95. *An Azeotrope of Nicotine and Water.*

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

Distillation constants have been applied to the examination of binary mixtures of liquids which form azeotropes. Mixtures of nicotine and water have thereby been proved to form an azeotrope, and this has been confirmed by investigation of the liquid–vapour equilibrium curve.

The authors showed (J., 1941, 275) that nicotine could be extracted from aqueous solutions by means of trichloroethylene, and fractional distillation of such solutions demonstrated the formation of an azeotrope of nicotine and water (*Nature*, 1941, **148**, 438). This has now been confirmed by determination of the distillation constants of aqueous solutions of nicotine and of the liquid–vapour equilibrium curve.

The distillation constants were determined by the method of Virtanen and Pulkki (*J. Amer. Chem. Soc.*, 1928, **50**, 3138). Reilly and Kelly ("Thorpe's Dictionary of Applied Chemistry," London, 1940, Vol. IV) have pointed out that the distillation constant, K, of a binary mixture determined by this method is the same as the relative volatility, α (Walker, Lewis, and McAdams, "Principles of Chemical Engineering," New York, 1937), of the constituents of the mixture. The similarity of K and α was considered to hold only on the condition that the constituents of a mixture obeyed Raoult's law. For a mixture composed of x_1 parts by weight of one liquid (*e.g.*, nicotine) and y_1 of another (*e.g.*, water) K is defined (following Virtanen and Pulkki, *loc. cit.*) by

$$K = (\log x_1 - \log x_2)/(\log y_1 - \log y_2) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

which is derived from Brown's equation (J., 1881, **39**, 531) : x_2 and y_2 are the number of parts by weight of the respective constituents left in the mixture after a partial distillation.

To show the more general relationship of K and α the distillation of a binary mixture may now be viewed as follows. If A and B are the number of g.-mols. of the respective pure components (A and B) in a mixture being distilled, and if an infinitesimal amount of the mixture be boiled off (at its particular boiling temperature) then

$$-\,\mathrm{d}A/-\,\mathrm{d}B = p_A/p_B \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

where p_A and p_B are the respective partial vapour pressures at that temperature. If α is the relative volatility of the components in the mixture, then by definition (Walker *et al.*, *op. cit.*)

$$\alpha = v_A/v_B = (p_A/m_A)/(p_B/m_B) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

where v_A and v_B are the volatilities of the pure components (at the particular temperature of the boiling point) and m_A and m_B are the mol.-fractions of the respective components in the mixture. Substitution of the values $m_A = A/(A + B)$ and $m_B = B/(A + B)$ in (3) and rearrangement gives

$$p_A/p_B = \alpha A/B \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

and substitution of this value of p_A/p_B in (2) gives

$$-\mathrm{d}A/-\,\mathrm{d}B = \alpha A/B \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

If α is a constant for a finite partial distillation, then (5) gives on integration:

$$\ln(A_1/A_2) = \alpha \ln(B_1/B_2) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

or

$$(\log A_1 - \log A_2)/(\log B_1 - \log B_2) = \alpha \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

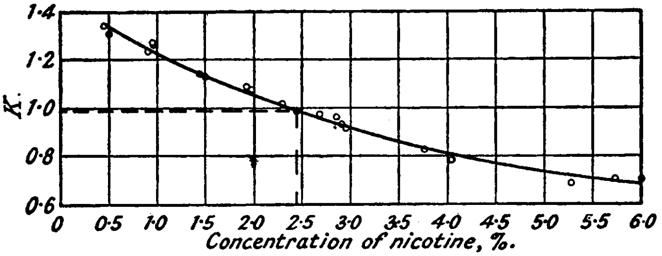
the subscripts 1 and 2 relating, respectively, to the composition of the "distilland" at the beginning and the end of the partial distillation. The same relationship (7) holds if composition is expressed by weight instead of by g.-mols. Equations (1) and (7) are therefore identical provided the relative volatility of the components be constant through the temperature range of the partial distillation. This condition is approximately observed in practice. Walker *et al.* (*op. cit.*) point out that, on change of temperature, although volatilities vary widely, yet relative volatilities, in general, vary but little. In practice, K will closely approximate to α; for an infinitesimally small distillation, the two would be identical. Azeotropic components deviate from Raoult's law, and with these, the identity will not hold in general : K will approximate to α if the deviations are small or if they nearly cancel. Experimental determination of K (or α) will indicate the existence of an azeotrope.

The experimental determination of true relative volatility, α, *e.g.*, by way of the liquid–vapour equilibrium points, is tedious, but Virtanen and Pulkki's method (*loc. cit.*) enables K to be determined easily and rapidly. Briefly, in this method, a mixture is distilled into separate small portions of distillate, leaving some residual "distilland," and the compositions of each are ascertained. The first portion of distillate being considered as arising from the combined remaining portions plus the residual "distilland," etc., values of K for a set of compositions equal to the number of portions of distillate are obtained. During any one partial distillation, it is assumed that the pertaining value of K of the components does not vary widely. The variation in K (or α approximately) over the whole range of compositions taken may be obtained quickly by finite partial distillation experiments even in the case of azeotropic components. In the latter case K will be determined for compositions which will fall to one side or other of the azeotropic composition.

The variation with composition of α is of interest in the case of binary mixtures forming azeotropes. If the components are present in the exact azeotropic composition, α is unity. At other compositions α is greater than or smaller than unity depending on which component is present in excess of this composition. When plotted, the curve of α–composition will go through the point $\alpha = 1$ at a point corresponding to the azeotropic composition. The same will hold true for K, which would remain constant at $K = 1$ throughout the distillation of an azeotropic mixture. Hence, determination of K for pairs of liquids by the rapid technique of Virtanen and Pulkki (*loc. cit.*) should afford, at least, a preliminary means of detecting the existence of an azeotrope. Distillation into separate portions of distillate could also be carried out by the more elaborate method of Rosanoff, Bacon, and White (*J. Amer. Chem. Soc.*, 1914, **36**, 1803), devised primarily for construction of liquid–vapour equilibrium curves. In that case, in addition to " extrapolating to zero " to obtain equilibria points, a series of values for K could be calculated for preliminary purposes.

For various nicotine–water mixtures K was determined by Virtanen and Pulkki's method. The results obtained are given in Table I. Curves of the first, second, and third degree were successively fitted to the data by using orthogonal polynomials and the method of least squares. Analysis of variance showed that the cubic did not materially improve the fit, and it was therefore not necessary to proceed beyond the second degree. The fitted quadratic was (q being the percentage of nicotine) $K = 1{\cdot}440427 - 0{\cdot}221455\,q + 0{\cdot}015837\,q^2$, and this curve, together with the data of Table I, are shown in Fig. 1. With this curve, $K = 1$ when $q = 2{\cdot}40$. The cubic curve gave $K = 1$ when $q = 2{\cdot}43$, which may be taken as the approximate composition of the azeotrope.

Fig. 1.



The experimental results tend to make K constant (*ca.* 0·7) for nicotine concentrations exceeding 5%, corresponding to the region where there are two liquid phases in the flask at the distillation temperature. In this region, the boiling point of the mixture is above the lower critical solution temperature of nicotine and water : the region represents compositions within the loop of the well-known closed solubility curve for nicotine–water solutions. It is noteworthy, too, that the distilland (at room temperature) and the distillates obtained in this region are one-phase liquid systems. When two liquid layers exist in the distilling flask (at the temperature of the boiling point of the mixtures) the distillation must be looked upon as follows : each layer, being a saturated solution, will maintain constant composition throughout the distillation, and the composition of the distillate (as well as the boiling point) will also be constant. Under these conditions, K must have a constant value as required by equation (1).

An aqueous solution containing 2·45% of nicotine distilled unchanged, K being approximately unity (actually 0·99) throughout the distillation, so this was taken to be the azeotropic composition. The azeotrope boiled at 99·6°/760 mm., and is a homoazeotrope of minimum boiling point (Swietoslawski, " Ebulliometry," New York, 1937) or a " pseudo-azeotrope " (Walker *et al.*, *op. cit.*). The latter term, however, does not imply that the present azeotrope does not behave like a true azeotrope : it is not clear whether the term is reserved only for a two-liquid-phase mixture which distils unchanged and thus corresponds to the binary heteroazeotrope of Swietoslawski (*op. cit.*).

There are but few experimental illustrations of liquid–vapour equilibria in partially miscible systems (see Glasstone, " Textbook of Physical Chemistry," London, 1940, p. 722) : the present azeotrope may correspond to the apparently theoretical case II discussed by Glasstone (*loc. cit.*).

By Othmer's method (*Ind. Eng. Chem., Anal.*, 1932, **4**, 232) we determined the liquid–vapour equilibrium curve of nicotine and water directly, thus confirming the existence of the azeotrope. The curve obtained is given in Fig. 2; it intersects the diagonal at a composition corresponding to 2·45% of nicotine, *i.e.*, that of the azeotrope.

EXPERIMENTAL.

The materials used and the method of determining the nicotine concentrations were the same as those described in our previous paper (*loc. cit.*). For the distillation experiments, Virtanen and Pulkki's method and apparatus (*loc. cit.*) were employed. Solutions of nicotine and water were distilled (at a rate of *ca.* 1 c.c./min.), and the distillate collected in successive portions. The values of K obtained for different concentrations are given in Table I and plotted in Fig. 1, showing the approximate azeotropic composition. When 150 c.c. of a 2·45% solution of nicotine in water

TABLE I.

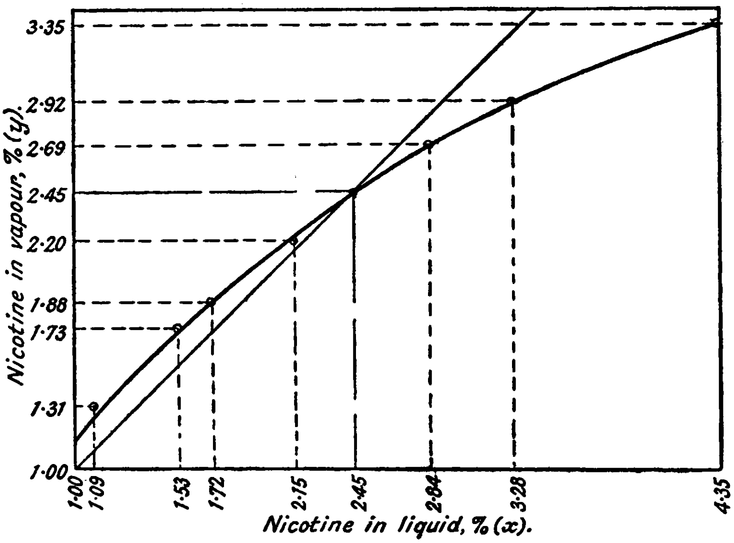
Nicotine, %	0·45	0·50	0·91	0·94	0·95	1·46	1·51	1·92	1·97	2·27	2·28
K	1·34	1·31	1·24	1·27	1·26	1·14	1·13	1·09	1·08	1·02	1·019
Nicotine, %	2·45	2·68	2·86	2·90	2·95	3·76	4·02	5·28	5·72	6·01	
K	0·99	0·97	0·96	0·93	0·92	0·82	0·78	0·69	0·7	0·7	

were distilled into 5 portions of distillate (*ca.* 25 c.c. each), no change in composition was found (apart from a negligible change in the last two) and a constant value of K was obtained (see Table II).

TABLE II.

Nicotine, %	2·45	2·45	2·45	2·46	2·46
K	0·99	0·99	0·99	0·99	0·99

FIG. 2.



The values given in Table III were obtained for equilibrium points in the liquid–vapour equilibrium curve (Fig. 2) as determined by Othmer's method (*loc. cit.*). An aqueous solution of nicotine was boiled in a still of the prescribed type until equilibrium was set up. Samples were drawn off from the still and distillate receiver, and their compositions ascertained as before. The figures obtained gave a pair of equilibrium compositions, and further pairs were determined similarly. Unduly prolonged boiling in the apparatus was avoided, for the solutions became brown.

TABLE III.

Nicotine in liquid (x), %	1·09	1·53	1·72	2·15	2·84	3·28	4·35
Nicotine in vapour (y), %	1·31	1·73	1·88	2·20	2·69	2·92	3·35
α	—	1·11	1·10	1·02	0·92	0·89	0·76

The true relative volatilities, α, of nicotine and water are also given in Table III for the respective equilibrium compositions. These values of α are calculated from the expression $\alpha = (b/a)[(1 - a)/(1 - b)]$, where a and b are the equilibrium compositions (expressed as proportion of nicotine) of liquid and vapour respectively. The value of α for the first pair of compositions was not calculated as this pair of values did not lie on the smooth curve.

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UNIVERSITY COLLEGE, CORK.

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