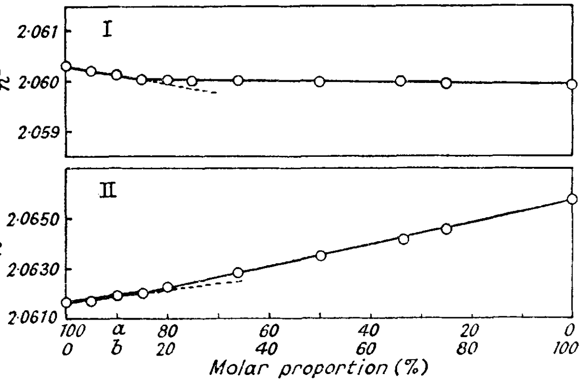

FIG. 7. *Relation between square of refractive index and component ratio in solutions of binary mixtures.*

I: *a*, Phenol; *b*, glucose. Solvent: ethylene glycol.

II: *a*, Water; *b*, glucose. Solvent: ethylene glycol.

[Evidence of interaction between aliphatic aldehydes and alcohols in binary liquid mixtures, interpreted as being due to hemiacetal formation, is given by refractive-index measurements [8] (1 : 1-complexes in several examples) and by infrared spectroscopy.[9]]

Carbohydrates.—The reactions of glucose and cellobiose in water (Table 1) show that they each behave monofunctionally towards reactive second solutes and that their reactions are identical with those of aliphatic aldehydes. It is, therefore, assumed that these carbohydrate molecules react through the aldehyde group in their open-chain forms, and not as the pyranose ring structures. The normal equilibrium state of glucose in water is strongly in favour of the α- and β-ring structures, only a small percentage of the open-chain aldehyde being present. If, however, in the equilibrium mixture the aldehyde group

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[8] Adkins and Broderick, *J. Amer. Chem. Soc.*, 1928, **50**, 499.

[9] Ashdown and Kletz, *J.*, 1948, 1454.

alone can form an intermolecular bond with, for example, pyridine or triethylamine (the hydroxy- and ether groups probably being protected by the water), then complex-formation will disturb the equilibrium, causing more open-chain compound to form, and sufficient of the intermolecular complex must ultimately be produced to affect perceptibly the curves examined. If this is so, triethylamine in water should be unable to form complexes, *e.g.*, with the ketoses, and, in fact, none is detected with either fructose or sucrose.

The non-reactivity of the hydroxy-groups of the carbohydrates towards most other solutes is consistent with other evidence (Table 1) of their behaviour in water, but the non-reactivity of phenol with glucose and with cellobiose is unexpected because phenol does normally combine with alcoholic groups in water, even with each such group in a straight-chain polyhydric alcohol, *e.g.*, mannitol. The experiment with glucose and phenol (Fig. 6) in water was repeated at different temperatures, and the result was checked and confirmed by determination of the apparent molecular weight (Fig. 6); there thus appears to be no doubt that interaction does not occur. This fact may be explained as follows: the aldehyde group is inactive towards phenol in water, so that the open-chain form of glucose will not, following the argument above, be stabilised by phenol. It follows that the inactivity of glucose hydroxy-groups towards phenol in water is a property of the ring form. It seems likely, in fact, that the water-attracting power of the hydroxy-groups is greater in the ring than in the open-chain form. Models demonstrate that the solvated water molecules on opposite sides of the glucose molecule must be closer together at their nearest distance, and so must experience greater mutual attraction, in presence of the ring form than in presence of the open-chain form in its most probable crumpled state. (The shortest distances of separation are about 4 and 6·5 Å respectively.) This increased affinity of the surrounding water must stabilise the ring structure and act as a protective atmosphere against weak interaction with other solutes.* Its stabilising action would also account

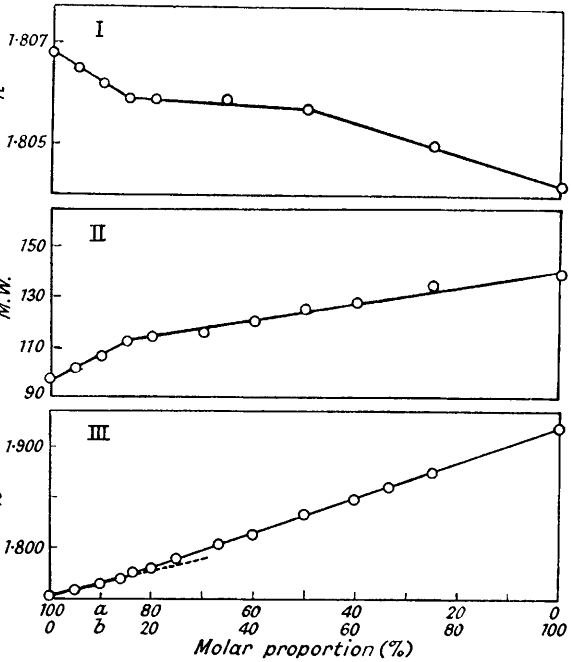

FIG. 8. *Relation between molar ratio, square of refractive index, and apparent molecular weight in solutions of ternary mixtures containing glucose.*

I : *a*, Phenol; *b*, glucose–triethylamine (1 : 1 molar ratio). Solvent : water.

II and III : *a*, Phenol; *b*, glucose–pyridine (1 : 1 molar ratio). Solvent: water.

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* [*Added, October* 16*th*, 1955.] A detailed study of the thermodynamic properties of glucose solutions has been published by Taylor and Rowlinson (*Trans. Faraday Soc.*, 1955, **51**, 1183) in which they find that both glucose and sucrose solutions "show negative excess heats, entropies, free energies, and volumes, indicating that there is strong hydrogen-bonding between the sugars and the surrounding water molecules. This bonding is apparently stronger, or more abundant, than that between the water molecules themselves."

for the ring structures' being favoured in water, instead of the more statistically probable open-chain form.

Confirmation of this hypothesis was obtained by the examination of solutions in ethylene glycol, and the use of certain solutions of ternary mixtures, as follows.

(*a*) *Solutions in ethylene glycol.* The alcoholic chelate rings persist in this solvent (see mannitol, Table 1) and its use should show whether the non-reactivity of the glycosidic groups in water may be due to chelation. 1 : 6-Complexes are formed between glucose and either phenol or water in this solvent (Fig. 7), so that the groups must be unchelated.

(*b*) *Use of solutions of ternary mixtures.* On the above arguments the addition of pyridine or triethylamine to an aqueous solution of a binary mixture of glucose and phenol should stabilise the open-chain glucose molecule and enable each of its hydroxy-groups to combine with phenol. Accordingly refractive-index measurements were made on two series of glucose–phenol solutions of constant molarity, to which there had been added pyridine and triethylamine respectively, in equimolar proportion to the glucose in every solution. The results (Fig. 8) confirm that in both cases a 1 : 6-complex is formed with phenol (the sixth phenol molecule is probably combined with the added base itself). The apparent molecular-weight curve, determined on one series of these solutions, gave a similar result (Fig. 8).

In confirmation that these complexes are not formed merely by an increased reactivity of phenol produced by the alkalinity of the added base, it was shown that in solutions of binary mixtures of glucose and phenol buffered at the pH (8·4) of the pyridine solutions, no complexes can be detected.

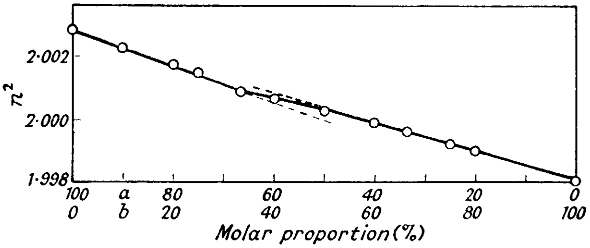

FIG. 9. *Relation between the square of the refractive index at* 17·5° *and component ratio in solutions of binary mixtures* (cf. Fig. 5 and footnote, *J.*, 1955, 70, in Part II[6]).
a, Resorcinol; *b*, diethylamine. Solvent : dioxan.

Cross-linking of Glucose Derivative by Water.—Examination of tetramethylglucopyranose, which retains one unsubstituted hydroxy-group, shows that it forms both 1 : 2- and 2 : 1-complexes with water; the latter must be a cross-linked compound.

Adsorption Properties of Cellulose.—The present work helps to explain some of the adsorption phenomena exhibited by cellulose. Adsorption on this substrate must take place, if at all, on molecular chains in non-crystalline regions, and in aqueous solutions these presumably resemble glucose and cellobiose in being surrounded by an atmosphere of water molecules bound so firmly that other solutes cannot normally penetrate it. It seems clear, therefore, that in presence of excess of water cellulose does not normally adsorb solutes by hydrogen bonding. This explains why phenol, which is readily absorbed from dilute aqueous solution by fibrous substrates capable of hydrogen bonding, *e.g.*, nylon, wool,[10] and cellulose acetate,[11] is entirely unadsorbed under similar conditions by regenerated cellulose [11] or cotton.[12] Preston and Nimkar [13] by studying freezing-point curves of adsorbed moisture in cellulose fibres, have shown that the non-crystalline parts of the fibre are in a state resembling solution in the water, so they should behave as glucose.

Ketones.—The few tests so far made point to the ketone group's being bifunctional in combination with alcohols or phenols; it is inactive towards all other solutes in benzene, ether, or water, and there is no evidence that ketones can act as hydrogen-donors.

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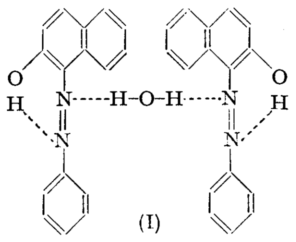
[10] Chipalkatti, Giles, and Vallance, *J.*, 1954, 4375.
[11] Marsden and Urquhart, *J. Textile Inst.*, 1942, **33**, T105.
[12] Giles, Jain, and Hassan, *Chem. and Ind.*, 1955, 629.
[13] Preston and Nimkar, *Textile Res. J.*, 1953, **23**, 119.

Quinones.—2 : 3-Benz-9-anthrone was included to test the reactivity of a single quinone oxygen atom; this reacts apparently as do the individual oxygen atoms in normal quinones which each combine with one phenolic group or with two amide groups.


(I)

Water.—Used as a solute, water can act either monofunctionally or bifunctionally, presumably as a cross-linking agent, both hydrogen atoms being involved in bonds (cf. Fig. 1) *e.g.*, with 1-phenylazo-2-naphthol * as in (I). In the styrene–water 2 : 1-complex one of the hydrogen atoms of the double bond of each styrene molecule must be involved in a bond with the oxygen of the water.

Solvent-protection.—For convenience, the examples already discussed of the prevention of intermolecular bonding by solvation are summarised in Table 3.

TABLE 3. *Solvation effects in intermolecular hydrogen bonding.*

Groups		Solvent (see Table 1)	
a	*b*	*a* Reactive with *b* in	Inactive in
OH (alk)	OH (alk)	Cs, D	W
,,	OH (ar)	T, W	None
OH (ar)	OH (ar)	D, T, W	None
CHO (alk; ar)	OH (alk, ar)	C, T	W
,,	$\cdot N_2\cdot$, $\cdot NR_3$, etc.	All	None
C=O (keto)	All	C, D, T	B, E, W

Negative results in these tests are not necessarily conclusive (cf. Parts II[6] and III[6]).

EXPERIMENTAL

Materials.—All compounds were either of Analytical Reagent quality or were purified commercial or laboratory-prepared products. All solvents were completely dried. Dioxan and methanol were of the " specially dried " quality (B.D.H.) used for Karl Fischer titrations. Ethylene glycol was first fractionated and then passed through activatedalumina. 2 : 3-Benz-9-anthrone was prepared by Fieser's method[15]; it formed buff crystals, m. p. 176°. As it did not couple with diazonium solutions it must exist as the ketone. The preparation of *N*-*n*-butylpropionamide was described in Part I.[1] Formaldehyde was prepared by heating paraformaldehyde, collecting the gas in water, and determining its concentration volumetrically by oxidation with hydrogen peroxide in presence of sodium hydroxide.

Infrared Spectroscopy.—The following were examined : (i) solutions in carbon tetrachloride of (*a*) phenol (0·1M), (*b*) pyridine (0·1M), (*c*) propionaldehyde (0·1M), (*d*) phenol (0·05M) and propionaldehyde (0·05M), (*e*) pyridine (0·05M) and propionaldehyde (0·05M), and (ii) (*f*) *iso*butyraldehyde (pure) and (*g*) an equimolar mixture of *iso*butyraldehyde and pyridine. There was evidence of a small increase in hydrogen bonding of the phenolic group in (*d*), the optical densities of the free and bonded OH-stretching frequencies of phenol alone (0·1M) being 0·505 and 0·097 respectively, and of phenol (0·05M) in presence of propionaldehyde, 0·0315 and 0·105, respectively. The bonded OH band also broadened and shifted slightly from 3460 cm.$^{-1}$ to 3440 cm.$^{-1}$. In the mixed solutions or mixtures containing pyridine, the indications were inconclusive; thus the pyridine–propionaldehyde curve could not be properly evaluated owing to the presence of some propionic acid in the propionaldehyde reference spectrum, evidently arising from aerial oxidation, though little or no acid was evident in the mixture itself; and in the *iso*butyraldehyde–pyridine mixture there also appeared to be traces of carboxylic acid, which interfered with examination of the aldehyde bands; slight shifts actually observed in these were not considered significant.

This, however, does not constitute evidence of non-interaction, because even in the phenol–aldehyde solution, in which interaction is demonstrable, there was no evidence of changes in the characteristic bands of the aldehyde group; and moreover, whereas the solution of aldehyde alone gave evidence of the presence of very little free carboxylic acid produced by aerial

* Brode, Sheldin, Spoerri, and Wyman [14] have attributed the appearance of a new band in the light-absorption spectra of alcoholic solutions of certain azo-compounds, on addition of water, to a hydrogen bond between the azo-group and water.

[14] Brode, Sheldin, Spoerri, and Wyman, *J. Amer. Chem. Soc.*, 1955, **77**, 2762.

[15] Fieser, *ibid.*, 1931, **53**, 2329.

oxidation, free acid was detected in either of the mixed solutions (*d*) or (*e*). Whatever the reason for this may be, it seems conclusive that pyridine influences the aldehyde group chemically.

The spectroscopic results therefore give no decisive evidence either for or against the hypothesis of bonding by the hydrogen of the aldehyde group.

Instruments and Procedure.—These have already been described in Parts I[1] and II;[6] a Bellingham and Stanley Pulfrich refractometer was also used in many of these experiments of this work. Infrared spectra were recorded in 1 mm. cells (solutions) on a Perkin-Elmer Model 13 instrument or in 0·05 and 0·025 mm. cells (pure liquids) on a Grubb-Parsons instrument, both with sodium chloride prism.

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