302. *Studies in Dielectric Polarisation. Part XXIV. The Solvent Effect on the Dipole Moments of Some Amines.*

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The polarisations and moments of some amines in various solvents have been determined and the results considered in relation to the effect of the solvent. The variations observed between the measurements are small. Mention is made of the results obtained with certain other compounds which show a similar behaviour and a discussion of the influence of the solvent on these substances is given.

MEASUREMENTS of the dipole moments of various compounds in solution and in the vapour state have shown that substances may be divided into three groups with respect to the influence of the solvent, according to whether the moments in solution are smaller than (negative solvent effect), larger than (positive solvent effect), or the same as those in the vapour state. The distinction between these classes depends mainly upon the shape of the polar molecule and the location of its dipole. (This classification omits those compounds which show specific behaviour in a particular solvent and others, such as dichloroethane, which possess an entirely different solvent dependence.)

The compounds previously employed in this series of investigations belong to the class (1) (Cowley and Partington, *J.*, 1936, 1184; 1937, 130; this vol., p. 977) and the work has now been extended to some amines, which are representative of the other types. The results, given in the table below, refer to determinations of the dipole moments of aniline and α- and β-naphthylamines at 20°, measured in the solvents used in the earlier work, carbon tetrachloride and carbon disulphide being excluded on account of their interactions with some amines. The values of the dielectric constant of the solvent, and the total polarisation at infinite dilution, $P_{2\infty}$, the electronic polarisation, P_E, and the moment, μ (in Debye units), of the solute are given.

Amine.	Solvent.	ϵ of solvent.	$P_{2\infty}$, c.c.	P_E, c.c.	μ.
Aniline	Hexane	1·90	77·0	30·6	1·48
	*cyclo*Hexane	2·02	77·4	30·6	1·49
	Benzene	2·28	80·0	30·6	1·53
	Toluene	2·38	79·5	30·6	1·52
α-Naphthylamine	*cyclo*Hexane	2·02	92·0	46·2	1·47
	Benzene	2·28	96·0	46·2	1·53
	Toluene	2·38	92·6	46·2	1·48
β-Naphthylamine	Benzene	2·28	112·0	46·2	1·76
	Toluene	2·38	109·3	46·2	1·73

The differences between the polarisations and moments of aniline in the various solvents are small but there is a tendency for the values to rise with increase of the dielectric constant of the solvent. These results may be compared with the dipole moment of aniline (at 25°) measured in hexane (1·50), benzene (1·54), and ether (1·67) (Higasi, *Bull. Inst. Phys. Chem. Res. Tokyo*, 1934, **13**, 1167), and it is evident that the first two values are in good agreement with the present results. Recently, the moment of the vapour of aniline has been found, the result (1·48) being corrected for the atomic polarisation, assumed to be 5% of the electronic polarisation (Groves and Sugden, *J.*, 1937, 1782). From this figure, the total polarisation of aniline in the vapour state at 20° is found to be 78·4 c.c., a value a little greater than the polarisations measured in hexane and *cyclo*hexane and somewhat smaller than those in benzene and toluene solutions. The differences between the vapour and the solution moments of this compound are therefore slight.

Small variations in the polarisation of α-naphthylamine in different solvents also occur, but in this case no value of the moment of the vapour is available. Similar results are found with β-naphthylamine, but the solubility of this compound was too small to permit of measurements in more than two solvents. Previous results for the moments of α- and β-naphthylamines in benzene at 22° are 1·44 and 1·74 respectively (Bergmann and Weizmann, *Trans. Faraday Soc.*, 1936, **32**, 1320), compared with the present values of 1·53 and 1·76 in benzene at 20°. For each of the compounds here investigated, the moment

in toluene solutions was a little lower than that in benzene solutions. For aniline and α-naphthylamine these values lie out of the sequence of the other determinations, which show a slight increase in the moment as the dielectric constant of the solvent increases. The slightly polar properties of toluene may account for this behaviour.

The majority of organic compounds possess a negative solvent effect and the variation of the polarisation of some substances belonging to this class has been previously considered (Parts XX, XXI, and XXII, *loc. cit.*). The positive solvent effect is exhibited by a small number of compounds and the following table refers to some of the more notable examples, *viz.*, some amines, ethers, alcohols and chloroform. The total polarisations of the substances are given, the values for the vapours having been calculated from the published data for the temperatures stated.

Values of the total polarisation.

Compound.	Vapour result.	Solution results.*
Diethylamine	36 (25°) [1]	49·4 (H., 25°) [2]; 50·7 (B., 25°) [2]
Triethylamine	36 (25°) [1]	45·3 (H., 25°) [2]; 46·6 (B., 25°) [2]
Methyl alcohol	69·9 (20°) [3]	59 (H., 20°) [4]; 70 (B., 20°) [4]; 67·8 (B., 20°) [5]; 60 (C., 20°) [4]
Ethyl alcohol	73·2 (20°) [3]	76·3 (B., 20°) [5]
n-Propyl alcohol	75·4 (20°) [6]	76 (H., 20°) [4]; 81 (B., 20°) [4]; 77·6 (B., 20°) [5]; 76 (C., 20°) [4]
n-Butyl alcohol	78·5 (20°) [6]	83·1 (B., 20°) [5]
Dimethyl ether	48·6 (20°) [7]	—
Diethyl ether	52·6 (20°) [7]	57 (H., 20°) [4]; 58·5 (B., 20°) [4]; 57 (C., 20°) [4]
Di-*n*-propyl ether	62·8 (20°) [7]	62·0 (H., 20°) [8]
Di-*n*-butyl ether	71·8 (25°) [7]	68·6 (H., 25°) [9]; 74·5 (B., 25°) [9]
Diamyl ether	—	74·5 (H., 25°) [9]; 78·6 (B., 25°) [9]
Chloroform	46 (20°) [10]	51 (H., 20°) [11]; 52 (B., 20°) [11]; 47·5 (C., 20°) [11]

* Solvents : H., hexane; B., benzene; C., carbon disulphide.

[1] Ghosh and Chatterjee, *Physical Rev.*, 1931, **37**, 427; [2] Higasi, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1937, **31**, 311; [3] Kubo, *ibid.*, 1935, **26**, 242; [4] Müller and Mortier, *Physikal. Z.*, 1935, **36**, 371; [5] Wolf and Gross, *Z. physikal. Chem.*, 1931, B, **14**, 305; [6] Kubo, *Sci. Papers Inst. Phys. Chem. Res., Tokyo*, 1935, **27**, 65; [7] Groves and Sugden, J., 1937, 1779; [8] Meyer and Büchner, *Physikal. Z.*, 1932, **33**, 390; [9] Thomson, J., 1937, 1056; [10] Sänger, *Physikal. Z.*, 1926, **27**, 556; [11] Müller, *ibid.*, 1933, **34**, 689.

These results illustrate several interesting points. In these examples, the differences between the polarisation values as measured in the vapour state and in solution are small, but none of the substances possesses a very large moment. Compounds with negative solvent effects often show a much greater influence of the solvent, and this is partly due to the greater moments which they frequently possess. Even with compounds of similar moments, however [*e.g.*, bromobenzene, total polarisations at 20°, 97·6 (vapour), 86·0 (hexane), 83·6 (benzene), 75·4 (carbon disulphide); J., 1937, 130], the variation is usually greater than is shown by the above substances. In the second place, the variations of polarisation observed with the change of dielectric constant of the medium are by no means so regular as for other substances. In particular, the values obtained from carbon disulphide solutions are lower than would be anticipated from the dielectric constant of the solvent, a result similar to that previously observed with compounds showing a negative solvent effect (cf. Higasi, *Bull. Inst. Phys. Chem. Res. Tokyo*, 1936, **15**, 766). The trend of the results for the higher ethers appears to be somewhat irregular, the vapour polarisations of di-*n*-butyl ether lying between the polarisations found in solutions in hexane and benzene. This point is discussed below.

The earlier empirical rules governing the solvent effect are applicable only to compounds possessing smaller moments in solution than in the vapour state. The first theoretical explanation of a positive solvent effect was given by Higasi (*Bull. Inst. Phys. Chem. Res. Tokyo*, 1934, **13**, 1167; *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1936, **28**, 284), who showed that the sign of the solvent effect is the reverse of that of the Kerr constant, and only a few exceptions to this rule are known, *e.g.*, methylene chloride (Higasi, *loc. cit.*, p. 306) and di*iso*propyl ketone (*idem, ibid.*, 1937, **31**, 317). The theories of Govinda Rau (*Proc. Indian Acad. Sci.*, 1935, *A*, **1**, 498) and of Frank (*Proc. Roy. Soc.*, 1935, *A*, **152**, 171) also explain both positive and negative solvent effects. [For a fuller account, see Cowley and Partington, J., 1936, 1184.]

Examination of the molecular structures of the compounds under investigation gives an indication of the type of solvent effect which might be expected from a consideration of the foregoing theories. It has been established that the ammonia molecule is pyramidal, the nitrogen atom being situated at the apex of a flat tetrahedron. In this molecule the three $\overset{-|\longrightarrow}{\text{H—N}}$ moments give a resultant which acts through the nitrogen nucleus and perpendicular to the plane of the three hydrogen atoms. The amines may be regarded as derived from ammonia by substitution of the hydrogen atoms by alkyl or aryl groups. Recent electron-diffraction experiments have shown that the C–N–C angle in trimethylamine is $108° \pm 4°$ (Brockway and Jenkins, *J. Amer. Chem. Soc.*, 1936, **58**, 2036), a range including the tetrahedral angle. In this molecule the angle between the dipole axis (which is also the axis of symmetry) and the N–C bonds is approximately 70°, and so a positive solvent effect would be expected (Frank, *loc. cit.*). It has been found that the moments of di- and tri-ethylamine in hexane and benzene are greater than those in the vapour state (Higasi, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1937, **31**, 311), in agreement with theoretical expectation. The axis of maximum polarisability of the trimethylamine molecule would lie in the plane containing the carbon atoms, the resultant moment acting through the nitrogen atom and perpendicular to this plane.

The configuration of the nitrogen atom in aniline will presumably be similar, and the moment of this compound therefore acts approximately in the same direction as in the above molecule. The Kerr constant of aniline is negative (see, *e.g.*, Briegleb and Wolf, *Fortschr. Chem.*, 1931, **21**, Part 3, p. 36), indicating that the direction of the dipole is inclined at a considerable angle to the axis of maximum polarisability in the molecule. Since this axis lies in the plane of the benzene ring in aniline, the angle between the direction of the dipole and the axis of maximum polarisability is about 70°, and so a positive solvent effect is anticipated (Frank, *loc. cit.*). As pointed out above, the polarisations of this compound in benzene and toluene are slightly greater than that of the vapour, whereas those measured in hexane and *cyclo*hexane are somewhat smaller. The effect of the solvent is small and is lower than might be expected from consideration of the moment and shape of the molecule. The influence of the solvent is far less marked than in the case of the ethylamines (Higasi, *loc. cit.*), which have smaller moments. Here the plane of maximum polarisability is in a somewhat different position relative to the dipole.

It is evident that the theoretical formulæ of Higasi (*loc. cit.*) and Rau (*loc. cit.*) predict that for aniline the solvent effect should increase as the dielectric constant of the solvent increases, and that all the solution moments should be greater than the result for the vapour. Since the actual variation is not regular, moments calculated for aniline could not reproduce the experimental figures. The constants necessary for the calculation are not available, but a rough value of B in Higasi's formula, estimated from the molecular shape, indicates a positive solvent effect of greater magnitude than that experimentally found. A somewhat similar variation of the total polarisation of di-*n*-butyl ether with the dielectric constant of the medium is observed, but the moments of di-*n*-propyl ether in the vapour state and in benzene are practically the same (see above table). The Kerr constant decreases from the dimethyl to the di-*n*-propyl member of this series, and so probably decreases in the higher compounds, although the constants for these substances are not available. Rotation of the more distant parts of the chain might influence the solvent effect slightly in the ethers, but in aromatic molecules like aniline this would not be possible.

Naphthylamine molecules are similar in structure to those of aniline, but here the comparison of the vapour with the solution results cannot be made. The moments of aniline and α-naphthylamine are equal under the same conditions (1·53 in benzene at 20°), thus showing the same relationship as is found for other phenyl and α-naphthyl compounds. The moment of β-naphthylamine under the same conditions is larger (1·76), a result also true for other similar compounds. The difference in moment between α- and β-chloronaphthalenes has been attributed (Hampson and Weissberger, *J.*, 1936, 393) to the polarising effect of the dipole upon the unsubstituted ring, and a similar explanation may possibly account for the difference observed with the present compounds.

EXPERIMENTAL.

The apparatus and method of calculation were as described in the previous papers.

Preparation of Materials.—The solvents used for these measurements were purified as described in Part XX (*loc. cit.*).

Amines. These compounds were obtained from Kahlbaum. Aniline was thrice fractionated through a long column under reduced pressure. The physical constants of the colourless distillate were : b. p. $77 \cdot 0°/15$ mm., $D_4^{20°}$ $1 \cdot 2017$, $n_D^{20°}$ $1 \cdot 5863$, $[R_L]_D^{20°}$ $30 \cdot 6$ c.c. α-Naphthylamine was crystallised repeatedly from light petroleum, and obtained in colourless needles, m. p. $49 \cdot 2°$. β-Naphthylamine was crystallised several times from absolute alcohol, and formed colourless plates, m. p. $111 \cdot 0°$.

Results.—The measurements relate to solutions of the amines in various solvents at 20°. The symbols are those used in previous papers in this series.

Solute : Aniline.

f_2.	ϵ.	$D_4^{20°}$.	P_{12}, c.c.	P_2, c.c.	f_2.	ϵ.	$D_4^{20°}$.	P_{12}, c.c.	P_2, c.c.
	In hexane.					In cyclohexane.			
0·000000	1·902	0·6746	29·52	—	0·000000	2·019	0·7781	27·41	—
0·011834	1·929	0·6778	30·08	76·8	0·011873	2·050	0·7801	27·99	77·3
0·023387	1·955	0·6807	30·61	76·3	0·024430	2·084	0·7822	28·62	76·8
0·034111	1·980	0·6833	31·13	76·7	0·035565	2·115	0·7841	29·18	77·1
0·043961	2·004	0·6858	31·61	77·0	0·045066	2·142	0·7859	29·65	77·1

$P_{2\infty} = 77 \cdot 0$ c.c. ; $P_E = 30 \cdot 6$ c.c. ;
$P_{2\infty} - P_E = 46 \cdot 4$ c.c. ; $\mu = 1 \cdot 48$.

$P_{2\infty} = 77 \cdot 4$ c.c. ; $P_E = 30 \cdot 6$ c.c. ;
$P_{2\infty} - P_E = 46 \cdot 8$ c.c. ; $\mu = 1 \cdot 49$.

f_2.	ϵ.	$D_4^{20°}$.	P_{12}, c.c.	P_2, c.c.	f_2.	ϵ.	$D_4^{20°}$.	P_{12}, c.c.	P_2, c.c.
	In benzene.					In toluene.			
0·000000	2·281	0·8789	26·58	—	0·000000	2·383	0·8664	33·54	—
0·011505	2·323	0·8807	27·19	79·5	0·012169	2·420	0·8679	34·10	79·1
0·022418	2·363	0·8824	27·76	79·2	0·021681	2·448	0·8690	34·51	78·1
0·033231	2·403	0·8839	28·33	79·1	0·032635	2·481	0·8706	34·97	77·4
0·044604	2·445	0·8857	28·90	78·6	0·042466	2·511	0·8719	35·40	77·2

$P_{2\infty} = 80 \cdot 0$ c.c. ; $P_E = 30 \cdot 6$ c.c. ;
$P_{2\infty} - P_E = 49 \cdot 4$ c.c. ; $\mu - 1 \cdot 53$.

$P_{2\infty} = 79 \cdot 5$ c.c. ; $P_E = 30 \cdot 6$ c.c. ;
$P_{2\infty} - P_E = 48 \cdot 9$ c.c. ; $\mu = 1 \cdot 52$.

Solute : α-Naphthylamine.

f_2.	ϵ.	$D_4^{20°}$.	P_{12}, c.c.	P_2, c.c.	f_2.	ϵ.	$D_4^{20°}$.	P_{12}, c.c.	P_2, c.c.
	In cyclohexane.					In benzene.			
0·000000	2·019	0·7780	27·42	—	0·000000	2·280	0·8789	26·57	—
0·007751	2·041	0·7809	27·92	91·4	0·010760	2·323	0·8829	27·31	95·3
0·010560	2·050	0·7820	28·10	91·9	0·021168	2·366	0·8869	28·03	95·7
0·013409	2·058	0·7830	28·27	91·5	0·031277	2·406	0·8906	28·70	94·9
0·018588	2·073	0·7850	28·60	91·1	0·042377	2·451	0·8946	29·46	94·7

$P_{2\infty} = 92 \cdot 0$ c.c. ; $P_E = 46 \cdot 2$ c.c. ;
$P_{2\infty} - P_E = 45 \cdot 8$ c.c. ; $\mu = 1 \cdot 47$.

$P_{2\infty} = 96 \cdot 0$ c.c. ; $P_E = 46 \cdot 2$ c.c. ;
$P_{2\infty} - P_E = 49 \cdot 8$ c.c. ; $\mu = 1 \cdot 53$.

f_2.	ϵ.	$D_4^{20°}$.	P_{12}, c.c.	P_2, c.c.	f_2.	ϵ.	$D_4^{20°}$.	P_{12}, c.c.	P_2, c.c.
				In toluene.					
0·000000	2·383	0·8664	33·54	—	0·034156	2·494	0·8776	35·55	92·3
0·012579	2·424	0·8705	34·28	92·6	0·046945	2·537	0·8816	36·31	92·5
0·023489	2·459	0·8741	34·92	92·4					

$P_{2\infty} = 92 \cdot 6$ c.c. ; $P_E = 46 \cdot 2$ c.c. ; $P_{2\infty} - P_E = 46 \cdot 4$ c.c. ; $\mu = 1 \cdot 48$.

Solute : β-Naphthylamine.

f_2.	ϵ.	$D_4^{20°}$.	P_{12}, c.c.	P_2, c.c.	f_2.	ϵ.	$D_4^{20°}$.	P_{12}, c.c.	P_2, c.c.
	In benzene.					In toluene.			
0·000000	2·280	0·8790	26·56	—	0·000000	2·380	0·8664	33·49	—
0·011379	2·339	0·8834	27·53	111·5	0·011323	2·428	0·8701	34·35	108·9
0·018432	2·376	0·8861	28·13	111·8	0·015538	2·446	0·8715	34·66	109·0
0·024679	2·409	0·8884	28·66	111·4	0·019366	2·463	0·8728	34·96	109·3
0·031397	2·444	0·8909	29·22	111·2	0·023204	2·480	0·8740	35·26	109·6

$P_{2\infty} = 112 \cdot 0$ c.c. ; $P_E = 46 \cdot 2$ c.c. ;
$P_{2\infty} - P_E = 65 \cdot 8$ c.c. ; $\mu = 1 \cdot 76$.

$P_{2\infty} = 109 \cdot 3$ c.c. ; $P_E = 46 \cdot 2$ c.c. ;
$P_{2\infty} - P_E = 63 \cdot 1$ c.c. ; $\mu = 1 \cdot 73$.