Studies of Trifluoroacetic Acid.   Part IX.*   The Electrical Conductivities of the Ternary System, Trifluoroacetic Anhydride–Acetic Anhydride–Water.

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Measurements of the electrical conductivities of equilibrium mixtures of trifluoroacetic anhydride, acetic anhydride, and water are reported, and the observed conductivities of the anhydrous mixtures are discussed.

The conductivities of solutions of strong acids in acetic acid have been investigated extensively [Hantzsch and Langbein, *Z. anorg. Chem.*, 1932, **204**, 193; Hall and Voge, *J. Amer. Chem. Soc.*, 1933, **55**, 239; Kolthoff and Willman, *ibid.*, 1934, **56**, 1007; Weidner, Hutchison, and Chandlee, *ibid.*, p. 1285 (H_2SO_4) ; Taylor and Follows, *Canad. J. Chem.*, 1951, **29**, 461 (HNO_3) ; Kendall and Gross, *J. Amer. Chem. Soc.*, 1921, **43**, 1426 ($CCl_3 \cdot CO_2H$) ; many other studies have been reported also]. A complete conductivity diagram for the system sulphuric acid–acetic acid–water has been worked out (Hall and Voge, *loc. cit.*).

The present investigation was undertaken in order to obtain information about the species present in equilibrium mixtures of trifluoroacetic anhydride and acetic acid and hence to explain the reactivity of the medium as an acetylating agent (*J.*, 1949, 2976; 1951, 718). To complete the conductivity studies it was necessary to investigate mixtures of trifluoroacetic acid and acetic anhydride, as well as mixtures of the two acids, and it was decided to make a complete investigation of the ternary system, trifluoroacetic anhydride–acetic anhydride–water. So far as we are aware no similar system has been studied previously, although Hall and Voge (*loc. cit.*) attempted to extend their investigation to sulphur trioxide and acetic anhydride, but were unable to do so owing to rapid irreversible chemical changes in the media. The object of the investigation was to obtain a large number of reproducible readings, rather than a few of the highest accuracy. In spite of this, a fairly complicated apparatus had to be built to ensure four essential requirements : (i) the complete exclusion of moisture; (ii) perfect mixing of the electrolyte; (iii) the ability to vary the composition of the electrolyte by the addition of any of the three components; and (iv) the ability to measure conductivities varying from 10^{-9} mho to greater than 10^{-2} mho. The apparatus described below was built after considerable experience had been gained from an earlier model which provided some preliminary data on the conductivities of the mixtures. All the data now reported were obtained, however, from the apparatus now described.

Experimental

The Conductivity Apparatus.—The apparatus is represented in Fig. 1. The components of the system were introduced into the mixing vessels 5 and conductivity cell from graduated burettes 1*A*, 1*B*, and 1*C*, having capacities of 20, 10, and 5 c.c., respectively, and charged in turn from graduated reservoirs 2*A*, 2*B*, and 2*C*, by adjustment of the mercury reservoirs and levels 3*A* and 3*BC*. 3*BC* could be connected to either component reservoir 2*B* or 2*C* by the three-way tap 12 (2*C* is not shown in the diagram; it was identical with 2*B*). The burette taps 4*A*, 4*B*, 4*C*, had " Fluon " (polytetrafluoroethylene) plugs (see Fig. 2) ; these required no lubricant and were interchangeable with glass plugs if necessary. Trifluoroacetic acid dissolves Vaseline-based greases, " Fluorolubes," and silicones. The mixing vessels and conductivity cell 5 were immersed in an oil-bath maintained at 25°. The three electrodes 6, 6′, and 6″ were used in pairs : 6′ and 6″ for low conductivities and 6 and 6′ for high conductivites. Mixing was carried out by repeated changing of the mercury levels in the reservoirs 7 and 7′. The vessel 5 had an opening with a " Fluon " stopper 8 through which a thermometer was fitted. At the end of a set of readings the stopper 8 was removed and the bulk of the electrolyte was withdrawn by suction. Further spent electrolyte was removed by flushing the vessel with low-boiling

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solvents (withdrawn in the same manner), and finally the whole apparatus was sealed and evacuated by means of a " Hyvac " pump, the trap 9 being cooled in liquid air. Nitrogen from a cylinder was fed into the evacuated apparatus through a column 10 filled with phosphoric oxide and glass beads surmounted by tightly packed glass wool. Reagents could be added or distilled directly into the apparatus through ground joints 11*A*, 11*B*, and 11*C* in the reservoirs 2*A*, 2*B*, and 2*C*. These joints were normally fitted with " Fluon " stoppers.

Note on " Fluon " tap-plugs and stoppers (Fig. 2). These units, essential features of the apparatus, were extremely satisfactory, but certain precautions had to be observed owing to the large coefficient of thermal expansion of " Fluon." If stuck, the taps and stoppers could be loosened by *cooling* (heating caused rapid expansion of the " Fluon " and breaking of the glass).
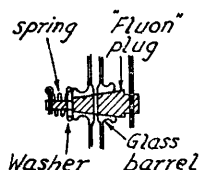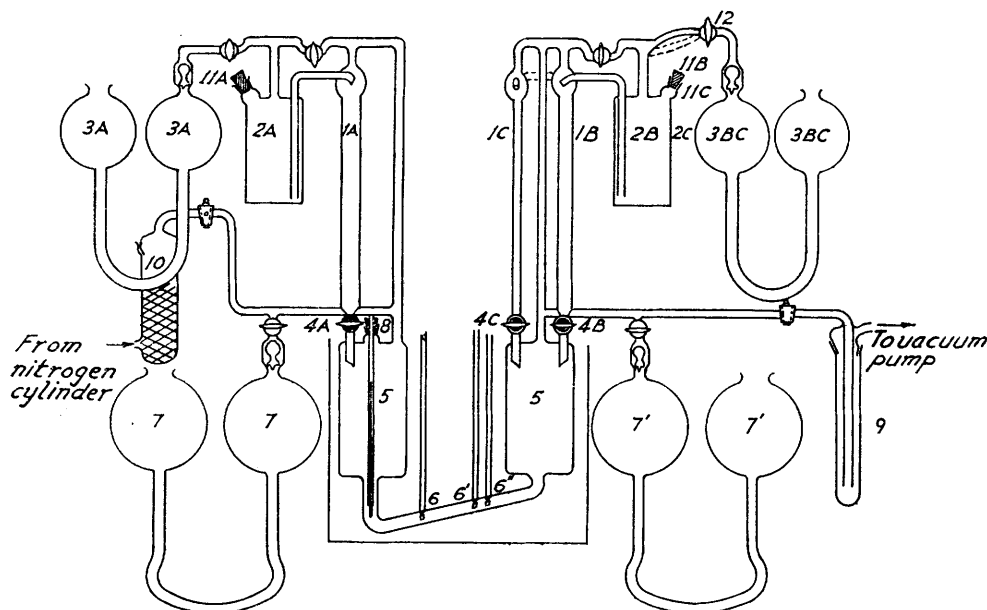
FIG. 1. *Conductivity apparatus.*

FIG. 2. *Section through " Fluon " taps (4A, 4B, and 4C).*

The polymer is easily scratched so that all surfaces had to be scrupulously cleaned before assembly. When the apparatus was left to stand, the " Fluon " parts were replaced by interchangeable glass pieces.

The Electrical Circuit.—A simple Wheatstone's bridge network was employed, one end of the bridge being connected to earth and the other to a double-beam Cossor Oscilloscope which was used as a detector. In addition to the cell, the remainder of the bridge circuit consisted of two Muirhead ratio units with a decade capacity box arranged to be put in parallel with either arm if necessary, and a Muirhead decade resistance box with a second decade capacity box in parallel. Measurements were made at various frequencies, but the network was found to be most sensitive at 500 cycles, and all the readings reported were made at this frequency. In spite of careful shielding, considerable pick-up from the 50-cycle mains occurred, but this could be separated easily from the oscillator's output on the oscilloscope.

Components.—Trifluoroacetic acid was prepared by mixing the commercial acid with trifluoroacetic anhydride (2%) and distilling the mixture through a column (18″ long) packed with glass helices; only the middle fraction, which had b. p. 70·5°, specific conductivity (κ) 3·5—

$4 \cdot 2 \times 10^{-7}$ mho at $25°$, was used.   Dannhauser and Cole (*J. Amer. Chem. Soc.*, 1952, **74**, 6105) gave κ 3—5 $\times 10^{-7}$ mho.

Trifluoroacetic anhydride was prepared by distillation of the acid over phosphoric oxide; the crude anhydride so obtained (b. p. 39—40°) was redistilled over fresh phosphoric oxide and then fractionated.   The material used for the conductivity measurements had b. p. $38 \cdot 5$—$38 \cdot 7°$, κ *ca.* $1 \cdot 0$—$1 \cdot 1 \times 10^{-9}$ mho at $25°$.

Acetic acid was prepared from the commercial acid (m. p. $16 \cdot 00°$) by fractional crystallisation.   After three recrystallisations the acid had m. p. $16 \cdot 60$—$16 \cdot 62°$; further crystallisation failed to alter the m. p., although the conductivity was decreased.   The material used for the conductivity measurements had m. p. $16 \cdot 60$—$16 \cdot 62°$, κ $3 \cdot 5$—$4 \cdot 7 \times 10^{-8}$ mho at $25°$.

Acetic anhydride was distilled through a column (36″ long) packed with nickel gauze spirals; the middle fraction, having b. p. 137—$137 \cdot 9°$, κ $3 \cdot 0$—$3 \cdot 5 \times 10^{-7}$ mho at $25°$, was used in the conductivity measurements.

Distilled water was boiled whilst a stream of nifrogen was bubbled through it, the nitrogen stream being continued until the water was cool, whereupon it was used directly; it had κ $4 \cdot 0$—$5 \cdot 5 \times 10^{-6}$ mho at $25°$.

FIG. 3.   *Conductivity of the systems, A,* $(CF_3 \cdot CO)_2 O$–$CH_3 \cdot CO_2 H$ *and B,* $(CF_3 \cdot CO)_2 O$–$(CH_3 \cdot CO_2 H + 3\%$ *of* $H_2 O)$.

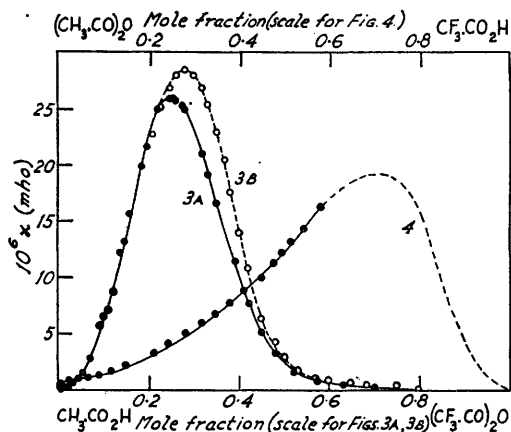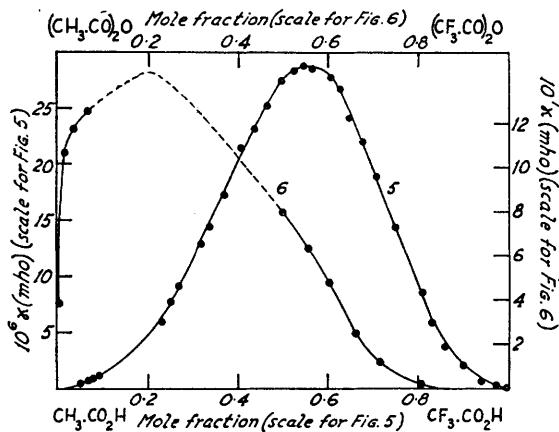FIG. 4.   *Conductivity of the system,* $CF_3 \cdot CO_2 H$–$(CH_3 \cdot CO)_2 O$.

FIG. 5.   *Conductivity of the system,* $CF_3 \cdot CO_2 H$–$CH_3 \cdot CO_2 H$.

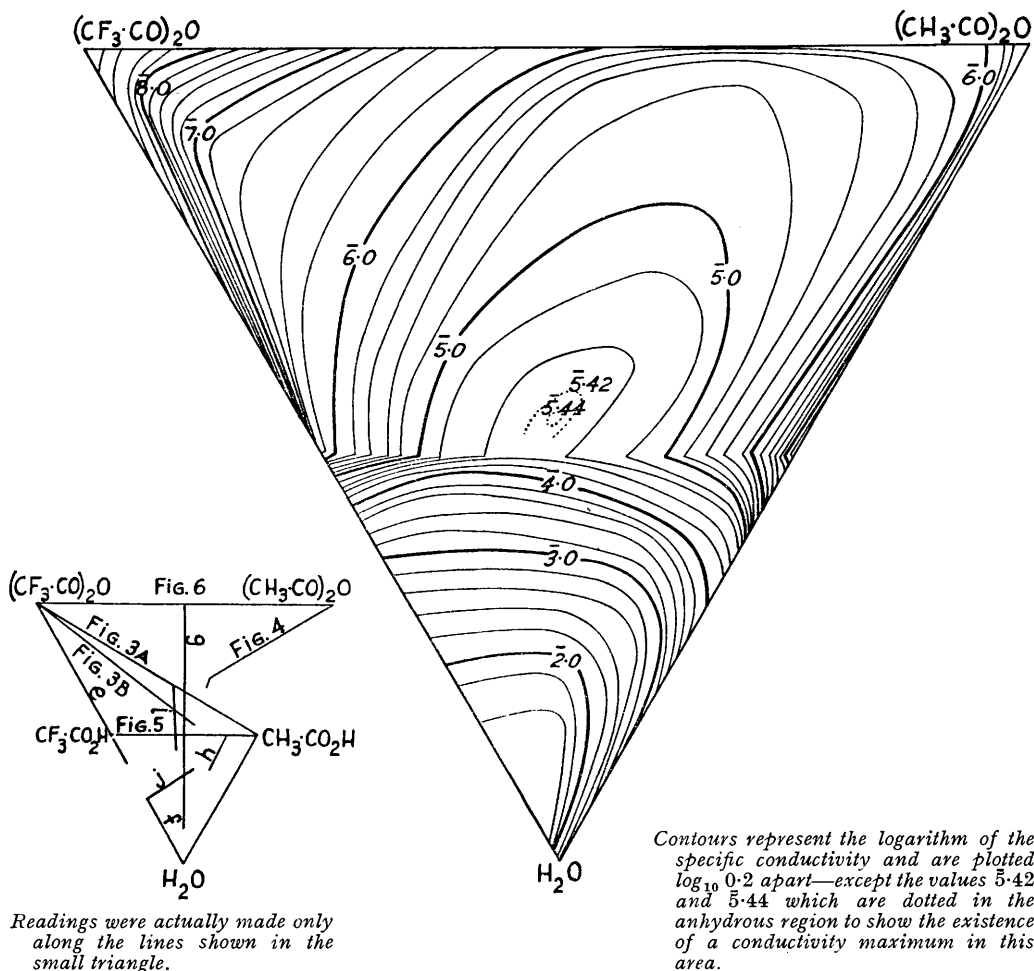FIG. 6.   *Conductivity of the system,* $(CF_3 \cdot CO)_2 O$–$(CH_3 \cdot CO)_2 O$.

Conductivities of Various Systems at $25°$.—(a) *Trifluoroacetic anhydride–acetic acid.*   Three series of readings were made of this system; two started from acetic acid, to which were added measured portions of (i) a 10% solution of trifluoroacetic anhydride in acetic acid, and (ii) pure trifluoroacetic anhydride respectively, and the third started with trifluoroacetic anhydride, to which acetic acid was added.   Considerable heat was evolved when the components were mixed, the equilibrium appeared to be reached rapidly, and the conductivities remained constant as soon as the temperature had become steady.   These conductivity values are plotted in Fig. 3 (curve *A*); the conductivities of the system obtained by addition of acetic acid containing water (3%) to trifluoroacetic anhydride (curve *B*) are also given.

(b) *Acetic anhydride–trifluoroacetic acid.*   Only a single series of readings was obtained for this system (Fig. 4); the curve was completed by interpolation from other readings.   When trifluoroacetic acid was first added to acetic anhydride the conductivity of the resulting mixture varied with time.   For the first three additions the conductivity initially rose to a maximum (*ca.* $1 \cdot 4 \times 10^{-6}$ mho) and then dropped slowly until after about $1\frac{1}{2}$ hr. it had definitely become constant (*ca.* $8 \cdot 0 \times 10^{-7}$ mho).   This initial high value for the conductivity was certainly not due to heat of reaction, which was small, the temperature returning to $25°$ within 5 min., but must have been due to the rapid formation of some fairly highly conducting species, which then decomposed slowly to give less highly conducting products.   This phenomenon was observed only for concentrations of trifluoroacetic acid less than $0 \cdot 05$ mole fraction.   In regions of greater concentration the conductivity reached a constant value the moment mixing was complete.

(c) *Trifluoroacetic acid–acetic acid.* Two series of readings contributed to Fig. 5, one in which a dilute solution of trifluoroacetic acid in acetic acid was added to acetic acid, and the other in which acetic acid was added directly to trifluoroacetic acid. The temperature changes associated with the mixing of these two components were small.

(d) *Trifluoroacetic anhydride–acetic anhydride.* Three series of readings were made for this system, but despite this it was not possible to obtain definite figures for the central part of the curve. At all points, but particularly in the range represented by a broken line (Fig. 6), it was

FIG. 7. *Contour diagram of the electrical conductivities of the ternary system,* $(CF_3 \cdot CO)_2O$–H_2O–$(CH_3 \cdot CO)_2O$.

Readings were actually made only along the lines shown in the small triangle.

Contours represent the logarithm of the specific conductivity and are plotted log_{10} 0·2 apart—except the values $\bar{5}$·42 and $\bar{5}$·44 which are dotted in the anhydrous region to show the existence of a conductivity maximum in this area.

extremely difficult to decide when the equilibrium conductivity was being measured. Directly mixing was complete, the conductivity showed a gradual increase; this rise was so slow that eventually it became impossible to decide whether it was due to changes in the equilibrium or to traces of moisture entering past the " Fluon " stopper. The broken line represents the conductivity of these mixtures about 3 hr. after mixing; the remainder of the curve which has been drawn represents points where the conductivity remained substantially constant after the first 20 min.

The conductivities of the other systems which were studied are reported in the Tables (e)—(j) (N = mole fraction). All these readings and those given in Figs. 3, 4, 5, and 6 have been used to compile Fig. 7 which represents a three-dimensional diagram for the complete ternary

system. The data for the water–acetic acid line are from "Landolt–Börnstein Tabellen," Vol. II (1920), Table 208*g*, p. 1075.

(e) *Water–trifluoroacetic anhydride.*

N_{H_2O}	κ_{25} (mho)	N_{H_2O}	κ_{25} (mho)	N_{H_2O}	κ_{25} (mho)	N_{H_2O}	κ_{25} (mho)
0	1.00×10^{-9}	0.42	5.49×10^{-8}	0.50_7	3.30×10^{-6}	0.59_5	4.14×10^{-4}
0.05	2.37×10^{-9}	0.43	7.04×10^{-8}	0.51	5.56×10^{-6}	0.61	6.43×10^{-4}
0.08	2.65×10^{-9}	0.44	9.38×10^{-8}	0.52	1.13×10^{-5}	0.62_5	9.56×10^{-4}
0.17	5.60×10^{-9}	0.45	1.18×10^{-7}	0.53	1.94×10^{-5}	0.64	1.48×10^{-3}
0.28	7.50×10^{-9}	0.46	1.84×10^{-7}	0.53_5	3.02×10^{-5}	0.66_5	2.31×10^{-3}
0.33	1.12×10^{-8}	0.47	1.96×10^{-7}	0.54	4.81×10^{-5}	0.68	3.02×10^{-3}
0.37	1.96×10^{-8}	0.49	3.00×10^{-7}	0.55	7.63×10^{-5}		
0.41	4.75×10^{-8}	0.50	4.16×10^{-7}	0.58	2.74×10^{-4}		

(f) *Trifluoroacetic anhydride–water.*

$N_{(CF_3 \cdot CO)_2O}$	κ_{25} (mho)	$N_{(CF_3 \cdot CO)_2O}$	κ_{25} (mho)	$N_{(CF_3 \cdot CO)_2O}$	κ_{25} (mho)	$N_{(CF_3 \cdot CO)_2O}$	κ_{25} (mho)
0	5.50×10^{-6}	0.043	2.90×10^{-2}	0.130	3.52×10^{-2}	0.180	2.34×10^{-2}
0.002	2.84×10^{-3}	0.052	2.97×10^{-2}	0.140	3.66×10^{-2}	0.190	2.04×10^{-2}
0.005	3.22×10^{-3}	0.076	3.15×10^{-2}	0.151	3.38×10^{-2}	0.199	1.88×10^{-2}
0.010	3.00×10^{-2}	0.087	3.28×10^{-2}	0.156	3.00×10^{-2}	0.200	1.63×10^{-2}
0.014	2.65×10^{-2}	0.109	3.39×10^{-2}	0.164	2.74×10^{-2}	0.227	1.33×10^{-2}
0.031	2.81×10^{-2}	0.115	3.52×10^{-2}	0.173	2.27×10^{-2}	0.236	1.12×10^{-2}

(g) *Water added to an equimolar mixture of trifluoroacetic anhydride and acetic anhydride.*

N_{H_2O}	κ_{25} (mho)	N_{H_2O}	κ_{25} (mho)	N_{H_2O}	κ_{25} (mho)	N_{H_2O}	κ_{25} (mho)
0	7.78×10^{-7}	0.43	2.98×10^{-5}	0.60	5.75×10^{-4}	0.77	1.34×10^{-2}
0.06_5	3.82×10^{-6}	0.45	3.08×10^{-5}	0.63	1.12×10^{-3}	0.79	1.74×10^{-2}
0.08	4.85×10^{-6}	0.47	2.97×10^{-5}	0.65	1.84×10^{-3}	0.80_5	2.09×10^{-2}
0.18	7.02×10^{-6}	0.49_5	2.45×10^{-5}	0.67	2.98×10^{-3}	0.83	2.49×10^{-2}
0.23	9.14×10^{-6}	0.50_5	2.60×10^{-5}	0.70	4.75×10^{-3}	0.86	2.60×10^{-2}
0.27	1.22×10^{-5}	0.52	5.00×10^{-5}	0.72	6.50×10^{-3}	0.88	2.58×10^{-2}
0.32	1.60×10^{-5}	0.54	1.12×10^{-4}	0.74	1.03×10^{-2}	0.90	2.23×10^{-2}
0.40	2.58×10^{-5}	0.56	1.89×10^{-4}				

(h) *Water added to a mixture of trifluoroacetic anhydride (0·158 mole) and acetic anhydride (0·342 mole).*

N_{H_2O}	κ_{25} (mho)	N_{H_2O}	κ_{25} (mho)	N_{H_2O}	κ_{25} (mho)	N_{H_2O}	κ_{25} (mho)
0.50	1.29×10^{-5}	0.62	5.53×10^{-4}	0.66	1.31×10^{-3}	0.75	7.37×10^{-3}
0.59	3.52×10^{-4}	0.63	7.10×10^{-4}	0.68	2.25×10^{-3}		
0.60	4.02×10^{-4}	0.65	9.40×10^{-4}	0.72	3.63×10^{-3}		

(i) *Water added to a mixture of trifluoroacetic anhydride (0·34 mole) and acetic anhydride (0·33 mole).*

N_{H_2O}	κ_{25} (mho)	N_{H_2O}	κ_{25} (mho)	N_{H_2O}	κ_{25} (mho)	N_{H_2O}	κ_{25} (mho)
0.33	1.72×10^{-5}	0.38	2.48×10^{-5}	0.45	3.01×10^{-5}	0.50	2.56×10^{-5}
0.37	2.32×10^{-5}	0.43	2.84×10^{-5}	0.47	2.92×10^{-5}	0.51	4.1×10^{-5}

(j) *Acetic acid added to a mixture of trifluoroacetic anhydride (0·24 mole) and water (0·76 mole).*

$N_{CH_3 \cdot CO_2H}$	κ_{25} (mho)	$N_{CH_3 \cdot CO_2H}$	κ_{25} (mho)	$N_{CH_3 \cdot CO_2H}$	κ_{25} (mho)	$N_{CH_3 \cdot CO_2H}$	κ_{25} (mho)
0	1.12×10^{-2}	0.05	8.98×10^{-3}	0.16	5.54×10^{-3}	0.33	2.54×10^{-3}
0.004	1.10×10^{-2}	0.07	8.12×10^{-3}	0.22	4.51×10^{-3}	0.37	2.07×10^{-3}
0.01	1.07×10^{-2}	0.11	7.15×10^{-3}	0.25	3.66×10^{-3}		
0.03	1.05×10^{-2}	0.12	6.26×10^{-3}	0.29	3.07×10^{-3}		

DISCUSSION

Complete interpretation of the electrical conductivity of a system is almost impossible without complete data of the dielectric constant and viscosity. These are not available for the present system, though the following figures for the pure components have been reported.

Dielectric constants and viscosities of the pure components.

Component	ε_{25}	η_{25} (poise)	Component	ε_{25}	η_{25} (poise)
$(CH_3 \cdot CO)_2O$	20·5 [a]	0·0086 [a]	$CF_3 \cdot CO_2H$	8·4 (20·0°) [b]	0·00876 [a]
$CH_3 \cdot CO_2H$	7·1 [a]	0·0112 [a]	H_2O	78·8	0·00916 [a]
$(CF_3 \cdot CO)_2O$	Unknown	Unknown			

[a] Landolt–Börnstein "Tabellen." [b] Dannhauser and Cole, *J. Amer. Chem. Soc.*, 1952, **74**, 6105; Simons and Lorentzen, *ibid.*, 1950, **72**, 1426, gave 40·2 (at 21·5°).

With the assistance of these values a few qualitative conclusions can be drawn from Fig. 7. In the aqueous region, *i.e.*, the whole of the diagram below a line joining trifluoroacetic acid to acetic acid, the ions present in greatest concentrations must be, presumably, H_3O^+ and $CF_3 \cdot CO_2^-$, those in smaller concentrations being, probably, $CH_3 \cdot CO_2H_2^+$, $CH_3 \cdot CO_2^-$, and even OH^-. Since trifluoroacetic acid is a considerably stronger acid than acetic acid, the ion $CF_3 \cdot CO_2^-$ is, in all probability, the principal negative ion throughout almost the whole region. The actual position of the point of maximum conductivity is presumably determined largely by the relatively large proton affinity and high dielectric constant of water.

Fig. 5 and the conductivities around the line joining the two acids (Fig. 7) are of considerable interest, since it must be in this region that the acetic acidium ion $CH_3 \cdot CO_2H_2^+$ replaces the hydroxonium ion H_3O^+ as the principal positive ion, and the rapid changes of conductivity reflect the decrease in total ionisation associated with this replacement. Comparison of the conductivity of trifluoroacetic acid in acetic acid (Fig. 5) with the conductivities of various other acids in the same solvent, reported by previous workers, shows that trifluoroacetic acid is a weak acid in this solvent. When the mole fraction of the second acid in acetic acid is one-tenth, the approximate conductivities are : sulphuric acid, $6 \cdot 0 \times 10^{-3}$ mho (Hall and Voge, *loc. cit.*); nitric acid, $1 \cdot 10 \times 10^{-5}$ mho (Taylor and Follows, *loc. cit.*); trifluoroacetic acid, $1 \cdot 4 \times 10^{-6}$ mho; whilst that of the weaker trichloroacetic acid is $3 \cdot 5 \times 10^{-7}$ mho (Kendall and Gross, *loc. cit.*).

The region above the line joining trifluoroacetic acid and acetic acid is the region of greatest interest. The most striking feature of this region is the occurrence of conductivities greater than any on the $CF_3 \cdot CO_2H$–$CH_3 \cdot CO_2H$ line. The principal conducting species present in mixtures of the acids only are clearly $CF_3 \cdot CO_2^-$ and $CH_3 \cdot CO_2H_2^+$, but the concentration of $CH_3 \cdot CO_2H_2^+$ should reach a maximum on the $CF_3 \cdot CO_2H$–$CH_3 \cdot CO_2H$ line, so that the greater conductivities above this line must be due either to contributions from other ions or to rapid changes in the viscosity and dielectric constant. The former explanation seems the more probable and the additional ions could be the acetic anhydridium ion $(CH_3 \cdot CO)_2OH^+$ and/or the acetylium ion $CH_3 \cdot CO^+$ (these ions are distinguished by the incorporation of a molecule of acetic acid in the former). Further evidence for the existence of such ions is provided by the fact that the conductivity of a dilute solution of trifluoroacetic anhydride in acetic acid is greater than the conductivity of a solution having twice this concentration of trifluoroacetic acid in acetic acid. Finally, between trifluoroacetic anhydride and acetic anhydride, where there can be no hydrogen ion of any kind, there is a conductivity maximum (Fig. 6). The conductivity of acetic anhydride is appreciably greater than the conductivity of acetic acid and, although the viscosity is much less, this has been put forward as evidence for partial ionisation of the anhydride $(CH_3 \cdot CO)_2O \rightleftharpoons CH_3 \cdot CO^+ + CH_3 \cdot CO_2^-$ (Mackenzie and Winter, *Trans. Faraday Soc.*, 1948, **44**, 159). On the other hand, trifluoroacetic anhydride has an extremely small specific conductivity, far lower than that of trifluoroacetic acid. A molecule of an unsymmetric anhydride would be expected to ionise more readily than one of a symmetric anhydride, especially when the two halves are derived from acids differing widely in strength. The partial ionisation of such an unsymmetric anhydride, derived from acetic and trifluoroacetic acids and formed from the mixtures studied here $(CF_3 \cdot CO \cdot O \cdot CO \cdot CH_3 \rightleftharpoons CF_3 \cdot CO_2^- + CH_3 \cdot CO^+)$, is the most probable explanation of the maximum in Fig. 6.

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