

*Studies in Hydrogen-bond Formation. Part II.\* The Use of Refractive-index Measurements to Detect Intermolecular Complex Formation in Solution.*

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(With an Appendix. By JOHN C. EATON.)

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The square of the refractive index may be used equally as well as the dielectric constant (see Part I\*) for detecting the ratio in which organic molecules associate intermolecularly in binary solution, with the added advantage that aqueous as well as non-aqueous solutions can be studied. In particular, hydrogen-bond complexes can be detected by this means, and typical results are given. Anion-cation association is also detectable, but no firm evidence has been obtained of the detection of other forms of association. The method appears equally useful for detecting strong or weak complexes. The reality of the existence of many compounds so detected has been demonstrated by a variety of procedures, including molecular-weight determination, preparation of solid complexes, and comparison with complexes previously reported, either by preparation in substance or detection by infra-red spectrophotometry. The method is rapid and simple, it requires only small quantities of substances (solutions at least as dilute as 0.01M have been used successfully), and it appears to have some advantages over hitherto-used procedures. It can be employed to detect intra- as well as inter-molecular bonds.

PART I\* described preliminary experiments upon the use of dielectric-constant measurements to detect intermolecular hydrogen-bonding between pairs of organic solutes in non-aqueous solutions. Plots of dielectric constant against molar ratio of the solutes (at constant total molarity) were shown to be linear, changes of slope occurring at ratios which were interpreted as corresponding to the composition of intermolecular complexes.

\* Part I, *J.*, 1952, 2799.

In Part I, p. 3800, last line of the second paragraph, for "hydrogen" read "carbon"; p. 3802, formula (III), lower line, for " $C_2H_5 \cdot OH$  =  $N \cdot C_4H_9$ ", read " $C_2H_5 \cdot C(OH) = N \cdot C_4H_9$ ."

The present paper describes an alternative method of detecting complex formation which may be used with both non-aqueous and aqueous solutions. The results obtained by the two methods are compared and a detailed examination is described of the validity of their interpretation as evidence of the presence of hydrogen-bond complexes.

*Use of Refractive-index Measurements.*—It was desired to work with aqueous solutions, and the dielectric-constant method used in Part I being unsuitable for this purpose, consideration was given to the measurement of some other physical constant. The refractive index appeared to fulfil the criterion of ready determination to a high degree of precision with small amounts of materials. By Maxwell's law, the square of the refractive index of a substance is equal to its dielectric constant, and therefore this parameter should, like the dielectric constant, vary linearly with the concentration of a solution. Since refractive index and dielectric constant cannot be measured at the same field frequency, and because anomalous dispersion occurs in dipolar substances, Maxwell's law is not generally

Relation between square of refractive index and molar concentration.

FIG. 1. Non-aqueous solutions.

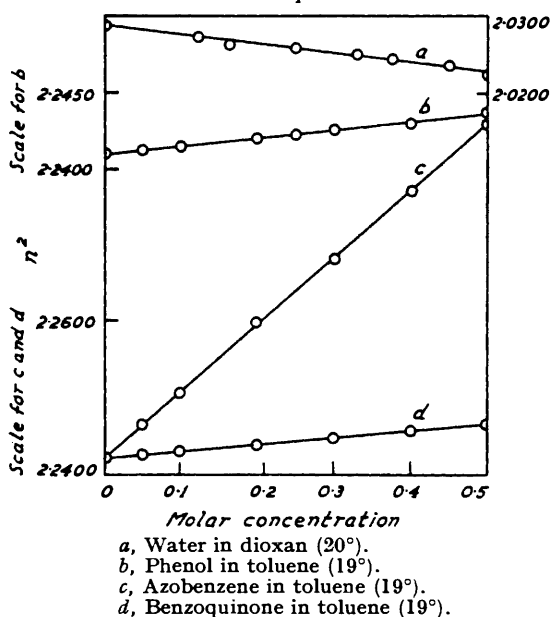
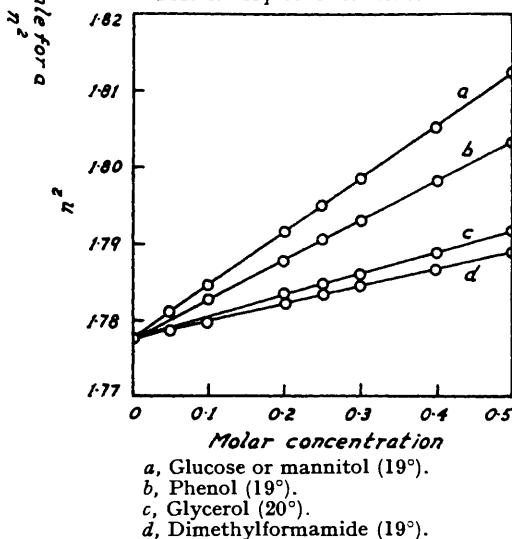


FIG. 2. Aqueous solutions.



obeyed. It was therefore necessary to examine empirically the relationship between the square of the refractive index and the concentration of non-aqueous and aqueous solutions over the limited range of concentrations proposed to be employed. The results of this examination are summarised in Figs. 1 and 2, which show that the relationship is quite linear\* for a variety of typical compounds in both non-aqueous and aqueous solutions up to at least double the maximum concentration (0.25M) used in the present work.

This test was then followed by one for additivity. Fig. 3 shows that the square of refractive index is truly additive for binary solutions, of constant molarity, of azobenzene and benzoquinone, two substances not capable of hydrogen-bond interaction. When, however, substances which are capable of interaction are examined, *viz.*, azobenzene and phenol (Fig. 7), the curve is virtually linear, but shows two slope changes, corresponding to intermolecular complexes of 1 : 1 and 1 : 2 ratio, as detected also by the dielectric-constant method (Part I, Fig. 2). An examination of some 33 different non-aqueous binary solutions, of which details will be given in later papers, then revealed that the changes in

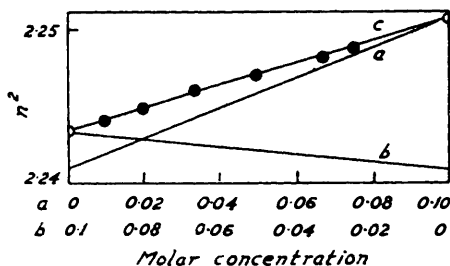
\* When the change in  $n$  is very small it is of course unnecessary to plot  $n^2$ , for  $n$  itself then varies linearly with concentration.

slope observed occur at the same respective ratios whether measurement is made by dielectric-constant or refractive-index methods. Further, it was found that aqueous solutions give the same type of curves as do non-aqueous solutions when examined by the latter method, changes in slope occurring at molar ratios which correspond in many cases to the occurrence of an expected hydrogen-bond complex.

*Previous Work.*—Apparently, refractive-index determinations have not hitherto been used thus, but Pushin and Matavulj (*Z. physikal. Chem.*, 1932, *A*, 158, 290; *A*, 161, 341; *A*, 162, 415; 1933, *A*, 164, 80), Pushin and Rikovski (*ibid.*, 1932, *A*, 161, 336), Pushin, Matavulj, Rikovski, and Nenadović (*Bull. Soc. chim. Belgrade*, 1940—1946, 11, 72; through *Chem. Abs.*, 1948, 42, 2167), and Pushin, Matavulj and Rikovski (*ibid.*, 1948, 13, 38, 165, 173; through *Chem. Abs.*, 1951, 45, 6475; 1952, 46, 2894), using binary mixtures of certain organic liquids, plotted refractive index, *f. p.*, etc., directly against molar composition. They observed many examples of systematic variation from arithmetic mean values, and obtained curves showing maxima corresponding in many cases to intermolecular complex formation. They detected, *e.g.*, complexes of piperidine with phenols; of acetic acid with certain primary, secondary, and tertiary amines (in several cases corresponding to known solid complexes; *e.g.*, equimolar complexes with phenylhydrazine, piperidine, pyridine, or quinoline); of aniline (1 mol.) with phenol or *o*-chlorophenol (1 mol.) or acetic acid (2 mols.); of formic acid (2 mols.) with aniline, mono- or di-methylaniline, pyridine or

FIG. 3. Additivity of square of refractive index for non-interacting solutes in toluene.

- a, Azobenzene.  
b, Benzoquinone.  
c, Binary solution.



quinoline (1 mol.); of benzylamine (1 mol.) with thymol (probably 1 mol.); and undefined complexes of quinol with *o*- and *p*-chlorophenol, cresols, guaiacol, or thymol; no complexes were detected between aniline and *p*-chlorophenol, cresols, or guaiacol. Evidence of molecular association of a second component mixed with benzene or toluene was obtained in some cases.

*Confirmation of Complex Formation by Other Methods.*—There were thus good grounds for believing that either of the present methods gives valid evidence of the presence of intermolecular complexes, but it was nevertheless considered that confirmation of this belief by as many other independent methods as possible would be desirable. Accordingly, a variety of procedures has been adopted in order to check the validity of the method. These include: (a) comparison with the composition of known solid complexes; (b) molecular-weight determinations; (c) comparison with infra-red spectrophotometric data; (d) examination of compounds known to contain chelate bonds; (e) comparison with certain interactions in monolayers; (f) a further study of the theoretical basis of the curves obtained; (g) examination of the consistency of the results and their relation to the known association properties of various compounds used. These results are now discussed.

(a) *Solid complexes.* In Table 1 a number of solid complexes between various organic compounds and alcohols or phenols, described by Pfeiffer (*Organische Molekülverbindungen*, Stuttgart, F. Enke, 2nd edn., 1932), are shown, in comparison with identical or closely similar complexes detected in solution by the present methods. Fig. 4 shows evidence given by refractive-index measurements confirmatory of the existence of one of these complexes (benzoquinone + quinol, 1 : 1) in (dioxan) solution.

The same type of complex will not necessarily exist both in the crystalline state and in solution, and in fact a number of examples in Table 1 show that the solvent itself may

prevent interaction. (This point will be considered more fully in a later paper.) Nevertheless, there is good agreement between the data from the different sources.

It was hoped that this information could be supplemented by examination of solid complexes prepared from the solutions used in the present work. Only four such solutions have actually been found satisfactorily to deposit solid complexes, *viz.*, ether (or toluene)

TABLE 1. *Intermolecular complexes of hydroxylic compounds.*

Components	Molar ratio	
	As solid (Pfeiffer)	In solution* (present work)
<i>Aldehydes and ketones</i>		
Acetaldehyde-ethanol .....	1 : 1	1 : 1 (W)
Benzaldehyde-ethanol .....	—	1 : 1 (W)
Acetone-methanol .....	—	1 : 2 (C) (D)
Acetone-phenol .....	1 : 2	† (E, W)
Diisobutyl ketone-phenol .....	—	1 : 2 (D)
<i>Amine</i>		
Aniline-phenol .....	1 : 1	1 : 1; (1 : 2); † (W) (T)
<i>Carboxylic acids</i>		
Acetic acid-phenol .....	—	1 : 1 (T)
Benzoic acid-phenol .....	—	1 : 1 (T)
Trichloroacetic acid-phenol .....	1 : 1	1 : 1 (T)
<i>Esters</i>		
Dimethyl oxalate-phenol .....	1 : 2; 1 : 4	1 : 2 (D)
Dimethyl terephthalate-phenol .....	—	1 : 4 (T)
Ethylene glycol dibenzoate-phenol .....	—	1 : 4 (T)
<i>Quinone</i>		
Benzoquinone-phenol .....	1 : 2	2 : 1; 1 : 2 (T)
Benzoquinone-quinol .....	1 : 1	1 : 1 (D)

\* Solvents: B = benzene; C = carbon tetrachloride; D = dioxan; E = diethyl ether; T = toluene; W = water. Data in parentheses denote uncertain indications.

† No complex detected.

solutions of diethylamine with *p*-nitrophenol and resorcinol respectively. Analyses of these complexes when previously prepared (see Part I) did not exactly correspond to an integral ratio of the components. The discrepancies were attributed to possible selective solution of one component by the solvent used for washing. The preparations have now been repeated with suitable precautions and the elementary analyses now correspond with integral ratios of components (1 : 2 in both cases), though it is admittedly not easy to formulate the structure of such complexes. On account of precipitation, refractive-index measurements cannot be carried out with solutions in the same solvent as used for the preparations, but by using dioxan as a solvent, in which the complexes are quite soluble, no precipitation occurs and curves can be obtained (Fig. 5) which show changes of slope corresponding to the analyses of the solids; the change in the diethylamine-*p*-nitrophenol curve is slight, but definite, that in the diethylamine-resorcinol curve at the 2 : 1-ratio is only just discernible,\* but there is a clear indication of a 1 : 1-complex, not obtained in solid form. Solutions in water give evidence of complexes of different integral ratios.

(b) *Molecular-weight determination.* Four pairs of compounds were selected for examination by the f. p. method in benzene. One of these, azobenzene-phenol, was chosen because, when examined by both the present methods (see above) it appears to form two distinct complexes of different ratio; the other three, because they appear to form unusual complexes perhaps by the less common mechanism of bonding through hydrogen attached to carbon. This will be discussed later. From data plotted on the basis shown (Figs. 7—10), *viz.*, apparent molecular weight of combined solute against molar ratio, the presence of an intermolecular complex should normally be demonstrated by a maximum in the curve at the appropriate ratio(s). In fact, all the expected

\* *Added in Proof.*—This change in the curve has now been confirmed by use of a refractometer of higher precision.

discontinuities are evident, though in three of the five instances they are only just so. In two systems (Figs. 8 and 10) minima are obtained, *i.e.*, complex formation *lowers* the apparent molecular weight. Low molecular-weight values can be attributed to solvation of solute by solvent (cf. Skau and Wakeham in "Physical Methods of Organic Chemistry," Vol. I, ed. Weissberger, New York, Interscience Publishers, Inc., 1945, Chap. I; see also Chipkatti, Giles, and Vallance, *J.*, 1954, 4375). The azobenzene-phenol system is clearly complicated by association of the phenol itself and the curve is difficult to interpret. Even

Relation between square of refractive index and component ratio in binary solutions in dioxan.

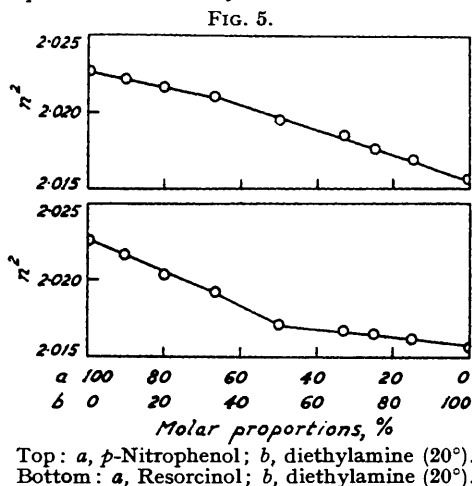
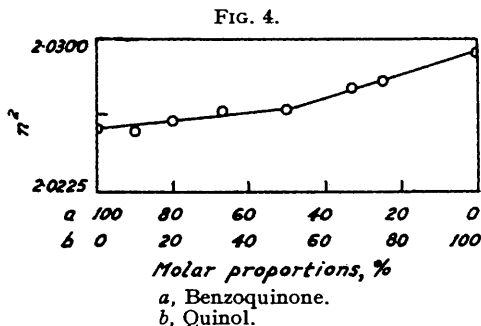
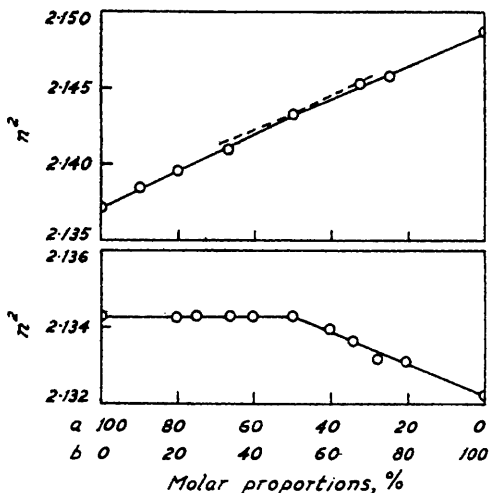


FIG. 6.  
 Top: a, Benzyl alcohol;  
 b, Azobenzene (0.1M) at 20°.  
 Bottom: a, Dimethylformamide;  
 b, Phenol (0.05M) at 16°.  
 Solvent: Carbon tetrachloride.

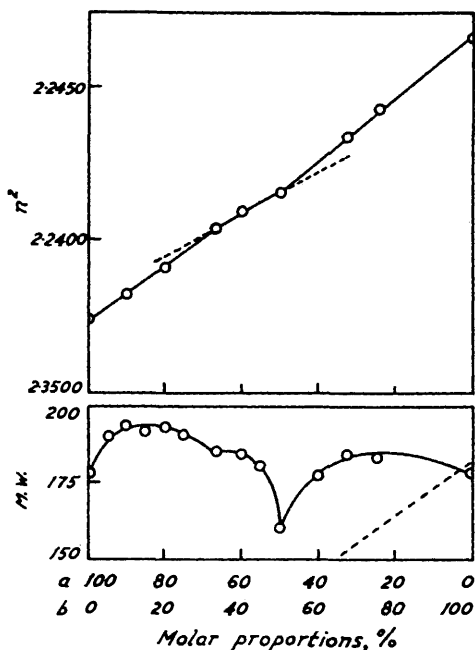


so, the discontinuities are above the theoretical line for no combination. The high intermediate sections of the curve must represent separation of complex on freezing, which can in fact be observed owing to the colour of azobenzene. Whatever the detailed interpretation of the discontinuities in these curves may be, they and the corresponding dielectric-constant or refractive-index plots agree in showing that at certain simple integral molar ratios of the solutes, some physical change occurs in the properties of the solutions.

In addition, Pushin and Matavulj (*loc. cit.*) confirmed the molar ratios of complexes detected in binary liquid mixtures, by f. p. determinations, and Laurent (*Compt. rend.*, 1935, 201, 554) obtained a solid complex of phenol and aniline with a molar ratio (2 : 1) the same

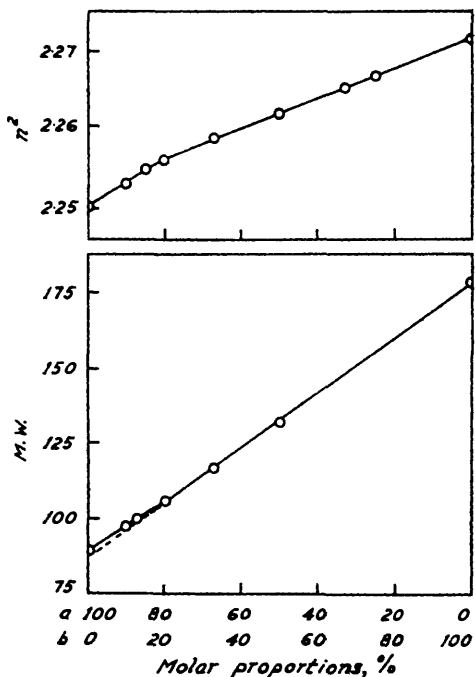
Relation between molar ratio, square of refractive index, and apparent molecular weight in binary solutions

FIG. 7.



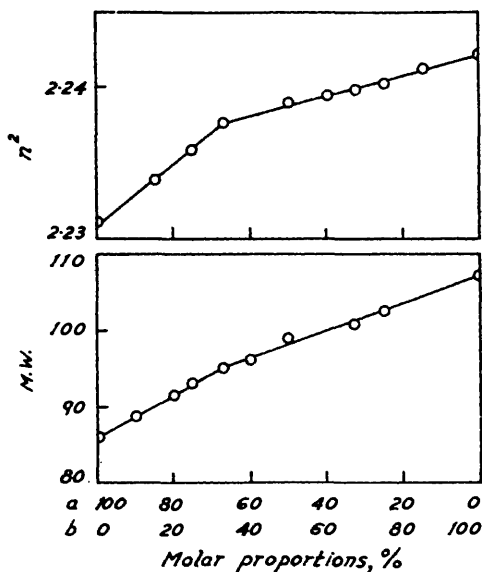
a, Phenol; b, Azobenzene. Solvent: benzene. Broken line in lower graph is theoretical plot for no combination and no association.

FIG. 8.



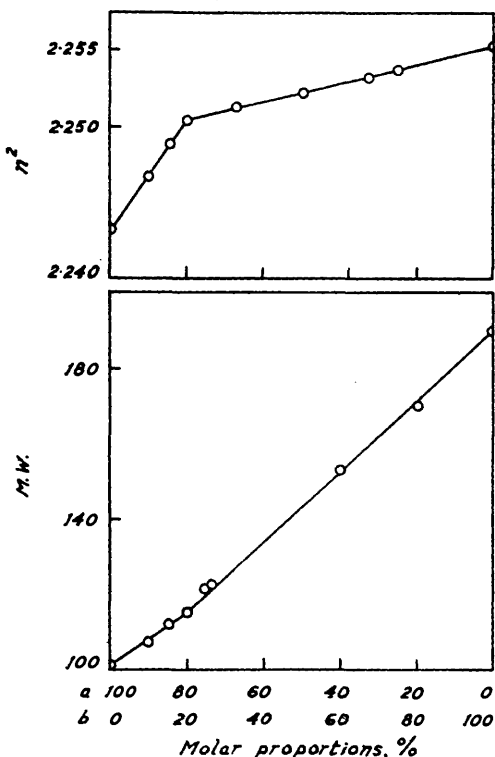
a, Ethyl acetate; b, azobenzene. Solvents: Top, toluene (17°); bottom, benzene.

FIG. 9.



Top: a, isoPropyl acetate; b, benzoquinone. Solvent: toluene. Bottom: a, Ethyl acetate; b, benzoquinone. Solvent: benzene.

FIG. 10.

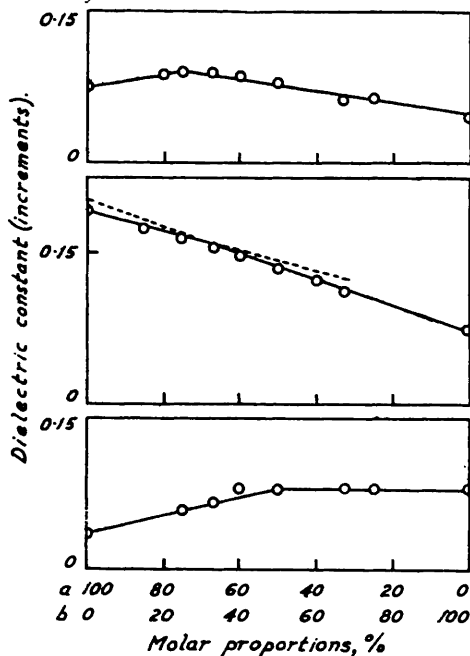


a, Triethylamine; b, dimethyl terephthalate. Solvents: Top, toluene; bottom, benzene.

as found by dielectric-constant measurements on binary solutions, and also confirmed by cryoscopic measurements.

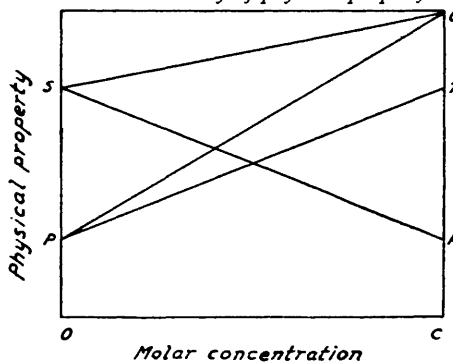
(c) *Infra-red spectrophotometry.* Flett (*J. Soc. Dyers Col.*, 1952, **68**, 59) and Tsuboi (*Bull. Chem. Soc. Japan*, 1952, **25**, 60) have given thermodynamic data for hydrogen-bond formation between pairs of aromatic compounds in carbon tetrachloride solutions, obtained by infra-red spectrophotometry. They determined heats, etc., of reaction by the method of measuring the change in height of an absorption band with change in temperature. This does not actually give an unequivocal measure of the ratio of components in the complex, but the ratio can usually be estimated, at least if the number of participating

FIG. 11. Detection of intramolecular bonding by the dielectric constant method.



Top : a, Phenol; b, *p*-nitrophenol.  
Middle : a, Phenol; b, nitrobenzene.  
Bottom : a, Phenol; b, *o*-nitrophenol.

FIG. 12. Linearity of physical property.



molecules is not more than about three or four, from the magnitude of the heat changes. In Table 2 some of Flett's and Tsuboi's data for compounds most resembling those we have examined are compared with our own. The systems studied are closely similar and in two

TABLE 2. Comparison of present results with those of infra-red spectrophotometry.

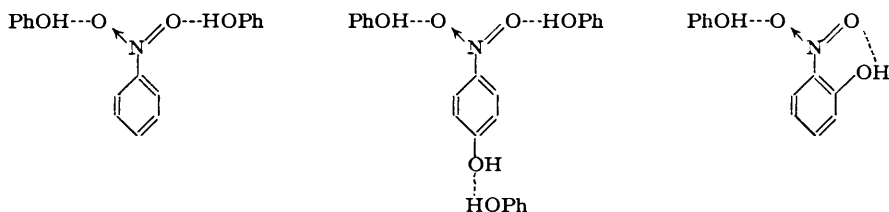
Complex between	Molar ratio and solvent *		
	Flett †	Tsuboi †	Present method
Anisole, benzyl alcohol .....	1 : 1	—	—
Anisole, phenol .....	—	—	1 : 1 (B)
Benzaldehyde, phenol .....	—	1 : 1	1 : 1 (W)
Benzyl acetate, phenol .....	1 : 1	—	—
<i>iso</i> Propyl acetate, phenol .....	—	—	1 : 1 (T)
Dimethylformamide, diethylamine .....	—	—	1 : 1 (B)
Dimethylformamide, diphenylamine .....	1 : 1	—	—
Dimethylformamide, phenol .....	1 : 1	—	1 : 1 (B; C; D; W)
Azobenzene, benzyl alcohol .....	1 : 1	—	1 : 1 (C)
Nitrobenzene, phenol .....	—	1 : 1	1 : 2 (B)

\* Solvents : B = benzene; C = carbon tetrachloride; D = dioxan; T = toluene; W = water.

† Both these workers used carbon tetrachloride as solvent, and the ratios are assumed.

examples (cf. Fig. 6) are in fact identical. In all cases the two methods give parallel results.

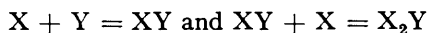
(d) *Chelated compounds.* If true complex formation is shown by these methods, then the masking of the reactivities of pairs of individual groups in a molecule by chelation should be capable of demonstration thereby, since it will lead to a corresponding reduction in the number of possible intermolecular bonds. This has been tested and found to apply in a number of cases, which will be discussed in detail in a subsequent paper (see also Table 3), but a particular example may be quoted here, *viz.*, the evidence that phenol forms with nitrobenzene, *p*-nitrophenol, and *o*-nitrophenol, 2 : 1, 3 : 1, and 1 : 1 complexes, respectively (Fig. 11), which may be formulated as below



(e) *Monolayer experiments.* Evidence of the formation of complexes of closely related types to some detected in this work has been obtained from the results of experiments with monolayers on water. These types include 1 : 1 complexes between quinol and benzoquinone derivatives, 2 : 1 complexes between *o*-hydroxyazo-compounds and quinol, etc. (see, *e.g.*, Giles and Neustädter, *J.*, 1952, 3806).

*Theoretical Treatment.*—The theoretical treatment given in the Appendix of Part I (*loc. cit.*) showed that linear curves with a change of slope at the point of complex formation are to be expected if the value of  $K$  for the reaction is high, *i.e.*, if the complex is very stable, and in the particular case of a 1 : 1 complex. Many of the complexes now detected, however, cannot be very stable, and indeed Flett (*loc. cit.*) has already shown that, in 12 binary systems (in carbon tetrachloride) similar to those we have examined, the values of  $K$  are often quite low, the lowest, at room temperature, being 3.82, yet the curves given by this method are always apparently linear, within the limits of accuracy. It was therefore necessary to re-examine the theoretical basis of the method in an entirely general way with a view to determine whether unstable complexes also should be detectable. At the same time the opportunity was taken to examine cases where a complex exists having a ratio other than 1 : 1, or where more than one complex is present simultaneously. The full treatment is given in the Appendix. It is there shown that the graph of the physical constant used against solute molar ratio can be expressed simply in terms of a deviation  $z(S_{XY} - S_X - S_Y)$ , where  $z$  is the number of molecules of complex  $X_mY_n$  formed, and  $S_{XY}$ , etc., are the slopes of the curves for the constants of the respective individual components of the solution. The graph of  $z$  against the number of molecules of  $X$  present consists of two straight lines, intersecting at the point corresponding to the composition of the complex, only if  $K = \infty$ , but for all values of  $K$  the graph has a single maximum at this same point. This will give a maximum or a minimum in the curves as plotted in this work, according as the value of  $(S_{XY} - S_X - S_Y)$  is positive or negative. Thus in the special circumstance where  $S_{XY} = S_X + S_Y$ , *i.e.*, where the physical constant of the complex is the additive value of those of its components, no deviation at all should occur. This has been experienced in practice, as mentioned below, but it appears to take place only at one temperature, and at temperatures above and below this deviations are observed. The graphs for all the systems studied are thus strictly not linear, but it will be seen from the figures that the deviations from linearity are barely discernible.

The argument may be extended to cases in which two compounds,  $X$  and  $Y$ , combine to form more than one complex, *e.g.*,  $XY$  and  $X_2Y$ . Here there are two equilibria co-existing in the solution :





and the concentrations of the reactants will adjust themselves so that the equilibrium constants in the mixture are the same as in the separate systems. The curve can therefore be divided into halves, at least to a first approximation, one of which, between  $X = Y$  and  $X = 0$ , has no change of slope, and the other, between  $X = Y$  and  $Y = 0$ , has one corresponding to  $X_2Y$ , there being also a change at the intersection of the halves. A similar treatment may, in fact, be applied to conditions where more than two complexes can be formed, and in the present work as many as three have sometimes been detected in the same solution.

*Relation of Results to Known Properties of Typical Solutes.*—A series of compounds was selected for test to determine whether pairs of simple hydrogen-bonding substances would be found to have the expected complex ratios by this method, and in fact Table 3, (ii) and (iii), shows that they did (cf. also Part I, Table 1); and also to determine whether other forms of intermolecular association would be discernible in the curves, particularly (a) anion-cation association, (b) association between aromatic nuclei in planar molecules arising from short-range physical forces, and (c) various types of dipole-dipole interaction. The results [Table 3 (i), (iv), (v)] show that (i) is certainly detectable, but the series of tests

TABLE 3. Typical results of refractive-index measurements.

Solute <sup>a</sup>		Solution		Temp.	Mol. ratio of complex (a : b)
	b	Solvent *	Total mol. concn.		
(i) Acids and bases					
Sulphanilic acid → β-naphthol .....	Glycine	W	0.1	19°	1 : 1
Aniline → 2-naphthol-3 : 6-disulphonic acid ...	Triethylamine	W	0.05	20	1 : 2
(ii) Phenol-phenol and phenol-quinone pairs					
Quinol .....	Phenol	W	0.25	19, 35	1 : 2
" .....	Benzoquinone	D	0.1	20	1 : 1 (Fig. 4)
(iii) Phenol with chelated, unchelated, and isomeric compounds					
Nitrobenzene .....	Phenol	B	0.25	18	1 : 2 (Fig. 11)
o-Nitrophenol .....	"	—	"	"	1 : 1 "
p-Nitrophenol .....	"	—	"	"	1 : 3 "
Aniline → 2-naphthol-3 : 6-disulphonic acid ...	"	W	0.05	20	1 : 1 —
Sulphanilic acid → 1-naphthol .....	"	"	0.25	20	1 : 1 ; 1 : 2 ; 1 : 3
Sulphanilic acid → 2-naphthol .....	"	"	"	18	1 : 1
(iv) Electron-donor pairs					
Acetone .....	Benzoquinone	C	0.05	20	†
" .....	Azobenzene	D	0.1	18	†
Pyridine .....	"	C	0.05	17	†
" .....	Triethylamine	C	0.1	20	†
Benzoquinone .....	Azobenzene	T	0.1	19	† (Fig. 3)
" .....	Diisobutyl ketone	C	0.05	20	†
Aniline → 2-naphthol .....	Pyridine	B	0.25	20	†
(v) Pairs with hydrocarbons					
Benzene .....	Ethylene dichloride	C	0.05	20	†
" .....	Naphthalene	C	0.1	—	(1 : 1) (?)
" .....	Phenol	C	"	—	2 : 1 ; 1 : 2
Toluene .....	Phenol	C	"	—	†
Naphthalene .....	2-Naphthol	C	"	—	†

\* Solvents : B = benzene; C = carbon tetrachloride; D = dioxan; T = toluene; W = water.

† No evidence of complex formation.

with pairs of donor compounds representative of many intended to be used in later work gives no evidence of (c), and the evidence for detection of (b) is doubtful for, even in the case of the two complexes between phenol and benzene, the possibility of hydrogen-bond formation cannot be entirely ruled out, because Jones and Badger (*J. Amer. Chem. Soc.*, 1951, **73**, 3132; cf. Badger, *J. Chem. Phys.*, 1940, **8**, 228) obtained infra-red spectro-

photometric evidence of intermolecular hydrogen bonding between methanol and the hydrogen of aromatic rings in benzene and other hydrocarbons in binary solutions in organic solvents. They also consider that the weaker association of phenol in benzene than in carbon tetrachloride may be evidence of a phenol-benzene hydrogen bond (cf. also Mecke, *Discuss. Faraday Soc.*, 1950, 9, 161).

Subsequent papers will describe a number of other experiments, including studies of the interactions, e.g., of various hydroxylic solutes, including water, with carbohydrates, and with amides and amines.

*Conclusions.*—(a) It is reasonably certain that the method can give valid evidence of the molar ratio of intermolecular complexes in aqueous or non-aqueous solution, and that it may also be capable of detecting intramolecular chelation. (b) There is so far no firm evidence that any other than the acid-base and hydrogen-bond types of association are detectable, though this possibility must be allowed for in the interpretation of results.

*Advantages of Present Methods.*—The present method appears to be somewhat more versatile than most of the commonly used hydrogen-bond detection procedures,\* because it can be employed with a very wide variety of solutes and solvents, including water; it requires quite small quantities of material (normally ca. 5 mmoles of each solute, though results might be obtained, if necessary, with as little as 0.05 mmole); it is rapid; and it can give information not readily obtained by most of the other methods. In a subsequent paper it will be shown that a qualitative estimate of the relative strength of bonds is possible in some cases; and it is proposed to attempt to obtain quantitative thermodynamic data of bond energies, etc., by this means.

## EXPERIMENTAL

*Materials.*—The organic solvents used were dried by the usual methods, except dioxan, which was of the "specially dried" quality (B.D.H.) used for Karl Fischer titrations.

*Instruments and Procedure.*—The dielectric-constant meter has been described in Part I (*loc. cit.*). The following refractometers were employed, both with sodium light: Bellingham and Stanley (Abbe type, reading to  $10^{-4}$  unit) and Zeiss (Pulfrich type, reading to  $10^{-5}$  unit). These require respectively ca. 0.1 and 1.0 c.c. liquid for each determination. In all cases a mean of at least two or three independent readings (in special cases up to six) was taken for each solution.

*Procedure.*—The general procedure followed was identical with that described in Part I, some 8–12 or more separate binary solutions of different molar ratios being used for each pair of solutes. Experiments were repeated in many cases where the position of the change of slope on the curve was uncertain, but normally one set of determinations is sufficient. A concentration of 0.1M or 0.25M is normally used, but in special cases 0.01M-solutions have been employed quite satisfactorily.

It is sometimes advisable to warm the solutions slightly after mixing, and allow them to cool again before use. This avoids irregularities due to imperfect mixing of some liquids which are slow to dissolve in each other. Incomplete solution cannot always be detected by eye.

Over certain temperature ranges some of the curves pass from convex to concave, relative to the  $x$ -axis, and thus at an intermediate temperature there is no evidence of complex formation. Therefore, if it was important to establish the reality of negative results with a particular group in a solute, determinations were made at more than one temperature, or a variety of second solutes was used, in one solvent, since it is unlikely that a fortuitous negative result would be repeated under similar conditions in a variety of systems.

*Preparations of Solid Complexes.*—Concentrated solutions in toluene of diethylamine and either *p*-nitrophenol or resorcinol, respectively, were mixed and the crystalline precipitates collected, carefully washed with a minimum of ether, and dried *in vacuo*. The *p*-nitrophenol complex separates out at once, that from resorcinol only slowly; the mixed solutions with resorcinol were therefore kept for several days in the cold before the precipitate was collected. *p*-Nitrophenol complex, yellow needles, m. p. 90° (Found: C, 54.8; H, 5.9; N, 11.85.  $C_{16}H_{11}O_4N_3$  requires C, 54.9; H, 6.0; N, 12.0%). Resorcinol complex, buff platelets, m. p. 119° (Found: C, 65.6; H, 8.3; N, 4.81.  $C_{16}H_{23}O_4N$  requires C, 65.5; H, 7.85; N, 4.8%).

\* See, e.g., Hunter, *Ann. Reports*, 1946, 43, 141.

*Determination of "Apparent Molecular Weight."*—The Beckmann f. p. method was used, with "molecular-weight quality" benzene, and a series of 0.1M-binary solutions. The apparent molecular weight is the value calculated on the assumption that only one compound is present, and is equal to the sum of the products of the true molecular weights of each solute multiplied by their respective molar fractions. The points shown in Figs. 7—10 are each the mean of two or three separate determinations.

Some attempts were made to detect bonding between amino-acids and glucose in aqueous solutions by measurement of specific rotation in a polarimeter, but the acids were insufficiently soluble to give any useful result.

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## APPENDIX

(By JOHN C. EATON, Department of Mathematics, Royal Technical College, Glasgow, C.1.)

*Theoretical Treatment of Relation between a Physical Constant and Molar Concentration of Binary Solutions.*—A physical property  $e$  varies linearly with concentration of a substance X in a given quantity of solvent; *i.e.*,

$$e_1 = e_0 + (x/C)S_X \text{ (cf. } PQ, \text{ Fig. 12)}$$

where  $e_0$  is the value for the pure solvent;  $C$  is the total number of molecules at maximum concentration;  $x$  is the number of molecules of X at any intermediate point; and  $S_X$  is a constant for the substance (of the dimensions of  $e$ ).

The same is true for a second substance Y; thus

$$e_2 = e_0 + (x/C)S_Y \text{ (cf. } PT, \text{ Fig. 12)}$$

(where  $S_Y$  is the constant for the substance Y) except that rate of increase  $S_Y$  differs from  $S_X$ . If, now, the number of molecules of Y is allowed to vary from  $C$  to 0 instead of from 0 to  $C$ , then

$$e_3 = e_0 + [(C - x)/C]S_Y \text{ cf. } RS, \text{ Fig. 12)}$$

so that if  $x$  molecules of X and  $C - x$  molecules of Y are simultaneously dissolved, and there is no interaction between X and Y, *i.e.*, the total number of molecules of X and Y remains constant at  $C$ , then

$$e_4 = e_0 + S_Y + (S_X - S_Y)x/C = e_1 + e_3 - e_0$$

This gives the line  $SQ$  (Fig. 12; cf. Fig. 3).

Finally if  $p$  molecules of X combine with  $q$  molecules of Y to form  $r$  molecules of  $X_pY_q$  (subsequently called XY for clarity), then

$$e_5 = e_0 + (x - pz/r)S_X/C + (C - x - qz/r)S_Y/C + zS_{XY}/C$$

[ $S_{XY}$  being the (unknown) value for the complex XY]

$$\begin{aligned} &= e_0 + S_Y + (S_X - S_Y)x/C + (S_{XY} - pS_X/r - qS_Y/r)z/C \\ &= e_4 + (S_{XY} - pS_X/r - qS_Y/r)z/C \end{aligned}$$

so that the deviation of  $e_5$  from the line  $SQ$  is proportional to  $z$ .

Now  $z$  is determined according to the mass-action law :

$$K = z^r / [(x - pz/r)^p (C - x - qz/r)^q] \text{ where } K \text{ is the reaction constant,}$$

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

Differentiating this with respect to  $x$ ,  $z$  being treated as a function of  $x$ , we obtain

$$K[(C - x - qz/r)^q p(x - pz/r)^{p-1} (1 - pz'/r) + (x - pz/r)^p q (C - x - qz/r)^{q-1} (-1 - qz'/r)] = rz^{r-1}z'$$

Solving for  $z'$ , we obtain,

$$z' = \frac{K(x - pz/r)^{p-1} (C - x - qz/r)^{q-1} [Cp - (p+q)x]}{rz^{r-1} - K(x - pz/r)^{p-1} (C - x - qz/r)^{q-1} [(p^2 - q^2)x/r + pq(p+q)z/r^2 - Cp^2/r]}$$

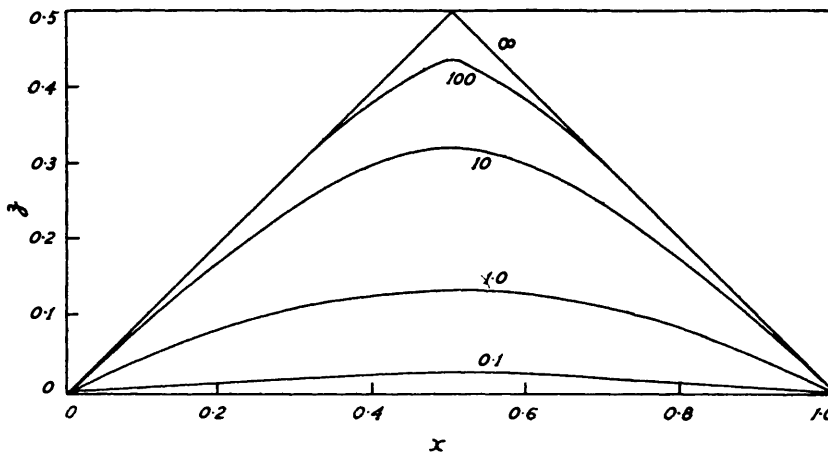
Now  $p, q, r, x, z$ , and  $C$  are positive integers, and  $K$  is also positive, while  $x - pz/r > 0$  and  $C - x - qz/r > 0$ , since otherwise  $K$  would be infinite (which, for the moment, we do not consider), so that  $z' = 0$  only if  $Cp - (p+q)x = 0$ , i.e., if  $x = pC/(p+q)$ .

Consider now the sign of  $(p^2 - q^2)x/r + pq(p+q)z/r^2 - Cp^2/r$  (= say,  $D$ ). The maximum value that  $z$  possibly can have is  $Cr/(p+q)$ , when  $Cp/(p+q)$  molecules of X combine with  $Cq/(p+q)$  molecules of Y, all of X and Y combining. Over the range  $0 \leq x \leq Cp/(p+q)$ , we have

$$\begin{aligned} D &= [(p - q)x/r + pqz/r^2 - Cp^2/r(p+q)](p+q) \\ &\leq [(p - q)Cp/r + pqCr/r^2 - Cp^2/r] = 0 \end{aligned}$$

Consider next the range  $Cp/(p+q) < x \leq C$ , which requires  $z < (C - x)r/q$ .

FIG. 13. Relation between  $z$  and  $x$  for the values of  $K$  shown on the curves.



Here

$$\begin{aligned} D &< (p^2 - q^2)x/r + pq(p+q)(C - x)r/qr^2 - Cp^2/r \\ &= (1/r)[pqC - qx(p+q)] \\ &< (1/r)[pqC - q(p+q)Cp/(p+q)] = 0 \end{aligned}$$

Thus  $D$  is negative for all values of  $x$  except  $pC/(p+q)$ , when it is zero, and thus the denominator of  $z'$ , viz.,

$$rz^{r-1} - K(x - pz/r)^{p-1} (C - x - qz/r)^{q-1} D$$

is positive for all values of  $x$ ;  $z'$  therefore has the same sign as  $Cp - (p+q)x$ . Thus  $z'$  is positive over the range  $0 \leq x < pC/(p+q)$ , and is negative over the range  $pC/(p+q) < x \leq C$ , i.e., there is a single maximum at  $x = pC/(p+q)$ , no matter how large  $p, q, r$  may be.

When  $p = q = r = 1$ , the mass-action law leads to a quadratic equation for  $z$ , and the graph of  $z$  against  $x$  is a hyperbola; for larger values of  $p, q, r$ , the mass-action law leads to curves of higher degree, but we have shown that they have only one maximum in the range  $0 \leq x \leq C$ , and hence  $e_5 - e_4$ , the deviation from the line  $SQ$ , will have only one turning value, a maximum or minimum according as  $S_{xy} - pS_x/r - qS_y/r$  is greater than or less than zero.

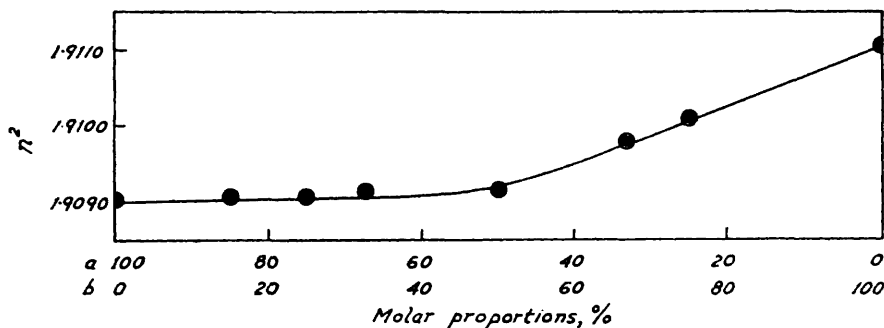
If values of  $e_5$  are determined experimentally for sufficient values of  $x$  to determine the graph of  $e_5$  against  $x$  accurately, and if the graph is found to be very nearly two straight lines, then the abscissa of their intersection will be close to  $pC/(p+q)$ , and hence the ratio  $p/q$  may be determined.

When  $K \rightarrow \infty$ , whatever the values of  $p$  and  $q$  the graph becomes a pair of straight lines which intersect at  $x = pC/(p+q)$ .

It should be noted that if  $e_s$  gives a single straight line  $SQ$ , this does not necessarily imply that no interaction takes place, as this result must follow even if there is interaction, provided  $rS_{XY} = pS_X + qS_Y$ .

Fig. 13 shows the variation in the graph of  $z$  against  $x$  for different values of  $K$  when  $p = q = r = 1$ . Figs. 6 and 14 show the experimental points for three typical systems giving 1 : 1 complexes. In the systems shown in Fig. 6 the values for  $K$  at room temperature are given

FIG. 14. *Theoretical (curve) and experimental (points) relation between square of refractive index and component ratio in binary solutions.*



a, Methanol; b, erythritol; solvent, 2-ethoxyethanol.

by Flett (*loc. cit.*) as 4.80—7.10 for azobenzene + benzyl alcohol and 381—461 for dimethylformamide + phenol, but in the system shown in Fig. 14 the value is unknown and an arbitrary figure of  $K = 10$  has been assumed, and from this the value of the constant ( $n^2$ ), corresponding to  $S_{XY}$ , for the complex is then computed from the treatment above, and the theoretical curve obtained thereby is shown.

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