389. *Indicator Measurements in the Solvent Systems* $ZnCl_2$–$CH_3{\cdot}CO_2H$ *and* $ZnCl_2$–HCl–$CH_3{\cdot}CO_2H$.

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The ionisation ratios of Brønsted bases and of 4 : 4′-dimethoxydiphenylmethyl compounds in solutions of zinc chloride in acetic acid increase with rising zinc chloride concentration. In the presence of hydrogen chloride the ionisation ratios pass through a maximum, decrease to a minimum, and then rise again, as the concentration of zinc chloride is raised. The measurements are interpreted as reflecting corresponding changes in the acidity (in the Brønsted–Lowry sense) of the media. The characteristic dependence of the ionisation ratios upon zinc chloride concentration is attributed to two different forms of chemical interaction between zinc chloride and hydrogen chloride. Secondary differences in behaviour between the two types of indicator are discussed.

To complement kinetic studies * on aromatic alkylation [1] and hydrogen-isotope exchange [2] in the systems $ZnCl_2$–$CH_3{\cdot}CO_2H$ and $ZnCl_2$–HCl–$CH_3{\cdot}CO_2H$, the ionisation of various indicators in these media has been investigated. The compositions of the media were such that acetic acid always constituted the largest component, acting both as solvent for

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* See following papers.

[1] Bethell and Gold, *J.*, 1958, 1930.

[2] Satchell, preceding paper.

the other species and as a potential Brønsted acid. No previous studies of indicator ionisation in the presence of both Lewis and Brønsted acids have been reported, though the high level of acidity often shown by such combinations is well known from other work.[3]

Three kinds of indicator were used: (1) Brønsted base indicators of the type used by Hammett in his studies with strongly acidic media;[4] (2) 4 : 4′-dimethoxydiphenylmethyl compounds; (3) (for a few measurements) triphenylmethyl chloride. The nature of the equilibria in which these substances engage in the present media is now discussed.

1. *Brønsted Base Indicators.*—(i) *Solvent system* $ZnCl_2$–$CH_3{\cdot}CO_2H$. The ionisation of four of the indicators usual in acidity-function studies,[4] namely, *p*-nitroaniline, *o*-nitroaniline, 4-chloro-2-nitroaniline, and *p*-nitrodiphenylamine, was investigated. The last three exist solely in their basic forms in pure acetic acid.[5] Solutions of the more basic *p*-nitroaniline in the pure solvent have finite absorption at the wavelength of maximum absorption of the ionised form. It is difficult to decide whether this absorption is due to the ionised or the un-ionised form by direct experiment, because added bases (*e.g.*, sodium acetate) will have no effect on equilibria of the type [6]

$$\mathrm{B} + \mathrm{AcOH} \rightleftharpoons \mathrm{B\overset{+}{H}\overset{-}{O}Ac} \quad \text{(ion pair)}$$

However, it is known [6] that *p*-naphtholbenzein † is not detectably ionised in acetic acid, and since this compound is not much less basic than *p*-nitroaniline it follows that *p*-nitroaniline itself can only be negligibly ionised. This conclusion is supported by results to be discussed below.

When anhydrous zinc chloride is added to a solution of one of the aforementioned indicators in acetic acid, the absorption spectrum of the indicator changes gradually from that of the basic form to that characteristic of the ionised, or acidic, form, as on addition of Brønsted acids such as hydrogen chloride or sulphuric acid. Measurement of indicator ratios, I (ratio of acidic to basic form), at various zinc chloride concentrations, is thus possible. This colour change of the indicators is considered to be a manifestation of their basicity in the Brønsted sense, *i.e.*, the indicators are thought to receive a proton, rather than to be involved in any direct interaction with zinc chloride.[2]

For solutions of the common mineral acids in acetic acid, plots of log I against acid concentration for different indicators of the type under consideration have constant separations.[7] However, for two given indicators the exact separations may depend on the mineral acid involved and may also differ from those found when water is the solvent. These discrepancies imply different relative basicities for the indicators in the different systems.[5]

The present system and indicators show behaviour analogous to that found with mineral acids.[5, 7] The plots of log I against the logarithm of the zinc chloride concentration (Fig. 1) provide a set of curves with reasonably constant separations, though *p*-nitrodiphenylamine shows some individual tendency. The behaviour of *p*-nitroaniline conforms with that of the other indicators, and this is additional circumstantial evidence for the assumption that this compound is effectively un-ionised in the pure solvent.

If the separations of the plots are taken to represent the relative basicities of the indicators, then the ΔpK_a's between *p*-nitroaniline and *o*-nitroaniline, between *o*-nitroaniline and 4-chloro-2-nitroaniline, and between 4-chloro-2-nitroaniline and *p*-nitrodiphenylamine are $-1{\cdot}66$, $-0{\cdot}95$, and $-1{\cdot}22$, respectively. The values in water are $-1{\cdot}28$,

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† *p*(or α)-Naphtholbenzein is a secondary base and in dissociating solvents may therefore respond to the J_0 function rather than to H_0 (cf. refs. 6, 14).

[3] *E.g.*, McCauley and Lien, *J. Amer. Chem. Soc.*, 1951, **73**, 2013; Kilpatrick and Luborsky, *ibid.*, 1953, **75**, 577; Brown and Brady, *ibid.*, 1952, **74**, 3570; Brown and Wallace, *ibid.*, 1953, **75**, 6268.

[4] Hammett, " Physical Organic Chemistry," McGraw-Hill Book Co. Inc., New York, 1940.

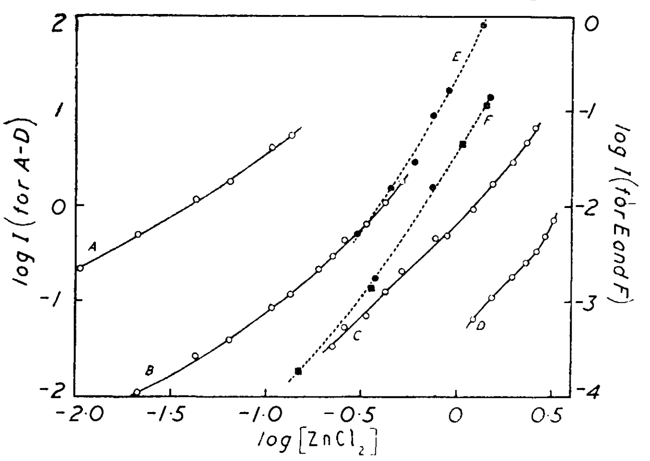
[5] Satchell, *J.*, 1958, 1916.

[6] Kolthoff and Bruckenstein, *J. Amer. Chem. Soc.*, 1956, **78**, 1.

[7] Paul and Hammett, *ibid.*, 1936, **58**, 2182; Hall and Spengeman, *ibid.*, 1940, **62**, 2487; Roček, *Chem. Listy*, 1956, **50**, 726.

$-0{\cdot}74$, and $-1{\cdot}45$ respectively.[8] Comparisons for the mineral acids in acetic acid show similar discrepancies.[5, 7] A comparison of the present data with those obtained for solutions of hydrogen chloride in acetic acid [5] shows that, for all the indicators common to both studies, the amount of ionisation produced by a given concentration of zinc chloride is much less than that brought about by the same stoicheiometric concentration of hydrogen chloride (Table 2). Thus the general level of acidity is much higher in the presence of hydrogen chloride.

FIG. 1. *Indicator ionisation in* $ZnCl_2$–$CH_3{\cdot}CO_2H$.



A: *p*-Nitroaniline. *B*: *o*-Nitroaniline. *C*: 4-Chloro-2-nitroaniline.
D: *p*-Nitrodiphenylamine. *E*: Triphenylmethyl chloride.
F { ● 4 : 4′-Dimethoxydiphenylmethyl chloride.
■ 4 : 4′-Dimethoxydiphenylmethanol.

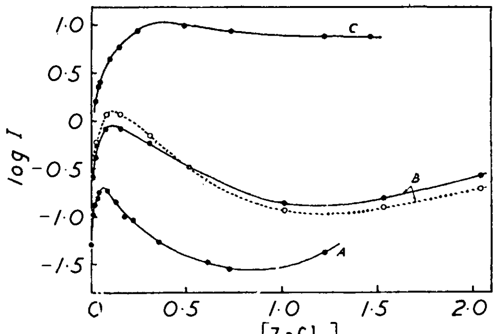


FIG. 2. *Ionisation of Brønsted bases in* $ZnCl_2$–HCl–$CH_3{\cdot}CO_2H$.

A: [HCl] = 0·013M.
B: [HCl] = 0·05M.
C: [HCl] = 0·42M.

●, 4-Nitrodiphenylamine.
○, 4-Chloro-2-nitroaniline.

(ii) *Solvent system* $ZnCl_2$–HCl–$CH_3{\cdot}CO_2H$. Measurements were made of the changes in indicator ionisation when increasing amounts of zinc chloride were added to acetic acid containing a constant quantity of hydrogen chloride. Three hydrogen chloride concentrations (0·013, 0·05, and 0·42M) were investigated, *p*-nitrodiphenylamine being used throughout. In the solutions containing 0·05M-hydrogen chloride, measurements were also made with 4-chloro-2-nitroaniline. Plots of log *I* against zinc chloride concentration are shown in Fig. 2. The shapes of the curves are very different from those obtained when either hydrogen chloride [5] or zinc chloride is used alone. The addition of small amounts

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[8] Paul and Long, *Chem. Rev.*, 1957, **57**, 1.

of zinc chloride to a constant quantity of hydrogen chloride markedly increases the ionisation—an increase much greater than that expected if the contributions of zinc chloride and hydrogen chloride [5] were simply additive. With further addition of zinc chloride the acidity passes through a maximum and a minimum, the positions of which depend on the hydrogen chloride concentration. (The increase in ionisation achieved at the maxima of the curves is roughly the same at each hydrogen chloride concentration, and amounts to a change in log I of about 1·5 units.)

Even when only one acidic species is present in solution the ionisation trends of different indicators are not always parallel.[5, 7, 8] In the present solutions it seems likely (as is argued more fully later) that more than one Brønsted acid is active and this is an additional and special reason for expecting such discrepancies.[5] The broken curve in Fig. 2 is a plot of log I — 1·45 for 4-chloro-2-nitroaniline at 0·05M-hydrogen chloride. Its general shape is very similar to that of the plot for *p*-nitrodiphenylamine at the same concentration, but detailed parallelism is lacking.

(iii) *Nature of the chemical species responsible for the ionisation.* The observed variations in indicator ionisation lead to the following conclusions.

(*a*) When zinc chloride is present alone there is at least one type of interaction with the solvent which results in the formation of an additional Brønsted acid species. This is quite plausible in view of the existence of compounds such as $BF_3,2CH_3{\cdot}CO_2H$. As has been previously mentioned, the ionisation curves in the presence of zinc chloride alone are similar to those obtained when a single mineral acid is used in this solvent. Thus, for these solutions the simplest interpretation is that zinc chloride is engaged in a single equilibrium with the solvent.

(*b*) When both hydrogen chloride and zinc chloride are present at least two further acidic complexes must be formed, and there is, in fact, some previous evidence of complex formation, of some kind, between zinc chloride and hydrogen chloride in both aqueous [9] and acetic acid [10, 11] solutions.

Unless *two* further acidic species are postulated it does not seem possible to explain the increase *and* subsequent decrease in ionisation. An alternative explanation of the decrease as due to deactivation of the indicators by complex formation with zinc chloride, is unlikely to be correct, since the phenomenon also occurs with indicators of a different type (see p. 1923) and in the exchange reaction with anisole [2] (see following paper), a compound for which ultraviolet absorption measurements show no evidence of complex formation.[1]

The ionisation maximum does not occur at a composition corresponding to any simple, or constant, stoicheiometry; in the range of hydrogen chloride concentrations studied it occurs when the concentration of zinc chloride is 1—5 times greater than that of the hydrogen chloride. Similarly, the positions of the acidity minima do not correspond to a fixed stoicheiometric ratio. These facts strongly imply the operation of mass-law effects in the interactions between hydrogen chloride and zinc chloride.

Specific chemical interpretation of the various forms of interaction between zinc chloride, hydrogen chloride, and acetic acid is handicapped by the paucity of modern work on the chemistry of zinc complexes in solution. In the solid state a large number of double salts of zinc halides have been reported and structural evidence indicates the considerable stability of the tetrahedral ion $ZnCl_4^{2-}$ and a general preference for four-co-ordinated structures.[12] By analogy, it seems likely that four-fold co-ordination gives rise to the most stable complexes in solution also, though there is evidence for the existence of both $ZnCl_3^-$ and $ZnCl_4^{2-}$ from Raman spectra of potassium chloride–zinc chloride melts,[13] where the three-fold co-ordination cannot be supplemented by solvent molecules.

The preference for four-fold co-ordination being borne in mind, the following suggestions

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[9] Hildebrand and Bowers, *J. Amer. Chem. Soc.*, 1916, **38**, 785.

[10] Davidson and Chappell, *ibid.*, 1939, **61**, 2164.

[11] Andrews and Keefer, *ibid.*, 1956, **78**, 4549, 5623; 1957, **79**, 4348.

[12] Bailar, " Chemistry of Co-ordination Compounds," Reinhold Publishing Co., New York, 1956.

[13] Bues, *Z. anorg. Chem.*, 1955, **279**, 104.

are thought to represent the simplest chemical interpretations of the present ionisation data.

In solutions of zinc chloride alone, the single equilibrium postulated is

$$ZnCl_2 + 2AcOH \rightleftharpoons H_2ZnCl_2(OAc)_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

the complex acid being responsible for the observed acidic effects. It seems reasonable to suppose that co-ordinated acetic acid will possess enhanced acidity, since the attachment of the electron-pair acceptor molecule will withdraw electrons from acetic acid. Zinc chloride is stable in acetic acid,[10] so that solvolysis to give some hydrogen chloride is not an alternative explanation.

When both zinc chloride and hydrogen chloride are present in the solvent the following equilibria seem the most likely:

$$2HCl + H_2ZnCl_2(OAc)_2 \rightleftharpoons H_2ZnCl_4 + 2AcOH \quad . \quad . \quad . \quad . \quad (2)$$

$$H_2ZnCl_4 + H_2ZnCl_2(OAc)_2 \rightleftharpoons 2H_2ZnCl_3(OAc) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

An alternative to the complex $H_2ZnCl_3(OAc)$, having the same $ZnCl_2 : HCl$ ratio, is $H_2Zn_2Cl_6$ with four-fold co-ordination achieved by a bridge structure similar to that in Al_2Cl_6. However, no such structure has previously been indicated for zinc compounds. A further possibility, with a higher $ZnCl_2 : HCl$ ratio, would be $H^+[ZnCl]^+[ZnCl_4]^{2-}$.

In terms of the above equilibria the qualitative explanation of the observed ionisation curves is as follows. When zinc chloride is added to a solution of hydrogen chloride in acetic acid the initial, sharp increase in acidity is to be attributed to the species H_2ZnCl_4, though this acid cannot be formed quantitatively since maximum ionisation occurs at a zinc chloride concentration greater than that corresponding to the ratio $ZnCl_2 : HCl = 1 : 2$. As more zinc chloride is added the acidity falls, and therefore H_2ZnCl_4 is clearly being replaced by a weaker acid with a higher $ZnCl_2 : HCl$ ratio, and having one of the formulæ indicated above. The formula $H_2ZnCl_3(OAc)$ seems the most likely, being intermediate in structure between H_2ZnCl_4 and $H_2ZnCl_2(OAc)_2$. The latter species will become increasingly important with further addition of zinc chloride, and accounts for the gradual recovery of acidity.

It is possible, on the above basis, to deduce an expression for I in terms of the various equilibrium constants and the stoicheiometric concentrations of hydrogen chloride and zinc chloride, but the equation is too complex to be of practical quantitative value.

The high acid strength of H_2ZnCl_4 calls for some comment. At the maximum of the ionisation curves there is certainly less H_2ZnCl_4 present than corresponds to the stoicheiometric hydrogen chloride concentration. Comparison of the ionisation produced with that produced by other acids in acetic acid [14] leads to the deduction that H_2ZnCl_4, in this solvent, is a stronger acid than perchloric, and probably stronger than any acid previously studied. It is, therefore, likely to be fairly completely ionised, since Kolthoff and Bruckenstein [6] give the ionisation constant for perchloric acid as unity.

Concerning the detailed structures of the complex acids—structures which must plausibly account for the differences in acidity—two views are possible. First, it may be assumed that in both H_2ZnCl_4 and $H_2ZnCl_3(OAc)$, all the hydrogen originating from the hydrogen chloride is completely ionised, giving ion-pairs or clusters of the type $2H^+[ZnCl_4]^{2-}$ and $H^+[ZnCl_3(AcOH)]^-$. The marked differences in strength between the two acids would then have to be attributed to the differences in the positions of the following equilibria involving the Brønsted base B:

$$B + 2H^+[ZnCl_4]^{2-} \rightleftharpoons BH^+[H]^+[ZnCl_4]^{2-} \quad . \quad . \quad . \quad . \quad (4)$$

$$B + H^+[ZnCl_3(AcOH)]^- \rightleftharpoons BH^+[ZnCl_3(AcOH)]^- \quad . \quad . \quad . \quad . \quad (5)$$

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[14] Smith and Elliott, *J. Amer. Chem. Soc.*, 1953, **75**, 3566.

i.e., it is necessary to postulate that equilibrium (4) lies much further to the right than equilibrium (5). In this scheme the hydrogen of the co-ordinated acetic acid molecules is regarded as only partially ionised.

Alternatively, it may be assumed that even the hydrogen originating from the hydrogen chloride is only partially ionised in the weaker acid. On this basis the relative strengths can be thought of as determined largely by the relative amounts of ionisation, which in turn would be determined by the relative stabilities of the ions $[ZnCl_4]^{2-}$, $[ZnCl_3(OAc)]^{2-}$, and $[ZnCl_2(OAc)_2]^{2-}$. These are certainly likely to be different, with $[ZnCl_4]^{2-}$ the most stable. The difficulty of this interpretation is to formulate an acceptable structure for the un-ionised species $H_2ZnCl_3(OAc)$ (or any of its alternatives considered). However, analogous problems exist in other cases.[15] The proton of the species $H[ZnCl_3(AcOH)]$ cannot be donated, in any way, to the complexed acetic acid molecule, since this molecule must be regarded as more acidic and less basic than the uncomplexed solvent, which will therefore receive a proton preferentially. The possibility of appreciable solvation or hydrogen bonding of incipiently ionised protons may be the governing factors for the formation of hydrogen halide–Lewis acid complexes, for there is evidence that, by themselves, boron trifluoride and hydrogen fluoride do not interact to form a significant amount [16] of HBF_4. Even in the present system it is not necessary to assume that the acids H_2ZnCl_4 and $H_2ZnCl_2(OAc)_2$ are capable of independent existence. The ions $[ZnCl_4]^{2-}$ (and $[ZnCl_2(OAc)_2]^{2-}$) need only be formed on the addition of a base (B), according to

$$2B + ZnCl_2 + 2HCl \rightleftharpoons 2BH^+[ZnCl_4]^{2-} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

However, it is essential to the explanation of the ionisation maximum to assume that some hydrogen chloride is actually bound to zinc chloride to form the intermediate (and less acidic) complex [of formula $H_2ZnCl_3(OAc)$ or one of its alternatives] in acetic acid solution. Such a compound must therefore exist, in spite of our present inability to give it an entirely satisfactory structural formula. The similar difficulties of formulation of H_2ZnCl_4 and $H_2ZnCl_2(OAc)_2$ are therefore no evidence against the existence of these compounds.

2. *The Indicators* 4 : *4'-Dimethoxydiphenylmethanol* (P), *its Chloride* (Q), *and Triphenylmethyl Chloride* (R).—(i) *Solvolysis of the indicators.* It has previously been shown [17] that dissolution of a small quantity of a diarylmethanol in sulphuric acid–acetic acid media results in a rapid conversion into the corresponding acetate. It seems reasonable to assume that a similar acid-catalysed reaction occurs in acetic acid rendered more acidic by the presence of zinc chloride. Solvolysis also occurs when a chloride, such as Q, is dissolved in acetic acid containing zinc chloride, as is indicated by the ultraviolet spectra of diphenylmethyl acetate. In the presence of a little zinc chloride, which for these compounds produces a spectrometrically undetectable amount of ionisation, both compounds give the spectrum characteristic of the acetate in the pure solvent.[1]

It may be concluded that, in the presence of zinc chloride, the solution of a diarylmethyl chloride will result in an equilibrium mixture of the alcohol, chloride, and acetate, with the last predominating. When both hydrogen chloride and zinc chloride are present initially in the solvent, dissolution of the alcohol will produce all three species, the acetate predominating though the amount of chloride present at equilibrium may depend on the concentration of hydrogen chloride. However, formation of an appreciable amount of diarylmethyl chloride is unlikely at the concentrations examined.[17] Triphenylmethyl chloride (R) is not substantially solvolysed in acetic acid.[18]

(ii) *Solvent system* $ZnCl_2$–$CH_3{\cdot}CO_2H$. In this system measurements were made with

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[15] Olah, Kuhn, and Olah, *J.*, 1957, 2174; Brown, Pearsall, Eddy, Wallace, Grayson, and Nelson, *Ind. Eng. Chem.*, 1953, **45**, 1462.

[16] Kilpatrick and Luborsky, *J Amer Chem. Soc.*, 1954, **76**, 5865.

[17] Bethell and Gold, *J.*, 1958, 1905.

[18] Evans, Price, and Thomas, *Trans. Faraday Soc.*, 1955, **51**, 481.

both the alcohol (P) and the chloride (Q) form of the diphenylmethyl indicator. The observed ionisation ratios for both compounds fall on the same curve (Fig. 1), as is to be expected if solvolysis of the chloride is rapid and practically complete, and the indicator concentration low, so that the hydrogen chloride produced in the solvolysis is present only to an insignificant extent. As for the Brønsted bases, increasing amounts of zinc chloride produce a steady increase in indicator ionisation, and at all zinc chloride concentrations the ionisation is much less than that produced by the same concentration of sulphuric acid; triphenylmethyl chloride (R) responds similarly to the addition of zinc chloride to the solution (Fig. 1).

(iii) *Solvent system* $ZnCl_2$–HCl–$CH_3{\cdot}CO_2H$. The ionisation of indicator P was again studied for increasing concentrations of zinc chloride in solutions containing a fixed concentration of hydrogen chloride (Fig. 3). Although the small number of experimental points allows some latitude in the drawing of the curves, it is evident that the maximum–minimum effects shown by the Brønsted bases (Fig. 2) are also displayed by this indicator. The parallelism is not exact, as the maxima now occur at larger concentrations of zinc chloride. The similarities of the curves suggest that the ionisation of P is largely, but not entirely, governed by the proton-donating power of the solution, and that the colour change is not due to direct association of zinc chloride with P.

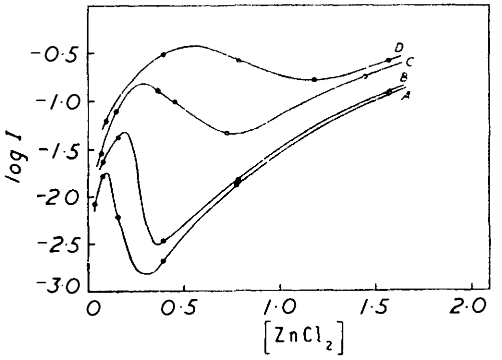

FIG. 3. *Ionisation of* 4 : 4′-*dimethoxy diphenylmethyl chloride in* $ZnCl_2$–HCl–$CH_3{\cdot}CO_2H$.

A: [HCl] = 0·0099M.
B: [HCl] = 0·016M.
C: [HCl] = 0·027M.
D: [HCl] = 0·054M.

(iv) *Differences between Brønsted bases and secondary bases.* The ionisation of the diarylmethanol–diarylmethyl acetate system under the influence of an acid catalyst in acetic acid has been discussed in a preceding paper.[17] For the case where the acetate is the predominant un-ionised form of the indicator, the ionisation ratio may be expressed in the form (ion-pair dissociation and the formation of higher aggregates being neglected)

$$I = \frac{\sum_i [R^+A_i^-]}{[ROAc]} = \sum_i \frac{K_i'}{K_E}\,\frac{(HA_i)\,f_{ROAc}}{(AcOH)\,f_{R^+A_i^-}} \quad . \; . \; . \; . \; . \; . \quad (7)$$

where the symbols have the significance previously defined,[17] the ratio K_i'/K_E also being the equilibrium constant for the reaction

$$ROAc + HA_i \rightleftharpoons R^+A_i^- + AcOH \quad . \; . \; . \; . \; . \quad (8)$$

For the Brønsted base indicators (B) previously discussed

$$I = \sum_i \frac{[BH^+A_i^-]}{[B]} = \sum_i \frac{(HA_i)}{K_a^{BH^+A_i^-}} \cdot \frac{f_B}{f_{BH^+A_i^-}} \quad . \; . \; . \; . \; . \quad (9)$$

where $K_a^{BH^+A_i^-}$ is the equilibrium constant for the reaction

$$BH^+A_i^- \rightleftharpoons B + HA_i \quad . \; . \; . \; . \; . \; . \; . \; . \quad (10)$$

Comparison of equations (7) and (9) reveals that they are of similar form, the most significant difference being the appearance of the activity of acetic acid in the denominator of (7). This difference is the same as that found for the two types of indicator in the system sulphuric acid–acetic acid and which was expressed[17]—without explicit consideration of ion association—as the difference between two "acidity functions" (H_0 and L^{OAc}). It is, therefore, intelligible that the ionisation ratios of the two types of indicator should show qualitatively the same sort of dependence on zinc chloride and hydrogen chloride concentration, but that there should be quantitative differences. If zinc chloride reduces the activity of acetic acid the maxima in the curves of Fig. 3 should be displaced towards higher zinc chloride concentrations than are found in Fig. 2 and the minima towards lower ones, as is observed. Furthermore, the detailed shapes of the various curves are likely to be very sensitive to small quantities of water in the solvent, since these may induce the acids to dissociate and will affect the alcohol–acetate–chloride equilibria for the secondary bases.

A more complex formula than (7) is obviously required for an indicator whose equilibrium mixture contains appreciable concentrations of alcohol and chloride, and may be obtained by an obvious elaboration of equation (4) in ref. 17.

EXPERIMENTAL

Materials.—Anhydrous acetic acid, hydrogen chloride, and stock solutions of the latter in the former were prepared as previously described.[5]

The anhydrous zinc chloride was supplied as fused sticks (B.D.H). Stock solutions of zinc chloride in acetic acid were made by dissolving sticks, the surfaces of which had first been washed in a separate portion of the anhydrous solvent. The sticks contain a little insoluble impurity and stock solutions were centrifuged to remove this. The compositions of the hydrogen chloride and zinc chloride solutions were determined by titration for chloride, by using either Fajans's or a modified Volhard procedure.

The *p*-nitroaniline, *o*-nitroaniline, 4-chloro-2-nitroaniline, and *p*-nitrodiphenylamine were recrystallised samples with m. p. 148°, 71·6°, 46°, and 135°, respectively.

4 : 4′-Dimethoxydiphenylmethanol was the specimen used in earlier work.[17] 4 : 4′-Dimethoxydiphenylmethyl chloride was prepared by passing a stream of hydrogen chloride through the ethereal solution of the alcohol and removing the water formed at several stages. After being dried ($CaCl_2$) the solution was neutralised (anhyd. Na_2CO_3) and filtered. The ether was distilled off and the colourless residue recrystallised from ether at a low temperature (m. p. 83—84). Triphenylmethyl chloride was a recrystallised commercial specimen.

Measurements of Ionisation Ratios.—The general procedure has been described before.[5, 17] The solutions containing known amounts of indicator, hydrogen chloride, and zinc chloride were made up, by volume, from stock solutions. The *p*-nitroaniline solutions were unstable, but not sufficiently so to prevent accurate measurements being made by a short extrapolation to zero time.

TABLE 1. *Ionisation of* (a) p-*nitroaniline,* (b) o-*nitroaniline,* (c) 4-*chloro*-2-*nitroaniline, and* (d) p-*nitrodiphenylamine in solutions of zinc chloride in acetic acid at* 18° ± 2°.

$ZnCl_2$ (M)	0·0106	0·0212	0·0424	0·0636	0·106	0·133		
log I_a	−0·67	−0·31	+0·06	0·25	0·61	0·74		
log I_b		−1·96	−1·58	−1·41	−1·08	−0·93		
log I_b − log I_a		−1·65	−1·64	−1·66	−1·69	−1·67		
$ZnCl_2$ (M)	0·186	0·222	0·255	0·333	0·420	0·510	0·765	
log I_b	−0·67	−0·53	−0·36	−0·19	+0·04	+0·26		
log I_c		−1·47	−1·28	−1·16	−0·91	−0·69	−0·34	
log I_c − log I_b		−0·94	−0·92	−0·97	−0·95	−0·95		
$ZnCl_2$ (M)	0·888	1·21	1·53	1·95	2·30	2·55	2·87	3·19
log I_c	−0·31	−0·03	+0·23	0·46	0·67	0·83		
log I_d		−1·19	−0·96	−0·74	−0·59	−0·47	−0·31	−0·14
log I_d − log I_c		−1·16	−1·19	−1·20	−1·26	−1·30		

TABLE 2. *Ionisation of* 4-*chloro*-2-*nitroaniline in acetic acid in the presence of* (a) *hydrogen chloride,* (b) *zinc chloride, at rounded molarities at* 18° ± 2°.

HCl (or $ZnCl_2$) (M)	0·2	0·4	0·6	0·8	1·0	1·2
log *I* (*a*)	+0·42	0·78	1·01	1·19	1·34	1·48
log *I* (*b*)	−1·56	−0·96	−0·60	−0·33	−0·18	−0·03

TABLE 3. *Ionisation of* (a) p-*nitrodiphenylamine and* (b) 4-*chloro*-2-*nitroaniline in acetic acid containing both hydrogen chloride and zinc chloride, at* 18° ± 2°.

(i) HCl = 0·013M							
$ZnCl_2$ (M)	0·0	0·0044	0·0133	0·0222	0·0355	0·044	0·088
log I_a	−2·13 *	−1·39	−0·98	−0·88	−0·81	−0·75	−0·73
$ZnCl_2$ (M)	0·132	0·176	0·220	0·352	0·610	0·720	1·22
log I_a	−0·85	−1·00	−1·04	−1·27	−1·48	−1·55	−1·38
(ii) HCl = 0·05M							
$ZnCl_2$ (M)	0·0	0·010	0·026	0·077	0·153	0·306	0·510
log I_a	−1·60 *	−0·58	−0·38	−0·08	−0·08	−0·23	−0·48
log I_b	−0·21 *	+1·07	1·23	1·52	1·52	1·30	0·97
$ZnCl_2$ (M)	1·02	1·53	2·04				
log I_a	−0·86	−0·81	−0·56				
log I_b	0·51	0·54	0·75				
(iii) HCl = 0·42 (M)							
$ZnCl_2$ (M)	0·0	0·0244	0·0373	0·0488	0·0976	0·146	0·244
log I_a	−0·60 *	+0·21	0·36	0·41	0·65	0·77	0·94
$ZnCl_2$ (M)	0·488	0·732	1·22	1·46			
log I_a	1·00	0·94	0·88	0·88			

* Values deduced from data given in reference 5.

TABLE 4. *Ionisation of* 4 : 4′-*dimethoxydiphenylmethanol* (P) *and its chloride* (Q) *in acetic acid containing both hydrogen chloride and zinc chloride, at* 18° ± 2°.

(i) HCl = 0·0M							
$ZnCl_2$ (M)	0·147	0·351	0·369	0·738	1·053	1·404	1·475
log I_Q	−3·73	—	−2·76	−1·80	—	—	−0·85
log I_P	—	−2·86	—	—	−1·34	−0·94	
(ii) HCl = 0·0099M							
$ZnCl_2$ (M)	0·039	0·079	0·157	0·393	0·786	1·571	
log I_P	−2·08	−1·79	−2·22	−2·69	−1·89	−0·93	
(iii) HCl = 0·016M							
$ZnCl_2$ (M)	0·079	0·157	0·393	0·786	1·571		
log I_P	−1·64	−1·39	−2·47	−1·82	−0·92		
(iv) HCl = 0·027M							
$ZnCl_2$ (M)	0·072	0·144	0·361	0·452	0·722	1·445	
log I_P	−1·55	−1·11	−0·90	−1·01	−1·34	−0·76	
(v) HCl = 0·054M							
$ZnCl_2$ (M)	0·157	0·393	0·786	1·178	1·571		
log I_P	−1·03	−0·51	−0·59	−0·79	−0·58		

TABLE 5. *Ionisation of triphenylmethyl chloride* (R) *in acetic acid in the presence of zinc chloride at* 18° ± 2°.

[$ZnCl_2$] (M)	0·298	0·447	0·596	0·745	0·894	1·341
log I_R	−2·29	−1·81	−1·53	−1·05	−0·78	−0·09

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