282. *Equilibrium Constants in Terms of Activities (Cryoscopic). Part V.* p-*Toluidine* o-*Chlorophenoxide and* p-*Chlorophenoxide in Benzene and in* p-*Dichlorobenzene.*

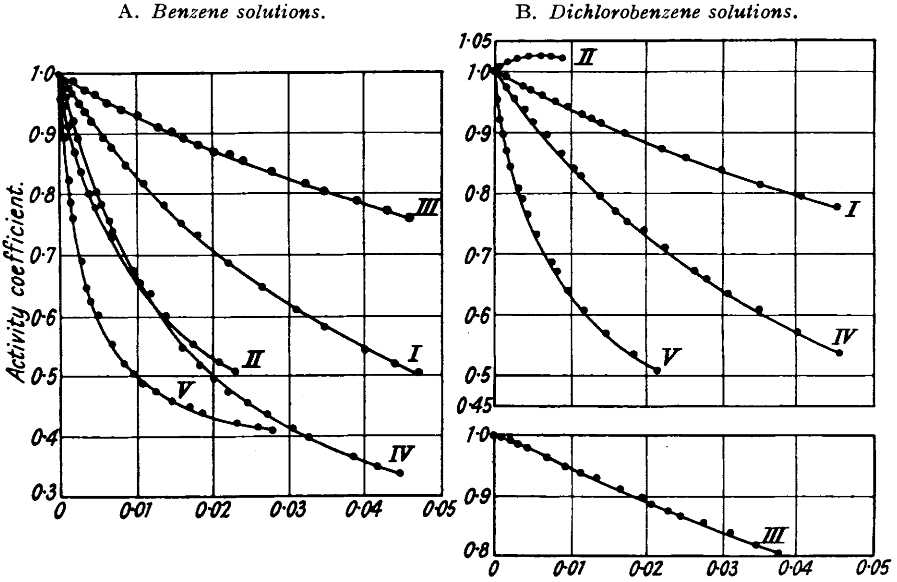
By W. R. Burnham and W. M. Madgin.

Some extension of the results reported in earlier parts of this series (J., 1934, 1292, and earlier references) seemed desirable. The existence of the *o*- and *p*-chlorophenoxides of *p*-toluidine as compounds has already been demonstrated (this vol., p. 789), and their dissociation in benzene and in *p*-dichlorobenzene has now been investigated.

If *o*-chlorophenol is chelated (Sidgwick and Callow, J., 1924, **125**, 527) but *o*-cresol is not, the heat of formation of *p*-toluidine *o*-tolyloxide might show some marked difference from that of the *o*-chlorophenoxide. Further, because of the widely different dipole moments of *o*- and *p*-chlorophenol, *viz.*, 1·2 and 2·3 respectively (Landolt–Börnstein, " Tabellen," 1931 and earlier), the heats of formation of the compounds of *p*-toluidine with each of these phenols seemed of interest. It was hoped that these results might contribute further to the problem as to whether compounds of the type amine–phenol all contain the same fundamental linkage.

Experimental.

p-Chlorophenol was purified as previously reported by us (*loc. cit.*), and other materials were as reported in earlier parts of this series (*loc. cit.*).



I. p-*Toluidine and* o-*chlorophenol together in solution* (γ).
II. p-*Toluidine* o-*chlorophenoxide, undissociated* (γ_{AB}).
III. p-*Chlorophenol* (γ_B).
IV. p-*Toluidine and* p-*chlorophenol together in solution* (γ).
V. p-*Toluidine* p-*chlorophenoxide, undissociated* (γ_{AB}).

Binary Systems.—The solutes selected form eutectic systems with both solvents and, with one exception, the various binary systems thus involved have been reported in earlier parts of this series. Sidgwick and Turner (J., 1922, **121**, 2256) found that the system *p*-chlorophenol–benzene was of the eutectic type.

Activity Coefficients.—Tables I, II, and III, together with the figure, give the results of the present work. The experimental cryoscopic method was as before, but the original method was simplified in the calculation of the molar ratios (m) of the uncombined constituents of amine-phenol complexes. The product $m^2\gamma_A\gamma_B$ was determined by the original experimental method, and plotted against m. The resulting curve has been used to determine m values corresponding to M values, since $(M\gamma)^2 = m^2\gamma_A\gamma_B$.

TABLE I.

Activity coefficients for p-*chlorophenol as solute.*

(M = Molar ratio of solute; ΔT = depression of f. p.)

Benzene solutions.						*p*-Dichlorobenzene solutions.					
10^3M.	ΔT.	γ_B.	10^3M.	ΔT.	γ_B.	10^3M.	ΔT.	γ_B.	10^3M.	ΔT.	γ_B.
0·766	0·050°	0·994	16·20	1·001°	0·893	0·988	0·048°	0·999	15·04	0·698°	0·919
1·551	0·101	0·988	17·97	1·107	0·883	1·983	0·096	0·994	16·63	0·768	0·911
2·357	0·153	0·982	20·37	1·242	0·869	2·402	0·116	0·991	18·93	0·869	0·899
3·592	0·232	0·972	22·09	1·341	0·863	3·260	0·157	0·986	20·81	0·936	0·889
4·315	0·278	0·967	24·08	1·452	0·852	3·401	0·178	0·985	23·00	1·042	0·875
4·884	0·314	0·963	27·88	1·663	0·835	4·438	0·213	0·980	24·68	1·112	0·869
6·288	0·402	0·953	32·11	1·893	0·815	4·905	0·235	0·976	27·73	1·238	0·855
8·109	0·515	0·942	35·13	2·056	0·802	6·892	0·328	0·962	31·27	1·382	0·838
10·00	0·631	0·929	38·88	2·248	0·787	8·058	0·382	0·958	32·14	1·420	0·835
12·48	0·781	0·915	42·86	2·451	0·772	8·932	0·432	0·953	37·86	1·641	0·808
14·00	0·871	0·905	45·79	2·600	0·759	9·598	0·453	0·949	41·09	1·765	0·795
14·64	0·909	0·901				11·50	0·540	0·939	45·57	1·931	0·776
						13·38	0·624	0·928			

TABLE II.

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

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

Benzene solutions.							*p*-Dichlorobenzene solutions.						
10^3M.	ΔT.	K_a.	γ.	γ_A.	γ_B.	γ_{AB}.	10^3M.	ΔT.	K_a.	γ.	γ_A.	γ_B.	γ_{AB}.
0·398	0·052°		0·993				0·505	0·049°		0·996			
0·605	0·079		0·986				1·022	0·099		0·994			
0·786	0·102	20·65	0·983	0·997	1·002	0·998	1·229	0·119		0·992			
1·182	0·153	20·97	0·975	0·995	1·004	0·997	2·396	0·231	8·37	0·984	1·003	1·010	1·001
1·553	0·200	21·17	0·968	0·994	1·005	0·995	2·700	0·260	8·41	0·981	1·004	1·012	1·001
2·106	0·270	21·17	0·958	0·993	1·006	0·991	3·120	0·300	8·68	0·979	1·005	1·015	1·002
2·406	0·307	20·75	0·951	0·992	1·007	0·989	3·774	0·362	8·65	0·978	1·006	1·017	1·002
2·939	0·373	20·69	0·942	0·991	1·008	0·987	4·588	0·439	8·63	0·971	1·006	1·020	1·003
3·218	0·408	21·10	0·938	0·990	1·009	0·983	5·662	0·540	8·75	0·964	1·007	1·023	1·005
4·065	0·511	21·06	0·923	0·988	1·011	0·971	6·251	0·595	8·79	0·960	1·007	1·026	1·006
4·487	0·561	21·01	0·915	0·987	1·012	0·964	7·799	0·739	8·78	0·952	1·006	1·031	1·007
5·794	0·715	20·87	0·892	0·985	1·015	0·955	9·420	0·888	8·89	0·943	1·004	1·034	1·009
6·673	0·816	21·02	0·878	0·982	1·017	0·945	9·946	0·936	8·88	0·939	1·003	1·037	1·009
8·722	1·051	21·09	0·850	0·978	1·020	0·912	11·29	1·058	8·86	0·931	1·000	1·038	1·012
10·98	1·303	20·97	0·819	0·973	1·022	0·871	12·58	1·170	8·81	0·927	0·998	1·040	1·013
13·58	1·564	20·79	0·788	0·970	1·024	0·838	13·82	1·285	8·63	0·919	0·994	1·040	1·014
16·05	1·799	21·05	0·753	0·964	1·025	0·796	14·95	1·385	8·79	0·913	0·992	1·040	1·015
17·91	1·985	20·73	0·731	0·959	1·025	0·762	17·08	1·572	8·67	0·902	0·985	1·039	1·017
22·20	2·376	21·07	0·686	0·954	1·024	0·730	20·03	1·826	8·78	0·884	0·977	1·037	1·021
26·64	2·762	20·91	0·645	0·950	1·022	0·674	22·48	2·034	8·53	0·874	0·970	1·035	1·022
31·14	3·120	20·90	0·609	0·947	1·019	0·637	25·02	2·246	8·56	0·862	0·962	1·033	1·023
35·24	3·437	20·60	0·581	0·945	1·017	0·596	30·02	2·656	8·45	0·839	0·949	1·028	1·025
39·78	3·738	20·61	0·548	0·944	1·014	0·551	35·13	3·066	8·63	0·817	0·938	1·021	1·026
44·09	4·003	20·59	0·519	0·942	1·012	0·524	40·19	3·456	8·44	0·796	0·928	1·012	1·026
47·11	4·213	20·60	0·503	0·940	1·010	0·508	45·16	3·834	8·59	0·777	0·920	1·004	1·025

Average values of K_a: in benzene, 20·95; in *p*-dichlorobenzene, 8·66.

Heats of Formation.—The average values of K_a (Tables II and III) have been applied in the isochore (cf. Part II, J., 1933, 1431), whence the heats of formation of *p*-toluidine *p*-chlorophenoxide ($Q = -$ 4200 cals.) and *o*-chlorophenoxide ($Q = -$ 3500 cals.) have been found. Each compound is formed exothermally ($T_1 = 277·0°$; $T_2 = 324·3°$).

TABLE III.

Equilibrium constants and activity coefficients for benzene and p-*dichlorobenzene solutions of* p-*toluidine* p-*chlorophenoxide at molar ratio,* M.

(γ_A, γ_B, and γ_{AB} = activity coefficients of *p*-toluidine, *p*-chlorophenol, and undissociated complex respectively.)

Benzene solutions.

10^3M.	ΔT.	K_a.	γ.	γ_A.	γ_B.	γ_{AB}.
0·525	0·068°	47·47	0·973	1·000	0·996	0·998
0·815	0·105	48·32	0·963	0·997	0·994	0·994
1·619	0·204	48·10	0·921	0·994	0·990	0·988
2·332	0·289	48·39	0·893	0·993	0·984	0·957
4·556	0·534	48·97	0·803	0·987	0·970	0·885
5·203	0·601	49·01	0·787	0·986	0·968	0·825
6·155	0·697	47·96	0·757	0·985	0·962	0·786
6·846	0·764	49·02	0·738	0·984	0·960	0·761
9·040	0·967	48·19	0·681	0·981	0·953	0·691
10·28	1·073	48·88	0·651	0·979	0·948	0·650
11·33	1·160	48·04	0·630	0·977	0·941	0·624
13·19	1·310	48·55	0·595	0·975	0·935	0·600
16·00	1·528	48·25	0·549	0·973	0·930	0·551
18·24	1·697	48·66	0·520	0·971	0·928	0·525
20·21	1·838	48·10	0·496	0·969	0·926	0·505
22·08	1·978	47·84	0·478	0·968	0·924	0·489
24·51	2·144	48·16	0·456	0·967	0·920	0·475
27·04	2·316	47·80	0·437	0·965	0·914	0·462
30·47	2·560	48·76	0·411	0·963	0·910	0·447
32·56	2·704	48·69	0·398	0·961	0·908	0·437
38·44	3·096	49·03	0·368	0·959	0·900	0·422
41·37	3·296	48·98	0·350	0·958	0·898	0·417
44·39	3·500	48·81	0·337	0·956	0·891	0·412

p-Dichlorobenzene solutions.

10^3M.	ΔT.	K_a.	γ.	γ_A.	γ_B.	γ_{AB}.
0·508	0·049°		0·991			
1·404	0·135	16·81	0·976	1·002	0·998	0·995
1·448	0·139	16·81	0·974	1·002	0·996	0·994
1·976	0·189	16·88	0·966	1·003	0·993	0·991
2·444	0·232	16·85	0·959	1·003	0·992	0·984
3·740	0·351	16·79	0·937	1·005	0·984	0·968
5·002	0·462	16·29	0·919	1·006	0·979	0·955
6·586	0·603	16·67	0·897	1·007	0·971	0·925
7·670	0·695	16·74	0·879	1·006	0·965	0·904
8·568	0·771	16·79	0·866	1·005	0·961	0·897
10·42	0·924	16·84	0·840	1·003	0·953	0·869
11·17	0·983	16·82	0·828	1·002	0·950	0·857
13·06	1·144	16·22	0·802	1·000	0·942	0·843
13·75	1·185	16·83	0·795	0·998	0·939	0·828
15·75	1·340	16·67	0·769	0·994	0·932	0·809
16·26	1·377	16·85	0·762	0·993	0·930	0·800
17·33	1·454	16·88	0·752	0·991	0·927	0·791
19·50	1·608	16·15	0·737	0·986	0·918	0·766
22·26	1·797	16·36	0·709	0·980	0·910	0·731
26·29	2·068	16·02	0·674	0·973	0·904	0·685
27·77	2·164	16·00	0·658	0·969	0·895	0·670
30·65	2·322	16·20	0·636	0·964	0·888	0·640
34·77	2·570	16·19	0·608	0·957	0·878	0·609
39·88	2·858	16·14	0·574	0·950	0·868	0·571
45·39	3·149	16·55	0·537	0·944	0·859	0·535
50·18	3·382	16·42	0·513	0·940	0·852	0·509

Average values of K_a: in benzene, 48·39; in *p*-dichlorobenzene, 16·54.

DISCUSSION.

The values of K_a (Tables II and III) are of the same order as those of *p*-toluidine *o*-tolyloxide (Part IV; J., 1934, 1292), and the stabilities of all of these complexes in solution are evidently similar. By contrast, the K_a values for pyridine and quinoline *o*-chlorophenoxides (Part III; J., 1934, 260, and earlier) are much larger, and these compounds are correspondingly more stable than those of *p*-toluidine.

To facilitate comparisons, the heats of formation already reported in earlier parts of this series are reproduced: pyridine *o*-chlorophenoxide, – 6800 cals.; quinoline *o*-chlorophenoxide, – 6800 cals.; *p*-toluidine *o*-tolyloxide, – 6000 cals.

The very different heats of formation of compounds of *o*-chlorophenol with *p*-toluidine ($Q = -3500$ cals.) and pyridine or quinoline ($Q = -6800$ cals.) are paralleled by the corresponding dipole moments of the bases, *viz.*, *p*-toluidine, 1·2; pyridine, 2·2; quinoline, 2·2 (Landolt–Börnstein, *op. cit.*).

If each of these complexes is formed by a co-ordinate link N—H (cf. Part IV), then the heat values suggest that such links do not show uniformity, but are considerably influenced by the chemical nature of the constituents of the complexes. This would be the case if dipole attraction is a contributory cause of co-ordination. Moelwyn-Hughes and Sherman (this vol., p. 101), discussing co-ordination, review different mechanisms which "are alternative attempts to describe the same phenomenon," and dipole attraction is one such mechanism.

In Part IV the ionisation constants were referred to as indicating probable relative heat values, but the heats of formation of the three *o*-chlorophenoxides cited would not be predicted by considering ionisation constants only.

Chelation will also be a factor. The presence of chelation in *o*-chlorophenol and its absence in *o*-cresol may be expected to give different heat values for the same base, *e.g.*, their compounds with *p*-toluidine. However, the actual difference (2500 cals.) may not be entirely accounted for by chelation; the two phenols have different ionisation constants and dipole moments.

p-Toluidine *p*-chlorophenoxide has a slightly greater heat of formation than the *o*-chlorophenoxide, as chelation considerations would suggest, although a greater difference might be anticipated. The value for *p*-toluidine *p*-chlorophenoxide (— 4200 cals.) seems surprising when compared with that for its *o*-tolyloxide (— 6000 cals.), since there is no chelation involved in either case. The dipole moments of the phenols are: *p*-chlorophenol 2·3, *o*-cresol 1·44. However, the actual length of the dipole is greater in the former, and compound formation may be retarded when two dipoles of dissimilar length are associating as in *p*-toluidine *p*-chlorophenoxide.

The activity coefficient, γ_{AB}, of *p*-toluidine *p*-chlorophenoxide (see fig.) is greater than 1, whereas, if such compounds associated in solution (cf. Sidgwick, "The Covalent Link in Chemistry," 1933), the value would be less than 1. Dipole association of the solvent, *p*-dichlorobenzene (cf. Part IV, p. 1295), may account for the present values of γ_{AB}.

SUMMARY.

The equilibrium constant, $K_a = a_{AB}/a_A a_B$, has been calculated for the dissociation of *p*-toluidine *o*- and *p*-chlorophenoxide in benzene and in *p*-dichlorobenzene.

Average values of K_a have been found for the two mean temperatures, $T_1 = 277{\cdot}0°$ and $T_2 = 324{\cdot}3°$, and the van 't Hoff isochore has been applied to calculate the heats of formation of the complexes.

These values have been compared with those previously reported, and the probable influences of dipole moments, dipole association, and chelation have been discussed.

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