48. *The Distribution of Nicotine between Trichloroethylene and Water.*

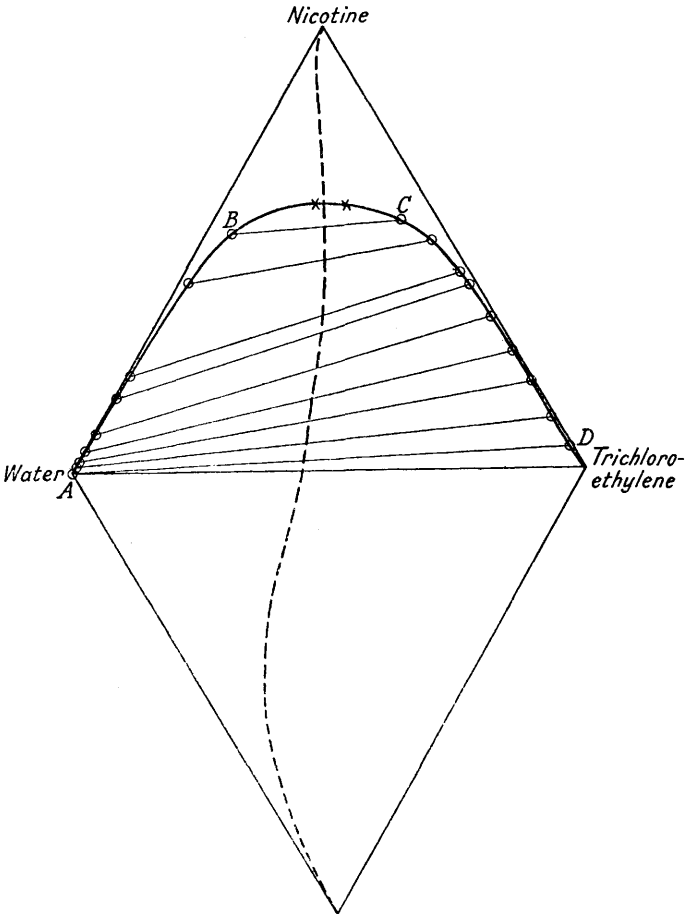
By J. Reilly, D. F. Kelly, and (Miss) M. O'Connor.

The distribution of nicotine between trichloroethylene and water has been investigated. The equilibrium curve is also drawn. A " cloud-point " method was employed to complete the construction of the equilibrium curve. A method for the quantitative estimation of trichloroethylene is recorded.

Trichloroethylene is completely miscible with nicotine but practically immiscible with water. When nicotine is distributed between trichloroethylene and water (below 61°, the limit of complete miscibility of nicotine and water), the system constitutes a typical three-component system containing two liquid phases.

It was considered that trichloroethylene could be employed to extract nicotine especially

from dilute aqueous solutions, such as would be obtained in the steam distillation of nicotine-containing material. Although the distribution of nicotine between water and various organic solvents has been recorded (*e.g.*, Leone, *Atti Congr. Naz. Chim.*, 1926, pp. 1209—1220; Kolosovskii and Kulikov, *Acta Univ. Central Asia*, 1935, No. 8), the system nicotine–trichloroethylene–water has not hitherto been studied. In the present work the distribution of the three components in equilibrium at some fixed temperatures has been investigated. A method has also been evolved for the quantitative estimation of trichloroethylene. In the distribution experiments the concentrations of nicotine and trichloroethylene in the " water " layer and of water in the " trichloroethylene " layer were determined directly. The remaining concentrations were calculated by difference. For 17°, the



distribution is shown in the figure. The conjugate line fixes the position of the plait-point. The smoothness of this line is noteworthy. With the change in the direction of the tie-lines, the plait-point occurs at about the summit of the equilibrium curve. There appear to be but relatively few cases of three-component systems with the plait-point at the summit of the equilibrium curve.

At 17° nicotine is completely miscible with either trichloroethylene or water, and these two solvents are regarded as being practically immiscible, for at 18° trichloroethylene dissolves 0·0250% (by wt.) of water, and at 16° the solubility of trichloroethylene in water is 0·081% (by wt.). The results plotted on the triangular diagram (cf. also table, p. 277) show, as expected, that, as the percentage of nicotine in the system increases, the mutual solubilities of the two solvents also increase: the water in the trichloroethylene layer increases from 0·66 to 6·81% as the total nicotine content of the system increases from

1·54 to 54·18%, but the trichloroethylene in the water layer increases only from 0·10 to 3·84% over the same range of nicotine concentration. The variation of the distribution ratio α (cf. table, below) with increase in nicotine concentration shows a falling away towards unity at the plait-point of the binodal curve. Further, from the point of view of extracting nicotine with trichloroethylene from dilute aqueous solutions, the high values of α at low concentrations of nicotine are of importance, as also is the small loss of trichloroethylene (due to its low solubility in the water layer). A relatively small number of washings of dilute aqueous nicotine solutions with trichloroethylene should suffice, in practical application, to extract the greater portion of the alkaloid. The separation of even relatively concentrated solutions of nicotine and trichloroethylene by fractional distillation should offer no difficulty owing to the widely different vapour pressures of the substances.

In practice, the extraction of nicotine from aqueous solution with trichloroethylene would be effected at room temperature, so the equilibrium data for 17° are of most interest. The application of a " cloud-point " method gave, for purposes of comparison, equilibrium curves (without tie-lines) for other temperatures. Such curves have shown that with increase in temperature there is a rise of nicotine content in what would be expected to be the plait-point mixtures.

Experimental.

The nicotine used was " Kahlbaum, specially purified "; by the silicotungstic acid method, it was found to contain 99·5—99·7% of nicotine. It had $d_4^{17°}$ 1·018. Trichloroethylene, specially purified and free from " stabilisers," was obtained from Imperial Chemical Industries, Ltd. Distilled water free from basic substances was employed.

Measured amounts of nicotine, trichloroethylene, and water were shaken vigorously in a separating funnel and kept at 17°. The layers were separated, and their compositions ascertained by analysis, nicotine being determined by addition of excess of standard hydrochloric acid solution, followed by the titration of the excess with standard sodium hydroxide solution, cochineal being the indicator (Young, *Analyst*, 1927, **52**, 15) (1 c.c. of 0·1N-acid = 0·0162 g. of nicotine). The water present in the trichloroethylene layer was estimated by the magnesium nitride method (Dietrich and Conrad, *Z. angew. Chem.*, 1931, **44**, 532), the ammonia evolved in the reaction $Mg_3N_2 + 6H_2O = 3Mg(OH)_2 + 2NH_3$ being determined by absorption in standard sulphuric acid; Kahlbaum's magnesium nitride, specially prepared for the process, was used. The portion of the trichloroethylene layer in which the water was to be estimated was allowed to flow slowly from a funnel into a flask containing the nitride. The funnel was then washed with anhydrous propyl alcohol, followed by anhydrous light petroleum—preliminary use of the former solvent having been found to lead to more accurate results. The flask was heated slowly on a wire gauze until about half of its contents had distilled. It was found unnecessary to " fix " the nicotine in the distilling flask with anhydrous tartaric acid.

No chemical method has been published for the determination of trichloroethylene, but its quantitative hydrolysis was found to be suitable. Under ordinary pressure, hydrolysis by aqueous potassium hydroxide solution is not quantitative, but at higher pressures potassium chloride is formed in amount equivalent to the total chlorine present, so reaction was carried out for 3 hours at 150° in a sealed Carius tube; the cooled solution was made faintly acid with nitric acid, and the chloride estimated by the Volhard method.

The experimental results obtained for the distribution experiments at 17° are in the following table; the distribution ratio α is that of nicotine in the trichloroethylene layer to that in the water layer (both in %). Concentrations are given in g. per 100 g. of solution.

Distribution Data.

Water layer.			Trichloroethylene layer.			
Nicotine, %.	C_2HCl_3, %.	H_2O, %.	Nicotine, %.	H_2O, %.	C_2HCl_3, %.	α.
0·49	0·10	99·41	5·02	0·66	94·33	10·24
1·34	0·08	98·58	11·54	0·74	87·72	8·61
3·09	0·12	96·79	19·46	0·40	80·14	6·30
4·80	0·10	95·10	26·42	0·57	73·01	5·50
9·28	0·16	90·56	34·63	1·23	64·14	3·73
17·06	0·25	82·69	41·30	1·96	56·74	2·42
22·08	0·40	77·52	44·29	2·25	53·46	2·01
42·33	1·59	56·08	51·95	2·46	45·59	1·23
53·34	3·84	42·82	56·64	6·81	36·55	1·06

These data give the binodal curves *AB* and *CD* with the appropriate tie-lines of the figure. It was not found possible to complete the curve by means of distribution experiments, but this was effected by a " cloud-point " method. A solution of nicotine in trichloroethylene (of concentration as indicated by the general direction of the binodal curves) is made up, and the water added drop by drop from a burette. At the point just before which the mixture clouds, the composition of the resulting homogeneous solution represents concentrations that will lie on the extension of one or the other of the binodal curves. The solution, conjugate to the homogeneous solution found as above, is not made so that the method does not give tie lines. By this means two " cloud-point " solutions were found which had the compositions shown below.

Composition of " Cloud-point " Solutions.

Nicotine, %.	C_2HCl_3, %.	H_2O, %.	Nicotine, %.	C_2HCl_3, %.	H_2O, %.
60·33	18·64	21·03	60·00	23·90	16·10

When these two " cloud points " are plotted, they give the points × × in the figure, which enable the equilibrium curve to be completed. The compositions of the solutions in this table are nearly the same, and the plait-point consequently lies close to these points.

The cloud-point method also enabled equilibrium curves (without tie-lines) to be constructed. In the present instance, an arbitrary but known mixture of trichloroethylene and nicotine was first made. Water was then added from a burette, and the " cloud point " determined. A further known amount of nicotine was added to the mixture, and a new " cloud point " then ascertained. The procedure was continued until sufficient points were obtained.

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