191. *The Polarisation of Aniline dissolved in Benzene.*

By R. J. W. LE FÈVRE, (MRS.) W. P. H. ROBERTS, and B. M. SMYTHE.

Disagreement between published sets of data for the dependence upon concentration in benzene of the total polarisation of aniline are probably explained by the shape of the curve, now more fully recorded, relating P_{aniline} with composition.

EMBLEM and McDOWELL (*J.*, 1946, 641) have directed attention to certain discrepancies in the literature dealing with the above subject. On consultation of their cited references, together with those of Higasi (*Bull. Inst. Chem. Phys. Res. Tokyo*, 1934, **13**, 1167) and Cowley and Partington (*J.*, 1938, 1598), the situation summarised in Table I is revealed. It does not correspond exactly with the statements of Emblem and McDowell.

TABLE I.

Source and temp.	Concn. range ($10^5 f_1$).	No. of solutions reported.	Corresponding polarisation range.	Change of P_1 with dilution.
Höjendahl,[1] 25°	5,517	6	74·3	Increase
	41,130 *		68·2	
Hassel & Uhl,[2] 18°	0·6787	3	49·7	Increase
	1·4219 †		48·3 †	
Tiganik,[3] 20°	566·9	4	79·6	Slight
	4,141·1		78·8	increase
Higasi,[4] 25°	2,133	3	79·3	Increase
	8,560 ‡		77·5	
Le Fèvre & Le Fèvre,[5] 25°	2,071·6	3	77·2	Slight
	3,681·5		77·5	decrease
Cowley & Partington,[6] 20°	1,150·5	4	79·5	Slight
	4,460·4		78·6	increase
Emblem & McDowell,[7] 20°	5,190	3	79·4	
	16,040		73·9	Increase

* Calculated from molarities and densities shown in Thesis (*loc. cit.*).

† Molarities and P_{A+O} respectively.

‡ $w_1 \times 10_5$.

References.—(1) Thesis, Copenhagen, 1928; *Physikal. Z.*, 1929, **30**, 391. (2) *Z. physikal. Chem.*, 1929, *B*, **8**, 187. (3) *Ibid.*, 1939, *B*, **14**, 135. (4) *Loc. cit.* (5) *J.*, 1936, 1130. (6) *Loc. cit.* (7) *Loc. cit.*

We have therefore re-studied the aniline–benzene system over a mixture range which is wider than that recorded by any *one* of the above groups of authors separately, and which, in fact, covers them all.

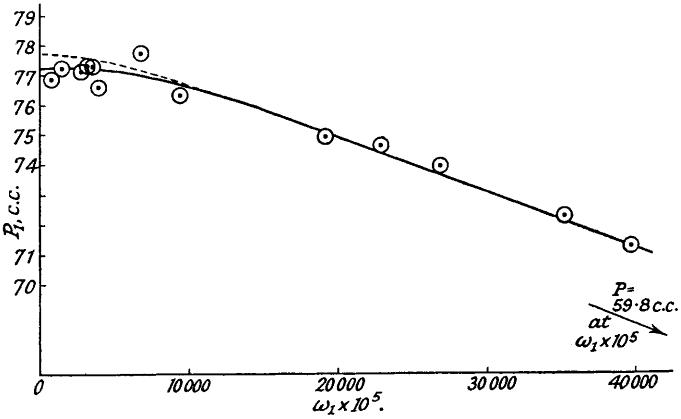
Measurements.—Details of the apparatus, etc., are given by Calderbank and Le Fèvre (*J.*, 1948, 1949), the present data therefore having been obtained with standard- and liquid-containing condensers, a circuit design, and components, which are all different from those previously used by Le Fèvre and Le Fèvre. The aniline was purified by distillation, drying (KOH), and redistillation at 20 mm. ($d_{4°}^{25°}$ 1·017); the benzene by the procedure described in "Dipole Moments" (Methuen, London, 1938, p. 29), wherein also the symbols used in Table II are defined. Concentrations are presented both as molar and weight fractions to simplify comparison with the results of other workers.

TABLE II.

$10^5 f_1$.	$10^5 w_1$.	$\varepsilon^{25°}$.	$\alpha\varepsilon_2$.	$d_{4°}^{25°}$.	βd_2.	P_1 (c.c.).
0	0	2·2725	—	0·87378	—	—
726·97	865·6	2·2978	2·92	0·87493	0·133	76·9
1,202·6	1,430·5	2·3144	2·93	0·87571	0·135	77·3
2,353·3	2,793·2	2·3549	2·95	0·87750	0·133	77·2
2,816·5	3,340·1	2·3716	2·97	0·87825	0·134	77·4
2,942·0	3,488·0	2·3765	2·98	0·87845	0·134	77·5
3,359·7	3,980·2	2·3896	2·94	0·87909	0·134	76·6
5,725·6	6,765·6	2·4762	3·01	0·88280	0·133	77·8
8,035·2	9,434·5	2·5612	3·06	0·88630	0·134	76·4
16,630·8	19,191·0	2·8944	3·24	0·89959	0·136	74·98
19,945·5	22,902·0	3·0355	3·33	0·90499	0·136	74·67
23,626·1	26,945·0	3·1899	3·33	0·91073	0·137	73·98
31,446·6	53,356·0	3·5228	3·54	0·92275	0·1385	72·29
35,676·2	39,750·0	3·7150	3·63	0·92913	0·139	71·34
10^5	10^5	6·68	—	1·017	—	59·8

The polarisations (last col.) are plotted against concentrations (col. 2) in Fig. 1. It is seen that at weight fractions greater than *ca.* 0·05, P_{aniline} diminishes with increasing concentration; from $w_1 = 0·25$ to $w_1 = 1$ this diminution is nearly rectilinear. Hence we confirm, for the appropriate composition ranges, the *directions* of the changes reported by Höjendahl, Hassel and Uhl, and Emblem and McDowell. The solutions of the remaining authors were dilute, and —in the light of Fig. 1—it is significant that for them the alteration of P_{aniline} with w_1 or f_1 has been much less definite. Since the uncertainties of P_1—evaluated as $M_1[p_2 + (p_{12} - p_2)/w_1]$—can theoretically become hyperbolically greater as w_1 is reduced (cf. Fig. 1 of Müller, *Trans. Faraday Soc.*, 1934, **30**, 729), it is doubtful whether much reliance should be placed on inequalities of a fractional c.c. order drawn from measurements at only 3 or 4 low concentrations. Nevertheless, we note that the data of Le Fèvre and Le Fèvre are satisfactorily superposable on Fig. 1, thus affording, in all, nine solutions at w_1 below 0·05. We suggest, therefore, on present evidence that as the solute concentration approaches zero, P_1 becomes approximately constant. We find, further, that the factors α and β [evaluated from the equations $\varepsilon_{12} = \varepsilon_2(1 + \alpha w_1)$ and $d_{12} = d_2(1 + \beta w_1)$, cf. Le Fèvre and Vine, *J.*, 1937, 1805] are not independent of w_1, but have themselves a straight-line relationship to it. If α and β, extrapolated to $w_1 = 0$, are used to calculate ${}_\infty P_1$, the polarisation (77·7 c.c.) so obtained is closely in the neighbourhood of that given by the direct graphical method (Fig. 1, broken and solid lines).

Fig. 1.



The matter under discussion scarcely affects the moment in more than the second decimal place. In Table III, we set out the values of μ derived from the polarisations recorded by previous observers when $[R_L]_D = 30·6$ is used consistently throughout.

Table III.

Summarised results in benzene solution.

Temperature	25°	25°	18°	20°	25°	25°	20°	20°	25°
P_{aniline} at infinite dilution	77·4	77·6	82·6	79·7	80·0	78·4	80·0	81·9	77·7
Moment, μ	1·50	1·51	1·56	1·53	1·54	1·52	1·53	1·56	1·51
Ref. (see Table I and below)	9	1	2	3	4	5	6	7	8

(8) Present work. (9) Estermann (*Z. physikal. Chem.*, 1928, *B*, **1**, 134) used the temperature method on one solution; the above ${}_\infty P_1$ has therefore been calculated by Hedestrand's formula from the mean of Estermann's figures for 20° and 30°. Vassiliev and Sirkin (*Acta Physicochim. U.R.S.S.*, 1941, **14**, 414; read in abstract only) quote μ_{aniline} as 1·54 D., but inaccessibility of experimental details prevents appropriate entries in Tables I and III.

It is noteworthy that from the $\varepsilon^{25°}$ and $d_{4°}^{25°}$ (Table II) of pure aniline, combined with $n_\infty^2 = 2·41$—from $[R_L]_\infty = 29·2$ (extrapolated from Landolt–Börnstein, "Tabellen")—the moment calculable *via* Onsager's expression (*J. Amer. Chem. Soc.*, 1936, **58**, 1436) for the orientation polarisation, *viz.*,

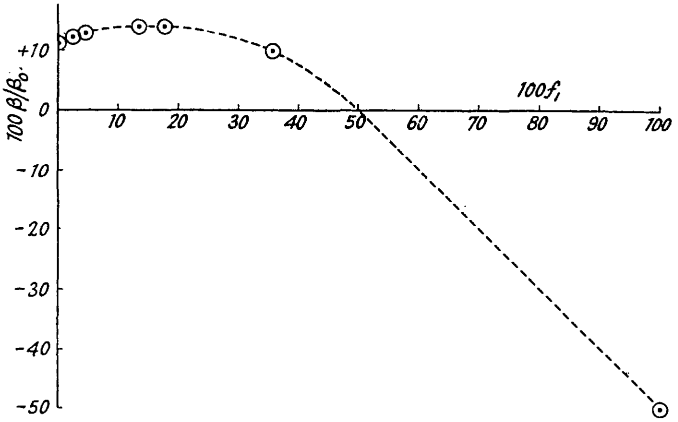
$$ {}_0P_{25°} = (\varepsilon - n_\infty^2)(2\varepsilon + n_\infty^2)M/\varepsilon(n_\infty^2 + 2)^2 d $$

is $0·22 \times (47·3)^{\frac{1}{2}} = 1·51$ D., while if $n^2 = 2·51$—from $[R_L]_D = 30·6$—μ becomes $0·22 \times (44·6)^{\frac{1}{2}} = 1·47$ D.

Groves and Sugden (*J.*, 1937, 1782) found $(P)_{\text{gas}}$ at 459° K. to be 61·55 c.c. If the same

$[R_L]_D$ is applicable to the gaseous and the liquid state (direct data seem to be lacking), then $(P)^{25°}_{\text{gas}} = 30{\cdot}6 + 31 \times 459/298 = 78{\cdot}3$ c.c. There is thus a possibility that the apparent moment of aniline in benzene solution is smaller than the true moment determined as a gas. Such a conclusion would be contrary to the opinions of a number of authors already cited (*e.g.*, Cowley and Partington, Higasi, etc.) who have harmonised the previously supposed fractional nature of the ratio $\mu_{\text{gas}}/\mu_{\text{soln.}}$ with the recorded *negative* Kerr constant of aniline (Briegleb and Wolf, *Fortschr. Chem.*, 1931, **21**, Part 3, 36; Lippmann, Diss., Dresden, 1912; Schmidt, Diss., Göttingen, 1901). We note, however, that it is only the electric double refraction (E.D.R.) of liquid aniline which is known to be negative; in this state molecular aggregates of some kind, perhaps cybotactates, may reasonably be supposed, the anisotropy of whose polarisability would not be the same as that of the separated molecules. Lippmann (*Z. Elecktrochem.*, 1911, **17**, 15) records the E.D.R. of mixtures of benzene with aniline: these (Fig. 2) indicate that from $100f_1 = 0$ to about 15, aniline contributes *positively* to the E.D.R. If, therefore, $\mu_{\text{gas}}/\mu_{\text{soln.}}$ is in fact greater than unity, aniline would merely be taking its place normally with other molecules with positive Kerr constants.

FIG. 2.



If the association of aniline takes place by hydrogen-bond formation, as infra-red spectroscopic studies have suggested (Gordy, *J. Chem. Physics*, 1939, **7**, 163; Buswell, Downing, and Rodebush, *J. Amer. Chem. Soc.*, 1940, **62**, 2759), the dimer will have some stereo-resemblance (the N–H–N arrangement being assumed rectilinear) to, *e.g.*, hydrazobenzene, the contribution of which to the E.D.R. of benzene is *negative* even at 0·9 mol. % (Lippmann, *loc. cit.*).

Finally, it is of interest that for many other properties, benzene–aniline mixtures seem to obey a normal additive law notwithstanding the fact that the apparent molecular weight of aniline in benzene is stated to rise with increasing concentration (Udovenko and Usanovitsch, *J. Gen. Chem. Russia*, 1940, **10**, 17).

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UNIVERSITY OF SYDNEY, N.S.W., AUSTRALIA.

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