644. *The Solvent Effect on the Dipole Moment of Aniline.*

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The molecular polarisation of aniline in dilute solution in *n*-heptane, carbon tetrachloride, and carbon disulphide has been studied at 25°, and the apparent dipole moments in these solvents have been found to be 1·477, 1·458, and 1·420 D., respectively. These results, compared with the value of about 1·48 D. for the moment of aniline in the vapour state, suggest that aniline may have a small negative solvent effect. This is shown to be compatible with the theories of Frank and of Higasi regarding the influence of the shape of the molecule on the variation of the dipole moment with the dielectric constant of the medium. The slight positive solvent effect previously attributed to aniline was based principally on the value of the moment in benzene solution, which appears to be anomalously high.

It was observed by Cowley and Partington (*J.*, 1938, 1598) that the molecular polarisation of aniline at infinite dilution in hexane or *cyclo*hexane was a little lower, and in benzene or toluene slightly higher, than the value for the vapour state. They inferred that, although the differences were small, there was a tendency for the molecular polarisation in solution to increase with increase in the dielectric constant of the solvent. When discussing this observation they suggested that the configuration of the nitrogen atom in aniline would presumably be similar to that in trimethylamine and triethylamine, for which, in accord with his theory, a positive solvent effect had been reported by Higasi (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1937, **31**, 311), and hence they inferred that the moment would act in approximately the same direction as in the trialkylamines. The negative value of the Kerr constant of aniline (Briegleb and Wolf, *Fortschr. Chem.*, 1931, **21**, Part 3, p. 36) indicated that the direction of the dipole was inclined at a considerable angle to the axis of maximum polarisability. As this axis lies in the plane of the benzene ring they suggested that it is inclined at an angle of about 70° to the axis of the dipole. Hence, according to the theory of Frank (*Proc. Roy. Soc.*, 1935, *A*, **152**, 171) a positive solvent effect would be expected, whilst Higasi's theory would indicate a positive solvent effect of greater magnitude than that actually observed.

This problem is of considerable interest, but the results of Cowley and Partington appeared to be rather inconclusive because they were based on measurements with only four solutions of low concentration in each case, whilst the values of the dielectric constant were expressed to three decimal places only. The interpretation of the results was thus subject to appreciable possible error, even as high as three units in the second decimal place of the moment. These measurements have therefore been extended to other solvents.

The molecular polarisation of aniline in *n*-heptane, carbon tetrachloride, and carbon disulphide has now been investigated. No previous measurements on solutions of aniline in these solvents appear to have been recorded. The results, together with the values found previously for aniline in benzene and dioxan (Few and Smith, this vol., p. 753) are recorded in Table I, which shows the dielectric constant (ε) of the solvent, the molecular polarisation at infinite dilution ($P_{2\infty}$), the molecular refraction ($[R_D]$), and the apparent moment (μ). The Table also includes the dipole moment for aniline in the vapour state, observed by Groves and Sugden (*J.*, 1937, 1782), together with the molecular polarisation of aniline vapour at 25° calculated from their measurements.

TABLE I.

Molecular Polarisation and Apparent Dipole Moment of Aniline in Various Solvents at 25°.

Solvent.	ε.	$P_{2\infty}$, c.c.	$[R_D]$, c.c.	μ (D.).
n-Heptane	1·909	77·20	31·1	1·477
Dioxan	2·204	95·11	30·9	1·750
Carbon tetrachloride	2·225	76·10	31·2	1·458
Benzene	2·272	78·35	30·7	1·505
Carbon disulphide	2·633	73·34	30·7	1·420
(Vapour)	1·00	77·5	30·6	1·48

The new observations suggest that aniline has a small but definite negative solvent effect, the values of $P_{2\infty}$ decreasing from the recalculated vapour result to the value in carbon disulphide solution. Whilst for dioxan solutions the value of $P_{2\infty}$ is much larger than would be expected for a solvent of dielectric constant 2·204, this anomaly can be accounted for by a definite interaction between the solute and solvent. For benzene solutions $P_{2\infty}$ is slightly higher than would be expected, and Cowley and Partington's measurements indicate that a similar high value occurs with toluene solutions. It has been noted in other cases, *e.g.*, nitrobenzene (Smith and Cleverdon, *Trans. Faraday Soc.*, 1949, **45**, 109), that the moments are anomalously high in benzenoid solvents, and if this is the case with aniline the data of Cowley and Partington for hexane and *cyclo*hexane solutions, which correspond to $P_{2\infty}$ values of 76·2 and 76·6 c.c., respectively, at 25°, also support the existence of a slight negative solvent effect.

It is also noteworthy that the data now available indicate that the molecular polarisation of aniline in benzene or toluene solution decreases appreciably with increasing concentration. A much more rapid decrease with increasing concentration was observed in the case of solutions in dioxan or in mixtures of dioxan and benzene, and is attributable to a large solvent effect of an aniline–dioxan complex (Few and Smith, this vol., p. 2663). In the other solvents which have been used, however, there is only a very slight change in the molecular polarisation with increasing concentration.

It is of interest to examine how far the difference between the values of the molecular polarisation of aniline in the vapour state and in solution can be reconciled with or accounted for by the various solvent-effect equations which have been suggested. The mode of variation of the molecular polarisation with concentration indicates immediately that the Sugden relation (*Nature*, 1934, **133**, 415) is not obeyed. Although for each solvent P_2 varies almost linearly with $(\varepsilon - 1)/(\varepsilon + 2)$ the slope of this line does not correspond to the orientation polarisation nor do the lines extrapolate to the gas value at $\varepsilon = 1$.

Müller's empirical equation (*Physikal. Z.*, 1933, **34**, 689), which may be written in the form $(P_{2\infty} - [R_D])_{\text{solution}}/(P_2 - [R_D])_{\text{vapour}} = 1 - 0{\cdot}075(\varepsilon - 1)^2$, represents well the change of polarisation of molecules with maximum polarisability along the dipole axis, but when applied to the data for aniline the calculated values for $(P_2 - [R_D])_{\text{vapour}}$ are much higher than the observed value. Closer accord is obtained if the value of the constant is reduced to 0·030, but the benzene result then still remains anomalously high. Other empirical relationships, such as that of Jenkins (*J.*, 1934, 480), are even more difficult to fit to the experimental data.

Owing to the fact that the aniline molecule cannot be regarded as being represented, even as a first approximation, by an ellipsoid of rotation, a theoretical derivation of the solvent effect of aniline by the method of Higasi (*Bull. Inst. Phys. Chem. Res. Tokyo*, 1934, **13**, 1167; *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1936, **28**, 284) is not possible. However Higasi pointed out that molecules with negative Kerr constants have dipole moments in solution which are higher that those observed for the vapour state, indicating their greater optical polarisation in the direction at right angles to the axis of the dipole, and the negative Kerr effect which had been reported was one of the main factors leading Cowley and Partington to the view that the solvent effect of aniline is positive. Since the present measurements were completed, however, it was pointed out by Le Fèvre, Roberts, and Smythe (this vol., p. 902) that the observations quoted referred to liquid aniline. In this state molecular aggregates may reasonably be supposed to exist, and the anisotropy of their polarisability would not be the same as that of the separated molecules such as exist in the vapour state or in dilute solution. They further point out that Lippmann (*Z. Elektrochem.*, 1911, **17**, 15) records data for mixtures of aniline and benzene which indicate that up to a molar fraction of about 0·15 aniline contributes positively to the electric double refraction. They therefore infer that if the solvent effect of aniline is negative it would be behaving normally as a molecule with a positive Kerr effect. Le Fèvre and his co-workers were concerned principally with the variation of the molecular polarisation of aniline with concentration. As this is rather anomalous when compared with results for other solvents it is evident that data for electric double refraction for other binary systems including aniline would be of considerable interest.

On the basis of his theory, Frank (*loc. cit.*) noted that for a molecule which possesses a single radical not on the dipole axis the sign and magnitude of the solvent effect depends largely on the polar co-ordinate θ of the radical. If this is less than 55° the solvent effect is negative, but when θ is greater than 55° it tends to become positive although it is only appreciable when θ approaches 90°. In calculating the angle between the direction of the dipole and the axis of maximum polarisability, Cowley and Partington neglected the mesomeric effect of the amino-group which operates when this group is linked directly to an aromatic nucleus. In aniline this effect will decrease the angle between the resultant dipole and the axis of the benzene ring, so that the dipole will not operate in the same direction as in an alkylamine.

The direction of the dipole may be calculated from the observed moments of aniline and of one of its *p*-substituted derivatives in which the dipole vector of the substituent group acts along the axis of the benzene ring, together with the moment of this substituent when linked to a phenyl group. Marsden and Sutton (*J.*, 1936, 599) calculated θ from data for several *p*-substituted anilines, and inferred that the most satisfactory substituent was the methyl group. Even the presence of this group in the molecule diminishes the mesomeric effect of the amino-group, with consequent change in the direction of the resultant dipole. From the data then available Marsden and Sutton deduced that θ was about 44°. However the calculated angle depends very critically upon the value assigned to the moment of *p*-toluidine. Recalculation of the value of this moment from the data of Donle and Gehrckens (*Z. physikal. Chem.*, 1932, *B*, **18**, 316) on the assumption that $P_{E+A} = 1{\cdot}05[R_D]$ leads to $\mu = 1{\cdot}33$ D., which, combined with the values for toluene (0·33 D.; Smythe and Lewis, *J. Amer. Chem. Soc.*, 1928, **50**, 94) and aniline (1·51 D.) leads to $\theta = 53°$. Although the possible error in this calculation is considerable this value is in accord with a very small negative solvent effect.

Lack of knowledge of the anisotropy parameters for aniline prevents the direct application of Rau's extension (*Proc. Indian Acad. Sci.*, 1935, *A*, **1**, 498) of the Raman and Krishnan treatment, but, for a particular solute, Ψ_2 and Θ_2 are approximately constant, and hence the introduction of the correction terms Ψ_1, which can be evaluated from Rau's data, should lead to " corrected " $P_{2\infty}$ values which should be linear with $(\varepsilon - 1)/(\varepsilon + 2)$. Actually after applying this " correction " the plot of $P_{2\infty}$ against $(\varepsilon - 1)/(\varepsilon + 2)$ was less linear than without it, and the best straight line did not extrapolate to the vapour value at $\varepsilon = 1$.

It is noteworthy that the very large value of Ψ_1 for benzene leads to the inference that the apparent dipole moments observed in benzene solution should be anomalously low, whereas they are usually higher than would be expected, and also that the decrease in the apparent molecular polarisation of the solute with increasing $(\varepsilon - 1)/(\varepsilon + 2)$ should be less rapid in benzene solution than, for instance, in carbon tetrachloride, whereas the reverse is generally the case. For this solvent, therefore, the correction for the anisotropy of the solvent molecule seems to operate in the wrong sense.

EXPERIMENTAL.

Materials.—Aniline was purified and stored as described previously (this vol., p. 753).

Carbon tetrachloride (commercial " pure " grade) was shaken 3 times with 50% sulphuric acid and then with 5% sodium hydroxide solution. After being washed with distilled water it was dried ($CaCl_2$) and refluxed for some time with mercury. It was then distilled from the mercury, dried [$Mg(ClO_4)_2$], and finally distilled through a 20-plate column. The middle fraction, of constant b. p. (within 0·05°), had b. p. 76·6°, d_4^{25} 1·5844$_5$, n_D^{25} 1·4576, ε^{25} 2·2252 (Jenkins and Sutton, *J.*, 1933, 609, found d_4^{25} 1·5848, ε^{25} 2·2245).

Carbon disulphide was purified by the method of Obach (*J. pr. Chem.*, 1882, **26**, 299). It was shaken with two portions of powdered potassium permanganate during 6-hour periods, distilled, dried (P_2O_5), and shaken with mercury for several hours. It was then distilled again, dried with phosphoric oxide, and fractionally distilled from this reagent. The middle fraction, of constant b. p. (within 0·05°), had b.p. 45·2°, d_4^{25} 1·2558$_0$, ε^{25} 2·6334 (Jenkins and Sutton found d_4^{25} 1·2558, ε^{25} 2·6328).

A sample of *n*-heptane conforming to the National Bureau of Standards Specification was dried (P_2O_5) and distilled in an all-glass apparatus. The middle fraction had d_4^{25} 0·6794$_8$, n_D^{25} 1·3852, ε^{25} 1·9095.

TABLE II.

Polarisation Data.

Aniline in n-heptane.

$100w_2$.	ε_{12}.	v_{12}.	p_{12}.	P_2.	n_D.	r_{12}.	$[R_D]$.	$\Delta\varepsilon/w_2$.	$\Delta v/w_2$.
0·0000	1·9095	1·47171	0·34238		1·38518	0·34503			
1·7660	1·9461	1·48353	0·35089	76·76	1·38736	0·34493	31·61	2·07	−0·463
2·8676	1·9695	1·45836	0·35619	76·72	1·38887	0·34481	31·41	2·09	−0·466
4·0306	1·9958	1·45292	0·36209	77·42	1·39051	0·34481	31·62	2·14	−0·466
4·9712	2·0169	1·44848	0·36669	77·42	1·39151	0·34454	31·21	2·160	−0·467
5·8055	2·0362	1·44444	0·37083	77·52	1·39257	0·34440	31·11	2·182	−0·470
5·8406	2·0370	1·44431	0·37101	77·53	1·39261	0·34440	31·12	2·183	−0·469
7·3927	2·0734	1·43678	0·37861	77·52	1·39470	0·34422	31·10	2·217	−0·473

$\alpha = 2{\cdot}050$; $\alpha' = 2{\cdot}26$; $\beta = -0{\cdot}4584$; $P_{2\infty} = 77{\cdot}20$ c.c.; $[R_D] = 31{\cdot}12$ c.c.; $P_\mu = 44{\cdot}55$ c.c.; $\mu = 1{\cdot}477$ D.

Aniline in carbon tetrachloride.

$100w_2$.	ε_{12}.	v_{12}.	p_{12}.	P_2.	n_D.	r_{12}.	$[R_D]$.	$\Delta\varepsilon/w_2$.	$\Delta v/w_2$.
0·0000	2·2252	0·63113	0·18301		1·45758	0·17208			
0·5910	2·2552	0·63312	0·18676	76·09	1·45878	0·17301	30·68	5·07	0·337
0·8405	2·2677	0·63405	0·18834	76·10	1·45938	0·17346	31·31	5·06	0·347
1·4121	2·2968	0·63604	0·19196	76·07	1·46057	0·17439	31·26	5·07	0·348
3·1030	2·3323	0·63842	0·19633	76·04	1·46183	0·17547	31·04	5·10	0·347
3·3105	2·3958	0·64260	0·20404	76·18	1·46455	0·17750	31·27	5·15	0·346
3·7571	2·4192	0·64410	0·20685	76·13	1·46544	0·17821	31·22	5·163	0·345
4·9175	2·4810	0·64813	0·21421	76·12	1·46776	0·18009	31·20	5·202	0·345
5·6873	2·5226	0·65072	0·21907	76·10	1·46940	0·18135	31·20	5·229	0·344

$\alpha = 5{\cdot}03$; $\alpha' = 3{\cdot}05$; $\beta = 0{\cdot}3474$; $P_{2\infty} = 76{\cdot}10$ c.c.; $[R_D] = 31{\cdot}20$ c.c.; $P_\mu = 43{\cdot}34$ c.c.; $\mu = 1{\cdot}458$ D.

Aniline in carbon disulphide.

$100w_2$.	ε_{12}.	v_{12}.	p_{12}.	P_2.	n_D.	r_{12}.	$[R_D]$.	$\Delta\varepsilon/w_2$.	$\Delta v/w_2$.
0·0000	2·6334	0·79631	0·28072						
1·0474	2·6740	0·79859	0·28602	73·26				3·88	0·218
1·2043	2·6804	0·79891	0·28683	73·39				3·90	0·216
2·0620	2·7146	0·80079	0·29123	73·60				3·94	0·217
2·9551	2·7498	0·80267	0·29570	73·35				3·94	0·215
5·4562	2·8512	0·80789	0·30829	73·20				3·992	0·212
6·0234	2·8754	0·80907	0·31122	73·30				4·018	0·212
6·8934	2·9120	0·81087	0·31563	73·30				4·042	0·211

$\alpha = 3{\cdot}865$; $\alpha' = 2{\cdot}57$; $\beta = 0{\cdot}2175$; $P_{2\infty} = 73{\cdot}34$ c.c.; $[R_D]$ (assumed) $= 30{\cdot}7$ c.c.; $P_\mu = 41{\cdot}11$ c.c.; $\mu = 1{\cdot}420$ D.

Experimental Methods.—The dielectric constants, specific volumes, and refractive indices were determined as previously described and the same methods were used in calculating the values of $P_{2\infty}$ and μ. The results are recorded in Table II, where the symbols have the same significance as previously.

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