An Investigation of Complex Formation by Partition of a Reactant between the Vapour Phase and Solution : The Determination of Association Constants and the Heats of Formation of Some Hydrogen Bonds.

By R. L. DENYER, A. GILCHRIST, J. A. PEGG, J. SMITH, T. E. TOMLINSON, and L. E. SUTTON.

[Reprint Order No. **6436**.]

A method of investigating complex formation between a volatile reactant and an involatile one in a volatile solvent, which involves partitioning between the liquid and the vapour phase, is described. It has been used to investigate hydrogen bonding between trimethylamine and some hydroxy-compounds, amines, and thiophenol. A regular variation in the association constant of the interaction is observed and cannot be explained satisfactorily. The results appear, however, to be suitable for internal comparison.

It is found that the strength of the O-H-N bond varies according to the acid strength of the OH group, and that a weak N-H-N bond is formed in some cases; no evidence for the formation of the S-H-N bond was obtained.

From measurements at different temperatures, values for ΔH can be derived; these agree quite well with values obtained calorimetrically.

ELECTRIC dipole moment measurements can, in principle, be applied to study chemical interactions between molecules. From the change in moment when a multimolecular complex is formed, information about the nature and the extent of the perturbation can be derived. Save for the stable co-ordination complexes, however, this application has not been made extensively, largely because, for the less stable ones, it is necessary to know the association constant before the electrical polarisation measurements can be fully used.

It is not generally practicable to derive both the association constant and the dipole moment of the complex from polarisation data alone (Earp and Glasstone, *J.*, 1935, 1709; Glasstone, *Trans. Faraday Soc.*, 1937, **33**, 200; Hammick, Norris, and Sutton, *J.*, 1938, 1755) though this may be done in special cases (Few and Smith, *J.*, 1949, 2781). Of the independent methods so far developed for determining the former, the most generally useful is the spectroscopic one, but this has some limitations.

The present communication describes a variant of another method of wide scope. Partitioning of a reactant between two liquids suffers from complications, particularly if one phase is aqueous (see *e.g.*, Anderson and Hammick, *J.*, 1950, 1089; Szyszkowski, *Z. phys. Chem.*, 1928, **131**, 175). If, however, one reactant (A) is volatile, the other (B) is involatile, and the solvent (S) also volatile, it is possible to partition between the liquid and the vapour phase. From a calibration it should be possible to obtain a relation between the A : S ratios in the two phases. If this were not generally affected by the presence of a third substance, then from the A : S ratio in the vapour over a solution of both A and B in S, it should be possible to obtain the ratio of free A to S in the liquid phase. If there is a specific reaction between A and B, and if the ratio of total A to S is known, the proportion of bound A can thus be derived. If then the reaction is simply : $A + B \rightleftharpoons C$ and the law of mass action is applicable, if c_A and c_B are the initial concentrations of A and of B, and c_C the concentration of the complex C, then :

$$K_{\text{assoc.}} = \frac{c_C}{(c_A - c_C)(c_B - c_C)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

From the measurements indicated, it is clearly possible to obtain K.

The fundamental assumptions are (i) that the A : S ratio in the vapour depends only on the free A : S ratio in the liquid, (ii) that the activity coefficients of the molecular species taking part in the reaction are unity, and (iii) that the complex is of the simple 1 : 1 type. Assumptions (i) and (ii) imply *inter alia* that the forces between A and B leading to complex formation are of very short range; and assumption (iii) implies that these are specific and saturable. A further, practical requirement is that the ratio of the saturated vapour pressures, of A to B, shall be large, *i.e.*, 10 : 1 or more if possible.

A type of system which conforms to most of these requirements is that in which A is a volatile amine such as trimethylamine, B is a relatively involatile substance with a moderately acidic hydrogen atom, *e.g.*, a phenol, and S is a non-polar saturated hydrocarbon, *e.g.*, *cyclo*hexane. Moreover, the investigation of hydrogen bonding in such systems is interesting for its own sake. Accordingly, a series of them has been examined, with B = phenol, *o*-, *m*-, and *p*-cresol, *p*-chlorophenol, α- and β-naphthol, triphenylmethanol, *n*-heptyl alcohol, 2 : 5-dimethylpyrrole, indole, and benzenethiol. The results of attempts to determine association constants are described; the application of these to electrical polarisation values is dealt with in the following paper.

EXPERIMENTAL

Theory of the Method.—The relative amounts of the two volatile components in the vapour phase over a ternary mixture are used to deduce the term $(c_A - c_C)$ in equation (1). To do this the ratio of the two components over the ternary mixture is compared with that over their binary mixture.

Consider the case of a binary mixture containing *a* moles of A and *s* moles of S, both A and S being volatile. The respective mole fractions are :

$$f_A = a/(a + s) \qquad f_S = s/(a + s)$$

If Raoult's law is obeyed, the partial vapour pressures above the solution are : $f_A p_A{}^\circ$ and $f_S p_S{}^\circ$, where $p_A{}^\circ$ and $p_S{}^\circ$ are the saturated vapour pressures of the pure components.

The amounts of vapour carried over when a stream of gas is swept over the surface of the mixture depends upon the flow rate of the carrier gas and the degree of saturation of the gas stream with respect to each vapour; but, if the degree of saturation is independent of the flow rate, the composition of a condensate from the gas stream will also be independent of it. The amounts of A and S carried over will then be proportional to $\alpha f_A p_A{}^\circ$ and $\beta f_S p_S{}^\circ$ moles, α and β being the factors indicating departures from Raoult's law and the degree of saturation of the gas stream, assuming that they can be so expressed. The proportionality factor will be the same in each case and will depend upon the volume of carrier gas passed.

The mole fraction of A in the condensate will therefore be :

$$N_A = \frac{\alpha f_A p_A{}^\circ}{\alpha f_A p_A{}^\circ + \beta f_S p_S{}^\circ} = \frac{\alpha f_A p_A{}^\circ}{\alpha f_A p_A{}^\circ + \beta p_S{}^\circ(1 - f_A)} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

This equation relates the mole fraction of A in the condensate to the mole fraction of A in the corresponding binary mixture and is the ideal equation of the calibration curve.

Consider the case of a ternary mixture, the third component, B, being involatile. Let *a′* moles of A, *s′* moles of S and *b′* moles of B be present, then the respective mole fractions are :

$$f_A{}' = a'/(a' + s' + b') \qquad f_S{}' = s'/(a' + s' + b')$$

Now, if the presence of B does not alter the values of α and β, the mole fraction of A in the condensate may be expressed as :

$$N_A{}' = \frac{\alpha f_A{}' p_A{}^\circ}{\alpha f_A{}' p_A{}^\circ + \beta f_S{}' p_S{}^\circ} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Furthermore, equation (2) holds for all values of *a* and *s* and in particular for the case where $a = a'$, $s = s'$, when

$$f_A = a'/(a' + s'), f_S = s'/(a' + s'), \textit{i.e.}, f_A/f_S = a'/s'$$

but, also,

$$f_A{}'/f_S{}' = a'/s' \quad \therefore f_A/f_S = f_A{}'/f_S{}' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

From equations (2), (3), and (4) we have

$$N_A{}' = \frac{\alpha(f_A/f_S) \cdot p_A{}^\circ}{\alpha(f_A/f_S) \cdot p_A{}^\circ + \beta p_S{}^\circ} = N_A$$

$N_A{}'$, the mole fraction of A in the condensate, may therefore be expressed in terms of $f_A = a'/(a' + s')$, *i.e.*, the mole fraction of A in the liquid mixture with respect to A and S only. If therefore the addition of B does not affect the relative activities of A and S in the ternary mixture, the same relation between the mole fractions of A in the condensate and solution will apply as in the case of the binary mixture of A and S, providing that in the case of the ternary solution the mole fraction of A is expressed in terms of A and S only. If the addition of B affects the activity of A this will no longer be true and the deviation may be used to determine an equilibrium constant for the interaction between A and B, on the assumption that this is of a certain type and that the activity of S remains unchanged. In the theory of this determination (below) weight fractions are used instead of mole fractions, but the above treatment still applies since corresponding weight and mole fractions may be related by a factor depending only on the values of a and s and the respective molecular weights.

The algebra used in the determination of the association constant K in a particular case is straightforward but somewhat involved; so it is convenient to give it in outline as follows:

Consider a ternary solution. Let W be its total weight, W_{A} the total weight of A, W_{A}' the weight of free A, W_{A}'' the weight of bound A, M_{A} the molecular weight of A, W_{S} the weight of solvent, M_{S} the molecular weight of S, W_{B} the total weight of B, and M_{B} the molecular weight of B.

The quantities known experimentally are:

$$x_a = W_{\mathrm{A}}'/(W_{\mathrm{A}}' + W_{\mathrm{S}}),\ y_a = W_{\mathrm{A}}/W,\ y_b = W_{\mathrm{B}}/W$$

Now

$$W = W_{\mathrm{A}}' + W_{\mathrm{A}}'' + W_{\mathrm{S}} + W_{\mathrm{B}} \quad \therefore x_a = \frac{W_{\mathrm{A}}'}{W - (W_{\mathrm{B}} + W_{\mathrm{A}}'')}$$

$$\therefore \frac{W_{\mathrm{A}}'}{W} = x_a\left[1 - \frac{W_{\mathrm{B}} + W_{\mathrm{A}}''}{W}\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

But

$$\frac{W_{\mathrm{A}}'}{W} = \frac{W_{\mathrm{A}} - W_{\mathrm{A}}''}{W} = y_a - \frac{W_{\mathrm{A}}''}{W}$$

$$\therefore \frac{W_{\mathrm{A}}''}{W} = \frac{y_a - x_a + (W_{\mathrm{B}}/W) \, . \, x_a}{1 - x_a} = \frac{y_a - (1 - y_b) \, . \, x_a}{1 - x_a} = \gamma$$

But the molar amount of a 1 : 1 complex $= m_c = W_{\mathrm{A}}''/M_{\mathrm{A}}$

I.e.,

$$m_c = W\gamma/M_{\mathrm{A}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Now the weight of free B $= Wy_b - m_cM_{\mathrm{B}}$

$$\therefore \text{ Molar amount of free B} = m_{\mathrm{B}} = \frac{W}{M_{\mathrm{B}}}\left[y_b - \frac{M_{\mathrm{B}}\gamma}{M_{\mathrm{A}}}\right] \quad . \quad . \quad . \quad . \quad (7)$$

Also the weight of free A $= W_{\mathrm{A}} - W_{\mathrm{A}}''$

$$\therefore \text{ Molar amount of free A} = m_{\mathrm{A}} = \frac{W}{M_{\mathrm{A}}}\left[y_a - \gamma\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

If m is the total number of moles present, by using molar fractions

$$K = \frac{(m_c/m)}{(m_{\mathrm{A}}/m) \, . \, (m_{\mathrm{B}}/m)} = \frac{m \, . \, m_c}{m_{\mathrm{A}} \, . \, m_{\mathrm{B}}}$$

Now, approximately, $m = W/M_{\mathrm{S}}$

$$\therefore K = \frac{W \, . \, m_c}{M_{\mathrm{S}} \, . \, m_{\mathrm{A}} \, . \, m_{\mathrm{B}}}$$

Whence, from equations (6), (7), and (8)

$$K = \frac{M_{\mathrm{B}}}{M_{\mathrm{S}}}\left\{\frac{\gamma}{(y_a - \gamma)(y_b - [M_{\mathrm{A}}/M_{\mathrm{B}}]\gamma)}\right\}$$

Although it is simpler for use in certain calculations, the association constant as defined above is not strictly a mass-action equilibrium constant because it involves molar fractions instead of molar concentrations. For the dilute solutions such as are used in this work, however, the following simple relation holds:

$$K_{\text{molar concn.}} = K_{\text{mol. fractn.}} \times V_s$$

where V_s is the molar volume of the solvent, which we took to be 0·1075 l. at 25°.

Apparatus and Technique.—(a) *Association constants.* In the notation of the previous section, the data required are x_a, y_a, and y_b. In our work A was in all cases trimethylamine and S *cyclo*hexane. y_a may be determined by acidimetric analysis of the reaction mixture. y_b is determined initially by weight when the reaction mixture is made up. Its value changes during an investigation, for distillation is involved and B is involatile; but, the initial weight of the solution and the amounts of A and of S removed on distillation and sampling being known, the successive values may be calculated. x_a is determined by the vapour partition method.

About 100 c.c. of the mixture were taken at the beginning of the investigation, during the course of which the volume decreased to about 50 c.c. The initial mixture was prepared by diluting approximately 10 times with dry *cyclo*hexane a stock solution of trimethylamine in *cyclo*hexane containing about 8% of trimethylamine by weight. In the investigation of a ternary mixture the involatile component B was weighed into the diluted solution and dissolved, the mixture was transferred to the saturator, and the weight so transferred determined by difference.

The mixture was shaken in a horizontal tubular glass vessel, having indentations (*L*), of about 250 c.c. capacity, the arc of shaking being about 20° and the frequency 200—220 per minute, giving effective break-up of the liquid surface with the formation of but little spray. The shaking vessel was contained in a water tank thermostatically controlled to 25° ± 0·05° c (see Fig. 1). It was shown experimentally that the calibration curve of the apparatus was not sensitive to small changes in temperature. During the shaking a stream of dry nitrogen, previously brought to the temperature of the thermostat, was swept over the mixture at rates of 40—60 c.c. per min., so that the time of contact of the gas stream with the mixture was about 3—4 min. It was shown also during one calibration experiment that an increase in the flow rate from 25 to 100 c.c. per min. did not produce a discontinuity in the curve and so did not affect the relative saturation of the vapour stream with trimethylamine and *cyclo*hexane. To prevent back diffusion while the carrier-gas stream was stopped during sampling, a clip was used to close the rubber tube (*R*).

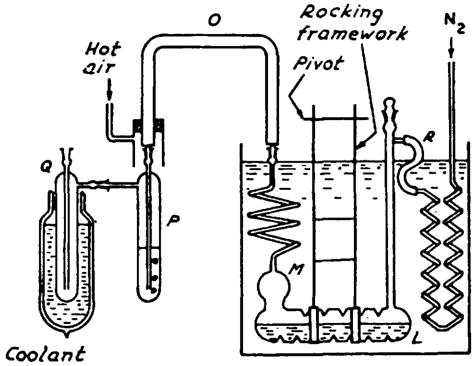


FIG. 1. *Saturator and condensers (not to scale).*

After passage through a splash bulb (*M*) and the flexible spiral above it the gas stream from the saturator was conveyed through a side-arm (*O*), which was lagged and electrically heated to prevent premature condensation, into a double condenser. It was found that a small column of liquid, always less than 2 cm. in length, usually collected in the glass spiral in the course of an experiment. Although the heating coil or lagging of the side-arm could not be continued below the water level, it is thought unlikely that this was a result of premature condensation, since the quantity was not dependent on the rate of flow of gas nor did it depend upon the intensity of heating of the side-arm. The column of liquid probably resulted from spray.

In the first compartment of the double condenser (*P*) the gas stream bubbled through 6—10 c.c. of approximately 0·1N-hydrochloric acid, which removed the trimethylamine from it. The second compartment (*Q*) was cooled in acetone–solid carbon dioxide and the solvent was condensed in it. No odour of trimethylamine could be detected in the gas stream issuing from the condensers, but, in case trimethylamine passed into, and was frozen out in, the second, the contents of the two compartments were always mixed before the standard acid was titrated.

The weight fraction of trimethylamine in the condensate was determined by measuring the gain in weight of the condensers and determining the amount of standard acid neutralised during the condensation. A similar weighing and titration procedure was used in analysing the reaction mixture, which was sampled with a pipette fitted with a rubber teat, at the beginning and the end of each distillation. The mean of the weight fractions found was taken for comparison with the weight fraction of trimethylamine in the condensate. Methyl-red was a satisfactory indicator, with a comparison flask, for these titrations, except when B was benzenethiol, in which case bromocresol-green was used as indicator in the analysis of the ternary solution. Because the total weight removed on analysis of the reaction mixture must be used in the calculation of successive values of y_b and all the sample cannot be transferred from the pipette to the flask containing standard acid, the length of the column of liquid remaining in the pipette was used as a measure of its weight in the application of a small correction.

(b) *Calorimetric measurements.* For the present work a precision of ±5% in the calorimetric determinations was deemed sufficient; so, since conservation of material was also desirable, the calorimeter was small. It consisted of a glass vessel with two legs. One, about 8·5 cm. long and 2·7 cm. in diameter, was the reaction compartment; this had a vacuum jacket and contained the hot junctions of the five-junction copper–constantan thermocouple. The other was a pocket for the cold junctions of the thermocouple, and contained *cyclo*hexane at the temperature of the thermostat bath in which the whole calorimeter was immersed. The temperature rise caused by reaction was observed; and when the temperature of the reaction compartment had again reached that of the bath, the electrical energy necessary to produce roughly the same rise in roughly the same time (*ca.* 25 sec.) was determined. The electrical heating coil was also used as a stirrer.

*cyclo*Hexane solutions containing 2—5% by weight of the reactants were used, and suitable amounts were weighed into the calorimeter from pipettes when required, both first being thermally equilibrated with the bath. The total volume of the mixed solutions was 2—3 c.c. From the initial concentrations of the two solutions, the quantities of each used, and the association constant K, the amount of complex formed could be calculated, and the heat of forming one mole of it thence derived.

Materials.—Nitrogen from a cylinder was used as carrier gas. It was dried by passage through concentrated sulphuric acid and then through a trap cooled in an acetone–solid carbon dioxide mixture.

Commercial *cyclo*hexane was purified by sulphonation and passage through a column of activated charcoal to remove aromatic impurities, followed by distillation from phosphoric oxide in a stream of dry air. Investigation of the range of temperature of freezing of the material showed that the content of impurity varied from 0·01 to 0·03 mole per 1000 g. of solvent, on the assumption that solid solutions were not formed on freezing. Aromatic impurities and thiophen were absent and the refractive index was reproducible to $\pm 5 \times 10^{-5}$. We believe that the impurities were methyl*cyclo*hexanes.

Two samples of trimethylamine were used. Both were prepared from the hydrochloride, made as described in *Organic Syntheses,* Coll. Vol. I, p. 514. The impure product of the first preparation was freed from unchanged ammonium chloride by recrystallisation from chloroform. The solution of trimethylamine in *cyclo*hexane was prepared by liberation of the compound from its salt by potassium hydroxide solution, passage of the gas over potassium hydroxide pellets to remove water, and liquefaction of the gas in a glass spiral cooled in dry ice. The liquid trimethylamine dropped into a flask containing dry *cyclo*hexane cooled in ice–water. This stock solution was used by two of us (J. A. P. and A. G.). In the course of the second preparation, it was observed that crystals of trimethylamine hydrochloric retain chloroform tenaciously, but may be freed from chloroform by recrystallisation from ethanol, though with considerable loss. A stock solution made as before from trimethylamine hydrochloride so purified was used by one of us (T. E. T.). It will be seen from the experimental results that the calibration curves of the apparatus with the two stock solutions differ slightly.

Commercial naphthalene, purified by recrystallisation twice from aqueous ethanol and dried *in vacuo* (P_2O_5), had m. p. 79·8° (cf. 80·10—80·27°; Timmermans, "Physico-chemical Constants of Pure Organic Compounds," Elsevier, Amsterdam, 1950).

p-Nitrotoluene, recrystallised from ethanol and dried (H_2SO_4) *in vacuo,* had m. p. 51° (cf. 51·6—52·1°; Timmermans, *loc. cit.*).

p-Dichlorobenzene was purified by recrystallisation from ethanol and dried *in vacuo*; it had m. p. 53° (cf. 53·0—53·2°; Timmermans, *loc. cit.*).

Anisole was dried (P_2O_5) and distilled twice. It had b. p. 155° (cf. 153·75—153·9°; Timmermans, *loc. cit.*).

Phenol was distilled four times at atmospheric pressure and dried (P_2O_5) *in vacuo* for several days [m. p. 39·8—40·2° (cf. 40·7—41·0°; Timmermans, *loc. cit.*)].

p-Chlorophenol was fractionally distilled under reduced pressure (b. p. 106°/17 mm.) and was dried (H_2SO_4) *in vacuo* [m. p. 42° (cf. 42·9°; Holleman and Rinkes, *Rec. Trav. chim.*, 1911, **30**, 83)].

o-Cresol was twice distilled at atmospheric pressure (b. p. 190°) and dried (P_2O_5) *in vacuo* for several days [m. p. 29·5—30° (cf. 30·35—30·94°; Timmermans, *loc. cit.*)].

m-Cresol was distilled at atmospheric pressure (b. p. 201—202°), followed by double fractional recrystallisation (m. p. 10·5—11·5°). It was then re-distilled [b. p. 201—201·5° (cf. b. p. 202·2—202·7°, m. p. 11·5—11·96°; Timmermans, *loc. cit.*)].

p-Cresol was distilled at atmospheric pressure (b. p. 195—197°) followed by double fractional recrystallisation and drying (P_2O_5) *in vacuo* for several days [m. p. 33—34° (cf. 34·4—34·6°; Timmermans, *loc. cit.*)].

Triphenylmethanol, recrystallised from carbon tetrachloride and dried at 90°, had m. p. 162·5° (cf. 164—165°; Stadnikow, *Ber.*, 1914, **47**, 2142).

n-Heptyl alcohol was shaken with successive lots of alkaline potassium permanganate solution until the solution was no longer decolorised after 15 min. It was then dried (K_2CO_3) and twice distilled at atmospheric pressure [b. p. 175—176° (cf. 175·6°; Butler, Thomson, and Maclennan, *J.*, 1933, 679)].

The 2 : 5-dimethylpyrrole used was prepared by Kofod, Sutton, and Jackson (*J.*, 1952, 1467). It was purified by redistillation under reduced pressure (b. p. 71°/19 mm.). Since it is rapidly oxidised in air the purified specimen was transferred direct from the receiver to the reaction mixture.

Indole was sublimed *in vacuo* [m. p. 52° (cf. 53°; Gluud, *Ber.*, 1915, **48**, 423)].

α- and β-Naphthol were recrystallised from boiling water and dried (P_2O_5) *in vacuo* for several days [m. p.s 95·5—96° and 122·5—123·5° respectively (cf. 94·2° and 121·6°; Kendall, *J. Amer. Chem. Soc.*, 1916, **38**, 1316).

Benzenethiol was distilled at atmospheric pressure [b. p. 168—168·5° (cf. 169·5°; Timmermans, *loc. cit.*)]. The purified specimen was used immediately.

EXPERIMENTAL RESULTS

Equilibrium Constants.—The symbols used are as follows (see also p. 3891). Weight fractions: v_a, of trimethylamine in the condensate; y_a, of total trimethylamine in solution in terms of the whole solution; y_a', of total trimethylamine in solution, in terms of trimethylamine and *cyclo*hexane only [$y_a' = W_A/(W_A + W_B)$]; x_a, of free trimethylamine in solution, in terms of free trimethylamine and *cyclo*hexane only; y_b, of involatile reactant in solution. K is the association constant in moles/litre.

The results of two of us (J. A. P. and A. G.) should be considered separately from those of the third (T. E. T.) since slightly different experimental calibration curves were used. The results are contained in Tables 1 and 2.

TABLE 1. *Results at 25°.*

Calibration curves

No. 1 (J. A. P.)

$100v_a$	15·14	14·65	14·44	13·85	13·84	13·12	13·08	12·15	12·00	11·12	10·91	10·18
$100y_a$	0·768	0·735	0·728	0·693	0·684	0·636	0·627	0·586	0·595	0·545	0·545	0·500
$100v_a$	10·11	9·34	9·19	8·36	7·96	7·43	7·00	6·33	5·96	5·40	4·57	4·32
$100y_a$	0·498	0·453	0·448	0·404	0·384	0·357	0·328	0·301	0·279	0·254	0·218	0·203
$100v_a$	3·33	3·15	2·40	2·08	1·62	17·46	15·96	15·85				
$100y_a$	0·158	0·139	0·112	0·093	0·072	0·892	0·836	0·797				

No. 2 (A. G.)

$100v_a$	13·3	12·0	11·6	10·3	9·77	8·71	7·71	7·31	7·07	4·30	3·62	2·09
$100y_a$	0·641	0·598	0·553	0·505	0·459	0·416	0·374	0·336	0·289	0·201	0·162	0·105

The best smooth curve through the first set of points is given by:

$$100v_a = 22{\cdot}09\ (100y_a) - 2{\cdot}93\ (100y_a)^2$$

and the second set of points agrees well with this.

No. 3 (T. E. T.)

$100v_a$	12·91	12·61	12·41	11·78	11·22	10·84	10·61	9·74	9·01	8·78	7·93	7·79
$100y_a$	0·608	0·626	0·585	0·545	0·541	0·502	0·486	0·462	0·426	0·412	0·362	0·362
$100v_a$	7·07	6·52	6·01	5·22	4·22	2·45	2·45					
$100y_a$	0·318	0·302	0·274	0·245	0·194	0·154	0·114					

These points are linear and the best straight line is given by:

$$100v_a = 21{\cdot}38\ (100y_a) + 0{\cdot}04$$

TABLE 1. (*Continued.*)

Naphthalene (J. A. P.)

$100v_a$	15·05	13·81	12·76	11·59	10·41	9·25	8·07	6·92	5·74	4·58	3·21	1·98
$100y_a'$	0·762	0·702	0·640	0·583	0·515	0·450	0·388	0·326	0·269	0·209	0·149	0·095
$100x_a$	0·762	0·694	0·632	0·570	0·550	0·447	0·386	0·328	0·269	0·216	0·149	0·094

p-*Nitrotoluene* (J. A. P.)

$100v_a$	15·89	15·47	14·71	13·40	12·59	11·44	10·10	8·82	7·53	6·10	4·05	2·96
$100y_a$	0·826	0·802	0·765	0·689	0·643	0·585	0·509	0·437	0·371	0·295	0·196	0·141
$100y_a'$	0·852	0·827	0·786	0·711	0·663	0·599	0·525	0·451	0·382	0·306	0·202	0·148
$100x_a$	0·804	0·780	0·739	0·667	0·620	0·560	0·490	0·425	0·357	0·285	0·188	0·138
$100y_b$	2·959	2·961	2·976	2·983	2·998	3·019	3·036	3·060	3·088	3·124	3·182	3·248
K	0·37	0·37	0·41	0·40	0·42	0·46	0·43	0·36	0·42	0·37	0·47	0·30

p-*Dichlorobenzene* (J. A. P.)

$100v_a$	15·24	14·42	13·54	12·28	11·00	9·60	8·28	7·06	5·44	4·17	2·74
$100y_a$	0·785	0·737	0·682	0·612	0·542	0·467	0·401	0·340	0·258	0·196	0·127
$100x_a$	0·762	0·708	0·655	0·590	0·527	0·457	0·402	0·334	0·255	0·192	0·121
$100y_b$	2·982	2·995	3·010	3·024	3·045	3·070	3·097	3·124	3·161	3·210	3·271
K	0·41	0·48	0·48	0·45	0·39	0·34	0·19	0·30	0·27	0·32	0·55

Anisole (T. E. T.)

$100v_a$	18·23	16·73	15·48	14·74	13·75	12·62	11·68	11·22	9·98	9·20	8·12	7·49
$100y_a$	0·963	0·865	0·797	0·741	0·688	0·635	0·590	0·537	0·485	0·443	0·405	0·369
$100x_a$	0·944	0·855	0·782	0·739	0·684	0·623	0·572	0·548	0·483	0·442	0·387	0·357
$100y_b$	4·708	4·743	4·762	4·779	4·799	4·818	4·836	4·857	4·883	4·908	4·933	4·960
K	0·21	0·18	0·22	0·16	0·17	0·21	0·24	0·09	0·16	0·15	0·29	0·25

Phenol (J. A. P.)

$100v_a$	16·38	15·85	14·68	13·50	12·70	11·78	10·85	9·42	8·30	8·03	7·25	6·32	5·54	4·77	4·05
$100y_a$	1·258	1·226	1·159	1·091	1·050	0·992	0·936	0·857	0·793	0·777	0·731	0·679	0·634	0·582	0·535
$100y_a'$	1·264	1·235	1·168	1·099	1·052	1·000	0·945	0·864	0·799	0·783	0·738	0·684	0·639	0·586	0·541
$100x_a$	0·835	0·806	0·733	0·670	0·635	0·578	0·529	0·462	0·403	0·390	0·348	0·303	0·267	0·223	0·183
$100y_b$	0·751	0·756	0·756	0·758	0·766	0·766	0·774	0·776	0·787	0·757	0·767	0·769	0·776	0·784	0·793
K	102	90	108	102	87	93	82	78	76	93	87	91	107	95	103

Phenol (A. G.)

$100v_a$	16·70	15·08	12·90	11·76	10·60	9·61	8·48	7·36	6·35	5·83	4·82	2·50	1·50	1·03
$100y_a$	1·371	1·268	1·120	1·055	0·995	0·928	0·856	0·797	0·750	0·695	0·625	0·469	0·398	0·341
$100x_a$	0·855	0·758	0·635	0·574	0·515	0·465	0·407	0·353	0·311	0·275	0·225	0·110	0·069	0·045
$100y_b$	0·857	0·863	0·868	0·873	0·882	0·888	0·896	0·904	0·907	0·916	0·928	0·983	1·03	1·09
K	324	175	100	94	97	81	72	78	81	75	72	96	111	127

Phenol (T. E. T.)

$100v_a$	10·28	9·75	8·92	8·44	7·46	6·59	5·87	5·17	4·38	3·68
$100y_a$	0·959	0·917	0·878	0·839	0·791	0·740	0·708	0·665	0·611	0·569
$100x_a$	0·498	0·471	0·428	0·404	0·355	0·311	0·277	0·242	0·203	0·171
$100y_b$	0·841	0·845	0·849	0·854	0·859	0·866	0·873	0·881	0·891	0·903
K	118	93	105	86	96	96	106	107	103	108

Phenol (T. E. T.)

$100v_a$	2·38	2·25	2·02	1·76	1·67	1·53	1·35	1·18	1·04	0·86
$100y_a$	0·497	0·489	0·473	0·451	0·435	0·420	0·405	0·391	0·376	0·359
$100x_a$	0·109	0·103	0·093	0·080	0·076	0·070	0·061	0·053	0·047	0·038
$100y_b$	1·024	1·031	1·041	1·052	1·065	1·080	1·096	1·115	1·138	1·171
K	108	111	115	124	118	118	126	136	140	156

p-*Chlorophenol* (J. A. P.)

$100v_a$	9·50	8·87	8·18	7·06	6·67	4·42	3·46	2·36
$100y_a$	0·893	0·859	0·794	0·757	0·678	0·609	0·553	0·492
$100x_a$	0·459	0·427	0·373	0·338	0·269	0·206	0·162	0·105
$100y_b$	1·007	1·006	1·014	1·024	1·038	1·050	1·069	1·095
K	350	330	228	205	186	201	193	246

TABLE 1. (*Continued.*)

p-*Cresol* (J. A. P.)

$100v_a$	11·35	9·40	8·79	7·63	6·35	5·19	3·98	3·05
$100y_a$	0·895	0·842	0·810	0·741	0·667	0·601	0·533	0·481
$100x_a$	0·500	0·453	0·424	0·366	0·301	0·244	0·185	0·139
$100y_b$	0·906	0·906	0·915	0·924	0·932	0·947	0·962	0·983
K	63	65	67	64	69	72	82	99

p-*Cresol* (T. E. T.)

$100v_a$	12·04	11·26	10·12	9·18	8·17	7·18	6·12	5·11	4·04	3·15
$100y_a$	0·898	0·835	0·794	0·746	0·691	0·633	0·560	0·505	0·464	0·400
$100x_a$	0·561	0·525	0·472	0·428	0·380	0·334	0·284	0·237	0·187	0·146
$100y_b$	0·718	0·721	0·725	0·729	0·734	0·740	0·746	0·754	0·764	0·777
K	96	59	77	77	73	69	59	62	83	75

o-*Cresol* (T. E. T.)

$100v_a$	2·68	2·48	2·29	2·14	1·96	1·79	1·65	1·36	1·28
$100y_a$	0·567	0·552	0·534	0·520	0·508	0·495	0·475	0·458	0·439
$100x_a$	0·124	0·114	0·105	0·098	0·090	0·082	0·075	0·062	0·058
$100y_b$	1·504	1·513	1·525	1·538	1·553	1·569	1·589	1·617	1·635
K	73	83	79	81	84	88	88	101	97

o-*Cresol* (T. E. T.)

$100v_a$	5·74	5·24	4·58	4·10	3·59	3·04	2·51
$100y_a$	0·660	0·622	0·583	0·547	0·510	0·476	0·439
$100x_a$	0·267	0·243	0·212	0·190	0·166	0·140	0·116
$100y_b$	1·008	1·015	1·023	1·032	1·043	1·056	1·073
K	74	70	73	71	71	78	73

m-*Cresol* (T. E. T.)

$100v_a$	10·25	9·24	8·17	6·95	6·39	5·38	4·45	3·43	2·74
$100y_a$	0·846	0·789	0·735	0·692	0·635	0·574	0·519	0·475	0·419
$100x_a$	0·478	0·430	0·380	0·323	0·297	0·250	0·206	0·159	0·126
$100y_b$	0·823	0·828	0·833	0·829	0·846	0·856	0·867	0·881	0·900
K	79	74	77	103	73	71	74	94	91

Triphenylmethanol (T. E. T.)

$100v_a$	12·60	11·35	10·19	9·86	8·82	8·08	7·17	6·50	5·88	5·30
$100y_a$	0·753	0·677	0·635	0·591	0·534	0·480	0·435	0·393	0·360	0·321
$100x_a$	0·621	0·554	0·493	0·476	0·423	0·386	0·340	0·307	0·277	0·247
$100y_b$	1·140	1·145	1·151	1·157	1·164	1·172	1·178	1·184	1·192	1·200
K	14·5	13·7	20·4	13·9	14·3	11·8	13·5	12·5	13·2	12·2

Triphenylmethanol (T. E. T.)

$100v_a$	16·67	15·83	14·26	13·16	11·98	10·78	9·94	9·17	8·26	7·47	6·73
$100y_a$	0·930	0·850	0·778	0·710	0·652	0·602	0·552	0·503	0·454	0·410	0·372
$100x_a$	0·850	0·802	0·713	0·652	0·589	0·524	0·480	0·440	0·394	0·365	0·317
$100y_b$	0·859	0·863	0·867	0·872	0·877	0:882	0·887	0·892	0·898	0·903	0·909
K	7·4	3·8	6·1	5·6	6·9	10·3	9·9	8·6	8·8	8·6	9·4

Triphenylmethanol (T. E. T.)

$100v_a$	8·14	7·15	6·46	5·67	4·80	4·21	3·51	2·92	2·41	1·92
$100y_a$	0·420	0·382	0·340	0·300	0·263	0·226	0·193	0·163	0·130	0·105
$100x_a$	0·370	0·333	0·300	0·263	0·223	0·195	0·162	0·135	0·111	0·088
$100y_b$	0·574	0·576	0·580	0·585	0·590	0·595	0·601	0·607	0·614	0·623
K	10·1	14·4	11·8	12·0	15·0	12·3	14·3	15·0	11·4	12·5

n-*Heptyl alcohol* (T. E. T.)

$100v_a$	8·72	8·10	7·35	6·75	6·30	5·81	5·05	4·68	4·28	3·89	3·55
$100y_a$	0·535	0·496	0·463	0·429	0·396	0·356	0·325	0·300	0·268	0·240	0·214
$100x_a$	0·418	0·386	0·348	0·319	0·297	0·273	0·236	0·218	0·198	0·181	0·164
$100y_b$	2·076	2·086	2·096	2·108	2·120	2·134	2·148	2·162	2·179	2·198	2·217
K	2·5	2·7	2·9	3·0	2·8	2·5	3·1	3·1	2·8	2·6	2·4

n-*Heptyl alcohol* (T. E. T.)

$100v_a$	9·25	9·03	8·21	7·64	7·06	6·57	6·24	5·29	4·69	4·16
$100y_a$	0·531	0·493	0·461	0·428	0·386	0·347	0·320	0·285	0·263	0·227
$100x_a$	0·406	0·395	0·355	0·327	0·300	0·278	0·265	0·221	0·194	0·171
$100y_b$	1·134	1·139	1·143	1·149	1·154	1·160	1·166	1·173	1·182	1·191
K	5·5	4·2	5·1	5·1	4·6	3·8	3·2	4·4	5·3	4·8

TABLE 1. (*Continued.*)

n-*Heptyl alcohol* (T. E. T.)

$100v_a$	7·53	7·06	6·57	5·60	5·26	4·77	4·32	3·63	3·18	2·67
$100y_a$	0·417	0·386	0·368	0·337	0·306	0·274	0·244	0·215	0·188	0·159
$100x_a$	0·350	0·328	0·305	0·265	0·244	0·221	0·200	0·168	0·147	0·123
$100y_b$	1·046	1·050	1·055	1·060	1·067	1·073	1·081	1·090	1·099	1·110
K	3·4	3·0	3·5	4·7	4·3	3·9	3·5	4·4	4·3	4·4

2 : 5-*Dimethylpyrrole* (T. E. T.)

$100y_a$	7·18	6·78	6·45	5·89	5·56	5·17	5·00	4·59	4·18	3·70
$100y_a$	0·395	0·380	0·352	0·332	0·313	0·296	0·283	0·259	0·236	0·213
$100x_a$	0·305	0·289	0·273	0·249	0·234	0·215	0·208	0·190	0·171	0·152
$100y_b$	1·184	1·188	1·192	1·197	1·202	1·206	1·210	1·216	1·223	1·232
K	3·7	3·9	3·5	4·0	4·0	4·5	4·3	4·2	4·3	4·5

Indole (T. E. T.)

$100y_a$	15·21	14·33	12·98	12·15	11·01	9·71	8·62	7·31	5·95	4·63	3·33
$100y_a$	0·913	0·843	0·766	0·715	0·653	0·583	0·513	0·436	0·358	0·277	0·209
$100x_a$	0·710	0·668	0·605	0·566	0·513	0·452	0·401	0·340	0·276	0·215	0·154
$100y_b$	0·631	0·634	0·637	0·641	0·645	0·649	0·655	0·662	0·670	0·681	0·694
K	20·3	14·8	13·4	12·3	11·9	11·9	10·2	9·4	9·2	8·1	9·5

α-*Naphthol* (T. E. T.)

$100v_a$	6·59	6·10	5·65	5·28	4·88	4·22	3·88	3·36	3·00	2·50
$100y_a$	0·434	0·415	0·398	0·375	0·352	0·332	0·311	0·286	0·263	0·244
$100x_a$	0·306	0·283	0·262	0·245	0·226	0·196	0·180	0·155	0·138	0·115
$100y_b$	0·398	0·399	0·400	0·401	0·404	0·406	0·408	0·411	0·415	0·418
K	96	119	150	123	113	184	160	179	155	204

α-*Naphthol* (T. E. T.)

$100v_a$	8·40	7·72	6·88	6·60	5·74	5·04	4·54	3·85
$100y_a$	0·509	0·482	0·455	0·425	0·393	0·363	0·335	0·303
$100x_a$	0·391	0·359	0·320	0·307	0·267	0·234	0·211	0·178
$100y_b$	0·359	0·360	0·362	0·364	0·364	0·368	0·370	0·373
K	84	114	272	100	166	208	171	203

β-*Naphthol* (T. E. T.)

$100v_a$	12·29	11·36	10·61	9·62	9·00	8·11	7·17	6·76	5·90
$100y_a$	0·645	0·612	0·580	0·541	0·500	0·462	0·429	0·395	0·357
$100x_a$	0·573	0·530	0·494	0·448	0·419	0·378	0·334	0·314	0·274
$100y_b$	0·222	0·222	0·223	0·224	0·225	0·226	0·227	0·228	0·230
K	580	1650	3740	—	1430	2190	—	1670	2230

β-*Naphthol* (T. E. T.)

$100v_a$	8·44	7·73	7·07	6·55	5·64	5·02	4·56	3·81	3·12
$100y_a$	0·513	0·475	0·445	0·410	0·374	0·340	0·305	0·277	0·249
$100x_a$	0·393	0·360	0·329	0·305	0·262	0·233	0·211	0·176	0·144
$100y_b$	0·297	0·299	0·300	0·302	0·303	0·306	0·308	0·311	0·314
K	8200	423	502	156	307	199	109	171	243

Benzenethiol (T. E. T.)

$100v_a$	9·08	8·65	7·75	7·08	6·53	5·82	5·02	3·65
$100y_a$	0·431	0·396	0·360	0·329	0·302	0·273	0·237	0·167
$100x_a$	0·423	0·402	0·361	0·329	0·304	0·207	0·232	0·168
$100y_b$	1·867	1·874	1·882	1·890	1·898	1·909	1·921	1·949
K	0·33	0·04	0·13	0·14	0·10	0·24	0·34	0·09

Calorimetric Measurements.—*Phenol.* Three separate determinations were made with a 3·7% (by wt.) phenol solution and a 4·9% (by wt.) trimethylamine solution. The three values of the molar heat of formation of the complex were 5·6, 5·9, and 5·5 kcal., leading to a mean heat of formation of the phenol–trimethylamine complex of 5·7 ± 0·2 kcal./mole.

p-*Chlorophenol.* Two separate determinations were made, at a *p*-chlorophenol concentration of 2·7% (by wt.) and a trimethylamine concentration of 4·9%. The two heats of formation were 7·4 and 8·6 kcal./mole, and it is therefore concluded that the heat of formation of the *p*-chlorophenol–trimethylamine complex is 8·0 ± 0·6 kcal./mole.

TABLE 2. *Results at* 43·7°.

Calibration curve (A. G.)

100v_a	14·85	13·65	13·10	12·30	11·56	10·30	8·53	7·08	5·39	3·44	2·53
100y_a	1·032	0·928	0·871	0·810	0·736	0·655	0·527	0·447	0·342	0·218	0·168

Phenol (A. G.)

100v_a	6·11	4·93	3·85	3·01
100y_a	0·825	0·717	0·628	0·554
100x_a	0·390	0·315	0·245	0·190
100y_b	0·963	0·986	1·010	1·044
K	50	45	47	49

p-*Chlorophenol* (A. G.)

100v_a	9·83	7·98	6·71	5·25	4·14	2·77
100y_a	0·995	0·886	0·782	0·688	0·603	0·524
100x_a	0·622	0·505	0·423	0·335	0·262	0·175
100y_b	0·908	0·919	0·933	0·948	0·967	0·993
K	114	157	92	108	97	138

p-*Cresol* (A. G.)

100v_a	6·57	5·39	4·45	3·68	2·94	2·12
100y_a	0·747	0·650	0·566	0·500	0·434	0·366
100x_a	0·415	0·340	0·282	0·235	0·198	0·132
100y_b	0·833	0·847	0·865	0·883	0·908	0·941
K	47	44	40	40	41	46

DISCUSSION

The first requirement for the present method to be satisfactory is that an inert second solute shall not change the relation between the A : S ratios in the vapour and liquid phases. That this is so is demonstrated by the results with B = naphthalene, shown in Fig. 2, in which the abscissa used is not $y_a = W_A/W$, but $y_a' = W_A/(W - W_B)$; if no complex is formed, and if there is no deviation from the simple theory, the experimental points will then lie directly on the calibration curve, as indeed they do.

If we use as B a substance which would not be expected to form hydrogen bonds but which, because it is dipolar, might cause a deviation from the simple theory, we find that the points do not now fall on the calibration curve but somewhat below it. Thus Fig. 2 shows that *p*-nitrotoluene has this effect; and the tabulated results show that *p*-dichlorobenzene and anisole have it too. In order to give these results some quantitative expression we may treat them as being due to the formation of a 1 : 1 complex, when we find for K values of 0·4, 0·35, and 0·2, in mole/l. units, respectively.

If, now, B is phenol which would be expected to form a hydrogen-bonded, 1 : 1 complex with trimethylamine, the experimental points show a marked departure from the calibration curve (Fig. 2) and an association constant can be calculated from each one. Series of such values obtained by three of the authors independently are plotted in Fig. 3. There is a considerable scatter of points between 60 and 100 for K, and, further, the curve of the points of any one run shows a minimum. The errors of precision between different experiments are about 20%, probably due to slight differences in starting conditions and particularly in the purity of the solvent, but the variation of K over a single experiment is too great to be explained by any obvious precision errors occurring therein. The K values lie on smooth curves in most of the systems wherein hydrogen bonding is indicated, although these curves do not always display minima. There is usually a rise at low concentrations.

If K is really constant, we can readily see that an anomalous increase in K corresponds to the trimethylamine's being less available in the ternary solution than it should be, relative to its availability in the binary amine–solvent mixture. This might be due to some kind of systematic error; but careful consideration of the possibilities has not revealed one. Because of the difficulty of fixing the starting conditions, it is not practicable to repeat the points obtained in the later stages of a previous run as the first points in a subsequent run, *i.e.*, the obvious tests of reproducibility are not easy to apply.

The next possibility considered was that the anomalies arise from over-simplification in the theory. The assumption that only short-range, specific forces need be considered is not quite correct, as the results with *p*-nitrotoluene, *p*-dichlorobenzene, and anisole show.

Therefore attempts were made to allow for inter-dipolar forces between the trimethylamine and the phenol, and also between it and the polar, hydrogen-bonded complex. From the results for the above three compounds in relation to their total *scalar* dipole moments (4·4, 3·1, and 1·28 D, respectively) it is possible to assess roughly the K values for these two interactions, with phenol ($\mu = 1{\cdot}54$ D, see Hulett, Pegg, and Sutton, following paper) and with the complex ($\mu = 3{\cdot}24$ D, *idem, ibid.*). Another correction is needed for the self-association of phenol. This was attempted by using the constant for dimerisation in carbon tetrachloride calculated from Fox and Martin's results (*Proc. Roy. Soc.*, 1937, *A*, **162**, 419). These calculations, which are equivalent to trying to obtain activity coefficients for the two reactants, though but approximate, suffice to show that these causes are quite inadequate to account for the variation in K. It is indeed difficult to see how any explanation based on activities can explain an anomaly which increases as infinite dilution is approached.

FIG. 2. *The effect of naphthalene* (○), *p-nitrotoluene* (●), *and phenol* (×) *on the vapour-phase concentration of trimethylamine. The calibration curve is shown as a solid line.*

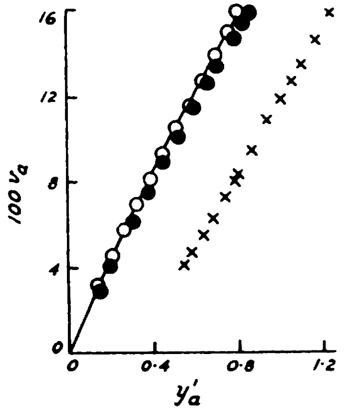
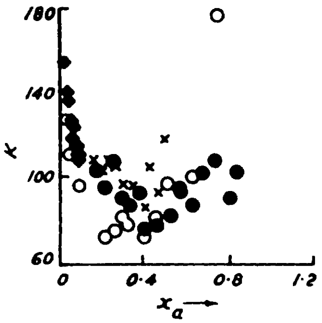


FIG. 3. *The variation of K for phenol–trimethylamine between runs, and with concentration.*



● *Run no.* 1; ○ *run no.* 2;
× *run no.* 3; ◆ *run no.* 4.

Another possible cause is that the complexes are not simply 1 : 1 (Davies, *Ann. Reports*, 1946, **43**, 5; McDougall, *J. Amer. Chem. Soc.*, 1941, **63**, 3420): this seems unconvincing because the anomaly for indole–trimethylamine is similar. Yet another is that there is not merely one kind of 1 : 1 complex but an infinite variety because the forces between the amine nitrogen atom and the acidic hydrogen atom are relatively long range, so that the treatment by a single equilibrium is inadequate. These possibilities have been considered in greater detail, but attempts to treat them rigorously were unsatisfactory.

We have therefore been forced to the conclusion that the variations may be real, and that we cannot at present explain them satisfactorily. Because of the possibility that values outside the range of those now observed might be obtained under different conditions, the quantitative significance of the K values is uncertain. Nevertheless the minimum values of K appear to be characteristic of particular associations (Fig. 3) and appear at least to be qualitatively useful and informative because the range thereof is so very large. In the rest of the discussion, comparisons will be made between them.

The best values of K thus obtained are shown in Table 3.

From Fig. 4, in which the logarithms of the dissociation constants in water (k) * and of the association constants with trimethylamine in *cyclo*hexane (K) are plotted against each other, it is clear, despite all the uncertainties, that the more acidic a compound is in water the stronger in general is the complex which it forms with the amine in a non-polar solvent. This is to be expected on the electrostatic theory of hydrogen-bond formation if there is also a parallel between the electric dipole moment of the X–H bond and the acid

---

* k_{water} for *p*-chlorophenol is taken, by analogy with the values for *p*-fluorophenol, to be four times the value in 30% ethanol–water (Bennett, Brooks, and Glasstone, *J.*, 1935, 1821).

TABLE 3.

B	*K* (mole fraction units)	*K* (mole/l. units)	Type of bonding
	At 25°		
Naphthalene	0	0	Nil
p-Nitrotoluene	3·5 ± 1	0·4	Dipole–dipole
p-Dichlorobenzene	2·7 ± 1	0·35	„
Anisole	1·8 ± 1	0·2	„
Benzenethiol	2·5 ± 1	0·3	„
Phenol	800 ± 200	86	Hydrogen bonding
o-Cresol	650 ± 150	70	„
m-Cresol	650 ± 150	70	„
p-Cresol	600 ± 150	65	„
p-Chlorophenol	1700 ± 300	200	„
α-Naphthol	1000 ± 200	110	„
β-Naphthol	2100 ± 400	230	„
Triphenylmethanol	110 ± 20	12	„
n-Heptyl alcohol	32 ± 8	3·5	„
2 : 5-Dimethylpyrrole	32 ± 8	3·5	„
Indole	85 ± 15	9	„
	At 43·7°		
Phenol	430	46	—
p-Chlorophenol	720	76	—
p-Cresol	380	40	—

dissociation constant in water of the molecule containing it. The compounds, triphenylmethanol, *n*-heptyl alcohol, 2 : 5-dimethylpyrrole, and indole, which do not appear in this graph because their acid dissociation constants are small and not easily measurable, form complexes which are much less stable than those with the phenols but which nevertheless are distinct from those formed by polar molecules without acidic hydrogen atoms.

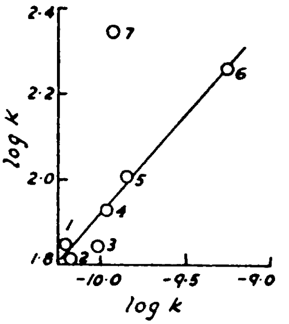


FIG. 4. *The relation between association constant K and electrolytic dissociation constant in water k.*
1, o-*Cresol;* 2, p-*cresol;* 3, m-*cresol;* 4, *phenol;* 5, α-*naphthol;* 6, p-*chlorophenol;* 7, β-*naphthol.*

There are two exceptions to this rule. Benzenethiol forms a very much less stable complex than would be expected : it is no stronger than a so-called dipole–dipole complex. By comparison with anisole the electric dipole moment of benzenethiol (1·33 D) should give a *K* value of about 0·2, while the actual value is 0·3. Gordy and Stanford (*J. Amer. Chem. Soc.*, 1940, **62**, 497) conclude that, in benzene solution, benzenethiol does not associate and that complex formation does not occur between thiophenol and amines less basic than pyridine, while with tripentylamine there seems to be salt formation. Trimethylamine probably has an intermediate basicity, so on this evidence a hydrogen-bonded complex might be expected. Copley, Marvel, and Ginsberg (*J. Amer. Chem. Soc.*, 1939, **61**, 3161) interpreted anomalous heats of mixing of some oxygen and some nitrogen compounds with benzenethiol as evidence of hydrogen-bond formation, though these were less than those when the same compounds were mixed with phenylacetylene and much less than those with chloroform. The experiments were, however, carried out at much higher concentrations than were ours.

The apparent paradox between this result for benzenethiol and its acid dissociation constant relative to that of phenol needs some consideration. An empirical explanation is provided by Schwarzenbach's observation that its dissociation constant is much more sensitive to the dielectric constant of the solvent than is that of phenol. He found (*Helv. Chim. Acta*, 1932, **15**, 1468) that in 60% ethanol–water, *k* for benzenethiol is $2{\cdot}31 \times 10^{-10}$

while in water (by extrapolation) it is $2{\cdot}89 \times 10^{-7}$; this is an increase of a thousandfold, whereas for phenol the increase is only about sixfold. The stability of the benzenethiol–trimethylamine complex will depend essentially upon the polar character of the X–H bond, and it is likely that this is considerably less in S–H than in O–H, at least in a medium of low dielectric constant. The moment of benzenethiol might arise largely from unshared electrons on the sulphur atom.

The second exception is the anomalous stability of the β-naphthol complex, which might be due to the greater heat of formation of the hydrogen bond, or to the partial screening of the α-hydroxyl group by the *peri*-hydrogen atom on the second ring. This matter is more appropriately discussed in the following paper which deals with the electric dipole moment changes.

From the results for K at 25° and 43·7° for three phenols, it is possible to calculate ΔH, and thence, from the ΔF values given by the association constants, rough values of ΔS can be derived. The results of the calorimetric measurements are given in Table 5 for comparison : these, of course, require a knowledge of K values for their evaluation.

TABLE 5.

Compound	ΔF (kcal./mole)	ΔH (kcal./mole) Thermodynamic	Calorimetric	ΔS (cal./mole/°c)
Phenol	−2·6	−5·8	−5·7	−10
p-Chlorophenol	−3·1	−7·0	−8·0	−13
p-Cresol	−2·4	−3·8	—	− 5

The values are all quite rough, but the agreement of the " thermodynamic " and the calorimetric values for ΔH, and the general reasonableness of the results support the view that the method of investigating equilibria described herein gives association constants of more than qualitative significance. The wider significance of these ΔH values will be considered in the following paper.

THE PHYSICAL CHEMISTRY LABORATORY,
OXFORD.

[*Received, May 16th,* 1955.]