680. *The Dielectric Polarisation of Solutions. Part I. The Polarisations and Apparent Dipole Moments of Various Primary, Secondary, and Tertiary Amines in Solutions in Non-polar Solvents and in the Liquid State.*

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The polarisations and apparent dipole moments of 18 aliphatic and aromatic amines have been determined in non-polar solvents, and those of 15 liquid amines in the pure state. Further measurements on aniline indicate that, in the majority of solvents, the dipole moment is lower than in the vapour state. In most of the compounds, the effect of the solvent on the moment of the solute is small. *n*-Propyl- and *n*-butyl-amine show larger moments in all the solvents used than in the vapour state. The changes in moment in the corresponding primary, secondary, and tertiary amines are compared. The variation of polarisation with change of concentration from infinitely dilute solution to the pure amine is considered and shown to depend on the type of amine and its dielectric constant. Calculations of the polarisations of the vapours according to Onsager's theory, from the physical constants of the liquid amines, do not give good agreement with experimental values which are available in only a few instances. Small, but definite, changes in the apparent molecular solution volumes of the amines in the different solvents are found and these results are qualitatively discussed.

The objects of this work were the study of the effect of hexane and benzene on the polarisations and apparent moments of amines, the investigation of the changes in moment produced by different alkyl and aryl groups attached to the nitrogen atom, and the comparison of the polarisations of the pure amines with those of the amines in solution at infinite dilution and, where possible, in the vapour state.

The polarisations and apparent dipole moments of aniline in four non-polar solvents at 20° were measured by Cowley and Partington (*J.*, 1938, 1598), who found that the values in benzene and toluene were slightly greater, and those in hexane and *cyclo*hexane were lower, than the moment of the vapour (Groves and Sugden, *J.*, 1937, 1782). The present research (Cowley, *Nature*, 1951, **168**, 705) reports further results for aniline in three other non-polar solvents as well as measurements of the dipole moments of various other amines mainly in hexane and benzene at 20°. Table 1 contains the values of the polarisations of the solutes at infinite dilution, $P_{2\infty}$, the electronic polarisations of the solutes, P_E, measured as the molecular refraction for sodium D light, and the apparent dipole moments, in Debye units, calculated either from $(P_{2\infty} - P_E)$ or from $(P_{2\infty} - P_{E+A})$, where P_{E+A} is taken as 1·05 $[R]_D$; both these methods of calculation have been used in the results quoted below. The solvent and its dielectric constant are stated for each measurement and all the values refer to 20·0°.

The Solvent Effect on the Moment of Aniline.—Cowley and Partington (*loc. cit.*) showed that their experimental moments of aniline increased slightly (0·05 D) with the dielectric constants of the four solvents used, but drew no final conclusion regarding the sign of the solvent effect. In the previous work, carbon tetrachloride and carbon disulphide were not at first used as solvents for, on storage, solutions of aniline in these liquids showed evidence of interaction, but later it was found that consistent results could be obtained if measurements were made on freshly prepared solutions. The results obtained, together with that in tetralin, shown in Table 1, indicate a fall in polarisation with an increase in the dielectric constant of the solvent. Thus, apart from the results in benzene and toluene, the dipole moments of aniline in the remaining five solvents are smaller than the moment of the vapour. Since Cowley and Partington's paper, several authors have published work on aniline. Emblem and McDowell (*J.*, 1946, 641) determined the moment (corrected for P_A) in benzene as 1·54 at 20°. Le Fèvre, Roberts, and Smythe (*J.*, 1949, 902) studied the variation of polarisation with concentration of aniline in benzene, and pointed out that it is only for liquid aniline that the electric double refraction is known to be negative, and that the separate molecules in solution contribute positively to the electric double refraction, as is indicated by Lippmann's results (*Z. Elektrochem.*, 1911, **17**, 15) for benzene–aniline mixtures.

TABLE 1. *Polarisations and apparent moments of various amines at 20°.*

Amine	Solv.	ε	$P_{2\infty}$	P_E	P_{O+A}	μ	P_{E+A}	P_O	$\mu_{corr.}$*
NH_2Pr^n	C_6H_{14}	1·894	59·0	19·4	39·6	1·38	20·4	38·6	1·36
	C_6H_6	2·283	57·3	19·4	37·9	1·35	20·4	36·9	1·33
$NHPr^n_2$	C_6H_{14}	1·894	55·5	33·5	22·0	1·03	35·2	20·3	0·99
	C_6H_6	2·281	57·1	33·5	23·6	1·07	35·2	21·9	1·03
NPr^n_3	C_6H_6	2·283	59·5	47·7	11·8	0·75	50·0	9·5	0·68
NH_2Bu^n	C_6H_{14}	1·895	62·0	24·1	37·9	1·35	25·3	36·7	1·33
	C_6H_{12}	2·019	61·8	24·1	37·7	1·35	25·3	36·5	1·32
	C_6H_6	2·282	64·5	24·1	40·4	1·39	25·3	39·2	1·37
$NHBu^n_2$	C_6H_{14}	1·897	65·8	42·8	23·0	1·05	44·9	20·9	1·00
	C_6H_6	2·276	67·3	42·8	24·5	1·09	44·9	22·4	1·04
cyclo-$C_6H_{11}\cdot NH_2$	C_6H_{14}	1·891	68·7	31·3	37·4	1·34	32·8	35·9	1·31
	C_6H_6	2·280	66·0	31·3	34·7	1·29	32·8	33·2	1·26
$NH_2\cdot CH_2Ph$	C_6H_{14}	1·895	68·8	34·4	34·4	1·29	36·2	32·6	1·25
	C_6H_{12}	2·019	69·6	34·4	35·2	1·30	36·2	33·4	1·27
	C_6H_6	2·280	71·2	34·4	36·8	1·33	36·2	35·0	1·30
	C_7H_8	2·379	66·9	34·4	32·5	1·25	36·2	30·7	1·21
$NH(CH_2Ph)_2$	C_6H_{14}	1·898	87·0	63·6	23·4	1·06	66·7	20·3	0·99
	C_6H_6	2·280	88·0	63·6	24·4	1·08	66·7	21·3	1·01
$N(CH_2Ph)_3$	C_6H_6	2·280	107·0	93·4	13·6	0·81	98·1	8·9	0·65
NH_2Ph	CCl_4	2·236	76·2	30·6	45·6	1·48	32·1	44·1	1·46
	CS_2	2·641	75·0	30·6	44·4	1·46	32·1	42·9	1·44
	$C_{10}H_{12}$	2·757	71·7	30·6	41·1	1·41	32·1	39·6	1·38
$NHPh_2$	C_6H_{14}	1·894	79·7	58·2	21·5	1·02	61·1	18·6	0·95
	C_6H_6	2·280	79·9	58·2	21·7	1·02	61·1	18·8	0·95
NPh_3	C_6H_6	2·283	92·0	83·3	8·7	0·65	87·5	4·5	0·47
$NHPhMe$	C_6H_{14}	1·884	96·6	35·7	60·9	1·71	37·5	59·1	1·69
	C_6H_6	2·285	93·4	35·7	57·7	1·67	37·5	55·9	1·64
$NPhMe_2$	C_6H_{14}	1·884	92·7	40·7	52·0	1·58	42·8	49·9	1·55
	C_6H_6	2·280	93·5	40·7	52·8	1·59	42·8	50·7	1·56
$NHPhEt$	C_6H_{14}	1·884	100·2	40·4	59·8	1·70	42·4	57·8	1·67
$NPhEt_2$	C_6H_{14}	1·895	120·8	50·2	70·6	1·84	52·7	68·1	1·81
	C_6H_6	2·276	120·0	50·2	69·8	1·83	52·7	67·3	1·80
$NHPhPr^n$	C_6H_{14}	1·885	104·8	45·1	59·7	1·69	47·4	57·4	1·66
	C_6H_6	2·285	104·1	45·1	59·0	1·68	47·4	56·7	1·65
$NPhEtPr^n$	C_6H_{14}	1·895	124·1	54·9	69·2	1·82	57·7	66·4	1·79
	C_6H_6	2·284	125·2	54·9	70·3	1·84	57·7	67·5	1·80

* Corrected for P_A.

Few and Smith (*J.*, 1949, 753) attributed the higher value of the dipole moment of aniline in dioxan than in benzene to hydrogen bonding between the hydrogen of the amino-group and the oxygen atoms of the solvent molecules (cf. Kumler and Halverstadt, *J. Amer. Chem. Soc.*, 1941, **63**, 2182; Wassiliew and Syrkin, *Acta Physicochim. U.R.S.S.*, 1941, **14**, 414). It may be noted that Higasi (*Bull. Inst. Phys. Chem. Res. Tokyo*, 1934, **13**, 1167) found that the dipole moment of aniline in ether is appreciably larger than the values in hexane or benzene. In a further paper, Few and Smith (*J.*, 1949, 3057) measured the dipole moment of aniline in *n*-heptane (1·477), carbon tetrachloride (1·458), and carbon disulphide (1·420) [all results at 25° calculated from $(P_{2\infty} - 1{\cdot}05[R]_D)$]. The results in carbon tetrachloride and carbon disulphide are close to those in Table 1, but Few and Smith used values of the molecular refraction determined in the various solvents, whereas the value for the pure liquid is used here.

Few and Smith (*loc. cit.*, p. 3057) suggest that aniline has a slight negative solvent effect, their values of the moment in solution lying below the vapour result and falling with the dielectric constant of the solvent, and that the value in benzene is slightly higher than expected. This is similar to the conclusion drawn for nitrobenzene that the moment is anomalously high in benzenoid solvents (Smith and Cleverdon, *Trans. Faraday Soc.*, 1949, **45**, 109). Few and Smith calculated the angle between the resultant dipole and the benzene ring in aniline as 53°, allowance being made for the mesomeric effect. This angle is slightly less than that given by Frank's theory (*Proc. Roy. Soc.*, 1935, *A*, **152**, 171), which predicts a negative solvent effect in molecules with a single radical not on the dipole axis when the angle between the radical and the dipole axis is less than 55° (cf. discussion by Cowley and Partington, *loc. cit.*).

Thus Cowley and Partington (*loc. cit.*) and Cowley (present research) have determined the dipole moment of aniline in seven solvents, and Few and Smith (*loc. cit.*) in five, and in all cases its moment as solute is less than that as vapour, the results in benzene, toluene, and dioxan being excluded. The weight of the evidence, therefore, is that aniline shows the more usual negative solvent effect, the differences, however, being fairly small.

Comparison of Moments of Amines.—The measurements on eight of the amines recorded in Table 1 are new, and there are no earlier values of the dipole moments of any of the compounds (apart from aniline) listed in Table 1 in hexane, *cyclo*hexane, or toluene. The dipole moments of amines investigated by other workers (several after this work was completed) are given with the relevant details in Table 2.

As already pointed out (Cowley, *loc. cit.*), the results of the present research for six amines, *viz.*, *n*-propyl-, *n*-butyl-, and diphenyl-amine, and methyl-, dimethyl-, ethyl-,

TABLE 2. *Published values of molar polarisations and dipole moments of amines.* (All were in benzene solution except those marked * which were as vapour; and all relate to 25° except where noted or where vapour was used.)

Amine	P_∞	$[R]_D$	μ calcd. from :	μ	Ref.
NH_2Pr^n	—	—	slope P–$1/T$ line $8301\cdot7$; intercept $23\cdot18$	1·17 *	1
	55·9	19·4	32·7	1·26	1
			$P_\infty - [R]_D$	1·34	1
NH_2Bu^n	—	—	slope P–$1/T$ line $6130\cdot72$; intercept $34\cdot10$	1·00 *	1
	63·7	24·5	29·6	1·20	1
			$P_\infty - [R]_D$	1·38	1
	64·0	24·06	$P_\infty - [R]_D$	1·40	2
	61·13	24·22	$P_\infty - 1\cdot05[R]_D$	1·32	3
cyclo-$C_6H_{11}\cdot NH_2$	65·7	30·5	$P_\infty - [R]_D$	1·32	4
NHPhMe	93	36	57	1·64	5
	93·20	35·81	55·20	1·643	6
	$93\cdot1_3$	35·68	$P_\infty - [R]_D$	1·67	1
$NPhMe_2$	—	—	$P - 1\cdot05[R]_D$	1·61 *	7
	—	—	—	1·39 †	8
	94	41	53	1·58	5
	97·6	46·7 (P_{E+A})	$P_A = 15\%$ of P_E	1·55	9
	94·06	41·17	50·83	1·577	6
	93·6	41·6	$P_\infty - [R]_D$	1·58	10
				1·53 †	11
	$94\cdot1_4$	40·82	$P_\infty - [R]_D$	1·61	1
NHPhEt	100	40	60	1·68 §	12
	$99\cdot5_4$	40·44	$P_\infty - [R]_D$	1·70	1
$NPhEt_2$	108	50·2	$P_\infty - [R]_D$	1·65 †	13
	117·5	50·20	$P_\infty - [R]_D$	1·81	1
$NHPh_2$	93·7	58·4 (P_{solid})	35·3	1·3 §	14
	79·8	57·3	22·5	1·04	15
	81·22	57·3	$P_\infty - [R]_D$	1·08	16
	79·0	57·6	$P_\infty - [R]_D$	1·0	1
NPh_3	—	—	$P_\infty - P_E = 1\cdot43$	0·26 ‡	17
			$(P_A = 0)$	0·71	18

† See notes in relevant references. § At 20°. ‡ At 15°.

References: (1) Barclay, Le Fèvre, and Smythe, *Trans. Faraday Soc.*, 1951, **47**, 357. (2) Rogers, *J. Amer. Chem. Soc.*, 1947, **69**, 457. (3) Few and Smith, *J.*, 1949, 2663. (4) Lewis and Smyth, *J. Amer. Chem. Soc.*, 1939, **61**, 3067. (5) Fogelburg and Williams, *Physikal. Z.*, 1931, **32**, 27: recalculation of μ gives 1·67 for methylaniline and 1·61 for dimethylaniline. (6) Few and Smith, *J.*, 1949, 753: μ calculated from $P_\infty - 1\cdot05[R]_D$. (7) Groves and Sugden, *J.*, 1937, 1782. (8) Højendahl, *Nature*, 1926, **117**, 892: method of calculation and temp. not stated. (9) Hertel and Dumont, *Z. physikal. Chem.*, 1935, *B*, **30**, 139. (10) Marsden and Sutton, *J.*, 1936, 599. (11) Fischer, *Nature*, 1950, **165**, 239: solvent, temp., and method of calculation not stated. (12) Cowley and Partington, *J.*, 1933, 1257. (13) Krasilnikov, *J. Phys. Chem., U.S.S.R.*, 1944, **18**, 174: temp. apparently 20°. (14) Estermann, *Z. physikal. Chem.*, 1928, *B*, **1**, 134. (15) Leonard and Sutton, *J. Amer. Chem. Soc.*, 1948, **70**, 1565: μ 0·99 with $P_A = 5\%$ of P_E. (16) Smith, *J.*, 1950, 3532: μ 1·016 from $P_\infty - 1\cdot05[R]_D$. (17) Bergmann and Schütz, *Z. physikal. Chem.*, 1932, *B*, **19**, 401. (18) Warburton, result quoted by Leonard and Sutton (ref. 15): μ 0·55 with $P_A = 5\%$ of P_E.

and diethyl-aniline in benzene at 20° are in close agreement with those of Barclay, Le Fèvre, and Smythe (*loc. cit.*) in the same solvent at 25°, the comparison being made between the dipole moments calculated with the same assumptions regarding the distortion polarisation. The latter authors' value of $[R]_D$ of *n*-butylamine is slightly higher than the present value, which confirms that of Rogers (*loc. cit.*) : when the present value of the molecular refraction is used, their moment is identical with the result now reported (1·39). All these results for *n*-butylamine are slightly higher than that of Few and Smith (*loc. cit.*), *viz.*, 1·34 in benzene at 25°, if calculated from $P_\infty - [R]_D$. The difference between the moments of *cyclo*hexylamine in benzene reported here and that of Lewis and Smyth (*loc. cit.*) is also due to use of different values of molecular refraction, the present value agreeing closely with Vogel's result (*J.*, 1948, 1825). Recalculation of Lewis and Smyth's result using this figure gives 1·30, compared with 1·29 (Table 1).

The moment of methylaniline found here and by Le Fèvre *et al.* (*loc. cit.*) is slightly greater than that found by Few and Smith (*loc. cit.*), and our value for dimethylaniline agrees with three of the earlier published results. Barclay, Le Fèvre, and Smythe's value for ethylaniline is close to that of Cowley and Partington (*loc. cit.*), but the former authors' result for diethylaniline, now confirmed, is considerably greater than that of Krasilnikov (*loc. cit.*). For diethylaniline the latter worker found a variation of polarisation with concentration from infinite dilution to the pure amine of the shape found for some alcohols, and this is different from the results now reported for benzene and hexane solutions over the range of mole-fraction from zero to 0·04. Krasilnikov's result may be explained by the fact that the dielectric constants are given to only three significant figures, which would greatly affect the results for dilute solutions. The present values of the moment of di- and tri-phenylamine are in satisfactory agreement with the other results.

Variation of Moment of Amines.—The results show that the change of moment from *n*-propyl- to *n*-butyl-amine is small, the moments of benzyl- and *cyclo*hexyl-amine being a little lower than the mean of the values for the other compounds. Smyth (*J. Amer. Chem. Soc.*, 1924, **46**, 2151) calculated the moments of benzyl- and dibenzyl-amine as approximately 1·14 and 1·15, which the experimental figures now show to be of the right order. The branched-chain primary butylamines have lower moments than *n*-butylamine, *viz.*, *iso*- 1·27 (Barclay, Le Fèvre, and Smythe, *loc. cit.*), *sec.*- 1·28, *tert.*- 1·29 (Rogers, *loc. cit.*), and 1·34 (Few and Smith, *J.*, 1949, 2663); all values relate to benzene solution at 25° and are calculated from the difference ($P_\infty - [R]_D$).

TABLE 3. *Change in dipole moment from primary to secondary to tertiary amine in benzene solution.*

Group or groups (R) in amine	μ of primary amine	Difference in μ : $NH_2R - NHR_2$	Difference in μ : $NHR_2 - NR_3$
Me	1·46	0·29	0·31
Et	1·28	0·25	0·11
Pr^n	1·35	0·28	0·32
Bu^n	1·39	0·30	—
CH_2Ph	1·33	0·25	0·27
Ph	1·53	0·51	0·37
Anilines :	methyl	−0·14	0·08
	ethyl	−0·15	−0·15
	n-propyl	−0·15	−0·16 *

* Difference between moments for *n*-propyl- and ethyl-*n*-propyl-aniline.

The changes in moment produced as the hydrogen atoms of the primary amine group are successively replaced by further alkyl or aryl groups are given in Table 3, all the data referring to results in benzene solution. (The values of the moments determined in hexane show approximately the same variation.) The values are those of the present research, except those for the methylamines (Le Fèvre and Russell, *Trans. Faraday Soc.*, 1947, **43**, 374), the ethylamines (Barclay, Le Fèvre, and Smythe, *ibid.*, 1950, **46**, 812; Le Fèvre, *ibid.*, 1952, **48**, 580), and aniline (Cowley and Partington, *loc. cit.*).

In the alkylamines, an approximately constant difference exists between the moments of the corresponding primary and secondary amines and also between the corresponding secondary and tertiary amines, with the exception of the smaller differences found between the ethylamines. The differences between the benzylamines are slightly smaller than those in the alkylamines, but in the series aniline, diphenylamine, triphenylamine the differences in moment are larger, that between the first two being much greater than that between the last two. In the replacement of the remaining hydrogen of the imino-group, the change from methyl- to dimethyl-aniline produces a small decrease in moment, but replacement by an ethyl group in either ethyl- or *n*-propyl-aniline causes in both cases the same increase in moment, *viz.*, 0·15.

The angles between the groups in these compounds are not available from direct measurements except for trimethylamine, where the C–N–C angle is 108°±4° (Brockway and Jenkins, *J. Amer. Chem. Soc.*, 1936, **58**, 2036). Leonard and Sutton (*loc. cit.*) have calculated this angle in di- and tri-phenylamine as 113° and 114°, respectively, from the dipole moments of the amines, the *p*-substituted fluoro-derivatives of these amines, and fluorobenzene. They regard the differences between these angles and that in trimethylamine as real and as indicating resonance with structures involving the grouping $=\overset{+}{N}<$, although neither amine is coplanar. Similarly, the difference in moment of the amino-group in the aliphatic and aromatic series is usually attributed to the mesomeric effect of the amino-group, which gives rise to the resonance.

Polarisations of Amines as Vapours or Liquids.—Of the compounds now used, only *n*-propylamine, *n*-butylamine, and dimethylaniline have been investigated in the vapour state, the polarisation then being lower for the first two, but higher for the last, than the corresponding solution results, as shown in Table 4. The moments of *n*-propylamine and *n*-butylamine are compared in Table 5 with the apparent moments of the pure liquids, calculated from the difference of the polarisation of the liquid and the molecular refraction (see Table 6), and with the earlier results for methyl- and ethyl-amine.

TABLE 4. *Total polarisation of amines in the vapour state and in solution at* 20°.

		Total polarisation:			
Amine	$\mu_{vap.}$	Vapour	In C_6H_{14}	In C_6H_{12}	In C_6H_6 [1]
n-Propylamine	1·17	51·7 [2]	59·0	—	57·3
n-Butylamine	1·00	50·4 [2]	62·0	61·8	64·5
Dimethylaniline	1·61	96·7 [3]	92·7	—	93·5

[1] All solution results from present research. [2] Calculated from the results of Barclay, Le Fèvre, and Smythe (*Trans. Faraday Soc.*, 1951, **47**, 357). [3] Calculated from the results of Groves and Sugden (*loc. cit.*).

TABLE 5. *Dipole moments of aliphatic amines.*

Amine	Condition	Mono-	Di-	Tri-	Amine	Condition	Mono-	Di-	Tri-
Me [1]	Gas	1·28	1·02	0·64	Et [2]	Gas	1·22$_5$	0·92$_0$	0·66$_0$
	C_6H_6 soln.	1·46	1·17	0·86		C_6H_6 soln.	1·28 [5]	1·02$_6$	0·91$_3$
	Liquid	1·08	1·13	0·72		Liquid	1·09	1·11	0·75$_8$
Pr^n	Gas	1·17 [4] (1·25)	—	—	Bu^n [3]	Gas	1·00 [4] (1·12)	—	—
	C_6H_{14} soln.	1·38	1·03	—		C_6H_{14} soln.	1·35	1·05	—
	C_6H_6 soln.	1·35	1·07	0·75		C_6H_6 soln.	1·39	1·09	—
	Liquid	1·18	1·04	0·67		Liquid	1·23	1·10	—

[1] Le Fèvre and Russell, *loc. cit.* [2] Barclay, Le Fèvre, and Smythe, *Trans. Faraday Soc.*, 1950, **46**, 812. [3] Present research. [4] Ref. 2, Table 4: μ's calculated from slope of P–$1/T$ line; the figures in parentheses have been calculated from the total polarisation of the vapour $-$ $[R]_D$. [5] Le Fèvre *ibid.*, 1952, **48**, 580.

The apparent moment of pure liquid *n*-propylamine is lower than that for the vapour or solution, thus resembling the values for methyl- and ethyl-amine, while that of *n*-butylamine lies between the moments of the vapour and that found from solutions. The apparent moments of pure liquid di-*n*-propyl- and di-*n*-butyl-amine are little different from the values found in hexane and benzene, and the difference in apparent moments of tri-*n*-propylamine is relatively small.

Table 6 gives the polarisations and apparent moments of all the liquid amines used in this work. The polarisations of the liquids have been calculated from the dielectric constants and densities at 20° of the pure materials (see Table 10) by the Clausius–Mossotti equation, and the apparent moments by the Debye equation.

TABLE 6. *Polarisations and apparent dipole moments of liquid amines, at 20°.*

Amine	$P_{\text{liq.}}$	P_{O+A}*	μ	P_O*	$\mu_{\text{corr.}}$†	Amine	$P_{\text{liq.}}$	P_{O+A}*	μ	P_O*	$\mu_{\text{corr.}}$†
NH_2Pr^n	48·6	29·2	1·18	28·2	1·16	NH_2Ph	61·0	30·4	1·21	28·9	1·18
$NHPr^n_2$	55·9	22·4	1·04	20·7	1·00	NHPhMe	67·7	32·0	1·24	30·2	1·21
NPr^n_3	57·1	9·4	0·67	7·1	0·58	$NPhMe_2$	72·5	31·8	1·24	29·8	1·20
NH_2Bu^n	55·8	31·7	1·23	30·5	1·21	NHPhEt	78·1	37·7	1·35	35·7	1·31
$NHBu^n_2$	68·0	25·2	1·10	23·1	1·05	$NPhEt_2$	93·1	42·9	1·44	40·4	1·39
cyclo-$C_6H_{11}{\cdot}NH_2$	63·4	32·1	1·24	30·6	1·21	$NHPhPr^n$	85·8	40·6	1·40	38·4	1·36
$NH_2{\cdot}CH_2Ph$ ...	63·5	29·1	1·18	27·3	1·14	$NPhEtPr^n$......	99·9	44·9	1·47	42·2	1·42
$NH(CH_2Ph)_2$ ...	86·3	22·7	1·04	19·6	0·97						

* $P_{O+A} = P_{\text{liquid}} - P_E$; $P_O = P_{\text{liquid}} - P_{E+A}$: for values of P_E and P_{E+A} see Table 1.
† See footnotes to Table 1.

Comparison of results for the pure liquids and for the same amines as solutes shows that the apparent moments of the liquids (Table 6) exhibit a variation similar to that found at infinite dilution in the non-polar solvents (Table 1). It is noteworthy that for the secondary aliphatic or benzyl amines, the moments are very close, but for the other compounds the apparent moments of the liquids are smaller. These amines can be grouped according to the difference between the polarisation at infinite dilution in solution and that of the pure liquid, which is mainly determined by the structure and the dielectric constant of the amine. This difference is very small if the dielectric constant of the secondary amine is 2—3·5; but it is 5—9 c.c. for primary aliphatic amines, benzylamine, and *cyclo*hexylamine, where the dielectric constant is approximately 5; and for the aromatic amines, it is 20—25 c.c. when the dielectric constant is equal to or greater than 5.

Association of Amines.—Attempts to obtain evidence of association in the liquid from the variation of polarisation with change of concentration of the solute in a non-polar solvent have been made, *e.g.*, by Smyth ("Dielectric Constant and Molecular Structure," The Chemical Catalog Company, New York, 1931, ch. 9, p. 169). Davy and Sidgwick (*J.*, 1933, 281) investigated the association of nitrobenzene in benzene and *cyclo*hexane by comparing the change of polarisation in these solvents with the molecular weights determined cryoscopically; since the association did not obey the law of mass action, they concluded that there is no chemical combination between the solute molecules, the fall in activity and polarisation being explained by orientation of the polar molecules under the influence of their mutual attractions.

It is improbable, therefore, that the cause of the fall of polarisation which occurs in "normal" liquids, like nitrobenzene, is chemical association. Van Arkel and Snoek (*Trans. Faraday Soc.*, 1934, **30**, 707) showed that the variation of polarisation with concentration was expressed by the formula

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4}{3}\pi n\left[\alpha + \frac{\mu^2}{3kT + Cn\mu^2}\right]$$

The constant C was usually independent of n, the number of molecules per c.c., of the nature of the solvent, and largely of the solute molecule, but, in some cases, it varied with concentration and had abnomal values (*e.g.*, with alcohols). It was shown that in many cases C was between 1 and 2, but the amines formed one of several groups of substances which did not obey the equation.

The distinction between dipole association and chemical association is stressed by Wilson (*Chem. Reviews*, 1939, **25**, 377). The dipole association is divided into two classes: co-association, in which dipoles are oriented head to tail so that the dipole moments reinforce each other, and contra-association in which dipoles tend to be oriented in antiparallel configurations, so that the moments cancel each other. Wilson showed that for a few simple molecules it is possible to decide on the type of association from considerations of potential energy.

The changes in polarisation of these amines with concentration are mentioned above. It is found that in every case the polarisation either falls or remains practically unchanged, but it is only in the aromatic series that there is an appreciable fall. It follows that, apart from the latter group, the effect of dipole association is slight.

Other evidence regarding association in these amines is sparse. Turner and Merry

(*J.*, 1910, **97**, 2069) concluded, from a study of the propyl-, amyl-, and benzyl-amines, that the primary amines were slightly associated, and the secondary and tertiary amines non-associated, in the liquid state, and this was confirmed for amyl- and benzyl-amines by molecular-weight determinations in benzene (cf. Turner, "Molecular Association," Longmans, Green and Co., London, 1915, p. 61). The value of Ramsay and Shields's constant increased in the order primary to secondary to tertiary propyl- or benzyl-amine, but since the molecular surface energies of various secondary and tertiary amines were proportional to the temperature, it was concluded that Ramsay and Shields's formula was not valid in these cases. Mussell, Thole, and Dunstan (*J.*, 1912, **101**, 1008), who showed that the ratio of viscosity to molar volume had high values for associated liquids, concluded that the primary amines had the highest ratio for the aliphatic amines. There was a large increase over these values in passing to the aromatic series, although the order primary, secondary, tertiary amine was preserved. Whereas aniline was regarded as associated, benzylamine was normal.

Theoretical Calculation of the Moments of Vapours of Amines.—The experimental moments and those calculated from Onsager's equation (*J. Amer. Chem. Soc.*, 1936, **58**, 1486) are compared in Table 7. The equation may be written

$$P_O\ (\text{vapour}) = \frac{(\varepsilon - n_\infty^2)(2\varepsilon + n_\infty^2)}{\varepsilon(n_\infty^2 + 2)^2} \cdot \frac{M}{d}$$

where ε is the dielectric constant of the pure liquid, n_∞ the refractive index for infinite wave-length, M the molecular weight, and d the density of the liquid. The equation has been tested by Böttcher (*Physica*, 1939, **6**, 59) and in many cases the calculated moments of the vapours are in reasonable agreement with the experimental values. Onsager's expression has been criticised by Wilson (*loc. cit.*) because of the assumed spherical shape of the solute molecule with a central dipole, the treatment of the molecule as a homogeneous continuum, and the arbitrary choice of the cavity used in the deduction: the reaction field, which arises from the polarisation of molecules close to the central dipole, will thus be in error. Wilson deduced a modified equation, which takes account of the optical anisotropy of the polar molecule, and the calculations made from it are in closer agreement with the vapour values than are Böttcher's results.

As the necessary constants for the application of Wilson's equation are lacking, the calculations are now made by means of Onsager's equation. The refractive index for infinite wave-length is obtained from the molecular refraction for the C and the G' line given by Vogel (*loc. cit.*), by using the formula

$$R_\infty = (\lambda_2^2 - \lambda_1^2)/(\lambda_2^2/R_2 - \lambda_1^2/R_1)$$

where R_1 and R_2 are the molecular refractions for the wave-lengths λ_1 and λ_2. The dielectric constants used are recorded in Table 10. The results from Onsager's equation are also compared with values calculated from Wyman's equation (*J. Amer. Chem. Soc.*, 1936, **58**, 1482), *viz.*, P_O (total polarisation of the vapour) $= M(\varepsilon + 1)/8{\cdot}5d$, where ε and d refer to the pure liquid. This is in accordance with Onsager's equation for high values of the dielectric constant.

The calculated values can be compared with the experimental values of the orientation polarisation of the vapour in only four cases, *viz.*, *n*-propylamine 28·5, *n*-butylamine 20·8, dimethylaniline 53·9, and aniline 46·3 (values at 20° of P_O in c.c.). The two sets of figures are not in good agreement, all the calculated values being too large. It is found, however, that the values given by the Onsager and the Wyman equation in some cases are quite close to each other and in the *N*-substituted anilines are little different from the values found in the non-polar solvents. No general conclusion regarding the applicability of Onsager's equation to these amines can be drawn in the absence of determinations for the vapours. Le Fèvre *et al.* have found that the moments calculated from Onsager's equation do not give good agreement for the methyl- and ethyl-amines and that the calculated values are too large, as is found here for *n*-propyl- and *n*-butyl-amine. They applied Barclay and Le Fèvre's expression (*J.*, 1950, 556) to some of the aliphatic amines.

The other theoretical solvent-effect equations (see, *e.g.*, Cowley and Partington,

TABLE 7. *Comparison of experimental values of* P_O *and* μ *from hexane and benzene solutions with values calculated from Onsager's and Wyman's equations.*

				P_0, c.c.				μ calc. from P_0 for			
				calc. from equation :		found in :		vapour		solution	
Amine	$R_{\infty}^{20°}$	n_{∞}^{20}	ε	Onsager	Wyman	C_6H_{14}	C_6H_6	Onsager	Wyman	C_6H_{14}	C_6H_6
NH_2Pr^n	19·00	1·378	5·31	43·6	40·8	38·6	36·9	1·45	1·40	1·36	1·33
NH_2Bu^n	23·41	1·391	4·88	45·0	43·0	36·7	39·2	1·47	1·44	1·33	1·37
$NHPr^n_2$	32·75	1·395	3·068	26·0	30·2	20·3	21·9	1·12	1·21	0·99	1·03
$NHBu^n_2$	41·82	1·407	2·998	29·1	35·1	20·9	22·4	1·18	1·30	1·00	1·04
NPr^n_3	46·52	1·406	2·277	10·4	23·1	—	9·5	0·71	1·05	—	0·68
cyclo-C_6H_{11}·NH_2	30·55	1·447	4·73	43·9	44·2	35·9	33·2	1·45	1·46	1·31	1·26
NH_2·CH_2Ph ...	33·17	1·520	5·18	41·3	43·1	32·6	35·0	1·41	1·44	1·25	1·30
$NH(CH_2Ph)_2$ ...	—	1·565[1]	3·446	26·2	33·8	20·3	21·3	1·12	1·28	0·99	1·01
NH_2Ph	29·09	1·551	7·07	51·2	53·4	44·9[3]	47·9[3]	1·57	1·63	1·47[3]	1·52[3]
NHPhMe	33·88	1·536	5·96	49·2	51·4	59·1	55·9	1·54	1·57	1·69	1·64
NHPhEt	38·50	1·522	5·87	57·7	59·7	57·8	58[2]	1·67	1·69	1·67	1·66[2]
$NHPhPr^n$	43·08	1·512	5·48	60·2	61·9	57·4	56·7	1·70	1·72	1·66	1·65
$NPhMe_2$	38·74	1·524	5·02	45·0	46·9	49·9	50·7	1·47	1·50	1·55	1·56
$NPhEt_2$	47·80	1·511	5·20	59·0	63·6	68·1	67·3	1·68	1·75	1·81	1·80
$NPhEtPr^n$	—	1·505[1]	4·90	63·0	64·9	66·4	67·5	1·74	1·77	1·79	1·80

[1] Estimated value. [2] Cowley and Partington, *J.*, 1933, 1257. [3] *Idem*, *J.*, 1938, 1598.

J., 1936, 1184; 1937, 186) cannot yet be applied to the amines as the necessary constants are not available.

Molecular Solution Volumes of Amines.—The density data recorded in the Experimental section have been used to calculate the apparent molecular solution volumes of the amines at 20° (Table 8). The relationship, $V_{12} = V_1x_1 + V_2x_2$, where V is the molar volume and x the mole-fraction and the suffixes 1, 2, and 12 refer to solvent, solute, and solution, respectively, is assumed, and so any volume change is included in the molecular solution volume of the solute. The molar volumes of the pure liquids are calculated from the molecular weights and the densities at 20°.

It is found that the apparent molecular volumes of the aliphatic amines in hexane or benzene are greater than those of the pure liquids. The apparent molecular solution volumes of the *N*-alkyl-substituted anilines and dibenzylamine are smaller than the molar volumes of the liquids, with the exception of the values for diethyl- and ethyl-*n*-propylaniline, which are slightly larger in benzene. For *cyclo*hexylamine and benzylamine the values in hexane are smaller than those in benzene, the molar volumes of the liquids lying between them. Few and Smith (*J.*, 1949, 753) note that the apparent specific volumes of aniline, methylaniline, and dimethylaniline in benzene are lower than the specific volumes of the pure liquids. With the exception of some aliphatic amines, the apparent molecular solution volume is generally greater in benzene than in hexane. The molar volumes of the amines and the values of the atomic volume of nitrogen, deduced from them, are considered in detail by Le Bas ("The Molecular Volumes of Liquid Chemical Compounds," Longmans, Green and Co., London, 1915, p. 197).

Many attempts have been made to correlate volume changes on mixing with the properties of the constituents of the mixture. It has long been recognised that the compressibility and internal pressure are factors influencing volume changes on mixing liquids (*e.g.*, Dawson, *J.*, 1910, **97**, 1896). Tyrer (*ibid.*, p. 2620) placed solvents in order with respect to the magnitude of volume change of the solute, and found that the product of the compressibility and molar volume for the solutes gave the same order as the variation of the specific volume of the solute. The forces of attraction between the solute and solvent molecules were considered to be nearly constant for the substances examined.

Meares (*Trans. Faraday Soc.*, 1949, **45**, 966) studied the volume changes on mixing esters, and analysed the results with respect to the contributing effects. He showed that changes both in geometrical arrangement and in intermolecular forces may occur, and that these effects often act in opposition in their contributions to the resulting volume change. If a geometrical arrangement of molecules occurs, the volume change results from modification of the number of nearest neighbour contacts. This is more likely with molecules of different diameters. Similarly, the nature of the chemical groups in the

TABLE 8. *Apparent molecular solution volumes of amines at 20°.*

Amine	Molar vol. of pure amine	Molecular solution vol. in : C_6H_{14}	C_6H_{12}	C_6H_6	C_7H_8
NH_2Pr^n	82·42	87·6	—	83·7	—
NH_2Bu^n	98·94	100·6	103·8	100·4	—
$NHPr^n_2$	136·97	137·8	—	137·5	—
$NHBu^n_2$	170·04	170·4	—	171·8	—
NPr^n_3	189·33	—	—	192·2	—
cyclo-$C_6H_{11}\cdot NH_2$	114·42	114·4	—	115·4	—
$PhCH_2\cdot NH_2$	109·14	107·6	115·4	109·2	109·9
$NH(CH_2Ph)_2$	192·12	189·0	—	191·6	—
NH_2Ph *	91·15	90·2	96·5	90·4	92·1
NHPhMe	108·64	106·7	—	108·1	—
NHPhEt	126·16	124·9	—	—	—
$NHPhPr^n$	143·10	140·9	—	141·1	—
$NPhMe_2$	126·74	126·2	—	126·7	—
$NPhEt_2$	159·68	157·2	—	160·2	—
$NPhEtPr^n$	176·67	171·8	—	177·3	—
Molar vol. of solvent		128·4	108·2	89·0	106·4

* The molecular solution volume of aniline in carbon tetrachloride is 89·7 (96·5), carbon in disulphide 93·9 (60·2), and in tetralin 91·6 c.c. (136·5), the molar volumes of the corresponding solvents being given in parentheses.

molecules determines the attractive force between the molecules, and so the volume occupied by the mixture may be different from the sum of the separate volumes. The intermolecular energies fall rapidly with distance, so the attractive force is localised in the few atoms in contact on the molecular surfaces. Meares applied Scatchard's theory (*ibid.*, 1937, **33**, 160) to the change of volume, due to modification of geometrical arrangement, of compressibility, and of intermolecular forces, with alteration in the relative amounts of the constituents.

The compressibilities of only a few of the amines used here are available. These figures have been used in the calculation of the internal pressures (P_i) of the liquids (Table 9), where $P_i = T\alpha/\kappa$ in atm. at 293° K.

TABLE 9. *Compressibilities* (κ), *coefficients of expansion* (α), *and internal pressures of some amines and solvents at* 20°.

Compound	$10^5\kappa$ per atm.[1]	Press. range (unit : 10^6 dynes)	$10^4\alpha$[2]	P_i	Compound	$10^5\kappa$ per atm.[1]	Press. range (unit : 10^6 dynes)	$10^4\alpha$[2]	P_i
NH_2Ph	4·51	1—9	8·46	4370	C_6H_{14}	1·05	100—500	13·19	3670
NHPhMe	4·36	100—500	8·19	5510	*cyclo*-C_6H_{12}	9·42	100—200	11·64	3620
NHPhEt	4·76	100—500	8·74	5370	C_6H_6	7·29	100—500	12·12	4870
$NPhMe_2$	4·86	100—500	8·56	5160	PhMe	6·99	100—500	10·67	4470
$NPhEt_2$	5·17	100—500	8·45	4790					

[1] I.C.T., 1928, **3**, 35. [2] Results calculated from density–temperature data (*ibid.*, p. 27); ethylaniline from Vogel's results (*J.*, 1948, 1832).

The internal pressures of liquids calculated from the above expression usually give values of 2000—8000 atm. (Hildebrand and Scott, "The Solubility of Non-Electrolytes," Reinhold Publ. Corp., New York, 3rd edn., 1950, p. 96). It is necessary to use in comparisons values determined between the same pressure limits, since the compressibilites vary considerably with differences in pressure ranges. The compressibilites and internal pressures of these *N*-alkylanilines differ more from the values for hexane than from those for benzene, and the greater change of molecular solution volume from that of the corresponding pure amine is found in the hexane solution values.

The effects of the sizes and shapes of the molecules in the mixture must also be considered. Clausius's expression (see Debye, "Polar Molecules," The Chemical Catalog Company, 1929, p. 15) gives the volume occupied by the spherical molecules in the gram-molecular volume as equal to the molecular refraction of the compound. Although the assumption of spherical shape is an approximation, molecules of unassociated liquids at temperatures not near to their freezing points may usually be regarded as occupying spherical volumes, since in the absence of strongly localised fields the molecules can probably rotate freely (Meares, *loc. cit.*). The ratio of molecular refraction to molar volume will give, therefore, the fraction of the molar volume actually occupied by the molecules. For the amines used here, this fraction, calculated from $[R]_D$/(molar volume of liquid at 20°), has the values: aliphatic amines, 0·24—0·25; *N*-alkylanilines, 0·31—0·33; *cyclo*hexylamine, 0·27; and the benzylamines, 0·31—0·33. The corresponding values for hexane and benzene are 0·23 and 0·30, respectively. The fractions for the aromatic amines are closer to that for benzene than the value for hexane, and the greater free space in the latter solvent might lead to the expectation of a larger decrease in molecular solution volume of the aniline in hexane, as is found. The order here is the same as is found for the internal pressures. The range of concentration used in these solutions is comparatively small, and in most mixtures the variation of molecular solution volume with concentration is no larger than the probable error in the calculations.

EXPERIMENTAL

Measurement of Dielectric Constants.—Some of the determinations were made with the apparatus used by Cowley and Partington (*J.*, 1935, 604; 1936, 1184); the others were made with a redesigned heterodyne-beat apparatus, operating at 1870 kc. The standard condenser was a Muirhead variable air-condenser, with an N.P.L. calibration over the whole scale. The error on the dielectric constants is not more than a few parts per 10,000. The figures have been recorded to three places of decimals and therefore the possible error does not affect these values of the dielectric constant. The higher dielectric constants of some of the pure amines are evidently less accurate and are given to two places of decimals. A check of these results was made by using purified samples of liquids of known dielectric constants and of approximately the same magnitudes as that of the liquid being investigated.

The previously described dielectric cells were used. Some of the measurements were made with a glass dielectric cell with concentric silvered surfaces, fitted with tubes, closed with glass caps, for filling the annular space in the cell. The platinum leads, sealed through glass supporting tubes, made contact with mercury cups on the dielectric-constant apparatus. The cell could also be used for density determinations and it was calibrated with specially purified benzene.

Purification of Materials.—*Amines.* The amines, of the purest grade obtainable, were all purified carefully before use. The liquid amines were dried (KOH) and repeatedly fractionated. The purified aliphatic amines, *cyclo*hexylamine, benzylamine, and dibenzylamine, were distilled into the solution vessels in a Brühl receiver, so that there was no possibility of contact with atmospheric moisture or carbon dioxide. The *N*-substituted anilines were fractionated several times under reduced pressure and were colourless when used. The solid amines were recrystallised until their m. p.s were constant. Absolute alcohol was the solvent for crystallisation of tribenzylamine and triphenylamine, and light petroleum for diphenylamine. The physical constants of the amines are given in Table 10: they may be compared with the following determinations:

TABLE 10. *Physical constants of amines used.*

Amine	B. p./mm.	d_4^{20}	n_D^{20}	ε^{20}	$[R]_D^{20}$, c.c.	$P_{liq.}$, c.c.
NH_2Pr^n	47·0—47·8°/747	0·7172	1·3872	5·31	19·42	48·6
$NHPr^n_2$	109·0—109·5/756	0·7387	1·4045	3·068	33·53	55·9
NPr^n_3	156·5—157·2/764	0·7567	1·4178	2·277	47·65	57·1
NH_2Bu^n	77·0—77·4/762	0·7392	1·4014	4·88	24·06	55·8
$NHBu^n_2$	159·5/770	0·7601	1·4176	2·998	42·78	68·0
cyclo-$C_6H_{11}\cdot NH_2$	134·5—134·6/767	0·8668	1·4592	4·73	31·28	63·4
$NH_2\cdot CH_2Ph$	81·0/20	0·9818	1·5439	5·18	34·45	63·5
$NH(CH_2Ph)_2$	174·0—175·0°/6	1·0270	1·5757	3·446	63·56	86·3
$N(CH_2Ph)_3$	92·0 *	—	—	—	93·4	—
NH_2Ph	76·0/12	1·0220	1·5856	7·07	30·57	61·0
$NHPh_2$	53·0 *	—	—	—	58·2	—
NPh_3	127·0 *	—	—	—	83·3	—
NHPhMe	78·2—78·3/5	0·9863	1·5708	5·96	35·68	67·7
$NPhMe_2$	70·0/3	0·9561	1·5574	5·02	40·73	72·5
NHPhEt	94·8—95·0/6	0·9606	1·5540	5·87	40·43	78·1
$NPhEt_2$	90·7/3	0·9346	1·5414	5·20	50·21	93·1
$NHPhPr^n$	99·6—100·0/4	0·9443	1·5428	5·48	45·11	85·8
$NPhEtPr^n$	122·0—123·0/11	0·9240	1·5340	4·90	54·91	99·9

* M. p.s.

Amines: *n*-propyl, b. p. 48°/750 mm., d_4^{20} 0·7173, n_D^{20} 1·38815;[1] di-*n*-propyl, b. p. 108°/751 mm., d_4^{20} 0·7400,[1] 0·7390,[2] n_D^{20} 1·40499,[1] ε at 22° 2·90;[3] tri-*n*-propyl, b. p.

156·5°/760 mm., d_4^{20} 0·7558,[1] 0·7567,[4] n_D^{20} 1·41760;[1] *n*-butyl, b. p. 77°/750 mm., d_4^{20} 0·7414, n_D^{20} 1·40086,[1] ε at 21° 5·3;[3] di-*n*-butyl, b. p. 159°/761 mm., d_4^{20} 0·7601, n_D^{20} 1·41766;[1] *cyclo*hexyl, b. p. 133°/756 mm., d_4^{20} 0·8671, n_D^{20} 1·45926;[1] benzyl, b. p. 185°/767 mm., d_4^{20} 0·9816, n_D^{20} 1·5438,[1] ε at 20·6° 4·6,[5] at 19·4° 5·2;[6] dibenzyl, b. p. 177·5—178·0°/16 mm., d_4^{20} 1·0272,[4] 1·0276,[2] $n_D^{21\cdot6}$ 1·57432,[4] ε at 20° 3·55,[3] at 23° 3·6;[7] tribenzyl, m. p. 92°,[8] 91·3°;[9] aniline, b. p. 184·5°/750 mm., d_4^{20} 1·0221, n_D^{20} 1·58547,[1] ε at 18° 7·316,[10] at 25° 6·90,[11] at 20° 7·21;[12] diphenyl, m. p. 53°;[13] triphenyl, m. p. 127°.[14]

Anilines: methyl, b. p. 193°/738 mm., d_4^{20} 0·9867,[1] 0·9863,[4] n_D^{20} 1·57094,[1] ε at 20° 5·8,[3] at 20·8° 5·93,[15] at 23° 5·3;[7] dimethyl, b. p. 194°/760 mm., d_4^{20} 0·9571, n_D^{20} 1·55776,[1] ε at 20° 5·07,[3] at 18° 5·0;[7] ethyl, b. p. 202·5°/750 mm., d_4^{20} 0·9601, n_D^{20} 1·55397,[1] ε at 19·8° 5·9,[15] at 20° 5·76,[16] at 19° 5·4;[6] diethyl, b. p. 214·5°/748 mm., d_4^{20} 0·9353,[1] 0·9344,[17] n_D^{20} 1·54178,[1] ε at 18·5° 5·5;[6] *n*-propyl, b. p. 96°/9 mm., d_4^{20} 0·9426, n_D^{20} 1·54217.[1]

[1] Vogel, *J.*, 1948, 1829—1833. [2] Turner and Merry, *J.*, 1910, **97**, 2069. [3] Schlundt, *J. Phys. Chem.*, 1901, **5**, 157. [4] Brühl, *Z. physikal. Chem.*, 1895, **16**, 193. [5] Walden, *ibid.*, 1910, **70**, 569. [6] Dobroserdov, *J. Russ. Phys. Chem. Soc.*, 1911, **43**, 124. [7] Mathews, *J. Phys. Chem.*, 1905, **9**, 665. [8] Mailhe, *Ann. Chim.*, 1920, **13**, 189. [9] Cannizzaro, *Jahresber.*, 1856, **9**, 582. [10] Turner, *Z. physikal. Chem.*, 1900, **35**, 385. [11] Lunt and Rau, *Proc. Roy. Soc.*, 1930, *A*, **126**, 213. [12] I.C.T., 1929, **6**, 82. [13] Leonard and Sutton, *J. Amer. Chem. Soc.*, 1948, **70**, 1565. [14] Piccard and Kharasch, *ibid.*, 1918, **40**, 1077. [15] Walden, *Z. physikal. Chem.*, 1910, **70**, 569. [16] Walden, Ulich, and Werner, *ibid.*, 1925, **116**, 261. [17] Richards and Mathews, *J. Amer. Chem. Soc.*, 1908, **30**, 10.

The values for the atomic refraction of nitrogen, calculated from the molecular refractions given in Table 10, are in most cases very close to Vogel's results (*loc. cit.*, p. 1825).

Solvents.—Hexane, *cyclo*hexane, carbon tetrachloride, benzene, and carbon disulphide were purified as previously described (Cowley and Partington, *J.*, 1933, 1252; 1936, 1184). The physical constants of the samples used are given with the individual measurements. Toluene was boiled under reflux with mercuric acetate solution, the yellow precipitate and water were removed, and the liquid washed with water and dried ($CaCl_2$ and finally Na); it was purified by

TABLE 11. *Properties of solutions of amines.*

10^6x_2	ε	d_4^{20}	P_{12}	P_2	10^6x_2	ε	d_4^{20}	P_{12}	P_2
				n-*Propylamine.*					
		In hexane.					In benzene.		
0	1·894	0·6695	29·55	—	0	2·283	0·8778	26·66	—
20,290	1·925	0·6695	30·14	58·6	19,638	2·327	0·8746	27·25	57·1
35,356	1·947	0·6696	30·53	57·3	35,374	2·362	0·8721	27·72	56·9
41,612	1·957	0·6697	30·71	57·5	49,012	2·393	0·8699	28·13	56·8
57,011	1·980	0·6699	31·11	56·9	59,127	2·416	0·8683	28·43	56·6
				Di-n-*propylamine.*					
		In hexane.					In benzene.		
0	1·894	0·6695	29·55	—	0	2·281	0·8779	26·62	—
14,255	1·907	0·6704	29·91	55·2	10,299	2·292	0·8757	26·93	56·7
20,840	1·913	0·6709	30·08	54·9	21,835	2·305	0·8732	27·29	57·1
26,384	1·918	0·6713	30·22	54·8	30,121	2·314	0·8714	27·54	57·1
32,963	1·924	0·6718	30·38	54·7	38,958	2·324	0·8695	27·82	57·3
				Tri-n-*propylamine.*					
				In benzene.					
0	2·283	0·8778	26·66	—	36,224	2·286	0·8679	27·82	58·9
12,565	2·285	0·8742	27·08	60·3	44,785	2·287	0·8657	28·10	58·9
30,463	2·286	0·8695	27·64	59·0					
				n-*Butylamine.*					
		In hexane.					In *cyclo*hexane.		
0	1·895	0·6693	29·58	—	0	2·019	0·7779	27·42	—
19,076	1·924	0·6702	30·19	61·4	14,813	2·045	0·7768	27·93	61·8
38,091	1·954	0·6710	30·80	61·6	29,968	2·072	0·7757	28·45	61·7
60,014	1·988	0·6720	31·48	61·2	35,868	2·083	0·7754	28·66	61·8
77,650	2·015	0·6727	32·00	60·7	48,802	2·107	0·7745	29·09	61·7
				In benzene.					
0	2·282	0·8779	26·64	—	24,838	2·342	0·8737	27·59	64·9
9,588	2·305	0·8763	27·00	64·1	30,436	2·355	0·8728	27·79	64·5
11,738	2·310	0·8760	27·08	64·4	49,102	2·401	0·8697	28·50	64·5
22,481	2·336$_5$	0·8741$_5$	27·50	64·8					

TABLE 11.—*Continued.*

10^6x_2	ε	d_4^{20}	P_{12}	P_2	10^6x_2	ε	d_4^{20}	P_{12}	P_2
				Di-n-*butylamine.*					
		In hexane.					In benzene.		
0	1·897	0·6763	29·33	—	0	2·276	0·8778	26·55	—
10,537	1·908	0·6775	29·71	65·7	10,894	2·288	0·8752	27·00	67·1
20,292	1·918	0·6785	30·06	65·4	22,805	2·300	0·8722	27·48	67·4
31,292	1·929	0·6797	30·45	65·1	31,014	2·310	0·8706	27·82	67·5
42,594	1·941	0·6809	30·86	65·3	38,517	2·318	0·8688	28·13	67·4
				cyclo*Hexylamine.*					
		In hexane.					In benzene.		
0	1·891	0·6695	29·47	—	0	2·280	0·8770	26·63	—
14,355	1·915	0·6720	30·03	68·6	12,101	2·306	0·8767	27·11	65·6
25,869	1·934	0·6740	30·48	68·4	23,661	2·332	0·8765	27·57	66·4
38,794	1·956	0·6762	30·97	68·2	36,209	2·360	0·8763	28·07	66·4
49,886	1·975	0·6782	31·40	68·1	46,486	2·380	0·8761	28·44	65·5
				Benzylamine.					
		In hexane.					In *cyclo*hexane.		
0	1·895	0·6693	29·58	—	0	2·019	0·7779	27·42	—
11,944	1·916	0·6727	30·05	68·9	14,160	2·047	0·7802	28·01	69·0
21,155	1·932	0·6752	30·41	68·6	21,370	2·062	0·7813	28·32	69·4
32,982	1·953	0·6783	30·87	68·7	30,090	2·078	0·7827	28·66	68·6
44,598	1·974	0·6814	31·33	68·8	40,399	2·099	0·7843	29·10	68·9
		In benzene.					In toluene.		
0	2·280	0·8789	26·58	—	0	2·379	0·8643	33·57	—
11,969	2·312	0·8804	27·11	71·3	13,516	2·405	0·8657	34·02	66·4
22,499	2·340	0·8818	27·58	71·0	24,369	2·427	0·8671	34·38	66·8
31,638	2·364	0·8828	27·98	70·9	33,706	2·447	0·8683	34·72	67·5
42,394	2·394	0·8843	28·47	71·1	44,356	2·467	0·8695	35·05	66·9
				Dibenzylamine.					
		In hexane.					In benzene.		
0	1·898	0·6698	29·64	—	0	2·280	0·8775	26·62	—
14,489	1·923	0·6778	30·47	87·1	12,621	2·306	0·8815	27·39	87·3
25,612	1·942	0·6840	31·10	86·7	24,398	2·331	0·8853	28·12	88·2
39,251	1·967	0·6919	31·89	87·1	35,737	2·354	0·8888	28·82	88·1
49,468	1·984	0·6973	32·47	86·9	44,028	2·371	0·8914	29·33	88·1
				Tribenzylamine.					
				In benzene.					
0	2·280	0·8779	26·61	—	24,583	2·321	0·8903	28·59	107·1
8,356	2·294	0·8823	27·28	106·7	31,811	2·333	0·8937	29·18	107·4
16,687	2·308	0·8864	27·94	106·7					
10^6x_2	n_D^{20}	d_4^{20}	$[R_D]_{12}$	$[R_D]_2$	10^6x_2	n_D^{20}	d_4^{20}	$[R_D]_{12}$	$[R_D]_2$
0	1·5009	0·8779	26·21	—	25,922	1·5082	0·8911	$27·94_5$	93·25
8,900	1·5035	0·8824	26·81	93·51	33,361	1·5103	0·8948	$28·45_5$	93·59
16,127	1·5055	0·8861	27·29	93·24	38,773	1·5117	0·8974	28·82	93·49
20,193	1·5066	0·8882	27·56	93·27				$[R_D]_{2\infty}$	93·4
10^6x_2	ε	d_4^{20}	P_{12}	P_2	10^6x_2	ε	d_4	P_{12}	P_2
				Aniline.					
		In carbon tetrachloride.					In carbon disulphide.		
0	2·236	1·5941	28·15	—	0	2·641	1·2639	21·30	—
10,375	2·268	1·5887	28·65	75·8	10,953	2·695	1·2593	21·88	74·5
20,312	2·300	1·5835	29·13	76·2	21,846	2·749	1·2548	22·46	74·3
30,837	2·334	1·5778	29·64	76·3	32,312	2·799	1·2506	22·99	73·6
41,194	2·368	1·5724	30·14	76·4	42,975	2·852	1·2463	23·54	73·5
				In tetralin.					
0	2·757	0·9682	50·43	—	35,990	2·834	0·9693	51·18	71·2
11,513	2·782	0·9686	50·68	72·1	45,918	2·857	0·9696	51·42	71·9
23,054	2·806	0·9689	50·92	71·5					
				Diphenylamine.					
		In hexane.					In benzene.		
0	1·894	0·6695	29·55	—	0	2·280	0·8779	26·61	—
13,028	1·917	0·6763	30·20	79·8	11,632	2·307	0·8824	27·22	79·2
19,451	1·928	0·6796	30·52	79·3	22,214	2·332	0·8864	27·80	80·1
24,608	1·938	0·6825	30·79	79·9	34,819	2·361	0·8912	28·46	80·0
31,324	1·950	0·6860	31·12	79·8	43·696	2·383	0·8945	28·96	80·4

TABLE 11.—*Continued.*

In benzene.

10^6x_2	n_D^{20}	d_4^{20}	$[R_D]_{12}$	$[R_D]_2$	10^6x_2	n_D^{20}	d_4^{20}	$[R_D]_{12}$	$[R_D]_2$
0	1·5002	0·8779	26·18	—	34,374	1·5106	0·8913	27·29	58·44
17,504	1·5055	0·8845	26·74	58·34	39,174	1·5118	0·8930	27·44	58·29
24,203	1·5074	0·8872	26·95	57·99	45,791	1·5136	0·8955	27·64	58·08
31,059	1·5095	0·8900	27·17	57·99				$[R_D]_{2\infty}$	58·2

Triphenylamine.

In benzene.

10^6x_2	ε	d_4^{20}	P_{12}	P_2	10^6x_2	ε	d_4^{20}	P_{12}	P_2
0	2·283	0·8779	26·65	—	28,625	2·333	0·8940	28·53	92·1
10,653	2·302	0·8839	27·35	92·4	29,785	2·335	0·8947	28·60	92·0
21,656	2·320	0·8901	28·05	91·4					

10^6x_2	n_D^{20}	d_4^{20}	$[R_D]_{12}$	$[R_D]_2$	10^6x_2	n_D^{20}	d_4^{20}	$[R_D]_{12}$	$[R_D]_2$
0	1·5009	0·8779	26·21	—	27,936	1·5124	0·8938	27·81	83·65
10,200	1·5052	0·8838	26·79	83·15	35,696	1·5155	0·8977	28·26	83·80
15,173	1·5072	0·8867	27·07	82·89	41,657	1·5180	0·9016	28·51	83·20
20,744	1·5095	0·8897	27·39	83·24				$[R]_{D2\infty}$	83·3

Methylaniline.

10^6x_2	ε	d_4^{2}	P_{12}	P_2	10^6x_2	ε	d_4^{20}	P_{12}	P_2
		In hexane.					In benzene.		
0	1·884	0·6694	29·30	—	0	2·285	0·8771	26·71	—
11,256	1·916	0·6726	30·05	96·1	10,918	2·331	0·8786	27·43	92·8
23,588	1·951	0·6760	30·86	95·4	20,947	2·373	0·8799	28·09	92·5
34,817	1·983	0·6791	31·58	94·8	30,680	2·414	0·8815	28·71	91·8
45,327	2·013	0·6820	32·24	94·3	41,766	2·461	0·8830	29·42	91·6

Dimethylaniline.

10^6x_2	ε	d_4^{2}	P_{12}	P_2	10^6x_2	ε	d_4^{20}	P_{12}	P_2
		In hexane.					In benzene.		
0	1·884	0·6694	29·30	—	0	2·280	0·8788	26·58	—
10,764	1·911	0·6725	29·98	92·5	10,457	2·320	0·8800	27·28	93·1
18,889	1·932	0·6749	30·50	92·7	21,653	2·362	0·8812	28·01	92·5
29,121	1·958	0·6779	31·13	92·2	30,329	2·395	0·8822	28·57	92·3
38,109	1·982	0·6807	31·70	92·4	40,418	2·432	0·8832	29·21	91·7

Ethylaniline.

In hexane.

10^6x_2	ε	d_4^{2}	P_{12}	P_2	10^6x_2	ε	d_4^{20}	P_{12}	P_2
0	1·884	0·6694	29·30	—	31,829	1·975	0·6787	31·54	99·8
11,151	1·915	0·6727	30·09	100·1	41,780	2·004	0·6814	32·24	99·8
20,752	1·943	0·6755	30·76	99·9					

Diethylaniline.

10^6x_2	ε	d_4^{2}	P_{12}	P_2	10^6x_2	ε	d_4^{20}	P_{12}	P_2
		In hexane.					In benzene.		
0	1·895	0·6713	29·49	—	0	2·276	0·8787	26·53	—
11,215	1·932	0·6751	30·51	119·7	10,248	2·327	0·8796	27·48	119·9
20,519	1·964	0·6784	31·35	120·1	20,933	2·380	0·8807	28·48	119·7
29,604	1·994	0·6814	32·16	119·4	30,117	2·426	0·8815	29·33	119·5
41,635	2·033	0·6855	33·18	118·0	39,342	2·472	0·8824	30·18	119·4

n-*Propylaniline.*

10^6x_2	ε	d_4^{2}	P_{12}	P_2	10^6x_2	ε	d_4^{20}	P_{12}	P_2
		In hexane.					In benzene.		
0	1·885	0·6694	29·32	—	0	2·285	0·8776	26·69	—
10,132	1·914	0·6727	30·09	104·7	11,285	2·333	0·8790	27·56	103·9
19,195	1·940	0·6756	30·76	104·4	22,132	2·379	0·8805	28·39	103·5
29,943	1·972	0·6790	31·58	104·9	26,563	2·399	0·8808	28·75	104·3
40,568	2·004	0·6822	32·40	105·1	34,561	2·432	0·8818	29·34	103·4
					43,419	2·470	0·8831	30·01	103·1

*Ethyl-*n*-propylaniline.*

10^6x_2	ε	d_4^{2}	P_{12}	P_2	10^6x_2	ε	d_4^{20}	P_{12}	P_2
		In hexane.					In benzene.		
0	1·895	0·6713	29·49	—	0	2·284	0·8779	26·67	—
11,190	1·932	0·6755	30·54	123·0	14,572	2·356	0·8791	28·10	124·7
22,552	1·971	0·6799	31·61	123·5	24,313	2·404	0·8799	29·05	124·5
33,566	2·006	0·6835	32·60	122·1	29,969	2·432	0·8804	29·60	124·5
43,256	2·039	0·6870	33·51	122·3	40,622	2·483	0·8814	30·61	123·8

several fractionations. Tetralin was purified by drying ($CaCl_2$) and repeated fractionation under reduced pressure : b. p. 69·5—71·5°/1 mm., d_4^{20} 0·9682, ε at 20° 2·757. Govinda Rau and Satyanarayana Rao (*Proc. Indian Acad. Sci.*, 1935, *A*, **2**, 232) give d_4^{20} 0·9679, ε at 20° 2·756.

Results.—The molar polarisations of the solvent, solution, and solute are expressed by P_1, P_{12}, and P_2, respectively. The mole-fraction x_2 of the solute and the dielectric constant and density of the solution are given and all results refer to 20·0°. The extrapolated value of the polarisation of the solute at infinite dilution, $P_{2\infty}$, is given in Table 1 with the dipole moment. In the majority of the measurements recorded in Table 11, the change of P_2 with concentration is small and the uncertainty in the extrapolation should not be greater than a few tenths of a c.c.

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