# 56. *Equilibrium Constants in Terms of Activities derived from Cryoscopic Data: The Dissociation of Pyridine* o-*Chlorophenoxide in Benzene.*

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IN using cryoscopic data to calculate equilibrium constants for the dissociation of molecular compounds of organic substances in solution, the main problem is to determine the correct concentrations for the undissociated molecules and products of dissociation, since the ideal solution laws are not strictly applicable in many cases.

Brown (J., 1925, **127**, 345) has determined equilibrium constants for naphthalene–trinitrotoluene and naphthalene–picric acid in nitrobenzene, but the extreme values differ by about 30%; also Hatcher and Skirrow (*J. Amer. Chem. Soc.*, 1917, **39**, 1939), using compounds of cresols with pyridine in benzene or naphthalene, were unable to obtain a reasonable constant. Studying ester–acid complexes in solution, Kendall and Booge (J., 1925, **127**, 1768) state : " The exact degree of dissociation at any given dilution cannot, however, be determined, since we have no means of knowing whether the curve for the undissociated compound follows the ideal or not."

Hence there seems some justification for an attempt to use the activity concept (Lewis and Randall, " Thermodynamics," 1923) to calculate equilibrium constants, for the activities of solutes describe the extent of deviation from ideal behaviour and represent corrected concentrations.

Lewis and Randall (*op. cit.*, p. 286) have derived an expression for the activity coefficient of a single non-dissociating solute in aqueous solution, *viz.*,

$$\log_e a/m = -\int_0^m j\,.\,d\log_e m - j + \int_0^m 0{\cdot}00057\ \theta/m\,.\,d\theta \quad . \quad . \quad . \quad . \quad (1)$$

where $a$ = activity of solute, $m$ = molality of solute, $a/m$ = activity coefficient, $\theta$ = depression of f. p. of the solvent produced by the solute, and $j = 1 - \theta/\lambda m$, where $\lambda$ is the molal lowering of f. p. of the solvent in a solution of infinite dilution. The factor 0·00057 is specific for water as a solvent.

The problem now under consideration is the calculation of the activities for a molecular compound, existing as undissociated molecules, and two products of dissociation, all in equilibrium in the same solution. It is desirable to consider first the dissociation of an electrolyte in aqueous solution, since this problem has been treated from the activity point of view. The mean activity coefficient for a uni-univalent electrolyte in aqueous solution can be calculated from f. p. data by a modified form of (1) (Lewis and Randall, *op. cit.*, p. 347), *viz.*,

$$\log_e \gamma = -\int_0^M j\,.\,d\log_e M - j + 0{\cdot}00057\int_0^M \theta\,.\,d\theta/\nu M \quad . \quad . \quad . \quad (2)$$

where $\gamma$ = mean activity coefficient of the ions, $M$ = molality of the electrolyte, $\nu$ = number of ions formed from one molecule of electrolyte, and $j = 1 - \theta/\nu\lambda M$; $\theta$, $\lambda$, and 0·00057 are the same as in (1).

The mean activity coefficient for a uni-univalent electrolyte ($\nu = 2$) is defined as $\gamma = a_{\pm}/M = \sqrt{a_{+}a_{-}}/M$, where $a_{+}$ and $a_{-}$ are the activities of positive and negative ions respectively and $a_{\pm}$ ($= M\gamma$) is the mean activity of the ions. By using activities, instead of stoicheiometric concentrations, a true equilibrium constant, $K_a = a_2/a_{+}a_{-}$, should be found, $a_2$ being the activity of the undissociated compound present in solution and $\sqrt{a_2/K_a} = a_{\pm}$ or $\frac{1}{2}\log_e a_2/K_a = \log_e a_{\pm}$. Hence

$$d\log_e a_2 = 2d\log_e a_{\pm} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Lewis and Randall (*op. cit.*, p. 342) use a similar equation to derive (2) from $(d\log_e a_2)/\nu = d\log_e a_{\pm} = d\theta/\nu\lambda M$ but they choose arbitrarily a standard state such that $K_a = 1$. This seems unnecessary when $K_a$ does not occur in (3). $M\gamma$ is therefore the true mean activity of the ions.

Being thermodynamically derived and independent of the nature of the solutes and solvents forming solutions, the general form of equation (2) should be applicable to any equilibrium in dilute solution for any value of $K_a$, *e.g.*, a molecular compound (pyridine *o*-chlorophenoxide; Bramley, J., 1916, **109**, 469) dissociating in benzene. In such a case, $M\gamma$ would now be the true mean activity of the dissociation products, analogous to the ions.

Since (3) cannot be used to find $a_2$ without introduction of $K_a$, the activity of undissociated molecules must be found by some other method. The following general method, applied to an equilibrium of the type A + B $\rightleftharpoons$ AB in a solvent, shows how this can be done. The components A and B are organic substances. Such equilibria possess an advantage over electrolytic dissociation into ions because the activity coefficients of A and B may be determined for each singly in solution, from cryoscopic measurements, by using

(1). In this way a graph can be constructed showing the variation of the activity coefficients of the two components A and B ($\gamma_A$ and $\gamma_B$) with concentration (see *e.g.*, Fig 2).

Equation (2), with the constant 0·00057 altered for the solvent used, will give the mean activity coefficients ($\gamma$) of A and B together in equimolecular amount in solutions. For any solution of molality $M$ and mean activity coefficient $\gamma$, $M\gamma = \sqrt{a_A a_B}$ or $(M\gamma)^2 = a_A a_B$, where $a_A$ and $a_B$ are the activities of A and B respectively. If $m$ is the actual molality of A or B at equilibrium in solution ($m$ is the same for A and B in the present case), then corresponding to $m$ there are two activity coefficients, $\gamma_A$ and $\gamma_B$, and it follows that $\gamma_A m = a_A$ and $\gamma_B m = a_B$; whence,

$$a_A a_B = (M\gamma)^2 = \gamma_A \gamma_B m^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

At complete dissociation $m = M$.

The assumption is now made that in a given dilute solution, containing the solutes A and B together with undissociated compound AB, the activity of any one of the three solute species is the same as it would be in solution separately at the same concentration.

It follows that reference to graphs, such as Fig. 2, will give (by trial) the values of $m$, $\gamma_A$, and $\gamma_B$ which satisfy any value of $(M\gamma)^2$ found experimentally from (2). Therefore, $(M - m)$ gives the stoicheiometric molality of the compound AB present in solution at equilibrium. As the variation of freezing-point depression with concentration is known for each of the components, A and B, in solution separately, the two depressions for solutions of A and B ($\Delta t_A$, $\Delta t_B$) of molality $m$ can be found.

The depression ($\Delta t_M$) for a solution containing the equimolecular mixture of A and B will be greater than $\Delta t_A + \Delta t_B$ by the amount of the depression due to molecules of AB of molality $(M - m)$ in solution, *i.e.*, $\Delta t_{AB} = \Delta t_M - (\Delta t_A + \Delta t_B)$.

A series of values of $\Delta t_{AB}$, for solutions of different concentrations, can be found and applied in (1) to find activity coefficients of the compound AB $[\gamma_{AB} = a_{AB}/(M - m)]$.

The equilibrium constant, in terms of activities, now takes the form [from (4)]

$$K_a = \frac{a_{AB}}{a_A a_B} = \frac{(M - m)\gamma_{AB}}{m^2(\gamma_A \gamma_B)} = \frac{(M - m)\gamma_{AB}}{(M\gamma)^2}$$

With the object of testing the foregoing application of the activity concept to the determination of equilibrium constants, a cryoscopic investigation of the molecular compound pyridine *o*-chlorophenoxide in benzene has been undertaken. There is cryoscopic evidence that this compound exists in a partially dissociated condition in benzene (see *e.g.*, Madgin, Peel, and Briscoe, J., 1928, 707). Benzene forms a eutectic system with both pyridine (Hatcher and Skirrow, *loc. cit.*) and *o*-chlorophenol (Sidgwick and Turner, J., 1922, **121**, 2256) and may thus be regarded as an inert solvent. The constant $K_a$ has also been compared with the constant $K_c$, obtained by using concentrations only.

## EXPERIMENTAL.

By using a standard Beckmann apparatus and reading temp. to 0·001°, the f. p. depressions for $C_6H_6$ solutions of $C_5H_5N$ and *o*-chlorophenol, separately and mixed together, have been determined. Materials were specially purified by the methods of Bramley (*loc. cit.*).

The formation of pyridine *o*-chlorophenoxide was further examined by mixing equidepression solutions of the components, of known comp. (cf. Madgin, Peel, and Briscoe, *loc. cit.*), in various proportions. The solution which contained the separate solutes in equimol. amount gave a depression which deviated most from the original value and evidently the greatest proportion of compound was here formed (see Fig. 1).

*Equilibrium Constant.*—In calculating this const. for the formation of pyridine *o*-chlorophenoxide in terms of stoicheiometric concns. in $C_6H_6$, it is necessary to know the state of association of the *o*-chlorophenol and $C_5H_5N$ separately in solution.

This was found by determining the mol. wts. of the two solutes from the formula $\Delta T = kn_u/(n_u + n_v)$ (Brown and Bury, J., 1924, **125**, 2219); $k = 65{\cdot}64$ for $C_6H_6$ as solvent.

Pyridine has an apparent mol. wt. 88 uniformly over a range of concn., and this represents a degree of association such that there will be 1 double mol. for every 8 single mols. Similar

TABLE I.

*Variation of mol. wt. with concn. for separate solutes.*

(Concn. is in g. per 100 g. of solvent.)

Series 1. *o*-Chlorophenol.

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Concn. | 1·022 | 1·532 | 2·035 | 3·005 | 4·558 | 5·119 | 6·535 | 7·235 |
| Mol. wt. | 125·6 | 127·2 | 126·1 | 127·2 | 130·1 | 128·5 | 127·2 | 126·9 |

Series 2. Pyridine.

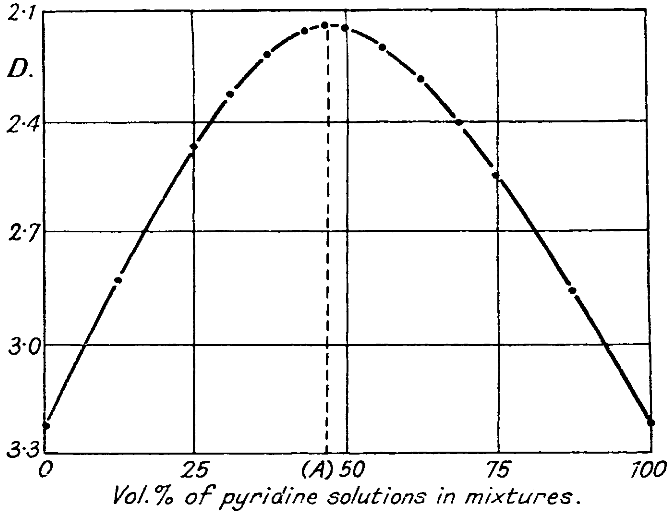
| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Concn. | 0·587 | 0·973 | 1·532 | 2·159 | 2·523 | 3·137 | 3·928 | 5·776 | 6·122 |
| Mol. wt. | 88·25 | 88·0 | 87·5 | 87·6 | 88·5 | 88·2 | 87·7 | 86·9 | 86·8 |

apparently const. association has been found by Auwers (*Z. physikal. Chem.*, 1899, **30**, 300) for other solutes.

*o*-Chlorophenol (average mol. wt. 127·8; calc., 128·5) appears to be unassociated over the given concn. range, and this might be expected from a chelated compound (see Sidgwick and Callow, J., 1924, **125**, 527). In the following calculation it is presumed that these conditions of association of the separate components persist in all mixtures.

FIG. 1.

*Depressions (D) for mixtures of equi-depression solutions of pyridine and* o-*chlorophenol separately in benzene.*



*Composition (weight) of mixed solutes in* A = 37·9% *pyridine and* 62·1% o-*chlorophenol.*

The concn. equil. const. ($K_c$) can be calculated by the method of Brown (*loc. cit.*). In the present work the types of equilibria are $(A_2) = 2A$ and $2A + 2B = 2AB$, where A refers to pyridine and B to *o*-chlorophenol. For 1 g.-mol. of total B in $N$ g.-mol. of solvent a fraction $\alpha$ of compound AB is formed and, at equilibrium, the fractions of 1 g.-mol. are $[A_2] = 0{\cdot}1\,(1 - \alpha)$, $[A] = 0{\cdot}8\,(1 - \alpha)$, $[B] = 1 - \alpha$, and $[AB] = \alpha$; hence total solute mol. $= 0{\cdot}9\,(1 - \alpha) + (1 - \alpha) + \alpha = 1{\cdot}9 - 0{\cdot}9\alpha$; $\Delta T = k(1{\cdot}9 - 0{\cdot}9\alpha)/(1{\cdot}9 - 0{\cdot}9\alpha + N)$ and

$$\alpha = 2{\cdot}1 - 1{\cdot}1\Delta T \,.\, N/(k - \Delta T).$$

Concns. being expressed as mol. fractions in $K_c = [AB]/[A][B]$, then

$$K_c = 10\alpha\,(N + 1{\cdot}9 - 0{\cdot}9\alpha)/8(1 - \alpha)^2.$$

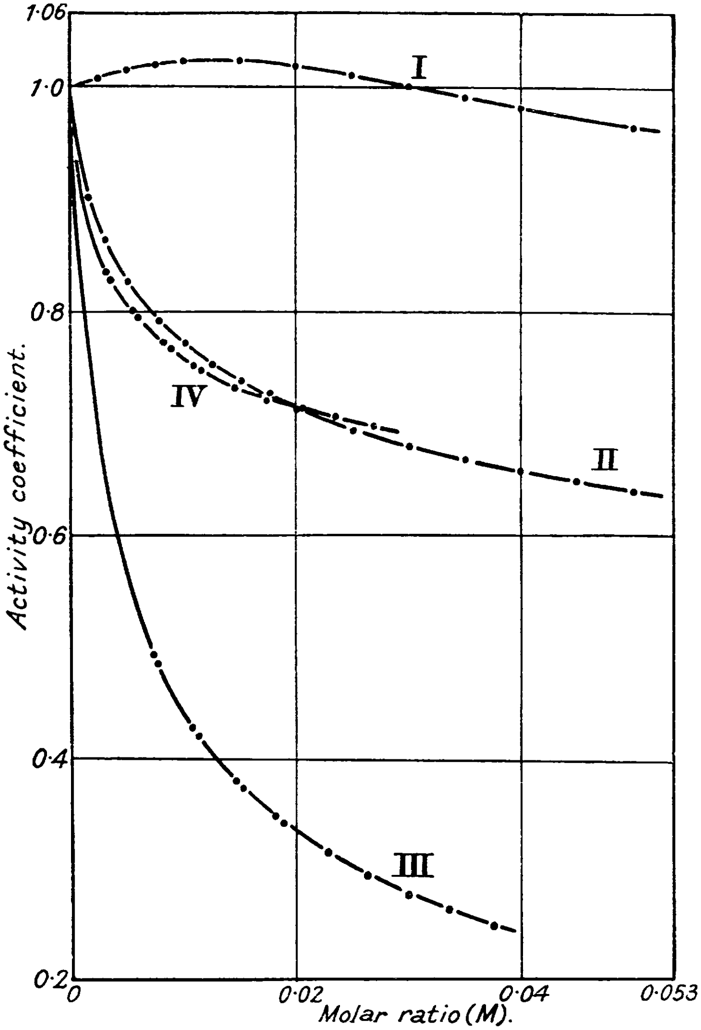
Values for $K_c$ are shown in Table II. When determining these data it was found that the results were independent of the method of preparing the solutions; *i.e.*, whether the pure phenoxide is added to benzene or equimol. solutions of the separate components are mixed.

*Activity Coefficients.*—Equations (1) and (2) have been applied to cryoscopic data in the present work but mol. ratios have been used for $m$ and $M$ instead of the molalities of the original definition. A specific const. for the solvent $C_6H_6$, in place of 0·00057 in (1) and (2), has been found by the method of Lewis and Randall [*op. cit.*, p. 283 (16)], and the necessary heat data for benzene were taken from Int. Crit. Tables. The new constant is 0·000106.

It has been found that $j = 1 - \theta/\lambda m = 1 - 0{\cdot}01526\ \theta/m$.

The activity coefficients ($\gamma_A$ and $\gamma_B$) for the single components (pyridine and *o*-chlorophenol) in separate benzene solutions have been calculated at round mol. ratios from (1), by using the f. p. depressions corresponding to Table I. These results (Fig. 2) enable the activity coefficients to be found for any concns. used experimentally.

FIG. 2.



I, *o-Chlorophenol* ($\gamma_B$) ; II, *pyridine* ($\gamma_A$) ; III, *pyridine and o-chlorophenol together in solution* ($\gamma$) ; IV, *pyridine o-chlorophenoxide, undissociated* ($\gamma_{AB}$).

The mean activity coefficients ($\gamma = \sqrt{a_A a_B}/M$) have also been found by using f. p. depressions ($\Delta T$, Table II), for equimol. mixtures of pyridine and *o*-chlorophenol, in (2).

The activity coefficients ($\gamma_{AB}$) for the undissociated compound, pyridine *o*-chlorophenoxide, have been found in the manner described above.

From these various coefficients (Table II) the corresponding activities can be calculated, and hence values for $K_a$ are found.

TABLE II.

*Equilibrium constants and activity coefficients for benzene solutions of pyridine* o-*chlorophenoxide at concn.* M = *mol. ratio.*

| | | | | Activity coefficients. | | | |
|---|---|---|---|---|---|---|---|
| $M \times 10^3$. | $\Delta T$. | $K_c$. | $K_a$. | $\gamma$. | $\gamma_A$. | $\gamma_B$. | $\gamma_{AB}$. |
| 7·196 | 0·67 | 393·8 | 222·7 | 0·4922 | 0·840 | 1·010 | 0·834 |
| 7·526 | 0·70 | 380·2 | 221·1 | 0·4856 | 0·838 | 1·010 | 0·830 |
| 10·65 | 0·956 | 367·1 | 221·1 | 0·4264 | 0·828 | 1·014 | 0·801 |
| 11·29 | 1·01 | 357·8 | 219·5 | 0·4178 | 0·825 | 1·015 | 0·795 |
| 14·62 | 1·275 | 338·5 | 216·0 | 0·3778 | 0·814 | 1·016 | 0·771 |
| 15·06 | 1·308 | 352·4 | 216·4 | 0·3730 | 0·812 | 1·016 | 0·769 |
| 18·02 | 1·536 | 336·2 | 213·2 | 0·3466 | 0·80 | 1·017 | 0·751 |
| 18·87 | 1·60 | 335·5 | 213·3 | 0·340 | 0·798 | 1·018 | 0·747 |
| 22·67 | 1·886 | 326·8 | 211·2 | 0·3149 | 0·790 | 1·019 | 0·732 |
| 22·94 | 1·910 | 318·4 | 210·7 | 0·3137 | 0·789 | 1·020 | 0·731 |
| 26·37 | 2·160 | 320·6 | 210·4 | 0·2952 | 0·782 | 1·020 | 0·722 |
| 30·01 | 2·396 | 297·1 | 214·0 | 0·2768 | 0·778 | 1·022 | 0·714 |
| 33·54 | 2·641 | 360·1 | 214·4 | 0·2629 | 0·774 | 1·023 | 0·705 |
| 37·61 | 2·874 | 454·4 | 220·2 | 0·2468 | 0·770 | 1·024 | 0·699 |

Average values: $K_c = 353$; $K_a = 216$. $\gamma_A$, $\gamma_B$, $\gamma_{AB}$ = activity coefficient of pyridine, *o*-chlorophenol, and undissociated pyridine *o*-chlorophenoxide, respectively. Activities may be found by applying equation (4) to the data in this table.

## DISCUSSION OF RESULTS.

The present results (Table II) include a very consistent set of values for $K_a$, the variation from average (less than 3% for extremes) being well within the limits of exptl. error. $K_c$ values, although divergent, are as consistent as those of other workers (cf. Brown, *loc. cit.*).

The numerical values of $K_a$ and $K_c$ suggest considerable stability of pyridine *o*-chlorophenoxide in benzene at temperatures above the m. p. (— 23°) of the pure substance: the average value of $K_a$ (216) shows that dissociation occurs in the benzene solutions examined to the extent of 30—50%, depending on dilution. From the results of Bramley (*loc. cit.*, p. 496) an equilibrium constant ($K_c$) has been calculated for an undiluted equimol. mixture of pyridine and *o*-chlorophenol. This constant shows the compound to have dissociated to the extent of only 11% and, by comparison, the present value of $K_a$ gives 9·5% dissociation in an infinitely concentrated solution (*i.e.*, pure solute).

The activity coefficient of undissociated molecules ($\gamma_{AB}$) enables the deviation from ideal behaviour to be found (cf. Kendall and Booge, *loc. cit.*), and the considerable difference between the average values of $K_a$ and $K_c$ in the present work is chiefly due to the fact that $\gamma_{AB}$ is always less than 1.

## SUMMARY.

The use of activities, instead of concentrations, to calculate true equilibrium constants is discussed for the dissociation of pyridine *o*-chlorophenoxide (AB) into pyridine (A) and *o*-chlorophenol (B) in benzene solution.

A method is devised to calculate the activity coefficients of products of dissociation and undissociated molecules, and thence to determine the activities $a_A$, $a_B$, and $a_{AB}$, from cryoscopic data.

The true constant, $K_a = a_{AB}/a_A a_B$, has been found for a series of solutions of different concentrations and the extreme values only differ from the average by some 3%. For purposes of comparison, the concentration constant, $K_c = [AB]/[A][B]$, has also been found, but the values are divergent. This would be expected, since the relevant concentrations are necessarily calculated on the assumption that the various solutes conform to the ideal solution laws.

It is concluded that the constant $K_a$ describes the condition of the pyridine *o*-chlorophenoxide in benzene, and the results are considered to give valuable evidence of the usefulness of the theory of activity of Lewis and Randall.

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