135. *The Electrical Polarisation of Concentrated Solutions of Nitrobenzene, with Special Reference to the Validity of the Sugden Relation.*

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THE electrical polarisations of nitrobenzene solutions are of interest for several reasons. Davy and Sidgwick (J., 1933, 282) showed that, for benzene solutions of nitrobenzene, degrees of association calculated from cryoscopic measurements are in approximate agreement with those obtained from electrical polarisations. However, marked disagreement results for *cyclo*hexane solutions of nitrobenzene, if it is assumed that the polarisation–concentration curve is of normal type, since abnormally high degrees of association are obtained from the freezing-point measurements. The form of the polarisation–concentration curve has therefore been determined and compared with those in other solvents.

Curves in benzene, carbon disulphide, *n*-hexane, and carbon tetrachloride have been studied in addition, in order to test the empirical relation formulated by Sugden (*Nature*, 1934, **133**, 415) and used by Fairbrother (*ibid.*, **134**, 458; J., 1934, 1946) and, in a different form, by Goss (*ibid.*, pp. 698, 1467) to determine electrical dipole moments.

EXPERIMENTAL.

The methods of preparation of pure materials, and of measuring dielectric constants and densities, were essentially the same as those previously described (Sutton, *Proc. Roy. Soc.*, 1931, *A*, **133**, 668; Jenkins, J., 1934, 480), except that a single solution condenser was used. This condenser is made of metal so far as possible (of brass, plated with platinum) and is designed so that it can easily be taken apart for cleaning but can be accurately re-assembled. The earthed electrode consists of a cylindrical jacket A (see Fig. 1), closed at the bottom, and a lid B, which is located uniquely by a pin in A and is held down by six screws. The lid carries a short piece of quartz C affixed coaxially with it into an annular channel D by means of solder (3 parts lead, 1 part tin). This tube carries and insulates a metal head E, affixed to it by solder, into which fits a stiff rod F which is located uniquely by a steady pin H and is pulled up tightly to the head E by a milled nut I, which in turn is locked by another one J that is also a terminal. The rod passes down through a hole in the lid and supports a cylinder G inside the earthed jacket;

the bottom of the insulated cylinder is a flat cone, so that no air bubbles may be entrapped. In order that as few lines of force as possible may pass through two media when solutions are in the cell, an attempt has been made to make the lines of force near the liquid surface (which is about 1 cm. below the lower side of the lid) run along radii of the cylindrical jacket, by having only a small clearance between the upper edge of the insulated cylinder and the jacket, and by cutting a depression in the top face of the cylinder. The air capacity is about 25 $\mu\mu$F. The condenser is made to take an interchangeable set of electrodes; the plug K can be replaced by a solid cylinder, and the solid cylinder G by a larger hollow one, so that the air capacity is approximately doubled.

FIG. 1.

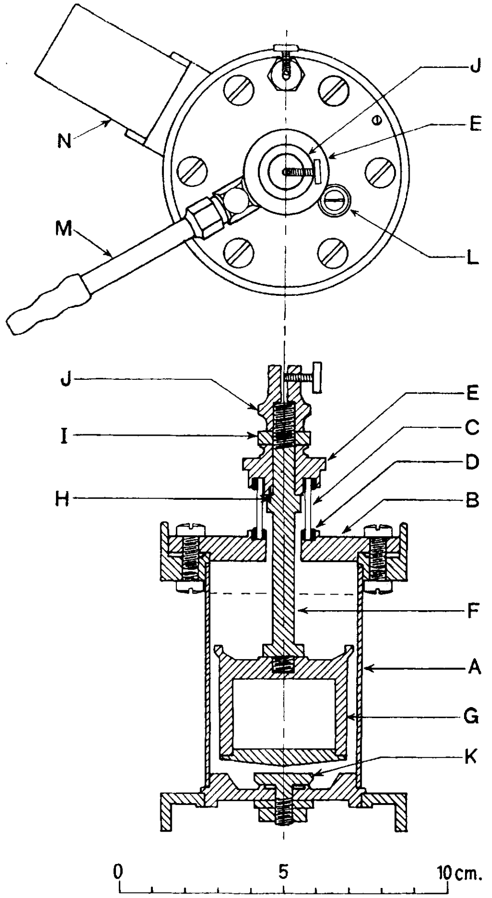
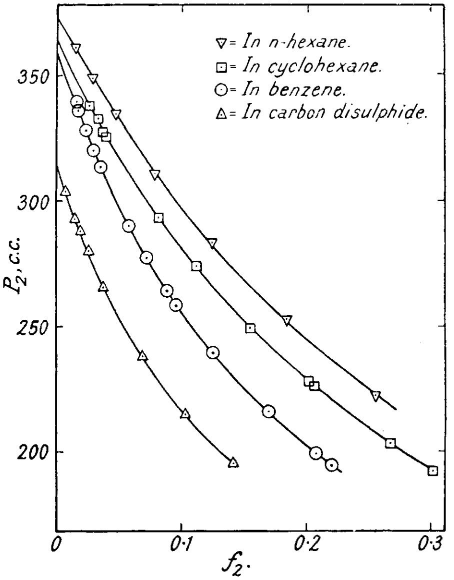


FIG. 2.



The condenser is filled through a hole in the lid, which can be closed with the screw plug L, with rather more solution than is required, and the excess above a certain level is then withdrawn by a special pipette, so that a definite volume of solution is left in the condenser. In order to prevent the ingress of moisture, a small positive pressure of dry air is maintained inside the condenser through the lead-in tube M; the efficacy of this method was shown on several occasions by the fact that the dielectric constant of carefully dried benzene, which is very hygroscopic, remained constant for several hours. The condenser is held in a thermostat by means of a tongue N which fits into a holder.

That the condenser is satisfactory was shown by the following facts : (*a*) reasonable concordance was obtained with Lange's results (*Z. Physik*, **1925**, **33**, 169) in benzene and carbon disulphide solutions, corrected to 25°; (*b*) the polarisations in the more dilute regions of these concentrated solution runs are consistent with the results in dilute solution previously obtained (Jenkins, *loc. cit.*) by using a different condenser; (*c*) the value found for the dielectric constant of chlorobenzene, a substance easily obtained pure, was 5·611, which is almost identical with that, 5·612, found by Sugden (J., **1933**, 768), using a resonance apparatus and a condenser of different air capacity and type; (*d*) the value found for the dielectric constant of chloroform was 4·727, while that found by Ball (J., **1930**, 596) was 4·724.

All the measurements were made at 25·0°. The results are given in the following tables where f_2 is the molecular fraction of nitrobenzene, ε_{25° the dielectric constant at 25·0°, $d_{4^\circ}^{25^\circ}$ the density, and $_{\mathrm{T}}P_2$ the total polarisation of the solute.

TABLE I.

f_2.	ϵ_{25°.	$d_{4^\circ}^{25^\circ}$.	$_{\mathrm{T}}P_2$.
	Nitrobenzene in benzene.		
0·0000	2·273	0·8736	—
0·0575	3·597	0·8954	289·9
0·0715	3·928	0·9008	277·4
0·0880	4·326	0·9068	264·2
0·0950	4·490	0·9092	258·8
0·1244	5·224	0·9202	239·8
0·1695	6·372	0·9365	215·8
0·2078	7·373	0·9502	199·4
0·2202	7·704	0·9545	194·8
	Nitrobenzene in cyclo*hexane.*		
0·0000	2·016	0·7739	—
0·0323	2·573	0·7860	332·7
0·0814	3·489	0·8053	293·3
0·1117	4·100	0·8171	273·8
0·1545	5·014	0·8343	249·7
0·2021	6·131	0·8534	228·0
0·2067	6·236	0·8554	225·8
0·2677	7·777	0·8798	203·0
0·3018	8·707	0·8942	192·0

f_2.	ϵ_{25°.	$d_{4^\circ}^{25^\circ}$.	$_{\mathrm{T}}P_2$.
	Nitrobenzene in carbon disulphide.		
0·0000	2·633	1·2558	—
0·0375	3·888	1·2508	266·0
0·0690	4·986	1·2468	238·0
0·1034	6·218	1·2426	214·9
0·1411	7·579	1·2378	195·3
	Nitrobenzene in n-*hexane.*		
0·0000	1·887	0·6615	—
0·0783	3·043	0·6974	310·6
0·1236	3·810	0·7181	283·5
0·1842	4·940	0·7458	252·5
0·2559	6·461	0·7800	222·6
	Nitrobenzene in carbon tetrachloride.		
0·0000	2·228	1·5848	—
0·0848	4·066	1·5522	276·4
0·1612	5·814	1·5229	226·9
0·2053	7·114	1·5061	210·9
0·2295	7·771	1·4968	201·4

DISCUSSION OF RESULTS.

The P_2–f_2 curves for nitrobenzene in the four solvents *n*-hexane, *cyclo*hexane, benzene, and carbon disulphide, of dielectric constants 1·887, 2·016, 2·273, and 2·633, are given in Fig. 2: values of $_{\infty}P_2$ and P_2 in dilute solution have been taken from a previous paper (Jenkins, *loc. cit.*). It is seen that the curves are displaced from one another in the order of the dielectric constant of the solvent, and also that the *cyclo*hexane curve is perfectly normal, which indicates that in this case there is no close relation between degrees of association calculated by the two methods.

Sugden has reported (*Nature*, 1934, **133**, 415; *Trans. Faraday Soc.*, 1934, **30**, 720) an empirical relation between the total polarisation of the solute ($_{\mathrm{T}}P_2$) at any concentration, and the volume polarisability, $(\varepsilon - 1)/(\varepsilon + 2)$, of the solution. It is

$$_{\mathrm{T}}P_2 = \alpha + {}^{\mathrm{G}}_{\mathrm{T}}P_2 - {}^{\mathrm{G}}_{\mathrm{O}}P_2\{(\varepsilon - 1)/(\varepsilon + 2)\}$$

where α is a small constant, ${}^{\mathrm{G}}_{\mathrm{T}}P_2$ is the total polarisation deduced from vapour measurements (Sugden uses $_{\mathrm{H}}P_2$), and ${}^{\mathrm{G}}_{\mathrm{O}}P_2$ is the orientation polarisation obtained from the same source.

In order to test the validity of this equation, answers to four questions have to be sought. (*a*) Is the equation of the right form for a solute in one particular solvent at one temperature? (*b*) Is the arbitrary constant α independent of solute, solvent, and temperature? (*c*) Is the slope of the $_{\mathrm{T}}P_2$–$(\varepsilon - 1)/(\varepsilon + 2)$ line, for one solute at one temperature, independent of the solvent? (*d*) Is this slope equal to $- {}^{\mathrm{G}}_{\mathrm{O}}P_2$?

(*a*) Fig. 3 shows such total polarisation–volume polarisation curves for nitrobenzene in different solvents, for concentrations ranging from infinite dilution to pure nitrobenzene: for the sake of clearness, the origin of ordinates has been displaced regularly for each solvent. The dielectric constant of pure nitrobenzene has been taken from Ball (*loc. cit.*) and Sugden (*loc. cit.*), and the density calculated from an equation given by Tyrer (J., 1914, **105**, 2544). It is seen that the benzene curve is almost perfectly straight over the entire range of concentration, but that the other solvents all give a curvature over the range as a whole as indicated by the broken lines. Such curvature has already been found for nitrobenzene in decane (di*iso*amyl) and *p*-xylene by Fairbrother (*loc. cit.*), and it is therefore quite clear that for this particular solute, in most non-polar solvents, the Sugden equation is approximately, but not exactly, of the right form.

(*b*) In answer to the second question, if the slight curvature noted above be ignored, and mean straight lines be drawn through the concentrated solution points for each solvent, then it is found that the intercepts on the ${}_{\rm T}P_2$ axis when $(\varepsilon - 1)/(\varepsilon + 2) = 0$ (*i.e.*, when $\varepsilon = 1$) are different, and therefore, if they are put equal to $\alpha + {}^{\rm G}_{\rm T}P_2$, that α varies with the solvent. Alternatively, since the intercepts at $(\varepsilon - 1)/(\varepsilon + 2) = 1$ (*i.e.*, $\varepsilon = \infty$) are also found to vary, and since these should be the sum of α and the atom and the electron polarisation, then again α is found to vary. These intercepts are given in Table II, which includes some results obtained by Lange (*loc. cit.*) for solutions in toluene. Furthermore, the value of α determined from the lower intercept for chlorobenzene in benzene solution, using the data of Rolinski (*Physikal. Z.*, 1928, **29**, 660), is not more than 1 c.c., whereas for nitrobenzene it is of the order of 30 c.c., for quinoline in benzene it is 18 c.c., for benzonitrile in benzene it is about 13 c.c., and for ethyl ether in benzene it is 28 c.c. That α depends upon both the solvent and the solute is thus clear.

FIG. 3.

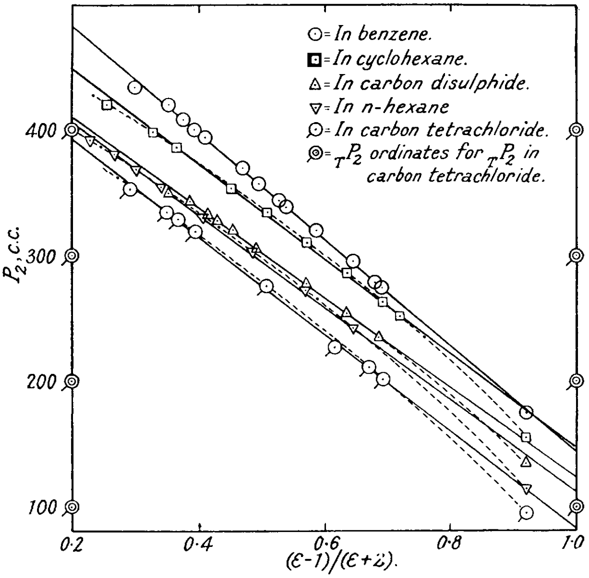


TABLE II.

Nitrobenzene in different solvents.

Solvent.	Intercept at $(\epsilon - 1)/(\epsilon + 2) = 0$.	Intercept at $(\epsilon - 1)/(\epsilon + 2) = 1$.	Slope.
Benzene	489	64	−425
Carbon tetrachloride	472	82	−390
Carbon disulphide	445	81	−364
n-Hexane	459	94	−365
*cyclo*Hexane	467	86	−381
Toluene	483	64	−419

The third part of the second question, regarding the temperature independence of α, has already been answered by Fairbrother, who found that for nitrobenzene in decane the intercepts at $(\varepsilon - 1)/(\varepsilon + 2) = 1$ appeared to be equal to within the limits of experimental error, but that if the intercepts at $(\varepsilon - 1)/(\varepsilon + 2) = 0$ have the significance attributed to them by the equation, then α must decrease with increasing temperature, because the moment calculated from the variation of the intercepts with temperature is abnormally high (see p. **614**).

(*c*) An answer to the third question can be obtained from Fig. 3, which shows that the slopes differ appreciably for nitrobenzene in different solvents at the same temperature. It appears that the benzenoid solvents, or the non-benzenoid solvents, are fairly consistent among themselves, but differ appreciably from each other in their effects upon the slope. The mean slopes are given in Table II, the variation being ± 7% of the average slope.

(*d*) The results given in Table II are relevant also to the fourth question. Since the gas orientation polarisation for nitrobenzene at 25·0° is 367 c.c. (calculated from the results of Groves and Sugden, J., 1934, 1094, and McAlpine and Smyth, *J. Chem. Physics*, 1935, **3**, 55), it is obvious that those for nitrobenzene in the non-benzenoid solvents at 25·0° confirm the conclusion of previous workers, that the slope multiplied by minus one is indeed very close to the gas polarisation : the slopes in the benzenoid solvents, on the other hand, are about 14% too great. In order to test this more generally, further data were collected from the literature, and a representative selection is given in Table III. The selection was made with several requirements in mind. One was that the solutes should be of as many different types as possible, another that in some cases the same solutes should be taken in different solvents, and a third that the gas orientation polarisation should have been determined experimentally in most cases. Some solutes are included, however, which are so polar that there is very little hope of determining the moments from the vapour, so that it is very interesting to see how likely a value is obtained from the Sugden relation. In Table III, col. 1 gives the solute, col. 2 the solvent, and col. 3 the temperature at which the polarisations were measured. Col. 4 gives the slope, multiplied by minus one, of the approximate straight line given by the Sugden relation, and col. 5 the orientation polarisation as calculated from the best values available for the dipole moment, the values determined in the vapour phase being taken when possible (these are marked with a subscript $_{G}$) ; col. 6 gives the ratio of the slope of the Sugden relation to the experimentally determined orientation polarisation value, and col. 7 the square root of this ratio, which is the ratio of the moments which would be obtained by using the two ways of calculating the orientation polarisation. The data were obtained from papers which are referred to in " A Table of Dipole Moments " (*Trans. Faraday Soc.*, 1934, **30**, Appendix).

Solute.	Solvent.	Temp.	−Slope.	$_{O}P_2$.	$-\frac{\text{Slope}}{_{O}P_2}$.	$\sqrt{-\frac{\text{Slope}}{_{O}P_2}}$.
Et_2O	C_6H_6	18°	9·2	$28{\cdot}0_G$	0·328	0·5727
	CCl_4	25	23·2	$27{\cdot}4_G$	0·847	0·9203
$CH_3{\cdot}CO_2Et$	C_6H_6	25	133	$64{\cdot}1_G$	2·075	1·4404
	CCl_4	25	98·4	$64{\cdot}1_G$	1·535	1·2389
$CHCl_3$	CCl_4	25	20·8	$20{\cdot}7_G$	1·005	1·0025
$COMe_2$	C_6H_6	22	170	$169{\cdot}8_G$	1·001	1·0005
	CCl_4	25	217	$168{\cdot}1_G$	1·291	1·1362
C_9H_7N	C_6H_6	18	115	100·7	1·142	1·0686
$SbCl_3$	C_6H_6	25	1115	322	3·463	1·8609
	CS_2	25	2240	322	6·956	2·6375
o-$NO_2{\cdot}C_6H_4{\cdot}CN$	C_6H_6	25	1160	790	1·468	1·2116
m- ,,	C_6H_6	25	360	296	1·216	1·1027
$NO{\cdot}C_6H_4{\cdot}NMe_2$	C_6H_6	25	1867	985	1·895	1·3766

From the preceding results it must be concluded that, although some solutes in particular solvents obey the Sugden relation very well, yet other solutes which are quite as normal, or the same solutes in equally normal solvents, fail to do so. Usually the slope is too great, but in one case it is much too small; furthermore, although benzene gives more anomalous results for some solutes than does carbon tetrachloride, the reverse is true in other cases. Hence it seems impossible to formulate any general rules about the discrepancies. Since from the empirical rules of both Müller (*Physikal. Z.*, 1933, **34**, 689) and Jenkins (*Nature*, 1934, **133**, 106) it is unlikely that the true orientation polarisation would be more than 20% greater than the value observed in benzene or carbon tetrachloride, it follows that neither *o*-nitrobenzonitrile nor *p*-nitrosodimethylaniline obeys the Sugden relation, the slopes being too great. The most marked anomalies are for antimony trichloride, and since these are so great, they may indicate some unusual solvation effects.

The general conclusions from all these tests may be briefly summarised. For one solute in one solvent, at one temperature, the Sugden relation is approximately, but not exactly, of the right general form. The empirical constant α can vary from 1 to 30 c.c. for different solutes in one solvent, and from 30 to 60 c.c. for one solute in different solvents; moreover, it may vary with temperature (see p. 612). The slope is not, in general, equal to ${}^{G}_{O}P_2$, although in some cases there is close agreement, so that the relation may have a physical significance akin to, but not quite so simple as, the one first given.

The qualitative explanation which Sugden gave for expecting the slope to be the orientation polarisation in the gas was that the diminution of the orientation polarisation by dipole association would be expected to be a function of the volume polarisation, $(\varepsilon - 1)/(\varepsilon + 2)$, but since this quantity was conceived from a physical model in which association was not considered, it is not clear why it should be a parameter for association.

The equation which Goss derived (*Trans. Faraday Soc.*, 1934, **30**, 751) from the Raman–Krishnan modification (*Proc. Roy. Soc.*, 1928, *A*, **117**, 595) of the Clausius–Mosotti–Debye equation is

$${}_{T}P_2 = {}^{G}_{T}P_2 + \{(\varepsilon - 1)/(\varepsilon + 2)\}(N\psi + N^2\Theta/3RT)$$

where ψ and Θ involve the effect of the anisotropy of the medium on ${}_{E}P_2 + {}_{A}P_2$ and on ${}_{O}P_2$ respectively. It has the same form as the Sugden relation, but differs from it in that the slope is $(N\psi + N^2\Theta/3RT)$ instead of $-{}^{G}_{O}P_2$, and that it includes no constant α. The difference in meaning attached to the slope in this and in the Sugden relation is unimportant at present, because the meaning which Sugden gave is, according to the present results, not generally correct, and because, ψ and Θ being known for but few substances, the general correctness of the meaning given by Goss cannot be tested. On the other hand, the fact that the experimental data call for a constant α which is not accounted for by the theory shows that the latter is imperfect. Raman and Krishnan elaborated the treatment given by Clausius and Mosotti to the problem of calculating the field on a molecule in a polarisable medium by allowing for the anisotropy of the medium outside the conventional cavity (which they took to be ellipsoidal). They neglected, however, the forces from the molecules inside the cavity, and therefore their relation, like the simple Clausius–Mosotti–Debye relation, should not apply for pure liquids or concentrated solutions of them. In such cases the total polarisation, ${}_{T}P_2$, will usually be too small; hence the slope of the total polarisation curve plotted against the volume polarisation will be too steep, and to a first approximation there should be a positive constant α included in the intercept on the polarisation axis where the volume polarisation is zero: this constant would be expected to depend upon solute, solvent, and temperature, all of which factors affect the conditions inside the cavity. As we have seen, this is actually the case, although it should be added that this explanation alone appears insufficient to account for the considerable values of α relative to ${}_{T}P_2$ found in some cases. Since it would be expected that the deviation of the actual curve from the ideal curve would not be linear but would increase with the concentration of the polar substance, it is not surprising to find that the curves, to a second approximation, are not straight but are concave relative to the abscissæ.

For these reasons, the simple method proposed by Goss (*loc. cit.*) to calculate a correct dipole moment cannot be of general validity; for even though the difference of the intercepts on the total polarisation axis, at $(\varepsilon - 1)/(\varepsilon + 2) = 0$, of two curves at two temperatures be used, the variation of α with temperature would vitiate the result, as pointed out by Fairbrother (*loc. cit.*). From the suggested origin of α it would be expected that it would decrease as the temperature increases, so that the apparent change of orientation polarisation found would be too large, and the values of the moments would be too high. In actual fact, Goss obtains moments of 1·20 *D* and 1·78 *D* for chloroform and methylene chloride respectively, whereas the values determined from the vapours are 1·00 *D* and 1·61 *D* (Sänger, *Physikal. Z.*, 1926, **27**, 556; Mahanti and Sen Gupta, *J. Indian Chem. Soc.*, 1928, **5**, 673; Sircar, *Indian J. Physics*, 1928, **3**, 673). Fairbrother's data (*loc. cit.*) for nitrobenzene lead to a value of about 4·5 *D*, whereas the values from vapour measurements are 4·19 *D* (McAlpine and Smyth, *loc. cit.*) and 4·23 *D* (Groves and Sugden, *loc. cit.*).

Since, as has been seen, there is no clear theoretical justification for expecting that the slope of the total polarisation–volume polarisation line would be $-\,{}^{\mathrm{G}}_{0}P_2$, and since in fact it frequently is not, the method of determining electric dipole moment proposed by Fairbrother also cannot be of general use. That the method gives a good mean value for nitrobenzene is fortuitous, as is emphasised by the drift of apparent moment with temperature, from 4·30 *D* at 20° to 4·19 *D* at 120°.

SUMMARY.

Electric polarisations of concentrated nitrobenzene solutions in benzene, carbon disulphide, *n*-hexane, *cyclo*hexane, and carbon tetrachloride have been determined. The nitrobenzene–*cyclo*hexane curve has been shown to be of normal type.

The Sugden relation has been discussed in the light of these results, and its use by Fairbrother and by Goss to evaluate electric dipole moments has been shown to have no general justification. A suggestion is made that the Goss method is in error on account of the approximate nature of the argument used by Raman and Krishnan in deriving their formula.

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