CCLXXXVII.—*Hydrochloric Acid Solutions of Iodine Monochloride.*

By Frederick Arthur Philbrick.

The stability of solutions of iodine monochloride in hydrochloric acid has commonly been attributed to the formation of a complex $HICl_2$ or ICl_2'. That they contain no iodine monochloride as ICl appears certain from the fact that carbon tetrachloride shaken with them, as in Andrews' titration, remains colourless, though iodine monochloride is soluble in carbon tetrachloride and gives solutions as strongly coloured as those of iodine. This fact might equally well be explained by assuming complete dissociation into $I^{\bullet}$ and Cl', and if this view is correct the addition of iodine monochloride to hydrochloric acid will raise the chloride-ion concentration, whereas if complex formation takes place it will reduce it : the object of the work now described was to decide between these views. Apart from its intrinsic interest, this appears to be an indispensable preliminary to the determination of the equilibrium constant of the reaction usually denoted by

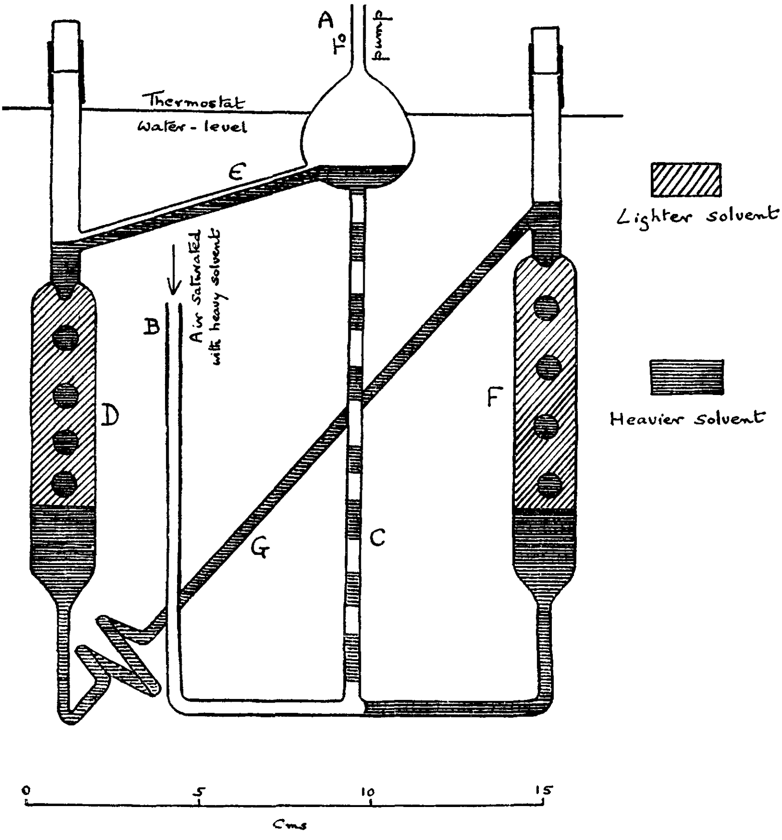
$$IO_3' + 2I_2 + 6HCl \rightleftharpoons 5ICl + Cl' + 3H_2O$$

and now of considerable importance in volumetric analysis.

The method selected was to compare the solvent power of the solutions on iodine with that of hydrochloric acid. The solubility of iodine in hydrochloric acid at 25° has been measured by Rây and Sarkar (J., 1922, **121**, 1449), and the work of Carter and Hoskins (J., 1929, 580), which was carried to hydrochloric acid concentrations of about $7N$, confirms their results. A study of the combined data shows that the solubility of iodine in millimoles per litre can be closely represented by the expression $2{\cdot}54a + 1{\cdot}36$, where a is the concentration of hydrochloric acid in moles per litre of solution. This linear relation follows from the constancy of the expression $[Cl'][I_2]/[ClI_2']$, since $[ClI_2']$ can be neglected in comparison with $[Cl']$. The distribution coefficient of iodine between hydrochloric acid and carbon tetrachloride at 25° has also been measured by Rây and Sarkar (*loc. cit.*), who found it to be only slightly dependent on the iodine concentration. Consequently the distribution coefficient of iodine between two hydrochloric acid solutions of concentrations a_1 and a_2 is $(2{\cdot}54a_1 + 1{\cdot}36)/(2{\cdot}54a_2 + 1{\cdot}36) = (a_1 + 0{\cdot}54)/(a_2 + 0{\cdot}54)$, and this relation can be used to measure chloride-ion concentrations in comparison with those prevailing in concentrated hydrochloric acid.

The solutions were prepared from potassium iodate, iodine, and hydrochloric acid, and comparison solutions were prepared containing equal concentrations of hydrochloric acid and potassium chloride but no iodine monochloride; the distribution coefficient of iodine between each pair of solutions was then measured by bringing both of them into equilibrium with the same solution of iodine in carbon tetrachloride. By this method there is automatic compensation for the presence of potassium chloride and also for any possible effect of carbon tetrachloride dissolved in the water layer. The apparatus finally adopted is shown in Fig. 1. Suction is applied to A and pure air saturated with the vapour of the heavier solvent is admitted at B. The heavier solution is carried up C and falls in drops or a thin stream through one of the aqueous solutions confined in D, is forced through G, falls through the comparison solution in F, and returns to C. When equilibrium has been reached, the stoppers are removed and the aqueous solutions in D and F withdrawn for analysis. In these experiments the apparatus and the air train were immersed in an 85-litre electric thermostat at 25°.

Fig. 1.

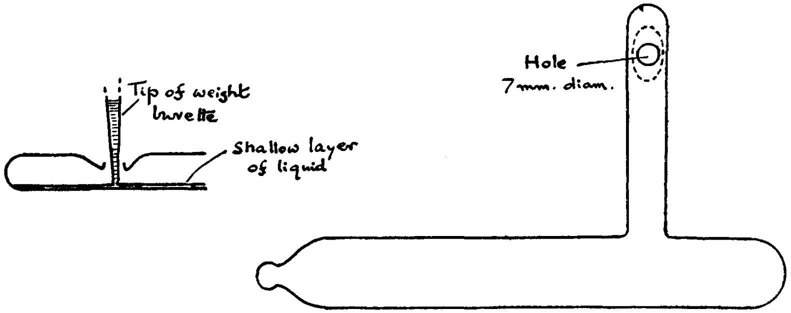


The three-liquid distribution apparatus.

Direct experiment showed that the air entering the apparatus was saturated with carbon tetrachoride vapour and also that the loss of iodine by volatilisation was negligible. Equilibrium is reached in an hour, but the time allowed was never less than 2 hours and ample time was allowed for the solutions to settle. On withdrawal they were sealed up and allowed to cool before analysis with potassium iodate by Andrews' method.

Since only two 5 c.c. portions of each solution, each containing from 1 mg. upwards of free iodine, were available for analysis, a titration vessel was designed to avoid the many disadvantages of the reagent bottle commonly recommended. In this vessel (Fig. 2) the tip of the weight burette can be brought into contact with the liquid to be titrated, so that one drop is no longer the smallest quantity of solution which can be added at a time, while no more than 0·3 c.c. of carbon tetrachloride is needed to indicate the end-point—a great gain in sensitivity. Additions are made while both limbs are horizontal and a shallow layer of liquid covers the floor of the side-tube; if the vessel is then shaken lengthways with the wide tube horizontal and the side-tube vertical, not a drop can be lost, but the final volume of the solution must not exceed half the capacity of the vessel. At the end of the titration the vessel is tipped so that the carbon tetrachloride runs into the small bulb, which it should just fill, and its colour is then viewed in diffused daylight against a white background. The solution to be titrated can be weighed into the titration vessel, which may be closed by a rubber stopper (Foulk and Morris, *J. Amer. Chem. Soc.*, 1922, **44**, 221) if the liquid contains free iodine, but in these experiments standardised pipettes were used. The vessel is very suitable for the estimation of from 0·5 to 5 mg. of iodine with thiosulphate : a trial analysis showed that 3 mg. can be estimated in this way with an accuracy of 0·1% (Taken: 3·077 mg. Found: 3·075, 3·073, 3·075 mg. of iodine). The accuracy by Andrews' method is, however, considerably less, and the concordance of the analyses on which this work is based averaged 0·5%.

FIG. 2.



Titration vessel for iodine.

At least two batches were prepared of all the materials, and the solutions were made independently. The potassium iodate (British Drug Houses A.R.) was twice recrystallised, and gave 99·9% on analysis. The potassium chloride was prepared by heating twice recrystallised potassium perchlorate in a fused silica crucible. The iodine was resublimed from potassium iodide and quicklime. The carbon tetrachloride was purified by the action of iodine monochloride, as recommended by Serra (*Gazzetta*, 1899, **29**, ii, 353). The hydrochloric acid (pure B.P.) was used without purification. All the materials were tested for purity by the usual methods and with satisfactory results.

The iodine monochloride solutions were made up by weighing potassium iodate and iodine (slightly in excess) into a standard flask, adding water, then a known volume of concentrated hydrochloric acid gradually and with constant cooling and the usual precautions, and filling the flask up to the mark the next day. There is no loss of chlorine by this method.

The results are in the table. The solutions more concentrated in iodine afford the best basis for calculation, since the expression for the distribution ratio is derived from measurements on saturated solutions. Let a_1 and a_2 be the concentrations of hydrochloric acid with the same chloride-ion concentrations as the iodine monochloride solutions; then (a_1 + 0·54)/(2·85 + 0·19 + 0·54) = 1·220 and (a_2 + 0·54)/(7·03 + 0·19 + 0·54) = 1·150, whence a_1 = 3·83 and a_2 = 8·38. The iodine monochloride has therefore raised the chloride-ion concentrations by 3·83 − 2·85 − 0·19 = 0·79 and 8·38 − 7·03 − 0·19 = 1·16 respectively, and the degree of ionisation of the iodine monochloride compared with that of the hydrochloric acid is 0·79/0·962 = 82% and 1·16/0·962 = 120·5%. That is, an approximately molar solution of iodine monochloride in 3*N*-hydrochloric acid is about 80% as fully dissociated as the acid, and in 7*N*-acid is considerably more dissociated than the acid. A more exact statement might be made in terms of activities, but in the absence of values for the chloride-ion activities serves little purpose; it is better to restrict the conclusions to the statement that

Chloride concentration of solutions (moles per litre).		Titratable iodine (millimoles per litre).		
ICl solution.	Comparison solution.	ICl solution.	Comparison solution.	Distribution ratio.
ICl, 0·962 HCl, 2·854 KCl, 0·192	ICl, none HCl, 2·854 KCl, 0·192	1·047	0·851	1·23(0)
		1·159	0·945	1·22(7)
		2·361	1·936	1·22(0)
		4·93	4·04	1·22(0)
ICl, 0·962 HCl, 7·03 KCl, 0·192	ICl, none HCl, 7·03 KCl, 0·192	2·530	2·194	1·15(3)
		4·37	3·80	1·15(0)
		7·97	6·93	1·15(0)

in hydrochloric acid solution iodine monochloride is a highly dissociated electrolyte. This conclusion is merely strengthened by any salting-out effect which the monochloride may have on iodine: the salting-out effect of hydrogen chloride is negligible (Carter and Hoskins, *loc. cit.*).

If $HICl_2$ or ICl_2' can exist at all in water, it should certainly be found in a solution nearly molar in iodine monochloride and 7*N* in hydrogen chloride, but the measurements leave no room for either undissociated monochloride or any compound of it with hydrochloric acid. Schützenberger (*Compt. rend.*, 1877, **84**, 389) claimed to have extracted $HICl_2$ from the acid solution with ether, but his product probably retained ether, which itself combines with hydrogen chloride. Sullivan (*Z. physikal. Chem.*, 1899, **28**, 523) considered that he had obtained evidence for complex formation, but his results appear on the whole to point to ionisation, whose possibility he did not discuss. The freezing-point measurements, on which he chiefly relied, were made with solutions which had not reached equilibrium and were slowly precipitating iodine, while, as he himself admits, the concordance of the results was unsatisfactory. He also found that the addition of iodine monochloride to solutions of the alkali-metal chlorides raised the electrical conductivity, a result most difficult to account for on the hypothesis of complex formation, and an experiment with acid solutions showed the iodine monochloride to have approximately the same equivalent conductivity as the dilute hydrochloric acid in which it was dissolved.

The ionisation of iodine monochloride in aqueous solution, in sharp contrast with the behaviour of iodine or bromine, strikingly confirms Fajans' view that the formation of electrovalencies is promoted by a large kation and a small anion (see, for instance, Sidgwick, "The Electronic Theory of Valency," p. 104). Since the valency shell of $I^{\cdot}$ contains only six electrons, it is to be expected that donor solvents will promote ionisation of the monochloride, and of this there is abundant evidence: it is a good conductor in ether (Solly, *Phil. Mag.*, 1836, **8**, 130, 400), dichloroacetic acid (Plotnikov, *Chem. and Ind.*, 1923, **42**, 750), sulphur dioxide, sulphuryl chloride, and above all in the pre-eminently donor solvent arsenic trichloride (Walden, *Z. physikal. Chem.*, 1903, **43**, 385).

The stability of iodine trichloride in hydrochloric acid can be accounted for in the same way, and there is similar evidence that the trichloride is ionised in non-aqueous solvents. The first to suggest the dissociation $ICl_3 \rightleftharpoons ICl_2^{\cdot} + Cl'$ appears to have been Oddo (*Gazzetta*, 1901, **31**, ii, 146, 151). Since in the ion $ICl_2^{\cdot}$ all three atoms have their full octets, it is not to be expected that the donor qualities of the solvent should have the same importance for the ionisation of the trichloride as for that of the monochloride, and while Walden found that in arsenic trichloride the equivalent conductivity of iodine trichloride was only some 4% of that of iodine monochloride under the same conditions, the cryoscopic measurements of Bruner and Galecki (*Z. physikal. Chem.*, 1913, **84**, 513) show that in nitrobenzene iodine trichloride is considerably dissociated but iodine monochloride is scarcely dissociated at all.

Summary.

1. An apparatus is described for circulating a heavy solvent between two lighter ones.
2. A description is given of a vessel for the micro-titration of iodine with which 3 mg. can be estimated with an accuracy of 0·1%.
3. Experiments on the distribution of iodine between hydrochloric acid and hydrochloric acid solutions of iodine monochloride show the latter to be highly ionised in aqueous solution. It is pointed out that this confirms modern views on the formation of electrovalencies. There is no evidence for the existence of $HICl_2$ or its anion in solution.
4. The dissociation of iodine monochloride and trichloride in non-aqueous solvents supports this conclusion.

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