391. *The Electrochemistry of Boron Trifluoride Co-ordination Compounds. Part III.* Boron Trifluoride–Mono(acetic Acid).*

By N. N. GREENWOOD and R. L. MARTIN.

The electrical conductivity, viscosity, and density of molten boron trifluoride–mono(acetic acid) have been measured in the temperature range 25—45°. At the m. p., 37·5°, the specific conductivity $\kappa = 2{\cdot}19_6 \times 10^{-3}$ ohm^{-1} cm.$^{-1}$, the dynamic viscosity $\eta = 25{\cdot}0$ centipoises, and the density $d_4^{37\cdot5} = 1{\cdot}4736$. Both electrical conductivity and viscosity vary exponentially with temperature, and plots of log κ and log η against $1/T$ show marked discontinuities in the region of the m. p. The temperature coefficient of the density shows no detectable change on passage from the ordinary to the supercooled state. Thermal decomposition of the compound commenced at temperatures above 47°. The measurements have been used to estimate activation energies, and the variation of degree of ionization of the compound with temperature.

GREENWOOD, MARTIN, and EMELÉUS * have shown that pure, molten boron trifluoride–mono(acetic acid), $BF_3,CH_3{\cdot}CO_2H$, is a good conductor of electricity. This was ascribed to ionization of the acetic acid molecule induced by co-ordination to boron trifluoride and, from analysis of the products of electrolysis, it was concluded that in the liquid ionization to a hydrogen ion and the acetoxytrifluoroborate anion occurred exclusively :

$$BF_3,CH_3{\cdot}CO_2H \longrightarrow H^+ + BF_3,CH_3{\cdot}CO_2^-$$

In accord with this it has been found that the addition of metallic sodium to the liquid results in the evolution of hydrogen.

In the present work measurements of the temperature variation of electrical conductivity, kinematic viscosity, and density of the complex have been made, in order to ascertain the extent to which ionization in the liquid occurs, and to determine its dependence on temperature. The temperature range was restricted to the region below and slightly above the melting point, in order to to avoid thermal decomposition of the complex.

The specific electrical conductivity between 25° and 45° is presented in Table I and the figure.

TABLE I.

Conductivity of boron trifluoride–mono(acetic acid) from 25° to 45°.

t.	$\kappa \times 10^3$, ohm^{-1} cm.$^{-1}$	μ, ohm^{-1} cm.^{2}	$\mathfrak{K} = \mu\eta$, ohm^{-1} cm.^{2} cp.	t.	$\kappa \times 10^3$, ohm^{-1} cm.$^{-1}$	μ, ohm^{-1} cm.^{2}	$\mathfrak{K} = \mu\eta$, ohm^{-1} cm.^{2} cp.
$25{\cdot}0_5$°	1·257	0·108	5·06	$36{\cdot}9_5$°	2·144	0·186	4·76
26·1	1·322	0·114	5·02	$37{\cdot}9_5$	2·229	0·194	4·73
27·4	1·405	0·121	4·94	39·0	2·321	0·202	4·70
28·8	1·510	0·130	4·92	40·2	2·428	0·211	4·67
30·0	1·595	0·138	4·90	$41{\cdot}1_5$	2·516	0·219	4·65
$31{\cdot}4_5$	1·700	0·147	4·86	42·4	2·637	0·230	4·63
$32{\cdot}8_5$	1·808	0·156	4·83	43·4	2·735	0·239	4·62
$34{\cdot}0_5$	1·908	0·165	4·82	$44{\cdot}2_5$	2·814	0·246	4·56
$35{\cdot}0_5$	1·982	0·172	4·78	45·1	2·901	0·253	4·55
36·0	2·061	0·179	4·76				

It increases with temperature, the relative temperature coefficient at the melting point $\left(\frac{1}{\kappa}\cdot\frac{d\kappa}{dt}\right)_{37.5}$ being 3·9%. The value of the conductivity κ at the melting point is $2{\cdot}19_6 \times 10^{-3}$ ohm^{-1} cm.$^{-1}$; that of glacial acetic acid $\kappa_{25} = 1{\cdot}12 \times 10^{-8}$ ohm^{-1} cm.$^{-1}$ (see Part II). Measurements of conductivity were not extended above 45°, for at higher temperatures the conductivity of the complex increased with time. For example, at $47{\cdot}2_5$° the conductivity rose by 2% during 100 hours. At lower temperatures the curve was accurately reproducible (see figure). The increase in conductivity at ~47° was accompanied by slow evolution of boron trifluoride which arose from thermal decomposition of the complex :

$$(1 + x)BF_3,CH_3{\cdot}CO_2H \xrightarrow{47°} xBF_3 + BF_3,(1 + x)CH_3{\cdot}CO_2H$$

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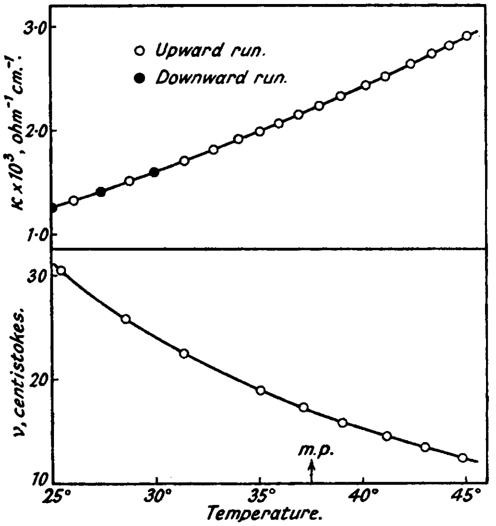
* Part II, *J.*, 1951, 1328.

The fact that this dissociation resulted in an increased conductivity is consistent with the conductivity–composition studies described in Part II.

Values for the molar conductivity, $\mu = M\kappa/d$, and the " reduced " conductivity, $\mathfrak{K} = \mu\eta$, are also given in Table I, and the temperature variation of these quantities, tabulated in the third and fourth columns, will be discussed later.

The density of molten boron trifluoride–mono(acetic acid) and its temperature dependence was required to calculate the molar conductivity and the dynamic viscosity of the complex.

Specific electrical conductivity and kinematic viscosity of boron trifluoride–mono(acetic acid).



The density, which does not appear to have been reported by previous investigators, was determined between 35° and 45° by means of a sealed Pyrex pyknometer (see Table II).

TABLE II.

Density of boron trifluoride–mono(acetic acid) from 35° *to* 45°.

t	35·0$_5$°	37·1°	39·0°	41·1$_5$°	43·0°	44·8°
d_4^t	1·4769	1·4742	1·4718	1·4689	1·4666	1·4643

The experimental values are reproduced to within 1 in the fifth significant figure by the equation : $d_4 = 1{\cdot}5220 - 0{\cdot}00129t$. The smoothness of the plot of these values indicates that there is no abnormal density change as the molten complex becomes supercooled. The density of the complex at its melting point is $d_4^{37\cdot5} = 1{\cdot}4736$.

The volume change per unit volume, $\Delta V/V_s$, on melting boron trifluoride–mono(acetic acid) was obtained by using a pyknometer for volume determination of solid and liquid. At the melting point, the volume change was $\sim$0·06. This value must be regarded as approximate, for the volume of the solid will depend on the closeness of packing of the individual crystals, during the freezing process.

The kinematic viscosity ν of the complex was required for calculation of the reduced conductivity $\mathfrak{K} = M\kappa\nu$, and was determined between 25° and 45° with a modified Ostwald U-tube viscometer (see Table III and figure). The values of the dynamic viscosity η, which is

TABLE III.

Viscosity of boron trifluoride–mono(acetic acid) from 25° *to* 45°.

t.	ν (cs).	η (cp).	t.	ν (cs).	η (cp).
25·4$_5$°	30·48	45·39	39·0°	15·81	23·28
28·5$_5$	25·80	38·32	41·1$_5$	14·46	21·24
31·3$_5$	22·43	33·24	43·0	13·42	19·68
35·0$_5$	18·87	27·87	44·8	12·40	18·16
37·1	17·24	25·42			

related to the kinematic viscosity by the equation, $\eta = \nu d^t_4$, are also tabulated. The viscosity decreases with rise in temperature with a relative temperature coefficient $-\frac{1}{\eta}\cdot\frac{d\eta}{dt}$ at the melting point of ~4·5%. At the melting point, the dynamic viscosity of boron trifluoride–mono(acetic acid) is 25·0 centipoises which is considerably higher than that of glacial acetic acid at the same temperature (0·93 centipoises; Thorpe and Rodger, *Phil. Trans.* 1895, **185**, 397).

DISCUSSION.

The present series of investigations has shown that in the molten state the co-ordination compounds of boron trifluoride are conductors of electricity. In the case of boron trifluoride–mono(acetic acid) it has been demonstrated that the conductivity of the complex arises from transport of current in the melt by hydrogen and acetoxytrifluoroborate ions. Furthermore, it has been found that the solid complex conducts electricity appreciably. For example, at 27·4°, the conductivity of the solid is $\kappa = 1{\cdot}9 \times 10^{-5}$ ohm^{-1} cm.$^{-1}$, indicating that it is, at least, partly ionized. The conductivity of the liquid at the same temperature is $\kappa = 1{\cdot}40_5 \times 10^{-3}$ ohm^{-1} cm.$^{-1}$, which gives a value of ~70 for the ratio κ_l/κ_s. Such increases in the conductivity of ionic conductors at the melting point have been ascribed to the large increase in the number of conducting entities on melting, and to the expansion in volume on fusion which reduces the activation energy for migration of the ions (see, *e.g.*, Ubbelohde, *Quart. Reviews*, 1950, **4**, 356). The volume change on fusion, $\Delta V/V_s$, in the present case is ~0·06 at the melting point but, as Ubbelohde has pointed out, correlation of this quantity with the structural and constitutional changes which occur on melting is not easy.

The variation, with temperature, of the conductivity of liquid boron trifluoride–mono(acetic acid) shown in the figure may arise from several factors. This necessitates the use of a "reduced" conductivity function for comparison purposes. The molar conductivity, $\mu = M\kappa/d$, effects a correction for density variations, and ensures that the conductivity is referred to a standard state in which there is always 1 mole of compound between electrodes 1 cm. apart. Values of this function for boron trifluoride–mono(acetic acid) are tabulated in the third column of Table I, where it is seen that a steady increase in molar conductivity occurs with rise in temperature. This may be caused by a corresponding increase in both the number and the mobility of ions in the melt. As ionic mobilities in pure liquids cannot be readily determined, the effect of this factor on the molar conductivity cannot be accurately assessed. However, an estimate may be made by assuming that ionic mobility in a medium of viscosity η is inversely proportional to η. In this way the molar conductivity is reduced to a standard of unit viscosity. The corrected function, $\mu\eta = M\kappa\eta/d$, will be termed the " reduced " conductivity and denoted by the symbol $\mathfrak{K}$. Values of the reduced conductivity of boron trifluoride–mono(acetic acid) at different temperatures are tabulated in the fourth column of Table I. The reduced conductivity at 25·0° is 5·06 ohm^{-1} cm.^{2} cp, and it is seen that increase in temperature effects a gradual linear decrease in the function, until at 45·1°, the value of $\mathfrak{K}$ is 4·55 ohm^{-1} cm.^{2} cp. It is significant that a mobility correction of this kind reduces an increase of 150% in the molar conductivity of the compound to a decrease of only 10% in the function $\mathfrak{K}$, in the temperature range studied. This implies that the observed increase with temperature of the specific conductivity arises primarily from increased mobility of the ions, and not from enhanced ionization of the complex.

An interesting feature of the conductivity results is that a plot of log κ against the reciprocal of the absolute temperature is accurately linear above the melting point. This indicates that the conductivity obeys an exponential law of the form, $\kappa = \kappa_0 e^{-E_\kappa/RT}$, where E_κ is the activation energy for ionic migration. A least-squares evaluation of the experimental points, above 37·5°, leads to the relation: $\log \kappa = 2{\cdot}530 - 1612{\cdot}3/T$, so that $\kappa_0 = 339$ ohm^{-1} cm.$^{-1}$ and $E_\kappa = 7{\cdot}38$ kcals.mole^{-1}. For the supercooled complex, the $(\log \kappa)$–$1/T$ curve is slightly concave to the conductivity axis, and the energy of activation for ionic migration is ~12% higher, having a mean value between 25° and 37·5° of 8·4 kcals. mole^{-1}. The discontinuity in slope of the $(\log \kappa)$–$1/T$ relation, in the range 25—45°, occurs in the region of the melting point.

This behaviour is paralleled by that of the viscosity of the compound. Both the kinematic and the dynamic viscosity vary exponentially with temperature, and discontinuities in the [log (viscosity)]–$1/T$ curves are observed near the melting point. The viscosity equation above 37·5° was evaluated by the method of least squares to be $\log \eta = -4{\cdot}597 + 1862{\cdot}1/T$. From this the activation energy for viscous flow was calculated to be $E_\eta = 8{\cdot}52$ kcals. mole^{-1}. The corresponding activation energy for glacial acetic acid is $E_\eta = 1{\cdot}93$ kcals. mole^{-1} (cf. Ward, *Trans. Faraday Soc.*, 1937, **33**, 88) so that co-ordination to boron trifluoride in equimolar proportions increases this quantity more than fourfold. The points for the supercooled liquid fall on a curve slightly concave to the viscosity axis. Again the activation energy below the melting point is considerably higher, having a mean value of ~11 kcals. mole^{-1}.

It is interesting that the activation energies for ionic migration and for viscous flow are of the same order of magnitude. This indicates that the configurational changes involved in ionic migration and viscous flow are similar, and suggests that free protons in the melt are solvated by molecules of the complex :

$$2BF_3,CH_3\cdot CO_2H \longrightarrow BF_3,CH_3\cdot CO_2H_2^+ + BF_3,CH_3\cdot CO_2^-$$

Because of the similarity in size and shape of these ions, the activation energies of the two processes would not be expected to differ greatly.

EXPERIMENTAL.

The preparation and purification of boron trifluoride–mono(acetic acid) was outlined in Part II of the present series.

Electrical conductivity was measured at 1000 cycles A.C. with a Wheatstone network as described in Part I. A modified Ostwald U-tube viscometer was employed for viscosity determinations. The time of efflux (t) varied between 250 and 620 secs. and was related to the viscosity by the relation $\nu = Ct - ct^{-1}$. The constant C was determined by comparing the times of outflow in this instrument with those in the viscometer described in Part I. *o*-Toluidine was used as the comparison liquid, and C had the value $4\cdot909 \times 10^{-3}$ centistokes sec.$^{-1}$. Kinetic-energy corrections were effected by the term containing the constant c, which was 2·4 centistokes sec. for the instrument used.

The temperature variation of density of the compound was determined by using a Pyrex glass pyknometer of standard design. The capacity of the bulb was ~9 ml., and the capillary had a uniform bore of diameter $2\cdot00 \pm 0\cdot01$ mm. The length of the capillary was ~20 cm., and the pyknometer was capped by a B7 ground joint to prevent access of moisture. Readings of the meniscus level with respect to a fiducial line etched on the capillary were made to ±0·02 mm. by means of a cathetometer. The portion of the pyknometer outside the thermostat was heated slightly to prevent distillation of the complex to cooler portions of the instrument. Standard buoyancy corrections were made, and the thermal expansion of the glass taken into account. Thermostatic control for all measurements was similar to that described previously.

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UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE.

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