160. *Molecular Polarisation and Molecular Interaction. Part I. The Apparent Dipole Moments of Aniline, Methylaniline, and Dimethylaniline in Benzene and 1 : 4-Dioxan Solutions.*

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From measurements of the dielectric constants, refractive indices, and specific volumes of dilute solutions, the apparent molecular polarisations at infinite dilution ($P_{2\infty}$) and molecular refraction ($[R_D]$) of aniline, methylaniline, and dimethylaniline in benzene and 1 : 4-dioxan solutions at 25° have been determined. For aniline and methylaniline the values of $P_{2\infty}$ are much greater in 1 : 4-dioxan than in benzene, whilst with dimethylaniline the difference is much smaller. These effects are attributable to the formation of hydrogen bonds between the amino-hydrogen atoms and an oxygen atom of the dioxan molecule, with resulting modification of the charge distribution. The values of $[R_D]$ for aniline and methylaniline are also slightly higher in 1 : 4-dioxan than in benzene solution or in the pure liquids. Assuming the total distortion polarisation to be $1{\cdot}05[R_D]$, the apparent dipole moments in benzene and 1 : 4-dioxan, respectively, are found to be : aniline, 1·505 and 1·750; methylaniline, 1·643 and 1·833; and dimethylaniline, 1·577 and 1·633 D. The value for aniline in benzene solution is slightly lower than observed by other investigators at 20°.

THE molecular polarisation and apparent dipole moments of amines in solution present an interesting problem in that, in these molecules, the axis of the dipole is inclined at an angle to the axis of maximum polarisability. Hence, according to the theories of Raman and Krishnan (*Proc. Roy. Soc.*, 1928, *A*, **117**, 589), Frank (*ibid.*, 1936, *A*, **152**, 171), and Higasi (*Sci. Pap. Inst. Phys. Chem. Res. Japan*, 1936, **28**, 284) they should show only a slight negative or a positive solvent effect.

The apparent dipole moment of aniline in various solvents has been studied previously by Højendahl (Thesis, Copenhagen, 1928), Hassel and Uhl (*Z. physikal. Chem.*, 1930, *B*, **8**, 193), Tiganik (*ibid.*, 1931, *B*, **14**, 139), Cowley and Partington (*J.*, 1938, 1598), Le Fèvre and Le Fèvre (*J.*, 1936, 1136), Higasi (*Bull. Inst. Phys. Chem. Res. Japan*, 1934, **13**, 1167), Vassiliev and Sirkin (*Acta Physicochim. U.R.S.S.*, 1941, **14**, 414), Kumler and Halverstadt (*J. Amer. Chem. Soc.*, 1941, **63**, 2182), and Emblem and McDowell (*J.*, 1946, 641). Methyl- and dimethyl-aniline have been investigated in benzene solution only by Fogelberg and Williams (*Physikal. Z.*, 1931, 32, 27). Recorded data for the molecular polarisations at infinite dilution ($P_{2\infty}$), the electronic polarisation (P_E) measured or assumed by each investigator, the value taken for the total distortion polarisation (P_{E+A}), and the orientation polarisation (P_μ) and apparent dipole moment (μ) deduced from these results are summarised in Table I, which also includes, for comparison purposes, the results for gaseous aniline and dimethylaniline recorded by Groves and Sugden (*J.*, 1937, 1782).

TABLE I.

Solvent.	Temp.	Observers.	$P_{2\infty}$, c.c.	P_E, c.c.	P_{E+A}, c.c.	P_μ, c.c.	μ, D.
		Aniline.					
Gas	186°	Groves and Sugden	61·5	30·6	32·1	29·4	1·48
Benzene	18	Hassel and Uhl	81·6	30·6	30·6	51·0	1·55
	20	Tiganik	79·7	30·6	30·6	49·1	1·52
		Cowley and Partington	80·0	30·6	30·6	49·4	1·53
		Emblem and McDowell	81·91	30·66	32·20	49·7	1·54
	25	Højendahl	76·0	29·0	29·0	47·0	1·51
		Le Fèvre and Le Fèvre	78·4	31	31	47·4	1·51
		Higasi	80·0	30·6	30·6	49·4	1·54
		Vassiliev and Sirkin	—	—	—	—	1·54
Hexane	20	Cowley and Partington	77·0	30·6	30·6	46·4	1·48
	25	Higasi	77·6	30·6	30·6	47·0	1·50
*cyclo*Hexane ...	20	Cowley and Partington	77·4	30·6	30·6	46·8	1·49
Toluene	20	Cowley and Partington	79·5	30·6	30·6	48·9	1·52
Dioxan	25	Vassiliev and Sirkin	—	—	—	—	1·77
		Kumler and Halverstadt	106	31	31	75	1·90
		do. (recalc.)	93·4	31	31	62·4	1·73
Diethyl ether...	20	Higasi	89·4	30·6	30·6	58·8	1·67
		Methylaniline.					
Benzene	25	Fogelberg and Williams	93	36	36	57	1·64
		Dimethylaniline.					
Gas	282	Groves and Sugden	78·0	40·8	42·8	35·2	1·61
Benzene		Højendahl	—	—	—	—	1·39
	25	Fogelberg and Williams	94	41	41	53	1·58

In the case of aniline in benzene the lack of accord is considerable, the values of μ reported ranging from 1·51 to 1·54 D. The divergence between the results is even greater than is suggested by these figures, since the observers who obtained the highest value made allowances for atomic polarisation which had not been included in computing the lower values.

From their investigations on solutions in 1 : 4-dioxan, Kumler and Halverstadt initially reported the value of $P_{2\infty}$, as derived by extrapolation of the values of P_2 to infinite dilution, as 106 c.c., leading to μ = 1·90 D., but these figures were later modified by them on the basis of their method of computation in which both the dielectric constant and the specific volume of the solutions were assumed to vary linearly with the weight-fraction of solute present. This change, which brought the value of μ more closely in accord with the measurements of Vassiliev and Sirkin, was made, however, at the cost of assuming that the true dielectric constant of the dioxan used relative to the values for the solvent differed from their measured value by no less than 0·0025. No actual data obtained by Vassiliev and Sirkin appear to be available, the publication quoting only the final moment deduced.

It may be inferred from the results, however, that the value of μ in hydrocarbon solvents is about equal to or slightly greater than for the gas phase, but that μ has much higher values in ether and in 1 : 4-dioxan solutions. Such high values would not be anticipated on the basis of normal "solvent effects" alone, so Vassiliev and Sirkin attributed the high value for dioxan solutions to the formation of complexes through hydrogen bonding.

No other data for the direct comparison of the apparent molecular polarisations of amines in oxygen-containing solvents with those in hydrocarbon solvents are available. It seems most probable, however, that the high values observed with aniline in the former class of solvent are due to hydrogen bonding between the hydrogen atoms of the amino-group and the donor oxygen atoms of solvent molecules, an effect which would give rise both to a lengthening of the N–H bond and a polarisation of the solvent molecule. The high value is therefore best regarded as due to an "interaction polarisation" in which the contributions of the solute and solvent molecules are inseparable. If these views are correct it would be anticipated that (*a*) there should also be a small increase in the apparent molecular refraction of aniline in solvents containing electron-donor atoms, and (*b*) the interaction polarisation would be decreased progressively when the amino-hydrogen atoms of the aniline molecule are successively replaced by methyl groups, the hydrogen atoms of which are less likely to engage in hydrogen bonding.

No data were available to test either of these inferences and therefore, in view of the uncertain character of the figures for aniline solutions, the dielectric constants, refractive indices, and specific volumes of dilute solutions of aniline, methylaniline, and dimethylaniline in benzene and 1 : 4-dioxan have been measured at 25°, and the values of the apparent molecular polarisations and apparent dipole moments deduced.

EXPERIMENTAL.

Materials.—Benzene (commercial " crystallisable " grade) was shaken with sulphuric acid, washed twice each with water and with 5% aqueous potassium hydroxide, and then further washed four times with water. After drying over phosphoric oxide it was fractionally crystallised until it formed a glassy crystalline mass on freezing, and after drying again over phosphoric oxide it was distilled from this reagent through a 20-plate all-glass fractionating column. The middle fraction was of constant b. p. within 0·01° and had $d_{4°}^{25°}$ 0·8737$_0$, $n_{\mathrm{D}}^{25°}$ 1·4981.

1 : 4-Dioxan (commercial " purissimus " grade) was purified by the method of Eigenberger (*J. pr. Chem.*, 1931, **130**, 75) by refluxing during 12 hours with N-hydrochloric acid whilst a stream of nitrogen was passed through it to remove aldehydes. The product was dried with two successive portions of potassium hydroxide pellets and then refluxed with sodium until the latter remained bright. It was finally fractionally crystallised once and distilled from sodium through the 20-plate column; the middle fraction of constant b. p. within 0·01° had $d_{4°}^{25°}$ 1·0280, $n_{\mathrm{D}}^{25°}$ 1·4202.

Amines. Pure commercial samples were dissolved in 40% sulphuric acid and free from non-basic material by passing steam through the solution during 1 hour, after which the base was liberated by addition of sodium hydroxide, steam-distilled, and dried over potassium hydroxide pellets.

Aniline was then twice distilled from zinc dust at 20 mm., dried with freshly prepared barium oxide, and finally distilled from a fresh sample of barium oxide in an all-glass apparatus at 20 mm.; $d_{4°}^{25°}$ 1·0174 (I.C.T., 1·0173$_6$).

The methylaniline gave no positive tests for primary or tertiary amines. It was further distilled at atmospheric pressure, dried over barium oxide, and finally distilled from freshly prepared barium oxide in nitrogen at 20 mm., the product being collected and stored under nitrogen in sealed containers; $d_{4°}^{25°}$ 0·9832$_2$.

Dimethylaniline. To ensure the absence of primary and secondary amines the dimethylaniline was further purified by the method of Brand and Krantz (*J. pr. Chem.*, 1927, **115**, 143). The dried base was distilled with acetic anhydride, and the fraction boiling at 185—190° consisted of dimethylaniline together with a trace of acetic anhydride. The product was washed five times with water and dried first with potassium hydroxide pellets and then with barium oxide. It was finally distilled and stored in the same manner as the methylaniline; $d_{4°}^{25°}$ 0·9519$_6$.

Experimental Methods.—*Dielectric constants.* These were determined with a heterodyne-beat apparatus, designed in conjunction with Mr. L. B. Witten, which will be described in another communication. By using a substitution technique the capacity of the cell containing the liquid under examination was compared directly with a Sullivan standard variable air condenser, thereby eliminating errors due to frequency drift. The dielectric cell, of a modified Sayce and Briscoe type, had a capacity of about 100 $\mu\mu$F. when filled with air, and measurements were made at a frequency of 10^6 cycles per second.

Refractive indices. These were measured with a Pulfrich refractometer, water from a thermostat being circulated rapidly through the heating block, whilst the liquid under test was pre-heated to the measurement temperature before introduction into the cell.

Specific volumes. These were determined with a 15-c.c. pyknometer, of a modified Sprengel type, fitted with ground-glass caps. All weights were corrected for buoyancy.

All the measurements were made at 25° ± 0·002°.

Calculation of Apparent Molecular Polarisation at Infinite Dilution, Molecular Refraction, and Apparent Dipole Moment.—The values of P_2 were derived by the method (Smith and Cleverdon, *Trans. Faraday Soc.*, 1949, **45**, 109) wherein the dielectric constant (ε_{12}) of the solution is assumed to vary with the weight-fraction (w_2) of solute present according to the relation $\Delta\varepsilon = \varepsilon_{12} - \varepsilon_1 = aw_2 + a'w_2^2$. Particularly in the case of aniline in benzene, the number of measurements were sufficient to permit a rough statistical treatment in which the solutions were divided into three groups, permitting the derivation of the values of ε_1, a, and a'. This procedure has the advantage that it places no greater weight on the actual measurement made on the pure solvent than on any other measurement, whereas the usual methods depend very critically on the accuracy of this measurement. The results for the solutions in benzene showed that within experimental error the specific volume (v_{12}) of the solutions varied linearly with w_2, but with the dioxan solutions this was not the case, and the value of β, the limiting value of $\mathrm{d}v_{12}/\mathrm{d}w_2$ at infinite dilution, had to be derived by the same treatment as used in determining a.

From the values of the parameters a and β so derived, $P_{2\infty}$ was calculated by the relationship $P_{2\infty} = M_2 p_{2\infty} = M_2 \times 3av_1/(\varepsilon_1 + 2)^2 + (v_1 + \beta)(\varepsilon_1 - 1)/(\varepsilon_1 + 2)$. The figures obtained in this way were checked by extrapolation of the curve produced by plotting the values of P_2 calculated for each concentration against the molar fraction of solute present, and of the best straight line through the points obtained by plotting P_2 against the volume polarisation $(\varepsilon_{12} - 1)/(\varepsilon_{12} + 2)$. Each of these methods led to values in good agreement with those derived from the parameters, but with a greater degree of uncertainty.

The molecular refraction of the solute ($[R_{\mathrm{D}}]$) appeared to be constant over the concentration ranges

TABLE II.

$100w_2$.	ε_{12}.	v_{12}.	p_{12}.	P_2.	n_D.	r_{12}.	$[R_D]$.	$\Delta\varepsilon$.	$\Delta\varepsilon/w_2$.	Δv.	$\Delta v/w_2$.	$\Delta\varepsilon$, calc.	Δv, calc.
						Aniline in benzene. Series I.							
0·0000	2·2725	1·14457	0·34089	—	1·4981	0·33557							
0·6341	2·2911	1·14362	0·34408	78·60	1·4987	0·33561	31·85	0·0185	2·93	—0·00095	—0·150	0·0186	—0·00109
0·7990	2·2962	1·14292	0·34482	78·60	1·4988	0·33547	30·08	0·0237	2·96	—0·00165	—0·206	0·0236	—0·00137
1·3396	2·3120	1·14228	0·34756	78·11	1·4992	0·33551	30·83	0·0395	2·95	—0·00229	—0·171	0·0396	—0·00230
2·9740	2·3613	1·13948	0·35567	77·99	1·5004	0·33537	30·62	0·0888	2·99	—0·00509	—0·172	0·0888	—0·00511
4·4540	2·4066	1·13691	0·36290	77·78	1·5016	0·33529	30·66	0·1341	3·011	—0·00766	—0·172	0·1341	—0·00766
5·6711	2·4444	1·13483	0·36880	77·59	1·5026	0·33524	30·71	0·1719	3·031	—0·00974	—0·172	0·1720	—0·00975
6·9460	2·4849	1·13266	0·37499	77·47	1·5036	0·33515	30·69	0·2124	3·058	—0·01191	—0·172	0·2124	—0·01195
9·2304	2·5582	1·12873	0·38584	77·10	1·5054	0·33500	30·65	0·2857	3·095	—0·01584	—0·172	0·2858	—0·01588
						Aniline in benzene. Series II.							
0·0000	2·2725	1·14457	0·34089	—	1·4981	0·33556							
0·8233	2·2968	1·14312	0·34500	78·23	1·4988	0·33554	30·92	0·0243	2·95	—0·00145	—0·176	0·0243	—0·00142
1·2121	2·3084	1·14244	0·34693	78·15	1·4991	0·33547	30·56	0·0360	2·97	—0·00213	—0·176	0·0358	—0·00208
2·2484	2·3402	1·14069	0·35223	78·72	1·4997	0·33536	30·77	0·0677	3·01	—0·00388	—0·173	0·0668	—0·00387
3·1073	2·3651	1·13925	0·35629	77·90	1·5006	0·33540	30·78	0·0926	2·98	—0·00532	—0·171	0·0928	—0·00534
4·4200	2·4056	1·13695	0·36273	77·76	1·5017	0·33534	30·78	0·1331	3·01	—0·00762	—0·172	0·1331	—0·00760
6·7970	2·4797	1·13285	0·37421	77·37	1·5035	0·33518	30·72	0·2072	3·048	—0·01172	—0·172	0·2074	—0·01169
7·9404	2·5164	1·13091	0·37970	77·25	1·5045	0·33514	30·76	0·2439	3·071	—0·01366	—0·172	0·2440	—0·01366
10·3710	2·5958	1·12672	0·39122	76·91	1·5063	0·33490	30·66	0·3233	3·117	—0·01785	—0·173	0·3232	—0·01780
						Aniline in 1 : 4-*dioxan. Series I.*							
0·0000	2·2037	0·97276	0·27854	—	1·4202	0·24627							
0·7572	2·2381	0·97268	0·28415	94·93	1·4215	0·24692	31·03	0·0344	4·54	—0·00008	—0·011	0·0342	—0·00009
1·0331	2·2508	0·97262	0·28619	94·89	1·4220	0·24716	31·03	0·0471	4·56	—0·00014	—0·014	0·0467	—0·00013
2·5391	2·3187	0·97245	0·29693	93·38	1·4245	0·24842	30·83	0·1150	4·53	—0·00031	—0·012	0·1149	—0·00031
3·7625	2·3744	0·97232	0·30550	92·66	1·4272	0·24977	31·60	0·1707	4·537	—0·00044	—0·012	0·1704	—0·00045
5·8920	2·4711	0·97209	0·31989	91·21	1·4304	0·25132	30·91	0·2674	4·538	—0·00067	—0·011	0·2673	—0·00067
6·8571	2·5150	0·97199	0·32615	90·60	1·4321	0·25216	30·92	0·3113	4·540	—0·00077	—0·011	0·3112	—0·00076
9·4320	2·6326	0·97179	0·34247	89·06	1·4367	0·25445	31·00	0·4289	4·547	—0·00097	—0·010	0·4290	—0·00099
11·0894	2·7090	0·96714	0·35263	88·16	1·4387	0·25540	30·59	0·5053	4·556	—0·00112	—0·010	0·5051	—0·00112
						Aniline in 1 : 4-*dioxan. Series II.*							
0·0000	2·2052	0·97281	0·27881	—	1·4202	0·24627							
1·0286	2·2514	0·97266	0·28630	93·77	1·4221	0·24720	31·33	0·0462	4·49	—0·00015	—0·015	0·0465	—0·00013
1·5562	2·2756	0·97261	0·29017	93·93	1·4228	0·24757	30·69	0·0704	4·52	—0·00020	—0·013	0·0703	—0·00020
2·6002	2·3221	0·97248	0·29747	92·78	1·4247	0·24849	30·87	0·1169	4·50	—0·00033	—0·013	0·1176	—0·00033
3·9667	2·3847	0·97235	0·30707	92·30	1·4271	0·24968	30·92	0·1795	4·525	—0·00046	—0·012	0·1797	—0·00048
5·6109	2·4596	0·97215	0·31818	91·30	1·4300	0·25111	30·95	0·2544	4·534	—0·00066	—0·012	0·2544	—0·00066
6·9709	2·5220	0·97202	0·32716	90·54	1·4324	0·25212	30·73	0·3168	4·545	—0·00079	—0·011	0·3164	—0·00080
8·2805	2·5816	0·97189	0·33550	89·66	1·4347	0·25344	30·98	0·3764	4·546	—0·00092	—0·011	0·3764	—0·00093
9·2921	2·6280	0·97178	0·34184	89·07	1·4365	0·25432	30·98	0·4228	4·550	—0·00103	—0·011	0·4228	—0·00101

TABLE II (*contd.*).

$100w_2$.	ε_{12}.	v_{12}.	p_{12}.	P_2.	n_D.	r_{12}.	$[R_D]$.	$\Delta\varepsilon$.	$\Delta\varepsilon/w_2$.	Δv.	$\Delta v/w_2$.	$\Delta\varepsilon$, calc.	Δv, calc.
Methylaniline in benzene.													
0·0000	2·2725	1·14458	0·34090	—	1·49817	0·33560							
0·7541	2·2953	1·14355	0·34485	92·65	1·4986	0·33556	35·39	0·0228	3·02	−0·00103	−0·137	0·0229	−0·00102
1·3651	2·3140	1·14273	0·34806	92·73	1·4992	0·33562	36·12	0·0415	3·04	−0·00185	−0·135	0·0415	−0·00184
2·7680	2·3571	1·14084	0·35534	92·43	1·4999	0·33551	35·61	0·0846	3·06	−0·00374	−0·135	0·0846	−0·00373
4·0207	2·3960	1·13915	0·36175	92·09	1·5018	0·33609	37·27	0·1235	3·07	−0·00543	−0·135	0·1234	−0·00542
6·0396	2·4595	1·13643	0·37193	91·58	1·5023	0·33554	35·85	0·1870	3·096	−0·00815	−0·135	0·1868	−0·00814
7·9037	2·5185	1·13393	0·38122	91·19	1·5035	0·33550	35·82	0·2460	3·113	−0·01065	−0·135	0·2460	−0·01065
8·6875	2·5437	1·13290	0·38490	90·80	1·5040	0·33548	35·81	0·2712	3·122	−0·01168	−0·135	0·2712	−0·01171
10·6890	2·6086	1·13021	0·39449	90·25	1·5053	0·33540	35·76	0·3361	3·144	−0·01437	−0·135	0·3362	−0·01441
Methylaniline in 1 : 4-dioxan.													
0·0000	2·2037	0·97279	0·27855	—	1·4201	0·24621							
0·7768	2·2368	0·97311	0·28407	105·99	1·4214	0·24696	36·73	0·0331	4·26	0·00032	0·041	0·0332	0·00033
1·2002	2·2552	0·97283	0·28710	106·19	1·4221	0·24738	36·83	0·0515	4·29	0·00049	0·041	0·0513	0·00051
2·4866	2·3098	0·97382	0·29596	104·87	1·4239	0·24847	36·12	0·1061	4·27	0·00103	0·0415	0·1063	0·00105
3·7038	2·3619	0·97436	0·30422	104·11	1·4259	0·24960	36·19	0·1582	4·27	0·00157	0·0423	0·1583	0·00157
5·7621	2·4503	0·97524	0·31782	102·87	1·4292	0·25152	36·26	0·2466	4·280	0·00245	0·0425	0·2466	0·00245
7·3098	2·5167	0·97590	0·32771	101·91	1·4315	0·25289	36·17	0·3130	4·282	0·00311	0·0426	0·3130	0·00311
8·6225	2·5732	0·97647	0·33591	101·13	1·4337	0·25414	36·23	0·3695	4·285	0·00368	0·0426	0·3694	0·00368
10·7581	2·6648	0·97739	0·34882	99·84	1·4370	0·25606	36·19	0·4611	4·286	0·00460	0·0428	0·4612	0·00460
Dimethylaniline in benzene.													
0·0000	2·2725	1·14456	0·34088	—	1·4982	0·33562							
1·0269	2·2976	1·14360	0·34529	93·34	1·4989	0·33572	41·85	0·0251	2·44	−0·00096	−0·091	0·0254	−0·00098
1·0915	2·2994	1·14350	0·34560	93·71	1·4989	0·33573	41·90	0·0269	2·46	−0·00106	−0·094	0·0270	−0·00104
1·7338	2·3154	1·14286	0·34836	93·59	1·4993	0·33575	41·16	0·0429	2·47	−0·00170	−0·096	0·0430	−0·00165
3·2551	2·3535	1·14145	0·35488	93·43	1·5000	0·33573	41·05	0·0810	2·488	−0·00311	−0·095	0·0810	−0·00311
4·3015	2·3796	1·14046	0·35925	93·06	1·5006	0·33577	41·10	0·1071	2·489	−0·00410	−0·095	0·1071	−0·00410
5·8788	2·4194	1·13895	0·36580	92·68	1·5015	0·33582	41·09	0·1469	2·500	−0·00561	−0·0949	0·1468	−0·00561
6·7394	2·4410	1·13813	0·36930	92·41	1·5019	0·33585	41·09	0·1685	2·500	−0·00643	−0·0949	0·1685	−0·00643
9·2670	2·5049	1·13574	0·37940	91·68	1·5034	0·33597	41·13	0·2324	2·508	−0·00882	−0·0949	0·2325	−0·00884
Dimethylaniline in 1 : 4-dioxan.													
0·0000	2·2038	0·97287	0·27859	—	1·4201	0·24626							
0·6470	2·2238	0·97342	0·28204	98·37	1·4210	0·24686	41·08	0·0200	3·09	−0·00055	0·085	0·0198	0·00054
1·0239	2·2351	0·97373	0·28397	97·43	1·4215	0·24720	40·97	0·0313	3·06	0·00086	0·084	0·0313	0·00086
2·2647	2·2730	0·97477	0·29040	96·95	1·4233	0·24835	41·02	0·0692	3·05	0·00190	0·084	0·0692	0·00191
3·5217	2·3112	0·97585	0·29679	96·39	1·4251	0·24958	41·27	0·1074	3·05	0·00298	0·085	0·1077	0·00298
4·7529	2·3494	0·97689	0·30308	96·20	1·4268	0·25072	41·21	0·1456	3·06	0·00402	0·085	0·1455	0·00403
5·7203	2·3787	0·97771	0·30788	95·81	1·4282	0·25162	41·20	0·1751	3·061	0·00484	0·0846	0·1751	0·00485
6·8337	2·4135	0·97868	0·31344	95·56	1·4298	0·25270	41·26	0·2097	3·068	0·00582	0·0851	0·2094	0·00582
8·5710	2·4663	0·98021	0·32181	94·99	1·4322	0·25433	41·24	0·2625	3·063	0·00734	0·0857	0·2629	0·00732

studied, so its mean value was deduced as $M_2[r_1 + \Sigma(r_{12} - r_1)/\Sigma w_2]$, where r = specific refraction. This method is more satisfactory than averaging the $[R_D]_2$ values for each solution, as in the latter case too great weight is placed upon the values for low concentrations, where the possible error is considerable. In computing P_μ and μ the total distortion polarisation P_{E+A} was taken as 1·05$[R_D]$.

Results.—The results obtained, together with the values of $\Delta\varepsilon/w_2$ and $\Delta v/w_2$ for each solution, are recorded in Table II, whilst the parameters deduced and the values of $P_{2\infty}$, $[R_D]$, P_μ, and μ derived from them are given in Table III. The figures given under $\Delta\varepsilon$ (calc.) and Δv (calc.) in Table II are derived by means of the parameters and confirm that the empirical relationships containing them represent the behaviour of the systems within the limits of experimental error.

TABLE III.

Polarisation data.

	α.	α'.	β.	β'.	$P_{2\infty}$, c.c.	$[R_D]$.	P_μ, c.c.	μ, D.
Aniline in benzene	2·933	1·77	−0·1720	—	78·35	30·70	46·12	1·505
Aniline in 1 : 4-dioxan(I)	4·520	0·32	−0·0127	0·023	95·11	30·92	62·64	1·750
,, ,, ,, (II)	4·510	0·40	−0·0131	0·023	94·93	30·92	62·46	1·748
Methylaniline in benzene	3·025	1·12	−0·1348	—	93·20	35·81	55·20	1·643
Methylaniline in 1 : 4-dioxan	4·271	0·15	+0·0421	0·006	106·72	36·23	68·68	1·833
Dimethylaniline in benzene	2·465	0·46	−0·0953	—	94·06	41·17	50·83	1·577
Dimethylaniline in 1 : 4-dioxan	3·054	0·15	+0·0839	0·018	97·79	41·21	54·52	1·633

TABLE IV.

Analysis of Previous Measurements on Solutions in Benzene.

$w_2 \times 10^2$.	ε_{12}.	v_{12}.	$\Delta\varepsilon$.	$\Delta\varepsilon/w_2$.	Δv.	$\Delta v/w_2$.	$\Delta\varepsilon$ (calc.).	Δv (calc.).
					Aniline.			
Tiganik (20°).								
0·0000	2·2825	1·1389	—	—	—	—	—	—
0·6752	2·3031	1·378	0·0206	3·05	−0·0011	−0·16	0·0206	−0·00115
1·1961	2·3191	1·1369	0·0366	3·06	−0·0020	−0·17	0·0368	−0·00204
2·5446	2·3609	1·1346	0·0784	3·08	−0·0043	−0·17	0·0784	−0·00435
4·8982	2·4352	1·1304	0·1527	3·117	−0·0085	−0·172	0·1527	−0·00835
Cowley and Partington (20°).								
0·0000	2·281	1·1378	—	—	—	—	—	—
1·3687	2·323	1·1355	0·042	3·06	−0·0023	−0·17	0·0419	−0·00233
2·6614	2·363	1·1333	0·082	3·08	−0·0045	−0·17	0·0820	−0·00453
3·9416	2·403	1·1313	0·122	3·09	−0·0065	−0·17	0·1222	−0·00672
5·2725	2·445	1·1290	0·164	3·11	−0·0088	−0·166	0·1646	−0·00899
Emblem and McDowell (20°).								
6·126	2·480	1·1280	0·199	3·25	−0·0098	−0·16	0·1920	−0·0104
7·374	2·512	1·1270	0·231	3·13	−0·0108	−0·15	0·2326	−0·0126
18·550	2·872	1·1059	0·591	3·19	−0·0319	−0·172	0·6169	−0·0316
Le Fèvre and Le Fèvre (25°).								
0·000	2·2725	1·1444	—	—	—	—	—	—
2·460	2·3448	1·1401	0·0723	2·94	−0·0043	−0·17	0·0732	−0·00423
3·182	2·3658	1·1389	0·0933	2·93	−0·0055	−0·17	0·0951	−0·00547
4·357	2·4036	1·1368	0·1311	3·01	−0·0076	−0·175	0·1311	−0·00749
Higasi (25°).								
0·000	2·273	1·1453	—	—	—	—	—	—
2·133	2·338	1·1416	0·065	3·05	−0·0037	−0·17	0·0634	−0·00367
4·556	2·413	1·1374	0·140	3·07	−0·0078	−0·173	0·1373	−0·00784
8·560	2·539	1·1305	0·266	3·11	−0·0147	−0·173	0·2641	−0·01472
					Methylaniline.			
Fogelberg and Williams (25°).								
0·000	2·276	1·1448	—	—	—	—	—	—
0·452	2·290	1·1442	0·014	3·1	−0·0006	−0·13	0·0127	−0·00061
1·135	2·310	1·1432	0·034	3·0	−0·0016	−0·14	0·0345	−0·00153
2·236	2·344	1·1418	0·068	3·0	−0·0030	−0·13	0·0682	−0·00301
3·317	2·376	1·1402	0·100	3·01	−0·0046	−0·14	0·1016	−0·00448
					Dimethylaniline.			
Fogelberg and Williams (25°).								
0·000	2·276	1·1448	—	—	—	—	—	—
0·449	2·287	1·1444	0·011	2·4	−0·0004	−0·09	0·0111	−0·00043
1·143	2·304	1·1438	0·028	2·4	−0·0010	−0·09	0·0282	−0·00109
2·216	2·331	1·1429	0·055	2·5	−0·0019	−0·09	0·0555	−0·00211
3·312	2·358	1·1416	0·082	2·5	−0·0032	−0·01	0·0821	−0·00316

The two series of measurements for solutions of aniline in benzene were made upon materials from different sources, but the results are in close accord with one another. Two series of measurement were also made with 1 : 4-dioxan as solvent, but in the one case the solvent was freshly dried and redistilled immediately before use whereas for the second series it had been kept in a stoppered bottle. Although the densities of the two specimens were almost identical, there was an appreciable difference between their dielectric constants at 25°, that of the freshly distilled sample (relative to benzene = 2·2725 at 25°) being 2·2037, in accord with the value 2·2038 ± 0·0002 which has been found consistently in these laboratories for pure dry 1 : 4-dioxan. The higher value for the other sample is attributable to traces of moisture absorbed during storage. The values of P_2 for aniline in the two samples differ only slightly, and the two values approach one another even more closely if, as is indicated by a rough statistical treatment, the values of ε_1 are about 0·0002 too low in the first series and the same amount too high in the second series relative to the values for the solutions. The measurements on methylaniline and dimethylaniline were all conducted with freshly dried and distilled solvent.

Comparison with Previous Measurements.—Previous results for benzene solutions are analysed in Table IV, which includes the values of ε_{12} reported by the investigators, together with the values of w_2 and v_{12} calculated from their concentration and density figures and the derived data by which comparison can be made. Cowley and Partington expressed ε_{12} to three decimal places only, but their values for aniline solutions all lie, within possible experimental error, on the curve indicated by the results of Tiganik, *viz.*, $\Delta\varepsilon = 3{\cdot}043w_2 + 1{\cdot}5w_2^2$. This, together with $\beta = -0{\cdot}1705$, leads to $P_{2\infty} = 79{\cdot}80$ c.c., and if this is combined with $P_{E+A} = 32{\cdot}23$ c.c., $P_\mu = 47{\cdot}57$ c.c. and $\mu = 1{\cdot}512$ D. The difference between this last figure and the value obtained at 25° in the present investigation seems to be outside the experimental error of either series of measurements.

The values of $\Delta\varepsilon$ (calc.) and Δv (calc.) in Table IV are derived from the above relations and the relations deduced from the present investigation, for the measurements at 20° and 25°, respectively.

The results of Emblem and McDowell are difficult to analyse, as they give no data for the characteristics of the pure benzene; the values used in these calculations are those found by Cowley and Partington, but comparison with the other available data suggests that their dielectric constant values may be in error in the second decimal place and their densities in the third place.

The results of Le Fèvre and Le Fèvre at 25° are in reasonable agreement with those of the present investigation, but the $\Delta\varepsilon$ values found by Higasi are higher than would be expected; they suggest, in fact, that the value taken for ε_1 is about 0·002 unit low relative to the values of ε_{12} for the solutions. On the other hand the density data accord well with the present measurements. The early measurements of Højendahl do not appear to have been very exact and are not included in this analysis.

The measurements of Fogelberg and Williams on benzene solutions of methyl- and dimethyl-aniline are in very good agreement with those now reported, although, as they expressed their dielectric constants to three decimal places only, the accord of the values of μ deduced from the two series of measurements is a little fortuitous.

The results of Kumler and Halverstadt for solutions of aniline in 1 : 4-dioxan fall almost into line with the present series if the dielectric-constant values of their pure solvent and their first solution were 0·0012 too low, and 0·0010 too high, respectively, relative to the figures for the other solutions.

DISCUSSION.

The results confirm that the molecular polarisation of aniline is much higher in 1 : 4-dioxan solution than in benzene solution, and show that a similar difference exists also with methylaniline, whereas with dimethylaniline the difference is relatively small. These observations support the view that in aniline and methylaniline solutions hydrogen bonding occurs between the amino-hydrogen atoms and the oxygen atoms of the 1 : 4-dioxan molecule. The slight difference between the molecular polarisation values of dimethylaniline in the two solvents is slightly greater than is normally encountered on passing from one solvent to another of almost equal dielectric constant, and may be associated with a tendency for hydrogen bonding between the activated *para*-hydrogen atom of the solute and the oxygen atoms of the 1 : 4-dioxan molecules. There is also evidence of a small increase in the molecular refractions of aniline and methylaniline on passing from benzene to dioxan solutions.

The apparent specific volumes of the amines in benzene solution, as given by the $v_1 + \beta$ terms, are in each case lower than the specific volumes of the pure liquids, the difference decreasing in the order aniline, methylaniline, dimethylaniline. For aniline, the value in 1 : 4-dioxan is much lower than in benzene, whereas with the other amines the values are higher in dioxan, that of dimethylaniline being greater than the specific volume of the pure liquid. The results of Cowley and Partington (*loc. cit.*) indicate that the apparent specific volumes of aniline in benzene, hexane, and *cyclo*hexane at 20° are about 0·967, 0·963, and 1·031, respectively, as compared with 0·9787 for pure aniline at the same temperature.

A further point of interest is that the apparent molecular polarisation in each case decreases with increasing concentration, *i.e.*, with increasing dielectric constant of the medium. The measurements have not been extended to sufficiently high concentrations to determine whether this increase is strictly linear with f_2, w_2, or $(\varepsilon_{12} - 1)/(\varepsilon_{12} + 2)$, but, in the cases of aniline and methylaniline the rate of decrease with each of these functions is much more rapid in 1 : 4-dioxan than in benzene. The decrease with increasing concentration with aniline is surprising in view of the fact that the apparent dipole moment is actually slightly greater than the gas value, and it suggests that the change in P_2 observed is not an effect attributable to the dielectric constant of the medium alone.

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