55. *Acetyl Chloride as a Polar Solvent. Part I. Solubility of Substances and Formation of Solvates in Acetyl Chloride.*

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Solubilities of substances, including Lewis acids and bases, and formation of solvates in acetyl chloride have been studied. Conductivities of the solutions of Lewis acids and bases indicate formation of ion pairs. The constitution of these solutions is discussed.

THE high dipole moment,[1] comparatively long and weak carbon–chlorine bond,[2,3] and high reactivity (in which respect it resembles nitrosyl chloride[4]) suggest that acetyl chloride ionizes into acetylium and chloride ions, just as nitrosyl chloride ionizes into nitrosyl and chloride ions.[5] The relatively high dielectric constant of acetyl chloride (15·9 at 20°; cf. carbonyl chloride 4·32 at 22° [7]) and its convenient working range (m. p. −112°, b. p. 51·8°) should render it a fairly good solvent.

The solubilities (*S*, in g./100 g. of solvent) of a number of chlorides at 30° ± 0·1° are recorded in Table 1(a). In some cases, the solubility was determined only qualitatively to explore the possibility of the formation of solvates. These results are given in Table 1(b).

Strongly ionic chlorides were insoluble in acetyl chloride, as were such other salts as silver and potassium nitrate, copper and cadmium carbonate, and sodium nitrite. During the determination of the solubility of oxides, it has been found that the mixtures with acetyl chloride of those oxides that form soluble chlorides do not attain a state of equilibrium as their solubility increases with time and rise in temperature. Organic bases, such as pyridine, quinoline, α-, β-, and γ-picoline, and dimethylaniline, are also soluble in acetyl chloride. The solubility and other properties of individual substances differ much, as seen from Table 1(b).

Titanium tetrachloride, stannic chloride, arsenic trichloride, phosphorus trichloride, phosphorus oxychloride and thiophosphoryl chloride are freely miscible with acetyl chloride. Development of colour when substances are dissolved in acetyl chloride indicates the formation of complexes.[9] Examination of such substances shows that they are either Lewis acids or are capable of producing these after solvolysis, or are bases such as pyridine. The constitution of these solutions is discussed later.

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[1] Koehl and Wenzke, *J. Amer. Chem. Soc.*, 1937, **59**, 1418.
[2] Allen and Sutton, *Trans. Faraday Soc.*, 1951, **47**, 236.
[3] (*a*) Phillips, Hunter, and Sutton, *J.*, 1945, 146; (*b*) Skinner, *Trans. Faraday Soc.*, 1945, **41**, 645.
[4] Ketelaar and Palmer, *J. Amer. Chem. Soc.*, 1937, **59**, 2629.
[5] Lewis and Wilkins, *J.*, 1955, 56.
[6] *International Critical Tables*, 1926, **6**, 82.
[7] Schlundt and Germann, *J. Phys. Chem.*, 1925, **29**, 353.

TABLE 1(a). *Solubility* (*g.*/100 *g. of solvent*) *of substances in acetyl chloride at* 30° ± 0·1°

Compound	S *	Colour of solution	Heat effect †	Solid phase	Compound	S *	Colour of solution	Heat effect †	Solid phase
$BiCl_3$	15·04	Yellow	0	$BiCl_3$	$ZnCl_2$	7·86	Yellow	0	$ZnCl_2$
$SbCl_3$	150·00	Red	—	$SbCl_3$	$SnCl_4$	Miscible	Yellow	+	
BiOCl	71·80	Dark red	++	BiOCl	$AsCl_3$	Miscible	Colourless	0	
SbOCl	92·13	Orange-yellow	++	SbOCl	$TeCl_4$	8·57	Dark red	+	$TeCl_4$
$SbCl_5$	24·12	Yellow	++	$SbCl_5$,AcCl	$TiCl_4$	Miscible	Yellow	+	
PCl_3	Miscible	Colourless	0		PCl_5	20·92	Colourless	+	PCl_5
$FeCl_3$	27·87	Red	0	$FeCl_3$	$PSCl_3$	Miscible	Colourless	0	
$HgCl_2$	3·12	Pale yellow	+	$HgCl_2$	$POCl_3$	Miscible	Colourless	0	
$SnCl_2$	4·47	Red	0	$SnCl_2$					

TABLE 1(b). (*Qualitative.*)

Compound	S	Colour of solution	Heat effect	Solid phase
Pyridine	Sparingly sol.	Orange-yellow	++	C_5H_5N,AcCl
α-Picoline	Freely sol.	Yellow	+	
β-Picoline	Sparingly sol.	Yellow	++	β-Picoline, AcCl
γ-Picoline	Sparingly sol.	Yellow	+	γ-Picoline, AcCl
Quinoline	Miscible	Pink	+	
Dimethylaniline	Miscible	Violet	+	
Diethylaniline	Miscible	Green	+	
$(C_7H_7NMe_3)Cl$	Sparingly sol.	Colourless	0	$(C_7H_7NMe_3)Cl$
$(C_7H_7NPhMe_2)Cl$	Fairly sol.	Colourless	0	$(C_7H_7NPhMe_2)Cl$
CaO	Insol.		++	CaO,2AcCl
CuO	Insol.		++	$3CuCl_2$,CuO,2AcC
CdO	Insol.		+	CdO
ZnO	Sparingly sol.	Red	++	$ZnCl_2$,2(ZnO,2AcCl)
HgO	Sparingly sol.	Yellow	++	HgO + $HgCl_2$
Sb_2O_5	Fairly sol.	Dark red	0	Sb_2O_5
As_2O_3	Fairly sol.	Nil	0	As_2O_3

* Miscible means freely soluble. Sparingly soluble and fairly soluble signify solubility of about <5% and 15%, respectively.

† 0 = Nil; — = cooling; + = slight; ++ = considerable.

Formation of solvates in acetyl chloride has been known since 1901 when a solvate of aluminium chloride was reported.[8] Conductivity measurements of solutions of ferric chloride in acetyl chloride have indicated the formation of complex ions in solution; [9] but attempts to isolate such a solvate of ferric chloride have failed, probably owing to the catalytic enolization of acetyl chloride. Solvates of boron trifluoride and boron trichloride,[11] and a monosolvate of magnesium bromide [12] are known. Recently Greenwood and Wade [13] reported the formation of a monosolvate of gallium trichloride with acetyl chloride. The formation of a compound of titanium tetrachloride and acetyl chloride in carbon disulphide has been mentioned.[14, 15] In the present work, this compound has been prepared by cooling a mixture of titanium tetrachloride and acetyl chloride. Stannic chloride, the solid solvate of which is known with phosphorus oxychloride [16] and selenium oxychloride,[17] does not give any solid solvate with acetyl chloride under ordinary conditions. Similar behaviour has also been noticed with sulphur monochloride [18] with which it is also freely miscible. The existence of its solvate, however, is quite evident from the results of conductivity measurements given below. While studying the properties of liquid sulphur dioxide, Seel [19] isolated a compound of antimony pentachloride with

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[8] Boeseken, *Rec. Trav. chim.*, 1901, **20**, 102.

[9] Wertyporoch, Kowalski, and Roeske, *Ber.*, 1933, **66**, 1232.

[10] Adkins and Thompson, *J. Amer. Chem. Soc.*, 1949, **71**, 2242.

[11] Meerwein and Maier-Huser, *J. prakt. Chem.*, 1932, **134**, 51.

[12] Menschutkin, *J. Russ. Phys. Chem. Soc.*, 1907, **39**, 102.

[13] Greenwood and Wade, *J.*, 1956, 1527.

[14] Bertrand, *Bull. Soc. chim. France*, 1880, **33**, 403.

[15] Cullinane, Chard, and Leyshon, *J.*, 1952, 4106.

[16] Garner and Sugden, *J.*, 1929, 1298.

[17] Smith, *Chem. Rev.*, 1938, **23**, 165.

[18] Hamdard, M.Sc. Thesis, 1956.

[19] Seel, *Z. anorg. Chem.*, 1943, **252**, 24.

acetyl chloride. We have prepared this compound by direct interaction of the two components.

Most of the oxides react with acetyl chloride to produce chlorides, but cupric oxide yielded an intermediate of the composition $3CuCl_2,CuO,2AcCl$, as a product of incomplete solvolysis, but calcium oxide gave a disolvate. The solvolytic reactions are discussed separately.

TABLE 2. *Formation of solvates in acetyl chloride.*

Substance	Solvate	M. p.	Substance	Solvate	M. p.
BF_3 [11]	$BF_3,CH_3{\cdot}COCl$	−70° to −60°	$SbCl_5$ [19]	$SbCl_6,CH_3{\cdot}COCl$	—
BCl_3 [11]	$BCl_3,CH_3{\cdot}COCl$	−54°	Pyridine [20]	$C_5H_5N,CH_3{\cdot}COCl$	98—100°
MgBr [12]	$MgBr_2,CH_3{\cdot}COCl$	—	α-Picoline	$2C_6H_7N,3CH_3{\cdot}COCl$	61—62°
$AlCl_3$ [8]	$AlCl_3,CH_3{\cdot}COCl$	—	β-Picoline	$C_6H_7N,CH_3{\cdot}COCl$	78—80°
$GaCl_3$ [13]	$GaCl_3,CH_3{\cdot}COCl$	46·5°	γ-Picoline	$C_6H_7N,CH_3{\cdot}COCl$	125—127°
$TiCl_4$ [14, 15]	$TiCl_4,CH_3{\cdot}COCl$	20·5°			

Dehn[20] reports that solvates and dihydrochlorides are formed simultaneously from bases, pyridine being an exception.[10] The solid solvates of pyridine and of β- and γ-picoline separate spontaneously, but that of α-picoline has been prepared by removing the excess of the solvent. It is apparent from Table 2 that most of the ionic chlorides do not form solvates with acetyl chloride.

Specific conductivities of solutions in acetyl chloride are given in Table 3. As acetyl chloride has a low dielectric constant, no attempt has been made to deduce the dissociation constants, etc., quantitatively. However, the results are significant from a qualitative point of view; for the solutions are much more conducting than either the solvent ($\kappa = 3{\cdot}5 \times 10^{-7}$ at 0°[23]) or the solutes stannic chloride[22] or titanium tetrachloride[21] which are non-conducting liquids.

TABLE 3. *Specific conductivity* (κ) *of acids and bases in acetyl chloride at* 30° ± 0·1°

(Specific conductivity of acetyl chloride, $3{\cdot}5 \times 10^{-7}$ ohm^{-1} cm.$^{-1}$ at 0°.[23])

Substance	Concn. (mole/l.)	$10^5\kappa$ (ohm^{-1} cm.$^{-1}$)	Substance	Concn. (mole/l.)	$10^5\kappa$ (ohm^{-1} cm.$^{-1}$)
Benzyltrimethylammonium chloride	0·0084	44·50	γ-Picoline	0·0094	6·134
Benzyldimethylphenylammonium chloride	0·0092	48·60	Quinoline	0·0088	21·8
α-Picoline	0·0119	8·624	Dimethylaniline	0·0093	3·569
β-Picoline	0·0090	5·707	Stannic chloride	0·0087	0·3834
			Titanium tetrachloride	0·0089	0·8735

Formation of conducting solutions can only be explained on the basis of the existence of solvates which behave as ion pairs in acetyl chloride. The Lewis acids, stannic chloride and titanium tetrachloride, are known to tend to form hexachlorostannate[24] and hexachlorotitanate ions.[25] On this basis the structure of their solvates in solutions of acetyl chloride can be represented as follows:

$$TiCl_4,AcCl \rightleftharpoons Ac^+ + TiCl_5^-$$

$$TiCl_4,AcCl + AcCl \rightleftharpoons 2Ac^+ + TiCl_6^{2-}$$

$$SnCl_4 + 2AcCl \rightleftharpoons 2Ac^+ + SnCl_6^{2-}$$

The structure of the solvate of pyridine, by analogy with its solvates in selenium oxychloride[17,26] and phosphorus oxychloride,[27] would be $C_5H_5N,AcCl \rightleftharpoons C_5H_5NAc^+ + Cl^-$. The ionization of the solvates of the picolines, and of solutions of quinoline and

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[20] Dehn, *J. Amer. Chem. Soc.*, 1912, **34**, 1399.

[21] Eingorn, *Ukrain. Khim. Zhur.*, 1950, **16**, 404.

[22] *International Critical Tables*, 1926, **6**, 142.

[23] *Ibid.*, p. 143.

[24] Dickinson, *J. Amer. Chem. Soc.*, 1922, **44**, 276.

[25] Rumpf, *Compt. rend.*, 1936, **202**, 950.

[26] Jackson and Smith, *J. Amer. Chem. Soc.*, 1940, **62**, 544.

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

dimethylaniline in acetyl chloride, can be similarly expressed. As these increase the chloride-ion concentration in acetyl chloride solutions, they will act as solvobases in acetyl chloride. On the other hand, the quaternary ammonium chlorides which are soluble in acetyl chloride give highly conducting solutions. These also increase the chloride-ion concentration and will act as ansolvobases.

The behaviour of these compounds as acids or bases is confirmed in Parts III and IV of this series in which the acid–base neutralization reactions have been studied by complex formation as well as conductometrically.

EXPERIMENTAL

Reagents.—Acetyl chloride, b. p. 50—52°, was redistilled over 10% of dimethylaniline and the fraction of b. p. 50·5—51·5° was refractionated over sodium. It was prepared in small quantities as needed. All other substances were dried before use according to standard methods, and in case of doubt, their purity was checked by analysis.

Estimation of Solubility.—Quantities of the anhydrous solids and acetyl chloride were mixed in glass ampoules, the solid being in excess. All transfers of materials were carried out in a dry box and the ampoules were immediately sealed and shaken in a thermostat kept at 30° ± 0·1°, and 40—48 hr. were allowed for equilibrium to be attained. The ampoule was broken, and the solution was quickly filtered through a sintered-glass funnel in the dry. The solubility of the substance was determined either by evaporating a known weight of the saturated solution to dryness in the dry or by determination of the cation from a known weight of the saturated solution.

Preparation of Solvates.—In the preparation of solvates, different substances (*ca.* 5 g.) were shaken in sealed tubes with acetyl chloride (*ca.* 15 g.) for about 24 hr. Care was taken to manipulate acetyl chloride and the anhydrous solids in a dry box. The mixture was filtered through a sintered-glass funnel and the residue was washed with acetyl chloride, a small quantity of dry light petroleum (b. p. 40—60°), and sometimes with carbon tetrachloride, and kept under vacuum to remove volatile solvent. In most of the cases, both solid and solution were examined for solvate.

Monosolvate of Antimony Pentachloride.—The *solvate* (3·5 g. from 4 g. of pentachloride) (Found: Cl, 54·1; Sb, 30·75%; Cl/Sb, 1·8. $SbCl_5,CH_3{\cdot}COCl$ requires Cl, 56·35; Sb, 32·3%; Cl/Sb, 1·75) did not melt but decomposed, had a pungent smell, and was fairly soluble in acetyl chloride and insoluble in light petroleum.

Monosolvate of Titanium Tetrachloride.—After drying in vacuum the *monosolvate* (1·5 g. from 2 ml. of tetrachloride) (Found: Cl, 64·8; Ti, 17·4. $TiCl_4,CH_3{\cdot}COCl$ requires Cl, 66·2; Ti, 17·9%) was very hygroscopic and freely soluble in acetyl chloride.

Monosolvate of Pyridine.—To ice-cold acetyl chloride (10 ml.), pyridine (2 ml.) was added dropwise and the mixture was stirred vigorously till a yellow solid appeared, then kept in an ice-bath for about ½ hr., with exclusion of moisture. This yellow solid was filtered off in a dry atmosphere and dried. The pyridine content was estimated according to Smith and Jackson;[26] nitrogen was computed from these results and chlorine was determined by Volhard's method (Found: Cl, 22·4; N, 8·55. $C_5H_5N,CH_3{\cdot}COCl$ requires Cl, 22·5; N, 8·9%). This *solvate* was hygroscopic and melted at 98—100°. It was sparingly soluble in acetyl chloride.

Solvate of α-Picoline.—α-Picoline (3 ml.) gave a dark yellow solution in acetyl chloride (15 ml.) and on addition of more base (1 ml.) and cooling, an oil separated. Excess of acetyl chloride was removed in a vacuum. A deep red solid was formed which was washed with dry light petroleum (b. p. 40—60°) and kept under vacuum to give the *solvate* (2·8 g.), which was analysed as described under pyridine (Found: Cl, 25·3; N, 6·2. $2C_6H_7N,3CH_3{\cdot}COCl$ requires Cl, 25·3; N, 6·65%). It was a reddish hygroscopic solid, m. p. 61—63°, freely soluble in acetyl chloride.

Monosolvate of β-Picoline.—β-Picoline (1·5 g.) on addition to cold acetyl chloride (15 ml.) gave a rose-coloured solid instantaneously, heat being evolved. This solid, when kept for about 1 hr. in ice and stirred, became a dirty yellow solid, which was filtered off and dried (2·1 g.). It was analysed as already described (Found: Cl, 20·4; N, 7·8. $C_6H_7N,CH_3{\cdot}COCl$ requires Cl, 20·7; N, 8·2%). The *solvate* was a very hygroscopic solid, and under high vacuum it changed to a dark red liquid. It melted at 77—78° and was sparingly soluble in acetyl chloride.

Monosolvate of γ-Picoline.—γ-Picoline (2 ml.) was added dropwise with stirring to ice-cooled acetyl chloride (15 ml.); an orange-yellow solid separated. The mixture was kept in ice for ½ hr. and then filtered in absence of moisture and kept under moderate vacuum. The *solvate* (1·8 g.), which smelt slightly of acetyl chloride, was analysed as already mentioned (Found: Cl, 20·3; N, 7·85%). This was a hygroscopic solid, m. p. 125—127°, and changed colour under vacuum. It was sparingly soluble in acetyl chloride and almost insoluble in dry light petroleum (b. p. 40—60°).

For resistance measurements we used a bridge-type instrument WBR No. 108 with logarithmic indicator amplifier (Type TAV, IKc, No. 034; Wissenschaftlich-Technische Werkstatten, Wielheim/Oby., Germany).

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