The Conductivity of Anhydrous Aluminium Bromide in Ethyl Bromide Solution.

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The conductivity of aluminium bromide in dry ethyl bromide solution, at 25°, has been measured in a totally enclosed system. The molar conductivity is of the order of 10^{-2} to 10^{-1} mho, most of which is due to the ionic dissociation of the aluminium bromide, probably into solvated $AlBr_2^+$ and $AlBr_4^-$. The conductivity of the solutions increases steadily with time, owing to the decomposition of the ethyl bromide–aluminium bromide complex into olefin and hydrogen bromide.

One piece of evidence which is frequently cited in support of the ionisation of an organic halide by an aluminium halide is the electrical conductivity shown by solutions of aluminium bromide in ethyl bromide, especially through the measurements of Wertyporoch (*Ber.*, 1931, **64**, 1369). Whilst denying neither the fact of the conductivity nor the concept of the ionisation, we felt that there was some doubt as to whether the conductivity was indeed experimental evidence of the ionisation of the ethyl bromide.

Since the experimental details and final results given by Wertyporoch (*loc. cit.*) do not indicate that any rigorous precautions had been taken to exclude traces of moisture, and since later work has so clearly emphasised the importance of this in all work with aluminium halides, the conductivity of anhydrous aluminium bromide in dry ethyl bromide has now been measured in a closed system, under strictly anhydrous conditions and over a greater range of concentrations. The results show a number of features which differ from those recorded by Wertyporoch.

Wertyporoch records that in dilute solution (up to 1·5% of $AlBr_3$) the conductivity rose with time, attaining a limiting value, in 30—45 minutes, of up to five times the initial value. In solutions containing about 5% of $AlBr_3$ the maximum was reached, at about 1½ times the initial value, after 10 minutes, whilst in 10% solution the final value was reached immediately. The final values of the molar conductivities were almost independent of the concentration.

In the present work, which covered a range of concentrations from 0·34 to 15·9% by weight of aluminium bromide, the conductivity in the freshly prepared solutions was less (by a factor of 1½—2 in equivalent concentrations) than that recorded above, whilst the increase was much slower and smaller in amount, provided that the solution was rigorously dry. In one solution (1·1% of $AlBr_3$) the rise of conductivity was followed for six days without reaching a limiting value. Examination of solutions which had been allowed to stand showed the presence both of free hydrogen bromide, which could be volatilised off with the ethyl bromide, and of unsaturated compounds in the liquid. It seems most probable that this increase in conductivity is chiefly due to the hydrogen bromide which originates from the decomposition of a C_2H_5Br–$AlBr_3$ complex, evidence for the formation of which has been given by Brown and Wallace (*J. Amer. Chem. Soc.*, 1953, **75**, 6279). The instability of solutions of aluminium bromide in ethyl bromide has been noted by other workers; *e.g.*, Brown and Wallace (*loc. cit.*) were unable to determine the molecular weight of the solute by vapour-pressure lowering, on account of the slow evolution of hydrogen bromide. They state, however, that their solutions were yellow, as were also those described by Wertyporoch. In the present work all solutions for which results are recorded were colourless : in fact, the absence of colour may be used as a criterion of purity. In a few other experiments, when probably by some accident the drying had been insufficient, the colour was yellow. In these solutions the initial conductivity was slightly greater and increased much faster than in the colourless solutions : these results are not recorded. Since, under these conditions, the hydrolysis of aluminium bromide is very slow (Fairbrother and Frith, *J.*, 1953, 2975) and in any case the amount of water initially present would be too small to account for the hydrogen bromide, it seems that the decomposition of the carbonium ion complex, $C_2H_5^+AlBr_4^-$, is catalysed by a trace of moisture.

EXPERIMENTAL

Ethyl bromide was purified by a method similar to that used by Smith (*J.*, 1931, 2573). A commercial product was mechanically shaken with cold concentrated sulphuric acid for several days, washed, and dried, first with calcium chloride and then with lithium hydride, and fractionated through a Fenske column; it then had b. p. 37·7°/746 mm. Aluminium bromide was prepared by direct synthesis from the elements, refluxed over aluminium turnings until all trace of colour had disappeared, distilled, and purified by seven sublimations *in vacuo*, at the end of which it was transferred, whilst still *in vacuo*, into fragile hook-ended ampoules.

The conductivity cell is shown in Fig. 1. The electrode assembly *E* consisted of two bright platinum plates, 2 × 2 cm., and 0·5 mm. thick, spaced about 2 mm. apart by fused glass beads. Several electrode assemblies were used during the work, the cell constants (by KCl calibration) varying between 0·0330 and 0·0449. The resistance of the solution did not vary with the amount of solution in the cell, provided this exceeded about 50 c.c.

The cell was constructed of Pyrex glass, the stout platinum electrode connections being sealed through short lengths of soda-glass which in turn were sealed to the Pyrex glass by graded seals. This quite overcame the difficulty of vacuum-tight seals associated with platinum sealed through Pyrex glass.

The cell was thoroughly evacuated and out-gassed through *C* which was then sealed, and cooled to −78°, pure aluminium bromide then being sublimed into it, without residue, from the weighed ampoule *A*. The tube *B* containing the broken fragments of the ampoule was removed at *D*. Dry ethyl bromide vapour was then admitted through *F* until about 50 c.c. of ethyl bromide (which is still liquid at −78°) had collected about the electrode assembly. After being sealed off at *F*, the cell was removed from the carbon dioxide bath and lowered into position in a large, well-stirred, water-thermostat at 25°, and the magnetic stirrer *S* rotated by a magnet outside and below the thermostat. The sequence of operations, from removal from the cooling bath to the completion of the first measurement, was timed and averaged about 4 min.

Resistance measurements were made, at 1000 c.p.s., with the usual a.c. Wheatstone's bridge and a visual null-point indicator. The latter was a highly sensitive modification of that described by Hazseldine and Woolf (*Chem. and Ind.*, 1950, 544) with a discrimination of the order of 1 in 10,000. Since both resistance and capacity out-of-balance were indicated separately by this arrangement, it could be observed that no polarisation difficulties were encountered by the use of bright platinum electrodes.

Readings of the resistance were made every 1—2 min. over a period of 30 min. After the first 8—10 min., which were required for attainment of temperature and composition equilibrium, the decrease of resistance with time became linear, which greatly facilitated extrapolation to zero time of preparation. This was taken as half way between the time of removal of the cell from the cooling mixture and the time of the first measurement; experiment showed that there was no variation of resistance over several minutes at −78°. The decrease in resistance during the first 30 min. varied between 0·069 and 0·255 of the average value for the period. The values recorded are those at zero time of mixing, obtained by extrapolation.

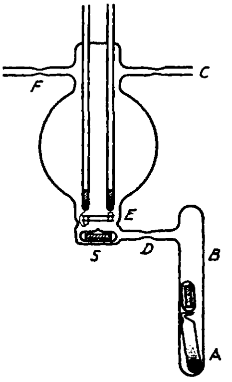


FIG. 1. *The conductivity cell.*

FIG. 2. *Molar conductivities of aluminium bromide–ethyl bromide solutions.*

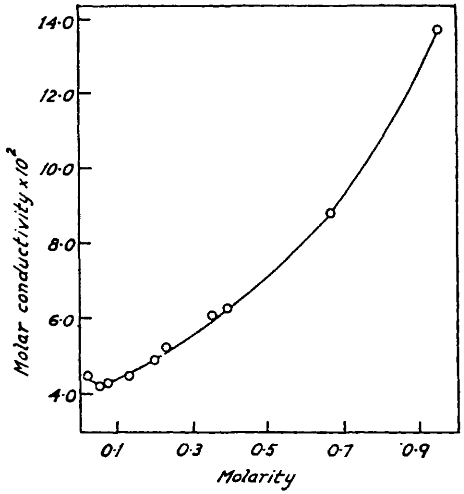
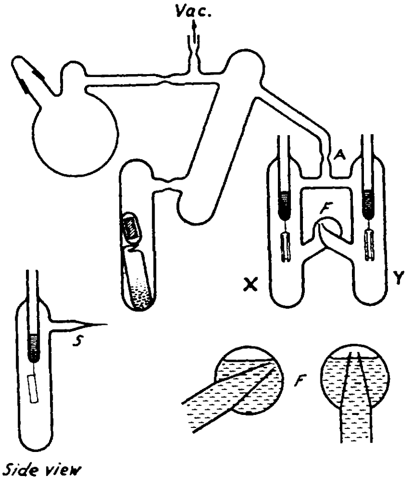


FIG. 3. *Apparatus for transport experiments.*



The weight concentrations of the solutions were obtained from the weight of aluminium bromide in the sealed ampoule and the weight of the electrode vessel empty and containing the solution. The volume concentrations (for the calculation of molar conductivities) were obtained from these with the aid of a separate series of pycnometric determinations of the densities of aluminium bromide–ethyl bromide solutions. The latter incidentally showed that aluminium bromide (d_4^{25} 3·01) dissolves in ethyl bromide with less than 1% contraction in total volume over this range.

The weight percentages (g. of $AlBr_3$/100 g. of solution) and specific conductivities are given in the following table. The molar conductivities are shown in Fig. 2.

$AlBr_3$, g./100 g. of soln.	0·3414	0·9361	1·285	2·339	3·570	4·094	6·246	6·899	11·44	15·90
Spec. conductivity (mho) × 10^5	0·084	0·216	0·302	0·578	0·972	1·19	2·14	2·45	5·85	13·0

Jacober and Kraus (*J. Amer. Chem. Soc.*, 1949, **71**, 2405) observed that the molar conductivity of aluminium bromide in methyl bromide at 0° and at −78° is of the order of 2—3 × 10^{-2} mho, indicating an ionic dissociation of order 10^{-4}. In the present work the conductivity in ethyl bromide solutions of similar concentrations was found to be only slightly higher : it is therefore apparent that even the total ionic strength is very low. The form of the conductivity curve, with a clear minimum at about 0·04M (Fig. 2), is of the general type for a weak electrolyte in a solvent of low dielectric constant, discussed by Fuoss and Kraus (*ibid.*, 1933, **55**, 2387). Jacober and Kraus (*loc. cit.*) claim a minimum in the case of aluminium bromide–methyl bromide, though this is not obvious from the data given.

It has been pointed out previously (Fairbrother, *J.*, 1941, 293; 1945, 503) that a review of the thermal energies involved and of other experimental data suggests that, although a rapid exchange of halogen atoms can take place between an aluminium and an organic halide, probably by an ionic mechanism, yet the proportion of organic halide molecules which are ionised at any one instant, even as undissociated ion-pairs, may be very small.

It is therefore pertinent to enquire to what extent this small observed conductivity is a result of the ionic dissociation of a binary complex involving the organic halide, and to what extent it is due to the ionisation of the aluminium bromide.

With this end in view, a number of transport experiments were carried out in the apparatus shown in Fig. 3. This was constructed of Pyrex glass and was totally enclosed without stopcocks, thus avoiding any possible contamination by lubricants. The cell was filled *in vacuo* in much the same manner as the conductivity cell, up to calibration marks on the electrode vessels, and was then sealed at *A*. The amount of current passed was measured by a copper voltameter in series with the electrolysis cell. At the conclusion of an experiment the anode and cathode compartments, *X* and *Y*, were separated by tilting the apparatus, whereby the connection between them was broken at *F*, as shown in the insets. Dry nitrogen was admitted, and the contents of *X* and *Y* were removed through tubes at the rear as shown in the side view at *S*.

With the object of diminishing the rate of decomposition of the solutions, the electrolyses were carried out at −78°. During the long time of electrolysis (8 hr.), however, some decomposition probably occurred and the results could only be considered as semi-quantitative. Nevertheless, they showed a net transport of aluminium to the cathode and of bromine to the anode, with the anion the predominant carrier.

Van Dyke (*J. Amer. Chem. Soc.*, 1950, **72**, 3619) came to somewhat similar conclusions from a study of the electrolysis of aluminium bromide in methyl bromide at −78°. He obtained liberation both of aluminium at the cathode and of bromine at the anode, and suggested that the ionic species responsible for the conduction were Br^- and $AlBr_2^+$.

In the present work we observed neither free bromine at the anode nor metallic aluminium at the cathode. The absence of free bromine in the anode compartment may be the result of its reaction with the unsaturated species present, since ethyl bromide solutions are much less stable than methyl bromide solutions, even at the same temperature. Any free Br^- ions would most certainly be attached to the strongly acceptor aluminium bromide molecules. The absence of metallic aluminium on the cathode and the somewhat greater mobility of the anion are best explained in this case, not by the formation of Br^- and $AlBr_2^+$, but of $AlBr_4^-$ and $C_2H_5BrAlBr_2^+$, of which the latter would break up at the cathode into aluminium bromide and discharged carbonium ion, or olefin and hydrogen ion.

Measurements of the rise of boiling point (Wertyporoch, *loc. cit.*) and of lowering of vapour pressure (Van Dyke, *loc. cit.*; Brown and Wallace, *loc. cit.*) all indicate that aluminium bromide is present in ethyl bromide solution essentially as a monomer, whilst Brown and Wallace's phase studies show that, at all events below 0°, it is present as a 1 : 1 complex. These results do not exclude the formation of small concentrations of the conducting species $AlBr_4^-$ and $C_2H_5BrAlBr_2^+$. It is clear, however, that the process responsible for the conduction is principally the dissociation of the aluminium bromide rather than of a simple electrolytic dissociation of an ion-pair $C_2H_5^+$ $AlBr_4^-$ which would give a transport of aluminium to the anode.

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