78. *Freezing Points of Solutions of Nitrobenzene in Benzene and* cyclo*Hexane, and their Relations to the Electrical Polarisation.*

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THE phenomenon of dipole association, the change of molecular polarisation with concentration which many polar substances show in non-polar solvents (see, *e.g.*, Debye, " Polar Molecules," 1930, p. 47; Errera, *Z. physikal. Chem.*, 1928, **138**, 332; Leipziger Vorträge, 1929, pp. 27, 109; Smyth, " Dielectric Constant and Molecular Structure," 1931, p. 180), is particularly marked with nitrobenzene, for which the polarisation is five times as great at infinite dilution as in the pure liquid. Its cause is still obscure; it may be due to an orientation of the separate polar molecules under the influence of their mutual attractions, or to their combination, through true chemical links or otherwise, to polymerides of lower or zero moment. To investigate this effect, it is desirable to compare it with that of the concentration on the molecular weight as determined cryoscopically. This comparison was made by Höjendahl ("Studies of Dipole Moment," Copenhagen, 1928, p. 33), but both his electrical and his cryoscopic data were rather limited; he quotes only the freezing-point data of Beckmann in 1888 (*Z. physikal. Chem.*, **2**, 734) and the polarisation values of Lange (*Z. Physik*, 1925, **33**, 169).

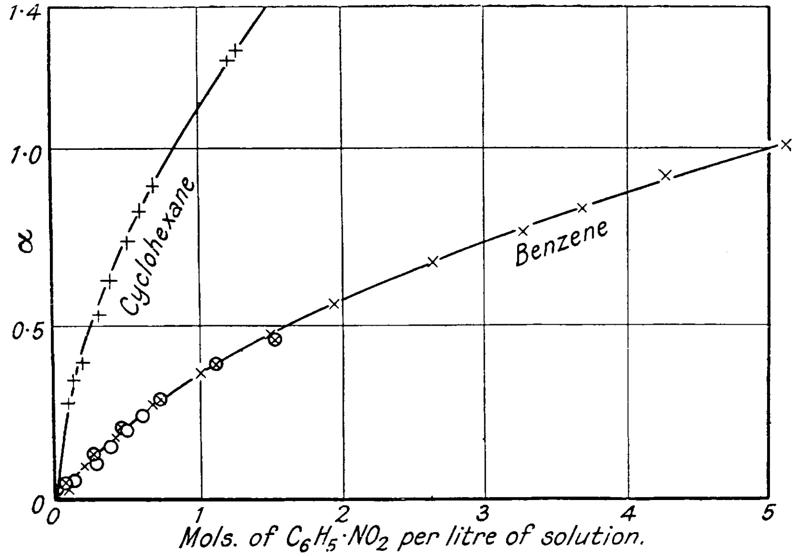
We have therefore re-examined the freezing points of nitrobenzene in benzene and in *cyclo*hexane, and compared the apparent association as calculated from these data with that deduced from the polarisation data now available.

EXPERIMENTAL.

Purification of Materials:—*Nitrobenzene.* This was made from thiophen-free C_6H_6, which was nitrated below 40° (Sidgwick and Ewbank, J., 1924, **125**, 2268). It was distilled under reduced press. below 100°, and then repeatedly frozen out until the f. p.'s of solid and mother-liquor were within 0·06° of one another.

FIG. 1.

Apparent association, a, of nitrobenzene in benzene and cyclo*hexane from cryoscopic measurements.*



For benzene solutions. ⊗ = Beckmann; ○ = Davy and Sidgwick; × = Dahms.
For cyclo*hexane solutions.* + = Davy and Sidgwick.

Benzene. A thiophen-free specimen was frozen out five times. After nine-tenths was frozen, the remaining liquid froze 0·2° below the solid.

cyclo*Hexane.* Eastman's "specially purified" material was frozen out until the difference of f. p.'s was reduced to 0·4°.

Method of Experiment.—A modified Beckmann's apparatus was used, with an electromagnetic stirrer. With a const. rate of stirring a const. degree of supercooling could be got, which was about 0·15° for C_6H_6, and much less, about 0·05°, for *cyclo*hexane. It was easy to get sharp and reproducible f. p.'s with both solvents. The effect of moisture was eliminated by adding a little P_2O_5 in every expt. To show that this had no action on the $PhNO_2$ used, the f. p. of a solution in C_6H_6 was measured in presence of the P_2O_5, and after the solution had stood overnight was found to be unchanged. For the more dil. solutions, a Beckmann thermometer was used, and for more conc., a 0·1° thermometer which was calibrated at the f. p.'s of H_2O and C_6H_6.

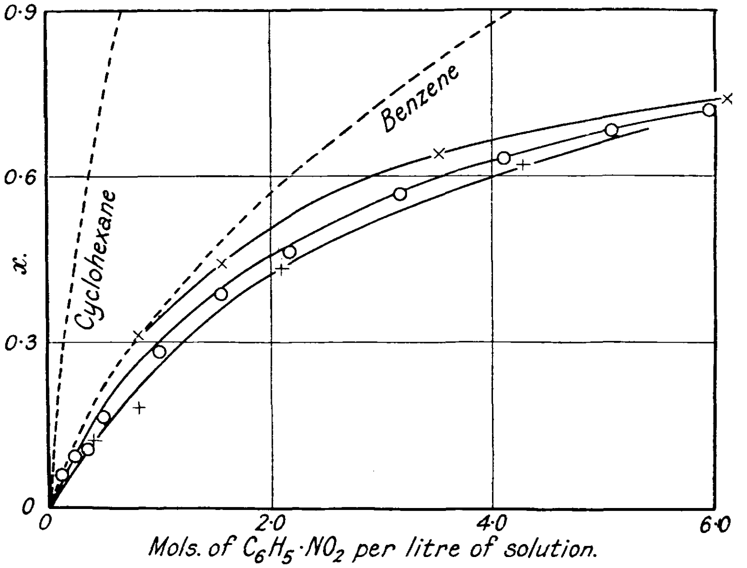
The agreement of our results in C_6H_6 at the lower concns. with those of Beckmann (*loc. cit.*) is so close that it seemed unnecessary to use more conc. solutions. After the work was finished, we found another series of measurements by Dahms (*Ann. Physik*, 1895, **54**, 496) which seem to have been generally overlooked; they are in good agreement with Beckmann's and our own.*

For calculating the mol. wts. we have used Jones and Bury's value (J., 1925, **127**, 1949) of 5·23 for 1 mol. in 1000 g. of solvent, and for *cyclo*hexane 20·0 (the values given in I.C.T. are from 20·0 to 20·3).

Results.—These are given in Tables I and II, and plotted in Fig. 1. Concns. are expressed in mols./l., since the object is to calculate the association const. In the tables, col. 1 gives the concn., col. 2 the obs. depression, and col. 3 the apparent mol. wt. If we make the simplest assumption, that the increase shown in col. 3 is due to a definite polymerisation of the $PhNO_2$ to double molecules, then if x is the fraction of single molecules polymerised, the number of solute molecules is reduced in the ratio $1 : (1 - x/2)$, so that $M_{\text{calc.}}/M_{\text{obs.}} = (1 - x/2)$, or $x = 2(M_{\text{obs.}} - M_{\text{calc.}})/M_{\text{obs.}}$. The values of x calculated on this hypothesis are given in col. 4, and are plotted in Fig. 2.

FIG. 2.

Apparent association of nitrobenzene in various solvents. Full curves from polarisation measurements; broken curves from cryoscopic measurements.



× = CS_2; ○ = CCl_4; + = hexane.

Measurements of Polarisation.—The mol. polarisation of $PhNO_2$ has been measured in C_6H_6 by Lange (*loc. cit.*; 24°), Hassel and Uhl (*Z. physikal. Chem.*, 1930, *B*, **8**, 199; 18·4°), Bergmann, Engel, and Sandor (*ibid.*, *B*, **10**, 412; 20·7°), Pal (*Phil. Mag.*, 1930, **10**, 265; 27°), Wehrle (*Physical Rev.*, 1931, **37**, 1135; 25°), and Tiganik (*Z. physikal. Chem.*, 1931, *B*, **13**, 440; 20°): in CCl_4 by Pal (*loc. cit.*); and in hexane and CS_2 by Williams and Ogg (*J. Amer. Chem. Soc.*, 1928, **50**, 98; 20°). The values obtained by different observers for P_∞ (*i.e.*, P_{A+O} at infinite dilution, P_E being taken as 32·7 c.c.), when corrected to 25° on the assumption that the polarisation is inversely proportional to the abs. temp., vary from 314 to 344 c.c., but the variations in different solvents are not greater than those found by different workers in the same solvent. We have therefore taken the mean value of 330 c.c. ($\mu = 3{\cdot}99$) in every case. From the data, the most probable polarisation–concentration curve for each solvent was drawn, and a series of values of P_C (P_{A+O} at concentration C) interpolated. On Höjen-

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* No other data of any accuracy seem to have been published, although Linard (*Bull. Soc. chim. Belge*, 1925, **34**, 363) and Meisenheimer and Dorner (*Annalen*, 1930, **484**, 130) give diagrams of the f. p. curves in C_6H_6, and the former also in *cyclo*hexane; these, however, are on too small a scale to be of any quant. use.

TABLE I.

Freezing Points: Nitrobenzene in Benzene. (See Fig. 3.)

1. Davy and Sidgwick. 2. Beckmann. 3. Dahms.

	C.	D_T.	*M.*	*x.*		*C.*	D_T.	*M.*	*x.*
1.	0·1200	0·689°	126·7	0·0584	3.	0·0874	0·51°	125·0	0·0320
	0·2862	1·632	129·7	0·103		0·1966	1·12	129·6	0·102
	0·3829	2·144	133·4	0·156		0·4144	2·31	135·6	0·186
	0·4945	2·727	136·9	0·203		0·6790	3·69	142·8	0·277
	0·5974	3·254	139·8	0·240		1·001	5·37	150·5	0·365
2.	0·0645	0·370	126·5	0·0553		1·497	7·98	160·8	0·470
	0·2584	1·445	132·0	0·136		1·953	10·36	171·4	0·565
	0·4649	2·550	137·1	0·206		2·631	14·08	184·9	0·669
	0·7357	3·945	143·7	0·288		3·266	17·67	198·6	0·761
	1·178	6·225	152·7	0·389		3·683	20·45	210·2	0·830
	1·526	8·015	159·5	0·458		4·268	24·20	277·8	0·920
						5·081	* 29·88	261·8	1·061

* Eutectic point.

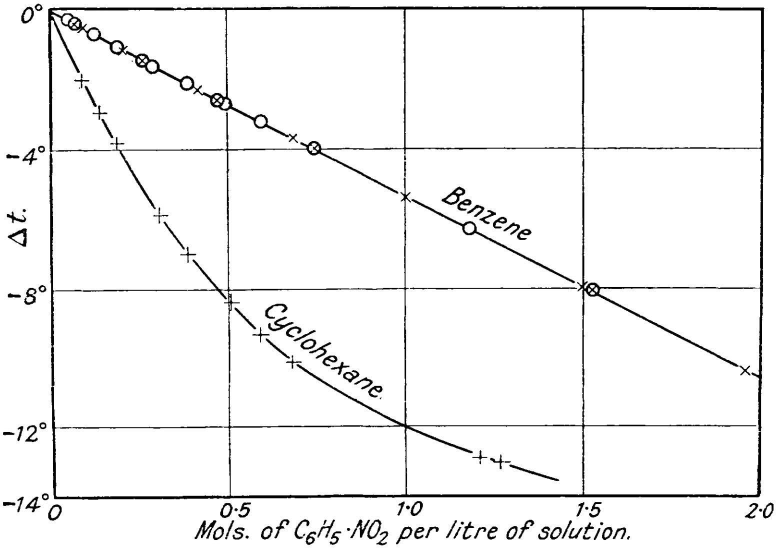
TABLE II.

Freezing Points: Nitrobenzene in cyclo*Hexane* (D. and S.). (See Fig. 3.)

C.	D_T.	*M.*	*x.*	*C.*	D_T.	*M.*	*x.*
0·0913	2·002°	143·0	0·280	0·5041	8·38°	194·7	0·736
0·1397	2·954	148·9	0·348	0·5944	9·30	208·6	0·820
0·1868	3·84	153·6	0·398	0·6800	10·07	221·9	0·892
0·3080	5·87	167·3	0·530	1·2075	12·82	324·3	1·242
0·3881	6·97	178·7	0·624	1·2692	12·96	339·4	1·275

FIG. 3.

Freezing-point depressions by nitrobenzene.



In benzene. ⊗ = Beckmann; ○ = Davy and Sidgwick; × = Dahms.
In cyclo*hexane.* + = Davy and Sidgwick.

dahl's assumption that double molecules are formed, and that these are non-polar, *x*, the fraction of single molecules which are polymerised, is given by $(P_\infty - P_C)/P_\infty$. The values of *x* so obtained are given in Table III, and compared with those derived from the f. p.'s. They are plotted on Fig. 2, in which the exptl. points are marked for solvents other than C_6H_6; the C_6H_6 curve itself is that which passes through the circles, being indistinguishable from the curve for CCl_4.

DISCUSSION OF RESULTS.

It will be seen from Fig. 2 that in benzene the cryoscopic values lie very close to those derived from the polarisations, until the solutions become concentrated. In *cyclo*hexane the polarisation has not been measured, but from the dielectric constant and the chemical character of this solvent we may assume that the degree of association will be between those in benzene and in hexane, and so but little different from that in benzene. On the other hand, the cryoscopic data for *cyclo*hexane indicate at every concentration a degree of association from 3 to 5 times as great as that found by polarisation in any solvent.

If the association is a real polymerisation, and a definite fraction of the nitrobenzene is present as double molecules, this should vary with the concentration according to the law of mass action :

$$K = \frac{[(C_6H_5 . NO_2)_2]}{[C_6H_5 . NO_2]^2} = \frac{C . x/2}{(1 - x)^2C^2} = \frac{x}{2(1 - x)^2C}.$$

The values of K in benzene and in *cyclo*hexane, obtained by this equation from the interpolated values of x, are given in Table III.

TABLE III.

Degree of Association of Nitrobenzene in Various Solvents.

(*a*) = derived from f. p. data; (*b*) = derived from polarisation data (polarisations at 25° : in CCl_4 also at 50°).

	C_6H_6.		CS_2.	CCl_4, 25°.	CCl_4, 50°.	Hexane.	*cyclo*Hexane.	*K*.		
								in C_6H_6.		in *cyclo*hexane.
C.	(*a*).	(*b*).	(*b*).	(*b*).	(*b*).	(*b*).	(*a*).	(*a*).	(*b*).	(*a*).
0·1	0·049	0·045	—	0·047	0·035	—	0·287	0·271	0·247	2·82
0·2	0·096	0·085	—	0·086	0·060	—	0·414	0·294	0·254	3·01
0·3	0·140	0·120	—	0·116	0·087	—	0·528	0·315	0·258	3·95
0·5	0·217	0·186	—	0·170	0·137	0·140	0·737	0·354	0·281	10·65
0·8	0·304	0·264	0·309	0·242	0·209	0·218	0·972	0·392	0·305	—
1·0	0·356	0·313	0·353	0·284	0·249	0·260	1·12	0·429	0·332	—
1·5	0·470	0·396	0·435	0·373	0·337	0·354	1·47	0·557	0·362	—
2·0	0·570	0·460	0·503	0·445	0·409	0·424	—	0·771	0·394	—
3·0	0·734	0·561	0·603	0·554	0·522	0·527	—	1·73	0·485	—
5·0	0·981	0·682	0·710	0·682	0·633	0·665	—	—	0·674	—
6·0	—	0·721	0·738	0·723	0·696	0·715	—	—	0·772	—
8·0	—	0·775	—	0·781	0·760	—	—	—	0·957	—

The results in benzene solution show that as the concentration increases the activity of the solute molecules diminishes; their effect in decreasing the vapour pressure of the solvent grows less, and so the molecular weights calculated from the freezing points increase; this is accompanied by a corresponding fall in the molecular polarisation. This effect may be due either to an orientation of the dipoles in the solution, or to an actual combination of the molecules with one another. The latter process, which is assumed in our calculation of x, involves a force active only when the molecules are close together, and falling off very rapidly as the distance between them increases : this is the condition for the law of mass action to hold. The values of K in Table III show that this does not occur; with increase of concentration K increases three or four times.* (Höjendahl reached the same conclusion about the association constant, but drew no inference from it.) It would thus seem that there can be no chemical combination or " dipole combination " between the molecules. The fall in activity and in polarisation is fully explained by the orientation of the polar molecules under the influence of their mutual attractions;

* It might be urged that the cryoscopic values of K would not be expected to be constant, since they are not obtained at the same temperature (though this does not apply to the polarisation values). This effect, however, is not serious. The range of m. p.'s from $C = 0·1$ to $C = 2·0$ (where K is 2·8 times as large as at $C = 0·1$) is 10°. The polarisation experiments of Pal (*loc. cit.*) show that in going from 50° to 10°, x in CCl_4 increases at $C = 1$ by 15·6%, and at $C = 4$ by 6·4%—say by 12% at $C = 2$: thus the corrected values for the m. p. of benzene would be, at $C = 2$, $x = 0·553$, and $K = 0·692$, *i.e.*, not 2·8 but 2·55 times as large as at $C = 0·1$. But the real error is much less than this, and may be in the opposite direction. Heats of fusion always fall slightly with a fall of temperature, and on the average by about 13 cals. per 1°. Thus in 10° that of benzene (2·37 kg.-cals. at the m. p.) will fall by about 0·13 kg.-cal., or 5%; hence the true observed molecular weight at $C = 2$ would be about 5% greater than that recorded. Thus the small effects of the 10° change in temperature on the association and on the cryoscopic constant oppose, and may be taken to cancel, one another.

in fact, the failure of the law of mass action in this case is very similar to that which occurs with strong electrolytes, except that the force between dipoles varies approximately as the inverse fourth power of the distance, and that between ions as the inverse square, so that the departure of the " constant " from constancy is less marked with the former.

This conclusion is in accordance with the general theory of chemical association, that its occurrence depends on the simultaneous presence in the molecule of donor and acceptor atoms. In nitrobenzene the oxygen atoms have a strong donor character, but there is no acceptor. In the alcohols on the other hand the hydroxyl hydrogen can act as acceptor, and co-ordination between the molecules is possible. The polarisation curves given by alcohols in non-polar solvents (see references, p. 281) are of an entirely different type from that of nitrobenzene: as the concentration increases from zero, the molecular polarisation at first rises, owing presumably to the new dipole of the co-ordinate link, and it is only at higher concentrations, when the polymerisation has nearly reached its maximum, and the dipole orientation of the polymerised molecules begins to have effect, that the polarisation diminishes (Sidgwick, *Z. Elektrochem.*, **1928**, **34**, 450).

In *cyclo*hexane we have a new phenomenon. The polarisation data in hexane indicate that the electrical behaviour of nitrobenzene will be much the same in *cyclo*hexane as in benzene, but the cryoscopic measurements point to a far higher degree of association in *cyclo*hexane. This suggests that in *cyclo*hexane the freezing points are affected by a new factor, which clearly is the tendency of the system to separate into two liquid layers, or, to speak more precisely, the highly positive partial vapour pressure curve of *cyclo*hexane in presence of nitrobenzene. Such a curve (a similar system is that of methyl alcohol and benzene) involves a complete breakdown of Raoult's law, and leads to values of the molecular weight from the freezing points far in excess of the truth. This explanation is confirmed by the observation of Linard (*loc. cit.*) that a mixture of nitrobenzene and *cyclo*hexane will separate into two layers in the metastable state, a few degrees below its freezing point.

It will be seen from Table III that the dipole association appears to vary somewhat (10—20%) with the solvent, in the order $CS_2 > C_6H_6 = CCl_4 > C_6H_{14}$. This is also the order of the dielectric constants (2·63, 2·29, 2·24, 1·88), and is the opposite of what we should expect, since on any hypothesis the force between the dipoles must increase as the dielectric constant of the solvent falls. Recently, Horst Müller (*Physikal. Z.*, **1932**, **33**, 731) has found by accurate measurements that the value of P_∞ for chlorobenzene varies about 10% in different non-polar solvents, being greatest in those of lowest dielectric constant. We have taken a constant (mean) value of P_∞ for nitrobenzene in all our solvents; this is presumably rather too high for carbon disulphide, which would exaggerate the association, and rather too low for hexane, which would make it appear too small. Hence this variation in association is probably not real; but the whole effect is small, and the existing data are not accurate enough to enable us to determine the individual values of P_∞ in different solvents.

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