

588. *Molecular Polarisation and Molecular Interaction. Part III. The Use of Dielectric Polarisation Measurements in studying the Extent of Molecular Interaction in Solution. The System Aniline-Dioxan-Benzene.*

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On the assumption that when two molecular species A and B associate in solution to give a complex AB the active masses can be represented by the molar concentrations, an equation has been derived relating the equilibrium constant (K) of the association process and the molecular polarisation (P_{AB}) of the complex with the apparent increase in the molecular polarisation of A at infinite dilution. This relation permits the values of K and of P_{AB} to be deduced from measurements of the molecular polarisation of A in various mixtures of B with an inert solvent. The method has been applied to data derived from measurements on dilute solutions of aniline in mixtures of dioxan with benzene, and leads to the inference that the dipole moment of the complex formed between aniline and dioxan is about 1.88 D., whilst at infinite dilution in pure dioxan about 65% of the aniline is in the form of complex.

DIELECTRIC polarisation measurements have long presented a potential means not only for detecting the formation of intermolecular complexes in the liquid state but also for determining the extent to which such complexes are formed. Earp and Glasstone (*J.*, 1935, 1709) considered the case of a mixture of compounds A and B which can yield an additive compound AB in which a definite linkage is formed. They supposed that the extrapolated value of the molecular polarisation of A at infinite dilution in B ($P_{A\infty}$), calculated on the assumption that the molecular polarisation of B (P_B) remains constant, gives the contribution of A and of the new linkage in the compound, and hence that the molecular polarisation of the compound is given by $P_{A\infty} + P_B$. From this value, combined with a knowledge of the value (P_A) of the molecular polarisation of A in solutions of equal dielectric constant in solvents in which no compound is formed, they interpreted the molecular polarisation of solutions containing finite concentrations of A in B in terms of the relation

$$P = P_A(f_A - x)/(1 - x) + P_B(f_B - x)/(1 - x) + P_{AB}x/(1 - x) \quad . \quad . \quad . \quad (1)$$

where f_A and f_B are the molar fractions of the initial components A and B, respectively, and x denotes the amounts of these which pass into the form of compound. This equation permits the calculation of x , which in turn allows the derivation of a mass-action constant $K = x(1 - x)/(f_A - x)(f_B - x)$ wherein the activities are expressed by the molar fractions.

This approach was criticised by Hammick, Norris, and Sutton (*J.*, 1939, 1755) on the grounds that unless K is infinite, all the A is not in the form of AB at infinite dilution. Further, they pointed out that in the calculation of P the mean molecular weight of the solution was taken by Earp and Glasstone as $M_A f_A + M_B f_B$, whereas its true value is $(M_A f_A + M_B f_B)/(1 - x)$, so that equation (1) should be written

$$P = P_A(f_A - x) + P_B(f_B - x) + P_{AB}x \quad \dots \quad (2)$$

Finally they also questioned the applicability of the mass-action law over the full composition range of binary mixtures.

Hammick, Norris, and Sutton tested various alternative methods for the solution of this problem, but reached the conclusion that the only dielectric-constant method which produced significant results involved measurements on dilute solutions of the two components in a third, unreactive, solvent. If the two reactive components were present in a constant proportion, the values of the molecular polarisation of the solution compared with those expected if no compound were formed (corrected for the variation of the molecular polarisations with the dielectric constant of the medium) were found to increase linearly with increasing concentration. They deduced that, if R is the difference between the observed and the theoretical value of the molecular polarisation of the mixture then

$$R = (P_{AB} - P_A - P_B)x/(f_A + f_B) \quad \dots \quad (3)$$

Hence either P_{AB} or x could be evaluated if the other were known, whereas, if neither was known, the function $(P_{AB} - P_A - P_B)x$ could be used to give comparative data.

It was found that this function was large for mixtures of chloroform and triethylamine, noticeable for chloroform and diisopropyl ether, and within experimental error for chloroform and nitromethane. As this was in accord with the known behaviours of tertiary amines, ethers, and nitro-compounds, respectively, as electron-donors in hydrogen-bond formation, it supported this general approach to the problem. The limitations of the method were well appreciated by the authors, but the method depends on the determination of the difference between the molecular-polarisation values for solutions of a mixture of A and B and of A and B separately in an inert solvent at finite concentrations of all three components. As the molecular polarisation of a polar solute decreases with increasing concentration in a manner which so far cannot be calculated on any theoretical basis, the results must be regarded as approximate and only comparative for various systems. Also, whilst the method gives an indication of molecular interaction, the extent to which the latter occurs cannot be deduced by this means.

A more promising approach seems to be the "Method 4" discussed by Hammick, Norris, and Sutton. This involves the determination of the apparent molecular polarisation at infinite dilution of a compound A in an active solvent B, in an inert solvent S, and in mixtures of B and S in constant proportion. This method was rejected by them on account of the results obtained with the system diisopropyl ether-chloroform-benzene, which led to different results according to whether the ether or the chloroform was considered as the solvent at low concentration. These grounds seem rather inadequate, as this system covers a wide range of dielectric constants, and examination of their experimental data shows that there was a considerable possible error in the values used for the molecular polarisation.

Such a system may, however, be treated as follows. If the weight fractions of A, B, and S in a solution are w_A , w_B , and w_S , respectively, and amounts Δw_A and Δw_B of A and B, respectively, pass into the form of a compound AB, then the total specific polarisation of the solution is given by $p = p_A(w_A - \Delta w_A) + p_B(w_B - \Delta w_B) + p_{AB}(\Delta w_A + \Delta w_B) + p_S w_S$ where p_A , p_B , p_{AB} , and p_S are the specific polarisations of A, B, the compound, and S, respectively. The apparent specific polarisation of A (p_A^*), calculated on the assumption of no compound formation, is given by $w_A p_A^* = p - w_B p_B - w_S p_S$, and hence $w_A(p_A^* - p_A) = p_{AB}(\Delta w_A + \Delta w_B) - \Delta w_B p_B - \Delta w_A p_A$. On introducing the relation $\Delta w_A/\Delta w_B = M_A/M_B$, where M_A and M_B are the molecular weights of A and B, respectively, we obtain the expression

$$P_A^* - P_A = \Delta P(\Delta w_A/w_A) \quad \dots \quad (4)$$

where $\Delta P = P_{AB} - P_A - P_B$, *i.e.*, the increase in molecular polarisation attending the formation of 1 g.-mol. of AB.

This expression is similar in form to equation (3) derived by Hammick, Norris, and Sutton, but with the increment in polarisation referred to the apparent increase of P_A instead of to the increase of P above the theoretical value. The equation should hold generally whether any inert third component is present or not, and, since for any particular system ΔP is constant,

the value of $P_A^* - P_A$ will be proportional to the fraction of the B present which passes into the form of compound.

Further, if the active masses of the reactants can be expressed by their concentrations in g.-mol. per c.c., then by the law of mass action it follows that $K = c_{AB}/c_A c_B = \Delta w_A/c_B(w_A - \Delta w_A)$, or

$$w_A/\Delta w_A = 1 + 1/Kc_B \quad \dots \quad (5)$$

But, from equation (4), $w_A/\Delta w_A = \Delta P/(P_A^* - P_A)$, and, as $c_B = w_B d/M_B$, where d is the density of the solution, therefore

$$\Delta P/(P_A^* - P_A) = M_B/Kw_B d + 1 \quad \dots \quad (6)$$

At infinite dilution of A in B or in mixtures of B and S in constant proportions, w_B is the actual weight fraction of B in the solvent mixture used, and hence the validity of the assumptions made can be tested by studying the apparent molecular polarisation of A in such solutions and deriving the values at infinite dilution in each case. From equation (6) a plot of $1/(P_A^* - P_A)$ against $1/w_B d$ should be linear, with a slope $M_B/K\Delta P$ and an intercept on the y axis equal to $1/\Delta P$.

Since the molecular polarisation of aniline varies only slightly with the dielectric constant of the medium, it appeared to be a suitable solute to study from this point of view, particularly as it shows abnormally high molecular polarisation, attributable to hydrogen bonding, in dioxan, a solvent the dielectric constant of which differs only a little from that of benzene (Few and Smith, this vol., p. 753). The apparent molecular polarisation of aniline in three constant-ratio mixtures of benzene and dioxan has therefore been studied, and the values at infinite dilution derived. The results are summarised in Table I, together with the figures for solutions of aniline in benzene and in dioxan recorded previously (*loc. cit.*). The symbols have the same significance as in the previous communications. As is to be expected the value of $P_{2\infty}$ increases progressively with increasing concentration of dioxan.

TABLE I.
Polarisation Data for Aniline in Benzene-Dioxan Mixtures.

Dioxan in solvent (wt.-%).	α .	α' .	β .	$P_{2\infty}$ (c.c.).	$[R_B]$ (c.c.).	P_μ (c.c.).	μ (D.).
0.00	2.933	1.77	-0.1720	78.35	30.7	46.12	1.505
9.07	3.122	1.36	-0.1604	80.79	30.9	48.35	1.540
15.52	3.244	1.12	-0.1517	82.32	30.9	48.85	1.563
49.21	3.780	0.73	-0.0982	88.28	30.9	55.78	1.655
100.00	4.520	0.32	-0.0127	95.11	30.9	62.64	1.750

TABLE II.

$w_B \times 100$.	d .	$1/w_B d$.	$1/(P_{A\infty}^* - P_{A\infty})$.	$P_{A\infty}^*$ (corr.).	$1/(P_{A\infty}^* - P_{A\infty})$ (corr.).
9.07	0.8823	12.49	0.410	80.76	0.415
15.52	0.8951	7.20	0.252	82.26	0.255
49.21	0.9442	2.152	0.101	87.96	0.104
100.00	1.0280	0.973	0.060	94.07	0.063

Table II shows the values of $1/w_B d$ and $1/(P_{A\infty}^* - P_{A\infty})$, where $P_{A\infty}$ is taken as the $P_{2\infty}$ value for benzene solution, and $P_{A\infty}^*$ as the corresponding value for solutions in the dioxan-containing solvent. The linearity of the plot of $1/w_B d$ against $1/(P_{A\infty}^* - P_{A\infty})$ supported the assumptions made in the derivation of equation (6). From the intercept of the best straight line through these points, derived by the method of least squares, the value of ΔP is 28.6 c.c., and thence from the slope (0.0301) K is 128.

However the apparent molecular polarisation of aniline in dioxan solution decreases fairly rapidly with increasing concentration, *i.e.*, with increasing dielectric constant of the medium (Part I), and in the present work it has been found that the rate of decrease in the mixed solvents, although less than in pure dioxan, is much greater than in benzene itself. That this rate of decrease is much greater than can be accounted for by the decrease in the proportion of aniline which passes into the form of complex, and hence that it is attributable to a large solvent effect, is shown by the following argument. On the assumption that the mass action law holds, $P_A^* - P_A$ should be proportional to the fraction of the aniline introduced which passes into the form of complex, *i.e.*, to $\Delta w_2/w_2$ (equation 4). For infinite dilution in pure dioxan this is $16.76/28.6 = 0.582$. Now equation (5) can be written $w_A/\Delta w_A = 1 + M_B/w_B d K$. For a solution of aniline in dioxan in which the weight fraction of aniline is 0.11089, $w_B = 0.88911$,

$d = 1.0292$ (Part I, Table II), and hence, on the assumption that $K = 128$ and $M_B = 88.1$, $\Delta w_A/w_A = 0.571$. This leads to a theoretical value of 16.44 for $P_A^* - P_A$ at this concentration, whereas the observed value was 9.81 as compared with benzene solution at infinite dilution or 11.66 relative to the molecular polarisation of aniline in benzene solution at the same dielectric constant.

As the decrease of molecular polarisation with increasing concentration must be due principally to the solvent effect, and only subsidiarily to the decrease in the degree of association, an approximate correction for the solvent effect has been made by interpolating the values of P_A^* in each solvent at a dielectric constant equal to that of benzene. This led to the modified values, $P_{A\infty}^*$ (corr.), shown in the fifth column of Table II. Using these "corrected" values, the plot of $1/w_B d$ against $1/(P_{A\infty}^* - P_{A\infty})$ leads to $\Delta P = 25.6$ and $K = 116$.

Whilst this treatment can be regarded as only approximate, if $\Delta P = 25.6$ c.c. the orientation polarisation of the complex is 71.6 c.c. and its dipole moment 1.88 D. This increase as compared with the moment of aniline in benzene seems reasonable if it is due to an increase in the mesomeric moment of aniline caused by the proton displacement towards the dioxan molecule and by a shift of the electrons in the dioxan molecule. This result leads to the inference that at infinite dilution of aniline in pure dioxan about 65% of the aniline is in the form of the complex.

EXPERIMENTAL.

The materials were purified by the methods described in Part I, and the same procedures were used for the determination of the dielectric constants, specific volumes, and refractive indices, and for the derivation of the values of $P_{2\infty}$ and μ . The benzene-dioxan mixtures were made up in batches by weight, and each group of aniline solutions was prepared from the same batch of solvent mixture.

The results are recorded in Table III, where the symbols have the same significance as previously.

TABLE III.
Polarisation Data for Solutions of Aniline in Benzene-Dioxan Mixtures.

$100w_2$	ϵ_{12}	v_{12}	p_{12}	P_2	n_D	r_{12}	$[R_D]$	$\Delta\epsilon/w_2$	$\Delta v/w_2$
9.074 wt.-% dioxan.									
0.0000	2.2689	1.12831	0.33538	—	1.4920	0.32733	—	—	—
1.0641	2.3024	1.12661	0.34104	80.77	1.4929	0.32738	30.94	3.15	-0.160
1.5949	2.3190	1.12577	0.34380	80.40	1.4935	0.32745	31.18	3.14	-0.159
2.3401	2.3427	1.12456	0.34769	80.22	1.4941	0.32746	30.99	3.154	-0.160
3.7367	2.3875	1.12233	0.35492	79.93	1.4953	0.32749	30.88	3.174	-0.160
5.4726	2.4436	1.11957	0.36372	79.46	1.4969	0.32753	30.82	3.192	-0.1597
6.3068	2.4713	1.11826	0.36797	79.35	1.4977	0.32763	30.93	3.209	-0.1594
7.5222	2.5114	1.11620	0.37395	78.98	1.4987	0.32756	30.79	3.237	-0.1610
10.1202	2.5988	1.11221	0.38667	78.43	1.5013	0.32783	30.94	3.260	-0.1591
15.524 wt.-% dioxan.									
0.0000	2.2658	1.11717	0.33150	—	1.4877	0.32170	—	—	—
1.1133	2.3020	1.11549	0.33760	81.90	1.4889	0.32191	31.71	3.25	-0.151
1.6537	2.3198	1.11467	0.34056	81.89	1.4895	0.32199	31.59	3.26	-0.151
2.4258	2.3453	1.11349	0.34470	81.54	1.4902	0.32204	31.26	3.28	-0.152
3.3157	2.3746	1.11217	0.34947	81.34	1.4909	0.32205	30.95	3.281	-0.151
5.2919	2.4405	1.10918	0.35982	80.71	1.4928	0.32223	30.89	3.301	-0.1510
5.9930	2.4642	1.10817	0.36347	80.55	1.4936	0.32239	31.03	3.311	-0.1502
7.3878	2.5116	1.10606	0.37058	80.13	1.4948	0.32244	30.89	3.327	-0.1504
8.2259	2.5403	1.10485	0.37485	79.95	1.4955	0.32248	30.83	3.339	-0.1498
49.211 wt.-% dioxan.									
0.0000	2.2474	1.05909	0.31104	—	1.4629	0.29167	—	—	—
1.6643	2.3105	1.05745	0.32149	87.44	1.4652	0.29246	31.58	3.79	-0.098
2.4221	2.3396	1.05669	0.32619	87.21	1.4661	0.29271	31.16	3.81	-0.099
3.3692	2.3757	1.05580	0.33194	86.73	1.4672	0.29305	30.88	3.81	-0.0976
4.5705	2.4219	1.05460	0.33912	86.18	1.4686	0.29351	30.90	3.818	-0.0982
5.8568	2.4716	1.05334	0.34665	85.59	1.4703	0.29403	30.92	3.828	-0.0982
7.4558	2.5343	1.05179	0.35590	85.00	1.4722	0.29463	30.86	3.848	-0.0979
8.2950	2.5667	1.05094	0.36055	84.55	1.4734	0.29506	30.98	3.849	-0.0982
9.7794	2.6241	1.04949	0.36861	83.79	1.4754	0.29570	31.00	3.852	-0.0982

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