CXIX.—*The Conductivity and Viscosity of Aqueous Solutions of Aniline Hydrochloride at 25°.*

By NEVIL VINCENT SIDGWICK and BERNARD HOWELL WILSDON.

IN connexion with the work described in the succeeding paper, we were led to determine the dissociation of aqueous solutions of aniline hydrochloride between decinormal and normal; and as the results seemed to have some intrinsic interest, the measurements were afterwards extended to stronger solutions.

The conductivity of aniline hydrochloride has been measured by various chemists, but always in very dilute solution, the object being to determine either the velocity of the anilinium ion, or the strength of the base by means of the hydrolysis of the salt (compare Bredig, *Zeitsch. physikal. Chem.*, 1894, **13**, 215; Walker, *ibid.* 1889, **4**, 335; Niementowski and Roszkowski, *ibid.*, 1897, **22**, 148; Lundén, *Med. från K. Vet. Nobelinst.*, 1907, **1**, 7, 4). We have not been able to find any measurements of solutions even as strong as decinormal. These stronger solutions, however, have an important bearing on the question of the relation between conductivity and viscosity. A solution saturated at 25° is more than four times normal, and has a viscosity nearly four times that of water.

Conductivity at Infinite Dilution.

This must be determined in presence of excess of aniline, in order to eliminate hydrolysis. Bredig (*loc. cit.*) found that the conductivity was the same in presence of $N/32$ - and $N/64$ -aniline, and hence assumed that the latter quantity was sufficient to render the hydrolysis inappreciable. He obtained at 25° $\mu_{\infty} = 113.5$. Lundén (*loc. cit.*), in presence of excess of aniline, the amount of which is not stated, obtained $\mu_{\infty} = 112.3$.

Our measurements were carried out in a cell of low resistance, having the electrodes sealed on to the glass cap. The cell contained the aniline solution, and the salt solution was added from a weight-pipette (the purification of the materials is described below). The cell was standardised with potassium chloride solutions of several different strengths. Two series of measurements were made, one with $N/58$ - and one with $N/22$ -aniline. The resulting values of μ were plotted against the square root of the concentration, and in both series gave a straight line within 1 part in 1000, from which

AQUEOUS SOLUTIONS OF ANILINE HYDROCHLORIDE AT 25°. 1119

the infinity value was obtained; the conductivity of the water, which is given in gemmhos, was subtracted. Temperature 25°.

I. Aniline $N/58$.
Water = 1·07 gemmhos.

V .	μ .
245·1	106·13
317·3	107·06
1377·0	110·51
∞	113·70

II. Aniline $N/22$.
Water = 1·20 gemmhos.

V .	μ .
191·4	104·15
478·0	107·22
680·3	108·06
1142·4	109·27
∞	112·70

These results show that a greater concentration of free aniline than was used by Bredig is necessary to eliminate hydrolysis completely. The value $\mu_{\infty} = 112·7$ was taken as correct.

Stronger Solutions: Viscosity and Conductivity.

The two properties were measured as far as possible with the same solutions. The aniline was purified by Hantzsch and Freese's method (*Ber.*, 1894, 27, 2966). It was dried over solid potassium hydroxide, and twice distilled. It passed over within 1° as a colourless liquid, with a distinct blue fluorescence. The hydrochloride was purified by repeated crystallisation from water, and was dried in a vacuum over potassium hydroxide and sulphuric acid. Analysis with silver nitrate showed it to contain the theoretical percentage of chlorine.

The solutions were made up by weight (in water of 0·8 to 1·3 gemmhos conductivity at 25°), and their composition checked by gravimetric analysis with silver. The densities were determined in a pycnometer of about 15 c.c. capacity, and the viscosities in two Ostwald viscometers of about three minutes period with water. In nearly every case the same solution was measured in both viscometers, and the results agreed to 2 parts in 1000, which about represents the limit of accuracy of this type of viscometer.

The conductivities were measured in a cell of the usual pattern, having the two electrodes widely separated. In order to eliminate hydrolysis, the water used for making the solutions contained $N/20$ -aniline. Three series of determinations were made, a fresh original solution being used for each.

In the following table three series are distinguished by the letters *A*, *B*, *C*. The second column gives the normality, the third the density, the fourth the molecular conductivity, and the fifth the viscosity. The density and viscosity are referred to water at 25° as unity.

1120 SIDGWICK AND WILSDON: CONDUCTIVITY AND VISCOSITY OF

Series.	Normality.	Density.	Molecular conductivity	Viscosity.	$\mu\eta$.	$\mu\eta^3$.
			$=\mu$.	$=\eta$.		
C.	4.1473	1.0970	21.69	3.648	79.14	51.40
C.	3.9182	[1.0921]	23.67	3.297	78.05	52.46
C.	3.4792	1.0827	27.74	2.784	77.22	54.90
C.	3.1149	[1.0752]	31.83	2.437	77.56	57.64
C.	2.7593	1.0685	35.65	2.156	76.86	59.50
B.	2.6608	1.0656	—	2.055	—	—
C.	2.1492	[1.0541]	42.61	—	—	—
B.	2.0470	1.0521	—	1.740	—	—
B.	1.4798	1.0383	52.26	1.498	78.28	68.42
A.	1.1807	1.0308	57.83	1.388	80.24	71.96
B.	1.1083	1.0297	58.59	1.363	79.87	72.02
A.	0.8447	1.0228	—	1.269	—	—
B.	0.8097	[1.0226]	64.90	1.261	81.81	75.63
A.	0.6222	1.0168	69.17	1.193	82.44	77.81
B.	0.6025	[1.0172]	69.70	1.195	83.29	78.49
A.	0.47573	1.0132	72.79	1.149	83.60	79.85
A.	0.36362	1.0107	—	1.118	—	—
A.	0.29308	1.0088	79.80	1.096	87.48	84.83
A.	0.19942	1.0065	84.00	1.070	89.87	87.87
A.	0.10536	1.0037	89.42	1.043	93.78	92.48

The values in brackets were obtained by interpolation.

The results are shown in the accompanying figure, in which the values of the products $\mu\eta$ and $\mu\eta^3$ are obtained from a series of points interpolated on the conductivity and viscosity curves.

It will be seen that the values of $\mu\eta$ attain a minimum at about $V=0.5$, and then on a further increase of concentration remain

nearly constant, with a slight tendency to rise. We can scarcely suppose that the further increase of concentration causes no diminution of dissociation; the true "intrinsic conductivity" must continually decrease with increasing strength, and hence the correction for viscosity in the expression $\mu\eta$ must be too great. If, however, we multiply by the two-thirds power of the viscosity, we get a regularly descending curve. A few values of α , the degree of ionisation, calculated on this latter assumption, are given below.

Normality.	$100 \alpha = \frac{100 \mu\eta^{\frac{2}{3}}}{\mu_{\infty}}$
0.1	82.35
0.5	70.82
1.0	65.21
2.0	56.56
3.0	51.78
4.0	46.34

It does not seem possible at present to establish any theoretical relation between ionic velocity and viscosity. It is a priori probable that some fractional power of the viscosity should be employed, since the viscosity due to the actual ion that is drifting under the potential gradient (which is part of the viscosity as measured in a viscometer) can hardly interfere with the motion of that ion. It is, however, quite possible that the proper index of η is itself a function of η , which approaches unity when η is small, but falls when it is large. Certainly our results indicate that when η is 2 or more, the index $\frac{2}{3}$ is more correct than 1; and this is in agreement with the work of Green (*Trans.*, 1908, **93**, 2023), who found the expression $\mu\eta^{0.7}$ to agree best with experiment for variations of η in the ratio 1:25.

It is to be remembered that at the point where $\mu\eta$ reaches a minimum, the percentage of salt is high (about 26 per cent.). At still higher concentrations a variety of disturbing factors may come in, which might possibly cause an abnormal increase in conductivity, especially the formation of complex ions, and the diminished hydration of the ions, owing to the fall in the concentration of the water. The diminution of hydration, if it occurs at all, must lead to an increase in ionic velocity, and therefore in conductivity; the formation of complex ions will only do so if these ions have a greater velocity than the simple ions, which we should scarcely expect. At any rate, a correction of the conductivity for the viscosity alone, whatever function of the latter may be used, can at best be only an approximation to the truth.

Bousfield (*Phil. Trans.*, 1906, **206**, A, 103) considers that the velocity is inversely proportional to the whole power of the viscosity, and to the radius of the ionic envelope, which latter he

derives on certain assumptions from the solution volume. We have calculated the dissociation constant of aniline hydrochloride on his hypothesis from our results, and find that it rises from 796 in the most dilute solution to 928 in the strongest. It therefore seems unnecessary to give the results of the calculation in full. The values obtained for α on this hypothesis are of the same order as those calculated by Bousfield for other strong electrolytes, such as sodium and potassium hydroxides.

DAUBENY LABORATORY,
MAGDALEN COLLEGE, OXFORD.