

**364.** *The Dielectric Polarisation of Hydrogen Chloride in Solution. Part II. Benzene, Ethyl Bromide, and Ethylene Dichloride as Solvents.*

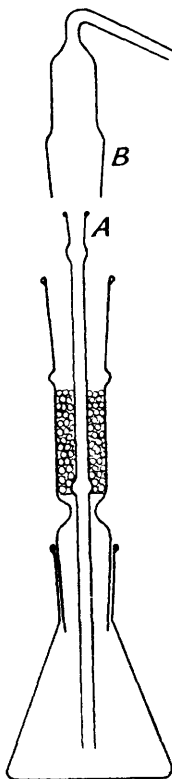
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IN a previous communication (J., 1932, 43), it was shown that the dielectric polarisability of hydrogen chloride in solution in benzene, cyclohexane, and carbon tetrachloride due to the electric moment of the molecules was more than 50% greater than in the gaseous state, leading to an apparent value of the electric moment of approximately  $1.3 \times 10^{-18}$  e.s.u. Those experiments have now been extended to include ethyl bromide and ethylene dichloride as solvents, and, with several improvements in technique, a further series of measurements in benzene has also been carried out.

Benzene (Kahlbaum's benzene "for analysis and molecular-weight estimations") was dried over purified phosphoric oxide and distilled. Ethyl bromide and ethylene dichloride (commercial products) were shaken with concentrated sulphuric acid, washed, dried, and fractionally distilled; b. p.'s 38.2—38.3°/760 mm. and 82.6—82.8°/743 mm. respectively. Samples of each gave no opalescence when tested with silver nitrate solution.

Each solvent was kept in the apparatus, in contact with purified phosphoric oxide for 4 or 5 days before distillation into the absorption vessel. The dielectric constants and densities of the solutions were measured as previously (*loc. cit.*), the method of correction for the inductance of the leads being more fully discussed elsewhere (Fairbrother, *Proc. Roy. Soc.*, 1933, A, 142, 173). The preparation and manipulation of the solutions were essentially the same as in Part I, with the following modifications. The hydrogen chloride was formerly passed over phosphoric oxide: in view of the possibility that this might have led to contamination of the solutions by phosphoryl chloride (compare preceding paper), phosphoric oxide was only used in the present work as a drying agent for the solvents. Hydrogen chloride was prepared by dropping pure sulphuric acid on A.R. ammonium chloride, passed through tubes filled with resublimed aluminium chloride, and condensed in a liquid-air bath. From this, it was fractionally evaporated, the most volatile two-thirds being passed into the solvent contained in an absorption vessel of the type previously described. The purified solvents were stored over the purified phosphoric

oxide in a separate flask, from which they were forced by compressed air, *via* a fine sintered-glass filter, into the distillation flask: this procedure avoided the possibility of any volatilisation of the phosphoric oxide during distillation. The solutions were varied in concentration either by the distillation of additional solvent into the more concentrated solutions or by removal of hydrogen chloride by a current of dry air. The solutions were forced into the condensers and pycnometer by air pressure as before, aluminium chloride, however, being used in the guard tubes instead of phosphoric oxide. A platinum plate condenser (*Proc. Roy. Soc., ibid.*), of about 215  $\mu\text{F}$  capacity when filled with dry air, was used for the solutions in benzene, and a silver plate condenser similar to that used in Part I, but of about 67  $\mu\text{F}$  capacity when filled with dry air, for the other solutions. Each condenser was fitted to the rest of the glass apparatus during filling by an interchangeable ground joint, and was then closed by ground caps and removed to the thermostat for the measurement of the dielectric constant. The estimation of the hydrogen chloride content of the benzene solutions was carried out with the aid of the apparatus shown in the fig.



The ground socket *A* fitted the end of one limb of the pycnometer which was, after the estimation of the density of a solution, inverted into *A* and the weighed contents blown into excess of 10% sodium hydroxide solution, free from chloride, contained in the flask below. The glass beads in the upper portion of the apparatus were also wetted with the alkali, which was then washed down into the flask. The outer ground joint *B* was provided in order that the solvent could be distilled away and collected. It was found more convenient, however, to remove the benzene by warming the flask and blowing filtered air through *A*. In this way, loss of hydrogen chloride was completely avoided, which is difficult of accomplishment when the solution is run on to the top of the alkali, even though the flask be stoppered immediately. The solutions in ethyl bromide and ethylene dichloride, which were heavier than water, were simply run from the pycnometer below the surface of solutions of A.R. sodium carbonate and sodium bicarbonate respectively. Sodium hydroxide was not used in these cases on account of the possible hydrolysis of the solvent. In all cases after evaporation of the solvent, the chloride content of the aqueous solution was estimated gravimetrically as silver chloride.

In the previous calculations of the electric moment of the hydrogen chloride, an allowance of 1.2 c.c. was made for the atom polarisation. Since there is some doubt as to the validity of this value (compare Part I), the sum of the atom and electronic polarisations ( $P_a + P_e$ ) will be taken as equal to 6.6 c.c., from the refractivity of the gas. (In view of the results of the refractive index measurements given in Part I, the refractive indices of the present solutions were not measured.) Any error arising from this procedure will hardly be greater than that introduced by the experimental uncertainty. The measurements described in Part I were made at 25°, but the present measurements were all made at 20.0°. The results are given in the table, in which the symbols have the same significance as in Part I,  $P_{2\infty}$  being taken simply as the average value of  $P_2$ , since any dependence of the latter on the concentration is clearly less than the experimental error.

Benzene.					Ethyl bromide.				
$f_2$ .	$\epsilon$ .	$\rho$ .	$P_{12}$ , c.c.	$P_2$ , c.c.	$f_2$ .	$\epsilon$ .	$\rho$ .	$P_{12}$ , c.c.	$P_2$ , c.c.
0.0000	2.282	0.8786	26.60	—	0.0000	9.449	1.4564	55.20	—
0.03621	2.358	0.8803	27.12	41.0	0.02253	9.478	1.4522	54.61	29.0
0.03185	2.349	0.8802	27.06	40.9	0.01737	9.481	1.4542	54.73	27.7
0.02453	2.332	0.8798	26.94	40.4	0.009698	9.477	1.4556	54.94	28.3
0.01410	2.311	0.8793	26.81	40.9	0.007507	9.486	1.4564	55.00	29.0
0.00882	2.301	0.8791	26.74	41.6					
$P_{2\infty} = 41.0$ c.c.; $P_a + P_e = 6.6$ c.c.; $\mu = 1.26 \times 10^{-18}$ e.s.u.					$P_{2\infty} = 28.5$ c.c.; $P_a + P_e = 6.6$ c.c.; $\mu = 1.02 \times 10^{-18}$ e.s.u.				
Ethylene dichloride.									
0.0000	10.580	1.2546	60.06	—	0.01729	10.574	1.2533	59.47	26.2
0.02463	10.561	1.2521	59.24	26.8	0.01666	10.580	1.2533	59.50	26.6
0.01936	10.571	1.2528	59.41	26.9					
$P_{2\infty} = 26.6$ c.c.; $P_a + P_e = 6.6$ c.c.; $\mu = 0.97 \times 10^{-18}$ e.s.u.									

The results for the solutions in benzene are in excellent agreement with those previously obtained, being experimentally hardly distinguishable from them, and are good evidence that no serious contamination of the hydrogen chloride by phosphoryl chloride had taken place.

The results for the solutions in ethyl bromide and in ethylene dichloride, on the other hand, lead to values of the electric moment which are almost the same as those obtained by Zahn for gaseous hydrogen chloride, *viz.*,  $1.03 \times 10^{-18}$  e.s.u. (*Physical Rev.*, 1924, 24, 400). The Debye equation on which the calculations are based only holds strictly for measurements in the vapour state or in very dilute solution in a non-polar solvent. When the solvent molecules are as polar as those of the solute, or more polar, as in the solutions in ethyl bromide and ethylene dichloride, the equation can only be roughly true. A closer agreement with the value for the moment in the gaseous state could not therefore be expected.

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