169. *A Conductimetric Study of Acid–Base Interactions in Non-aqueous Media.*

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The conductimetric titration technique has been extended in order to study interactions between organic acids and tertiary bases in acetone and acetonitrile. Various conductance curves have been interpreted in terms of the ionic species present in solution.

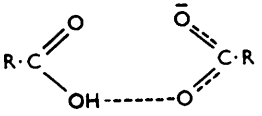
In contrast to the behaviour in hydroxylic media, the addition of acid to a salt in these solvents may enhance conductivity, over and above that due to any mass-law increase. This does not occur with strongly chelated acids such as 2 : 6-dinitrophenol and picric acid.

The submission that this effect is due to hydrogen bonding between acid and anion has been examined with due regard to the various physical and chemical changes involved, and in connection with the behaviour of salts undergoing acid–base dissociation.

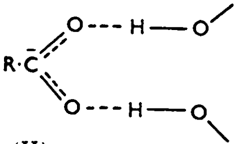
The attractions involved appear to be of exceptional strength, and, for carboxylic acids and their anions, are evident in solvents in which the acids are known to be monomeric.

The conductimetric study of acid–base interactions has been largely confined to operations of analytical significance. In aqueous solution the processes are well understood, and most of the changes examined are known to depend largely upon the concentrations of free hydroxyl and hydroxonium ions.[1] Non-aqueous media have been used [2] where the solvents or solutes are intensely reactive, thus avoiding side reactions in order to obtain results of quantitative significance.

Maryott,[3] however, performed conductimetric titrations with various organic acids and bases in benzene or dioxan. When base solutions were added to acid solutions, the appearance of a maximum in the specific conductivity curve, occurring before the accepted stoicheiometric equivalence point, was taken as evidence for the presence of a hydrogen-bonded complex (I) between anion and excess of acid. The resulting complex anion would be larger than the simple anion, so that its charge would be more effectively shielded, the Coulombic attractions reduced, and the dissociation consequently increased. However, the concentration of *free* acid anions in solvents of low dielectric constant must necessarily be very small, and the recorded conductivities are of the order of 10^{-10} to 10^{-12} ohm^{-1} cm.$^{-1}$.



(I)



(II)

The existence of acid salts of monobasic organic acids was first demonstrated by Gerhardt.[4] Pfeiffer *et al.*[5] prepared a series of normal and acid salts of carboxylic acids with pyridine, and ascribed the formation of the latter salts to interaction between the anion and the hydrogen atom of the acid. In more recent years, Speakman and his co-workers [6] carried out *X*-ray examinations of the crystals of various aromatic acid salts. The presence of hydrogen bonds was demonstrated, but claims concerning their symmetry

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[1] Kolthoff, *Ind. Eng. Chem. Anal.*, 1930, **2**, 225; Britton, "Conductometric Analysis," Chapman and Hall, London, 1934.

[2] Riddick, *Analyt. Chem.*, 1954, **26**, 77.

[3] Maryott, *J. Res. Nat. Bur. Stand.*, 1947, **38**, 527.

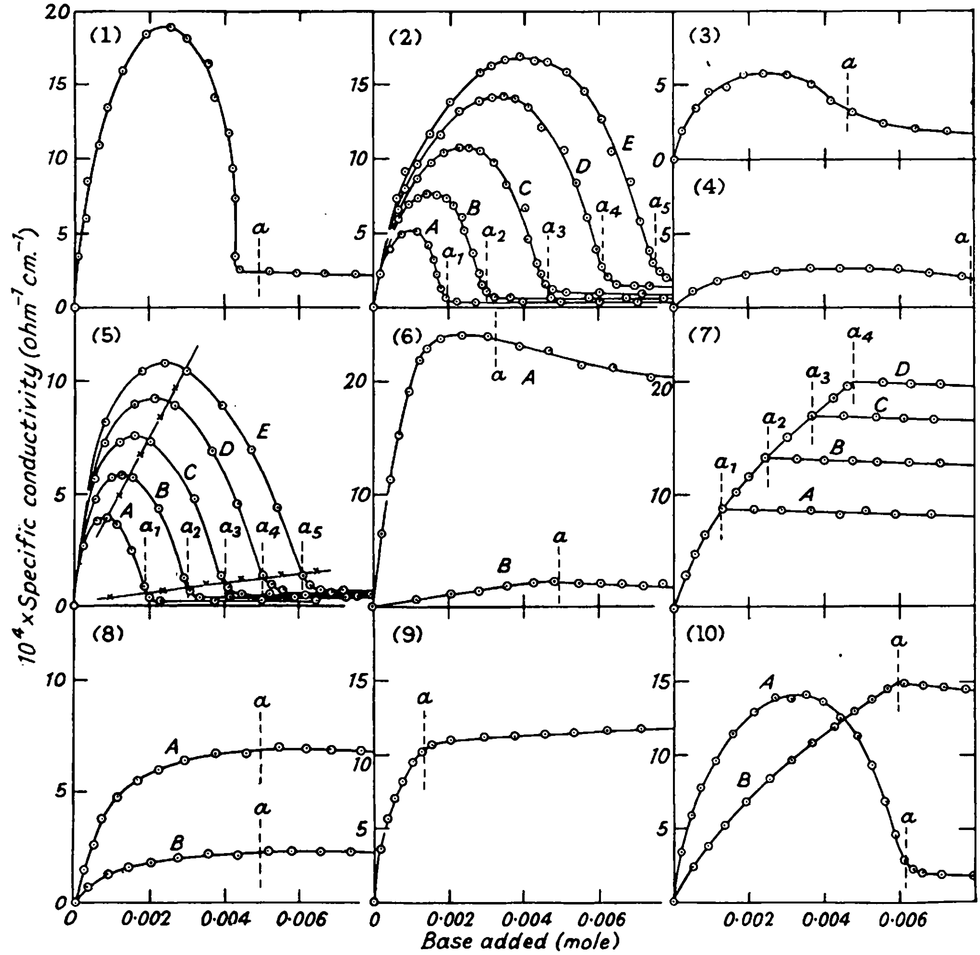
[4] Gerhardt, *Annalen*, 1853, **87**, 150.

[5] Pfeiffer, *Ber.*, 1914, **47**, 1580, and references to Birencweig, Hofmann, and Windheuser therein.

[6] Speakman, *J.*, 1949, 3357; Skinner and Speakman, *J.*, 1951, 185; Skinner, Stewart, and Speakman, *J.*, 1954, 180; Downie and Speakman, *ibid.*, p. 787.

have been discounted, from infrared evidence, by Davies and Thomas.[7] Further infrared studies, made by Barrow and Yerger,[8] on solutions containing primary, secondary, and tertiary bases with acetic acid in carbon tetrachloride or chloroform, showed the occurrence of acid–base equilibria, together with the formation of undissociated acid–anion–cation and anion–cation complexes, AH · · · A⁻ · · · HB⁺ and ⁻A · · · HB⁺. Further complexities, due to solute–solvent interaction, were adduced for the chloroform solutions.

FIG. 1. *Titrations with triethylamine* [except no. (9)].



(1) *Trichloroacetic acid* (0·165 *mole/l.*) *in acetone.*
(2) *Dichloroacetic acid* (*A*, 0·0653; *B*, 0·100; *C*, 0·154; *D*, 0·203; *and E*, 0·250 *mole/l.*) *in acetone.*
(3) *Monochloroacetic acid* (0·154 *mole/l.*) *in acetone.*
(4) *Acetic acid* (0·267 *mole/l.*) *in acetone.*
(5) 3 : 5-*Dinitrobenzoic acid* (*A*, 0·0612; *B*, 0·104; *C*, 0·134; *D*, 0·167; *and E*, 0·204 *mole/l.*) *in acetone, titrated with* Et_3N (*constant volume*).
(6) *A*, 3 : 5-*Dinitrophenol* (0·018 *mole/l.*); *B*, 2 : 6-*dinitrophenol* (0·164 *mole/l.*) *in acetone.*
(7) *Picric acid* (*A*, 0·0260; *B*, 0·0503; *C*, 0·0765; *and D*, 0·0991 *mole/l.*) *in acetone, titrated with* Et_3N (*constant volume*).
(8) *A*, m-*Nitrophenol* (0·165 *mole/l.*); *B*, o-*Nitrophenol* (0·166 *mole/l.*) *in acetone.*
(9) *Picric acid* (0·0430 *mole/l.*) *in acetone, titrated with pyridine.*
(10) *Dichloroacetic acid*: *A* (0·205 *mole/l.*) *in acetone*; *B*, (0·198 *mole/l.*) *in ethyl alcohol.*

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[7] Davies and Thomas, *J.*, 1951, 2858.

[8] Barrow and Yerger, *J. Amer. Chem. Soc.*, 1954, **76**, 5211; 1955, **77**, 4474; Yerger and Barrow, *ibid.*, p. 6206.

There is thus considerable evidence for the existence of a range of complex salts both in the crystalline state and in solution with aprotic solvents. The purpose of the present investigation is to determine if complex-formation by *free* anions can be demonstrated under more favourable conditions, and to extend the existing concepts regarding their mode of formation. This communication deals with the interactions between tertiary bases and monobasic organic acids, in acetone, acetonitrile, and ethyl alcohol.

RESULTS

Conductimetric titrations were carried out with solvents of higher dielectric constant than those used by Maryott;[8] addition of pure liquid base or acid instead of a solution then gave higher conductivities and smaller dilution effects. The results are shown in the Figs. 1—2, the specific conductivity being plotted against the molar fraction of base added to the acid in solution, or (Fig. 2) against the molar fraction of acid added to base solution. On all the

TABLE 1.

					Specific conductivity (ohm^{-1} cm.$^{-1}$ × 10^4)		
Curve type, Fig. 1	Acid	Solvent	Base	Acid concn. (mole/l.)	Initial solution of acid (approx.)	At max. pt.	At equiv. pt. *a*
(1)	$CCl_3\cdot CO_2H$	$COMe_2$	Et_3N	0·165	0·01	18·9	2·6
,,	,,	,,	Bu^n_3N	0·162	0·01	15·0	1·9
,,	,,	Me·CN	Et_3N	0·112	<0·03	31·7	8·9
(2)	$CHCl_2\cdot CO_2H$	$COMe_2$	,,	0·0653	<0·03	5·20	0·8
,,	,,	,,	,,	0·100	<0·03	7·59	1·1
,,	,,	,,	,,	0·154	<0·03	10·7	1·8
,,	,,	,,	,,	0·203	<0·03	14·2	3·0
,,	,,	,,	,,	0·250	<0·03	16·8	3·4
,,	,,	,,	Bu^n_3N	0·166	<0·03	9·50	2·3
,,	,,	Me·CN	Et_3N	0·0787	<0·03	17·5	3·8
(3)	$CH_2Cl\cdot CO_2H$	$COMe_2$	,,	0·154	<0·03	5·85	3·4
,,	,,	Me·CN	,,	0·176	<0·03	18·6	6·8
(4)	$CH_3\cdot CO_2H$	$COMe_2$	,,	0·267	<0·01	2·65	2·4
(5)	3 : 5-$C_6H_3(NO_2)_2\cdot CO_2H$ *	,,	,,	0·0612	<0·01	3·90	0·6
,,	,, *	,,	,,	0·104	<0·01	5·95	0·9
,,	,, *	,,	,,	0·134	<0·01	7·64	1·0
,,	,, *	,,	,,	0·167	0·01	9·22	1·5
,,	,, *	,,	,,	0·204	<0·03	11·0	1·7
(3)	*o*-$C_6H_4(NO_2)\cdot CO_2H$	,,	,,	0·164	<0·01	2·40	0·9
,,	*m*-$C_6H_4(NO_2)\cdot CO_2H$	,,	,,	0·163	<0·01	3·90	1·4
,,	*p*-$C_6H_4(NO_2)\cdot CO_2H$	,,	,,	0·163	<0·01	4·05	1·5
(6*A*)	3 : 5-$C_6H_3(NO_2)_2\cdot OH$	,,	,,	0·108	<0·03	24·3	24·0

* At constant vol.

TABLE 2.

					Specific conductivity (10^4 ohm^{-1} cm.$^{-1}$)	
Curve type, Fig. 1	Acid	Solvent	Base	Acid concn. (mole/l.)	Initial soln. of acid (approx.)	At equiv. pt. *a*
(7)	$C_6H_3(NO_2)_2\cdot OH$ *	$COMe_2$	Et_3N	0·0260	<0·1	8·89
,,	,, *	,,	,,	0·0503	0·1	13·4
,,	,, *	,,	,,	0·0765	0·1	17·4
,,	,, *	,,	,,	0·0991	0·1	20·3
(9)	,,	,,	C_5H_5N	0·0430	0·1	10·0
(8*B*)	*o*-$C_6H_4(NO_2)\cdot OH$	,,	Et_3N	0·166	<0·1	2·30
(8*A*)	*m*-$C_6H_4(NO_2)\cdot OH$	,,	,,	0·165	<0·1	6·90
,,	*p*-$C_6H_4(NO_2)\cdot OH$	,,	,,	0·0781	<0·1	8·80
(6*B*)	2 : 6-$C_6H_3(NO_2)_2\cdot OH$	,,	,,	0·164	<0·01	2·30
(10*B*)	$CHCl_2\cdot CO_2H$	EtOH	,,	0·0429	<0·03	5·10
,,	,,	,,	,,	0·113	<0·03	10·2
,,	,,	,,	,,	0·198	0·1	15·0
,,	,,	,,	,,	0·267	0·1	18·5
,,	3 : 5-$C_6H_3(NO_2)_2\cdot CO_2H$	,,	,,	0·0596	<0·03	7·00

* At constant volume.

curves, the point " *a* " shows the molar fraction of base equivalent to the acid content of the solution, or *vice versa.* The initial conductivities of the acid or base solutions were very low. On the addition of base, however, all the acid solutions showed a sharp increase in conductivity, the same effect being evident on addition of acid to a base solution.

The curves obtained by adding base to acid solutions are seen to be essentially of two types. Those in the first group, *e.g.*, Fig. 1 (1)—(6*A*) and (10*A*) (cf. Table 1), show maximum conductivity *before* the stoicheiometric equivalence point is reached. In some cases [Fig. 1 (1, 2, and 5)] this maximum is followed by a sharp fall and by a sudden change of direction in the vicinity of the equivalence point, producing a well-defined inflexion. In other instances [Figs. 1 (3, 4, and 6)] the curve falls away gradually, passing through the point of theoretical equivalence without an abrupt deviation.

Systems of the second type, *e.g.*, Fig. 1 (7 and 10*B*) are listed in Table 2. They have no preliminary maxima but show a rapid and regular rise in specific conductivity up to the equivalence point, where a sudden change of course may occur. Change in type can be brought about by change of acid [Fig. 1 (1 and 7)] or solvent [Fig. 1 (10)]. In acetone, this simpler type of curve was shown with picric acid and 2 : 6-dinitrophenol, in contrast to the behaviour of the other acids in this solvent. In ethyl alcohol, however, no preliminary maxima occurred with dichloroacetic or 3 : 5-dinitrobenzoic acid, unlike the corresponding solutions in acetone or acetonitrile. The reverse process, involving the addition of acid to base solution, is illustrated by the curves shown in Fig. 2, which were obtained in acetone and ethyl alcohol.

FIG. 2.

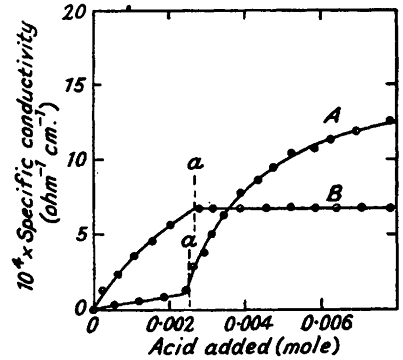

FIG. 3.

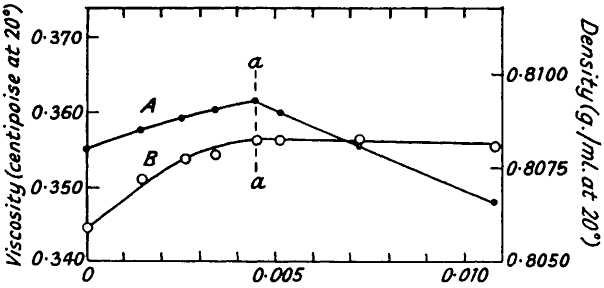

FIG. 2. *A, Tri*-n-*butylamine* (0·0918 *mole/l.*) *in acetone, titrated with* $CHCl_2{\cdot}CO_2H$. *B, Tri*-n-*butylamine* (0·0949 *mole/l.*) *in ethyl alcohol, titrated with* $CHCl_2{\cdot}CO_2H$.

FIG. 3. (*A*) *Density and* (*B*) *viscosity changes during titration of* 3 : 5-*dinitrobenzoic acid* (0·148 *mole/l.*) *in acetone, with* Et_3N.

The majority of the titrations involving addition of base were carried out with triethylamine; with tri-*n*-butylamine, the general contours of the curves were similar, but the maxima and the points corresponding to stoicheiometric equivalence both occurred at lower conductivities than for the triethyl analogue. Results obtained by titrating the various acids in acetone and acetonitrile were again similar, but the overall conductivities obtained with the nitrile solutions were higher.

In acetone or acetonitrile, no conductivity drifts were noted in the picric acid experiments, contrary to the observations recorded for benzene and dioxan.[3] During the titration of trichloroacetic acid with tertiary aliphatic bases in acetone, however, the conductivity tended to drift, with time, towards lower values as the equivalence point was approached. The final inflexion then occurred somewhat before this stage (Fig. 1). This effect was accentuated if the titration was carried out at 60° in phenylacetonitrile, and with addition of tri-*n*-butylamine. In this connection, however, trichloroacetic acid and tertiary bases are known to undergo further interaction to yield chloroform and carbon dioxide, presumably by way of betaines.[9] At 20° and at the concentrations used in the present work, no reaction other than salt formation was observed with mono- and di-chloroacetic acid.

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[9] Silberstein, *Ber.*, 1884, **17**, 2664; Verhoek, *J. Amer. Chem. Soc.*, 1934, **56**, 571.

Volume changes involved during a titration were not great. For a given initial concentration of acid in acetone, the result of adding triethylamine gave the following increases in volume, from the commencement up to the equivalence point:

Acid	3 : 5-Dinitrobenzoic		Picric
Initial concn. (mole/l.)	0·148	0·204	0·147
Increase in vol. (%)	1·5	2·2	1·7

These volume changes were calculated from the density determinations plotted in Figs. 3 and 4.

Figs. 3 and 4 also show the changes in viscosity occurring during the course of titrations involving triethylamine with 3 : 5-dinitrobenzoic and picric acids respectively, in acetone. The systems discussed here showed conductivities increasing to such an extent that the measurement of dielectric constant was inconvenient. Maryott,[3] however, treated 0·01M-solutions of acid in benzene or dioxan with 0·2M-solutions of base in the same solvents. With triethylamine and trichloroacetic acid the specific-conductivity curves showed well-defined maxima before the equivalence point, and the highest conductivities recorded were only of the order of 10^{-11} to 10^{-12} ohm^{-1} cm.$^{-1}$. Under similar conditions to those used by Maryott, the dielectric constant of the system was measured at intervals, for both dioxan and benzene, and the results are shown in Fig. 5.

FIG. 4.

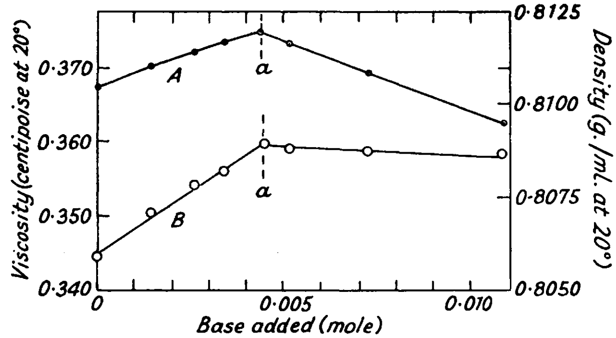

FIG. 5.

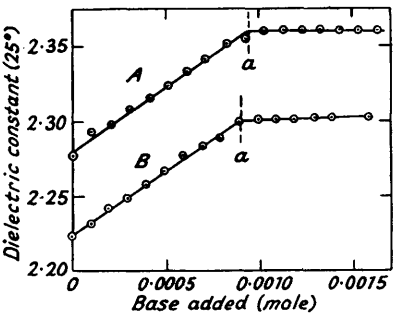

FIG. 4. *(A) Density and (B) viscosity changes during titration of picric acid* (0·147 *mole/l.*) *in acetone, with* Et_3N.

FIG. 5. *Dielectric constant changes: titration of (A) trichloroacetic acid* (0·000945 *mole/l.*) *with* Et_3N (0·205 *mole/l.*) *in benzene, and of (B) trichloroacetic acid* (0·000952 *mole/l.*) *with* Et_3N (0·199 *mole/l.*) *in dioxan.*

FIG. 6.

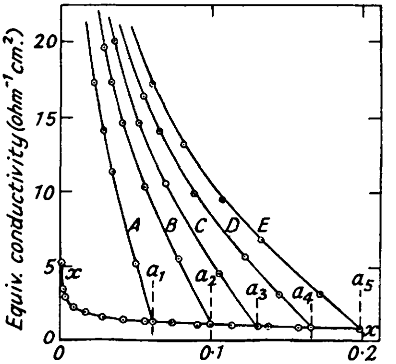

FIG. 7.

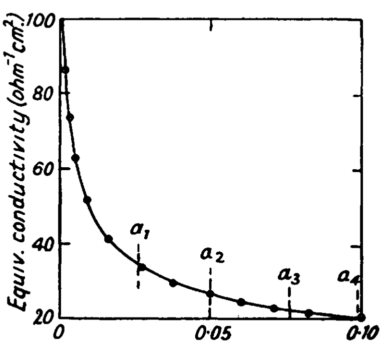

FIG. 6. *Equivalent conductivities of triethylammonium 3 : 5-dinitrobenzoate in acetone (x—x), and in acetone with decreasing excess of the corresponding acid (A—E).*

FIG. 7. *Equivalent conductivities of triethylammonium picrate in acetone, or in acetone with decreasing excess of corresponding acid.*

Preparation of the normal and the acid triethylammonium 3 : 5-dinitrobenzoate allowed conductivities to be measured, for these salts, at various concentrations in acetone. The results, expressed in terms of the equivalent base or salt content of the solutions, are superimposed on the titration diagram in Fig. 1 (5).

In order to compare the results of concentration changes at constant volume, sets of twelve acetone solutions, containing the same amount of 3 : 5-dinitrobenzoic acid, were treated with varying amounts of triethylamine and each made up to the same volume. Five such sets were prepared, and the specific conductances of the various solutions are shown in Fig. 1(5). These curves are, of course, essentially similar to the titration diagrams obtained with this system, the differences being trivial at the scale on which they are plotted. On the assumption that acid–base dissociation was small, the solutions containing one equivalent of base therefore contained one equivalent of normal salt. The equivalent conductivities of normal salt in various solutions, plotted against the concentration in moles per litre, are shown in Fig. 6. There the horizontal curve *x*—*x* shows the conductivity of the normal salt alone, whilst the curves joining the latter at the points a_1—a_5 represent the conductivity of one g.-equiv. of this salt during a conductimetric titration at constant volume. A similar experiment, performed with picric acid and triethylamine in acetone, gave a series of curves following a substantially identical course (Fig. 7), in common with the conductance curve for a pure sample of triethylammonium picrate.

DISCUSSION

In acetone or acetonitrile, the titration curves produced with tertiary bases and relatively strong acids are similar, in principle, to those reported for benzene or dioxan.[3] Ionic dissociation in the initial acid and base solutions must be very small, as can be seen from their low conductivities. It follows that the corresponding conjugate acids and bases are similarly little affected. As the formation of salt proceeds, however, non-conducting ion pairs or higher aggregates are formed. These entities are more or less dissociated into free conducting ions according to the thermal forces in the solution and to the degree of solvation of the ions. The thermal forces depend on the dielectric constant of the medium, and the solvation depends on the attractive forces between solute ions and between these ions and the solvent molecules.

Before the principle is accepted that the conductance maxima are due to complex-ion formation, it seems necessary to consider other changes which may occur during the conductance titrations.

(*a*) With very concentrated solutions of salts, etc., in aqueous solution, the specific conductances may, if solubility permits, rise to a maximum and then fall as the concentration is increased.[10] The occurrence of this maximum is ascribed to the opposing factors of rising electrolyte concentration and falling degree of dissociation and mobility.[11] Such salt solutions as are considered here, however, show no such maxima at the relevant concentrations [Fig. 1 (5)], and the anomaly occurs only when there is a progressive neutralisation of acid.

(*b*) Triple-ion formation is known to cause irregularities in conductance curves,[12] and these inflexions occur at higher concentrations for liquids of greater dielectric constant.[13] In acetone ($\epsilon_{20} = 21{\cdot}2$) [14] the equivalent conductances of both the acid and the normal triethylammonium 3 : 5-dinitrobenzoate show the usual hyperbolic fall with increase in concentration up to 0·2 equiv./l., and no such irregularity occurs. When the equivalent conductivity of the normal salt is plotted for a decreasing excess of acid and an increasing concentration (Fig. 6), the curves again show a smooth fall. With acetonitrile ($\epsilon_{20} = 37{\cdot}5$) then, this effect cannot be evident at commensurate concentrations.

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[10] Kohlrausch and Holborn, "Leitvermögen der Elektrolyte," Leipzig, 1898, pp. 145—158; Landolt–Börnstein, "Tabellen," 5th Edn., Vol. 2, pp. 1068—1078.

[11] Kortum-Bockris, "Textbook of Electrochemistry," Elsevier, New York, 1951, Vol. 1, p. 199.

[12] Fuoss and Krauss, *J. Amer. Chem. Soc.*, 1933, **55**, 2387.

[13] Kraus, *J. Phys. Chem.*, 1956, **60**, 129.

[14] Dielectric constants are from Maryott and Smith, "Tables of Dielectric Constants of Pure Liquids," N.B.S. Circular 514, 1951.

(*c*) The ionic dissociation constants of incompletely substituted ammonium salts are very low in non-polar solvents, and only of the order of 10^{-3} or 10^{-4} in such liquids as acetone or nitrobenzene.[15] At appreciable concentrations, then, the free ions may be regarded as moving in a medium consisting of solvent and undissociated aggregates. The increase in concentration will be accompanied by a change in the bulk dielectric constant and in the total viscosity, affecting both the dissociation of the ions and their mobility. It will be seen, however, from Figs. 3—5, that the increases are regular for both these properties up to the equivalence point for 1 : 1 salt formation, and remain so where a preliminary maximum occurs with the conductivity. Furthermore, the increase in dielectric constant is not great, whilst the viscosity rises are of comparable magnitude whether or not the system shows a preliminary maximum.

(*d*) The suggestion that the maxima are due to positive salt effects has been dealt with inasmuch as it applies to solutions in which the ionic strength is very low.[3] Even when the latter is higher, however, such an explanation would fail to account for the diverse behaviour of various acids when the solvent and base remain the same. Preliminary maxima are not always shown, and where they are shown with one solvent they may not occur with another. It will be seen below that this difference is of significance in interpreting the curves.

Interactions in the Solutions.—It is known that the presence of hydrogen bonds may cause profound effects upon electrolytes in certain solvents. Kraus and his co-workers [13,15] have demonstrated the existence of interactions between the anions and cations of partially substituted ammonium salts that are additional to the ordinary Coulombic forces. Thus, with an acid and tertiary base, we have :

$$R_3N + HA \longrightarrow (R_3NH^+ \cdots A^-) \rightleftharpoons R_3NH^+ + A^- \quad . \quad . \quad . \quad (i)$$

with the usual ion-pair attractions supplemented by those due to hydrogen bonds. The resulting salts then have low ionic dissociation constants in certain solvents such as acetone or nitrobenzene, whilst their tetrasubstituted counterparts may give constants some thousand times greater. Similarly, the ratios between the dissociation constants of partially substituted and quaternary base salts are shown to vary considerably amongst solvents of differing proton attraction, owing to the varying abilities which the solvents may show for interaction with the cations.

In solvents such as dioxan, acetone, or acetonitrile, the thermal dissociation of tertiary base salts will be somewhat augmented by hydrogen-bonding attractions between the solvent and the cation :

$$(R_3N^+ \cdots A^-) + S \rightleftharpoons (R_3N^+ \cdots S) + A^- \quad . \quad . \quad . \quad . \quad (ii)$$

but this influence will be opposed by the combined Coulombic and hydrogen–bonding forces between the two ions. With benzene, the thermal forces are very low, and the slight ionic dissociation must be attributed to the formation of triple ions, together with the known polarisability of the aromatic nucleus.[16] If the solution contains excess of acid, however, the latter will be associated with the anion. For equivalent amounts of acid and salt, the interactions affecting the salt pair may now be represented, in the simplest case, as :

$$(R_3NH^+ \cdots A^-) + HA \rightleftharpoons (R_3NH^+ \cdots A^- \cdots HA) \rightleftharpoons R_3NH^+ + A^- \cdots HA \quad (iii)$$

There is thus greater dissociation than with (ii) alone, so that the conductivity of the solution will be higher. The hydrogen-bonding tendency between anion and cation will contribute to a lowering of free-ion availability, whilst that between anion and acid will increase it. The attraction between acid and anion must therefore possess a strength at

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[15] (*a*) Kraus, *J. Phys. Chem.*, 1939, **43**, 231; (*b*) Taylor and Kraus, *J. Amer. Chem. Soc.*, 1947, **69**, 1731; (*c*) Witschonke and Kraus, *ibid.*, p. 2472.

[16] Andrews, *Chem. Rev.*, 1954, **54**, 713.

least comparable with that between the paired ions, where a similar attraction is augmented by Coulombic forces.

Interpretation of Conductivity Curves.—When strong bases are added to strong acids in solution [Figs. 1 (1, 2, and 5)], the shapes of the curves showing preliminary maxima depend on the opposing trends of rising salt concentration and falling degree of acid–anion association. The resulting increase in specific conductance, on addition of one equivalent of acid to one of salt, is at these concentrations greater than that produced by doubling the concentration of salt alone. Even in cases where an acid–base dissociation occurs, an increase of such magnitude cannot, therefore, be attributed to a mass-law effect. At the commencement of the titration, highly solvated salt is being formed in proportion to the amount of base added, but as the addition proceeds more of the free acid is used up in salt formation. The two effects are eventually in equilibrium, in terms of the conductance, when a maximum occurs; the precise position of the latter depends on the extent of the opposing forces. The curve then falls steeply until all the excess of acid is used up and only the normal salt remains in solution (eqn. ii). The subsequent slow fall in conductivity is then due largely to the effects of dilution. There is thus a sharp " end point " in all these titrations approximating to the point of theoretical equivalence. Similarly, if acid is added to base solution (Fig. 2*A*), the conductance rises slowly until the equivalent amount of salt is formed, and then much more rapidly as the latter is solvated by the acid.

If the salt undergoes acid–base dissociation, the free acid will not be completely removed at the theoretical equivalence point, so that some measure of its effect will be still apparent in an enhanced conductivity and a gradually falling titration curve :

$$\mathrm{R_3N} + \mathrm{H}\underbrace{\mathrm{A} \rightleftharpoons \mathrm{R_3NH^+} + \mathrm{A^-}} \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad \text{(iv)}$$

The addition of base to the solution of a salt formed from a weaker acid may then result in a fall in conductivity, rather than a rise. The magnitude of this effect will depend on the salt equilibrium and on the attractive force between anion and acid in each case. If there is parallelism between the relative strengths of acids in a range of solvents[17] the trend is illustrated with the series trichloroacetic, dichloroacetic, monochloroacetic, and acetic acid [Figs. 1 (1—4)], the respective values for K_a in water being 20,000, 5,000, 138, and $1{\cdot}75 \times 10^{-5}$. When the solvent, acetone, and the base, triethylamine, are the same throughout, the weaker the acid, the more gradual the fall in the curve and the higher the conductivity at the theoretical end point relative to that at the maximum. Even salts of the stronger acids used in acetone show a small acid–base dissociation at the theoretical equivalence point, there being a slight subsequent fall in conductivity before the practically constant value is obtained [Figs. 1 (2 and 5)].

A tendency to acid–base dissociation accounts for the instability of a number of the simple 1 : 1 salts with weaker bases. Thus Kench and Malkin [18] found that the ammonium salts of the higher fatty acids tended to pass into the acid salts. The normal pyridinium salts prepared by Pfeiffer *et al.* were converted into the acid salts on crystallisation from ethyl alcohol.[5] In the present investigation, it was found that pyridinium 3 : 5-dinitrobenzoate was similarly affected by crystallisation from acetone, or by exposure to moist air, whilst the corresponding triethylammonium salt was unchanged under these conditions.

With picric acid and triethylamine [Fig. 1 (7)], no preliminary maximum is evident in the acetone curves, in agreement with the results obtained in benzene or dioxan.[3] The same result is evident for 2 : 6-dinitrophenol in acetone [Fig. 1 (6*B*)], and both acids show contrary behaviour to the majority in this solvent. The significance of this result appears to have been missed, for both the aforementioned acids are known to contain intramolecular (chelated) hydrogen bonds, so that their hydrogen atoms have restricted availability

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[17] Dippy, *Chem. Rev.*, 1939, **25**, 151; Bell, " Acid–Base Catalysis," Methuen, London, 1952.

[18] Kench and Malkin, *J.*, 1939, 230.

for linkage with the anions. In this case the conductivity rises sharply as the practically non-conducting acid is successively replaced by the more highly dissociated salt. This rise ceases when the interaction is complete, and any excess of base has little effect on the conductivity. The reverse process of adding acid to base solution produces a similar diagram.[3]

With salts of chelated acids, the result of using a relatively weak acid or base causes further differences. The titration with *o*-nitrophenol [Fig. 1 (8*B*); $K_a = 0{\cdot}75 \times 10^{-7}$] gives a curve in which a slight continuous rise in conductivity is still evident after the equivalence point. Pyridinium picrate is known to show acid–base dissociation,[15c] and the successive addition of excess base causes a gradual rise in conductivity, rather than a fall [Fig. 1 (9)]. These results are consistent with the occurrence of a simple equilibrium $R_3N + HA \rightleftharpoons R_3NH^+ + A^-$. Where considerably weaker acids are used, the curves produced by adding base may not show a preliminary maximum, for the anion concentration is low. Thus *m*- and *p*-nitrophenol ($K_a = 1 \times 10^{-8}$ and $0{\cdot}96 \times 10^{-7}$ respectively) give diagrams [Fig. 1 (8*A*)] similar in type to the chelated *o*-isomeride [Fig. 1 (8*B*)], where the curvature is largely due to acid–base dissociation alone. Further, the anions are of relatively higher basic strength, so that a considerable excess of amine is necessary in order to decompose the acid associated entities. The curves may then reach their highest conductivity at a point beyond " *a*."

The fact that the preliminary maxima in the titration curves are absent in ethyl alcohol solutions [Fig. 1 (10*B*)] can also be attributed to hydrogen bonding. The curves are similar to those given with strongly chelated acids in acetone or acetonitrile, but the similarity arises from different causes. The equivalent conductivities (Λ) of triethylammonium 3 : 5-dinitrobenzoate solutions of similar or identical concentrations (*c*) are given, in the accompanying Table, for three different solvents, together with the dielectric constants (ε) and viscosities [19] (η) of the latter.

	c (equiv./l.)	Λ (ohm^{-1} cm.^{2})	ε_{20}	η_{20} (centipoises)
Acetone	0·0594	1·35	21·2	0·316
Ethyl alcohol	0·0596	11·8	25·1	1·72
n-Propyl alcohol	0·0594	3·16	20·8	2·23

The conductivities are higher for the alcohols, in spite of the fact that their dielectric constants are commensurate with that of acetone and their viscosities much greater. It is concluded that the ion dissociation is higher in the alcohols, for the hydroxyl groups should be capable of interacting with both anion and cation. In the acetone and acetonitrile titrations, acid associated with the anion is being progressively removed as the titration proceeds. In ethyl alcohol, however, hydrogen bonding with the anion is present throughout, as well as with the cation, and since the alcohol is in gross excess it is the more successful competitor for the anions, despite the fact that the bonding attraction is weaker than with acids. When acid is added to base solution (Fig. 2*B*), the alcohol curves are similar to those for the reverse process [Fig. 1 (10*B*)], unlike the results with the other two solvents. The whole effect is analogous to that shown by weak acids and bases in water.[1]

Further Interactions in Solution.—The solid complex salts are finite entities, with their hydrogen-bonded atoms locked within the crystal lattice. On the other hand their solutions must be regarded from a kinetic standpoint, the tendency to form hydrogen bonds serving to increase or decrease the various mutual attractions according to circumstance. The acid associated anion will be in equilibrium with its components, thus: $A^- + HA \rightleftharpoons (A^- \cdots HA)$. Furthermore, the carboxylate ion is capable of directly co-ordinating two equivalents of acid (II), and the acid molecules thus engaged are able to interact with others of their kind. Presumably these interactions will be weaker, for the subsequent additions will be further removed from the charge centre of the anion. When acid is added to base solution (Fig. 2*A*), the rise in conductance continues well

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[19] The value for acetone was separately determined, the other viscosities being taken from " International Critical Tables."

beyond the point at which equivalent amounts of salt and acid are present. This further rise may then be attributed to a growing concentration of complex anions and to an increase in their order of co-ordination.

During the present work, there was no sign of cation–amine interaction, in contrast to results with benzene or dioxan,[3] but in the systems discussed here several interactions involving either ions or uncharged entities may affect the degree of solvation of the former. Thus, an electron-donating solvent may show some measure of competition with the anion, for the attraction of the acidic hydrogen. Similarly, where acid–base dissociation of a salt occurs, there will also be some tendency to hydrogen bonding between acid and base, and between either or both and certain solvents. Further, the state of aggregation of carboxylic acid molecules varies from one solvent to another.[20] All these interactions must be considered in their relation to the normal dispersion, dipolar, polarisation, and repulsive forces known to affect the properties of liquid systems.[21]

Strength of Acid–Anion Attractions.—Complex-formation by the anions cannot be attributed to direct interaction with the dimeric forms of carboxylic acids, for Bell and Arnold [22] found that trichloroacetic acid, whilst dimeric in benzene, is entirely monomeric in dioxan. In addition, carboxylic acids have been stated to be monomeric in acetone.[23] Since acid–anion interaction is evident in these solvents, the attractive forces involved must be greater than those operating in the dimerisation. Klemperer and Pimental [24] measured the dissociation pressures of trifluoroacetic acid over two compounds with its simple sodium salt. One of these was found to be $CF_3{\cdot}CO_2Na{-}2CF_3{\cdot}CO_2H$ and the other probably $CF_3{\cdot}CO_2Na{-}CF_3{\cdot}CO_2H$. The heat of dissociation of the former was given as 14 kcal./mole of acid, in contrast to the value of 7 kcal./mole for the dissociation of the acid dimer.[25] These results are comparable with the figure of $\Delta H = 18$ kcal. found for the $^-F \cdots HF$ ion,[26] in contrast to the estimate of 10 kcal. given for the dissociation of $HF \cdots HF$ bonds.[27] This greater strength must arise through the formal negative charge on the anion, with its provision of additional electrostatic energy.

In spite of the known limitations of considering only the macroscopic dielectric constants and viscosities, there appears to be ample evidence, from the preceding arguments, that an exceptionally strong hydrogen-bonding attraction can exist between acids and their corresponding free anions in certain solvents, even though many interactions may modify the degree of association.

EXPERIMENTAL

Temperature readings were corrected.

Handling was performed either in a closed system or in an efficient dry box, and all the exits of the apparatus were guarded by phosphoric oxide tubes.

Materials.—Reagents and solvents used were purified and dried, and the latter were freshly distilled before use. The fractionating apparatus consisted of a lagged 18 in. Fenske column, surmounted with a Whitmore–Lux head, and distillations were conducted at a 10 : 1 reflux ratio, with liberal rejection of head and tail fractions.

Acetone ("AnalaR") was kept over anhydrous potassium carbonate for 7 days, then over anhydrous calcium sulphate for a similar period, with frequent shaking. The liquid was twice fractionated and the portion boiling at 56·1°/760 mm. reserved for use. This material had d_4^{20} 0·7904, n_D^{20} 1·3590, η_{20} 0·316 centipoise, κ 1×10^{-7} ohm^{-1} cm.$^{-1}$.

Acetonitrile (Eastman Spectroscopic Grade) was refluxed over phosphoric oxide for 8 hr. and twice fractionated. It had b. p. 81·7°/760 mm., d_4^{20} 0·7822, n_D^{20} 1·3440, κ 1×10^{-7} ohm^{-1} cm.$^{-1}$.

[20] Allen and Caldin, *Quart. Rev.*, 1953, **7**, 255.
[21] Davies, *Ann. Reports*, 1946, **43**, 7.
[22] Bell and Arnold, *J.*, 1935, 1432.
[23] Bell, Lidwell, and Vaughan-Jackson, *J.*, 1936, 1798.
[24] Klemperer and Pimental, *J. Chem. Phys.*, 1954, **22**, 1399.
[25] Lundin, Harris, and Nash, *J. Amer. Chem. Soc.*, 1952, **74**, 4654.
[26] Westrum and Pitzer, *ibid.*, 1949, **71**, 1940.
[27] Kreutzer, *Z. physikal. Chem.*, 1943, **53**, *B*, 213; Briegleb, *ibid.*, p. 225.

Ethyl alcohol (Burrough's "Alcohol Dehydratum", B.P. 1948), dried with aluminium ethoxide,[28] and twice fractionated, had b. p. 78·3°/760 mm., d_4^{20} 0·7896, n_D^{20} 1·3614, κ 3 × 10^{-8} ohm^{-1} cm.$^{-1}$.

Benzene was freed from thiophen in the usual manner[29] and purified by repeated fractional crystallisation and distillation. The product, b. p. 80·1°/760 mm., f. p. 5·5°, d_4^{20} 0·8789, n_D^{20} 1·5010, was stored over sodium.

1 : 4-Dioxan was freed from acetal[30] and partially frozen twice; the solid which separated was allowed to melt, and dried over potassium hydroxide. Refluxing over metallic sodium for 8 hr. was followed by fractionation, to yield a product of b. p. 101·3°/760 mm., f. p. 11·8°, d_4^{20} 1·0339, n_D^{20} 1·4223.

Triethylamine (from Imperial Chemical Industries Limited) was converted into its hydrochloride and this was recrystallised from industrial alcohol until its m. p. was sharp and constant (254°), then treated with aqueous sodium hydroxide, the liberated base being dried over potassium hydroxide and twice fractionated over metallic sodium in an atmosphere of nitrogen. The product had b. p. 89·3°/760 mm., d_4^{20} 0·7280, d_4^t 0·7463 − 0·00092t, n_D^{20} 1·4005.

Tri-*n*-butylamine (Eastman "White Label"), dried over metallic sodium and twice fractionated over the metal in an atmosphere of nitrogen, had b. p. 68°/3 mm., d_4^{20} 0·7788, d_4^t 0·7938 − 0·000747t, n_D^{20} 1·4294.

Pyridine ("AnalaR") was fractionated twice and converted into its zinc chloride complex.[31] The complex was crystallised twice from alcohol, and the base liberated with aqueous sodium hydroxide. Drying (KOH), followed by fractionation over barium oxide, gave material, b. p. 115·1°/760 mm., d_4^{20} 0·7832, d_4^t 1·0030 − 0·00099t, n_D^{20} 1·5096. The method was tedious and wasteful.

Dichloroacetic acid (B.D.H. "Laboratory Reagent"), twice fractionated, had b. p. 82·5°/7 mm., d_4^{20} 1·5647, d_4^t 1·5931 − 0·00142t.

The other acids used were purified by the customary methods until m. p. was sharp and constant, and were stored *in vacuo* over phosphoric oxide for at least 12 hr. before use.

Triethylammonium 3 : 5-*dinitrobenzoate* was prepared by adding triethylamine (5·05 g.) to a hot solution of the acid (10·6 g.) in acetone (25 ml.). The salt separated on cooling (79%, 12·45 g.), and formed prisms, m. p. 155° (decomp.), from acetone or benzene (Found : C, 49·7; H, 6·0; N, 13·5. $C_{13}H_{19}O_6N_3$ requires C, 49·8; H, 6·1; N, 13·4%).

Triethylammonium hydrogen bis-3 : 5-*dinitrobenzoate* separated as needles from a hot solution of 3 : 5-dinitrobenzoic acid (10·6 g.) and triethylamine (2·5 g.) in acetone (35 ml.) in 81% yield. Recrystallisation from acetone or benzene gave needles, m. p. 125·5° (Found : C, 45·7; H, 4·6; N, 13·3. $C_{20}H_{23}O_{12}N_5$ requires C, 45·7; H, 4·4; N, 13·3%).

Apparatus.—Four "Pyrex" glass cells were used for the various conductimetric titrations, all of the form shown in Fig. 8. The electrodes were of platinum (0·01 in. thick) with tungsten leads. For the calibration, a cell was constructed according to the recommendations of Jones and Bollinger[32] and standardised with 0·01D-potassium chloride.[33] This cell had κ 1·2103, and the titration cells were calibrated from this by stepwise measurements with various solutions of tri-*n*-butylammonium picrate in nitrobenzene. These cells had constants of 1·091, 0·3864, 0·0533, and 0·01678. The electrodes were covered with a "greyed" platinum surface, except when alcohol solutions were used. For the latter, a duplicate cell was prepared, having bright unplatinised electrodes and with κ 0·3326.

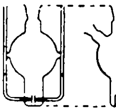

FIG. 8.

The bridge used for the titrations was of the Kohlrausch pattern, fitted with a Campbell constant-inductance slide-wire, calibrated directly in ohms and operated by means of a slow-motion dial. A capacitance balance was inserted in the variable arm. This system was fed by a 1000 c/s oscillator, the out-of-balance signals being passed, by way of a transformer, through a two-stage amplifier and displayed with a cathode-ray oscillograph. The sensitivity somewhat exceeded the accuracy of reading when the signal varied from 0·5 to 2 v.

The cell calibrations were carried out with a bridge designed largely from Luder's

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[28] Walden, Ulich, and Loun, *Z. physikal. Chem.*, 1925, **114**, 275.

[29] Richards and Shipley, *J. Amer. Chem. Soc.*, 1919, **41**, 2002.

[30] Weissberger, "Organic Solvents," Interscience Pub. Inc., New York, 1955, 2nd Edn., p. 372.

[31] Heap, Jones, and Speakman, *J. Amer. Chem. Soc.*, 1921, **43**, 1936.

[32] Jones and Bollinger, *ibid.*, 1931, **53**, 411.

[33] Jones and Bradshaw, *ibid.*, 1933, **55**, 1780; cf. footnote, *J.*, 1956, 4464.

recommendations,[34] the circuit being fitted with a Wagner earth, but the output was again amplified and balance indicated with a cathode-ray oscillograph.

Technique.—For the titrations, a known volume of the solution was placed in the cell, and the whole kept at 20° ± 0·1° (thermostat). Reagent was added from a calibrated microburette reading to 0·01 ml., inserted through the neck of the cell by means of a rubber stopper. After each addition, the whole assembly was vigorously shaken. The volume readings were converted to molar fractions by means of the known densities at the relevant temperature. If the reagent was added in small increments (equivalent to about 0·0003 equiv.), it was found that thermal conduction was sufficiently high to obviate detectable error due to heat of reaction.

Viscosities were measured by means of No. 0 B.S.S. viscometers.[35] Access to moisture was prevented,[36] and each measurement recorded was the mean obtained from two different instruments, of constants 0·0006069 and 0·0006913 respectively.

Dielectric constants were determined, during a titration, by drawing liquid upward into a Sayce–Briscoe pattern cell, kept at 25° ± 0·1°. Particular care was taken to " wash " the cell after each addition and it was found necessary to use an oil-filled thermostat. The cell was connected to a simple resonance circuit and detector [37] by means of rigidly attached co-axial cable, and the capacitances were measured by means of a Muirhead Type A 411-B variable condenser.

Densities were determined with a 10 ml. density bottle, and the results corrected for the buoyancy of air. Linear formulæ for the density of liquids were derived from determinations at 15°, 20°, 25°, and 30°, and the agreement with these results was within 1×10^{-4} g./ml.

We thank Mr. F. E. Charlton for microanalyses, and Dr. C. C. Addison and Mr. L. T. D. Williams for helpful discussions.

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[*Received, September 5th*, 1956.]

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[34] Luder, *J. Amer. Chem. Soc.*, 1940, **62**, 89.
[35] British Standard Specification 188/1937.
[36] *Ibid.*, appendix B, p. 28.
[37] Calderbank and Le Fèvre, *J.*, 1948, 1951.