

**156. The Electrochemistry of Boron Trifluoride Co-ordination Compounds. Part V.\* Boron Trifluoride-*n*-Alkyl Acetates.**

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The equimolar co-ordination compounds of boron trifluoride with the first four *n*-alkyl esters of acetic acid have been prepared and characterised by melting point, and by density and viscosity determinations over a range of temperatures. The compounds in the pure molten state conduct electricity, and the variation of specific conductivity with temperature and composition has been studied. Both electrical conductivity and viscosity vary exponentially with temperature, and activation energies for the processes of ionic migration and viscous flow have been calculated. A comparison of the densities, viscosities, and conductivities of the donor molecules with those of the boron trifluoride complexes demonstrates that formation of an oxygen-boron donor-acceptor bond in the system boron trifluoride-alkyl acetate is accompanied by large increases in each of these properties.

IN Part III (*J.*, 1951, 1795) certain physical properties of the compound boron trifluoride-mono(acetic acid),  $\text{BF}_3 \cdot \text{CH}_3 \cdot \text{CO}_2\text{H}$ , were reported, these being required as part of a general electrochemical investigation on the co-ordination compounds formed by boron trifluoride. The properties studied were density, viscosity, and electrical conductivity as these lead to estimates of the degree of ionic dissociation in the molten compounds. The present communication reports extension of the experiments to the homologous series of 1 : 1 addition compounds between boron trifluoride and *n*-alkyl acetates,  $\text{BF}_3 \cdot \text{CH}_3 \cdot \text{CO}_2\text{R}$ , where R is Me, Et, Pr<sup>n</sup>, or Bu<sup>n</sup>. These compounds were chosen partly because of their convenient melting points (cf. Table I) and partly because of the possibility of correlating their properties with the progressive variation in chain length of the addend.

Stable compounds of boron trifluoride and alkyl acetates were first reported by Bowlus and Nieuwland (*J. Amer. Chem. Soc.*, 1931, **53**, 3835), who concluded that methyl, ethyl, and *n*-propyl acetates gave equimolecular compounds of which the two lower members were solids. In the same year, Morgan and Taylor (*J. Soc. Chem. Ind.*, 1931, **50**, 869) also reported the first two of these compounds. Apart from some parachor measurements by Sugden and Waloff (*J.*, 1932, 1492) on Morgan and Taylor's samples, boron trifluoride-alkyl acetates do not appear to have received further study.

TABLE I. *Boron trifluoride-n-alkyl acetates.*

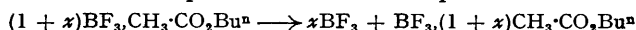
| Compound   | M. p.     |                                       | B. p.          |   |
|--|-----------|---------------------------------------|----------------|---|
|  | This work | Literature                            | This work      | Literature  |
| $\text{BF}_3 \cdot \text{CH}_3 \cdot \text{CO}_2\text{Me}$ .....   | 65.5°     | 60° <sup>a</sup> ; 61.5° <sup>b</sup> | —              | 110°/739 mm. <sup>a</sup> ; 112°/772 mm. <sup>b</sup> |
| $\text{BF}_3 \cdot \text{CH}_3 \cdot \text{CO}_2\text{Et}$ .....   | 32.5      | 26° <sup>a</sup> ; 31° <sup>b</sup>   | —              | 119/739 mm. <sup>a</sup> ; 123/772 mm. <sup>b</sup>   |
| $\text{BF}_3 \cdot \text{CH}_3 \cdot \text{CO}_2\text{Pr}^n$ ..... | 14.7      | Liquid                                | 127° (decomp.) | 126/743 mm. <sup>a</sup>                              |
| $\text{BF}_3 \cdot \text{CH}_3 \cdot \text{CO}_2\text{Bu}^n$ ..... | 17.9      | New compound                          | 135 (decomp.)  | New compound  |

<sup>a</sup> Bowlus and Nieuwland (*loc. cit.*). <sup>b</sup> Morgan and Taylor (*loc. cit.*).

In the present investigation the complexes were synthesised gravimetrically by passing purified boron trifluoride gas into a weighed amount of the ester. Absorption of an equimolar quantity of the gas was rapid and complete and, if local heating of the liquid was minimized by careful control of the flow rate and by cooling, the complexes were obtained as viscous water-white liquids. The methyl acetate compound crystallized rapidly on cooling below its m. p. (65.5°), and if the temperature of absorption fell much below 60° blockage of the boron trifluoride inlet tube occurred. On the other hand, the ethyl, *n*-propyl, and *n*-butyl complexes showed a strong tendency to supercool by as much as 10–20° unless crystallization was deliberately initiated. Fractional freezing of the liquids in dry air or nitrogen was the most effective means of purification. For each compound, four or five slow freezings at a temperature just below the m. p. sufficed to give a crop of transparent well-formed crystals, the m. p. being raised by about 1° (see Table I for final values).

\* Part IV, Greenwood and Martin, *J.*, 1951, 1915.

Table I shows that the m. p.s quoted by Bowlus and Nieuwland are particularly low; in fact, they failed to obtain boron trifluoride-*n*-propyl acetate (m. p. 14.7°) in solid form. Further, in view of their statement that the complexes are dissociated in the vapour phase, their procedure for purification by distillation seems suspect. The present investigation has shown that distillation of freshly prepared boron trifluoride-*n*-butyl acetate at atmospheric pressure results in copious evolution of boron trifluoride followed by a colourless, constant-boiling fraction at 135°. A middle fraction of this distillate was collected and shown to have m. p. 4°, *i.e.*, some 13° below the m. p. of the starting material. Analysis of the distillate confirmed that partial thermal decomposition had occurred:



The micro-analyses (C, 43.0; H, 6.8%) suggested that *x* was about 0.2, corresponding to ~15% dissociation of the complex.

Boron trifluoride-*n*-alkyl acetates fume copiously when exposed to a moist atmosphere, and hydrolyse rapidly in water:  $\text{BF}_3 \cdot \text{CH}_3\text{CO}_2\text{R} + 2\text{H}_2\text{O} \longrightarrow \text{BF}_3 \cdot 2\text{H}_2\text{O} + \text{CH}_3\text{CO}_2\text{R}$ . The solid complexes, after recrystallization, may be kept indefinitely in a dry atmosphere without apparent change. However, when molten, the compounds tend to decompose slowly, and become brown when kept for some months.

*Densities.*—The densities were determined over a range of temperatures by using the Pyrex-glass dilatometer described in Part III (*loc. cit.*). The results, which refer to both the normal and supercooled regions, are listed in Tables 2 and 3. Values were not affected

TABLE 2. Density of boron trifluoride-*n*-propyl acetate from 2° to 25°.

|                             |        |        |        |        |        |        |        |        |
|-----------------------------|--------|--------|--------|--------|--------|--------|--------|--------|
| <i>t</i> .....              | 2.00°  | 5.00°  | 9.00°  | 12.00° | 15.00° | 18.00° | 22.70° | 24.80° |
| <i>d</i> <sub>4</sub> ..... | 1.2211 | 1.2176 | 1.2128 | 1.2095 | 1.2058 | 1.2023 | 1.1963 | 1.1941 |

TABLE 3. Density of boron trifluoride-*n*-butyl acetate from 2° to 31°.

|                             |        |        |        |        |        |        |        |        |
|-----------------------------|--------|--------|--------|--------|--------|--------|--------|--------|
| <i>t</i> .....              | 2.15°  | 6.40°  | 10.75° | 13.80° | 19.60° | 22.95° | 26.30° | 30.90° |
| <i>d</i> <sub>4</sub> ..... | 1.1758 | 1.1709 | 1.1658 | 1.1624 | 1.1558 | 1.1520 | 1.1483 | 1.1432 |

by prolonged storage at the higher temperatures. The densities decrease linearly with rising temperature, and are consistent with the equations given in Table 4 to  $\pm 1$  in the fifth significant figure. The density of boron trifluoride-*n*-propyl acetate has been given by Bowlus and Nieuwland (*loc. cit.*) as  $d_4^{23}$  1.170; the present data lead to a value of  $d_4^{23}$  1.1964.

TABLE 4. Dependence of density upon temperature:  $d_4^t = A - 10^{-3}Bt$ .

|   | A      | B     |   | A      | B     |   | A      | B     |
|---|--------|-------|---|--------|-------|---|--------|-------|
| $\text{BF}_3 \cdot \text{CH}_3\text{CO}_2\text{H}^a$  | 1.5216 | 1.290 | $\text{BF}_3 \cdot \text{CH}_3\text{CO}_2\text{Et}^b$ | 1.276  | 1.23  | $\text{BF}_3 \cdot \text{CH}_3\text{CO}_2\text{Bu}^n$ | 1.1781 | 1.134 |
| $\text{BF}_3 \cdot \text{CH}_3\text{CO}_2\text{Me}^b$ | 1.324  | 1.17  | $\text{BF}_3 \cdot \text{CH}_3\text{CO}_2\text{Pr}^n$ | 1.2234 | 1.174 |   |        |       |

<sup>a</sup> The value  $d_4^0$  1.5220 quoted in Part III is 4 parts in 15,000 high owing to a small error in calibration of the dilatometer. <sup>b</sup> Sugden and Waloff, *J.*, 1932, 1492.

These data not only are necessary to calculate dynamic viscosities,  $\eta = \nu d_4^t$ , and molar conductivities,  $\mu = M\kappa/d_4^t$ , but also provide valuable information on the changes which accompany donor-acceptor bonding and on the constitution of the resulting adduct (Greenwood and Martin, Part VII, in preparation). The decrease in  $d_4^0$  for the boron trifluoride-alkyl acetates is linear with chain length, whereas the value for the acetic acid complex lies above the curve, being considerably greater than that expected from a linear variation. The latter behaviour may arise partly from molecular association due to hydrogen-bonding, although it is more likely that the predominant effect is considerable ionic dissociation leading to stronger electrical fields and tighter binding within the liquid complex.

*Viscosities.*—The viscous properties were examined by use of an Ostwald-Poiseuille viscometer described in Part I (Greenwood, Martin, and Emeléus, *J.*, 1950, 3030). The temperature dependence of kinematic viscosity,  $\nu$  centistokes, and dynamic viscosity,  $\eta$  centipoises, for the four complexes is recorded in Tables 5—8. The variation of dynamic viscosity with temperature is shown graphically in Fig. 1. The shapes of the  $\eta$ -*t* plots for

the ester compounds are similar and follow approximately the same curve, although there is a small displacement in viscosity with increasing chain length. By contrast, the  $\eta$ - $t$  curve for boron trifluoride-mono(acetic acid) lies considerably above those of the other complexes. This probably arises, as does the density anomaly, partly from the molecular association characteristic of hydroxylated liquids and partly from the greater ionic disso-

FIG. 1. *Dynamic viscosity of boron trifluoride-alkyl acetates.*

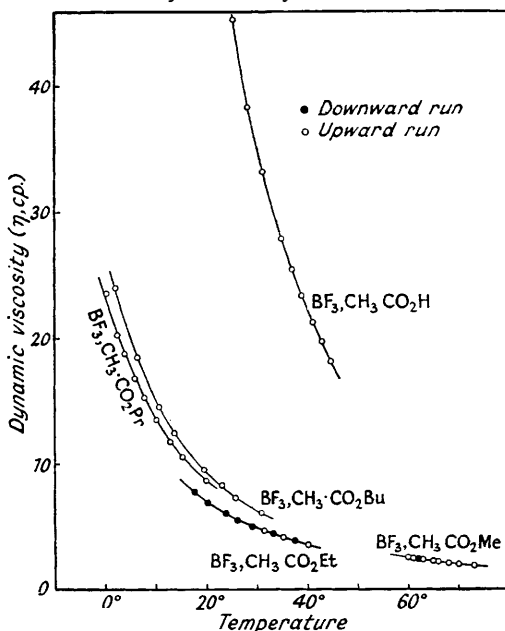
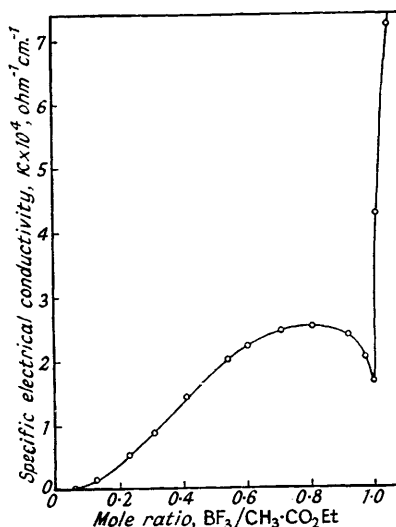


FIG. 2. *Conductivity-composition isotherm at 33.0°.*



ciation of this compound (cf. Part VII) leading to the formation of ionic clusters (Barrer, *Trans. Faraday Soc.*, 1943, 39, 48).

TABLE 5. *Viscosity of boron trifluoride-methyl acetate from 60° to 73°.*

|                      |       |       |       |       |       |       |       |       |       |
|----------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| <i>t</i> .....       | 60.0° | 61.0° | 62.0° | 63.0° | 65.0° | 66.0° | 68.0° | 70.0° | 73.0° |
| <i>v</i> (cs.) ..... | 2.06  | 2.01  | 1.97  | 1.92  | 1.83  | 1.79  | 1.72  | 1.65  | 1.55  |
| $\eta$ (cp.) .....   | 2.58  | 2.52  | 2.46  | 2.40  | 2.28  | 2.23  | 2.14  | 2.05  | 1.92  |

TABLE 6. *Viscosity of boron trifluoride-ethyl acetate from 17° to 40°.*

|                    |       |       |                     |       |       |                     |       |                     |       |                     |
|--------------------|-------|-------|---------------------|-------|-------|---------------------|-------|---------------------|-------|---------------------|
| <i>t</i> .....     | 17.7° | 20.3° | 23.8 <sub>5</sub> ° | 26.6° | 29.1° | 31.4 <sub>5</sub> ° | 33.3° | 35.1 <sub>5</sub> ° | 37.5° | 40.1 <sub>5</sub> ° |
| <i>v</i> (cs.) ... | 6.16  | 5.54  | 4.86                | 4.40  | 4.06  | 3.75                | 3.57  | 3.36                | 3.15  | 2.92                |
| $\eta$ (cp.) ...   | 7.73  | 6.93  | 6.06                | 5.47  | 5.03  | 4.64                | 4.41  | 4.14                | 3.88  | 3.58                |

TABLE 7. *Viscosity of boron trifluoride-n-propyl acetate from 0° to 20°.*

|                      |       |       |                    |                    |                    |                     |       |       |       |
|----------------------|-------|-------|--------------------|--------------------|--------------------|---------------------|-------|-------|-------|
| <i>t</i> .....       | 0.2°  | 2.5°  | 4.0 <sub>5</sub> ° | 6.0 <sub>5</sub> ° | 7.8 <sub>5</sub> ° | 10.2 <sub>5</sub> ° | 13.0° | 15.3° | 19.9° |
| <i>v</i> (cs.) ..... | 19.24 | 16.84 | 15.37              | 13.79              | 12.53              | 11.13               | 9.73  | 8.76  | 7.23  |
| $\eta$ (cp.) .....   | 23.53 | 20.55 | 18.73              | 16.77              | 15.21              | 13.48               | 11.76 | 10.55 | 8.68  |

TABLE 8. *Viscosity of boron trifluoride-n-butyl acetate from 2° to 31°.*

|                      |       |                    |                     |                     |       |                     |       |                     |
|----------------------|-------|--------------------|---------------------|---------------------|-------|---------------------|-------|---------------------|
| <i>t</i> .....       | 2.1°  | 6.4 <sub>5</sub> ° | 10.7 <sub>5</sub> ° | 13.8 <sub>5</sub> ° | 19.6° | 22.9 <sub>5</sub> ° | 26.3° | 30.8 <sub>5</sub> ° |
| <i>v</i> (cs.) ..... | 20.35 | 15.75              | 12.49               | 10.68               | 8.24  | 7.18                | 6.34  | 5.33                |
| $\eta$ (cp.) .....   | 23.93 | 18.44              | 14.56               | 12.41               | 9.53  | 8.27                | 7.28  | 6.09                |

In Table 9, the viscosities of the complexes are compared at their m. p.s; the viscosities of the donor molecules at 20° are also included, and the Table shows the large increase which accompanies co-ordination. That the formation of "salts" in an acid-base system is accompanied by a marked increase in viscosity appears to be a general law (Prideaux and Coleman, *J.*, 1937, 4), so the 10-fold increase observed in the present system,  $\text{BF}_3$ -

$\text{CH}_3\text{-CO}_2\text{R}$ , is not unexpected. The complexes also possess relatively high temperature coefficients of viscosity. Col. 5 lists values of the function  $(1/\eta)(d\eta/dt)$  at the m. p.s of the complexes over a temperature interval,  $dt = 6^\circ$ ; corresponding values for the donor molecules are in col. 4. The data show that formation of the co-ordination complex increases the temperature coefficient of viscosity about 3-fold. A parallel increase occurs in the activation energy of viscous flow,  $E_\eta$ . If  $\log \eta$  is plotted against the reciprocal of absolute temperature for the liquids above their m. p.s, linear plots are obtained, showing that dynamic viscosity is related to temperature by the exponential relation:  $\eta = \eta_0 e^{E_\eta/RT}$ . Values of  $E_\eta$  are listed in Table 10 together with the corresponding quantities for the free donor molecules.

TABLE 9. *Dynamic viscosity and its temperature coefficient.*

| Donor molecule                             | $\eta$ (cp.)     |                           | $(1/\eta)(d\eta/dt)$ , % |                           |
|--|------------------|---------------------------|--------------------------|---------------------------|
|  | Donor molecule * | Adduct with $\text{BF}_3$ | Donor molecule *         | Adduct with $\text{BF}_3$ |
| $\text{CH}_3\text{-CO}_2\text{H}$ .....    | 1.24             | 25.0                      | 1.3                      | 4.5                       |
| $\text{CH}_3\text{-CO}_2\text{Me}$ .....   | 0.38             | 2.26                      | 0.9                      | 2.3                       |
| $\text{CH}_3\text{-CO}_2\text{Et}$ .....   | 0.45             | 4.50                      | 1.1                      | 3.3                       |
| $\text{CH}_3\text{-CO}_2\text{Pr}^n$ ..... | 0.58             | 10.83                     | 1.2                      | 4.7                       |
| $\text{CH}_3\text{-CO}_2\text{Bu}^n$ ..... | 0.73             | 10.18                     | 1.4                      | 4.5                       |

\* Values calculated from: Bingham, White, Thomas, and Cadwell (*Z. phys. Chem.*, 1913, **83**, 641), Thorpe and Rodger (*Phil. Trans.*, 1897, **189**, 71), Bingham and de Turck (*J. Rheology*, 1932, **3**, 479).

TABLE 10. *Activation energies for viscous flow and ionic migration.*

| Donor molecule                             | $E_\eta$ , kcal. mole <sup>-1</sup> |                           | $E_\kappa$ , kcal. mole <sup>-1</sup><br>Adduct with $\text{BF}_3$ |
|--|-------------------------------------|---------------------------|--|
|  | Donor molecule *                    | Adduct with $\text{BF}_3$ |  |
| $\text{CH}_3\text{-CO}_2\text{H}$ .....    | 2.66                                | 8.53                      | 7.38   |
| $\text{CH}_3\text{-CO}_2\text{Me}$ .....   | 1.89                                | 4.97                      | 6.17   |
| $\text{CH}_3\text{-CO}_2\text{Et}$ .....   | 2.01                                | 5.68                      | 6.35   |
| $\text{CH}_3\text{-CO}_2\text{Pr}^n$ ..... | 2.23                                | 7.17                      | 6.30   |
| $\text{CH}_3\text{-CO}_2\text{Bu}^n$ ..... | 2.46                                | 6.92                      | 8.94   |

\* Calc. from data in the papers cited in Table 9.

Table 10 illustrates that combination between boron trifluoride and acetic acid and its esters leads to large increases in the activation energy of viscous flow. In a comprehensive review on the viscosities of liquids, Ward (*Trans. Faraday Soc.*, 1937, **33**, 88) has pointed out that values of  $E_\eta$  for molecular liquids (which include non-polar, dipolar, hydroxylated, and hydrogen-bonded liquids) fall in the range 0.4—3.5 kcal. mole<sup>-1</sup>, whereas for some metals, such as silver,  $E_\eta$  may attain a value as high as 4.9 kcal. mole<sup>-1</sup>. By contrast, activation energies of the magnitude recorded in Table 10 are characteristic of highly ionized molten salts such as fused sodium and potassium chlorides. There is therefore an interesting parallel between the behaviour of boron trifluoride co-ordination complexes, which may be regarded as salts formed in a Lewis acid-base system, and true inorganic salts, even though the degree of ionic dissociation of the complexes is much smaller. The viscosities of boron trifluoride-alkyl acetates in the supercooled state have been discussed elsewhere (Greenwood and Martin, *Nature*, 1951, **168**, 344; *Proc. Roy. Soc.*, 1952, **215**, A, 46).

*Electrical Conductivities.*—The electrical conductivity of boron trifluoride-alkyl acetates was determined by methods outlined in Parts I (*loc. cit.*) and II (*J.*, 1951, 1328). The conductivity of boron trifluoride is extremely low ( $<5 \times 10^{-10}$  ohm<sup>-1</sup> cm.<sup>-1</sup> at  $-120^\circ$ ; Woolf and Greenwood, *J.*, 1950, 2200) and the conductivities of alkyl acetates are  $\sim 10^{-6}$  ohm<sup>-1</sup> cm.<sup>-1</sup> or less. However, the conductivities of equimolar complexes of the two constituents are higher than those of the parent compounds by several powers of 10. This is summarized in Table 11, where values of specific electrical conductivity,  $\kappa$ , for the 1:1 addition complexes are compared with values for the donor molecules interpolated from data in the literature.

The variation of specific electrical conductivity with composition was determined for the systems boron trifluoride-methyl acetate and boron trifluoride-ethyl acetate. The characteristic features of these conductivity-composition isotherms are illustrated by the

results obtained for the latter system at 33.0° (see Fig. 2). Initially the conductivity of pure ethyl acetate was  $\ll 10^{-6}$  ohm<sup>-1</sup> cm.<sup>-1</sup>, but addition of boron trifluoride rapidly increased it so that at a mole ratio  $\text{BF}_3/\text{CH}_3\cdot\text{CO}_2\text{Et} = 0.06$  the specific conductivity was already  $0.71 \times 10^{-5}$  ohm<sup>-1</sup> cm.<sup>-1</sup>. Further additions of the gas increased the conductivity of the system until a maximum of  $2.5 \times 10^{-4}$  ohm<sup>-1</sup> cm.<sup>-1</sup> was reached in the vicinity of the mole ratio 0.8. Further increase in the concentration of boron trifluoride reduced the conductivity until a well-defined minimum was reached at equimolar proportions of the constituents. Practically no further absorption occurred at atmospheric pressure, although a mole ratio of 1.05 was eventually reached by prolonged passage of the gas through the molten complex. This produced a further rapid increase in the conductivity of the system.

TABLE 11. *Specific electrical conductivity at the m. p.*

| Donor molecule                                 | $\kappa$ , ohm <sup>-1</sup> cm. <sup>-1</sup> |                               |
|--|--|-------------------------------|
|  | Donor molecule *                               | Adduct with $\text{BF}_3$     |
| $\text{CH}_3\cdot\text{CO}_2\text{H}$ .....    | $1.1 \times 10^{-8}$ (25°)                     | $2.20 \times 10^{-3}$ (37.5°) |
| $\text{CH}_3\cdot\text{CO}_2\text{Me}$ .....   | $3.4 \times 10^{-6}$ (25°)                     | $6.82 \times 10^{-4}$ (65.5°) |
| $\text{CH}_3\cdot\text{CO}_2\text{Et}$ .....   | $1 \times 10^{-9}$ (25°)                       | $1.67 \times 10^{-4}$ (32.5°) |
| $\text{CH}_3\cdot\text{CO}_2\text{Pr}^n$ ..... | $< 10^{-6}$ (25°)                              | $6.37 \times 10^{-5}$ (14.7°) |
| $\text{CH}_3\cdot\text{CO}_2\text{Bu}^n$ ..... | $< 10^{-6}$ (25°)                              | $2.21 \times 10^{-5}$ (17.9°) |

\* Values taken from: Rabinowitsch (*Z. phys. Chem.*, 1926, **119**, 59), Patten (*J. Phys. Chem.*, 1902, **6**, 554), Kendall and Brakeley (*J. Amer. Chem. Soc.*, 1921, **43**, 1826), Sammis (*J. Phys. Chem.*, 1906, **10**, 593).

TABLE 12.

| $10^5\kappa$  | $10^3\mu$ | $\Sigma$ | $t$    | $10^5\kappa$        | $10^3\mu$ | $\Sigma$ | $t$    | $10^5\kappa$      | $10^3\mu$ | $\Sigma$ |        |
|---|-----------|----------|--------|---------------------|-----------|----------|--------|-------------------|-----------|----------|--------|
| <i>Conductivity of boron trifluoride-methyl acetate from 63° to 75°.*</i> |           |          |        |                     |           |          |        |                   |           |          |        |
| 62.9°   | 63.53     | 72.1     | 0.174  | 67.4°               | 71.64     | 81.7     | 0.177  | 71.0°             | 79.09     | 90.4     | 0.181  |
| 63.8  | 65.13     | 74.0     | 0.174  | 68.0                | 72.97     | 83.2     | 0.178  | 73.0              | 83.28     | 95.4     | 0.183  |
| 65.0  | 67.39     | 76.6     | 0.175  | 69.1                | 75.21     | 85.9     | 0.179  | 75.0              | 87.60     | 100.6    | 0.185  |
| 66.3  | 69.69     | 79.4     | 0.176  | 70.0                | 77.02     | 88.0     | 0.180  |                   |           |          |        |
| <i>Conductivity of boron trifluoride-ethyl acetate from 17° to 41°.</i>   |           |          |        |                     |           |          |        |                   |           |          |        |
| 16.8  | 8.93      | 11.1     | 0.0894 | 25.1                | 12.43     | 15.6     | 0.0903 | 35.5              | 18.48     | 23.4     | 0.0961 |
| 19.7  | 10.16     | 12.7     | 0.0896 | 27.8                | 13.97     | 17.5     | 0.0923 | 38.6              | 20.32     | 25.8     | 0.0967 |
| 21.8 <sup>s</sup>   | 10.92     | 13.6     | 0.0892 | 31.5                | 16.03     | 20.2     | 0.0937 | 41.0              | 22.20     | 28.2     | 0.0988 |
| 23.3  | 11.77     | 14.7     | 0.0911 |                     |           |          |        |                   |           |          |        |
| <i>Conductivity of boron trifluoride-n-propyl acetate from 0° to 25°.</i> |           |          |        |                     |           |          |        |                   |           |          |        |
| 0.0   | 3.178     | 4.41     | 0.1068 | 11.0                | 5.456     | 7.66     | 0.1012 | 19.0              | 7.568     | 10.71    | 0.0978 |
| 2.0   | 3.543     | 4.93     | 0.1060 | 12.0                | 5.703     | 8.01     | 0.1008 | 19.5              | 7.705     | 10.90    | 0.0977 |
| 4.0   | 3.925     | 5.47     | 0.1046 | 12.5                | 5.824     | 8.18     | 0.1003 | 20.0              | 7.850     | 11.12    | 0.0976 |
| 5.0   | 4.133     | 5.77     | 0.1043 | 13.0                | 5.943     | 8.36     | 0.0997 | 21.0              | 8.153     | 11.56    | 0.0958 |
| 6.0   | 4.333     | 6.05     | 0.1035 | 14.0                | 6.195     | 8.72     | 0.0995 | 22.0              | 8.445     | 11.98    | 0.0952 |
| 7.0   | 4.546     | 6.36     | 0.1029 | 15.0                | 6.462     | 9.11     | 0.0992 | 23.0              | 8.756     | 12.43    | 0.0948 |
| 8.0   | 4.762     | 6.66     | 0.1024 | 16.0                | 6.723     | 9.48     | 0.0988 | 24.0              | 9.033     | 12.84    | 0.0940 |
| 9.0   | 4.982     | 6.98     | 0.1018 | 17.0                | 7.008     | 9.89     | 0.0986 | 25.0              | 9.376     | 13.34    | 0.0938 |
| 10.0  | 5.216     | 7.31     | 0.1014 | 18.0                | 7.291     | 10.30    | 0.0982 |                   |           |          |        |
| <i>Conductivity of boron trifluoride-n-butyl acetate from 8° to 28°.</i>  |           |          |        |                     |           |          |        |                   |           |          |        |
| 8.0 <sub>s</sub>  | 1.247     | 1.96     | 0.0330 | 16.0                | 1.995     | 3.16     | 0.0353 | 20.1 <sub>s</sub> | 2.494     | 3.97     | 0.0369 |
| 10.0  | 1.414     | 2.23     | 0.0337 | 17.7 <sub>s</sub> † | 2.195     | 3.49     | 0.0358 | 21.9              | 2.725     | 4.35     | 0.0374 |
| 12.0  | 1.595     | 2.52     | 0.0343 | 18.0                | 2.221     | 3.53     | 0.0360 | 24.5 <sub>s</sub> | 3.121     | 4.99     | 0.0390 |
| 14.0  | 1.787     | 2.83     | 0.0348 | 18.1 <sub>s</sub>   | 2.240     | 3.56     | 0.0361 | 28.2              | 3.748     | 6.02     | 0.0407 |

\* The units of  $\kappa$ ,  $\mu$ , and  $\Sigma$  in this table are:  $\kappa$  in ohm<sup>-1</sup> cm.<sup>-1</sup>;  $\mu$  in ohm<sup>-1</sup> cm.<sup>2</sup>;  $\Sigma$  in ohm<sup>-1</sup> cm.<sup>2</sup> cp.  
 † Value remained constant during 36 hours.

The stoichiometric excess of boron trifluoride was evolved again when the molten complex was allowed to solidify.

The conductivity-composition plot for the system boron trifluoride-methyl acetate displays similar characteristics to those in Fig. 2. However, with this system it was necessary to add boron trifluoride initially at 25° to prevent distillation of the free ester (b. p. 57.1°). The system commenced to crystallize at a mole ratio  $\text{BF}_3/\text{CH}_3\cdot\text{CO}_2\text{Me} = 0.75$ , and the temperature was then raised to 70.2° for the remaining additions of gas. As a result of five experiments, the minimum in conductivity was placed at a mole ratio 1.002.

There is no fundamental reason why the minimum in conductivity should coincide exactly with stoichiometric proportions of the two components (cf. Prideaux and Coleman, *loc. cit.*; Kunzler and Giauque, *J. Amer. Chem. Soc.*, 1952, **74**, 804).

The temperature dependence of electrical conductivity of the four boron trifluoride-alkyl acetates was determined at a frequency of 1000 cycles; the values are given in Table 12. The conductivity data are also shown graphically in Fig. 3, where the logarithm of specific electrical conductivity,  $\kappa$ , is plotted as a function of temperature. For each compound, the values fall on a smooth curve slightly concave to the temperature axis, and a progressive decrease in the magnitude of specific conductivity with increasing chain length is apparent. This arises largely from differences in density and viscosity of the complexes, so that for comparison purposes the specific conductivities in Table 12 have been reduced to comparable density and viscosity conditions by use of the function,  $\mathfrak{K} = M\kappa\eta/d$ .

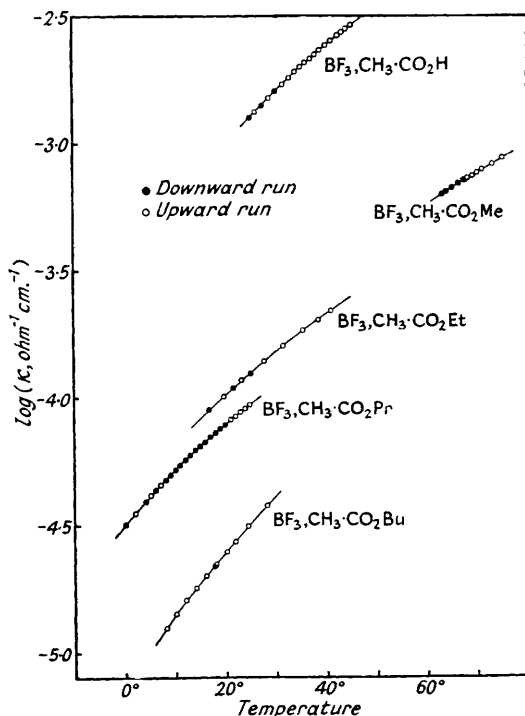


FIG. 3. *Electrical conductivity of boron trifluoride-alkyl acetates.*

Values of the reduced conductivity,  $\mathfrak{K}$ , are much less dependent on molecular weight, decreasing from about 0.18 for boron trifluoride-methyl acetate to 0.035  $\text{ohm}^{-1} \text{cm.}^{-2} \text{cp.}$  for boron trifluoride-*n*-butyl acetate. The Tables also list values of the molar conductivity,  $\mu = M\kappa/d$ . Further discussion of the conductivities and their variations with temperature is deferred to Part VII.

The specific conductivities recorded in Table 12 vary exponentially with the reciprocal of the absolute temperature, conforming to the equation  $\kappa = \kappa_0 e^{-E_\kappa/RT}$ , where  $E_\kappa$  is the activation energy for the process of ionic migration. Values of  $E_\kappa$  for the complexes above their melting points are given in Table 10. The values are of the same order of magnitude as the corresponding activation energies for viscous flow, with  $E_\kappa = E_\eta \pm 20\%$ . It is suggested that this indicates that similar configurational changes are involved in the processes of ionic migration and viscous flow in these liquids.

*Experimental.*—The procedures used have been described in earlier papers referred to in the text. The esters used were B.D.H. "Laboratory Reagent" grade, purified in the following way. Methyl acetate: repeated fractionation through an efficient column packed with Fenske glass helices, the final fraction, b. p. 57.0—57.1°,  $n_D^{20}$  1.3608, being retained. Ethyl, *n*-propyl, and *n*-butyl acetate: the esters were treated repeatedly with aqueous sodium carbonate,

washed thoroughly with water, and dried at 0° (CaCl<sub>2</sub>). They were then twice fractionated from phosphoric oxide through a Fenske column. Ethyl acetate had b. p. 76.6°/749 mm.,  $n^{20}_D$  1.3720; *n*-propyl acetate, b. p. 101.9°/767 mm.,  $n^{20}_D$  1.3838; *n*-butyl acetate, b. p. 126.0°/767 mm.,  $n^{20}_D$  1.3951. (All b. p.s are corrected.) Final purification of the boron trifluoride compounds was effected by repeated fractional crystallisation from the molten complex.

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