65. *Equilibrium Constants in Terms of Activities (Cryoscopic). Part III. The Dissociation of Quinoline* o-*Chlorophenoxide in Benzene and in* p-*Dichlorobenzene.*

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A STUDY has been made of the dissociation of quinoline *o*-chlorophenoxide, in the solvents benzene and *p*-dichlorobenzene, by methods precisely the same as those used in a similar study (J., 1933, 193, 1431) of pyridine *o*-chlorophenoxide. Each solvent forms a eutectic system with either quinoline or *o*-chlorophenol (see below) and this is a necessary condition for the present investigation. Bramley (J., 1916, **109**, 469) has shown that quinoline and *o*-chlorophenol form an equimolecular compound and, as this may be expected to contain the same type of valency bond as the analogous pyridine compound, it is of interest to know if the complete heat of formation is the same for both substances.

The activities of quinoline *o*-chlorophenoxide and its dissociation products have been calculated from freezing-point data, and values for the equilibrium constant, K_a, have been found; the latter have been used to calculate the heat of formation of quinoline *o*-chlorophenoxide by the van 't Hoff isochore (cf. *loc. cit.*).

" Pure synthetic " quinoline, after standing for 3 days over potassium hydroxide, was distilled in the dark from barium oxide (Walton and Wise, *J. Amer. Chem. Soc.*, 1922, **44**, 103) until the product was colourless. Other substances were as before (*loc. cit.*).

TABLE I.

Activity coefficients for quinoline as solute.

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

Series 1. Benzene solutions.						Series 2. *p*-Dichlorobenzene solutions.					
$M\times10^3$.	ΔT.	γ_A.	$M\times10^3$.	ΔT.	γ_A.	$M\times10^3$.	ΔT.	γ_A.	$M\times10^3$.	ΔT.	γ_A.
0·808	0·053°	0·995	11·03	0·702°	0·945	0·879	0·043°	1·013	20·32	0·997°	1·063
1·401	0·091	0·992	12·83	0·814	0·938	1·996	0·098	1·022	21·74	1·064	1·062
2·152	0·140	0·986	15·36	0·970	0·930	2·503	0·123	1·025	24·24	1·181	1·058
2·961	0·192	0·981	17·33	1·091	0·923	3·167	0·156	1·030	26·26	1·275	1·054
3·744	0·242	0·976	19·52	1·226	0·918	4·582	0·226	1·039	28·20	1·364	1·051
4·058	0·263	0·975	22·11	1·382	0·909	5·670	0·280	1·043	30·39	1·467	1·048
5·182	0·334	0·969	26·98	1·678	0·898	7·750	0·384	1·053	32·49	1·563	1·045
5·775	0·372	0·968	30·25	1·874	0·890	9·740	0·483	1·059	36·77	1·761	1·040
6·757	0·434	0·963	34·12	2·101	0·880	11·45	0·568	1·063	39·41	1·881	1·035
7·415	0·476	0·961	38·38	2·356	0·873	13·46	0·667	1·065	44·86	2·127	1·027
8·308	0·532	0·956	44·74	2·726	0·860	15·94	0·788	1·066	48·19	2·278	1·022
9·358	0·598	0·952				18·28	0·900	1·066	57·46	2·686	1·007

Cryoscopic data for quinoline (Table I) and for equimolecular mixtures of quinoline and *o*-chlorophenol (Table II) were determined.

We found that equimolecular mixtures give a minimum depression (cf. J., **1933**, **196**), showing maximum formation of quinoline *o*-chlorophenoxide, and we used such mixtures, prepared synthetically, in the solid form (m. p. 47·5°). Freezing-point depressions in *p*-dichlorobenzene were determined as before (J., **1933**, **1431**), but alumina was used to take up moisture in benzene

TABLE II.

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

(γ_A, γ_B, and γ_{AB} = activity coefficients of quinoline, *o*-chlorophenol, and undissociated quinoline *o*-chlorophenoxide respectively.)

(a) *Benzene solutions.*

$M \times 10^3$.	ΔT.	K_a.	γ.	γ_A.	γ_B.	γ_{AB}.
0·552	0·069°	214·3	0·902	0·996	1·002	0·991
0·845	0·103	217·8	0·860	0·995	1·003	0·980
1·105	0·132	218·7	0·828	0·993	1·004	0·969
1·360	0·160	218·6	0·800	0·992	1·004	0·958
1·863	0·214	214·4	0·755	0·990	1·005	0·936
2·243	0·251	222·5	0·719	0·989	1·005	0·924
3·047	0·330	218·3	0·668	0·986	1·007	0·901
3·841	0·403	220·0	0·623	0·984	1·008	0·876
5·236	0·524	220·5	0·562	0·981	1·009	0·838
6·398	0·627	219·6	0·522	0·979	1·010	0·806
7·605	0·713	222·3	0·486	0·977	1·011	0·781
9·078	0·827	221·6	0·452	0·975	1·012	0·754
10·68	0·944°	220·3	0·421	0·973	1·014	0·724
12·28	1·057	220·0	0·395	0·971	1·015	0·700
13·64	1·153	218·5	0·377	0·970	1·015	0·683
15·29	1·263	219·9	0·356	0·968	1·016	0·664
16·70	1·357	219·5	0·341	0·967	1·016	0·650
18·54	1·472	220·1	0·323	0·965	1·017	0·632
21·27	1·638	220·4	0·301	0·964	1·018	0·610
24·22	1·814	222·0	0·280	0·962	1·019	0·588
27·26	1·983	221·9	0·262	0·960	1·020	0·565
30·28	2·149	221·3	0·247	0·958	1·020	0·545
34·28	2·366	221·4	0·230	0·956	1·021	0·523

(b) p-*Dichlorobenzene solutions.*

$M \times 10^3$.	ΔT.	K_a.	γ.	γ_A.	γ_B.	γ_{AB}.
1·300	0·124	37·64	0·964	1·015	1·005	1·002
1·702	0·162	37·20	0·955	1·018	1·008	1·003
2·540	0·239	37·96	0·933	1·024	1·012	1·006
3·388	0·316	36·34	0·917	1·029	1·015	1·008
3·954	0·367	35·97	0·906	1·032	1·017	1·010
4·479	0·414	35·75	0·896	1·034	1·019	1·012
5·131	0·470	36·04	0·883	1·039	1·020	1·014
5·714	0·520	35·90	0·873	1·041	1·023	1·015
6·732	0·605	36·17	0·854	1·044	1·026	1·016
8·648	0·764	35·94	0·824	1·049	1·030	1·018
10·42	0·910	36·11	0·798	1·054	1·033	1·018
12·28	1·052	35·94	0·774	1·057	1·034	1·018
13·70	1·163	35·90	0·757	1·059	1·036	1·017
15·70	1·307	36·39	0·732	1·062	1·038	1·012
17·74	1·454	36·51	0·710	1·065	1·039	1·006
19·45	1·574	36·85	0·692	1·065	1·040	1·001
21·26	1·696	37·08	0·674	1·066	1·040	0·995
22·18	1·759	37·02	0·666	1·066	1·040	0·991
24·31	1·899	37·15	0·647	1·066	1·039	0·982
26·95	2·073	37·28	0·626	1·066	1·039	0·972
29·71	2·251	37·36	0·606	1·066	1·038	0·962
32·67	2·431	37·71	0·585	1·066	1·038	0·950
36·08	2·643	37·63	0·565	1·065	1·037	0·937
38·30	2·775	37·87	0·552	1·065	1·036	0·931

Average values of K_a: (*a*) (in benzene) = 219·8; (*b*) (in *p*-dichlorobenzene) = 36·74.

solutions (Jones and Bury, J., 1925, **127**, 1947). Concentrated (10%) solutions of quinoline or *o*-chlorophenol can be left in contact with alumina for 24 hours without any detectable variation of the f. p.'s of the solutions, and there is evidently no adsorption of these solutes on alumina.

All depression results now reported were determined in an apparatus provided with a mercury-sealed stirrer and a guard tube containing phosphoric oxide to exclude moisture.

Activity Coefficients.—The results of the present work, summarised in Tables I and II, were obtained as previously (*loc. cit.*), and the necessary values for γ_B, the activity coefficient of *o*-chlorophenol, are taken from earlier parts of this series of papers. Fig. 1 shows that, in *p*-dichlorobenzene solutions, all γ_A values and certain γ_{AB} values are greater than unity. Similar examples have been noted before (*loc. cit.*) and, in all cases, γ_{AB} values are generally lower than the corresponding γ_A or γ_B values.

Heat of Formation of Quinoline o-*Chlorophenoxide.*—The average values of K_a (Table II) have been applied in the isochore (cf. J., 1933, 1431); whence $Q = -6800$ cals., and the reaction is exothermal ($T_1 = 277·7°$ and $T_2 = 324·8°$). This value for Q is the same as that found for pyridine *o*-chlorophenoxide (*loc. cit.*).

Related Binary Systems (with Frederick Hunter).—In this and earlier parts of this series, the two solvents, benzene and *p*-dichlorobenzene, have been used because each forms a binary eutectic system with any of the solutes quinoline, pyridine, or *o*-chlorophenol. Data for four of these binary systems are now reported; Fig. 2 shows the results.

F. p.'s were determined by the usual thermometric cooling curve method, but the temperature at which solid first appeared was also observed, as an additional check, in many cases. This was rendered possible by the use of a transparent Dewar tube as container of freezing mixtures.

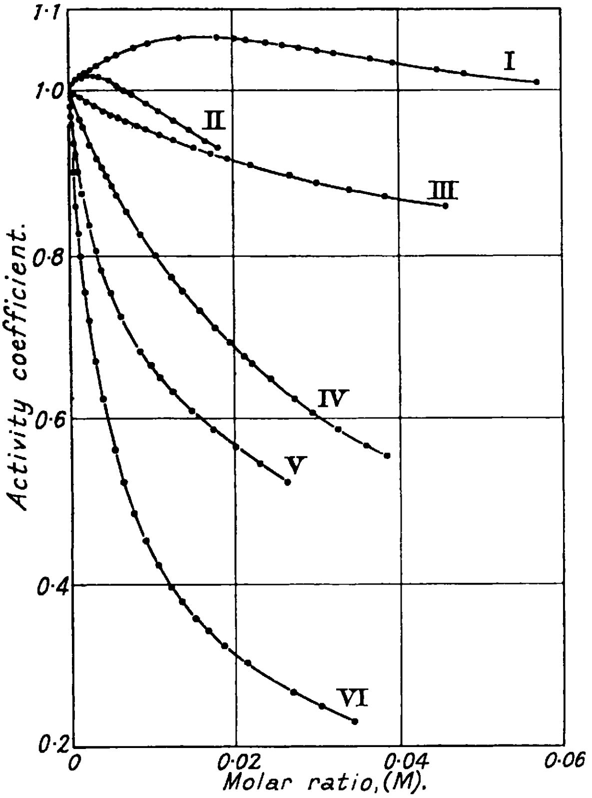
Freezing mixtures were varied to suit the range of temperature involved with the various mixtures; water, ice–water, ice–salt, and ether–solid carbon dioxide cover the entire range of temperatures (see Fig. 2).

The system benzene–quinoline showed very pronounced supercooling, and it was necessary to inoculate it with the solid phase to obtain satisfactory freezing points (cf. Glass, Laybourn, and Madgin, J., 1932, 874).

A mercury-in-glass thermometer (— 10° to + 60° by 0·1°) was used for temperatures above, and a toluene-in-glass thermometer (25° to — 80° by 1°) for those below 0°. The two thermometers were checked against each other over their common range and each was standardised against a thermocouple for the complete range. As an additional check, the f. p.'s of the pure components and the four eutectic mixtures have been determined with a thermocouple.

The diagrams in Fig. 2 suggested that each system is of the simple eutectic type, and this was confirmed by the eutectic arrests, also shown in the Fig. Further support for these conclusions was obtained for those systems which would be expected to deposit *p*-dichlorobenzene as solid phase. In several instances the solid was isolated, pressed on a porous tile, and the m. p. of the residue determined (cf. Wood and Scott, J., 1910, **97**, 1576). This m. p. was never more than 1° below that of pure *p*-dichlorobenzene (52·9°).

FIG. 1.



p-Dichlorobenzene solutions; I, II, and IV. *Benzene solutions*; III, V, and VI. I and III, *quinoline* (γ_A); II and V, *quinoline* o-*chlorophenoxide, undissociated* (γ_{AB}); IV and VI, *quinoline and* o-*chlorophenol together in solution* (γ).

DISCUSSION OF RESULTS.

The values of K_a now reported for quinoline *o*-chlorophenoxide are very similar, both numerically and by reason of their consistency, to those already reported (*loc. cit.*) for pyridine *o*-chlorophenoxide. Extreme values in the present results differ from average values by only 2% for benzene and 3% for *p*-dichlorobenzene solutions. Thus there seems to be evidence of marked similarity between the two bases, pyridine and quinoline.

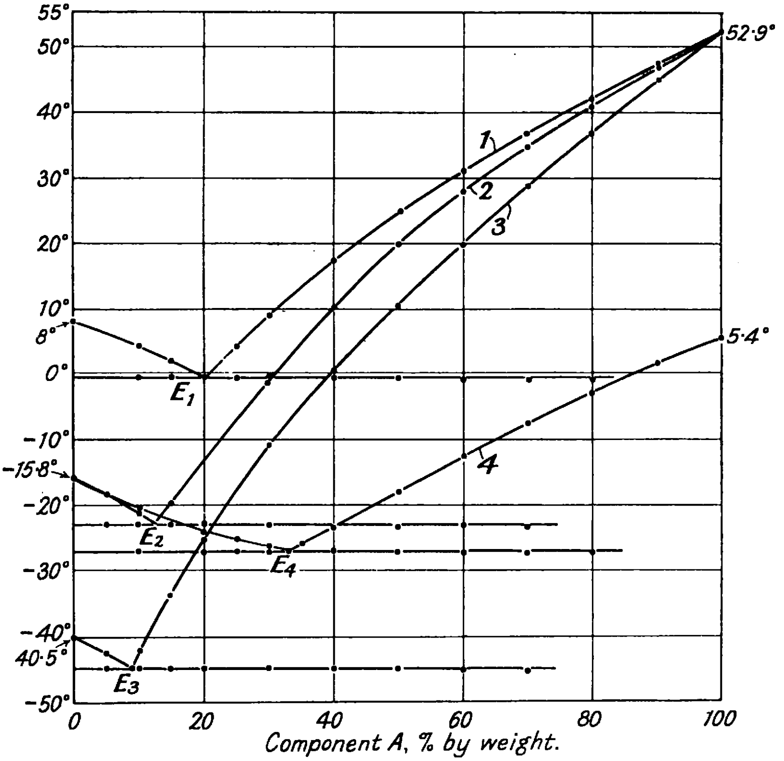
The large differences between γ_{AB} values in the two non-polar solvents benzene and *p*-dichlorobenzene (Fig. 1; II and V) require comment. In a case where the activity is independent of temperature, the activity coefficients would be expected to be almost the same in each of the two solvents now under consideration. Such solutions are referred to as semi-ideal (Guggenheim, "Modern Thermodynamics," London, 1933), and an example is to be found in the *o*-chlorophenol solutions already studied by us (*loc. cit.*). The γ_{AB} values in the present work presumably refer to non-ideal solutions, since they show large variations with temperature changes and thus resemble quinoline solutions (Fig. 1, I and III). The extents of such variations cannot be pre-determined but it would be expected that activity coefficients would approach unity on rise of temperature, the solutions thus becoming more ideal.

The specific effect shown by *p*-dichlorobenzene, *viz.*, enhancing the activities by comparison with benzene solutions, has been referred to already (J., 1933, 1431).

The heat of formation is identical (Q = — 6800 cals.) for the *o*-chlorophenoxides of both pyridine and quinoline; the heat value is for complete compound formation from g.-mol. quantities in the condition in which they exist in dilute solution. Probably this identity of heat of formation is due to some more fundamental cause than the similarity of pyridine and quinoline, and there seems reason to suppose that the same type of valency bond occurs in both *o*-chlorophenoxides. Following Sidgwick ("Electronic Theory of Valency," Oxford, 1927, p. 68), we may regard the nitrogen atom in each base as co-ordinating the hydrogen atom in *o*-chlorophenol, and should expect the product to be dissociated in, *e.g.*, benzene, into the original components, thus, $[BN \longrightarrow HO{\cdot}C_6H_4Cl] \rightleftharpoons BN + HO{\cdot}C_6H_4Cl$. Therefore it would seem that the heat values now determined indicate the energy of formation of the co-ordinate link $BN \longrightarrow HOR$.

We are continuing investigations similar to the present.

FIG. 2.



Freezing point–composition diagrams.

	1	2	3	4
A.	p-*Dichlorobenzene*	p-*Dichlorobenzene*	p-*Dichlorobenzene*	*Benzene*
B.	o-*Chlorophenol*	*Quinoline*	*Pyridine*	*Quinoline*

E_1 20% A (−0·4°); E_2 12·5% A (−22·9°); E_3 9% A (−44·9°); E_4 33% A (−27·0°).

SUMMARY.

The true equilibrium constant, $K_a = a_{AB}/a_A a_B$, has been calculated for the dissociation of quinoline *o*-chlorophenoxide in benzene and in *p*-dichlorobenzene. Thus, two average values of K_a have been found for the two mean temperatures, $T_1 = 277{\cdot}7°$ and $T_2 = 324{\cdot}8°$, and the van 't Hoff isochore has been applied to calculate the heat of formation ($Q = -6800$ cals.) of quinoline *o*-chlorophenoxide. Since pyridine *o*-chlorophenoxide has been shown (*loc. cit.*) to have the same heat of formation, an explanation of this equality has been suggested in terms of valency considerations.

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