605. *Solvent Effects upon the First Ultraviolet Absorption Band of Substituted* p-*Nitroanilines.*

By J. H. P. Utley.

The wavelengths of the maxima of the first ultraviolet absorption band of several substituted *p*-nitroanilines have been measured in " iso-octane," carbon tetrachloride, methanol, and dioxan, and in mixtures of the polar with the non-polar solvents. The position of the band is very solvent-dependent, red shifts accompanying changes to more polar solvents. These shifts are probably a result of both solvent–solute hydrogen bonding and solvent–solute dipole–dipole interactions. The large shifts observed at low concentrations of polar solvent are mainly a result of hydrogen bonding involving the amine-hydrogen atoms and the polar solvent. Such hydrogen bonding has been characterised by a study of the N–H stretching vibrations in polar solvent–carbon tetrachloride mixtures. A similar study of the symmetrical NO_2 stretching vibrations suggests that the nitro-group is not involved in specific solvent–solute interactions. For methanol–" iso-octane " mixtures of high dielectric constant (>10) dipole–dipole interactions can account for about 60% of the total shift. Shifts resulting from such interactions have been related to the dielectric constant of the solvent by adaptation of an equation derived by Onsager.

The position of the first ultraviolet absorption band of *p*-nitroaniline is very solvent-dependent, large red shifts accompanying changes to more polar solvents. Pearson[1] has demonstrated that the solvent-induced shift of the first ultraviolet absorption band of *p*-nitroaniline is related to the polarity of the solvent, as measured by its dielectric constant. Some dependence of the shift on the functional groups of the solvent is also noted by Pearson, and the relative importance of hydrogen bonding and dipole–dipole interactions is difficult to judge. Previous workers on such solvent effects had concluded that, when present, the effect of hydrogen bonding swamps that of other less specific interactions.[2] This is shown particularly by Brealey and Kasha's measurements on the blue shift of the 29,450 cm.$^{-1}$ band of pyridazine in ethanol–hexane mixtures.[3] This large shift was associated with hydrogen bonding between ethanol and the solute which was characterised for the system by ultraviolet and infrared studies. The present work is an attempt to distinguish between the types of solvation which produce red shifts of the first ultraviolet absorption band of *p*-nitroaniline.

The nature of the electronic transition associated with the first ultraviolet absorption band of *p*-nitroaniline is still not clear, but recent work suggests that the excited state has some charge-transfer character.[4,5] What is clear is that during the transition the dipole moment of the molecule is increased and lies in the same direction as the ground-state dipole.[6]

EXPERIMENTAL

Materials.—All the compounds investigated, except one, had been prepared in a condition suitable for physical measurements by previous workers in this laboratory. NN-*Di-n-hexyl*-p-*nitroaniline* was prepared during the present investigation. *NN*-Di-n-hexyl-*p*-nitrosoaniline[7] was oxidised with aqueous potassium permanganate. A benzene solution of the product was passed down an alumina column and the main, yellow, band collected. The product was an oil (Found: C, 70·5; H, 9·7; N, 9·0. $C_{18}H_{30}N_2O_2$ requires C, 70·55; H, 9·9; N, 9·1%).

---

[1] Pearson, *Proc. Chem. Soc.*, 1962, 78.
[2] Pimentel and McClellan, " The Hydrogen Bond," Freeman and Co., London, 1960, p. 159.
[3] Brealey and Kasha, *J. Amer. Chem. Soc.*, 1955, **77**, 4462.
[4] Lutskii and Konel'skaya, *J. Gen. Chem.* (*U.S.S.R.*), 1960, **30**, 3735.
[5] Dr. J. N. Murrell, personal communication.
[6] Czekalla and Wick, *Z. Elektrochem.*, 1961, **65**, 727.
[7] Brouwers, Bijlsma, Verkade, and Wepster, *Rec. Trav. chim.*, 1958, **77**, 1080.

Solvents.—" *Iso-octane.*" Phillips " spectrograde " iso-octane (mainly 2,2,4-trimethylpentane) was purified by Wepster's method.[8]

Methanol. Merck " pro analysi " methanol was used without further purification.

Dioxan. This was purified by Cavell, Chapman, and Johnson's method.[9]

Carbon tetrachloride. The commercial product was purified as described by Vogel.[10]

Dimethylformamide. Merck's dimethylformamide " for ultraviolet spectroscopy " was used without purification.

Measurements.—(*a*) *Ultraviolet absorption maxima in mixed solvents.* Mixtures were prepared by volume. Stock solution of the amine in the polar solvent was added to each of several graduated flasks. Suitable volumes of polar solvent were then added and the mixtures made up to the mark with " iso-octane." The final solute concentration was generally about $3{\cdot}0 \times 10^{-5}$M. Absorption maxima were measured with 1 cm. cells and a Beckman D.K.2 recording spectrophotometer. For some " iso-octane "–methanol mixtures it was necessary to warm the cell compartment to 40—50° to obtain complete miscibility.

(*b*) N–H *Stretching frequencies in mixed solvents.* Solutions of amine and polar solvent in carbon tetrachloride were prepared by weight. The solute concentration was generally about 6×10^{-3}M and the polar solvent concentration about 0·5M. Reference solutions containing only the two solvents were prepared in a similar way. The infrared spectra in the 3 μ region were measured by using 1 cm. quartz cells and a Beckman D.K.2 spectrophotometer.

(*c*) NO_2 *Stretching frequencies in mixed solvents.* Sample and reference solutions were prepared in the way described for the measurement of N–H stretching frequencies. The solute and polar solvent concentrations were generally similar to those used for the N–H stretching vibration measurements. The symmetrical stretching frequency of the nitro-group was measured with a Perkin-Elmer model 21 recording spectrophotometer.

(*d*) *Dielectric constants of mixed solvents.* Solutions of methanol (0—5% v/v), and dioxan (0—100% v/v), in " iso-octane " were prepared by weight. Dielectric constants of these mixtures were measured, at 25·0°, with a Wissenschaftlich-Technische Werkstätten dipole meter of type D.M.01.

(*e*) *Association constants in carbon tetrachloride.* (i) The intensity of the N–H stretching band was calibrated for various amine concentrations in carbon tetrachloride. Stock solutions of the amines and of the polar solvents in carbon tetrachloride were prepared by weight. Sample solutions of a given concentration in amine but of varying concentration in polar solvent were prepared by mixing suitable volumes of the stock solutions. Reference solutions with the same concentrations in polar solvent were also prepared. The spectra, at 20°, of the sample solutions were then measured in the 3 μ region with a Beckman D.K.2 spectrophotometer.

(ii) Calculation was based on Brealey and Kasha's method.[3]

$$\mathrm{R{\cdot}NH_2} + r(\text{Polar solvent}) \rightleftharpoons \mathrm{R{\cdot}NH_2}(\text{Polar solvent})_r \text{ Complex}$$

$$K = [\text{Complex}]/([\text{Polar solvent}]^r\,[\mathrm{R{\cdot}NH_2}])$$

Hence,

$$\log K + r \log\,[\text{Polar solvent}] = \log\,([\text{Complex}]/[\mathrm{R{\cdot}NH_2}]) \qquad (1)$$

From a plot of log ([Complex]/[R·NH_2]), known from the peak intensities, against log [Polar solvent]$_{\text{added}}$, approximate values of r were calculated. This value was used to calculate log [Polar solvent]$_{\text{true}}$, and r was recalculated. K was then calculated from eqn. (1) for each concentration of polar solvent.

DISCUSSION

Fig. 1 shows the red shifts, relative to " iso-octane " or carbon tetrachloride solutions, of the first ultraviolet absorption maxima of several substituted *p*-nitroanilines in mixed solvents. Table 1 gives the wavelengths of the absorption maxima of solutions in various pure solvents. The direction and magnitude of the observed shifts are probably a consequence of both hydrogen bonding and dipole–dipole solute–solvent interactions, and here we attempt to estimate the relative importance of the two causes. Intermolecular association

---

[8] Wepster, *Rec. Trav. chim.*, 1952, **71**, 1159.

[9] Cavell, Chapman, and Johnson, *J.*, 1960, 1413.

[10] Vogel, " Practical Organic Chemistry," Longmans, Green and Co., London, 1956, p. 176.

of the amines is of little significance at the concentration used in this study ($\sim 3 \times 10^{-5}$ mole $l.^{-1}$). Beer's law was found to be obeyed to within 2% for a change in solute concentration from $5{\cdot}8 \times 10^{-6}$ to $4{\cdot}7 \times 10^{-5}$ mole $l.^{-1}$. Solvent effects on the intensity of the ultraviolet spectra are noticeable. The effect on the molecular extinction coefficient of a continuous change of solvent from carbon tetrachloride to methanol is given for *p*-nitroaniline in Table 2. No explanation of the variation is offered in this paper.

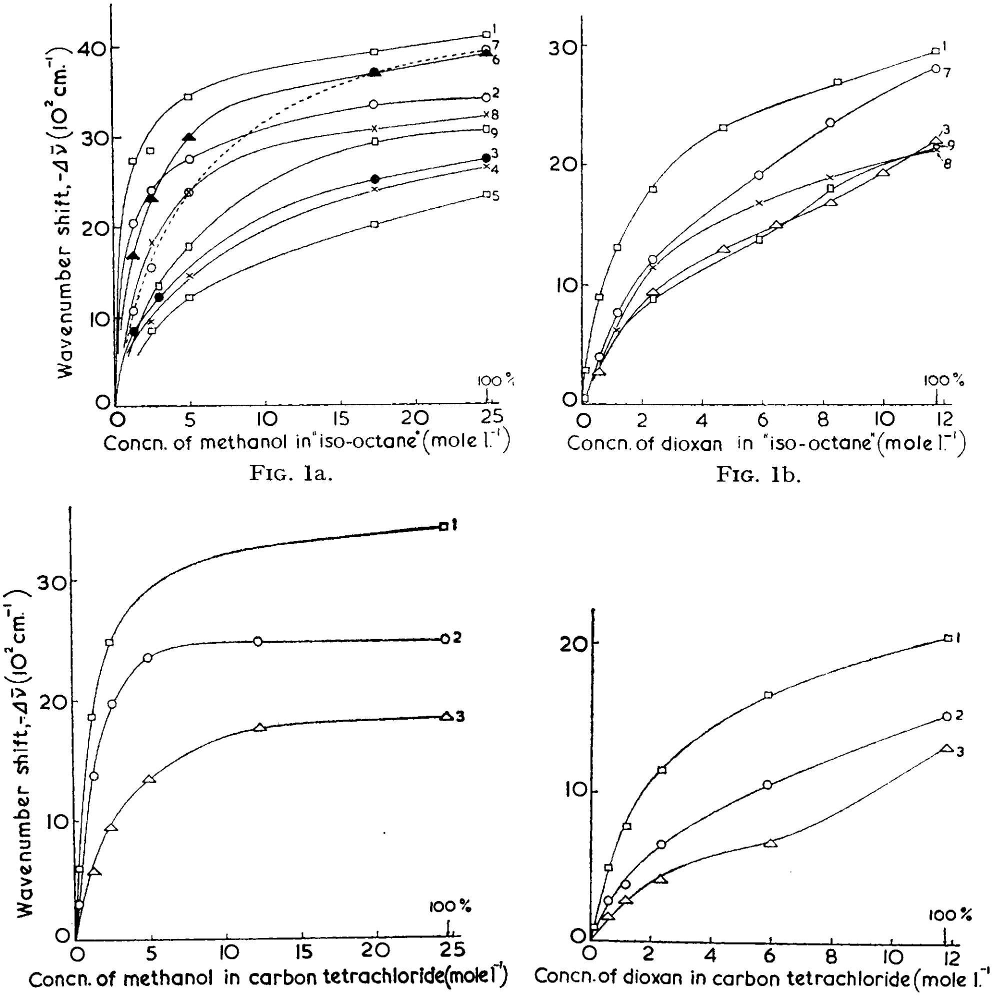

Fig. 1a.

Fig. 1b.

Fig. 1c.

Fig. 1d.

Fig. 1. Red shifts, relative to " iso-octane " or carbon tetrachloride solutions. For key see Table 1.

The Red Shift as a Result of Hydrogen Bonding.—It has been established that for hydrogen bonding between solute and solvent to result in a red shift of the absorption maximum the strength of the hydrogen bond must be increased in going to the excited state.[11] As the Franck–Condon principle must be obeyed the solvent molecules in the excited state are oriented as for the ground state and may not therefore be in a favourable position to form a stronger hydrogen bond in the excited state. In any case Pimentel[11]

---

[11] Pimentel, *J. Amer. Chem. Soc.*, 1957, **79**, 3323.

TABLE 1.

Absorption maxima (mμ) * of substituted *p*-nitroanilines in pure solvents.

Compound	Curve (see Fig. 1)	i-C_8H_{18}	CCl_4	Dioxan	MeOH	$H\cdot CO\cdot NMe_2$
p-$NO_2\cdot C_6H_4\cdot NH_2$	1	319·5	328·5	352·5	368·0	381·5
p-$NO_2\cdot C_6H_4\cdot NHMe$	2	338·0	349·0	368·0	383·5	—
p-$NO_2.C_6H_4\cdot NMe_2$	3	351·0	362·5	381·0	388·5	—
p-$NO_2\cdot C_6H_4\cdot NC_4H_8$ †	4	358·5	—	—	396·5	—
p-$NO_2\cdot C_6H_4\cdot N(C_6H_{13}\text{-n})_2$	5	365·0	—	—	399·0	—
4,2,6-$NO_2\cdot C_6H_2Me_2\cdot NH_2$	6	328·5	—	—	376·0	—
4,2,6-$NO_2\cdot C_6H_2Me_2\cdot NHMe$	7	335·0	—	369·5	386·5	—
p-$NO_2\cdot C_6H_4\cdot NHBu^t$	8	345·0	—	372·0	388·0	—
4,2,6-$NO_2\cdot C_6H_2Bu^t{}_2\cdot NH_2$	9	337·0	—	363·0	376·0	—

* In this region the measured wavelengths are judged to be accurate to ±0·5 mμ. † 1-*p*-Nitrophenylpyrrolidine.

TABLE 2.

Molecular extinction coefficients, at 20°, for *p*-nitroaniline in CCl_4–MeOH mixtures.

[MeOH] (mole l.$^{-1}$)	0	1·24	2·48	4·95	9·91	24·8
$10^{-4}\varepsilon$ *	1·34	1·22	1·20	1·32	1·32	1·52

* Values of ε are accurate to about ±3%.

has concluded from theory that a red shift should not exceed the ground-state strength of the hydrogen bond. For the transition under discussion hydrogen bonding giving a red shift must involve either the amino-group as a proton donor or the nitro-group or aromatic residue as a proton acceptor. These are the only hydrogen bonds possible whose strength could be greater in the excited than in the ground state.

In methanol–" iso-octane " mixtures (Fig. 1, Table 1) the larger shifts are about —4000 cm.$^{-1}$ (11·5 kcal./mole) even where only one hydrogen bond can be formed involving the N–H bond, *e.g.*, for *N*-methyl- and *N*,2,6-trimethyl-4-nitroaniline. If we assume that solvent interaction with the nitro-group contributes little to the red shift—and there is evidence to support this view (see below)—it is very unlikely that ground-state hydrogen bonds of at least 11·5 kcal./mole strength are formed in these systems. However, it is noticeable that, for the amines where hydrogen bonding involving the N–H bond is not possible, curves of the $\Delta\bar{\nu}$ against [MeOH] are substantially depressed. Such amines are *NN*-dimethyl-*p*-nitroaniline, 1-*p*-nitrophenylpyrrolidine, and *NN*-di-n-hexyl-*p*-nitroaniline. The plot of $\Delta\bar{\nu}$ against [MeOH] for 4-nitro-2,6-di-t-butylaniline is also depressed. From Bellamy, Eglington, and Morman's study[12] of hydrogen bonds formed by sterically hindered phenols it would be supposed that 4-nitro-2,6-di-t-butylaniline would not form strong hydrogen bonds involving the amine group. This has been confirmed experimentally by a study of the N–H stretching vibrations in mixed solvents (see below). The considerations of Kamlet[13] indicate that, for measurements in pure solvents, the difference in red shift between amines and the corresponding *N*-methylated compounds reflects the effect of hydrogen bonding. For a change in solvent from " iso-octane " to methanol the red shifts for *p*-nitroaniline and *NN*-dimethyl-*p*-nitroaniline are —4130 and —2750 cm.$^{-1}$, respectively. A shift for *p*-nitroaniline of —1380 cm.$^{-1}$ can therefore be attributed to hydrogen bonding involving the amine protons.

The qualitative trends seen for the methanol–" iso-octane " system are also found for the other systems studied although the overall shifts are less. However, even for compounds in which the amine-hydrogen atoms have been replaced by alkyl groups there is still a large red shift in going from non-polar to polar solvents.

N–H *Stretching vibrations in mixed solvents.* Strong evidence of specific solvent interaction with the N–H bond is found. In carbon tetrachloride solutions containing dioxan or dimethylformamide, peaks at lower N–H stretching frequencies appear although peaks

---

[12] Bellamy, Eglinton, and Morman, *J.*, 1961, 4762.

[13] Dr. M. J. Kamlet, personal communication.

with the original frequencies, but diminished intensity, remain. The new peaks probably represent the hydrogen-bonded species, whereas the original peaks represent the " free " molecule. Methanol absorbs too strongly in this region to be used in similar experiments, but indirect evidence of hydrogen bonds involving methanol comes from the measurements of nitro-group stretching frequencies (see below).

The measured frequencies are listed in Table 3. The antisymmetric and the symmetric stretching vibrations of the NH_2 group are represented by $\bar{\nu}_a$ and $\bar{\nu}_s$, respectively; $\Delta\bar{\nu}_{mean}$ refers to the mean of the displacements of $\bar{\nu}_a$ and $\bar{\nu}_s$. The displacement of the stretching frequencies, in wavenumbers, should give an indication of the strength of the hydrogen bond involved. Nakamoto, Margoshes, and Rundle[14] suggest that the quantity $\Delta\bar{\nu}/\bar{\nu}$ best represents the strength of such bonds. Bellamy and his co-workers[12] have demonstrated that in phenols substituents near the hydroxyl group can alter the equilibrium constant of hydrogen-bonding interactions, and large substituents will also increase the O • • • O bond distances and thus weaken the bond. For example, the association of 2,6-di-t-butylphenol with many solvents is weak. The smaller $\Delta\bar{\nu}/\bar{\nu}$ values for amines likely to be sterically hindered around the N–H bond are therefore understandable.

TABLE 3.

N–H stretching vibrations * of substituted *p*-nitroanilines.

Subst.	Solvent	$\bar{\nu}_a$ (cm.$^{-1}$)	$\bar{\nu}_s$ (cm.$^{-1}$)	$\Delta\bar{\nu}_{mean}$ (cm.$^{-1}$)	$10^2\Delta\bar{\nu}/\bar{\nu}$
None	CCl_4	3515	3422	—	—
,,	CCl_4–DMF †	3308	3245	192	5·53
,,	CCl_4–Dioxan	3370	3250	158	4·55
2,6-Me_2	CCl_4	3520	3430	—	—
,,	CCl_4–DMF	3323	3254	187	5·38
,,	CCl_4–Dioxan		No displacement		0
2,6-Bu^t_2	CCl_4	3557	3472	—	—
,,	CCl_4–DMF		Slight broadening		0
,,	CCl_4–Dioxan		No displacement		0
N,2,6-Me_3	CCl_4	—	3456	—	—
,,	CCl_4–DMF	—	3416	40	1·16
,,	CCl_4–Dioxan	—	Slight broadening		0
N-Bu^t	CCl_4	—	3436	—	—
,,	CCl_4–DMF	—	3336	100	2·91
,,	CCl_4–Dioxan	—	3373	63	1·83

* These frequency measurements are judged to be accurate to ±2 cm.$^{-1}$. † *NN*-Dimethylformamide.

TABLE 4.

NO_2 Group symmetrical stretching vibrations * of substituted *p*-nitroanilines.

Subst.	Solvent	$\bar{\nu}$ (cm.$^{-1}$)	$\bar{\nu}'$ (cm.$^{-1}$)	$\Delta\bar{\nu}$ (cm.$^{-1}$)
None	CCl_4	1339	—	—
,,	CCl_4–MeOH	1337	1313	24
,,	CCl_4–DMF	1333	1318	15
,,	CCl_4–Dioxan	1337	—	—
2,6-Bu^t_2	CCl_4	1330	—	—
,,	CCl_4–DMF	1326	—	—
,,	CCl_4–Dioxan	1330	—	—
NN-Me_2	CCl_4	1330	—	—
,,	CCl_4–MeOH	1328	—	—
,,	CCl_4–DMF	1325	—	—

* The frequency measurements are judged to be accurate to ±3 cm.$^{-1}$.

Nitro-group symmetrical stretching frequencies in mixed solvents. These measurements were made in an attempt to detect specific solute–solvent interactions involving the N–O bond. The results are summarised in Table 4 where the frequency of any displaced peak is under the heading $\bar{\nu}'$. The results show, however, that the expected splitting into

---

[14] Nakamoto, Margoshes, and Rundle, *J. Amer. Chem. Soc.*, 1955, **77**, 6480.

two peaks occurs only when it is probable that the amino-group is involved in hydrogen bonding. It is possible that hydrogen bonding of the amino-group alters its polar effect on the aromatic residue and therefore affects the NO_2 stretching vibration. There is no displacement of the NO_2 stretching frequency when only the nitro-group is likely to be involved in hydrogen bonding, *e.g.*, *NN*-dimethyl-*p*-nitroaniline in methanol–carbon tetrachloride. If, as it seems, there is little ground-state hydrogen bonding to the nitro-group then it is unlikely that solvent molecules will be oriented in directions suitable for extra stabilisation of the excited state. As they cannot be oriented during the transition to the Franck–Condon excited state there should be little shift in the absorption maximum due to hydrogen bonding of the nitro-group.

Association constants. The hydrogen-bonded complexes of *N*-methyl-*p*-nitroaniline with dioxan and *NN*-dimethylformamide in carbon tetrachloride were further characterised by determining the association constants. These are given in Table 5. *NN*-Dimethylformamide behaves similarly to methanol in producing large red shifts of the first ultraviolet absorption band even at low concentrations. For example, the band maximum is at 344·5 mμ for *p*-nitroaniline in a solution of 0·136M-*NN*-dimethylformamide in " iso-octane; " this corresponds to a red shift of —2270 cm.$^{-1}$ from the absorption in pure " iso-octane." Such shifts are much greater than those found in similar concentrations of dioxan. The association constants indicate that more of the amine is involved in the complex in the dimethylformamide solution. Values of *r* suggest that 1 : 1 complexes are formed although the uncertainty in *r* is such that no definite conclusion can be drawn.

TABLE 5.

Association constants for amine–polar solvent association in carbon tetrachloride at 20° ± 1°.

Amine	Solvent	*K* (l. mole^{-1})	*r*
p-$NO_2 \cdot C_6H_4 \cdot NHMe$	Dioxan	13·0 ± 4·0	1·17 ± 0·10
,,	DMF	84·0 ± 25·0	1·15 ± 0·10

The Red Shift as a Function of Dielectric Constant.—The other solute–solvent interactions strong enough to cause large shifts of absorption maxima in this system are dipole–dipole interactions. A polar molecule such as *p*-nitroaniline will orient polar solvent molecules around itself and thus stabilise the ground state of the molecule relative to the ground state in a non-polar solvent. During the transition to the excited state the dipole moment of the solute is increased and is in the same direction as in the ground state. The excited state molecule will therefore be stabilised more than the ground state by the oriented polar solvent. The energy separation between the ground and the excited state will be decreased and a red shift will result. Such a solvation effect should generally be a function of the dielectric constant of the solvent and Pearson's [1] measurements of the red shift, relative to n-hexane solution, show that a plot of $-\Delta\bar{\nu}$ against dielectric constant for *p*-nitroaniline in 31 solvents is similar in shape to Fig. 1a (curve 1).

The dielectric constants of methanol–" iso-octane " and dioxan–" iso-octane " mixtures have been measured during this investigation and are given in Table 6.

TABLE 6.

Dielectric constants (*D*), at 25·0°, of polar solvent–" iso-octane " mixtures.

[MeOH] (mole l.$^{-1}$)...	0·299	0·549	0·601	0·813	0·957	1·25	1·48
D	1·985	2·056	2·073	2·141	2·193	2·312	2·427
[Dioxan] (mole l.$^{-1}$)	1·07	1·46	2·72	4·78	8·00	9·47	11·8
D	1·920	1·950	2·003	2·073	2·173	2·219	2·285

From a knowledge of the variation of dielectric constant with concentration of polar solvent, and from the measured red shifts of *p*-nitroaniline and *NN*-dimethyl-*p*-nitroaniline, plots of *D* against $-\Delta\bar{\nu}$ have been made (Fig. 2). The approximate slope of the initial, linear, portion of Pearson's plot is also given and it is noteworthy that the initial increment in $-\Delta\bar{\nu}$ is greater in methanol–" iso-octane " than expected from the dielectric constants of the mixtures.

The Relative Importance of Hydrogen Bonding and Dipole–Dipole Interactions.—The infrared spectroscopic studies of the N–H and NO_2 stretching vibrations, and the measurements on the association, in carbon tetrachloride, between *N*-methyl-*p*-nitroaniline and polar solvents, indicate that several of the amines are hydrogen-bonded in the systems under study. Moreover, although the wavenumber shifts are related to the dielectric constant of the solvent mixtures in a way similar to that for single solvents, the large shifts at low dielectric constant suggest that hydrogen bonding is the dominant interaction in such solutions.

For solvent mixtures with a high dielectric constant it is probable that dipole–dipole interactions are important in the cases discussed here. This is because the dipole moment of molecules such as *p*-nitroaniline is greatly increased during the transition to the first excited state although its direction is unchanged. Attractive interactions in the ground state are therefore greatly strengthened in going to the excited state (see below). For a change from " iso-octane " to methanol solution the red shifts found for *N*-methyl-*p*-nitroaniline and *N*,2,6-trimethyl-4-nitroaniline are —3420 and —3960 cm.$^{-1}$, respectively. This represents a solvent stabilisation of the excited state extra to that of the ground state by about 11·5 kcal./mole. In the light of Pimentel's calculations [11] it is very unlikely that such a large shift can be accounted for in terms of hydrogen bonding only.

Onsager [15] calculated the effect on energy content of introducing a rigid dipole (μ) into a cavity of radius *a* in an unpolarised medium of dielectric constant *D*. Subsequent workers [16] have suggested that in these circumstances the gain in energy of such a dipole is given by

$$\delta E = \frac{-\mu^2}{a^3}\left[\frac{D-1}{2D+1}\right]. \qquad (2)$$

If, instead of one dipole and different solvents, the ground-state dipole (μ_g) and the excited state dipole (μ_e) are considered in the same solvent, the change in free energy of solvation due to the change in dipole moment is given by

$$\Delta\Delta F = \frac{-(\mu_g^2 - \mu_e^2)}{a^3}\cdot\left[\frac{D-1}{2D+1}\right]. \qquad (3)$$

Czekalla and Wick [6] estimated μ_g and μ_e for *p*-nitroaniline and *NN*-dimethyl-*p*-nitroaniline. Their calculations are based on measurements of electrical dichroism and are independent of solvent-induced wavelength shifts. Values of μ_g and μ_e were therefore substituted into eqn. (3), and for a series of values of *D* from 1·9 to 30·0 the differences in free energy of solvation between the ground and the excited state of *p*-nitroaniline calculated in terms of a^3, a constant. This represents a continuous change of solvent from, say, " iso-octane " to methanol, without account for the effects of weak van der Waal's interactions and hydrogen bonding; when the results of the calculation are plotted (Fig. 3) the shape of the curve is that found experimentally by Pearson. Further, it now seems unnecessary to give a different explanation for separate portions of the curve as Pearson does. That this treatment, coupled with the recent estimates of the excited-state dipole moment, can account for red shifts of about —2750 cm.$^{-1}$ can be shown by calculating *a* for *p*-nitroaniline in methanol. The shift of —2750 cm.$^{-1}$ is that part of the total shift not caused by hydrogen bonding (see p. 3255). The value of *a* required to fit the results is 4·4 Å, a reasonable figure. Similarly a value of 4·6 Å is required to fit the overall wavenumber shift of *NN*-dimethyl-*p*-nitroaniline in methanol. These two values were substituted into eqn. (3), the energy term being expressed in wavenumbers, and plots of

---

[15] Onsager, *J. Amer. Chem. Soc.*, 1936, **58**, 1486.

[16] Powling and Bernstein, *J. Amer. Chem. Soc.*, 1951, **73**, 1815; Berson, Hamlet, and Mueller, *ibid.*, 1962, **84**, 297.

calculated $-\Delta\bar{\nu}$ against D were constructed. A comparison of these with the experimental plots is shown in Fig. 2. At low dielectric constants linearity is predicted and indeed found when no hydrogen bonding of the amino-group is possible, *e.g.*, for *NN*-dimethyl-*p*-nitroaniline. Where there is such hydrogen bonding, however, the initial slope of the curves is much greater than predicted. From the total shifts in dioxan, values of a for *p*-nitroaniline and *NN*-dimethyl-*p*-nitroaniline have been calculated. These are smaller than is reasonable, 2·2 and 2·6 Å, respectively, probably because the dielectric constant is not a suitable measure of the polarity of dioxan (see p. 3260). A comparison of predicted and experimental plots of the type shown in Fig. 2 suggests for the dioxan–" iso-octane " system a conclusion similar to that drawn for the methanol–" iso-octane " system. Where hydrogen bonding is possible, large deviations from the predicted linearity are found. There is little deviation when hydrogen bonding is not possible. Fig. 2 shows that hydrogen bonding probably accounts for about 90% of the total shift for *p*-nitroaniline in a methanol–" iso-octane " mixture of dielectric constant 2·2. Dipole–dipole interactions probably become very significant in solutions with dielectric constants greater than 10 (Fig. 3). In such solutions hydrogen bonding accounts for about one-third of the total shift.

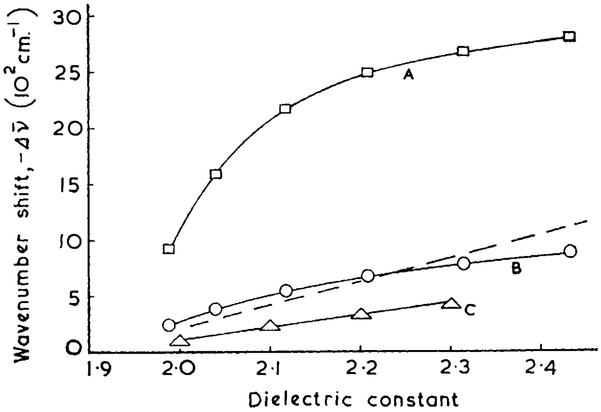

FIG. 2. Experimental curves for (A) *p*-nitroaniline and (B) *NN*-dimethyl-*p*-nitroaniline in methanol–" iso-octane," compared with (C) the calculated curve and (broken line) the experimental curve for *p*-nitroaniline in single solvents (ref. 1).

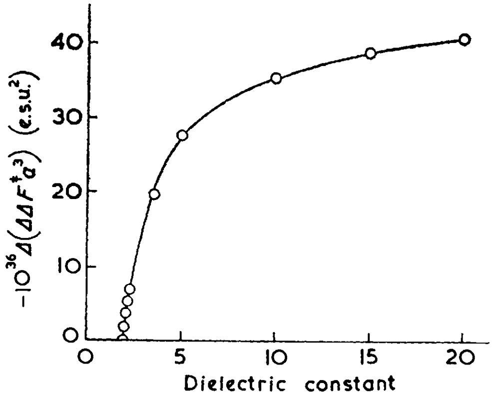

FIG. 3. Theoretical wavenumber shift plotted against dielectric constant; calculated from the Onsager equation.

According to Kamlet,[13] the difference in red shift between *p*-nitroaniline and *NN*-dimethyl-*p*-nitroaniline can be taken as a measure of the hydrogen-bonding effect. The shift due to hydrogen bonding, as measured by the separation of curves 1 and 3 in Fig. 1a, is at a maximum at a methanol concentration of about 3 mole l.$^{-1}$. It is possible that at this concentration there exists an optimum concentration of methanol monomer.

The significant red shift (—1320 cm.$^{-1}$) observed for *NN*-dimethyl-*p*-nitroaniline between carbon tetrachloride and dioxan solutions calls for special comment. In this case there is no possibility of suitable hydrogen bonding to the dimethylamino-group or to the nitro-group. Further, the dielectric constants of all the mixtures are very similar. It is probable that the red shift is still the result of dipole–dipole interaction although this is not reflected in the macroscopic dipole moment or dielectric constant of dioxan. Dipole–dipole forces vary with distance as the inverse fourth power and it is reasonable to suggest that, although dioxan has two opposed dipoles, the attractive interaction between the " positive " dimethylamino-group and the nearer " negative " oxygen atom is much stronger than other repulsive interactions at greater distances.

The unexpectedly large red shift for *p*-nitroaniline at low methanol concentrations could be the result of solvent sorting.[17] At low methanol concentrations the dielectric constant of the solvent surrounding the solute molecule may be considerably higher than that of the bulk of the solvent if methanol molecules predominate near the solute. The red shifts for *NN*-dimethyl-*p*-nitroaniline are, however, about the value expected from the bulk dielectric constant, which would not be the case if solvent sorting were significant.

I am very grateful to Professor B. M. Wepster for suggesting the topic and for many helpful discussions. I also thank the Technische Hogeschool, Delft, for its generous hospitality and the Department of Scientific and Industrial Research for a N.A.T.O. Fellowship.

THE TECHNISCHE HOGESCHOOL, DELFT, NETHERLANDS.
[Present address: UNIVERSITY COLLEGE, LONDON.]

[*Received, December 4th,* 1962.]

---

[17] Hyne, *J. Amer. Chem. Soc.*, 1960, **82**, 5129.