

1070. *Studies in Hydrogen-bond Formation. Part X.* Complex-formation between a Variety of Organic Solutes in Carbon Tetrachloride.*

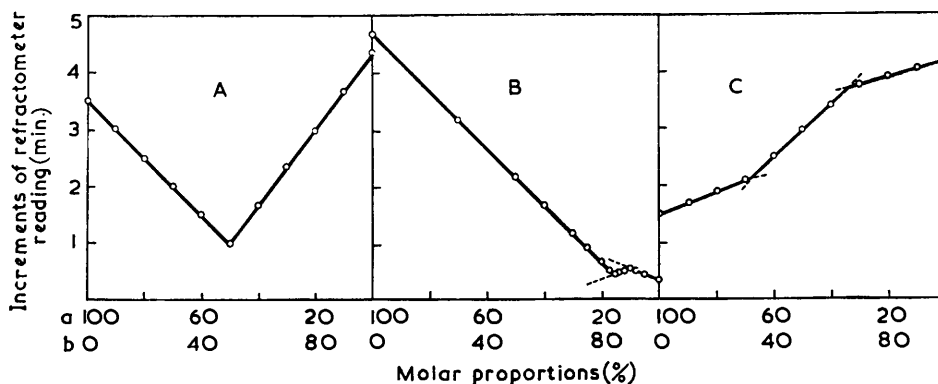
By C. H. GILES, R. B. MCKAY, and (in part) W. GOOD.

A number of pairs of solutes have been tested by the refractometric method in a non-bonding solvent, carbon tetrachloride. Intermolecular hydrogen-bonding of $\text{OH} \cdots \text{O}$, $\text{CH} \cdots \text{Cl}$, $\text{CH} \cdots \text{N}$, $\text{OH} \cdots \text{Cl}$, and $\text{ArOH} \cdots \text{ArH}$ types have been detected. The results agree with those obtained previously in hydrogen-bonding solvents, *e.g.*, benzene, dioxan, ethanol, water, and confirm the value of the method for measuring complex ratios in either bonding or non-bonding solvents. The theoretical basis of the linearity of the curves is discussed.

THE method of "continuous variations" with refractive index measurements is used in this work to measure the combining ratio of a variety of hydrogen-bonding organic solutes. Several hundred systems have been examined, and the complex ratios found, or

* Part IX, Giles and Nakhwa, *J. Appl. Chem.*, 1961, **11**, 197.

the reactivity of individual types of group, have in many cases been confirmed by other methods.¹⁻⁴ There are numerous cross-checks in the data, *e.g.*, the number of molecules of a solute B combined with a solute A agrees with the number of free bonding centres in A.



Relation between refractive index (as instrument reading) and ratio of components in carbon tetrachloride solution.

A: a, Chlorobenzene; b, phenol; 0.1M; 14.85°.

B: a, Hexachlorobenzene; b, phenol; 0.05M; 12.08°.

C: a, Benzene; b, phenol; 0.1M; 17.00°.

The method has also been used to detect intramolecular bonding, *e.g.*, in diols,² for which confirmation by infrared spectroscopy is available (ref. 5, p. 97). A recent comment on the method (ref. 5, p. 55) is that large numbers of the systems used here were examined in hydrogen-bonding solvents, *e.g.*, ethanol, benzene, and especially water, and that more positive value could be placed on the method if the only possibility for hydrogen bonding were between the two solutes. The present paper describes the application of this suggestion. It should, however, be emphasised that hydrogen bonding in aqueous solution is of the greatest importance in all biological systems and in many technical processes, and that in our view one of the principal advantages of this method is that it is almost the only simple one that can be used to study hydrogen-bonding combining ratios in dilute aqueous solution. Thus, of nearly thirty methods described by Pimentel and McClellan⁵ only about ten can be used with aqueous media, and few if any are as widely applicable as the present.

The method of continuous variations has also been used successfully to determine combining ratios between metals and a chelating organic solute.⁶

In this paper we describe tests in carbon tetrachloride solution with a variety of pairs of solutes, chosen to represent the most important types of intermolecular bond, within the limits imposed by the small range of compounds that are sufficiently soluble in this solvent. The results are shown in the Figure and Table 1 which includes the results with this solvent reported previously. All relevant comparisons with systems in water or other bonding solvents are also shown.

¹ Arshid, Giles, McLure, Ogilvie, and Rose, *J.*, 1955, 67.

² (a) Arshid, Giles, Jain, and Hassan, *J.*, 1956, 72; (b) Arshid, Giles, and Jain, *J.*, 1956, 559, 1272.

³ See, *e.g.*, Giles and Neustädter, *J.*, 1952, 3806; Allingham, Giles, and Neustädter, *Discuss. Faraday Soc.*, 1954, 16, 92; Cameron, Giles, and MacEwan, *J.*, 1957, 4304; Giles and MacEwan, *J.*, 1959, 1791.

⁴ Giles, in "Hydrogen Bonding," ed. Hadzi, Pergamon Press, London, 1959.

⁵ Pimentel and McClellan, "The Hydrogen Bond," W. H. Freeman & Co., San Francisco, 1960.

⁶ See, *e.g.*, Job and his collaborators, *Compt. rend.*, 1925—1935, 180—200; Vosburgh and Cooper, *J. Amer. Chem. Soc.*, 1941, 63, 437; and other papers quoted in ref. 2a.

TABLE I.
Comparison of results of complex-detection tests in carbon tetrachloride with those in bonding solvents.

Type of bond	Solutes	Solv.*	Total mol. concn.	Temp.	Mol. ratio of complex	
Alk-OH + Ar-OH	Butan-1-ol	Phenol	CCl ₄	0.1	15.85°	1:1
	Several alcohols		T, D, W			1:1
-CHO + Alk-OH	Acetaldehyde	Ethanol	CCl ₄	0.1	20	1:1
	Benzaldehyde		CCl ₄	0.1	20	1:1
	D-Glucose		W ^{2b}	0.25	20	0
	Propionaldehyde		CCl ₄ ^{2b}	0.2	17.5	1:1
-CHO + Ar-OH	n-Butyraldehyde	Phenol	W ^{2b}	0.2	17.5	0
			CCl ₄	0.1	13.08	0
	D-Glucose		W ^{2b}	0.25	20	0
			CCl ₄ ^{2b}	0.1	17	1:1(?)
			EG	0.2	18	1:1
-CHO + N<	Acetaldehyde	Diethylamine	W ^{2b}	0.25	20	1:1
			CCl ₄	0.1	13.08	1:1
	n-Butyraldehyde	Triethylamine	W ^{2b}	0.2	20	1:1
			W ^{2b}	0.25	20	1:1
	Formaldehyde		W ^{2b}	0.25	20	1:1
			CCl ₄ ^{2b}	0.2	18	1:1
	D-Glucose		W ^{2b}	0.2	18	1:1
			W ^{2b}	0.2	18	1:1
	Propionaldehyde	Dimethylformamide	CCl ₄ ^{2b}	0.2	18	1:1
			W ^{2b}	0.2	18	1:1
Terephthaldehyde	Triethylamine	T ^{2b}	0.2	18	1:2	
		W ^{2b}	0.1	17	1:2	
>C=O + Alk-OH	Acetone	Methanol	C ^{2b}	0.1	20	1:2
			D ^{2b}	0.1	20	1:2
>C=O + Ar-OH	Acetone	Phenol	W ^{2b}	0.1	20	0
			D ^{2b}	0.25	20	1:2
	Di-isobutyl ketone		CCl ₄	0.1	14.83	1:1, 1:2
			CCl ₄	0.1	17.00	2:1, 1:2
	Ethyl methyl ketone		CCl ₄	0.1	14.85	1:1
Ar-H + ArOH	Benzene	Phenol	EW [†]	0.1	20	1:1
			CCl ₄	0.05	12.08	1:6, 1:9
Ar-Cl + Ar-OH	Chlorobenzene	Phenol	CCl ₄ ^{2a}	0.1	22	1:1, 1:2
			B ^{2a}	0.25		1:1 [†]
-C-N< + ArOH	Hexachlorobenzene	Phenol	W ^{2a}	0.25	19.35	1:1
			CCl ₄ ^{2a}	0.1	20	1:1
-N=N- + ArOH	Azobenzene	Benzyl alcohol	CCl ₄ ^{2a}	0.1	20	1:1
			B ^{2a}	0.25	19	1:1, 1:2
-CO ₂ R + Ar-OH	Ethyl acetate	Phenol	CCl ₄ ^{2b}	0.1	13.11	1:1
			W ^{2b}	0.04	24	1:1(?)
-CO ₂ R + Ar-Cl	Ethyl acetate	Chlorobenzene	CCl ₄ [†]	0.1	14.85	1:1
			EW*	0.1	14	1:1
	Phenyl acetate		B [†]	0.1	21	1:1
			EW [†]	0.25	14	1:1

* Solvents and references (where no ref. is given, the test is new): B = benzene; D = dioxan; EW = ethanol-water (1:1 v/v); T = toluene; W = distilled water. † By dielectric constant measurement. ‡ Giles and Nakhwa, *J. Appl. Chem.*, 1961, **11**, 197.

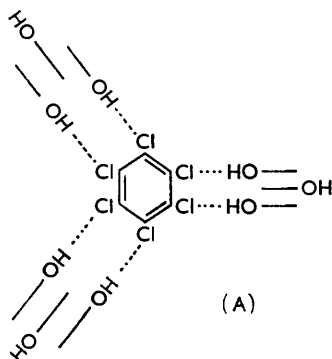
Experimental.—The solutes were recrystallised or redistilled, and the solvent was of infrared "AnalaR" quality. A Bellingham and Stanley (Pulfrich) refractometer was used, with water circulation, by suction, from a cool thermostat bath, controlled to $\pm 0.01^\circ$ by mercury-toluene regulator. The solutions in each series were aged for several hours in the bath before use, and were selected for test in a random manner, to avoid error due to possible progressive ageing.

The most consistent results are obtained if the refractometer is used by one operator only.

Comparisons between Results in Carbon Tetrachloride and Bonding Solvents.—In Table I the present results are set alongside others, in which the same type of bond is expected and which were made in bonding solvents. It will be seen that three conditions occur: (a) The bonding-ratio of each pair of groups is identical in carbon tetrachloride and in a bonding solvent; this is so for most cases. (b) A complex is formed in carbon tetrachloride but not in a bonding solvent; this applies only to aldehyde and ketone groups,

which in water are unreactive, presumably being protected by preferential bonding to the solvent. (c) No complex is formed in carbon tetrachloride, though its formation would be expected. This applies to one case only (butyraldehyde-phenol). This was not further investigated, but there are two possible causes: hindrance by the bulky butyl group, or inactivation of the carbonyl-oxygen atom by its intramolecular bonding in a 6-membered ring with hydrogen on the γ -carbon atom. Bonds of the latter type in carboxylic acids and ketones have been suggested by others.⁷

Complexes with Hexachlorobenzene.—This compound was used, with phenol, to discover whether high-ratio complexes can be detected in carbon tetrachloride solution. A 1 : 6 complex was expected, in which each chloro-group is bonded to a phenol molecule. In fact, this complex is clearly evident (Fig. 1), but in addition a 1 : 9 complex also appears. We suggest that the latter is formed when three extra phenol molecules each become sandwiched between a pair of those in the 1 : 6 complex (cf. A). There appears to be evidence that this type of structure can be formed between phenol and benzene also, in carbon tetrachloride. These solutes form both 1 : 2 and 2 : 1 complexes: presumably in one case the benzene molecules are sandwiched between two phenol molecules, and in the other phenol is between benzene. These complexes were detected previously,¹ but the test has been repeated for confirmation (Fig. 1).



Mixtures not Forming Complexes.—In the previous papers in this series about twenty systems in carbon tetrachloride were examined, and in nine of these (Table 2) no complex-formation was detected. In most of these nine the pairs of solutes would not be expected to form hydrogen-bond complexes. Systems indicated in Table 2 have now been

TABLE 2.
Systems giving no complex in carbon tetrachloride.

Solutes		Total mol. concn. (and ref.)	Temp.
Acetone	Benzoquinone	0.05 ¹	20°
2-Acetylpyridine	Di-isobutyl ketone	0.1 ^{2b}	21
Azobenzene	Pyridine	0.05 ⁷	17
Benzene	Ethylene dichloride	0.05 ¹	20
Benzoquinone	Di-isobutyl ketone	0.05 ¹	20
Dimethylformamide	Diphenylamine	0.05	13-33
		0.05 ^{2a}	17
Naphthalene	2-Naphthol	0.05	13-33
		0.1(?) ¹	20(?)
Phenol	Toluene	0.1	17-10
		0.1 ¹	20(?)
Pyridine	Triethylamine	0.1 ¹	20

re-examined at different temperatures, and the previous results confirmed. (A negative result at one temperature only is not conclusive evidence of non-bonding.¹)

APPENDIX (By W. GOOD)

Linearity of Curves.—In the Appendix of Part II¹ it was demonstrated that curves obtained as here, by the method of "continuous variations," for solutions in which a 1 : 1 complex is formed, should not consist of linear portions, except in the special case where the reaction constant, $K = \infty$. In practice however, all such curves appear to consist of linear portions, even where K must have quite a low value (see, especially, Fig. 1 here). Thus, Flett⁸ calculated

⁷ E.g., Evans, J., 1936, 785; Evans and Gordon, J., 1938, 1434; Dippy, J., 1938, 1222.

⁸ Flett, J. Soc. Dyers Colourists, 1952, 68, 59.

values of K for a wide variety of intermolecular hydrogen-bonding reactions between pairs of organic solutes in carbon tetrachloride at room temperature. These measurements, made from infrared absorption data, on solutions mainly in the range 0.005—1.00M, gave values of K between 3.0 and 150, except for one case (phenol-dimethylformamide) which gave values above 400. The probable explanation for the linearity is as follows.

The curves in Fig. 13 of Part II are calculated from the equation (p. 77¹),

$$K = z^r / [(x - pz/r)^p (C - x - qz/r)^q]$$

for the special case where $p = q = r = 1$, *i.e.*, where

$$K = z/(x - z)(c - x - z),$$

and thus they correspond to unit molarity. If the molarity is in fact $1/v$ (*i.e.*, 1 mole in v litres), z should be calculated from the relation

$$K/v = z/(x - z)(c - x - z),$$

i.e., from a curve which in Fig. 13 would be labelled K/v .

Thus it is clear that, the more dilute the solutions used, the more nearly linear are the portions of the curve. Conversely, the more concentrated the solutions, the less linear they are; and the limiting case occurs of course when two pure liquids are used, and there is no solvent. This type of system was investigated by, *e.g.*, Pushin and Matavulj, and by Burnham and Madgin, who in fact obtained non-linear curves (hyperbolæ) for values of refractive index against component percentage, by the method of continuous variations.⁹

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⁹ Pushin and Matavulj, *Z. phys. Chem.*, 1932, A, **158**, 290; Burnham and Madgin, *J.*, 1936, 789.