336. *Equilibrium Constants in Terms of Activities from Cryoscopic Data. Part II. The Dissociation of Pyridine* o-*Chlorophenoxide in* p-*Dichlorobenzene.*

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IT has been shown (this vol., p. 193) that an equilibrium constant, K_a, involving activities instead of concentrations, can be calculated for pyridine *o*-chlorophenoxide in benzene, but the necessary cryoscopic data only refer to a short temperature range near the freezing point of benzene, 5·5°. If a value for K_a could be found for a widely different temperature, it should then be possible to apply the van 't Hoff isochore and calculate the heat of formation of pyridine *o*-chlorophenoxide. We have therefore made a cryoscopic study of this compound in *p*-dichlorobenzene (freezing point 52·9°), since there are the following reasons for considering that this solvent and benzene have almost the same solvent influence on the dissolved substance. First, both solvents have practically the same dielectric constant (see Int. Crit. Tables) and the dipole moment of each substance is zero (Smyth, Morgan, and Boyce, *J..Amer. Chem. Soc.*, 1928, **50**, 1536); secondly, Mortimer (*ibid.*, 1923, **45**, 633) has shown from solubility measurements that these two solvents have equal relative internal pressures.

The difference (*ca.* 50°) between the freezing points of benzene and *p*-dichlorobenzene is sufficiently great to cause the variation in the dissociation of pyridine *o*-chlorophenoxide, between these two temperature limits, to preponderate considerably over any specific solvent effects due to either of these solvents.

We find that *p*-dichlorobenzene forms a eutectic system with both pyridine and *o*-chlorophenol and may therefore be regarded as an inert solvent resembling benzene. The data for these two eutectic systems will be given with others in a later communication.

Evidence is given below that the heat of formation of pyridine *o*-chlorophenoxide is practically constant over the temperature range considered here. There is thus some justification for the present application of the isochore.

The activities of pyridine *o*-chlorophenoxide and its dissociation products, pyridine and *o*-chlorophenol, in *p*-dichlorobenzene have been calculated in the manner previously described (*loc. cit.*), and the equations therein discussed have been appropriately altered to give the following for *p*-dichlorobenzene, *m* and *M* being mol. ratios :

$$\log_e a/m = -\int_0^m j\,.\,d\log_e m - j + 0{\cdot}00009354\int_0^m \theta/m\,.\,d\theta \quad . \quad . \quad . \quad . \quad (1)$$

$$\log_e \gamma = -\int_0^M j\,.\,d\log_e M - j + 0{\cdot}00009354\int_0^M \theta\,.\,d\theta/\nu M \quad . \quad . \quad . \quad . \quad (2)$$

The constant 0·00009354 has been calculated from the calorimetric data of Narbutt (*Z. Elektrochem.*, 1918, **24**, 339), and, in $j = 1 - \theta/\nu\lambda M$, $1/\lambda = 0{\cdot}02056$.

The equilibrium constant

$$K_a = \frac{a_{\text{AB}}}{a_{\text{A}}a_{\text{B}}} = \frac{(M - m)\gamma_{\text{AB}}}{(M\gamma)^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

is also of the same form as previously used and involves

$$a_{\text{A}}a_{\text{B}} = (M\gamma)^2 = \gamma_{\text{A}}\gamma_{\text{B}}m^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

EXPERIMENTAL.

" Purified " *p*-dichlorobenzene was recrystallised twice from ethyl alcohol and thoroughly dried over calcium chloride; m. p. 52·9°. Pyridine and *o*-chlorophenol were as before (*loc. cit.*).

The freezing-point depressions for *p*-dichlorobenzene solutions of pyridine and *o*-chlorophenol, separately and mixed together in equimolar proportion, were determined with a suitably modified Beckmann apparatus, and temperatures were read to 0·001°. The outer bath of the apparatus was a 1-litre tall Pyrex beaker heated with a winding of resistance wire and containing high-boiling liquid paraffin. This was shielded by immersion in a larger beaker lagged with asbestos.

The central tube, containing an experimental solution, was separated from the paraffin oil by the usual annular air space, and the mouth of this tube was specially enlarged to accommodate a rubber stopper which carried the thermometer, a mercury sealed stirrer, a guard tube containing phosphoric oxide, and two glass tubes to allow a current of dry air to pass. Dry air was passed through the central tube for ½ hour while solid was being fused, and a dry atmosphere was retained during each freezing-point determination. Preliminary tests showed that *p*-dichlorobenzene lost 0·2% of its weight by evaporation to this current of dry air, and a correction was applied on this basis to all solutions.

The outer oil-bath was mechanically stirred, and the temperature observed with a thermometer reading to 0·1°; it was maintained at 1·0° below the freezing point of each solution during investigation.

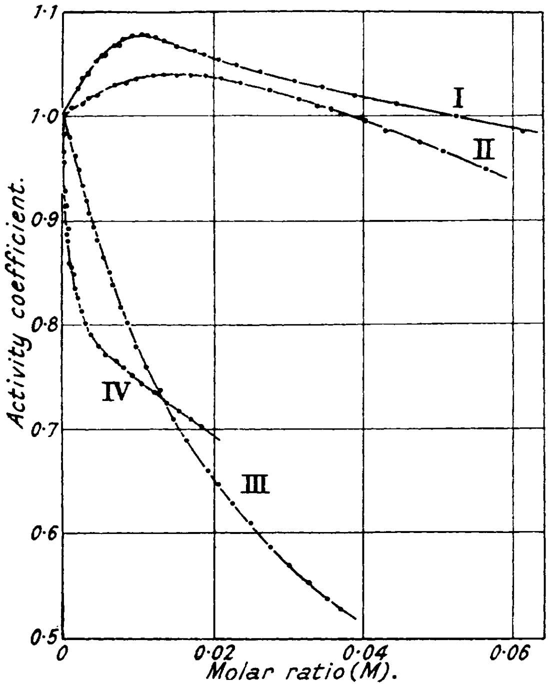
The solutes used were liquids in all cases, and these were weighed out in small sealed glass bulbs which were subsequently broken under the surface of the molten solvent. When mixed solutes were being used, an equimolecular mixture of the two components was first accurately made up, and suitable portions of this weighed off.

All freezing points here recorded have been corrected for the exposed stem of the thermometer. *p*-Dichlorobenzene does not exhibit supercooling to any marked extent : we found an average of 0·15°. An appropriate correction has been applied.

Activity Coefficients.—The activity coefficients (γ_{A} and γ_{B}, Table I) for the single components, pyridine and *o*-chlorophenol, in separate *p*-dichlorobenzene solutions have been calculated from (1), the freezing point results in Table I being used. Many of the γ_A and γ_B values are greater than unity (see Fig.), and thus the activity (*a*) exceeds the concentration (*m*). The molecular weight of the solute, calculated from $K = 0{\cdot}002T^2/L$, is therefore lower than the normal value.

In the results previously reported (*loc. cit.*), *o*-chlorophenol was found to behave similarly in benzene, but the activity coefficient of pyridine was continually less than unity. The abnormally high values for the activity coefficients in *p*-dichlorobenzene accord with comparable experimental results of other workers with this solvent (see Bruni and Gorni, *Gazzetta*, 1900, **30**, 127; Gomberg and Sullivan, *J. Amer. Chem. Soc.*, 1922, **44**, 1810). At high concentrations the activity coefficients become less than unity (cf. Mortimer, *loc. cit.*).

The mean activity coefficient γ, from (2), is used in (4) to find corresponding values for γ_A, γ_B, and *m*. From these, γ_{AB} values are found as before (*loc. cit.*), and K_a is now calculated. Table II summarises these results. The average value is $K_a = 34{\cdot}78$ for an average temperature of 51·8°, and, in benzene, it was found that the average value was $K_a = 216$ for an average temperature of 3·9°.



I, *Pyridine* (γ_A) ; *II* o-*chlorophenol* (γ_B) ; III, *pyridine and* o-*chlorophenol together in solution* (γ) ; IV, *pyridine* o-*chlorophenoxide, undissociated* (γ_{AB}).

Heat of Formation of Pyridine o-*Chlorophenoxide.*—The two average values of K_a have been applied in the isochore $2{\cdot}3 \log K_1/K_2 = Q(T_1 - T_2)/RT_1T_2$, where $K_1 = 216$, $K_2 = 34{\cdot}78$, $T_1 = 276{\cdot}9°$, and $T_2 = 324{\cdot}8°$; whence $Q = -6800$ cals., and the reaction is exothermal. An approximation of the variation of Q with temperature has been obtained by applying Kirchoff's equation to Bramley's specific-heat data (J., 1916, **109**, 496). From the average specific heats at the mean temperature 30°, Q varies by 100 cals. (1·5% of Q) for the entire temperature range $T_2 - T_1 = 48°$. In using these specific heats, we have considered pyridine *o*-chlorophenoxide to be 13·5% dissociated at 30°, since it was shown (*loc. cit.*) to be 9·5% dissociated at T_1 and has now been found to be 17% dissociated at T_2. Evidently Q may be regarded as constant in the preceding application of the isochore.

DISCUSSION OF RESULTS.

The present results include a set of 27 values for K_a, and the extreme values differ from the average by only 2·5%. Since this is within the limits of experimental error, one is justified in using the average value in calculations.

From $K_a = 34{\cdot}78$, it is found that pyridine *o*-chlorophenoxide is dissociated to the extent of 50—95% in *p*-dichlorobenzene, the latter figure being from more dilute solutions than previously used.

The heat of formation ($Q = -6800$ cals.) has been calculated for complete compound formation from g.-mol. quantities of pyridine and *o*-chlorophenol in the condition (association, etc.) in which they exist in dilute benzene or *p*-dichlorobenzene solutions. Bramley (*loc. cit.*) obtained — 4519 cals. for a g.-mol. mixture of the two pure components (no solvent) and this would include heat effects due to preliminary dissociation and other dilution phenomena. On the other hand, the present value ($Q = -6800$ cals.), being for complete compound formation from diluted components, probably represents the energy change involved in the formation of the co-ordination link present in pyridine *o*-chlorophenoxide.

TABLE I.

Activity coefficients for separate solutes.

(M = Molar ratio; ΔT = depression of freezing point.)

Series 1. Pyridine.						Series 2. *o*-Chlorophenol.					
$M \times 10^3$.	ΔT.	γ_A.	$M \times 10^3$.	ΔT.	γ_A.	$M \times 10^3$.	ΔT.	γ_B.	$M \times 10^3$.	ΔT.	γ_B.
1·951	0·096°	1·027	13·51	0·666°	1·070	1·148	0·056°	1·007	19·10	0·934°	1·038
2·792	0·138	1·036	15·32	0·751	1·066	2·605	0·127	1·009	21·00	1·025	1·035
3·624	0·179	1·041	17·66	0·858	1·058	3·514	0·172	1·017	23·70	1·150	1·031
4·467	0·222	1·052	18·90	0·918	1·057	4·573	0·224	1·020	27·59	1·330	1·024
5·138	0·256	1·057	20·72	1·003	1·054	5·348	0·263	1·025	31·39	1·502	1·016
5·630	0·280	1·058	23·29	1·121	1·047	6·972	0·343	1·030	33·84	1·608	1·008
6·933	0·346	1·068	26·38	1·263	1·041	8·233	0·405	1·032	35·58	1·689	1·006
7·463	0·372	1·068	30·94	1·474	1·034	9·723	0·479	1·036	40·11	1·886	0·994
8·021	0·401	1·073	34·43	1·633	1·028	12·05	0·593	1·040	42·96	2·005	0·985
9·316	0·466	1·077	38·86	1·832	1·019	13·58	0·668	1·040	47·58	2·204	0·974
10·79	0·539	1·078	44·57	2·097	1·011	15·03	0·738	1·039	50·60	2·326	0·965
11·18	0·557	1·078	52·31	2·439	1·0	17·05	0·835	1·038	56·33	2·554	0·947
12·28	0·638	1·074	61·20	2·821	0·983						

TABLE II.

Equilibrium constants and activity coefficients for p-*dichlorobenzene solutions of pyridine* o-*chlorophenoxide at molar ratio* = M.

			Activity coefficients.*							Activity coefficients.*			
$M \times 10^3$.	ΔT.	K_a.	γ.	γ_A.	γ_B.	γ_{AB}.	$M \times 10^3$.	ΔT.	K_a.	γ.	γ_A.	γ_B.	γ_{AB}.
0·811	0·078°	34·27	0·980	1·010	1·005	0·985	11·01	0·925°	35·44	0·759	1·072	1·033	0·803
1·644	0·157	34·70	0·962	1·027	1·009	0·965	12·67	1·053	34·69	0·737	1·075	1·035	0·791
2·116	0·200	34·09	0·949	1·028	1·010	0·955	14·62	1·192	34·69	0·710	1·076	1·037	0·779
2·687	0·252	34·55	0·932	1·031	1·012	0·927	16·28	1·310	34·61	0·690	1·077	1·038	0·771
3·180	0·296	34·89	0·919	1·035	1·013	0·914	19·07	1·504	34·76	0·660	1·075	1·039	0·766
3·518	0·324	35·70	0·908	1·039	1·015	0·892	20·54	1·604	34·57	0·646	1·074	1·040	0·759
4·123	0·377	35·63	0·894	1·044	1·017	0·886	22·43	1·729	34·44	0·628	1·071	1·040	0·751
4·692	0·427	35·08	0·882	1·048	1·018	0·882	24·89	1·887	34·55	0·606	1·069	1·040	0·744
5·344	0·480	35·48	0·865	1·052	1·020	0·859	27·55	2·059	34·34	0·586	1·065	1·040	0·735
6·085	0·542	35·38	0·850	1·055	1·023	0·857	29·97	2·215	34·02	0·570	1·063	1·039	0·725
6·679	0·591	35·26	0·838	1·057	1·025	0·849	32·60	2·372	34·17	0·552	1·060	1·038	0·718
7·809	0·682	34·93	0·817	1·061	1·028	0·835	35·12	2·523	34·22	0·537	1·058	1·038	0·710
8·541	0·738	35·28	0·802	1·064	1·030	0·826	36·79	2·623	34·00	0·528	1·056	1·038	0·703
9·754	0·830	35·42	0·779	1·068	1·030	0·814							

Average value : $K_a = 34{\cdot}78$.

* γ_A, γ_B, γ_{AB} = activity coefficient of pyridine, *o*-chlorophenol, and undissociated pyridine *o*-chlorophenoxide, respectively.

SUMMARY.

The true equilibrium constant, $K_a = a_{AB}/a_A a_B$, has been calculated for the dissociation of pyridine *o*-chlorophenoxide in *p*-dichlorobenzene by the method previously described (*loc. cit.*) for benzene solutions. The present results, in conjunction with those reported for benzene, give two series of values of K_a for different temperatures, *viz.*, the freezing

points of the solvents, and therefore the van 't Hoff isochore has been applied to calculate the heat of formation (Q) of pyridine *o*-chlorophenoxide. Since $Q = -6800$ cals., the compound is formed exothermally.

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