58. *Acetyl Chloride as a Polar Solvent. Part IV.*[1] *Conductometric Titrations in Acetyl Chloride.*

By BALDEV SINGH MANHAS, RAM CHAND PAUL, and SARJIT SINGH SANDHU.

The existence of solvoacids, solvobases, and ansolvobases in acetyl chloride, as already postulated, is confirmed conductometrically. The breaks in the curves correspond to acid : base molar ratios of 1 : 1 and 1 : 2, indicating the formation of normal and acid salts. Most of the complexes recorded in Part III are confirmed, and their formation is explained on the basis of the existence of ionic species in the solutions in acetyl chloride.

THE formation of acid–base neutralisation complexes which have been isolated and analysed as described in Part III[1] has been confirmed conductometrically and the existence of acidic and basic species in acetyl chloride has been indicated. Lewis acids such as stannic chloride[2] and titanium tetrachloride,[3] in the pure state, are non-conducting liquids but their solutions in acetyl chloride[4] are more conducting than the solvent itself ($\kappa = 3{\cdot}5 \times 10^{-7}$ ohm^{-1} at 0°;[5] cf. water, 4×10^{-8} ohm^{-1} at 18°). Similar observations have been recorded for solutions containing solvobases such as pyridine, picolines, quinoline, and dimethylaniline, and ansolvobases such as benzyltrimethylammonium and benzyldimethylphenylammonium chlorides. The mode of ionisation of solutions of all these compounds in acetyl chloride has already been indicated.[4]

Addition of titanium tetrachloride solution to a solution of benzyltrimethylammonium chloride in acetyl chloride results in separation of a light yellow solid, accompanied by a decrease in the conductance of the solution until it reaches a minimum at an acid : base molar ratio of 1 : 2 (Fig. 1), at which the precipitation is complete. On further addition of the acid solution, the precipitate begins to dissolve and the conductance shows a sharp increase. The second break appears when the molar ratio of the acid to base is 1 : 1 and the dissolution of the precipitate is almost complete. Further addition causes no appreciable increase in conductance, and no other break in the curve is observed.

---

[1] Part III, preceding paper.
[2] *International Critical Tables*, 1926, **6**, 142.
[3] Eingorn, *Ukrain khim. Zhur.*, **16**, 404 (1950).
[4] Paul, Singh, and Sandhu, Part I, *J.*, 1959, 315.
[5] *Op. cit.*, ref. 6, p. 143.

FIG. 1. FIG. 2. FIG. 3.

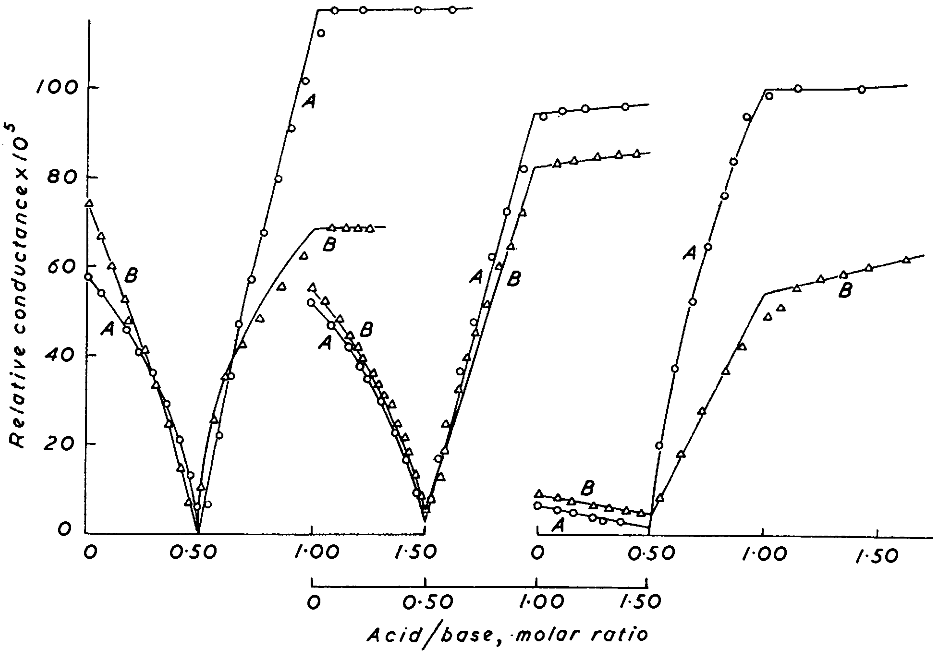

FIG. 1. *A, Stannic chloride* (0·01980 *mole*/100 *ml.*) *and benzyltrimethylammonium chloride* (0·0448 *g.*).
B, Titanium tetrachloride (0·03575 *mole*/100 *ml.*) *and benzyltrimethylammonium chloride* (0·0860 *g.*).

FIG. 2. *A, Stannic chloride* (0·01476 *mole*/100 *ml.*) *and benzyldimethylphenylammonium chloride* (0·0502 *g.*).
B, Titanium tetrachloride (0·01619 *mole*/100 *ml.*) *and benzyldimethylphenylammonium chloride* (0·0698 *g.*).

FIG. 3. *A, Stannic chloride* (0·02551 *mole*/100 *ml.*) *and α-picoline* (0·0246 *g.*).
B, Titanium tetrachloride (0·04494 *mole*/100 *ml.*) *and α-picoline* (0·02965 *g.*).

FIG. 4.

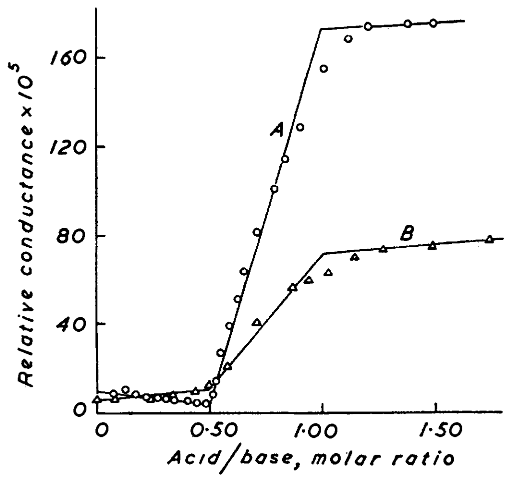

FIG. 5.

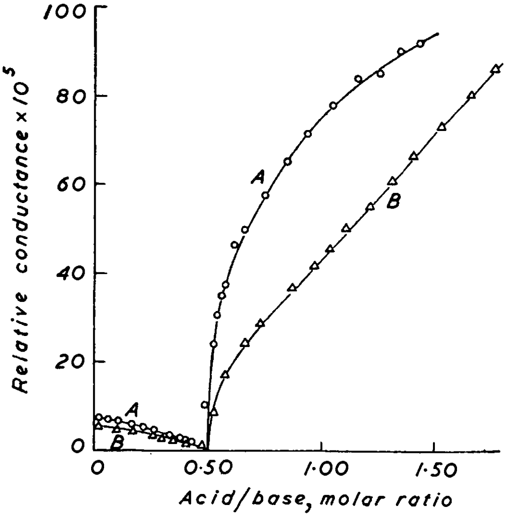

FIG. 4. *A, Stannic chloride* (0·0284 *mole*/100 *ml.*) *and β-picoline* (0·0578 *g.*).
B, Titanium tetrachloride (0·03510 *mole*/100 *ml.*) *and β-picoline* (0·0262 *g.*).

FIG. 5. *A, Stannic chloride* (0·01751 *mole*/100 *ml.*) *and pyridine* (0·0462 *g.*).
B, Titanium tetrachloride (0·02966 *mole*/100 *ml.*) *and pyridine* (0·0246 *g.*).

These results may be interpreted in terms of the existence of ionic species in the solutions.[1,4] Titanium tetrachloride yields a solvate with acetyl chloride which ionises in solution as $TiCl_4,AcCl + AcCl \rightleftharpoons 2Ac^+ + TiCl_6^{2-}$. Similarly with benzyltrimethylammonium chloride in acetyl chloride the appearance of the precipitate is attributed to formation of the hexachlorotitanate: $2Q^+ + 2Cl^- + Ac_2TiCl_6 \longrightarrow Q_2TiCl_6 + 2AcCl$. Hence, progressive removal of benzyltrimethylammonium and chloride ions from the solution results in a decrease in its conductance until precipitation is complete. Dissolution of the precipitate, accompanied by an increase in conductance, can be attributed to the formation and subsequent ionisation of the acid salt: $Q_2TiCl_6 + Ac_2TiCl_6 \longrightarrow 2QTiCl_6Ac \rightleftharpoons 2Ac^+ + 2[QTiCl_6]^-$.

As the acid salt $QTiCl_6Ac$ is more strongly ionised than Q_2TiCl_6 or Ac_2TiCl_6, its progressive formation results in an enormous increase in the conductivity of the solution. Once dissolution is complete, the conductance is scarcely affected by any further addition of the acid which itself is comparatively feebly ionised.

The results of observations in the titrations of the quaternary ammonium chlorides with titanium tetrachloride and stannic chloride are presented in Figs. 1 and 2, which show the characteristics described above. It is noteworthy that the neutralisation complexes of stannic chloride are more soluble in acetyl chloride and hence more conducting than those of titanium tetrachloride. The four compounds concerned have been isolated and identified,[1] but the corresponding acid salts are too soluble to be isolated.

α- and β-Picoline [7] and pyridine [2,6] have also been used for the conductometric titrations with stannic chloride and titanium tetrachloride in acetyl chloride. These bases form solvates [4] and a study of the conductivity of their solutions has shown that they ionise in acetyl chloride as $B + AcCl \longrightarrow B,AcCl \rightleftharpoons (BAc)^+ + Cl^-$. The results of the titration of α-picoline with titanium tetrachloride are presented in Fig. 3; the titrations closely follow the course described above for quaternary ammonium chlorides, the equations being: $2(BAc)^+ + Cl^- + Ac_2MCl_6 \longrightarrow (BAc)_2MCl_6 + 2AcCl$; $(BAc)_2MCl_6 + Ac_2MCl_6 \longrightarrow 2BAc,MCl_6,Ac \rightleftharpoons 2(BAc,MCl_6)^- + 2Ac^+$.

Stannic chloride and α-picoline in acetyl chloride behave analogously (Fig. 3). The acid salt has been isolated and analysed.[1]

Similar titrations of β-picoline and pyridine with titanium tetrachloride and stannic chloride are represented in Figs. 4 and 5. The novel feature about the titration of β-picoline with titanium tetrachloride is that both the normal and the acid salt are soluble; owing to the solubility and slight ionisation of the normal salt, the conductivity of the solution increases slightly up to the point of first inflection (Fig. 4). Then there is a sharp increase in the conductance due to the formation and ionisation of the acid salt. The titration of β-picoline with stannic chloride (Fig. 4) is, however, quite similar to the titrations of α-picoline already discussed.

In pyridine the titration curves obtained with the two acids (Fig. 5) show only one break, corresponding to the formation of normal salt. There is an increase in conductance due to the formation of the acid salt but the precipitate does not dissolve completely, even on addition of a further mole of acid per mole of base, so a second break is not observed.

Quinoline and dimethylaniline are freely miscible with acetyl chloride and do not form any solid solvate under ordinary experimental conditions. The existence of their solvates in solutions is, however, clearly indicated by the high specific conductivities of their solutions.[4] On the addition of a solution of quinoline to one of titanium tetrachloride in acetyl chloride, the conductance rises to a maximum at a point corresponding to a base : acid molar ratio of 1 : 1 (Fig. 6). Further addition of the base solution results in separation of a yellow precipitate and the conductance of the solution slowly decreases. At the molar ratio 2 : 1, a second break in the curve appears; further addition of base

---

[6] Gutmann, *Monatsh.*, 1954, **85**, 1077.

[7] Henery, Hazel, and McNabb, *Analyt. Chim. Acta*, 1956, **15**, 187.

then has only a slight effect on the conductance. The first two portions of the curve can be attributed to the successive processes

$$\mathrm{BAc)^+ + Cl^- + 2AcTiCl_6 \longrightarrow BAc,TiCl_6{\cdot}Ac + AcCl \rightleftharpoons (BAc,TiCl_6)^- + Ac^+}$$
$$\mathrm{(BAc,TiCl_6)^- + Ac^+ + (BAc)^+ + Cl^- \longrightarrow (BAc)_2TiCl_6 + AcCl}$$

The slight increase beyond the second break is due to addition of the comparatively weakly ionised base. In this titration acid salt begins to separate just before the molar ratio 1 : 1 is attained, so the relevant points do not fall on a regular curve. The two neutralisation complexes formed by quinoline with titanium tetrachloride have been isolated and analysed.[1]

Fig. 6.

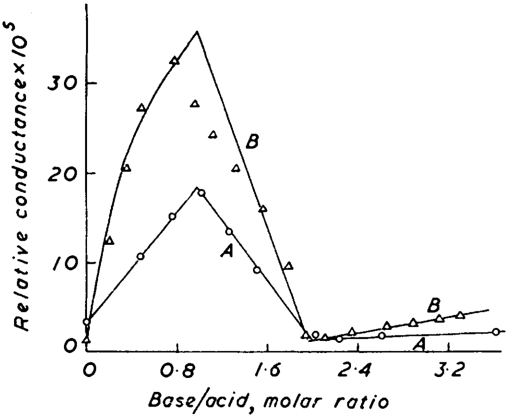

Fig. 7.

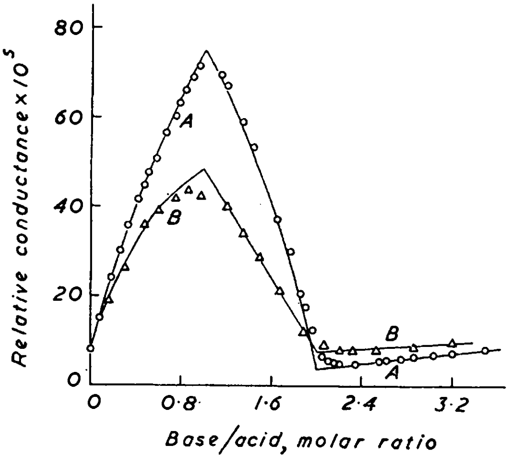

FIG. 6. *A, Quinoline* (0·02917 *mole*/100 *ml.*) *and stannic chloride* (0·0090 *g.*).
B, Quinoline (0·0443 *mole*/100 *ml.*) *and titanium tetrachloride* (0·0240 *g.*).
FIG. 7. *A, Dimethylaniline* (0·02655 *mole*/100 *ml.*) *and stannic chloride* (0·0702 *g.*).
B, Dimethylaniline (0·0352 *mole*/100 *ml.*) *and titanium tetrachloride* (0·0436 *g.*).

The curve obtained for the titration of quinoline against stannic chloride is similar to that just discussed and indicates the formation of both an acid and a normal salt.

The course of neutralisation of titanium tetrachloride and stannic chloride with dimethylaniline is similar to their neutralisation with quinoline (see Fig. 7). In these titrations also, the formation of the acid and the normal salts as reddish-yellow and light yellow solids is indicated. Both the normal salts have been isolated and analysed.[1]

These neutralisation reactions, in which the relatively undissociated molecules of acetyl chloride are formed, are similar to those in water or other polar solvents.

EXPERIMENTAL

Acetyl chloride was purified as already described,[8] and the fraction with a take off ratio of 1 : 10 was collected. Acids and bases were purified by fractional distillation, and quaternary ammonium chlorides were crystallised from lime-dried alcohol.

The solutions of acids and bases in acetyl chloride were prepared in a dry box and the transfer of solutions was carried out by using compressed dry nitrogen. A glass conductivity cell, with replaceable platinum electrodes in ground-glass joints and equipped with a micro-burette and calcium chloride guard tube, was employed. The resistance of solutions was measured at 30° ± 0·1° by using a precision measuring bridge type WBR No. 108 with logarithmic indicator amplifier type, TAV,IKc, No. 034 (Wissenschaftlich-Technische Werkstatten, Wielheim/Oby., Germany).

PANJAB UNIVERSITY, HOSHIARPUR, INDIA.
[*Present Address.*—KARNATAK UNIVERSITY, DHARWAR.]

[*Received, April 2nd*, 1958.]