[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WESTERN AUSTRALIA]

The Perturbation of the Ultraviolet Spectrum of Nitromethane in Mixed Solvents, with a Note on Complex Formation

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The 2800 Å. band of nitromethane has been measured in nine binary mixed solvents, with benzene, toluene and dioxane as active solvents which increase the intensity. The results are considered in terms of the alternative hypotheses of 1:1 complex formation and of physical solvent perturbation. It is shown that the alternatives are equally compatible with experiment, leading to the conclusion that other cases of assumed 1:1 complex formation can be the result of a physical solvent perturbation. Complex formation and physical solvent perturbation are shown to be different in principle.

In a recent study[1] of the effect of solvents on the ultraviolet absorption of nitromethane and other compounds it was found that the intensity of the nitromethane (2800 Å.) band was about doubled in benzene relative to the other solvents used. Subsequent experiments showed similar increases of the intensity in toluene and dioxane as solvents. In order to study this perturbation further, we have now measured the nitromethane (2800 Å.) band in nine binary solvent mixtures using benzene, toluene and dioxane as active solvents, namely, as those that increase the intensity relative to the inactive solvents *n*-heptane, isoöctane, carbon tetrachloride, methanol and water.

Experimental

All materials used were carefully purified by standard methods,[2] and their physical constants (density and refractive index) were in close agreement with literature values.[3] The mole fraction compositions of the binary solvent mixtures were determined either by making them up by weight or by density determination and interpolation on the appropriate density–composition curve. The nitromethane solutions (approx. 0.01 *M*) were made up directly by weight, and the volume concentrations calculated from the determined density of the solvent.

The spectrophotometric measurements were made on a Beckman instrument, model DU, at room temperature (about 20°). The slit width employed varied to some extent from system to system but was kept constant within each system to ensure comparability of results. Appropriate cell-constant corrections were applied to all measurements, which were reproducible to within 2%.

Results

Table I summarizes the maximum extinction coefficients ϵ_x of the nitromethane 2800 Å. band in the nine binary solvent mixtures. We define ϵ by the usual relation $\log_{10} I_0/I = \epsilon cl$, where I_0 and I are the incident and transmitted intensities, c is the concentration of nitromethane in mole liter^{-1}, and l is the path length in cm. We use ϵ_x to denote the maximum of ϵ in a mixture where x is the mole fraction of the active solvent. Benzene, dioxane and toluene are the three chosen active solvents; but it is to be noted that benzene is active with respect to dioxane in mixtures of the two. Carbon tetrachloride has been used, perhaps arbitrarily, as an inactive solvent even though it intensifies the band almost as much as dioxane. A typical set of absorption curves is shown in Fig. 1 for heptane–dioxane and dioxane–benzene as solvents. In dioxane it is to be noted that the enhancement of the nitromethane (2800 Å.) band is accompanied by the development of a more intense band at higher frequency. We followed this band to the limit of the range of the instrument, not only in dioxane but also in isoöctane and in the vapor, and at 4.6 kilokayser the absorption was still rising steeply with $\epsilon \sim 1000$ (vapor), 2400 (isoöctane) and > 2500 (dioxane). It is obviously a rather intense band with its maximum probably in the vacuum region, and which is displaced progressively to lower frequency in the order vapor, isoöctane and dioxane, the low frequency toe appearing only in dioxane in Fig. 1. Owing to solvent absorption the band could not be observed in solvent mixtures containing benzene, toluene or carbon tetrachloride.

TABLE I

EXTINCTION COEFFICIENTS OF NITROMETHANE

(i) Benzene as active solvent with

Dioxane		*n*-Heptane		Carbon tetrachloride	
x	ϵ_x	x	ϵ_x	x	ϵ_x
0.000	22.7	0.000	16.7	0.000	20.8
.196	24.0	.238	19.1	.206	22.9
.454	25.8	.378	21.5	.448	25.2
.794	28.2	.504	23.5	.792	27.6
.975	29.3	.765	26.5	.885	28.0
1.000	29.1	1.000	29.1	1.000	29.1

(ii) Dioxane as active solvent with

Water		*n*-Heptane		Methanol	
x	ϵ_x	x	ϵ_x	x	ϵ_x
0.000	14.9	0.000	16.7	0.000	15.0
.091	17.9	.166	17.7	.158	17.9
.169	21.6	.339	19.3	.285	18.9
.346	22.0	.501	19.7	.422	19.7
.480	21.9	.584	20.0	.557	20.7
.696	22.0	.704	20.7	.698	21.1
.859	22.3	.842	21.2	.841	21.9
1.000	22.7	1.000	22.7	1.000	22.7

(iii) Toluene as active solvent with

Carbon tetrachloride		Isoöctane		Methanol	
x	ϵ_x	x	ϵ_x	x	ϵ_x
0.000	20.8	0.000	17.5	0.000	15.0
.158	20.9	.173	19.9	.181	20.6
.338	22.6	.339	21.1	.323	22.4
.518	23.9	.511	22.1	.485	24.8
.661	24.6	.646	23.3	.653	25.5
.810	26.1	.839	25.3	.834	26.0
1.000	26.7	1.000	26.7	1.000	26.7

For record purposes we give in Table II the values of ν_m and ϵ_m in the pure solvents; they agree well with values found previously by Bayliss and McRae.[1]

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[1] N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1006 (1954).

[2] A. Weissberger and E. Proskauer, "Organic Solvents," Oxford Univ. Press, New York, N. Y., 1935.

[3] J. Timmermans, "Physico-chemical constants of pure organic compounds," Elsevier Press, Houston, Texas, 1950; for nitromethane —C. J. Thompson, H. J. Coleman and R. V. Helm, THIS JOURNAL, **76**, 3445 (1954).

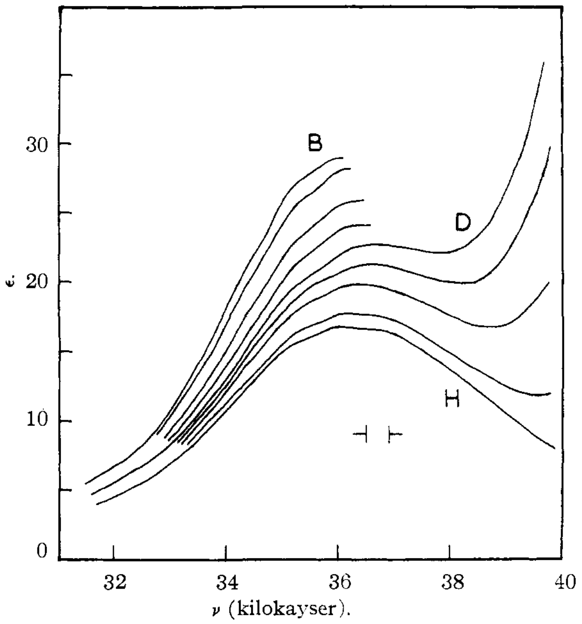

Fig. 1.—Nitromethane (2800 Å.) band in pure and mixed solvents: H, in pure *n*-heptane; D, in pure dioxane; B, in pure benzene. Intermediate curves refer to H–D and D–B mixtures, respectively. (Beckman spectrophotometer model DU; room temperature (20°); concn. approx. 0.01 *M;* path length 1 cm.; effective slit width 400 kayser.)

TABLE II

EXTINCTION COEFFICIENTS AND FREQUENCIES OF NITROMETHANE IN PURE SOLVENTS

Solvent	Benzene	Toluene	Dioxane	Carbon tetrachloride
ϵ_m	29.1	26.7	22.7	20.8
ν_m, kayser	36,000	35,400	36,700	36,000
Solvent	Isoöctane	*n*-Heptane	Methanol	Water
ϵ_m	17.5	16.7	15.0	14.9
ν_m, kayser	36,000	36,000	36,700	36,900

Discussion

In the literature there are many cases of solvent-induced perturbation of frequency and intensity that have been explained in terms of Lewis acid–base interaction forming 1:1 complexes between solvent (base) and solute (acid).[4–9] Since nitromethane is an acid and the active solvents benzene, toluene and dioxane are bases, an explanation of our results in terms of 1:1 complex formation must be considered. On the other hand, the perturbations in Fig. 1 are relatively small, so that the possibility must also be taken into account that the interaction is physical in nature. We therefore examine the results from the two theoretical viewpoints, which later will be shown to be distinct from one another in principle.

(a) **Assumption of 1:1 Complex Formation.**—In a mixture of an active and an inactive solvent, where x is the mole fraction of the active solvent, we consider the equilibrium for 1:1 complex formation

$$\text{nitromethane} + \text{active solvent} = \text{complex} \quad (1)$$

with the equilibrium constant $K = [\text{complex}]/x[\text{nitromethane}]$. In terms of our previous notation, ϵ_x is the maximum extinction coefficient of the nitromethane (2800 Å.) band, relative to the *total* nitromethane concentration. The maximum extinction coefficient in the pure inactive solvent is thus ϵ_0 $(x = 0)$, and in the pure active solvent is ϵ_1 $(x = 1)$. The maximum extinction coefficient of the postulated complex is denoted by ϵ_c. Then if equation 1 holds, Ketelaar, *et al.*,[10] have shown that

$$\frac{1}{\epsilon_x - \epsilon_0} = \frac{1}{(\epsilon_c - \epsilon_0)Kx} + \frac{1}{\epsilon_c - \epsilon_0} \quad (2)$$

This of course reduces to the Benesi–Hildebrand relation 4

$$1/\epsilon_x = 1/\epsilon_c Kx + 1/\epsilon_c \quad (3)$$

when ϵ_0 is very small compared with either ϵ_x or ϵ_c.

For reasons that will be apparent later, we transform equation 2 by introducing the factor $(\epsilon_1 - \epsilon_0)$ to give

$$\frac{\epsilon_1 - \epsilon_0}{\epsilon_x - \epsilon_0} = \frac{\epsilon_1 - \epsilon_0}{(\epsilon_c - \epsilon_0)Kx} + \frac{\epsilon_1 - \epsilon_0}{\epsilon_c - \epsilon_0} \quad (4)$$

Thus the existence of a complex according to (1) requires that the plot of $(\epsilon_1 - \epsilon_0)/(\epsilon_x - \epsilon_0)$ against $1/x$ shall be a straight line whose slope is $(\epsilon_1 - \epsilon_0)/K(\epsilon_c - \epsilon_0)$ and whose intercept on the axis $1/x = 0$ is $(\epsilon_1 - \epsilon_0)/(\epsilon_c - \epsilon_0)$.

One result of introducing the experimental factor $(\epsilon_1 - \epsilon_0)$ into equation 4 is to make the same scale of coördinates applicable to all cases regardless of the values of ϵ and K, since all the relevant straight lines must pass through the point (1, 1). The conformity of experimental results to the linear relations demanded by the essentially identical equations 2, 3 and 4 has been regarded by many authors as proof of the existence of 1:1 complex formation; however, the next section will show that similar linear, or almost linear, relations can be derived from the alternative hypothesis.

(b) **Assumption of a Physical Perturbation.**—We now examine the alternative that there is a physical perturbation of the intensity when solute and active solvent molecules are in close proximity in the solution. It will be seen that for present purposes the exact nature of the perturbation need not be specified. (In solutions with dioxane as active solvent it is not impossible that the perturbation is the contribution made by the far ultraviolet band to absorption in the 2800 Å. region; but our argument is equally valid if it has a different origin.)

Consider a solute nitromethane molecule surrounded by a cage of z nearest neighbor (n.n.) solvent molecules, where z is the average coördination number of the solute. In a mixed solvent some of the n.n. solvent molecules are of the active species,

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(4) H. A. Benesi and J. H. Hildebrand, THIS JOURNAL, **71**, 2703 (1949).

(5) (a) R. S. Mulliken, *ibid.*, **72**, 600 (1950); (b) **74**, 811 (1952); (c) *J. Phys. Chem.*, **56**, 801 (1952); (d) C. Reid and R. S. Mulliken, THIS JOURNAL, **76**, 3869 (1954).

(6) L. J. Andrews and R. M. Keefer, *ibid.*, **75**, 3776 (1953), and many papers in preceding years.

(7) H. McConnell, J. S. Ham and J. R. Platt, *J. Chem. Phys.*, **21**, 66 (1953).

(8) L. J. Andrews, *Chem. Revs.*, **54**, 713 (1954)—review.

(9) L. E. Orgel, *Quart. Rev. Chem. Soc.*, **8**, 422 (1954)—review.

(10) J. A. A. Ketelaar, C. van de Stolpe, A. Goudsmit and W. Dzcubas, *Rec. trav. chim. Pays-Bas*, **71**, 1104 (1952).

some of the inactive. We make the following simplified postulates:

(i) The perturbation is the result of the presence of active solvent molecules in the n.n. cage, and the effect of more distant active solvent molecules may be neglected.

(ii) The number of active solvent molecules in the n.n. cage in a mixed solvent is proportional to the mole fraction x of the active solvent. On the average therefore the cage consists of zx active and $z(1 - x)$ inactive solvent molecules. (This postulate is valid for ideal mixtures of molecules of equal size; it is probably a good approximation for regular solutions, but it will fail if there is a marked tendency to clustering on the part of one solvent species.)

(iii) The perturbation depends in some way on the number of active solvent molecules in the n.n. cage. The mode of this dependence is not easy to specify and may vary from case to case. One possibility would be to assume that the perturbation depends linearly on the number of n.n. active solvent molecules; this is most likely to be true if the perturbation is a weak one and if it is not too dependent on proper intermolecular orientation. Alternatively if the perturbation caused by one n.n. active solvent molecule is a strong one, the presence of additional active nearest neighbors may not be able to make it much greater; there could also be cases where it depends on favorable mutual orientation between the solute and active solvent molecules. Bearing these points in mind, the perturbation should be somewhere between the following extreme cases I and II : I. The perturbation is directly proportional to zx, the number of active solvent molecules in the n.n. cage. II. The perturbation reaches its maximum value when there is *one* active solvent molecule in the n.n. cage, and is not increased by the presence of additional n.n. active molecules.

I.—Case I obviously gives

$$\epsilon_x - \epsilon_0 = kzx \tag{5}$$

where the constant k must be subject to the condition that when $x = 1$

$$\epsilon_1 - \epsilon_0 = kz \tag{6}$$

Hence we derive the equation[11]

$$(\epsilon_1 - \epsilon_0)/(\epsilon_x - \epsilon_0) = 1/x \tag{7}$$

II.—The consequences of case II are obtained by considering an assembly of n.n. cages, each of z molecules, in which active and inactive solvent molecules in the ratio $x/(1 - x)$ are distributed at random. The probability that a cage shall contain *no* active solvent molecule is $(1 - x)^z$, and therefore the fraction of all cages that contain *at least one* active solvent molecule is $[1 - (1 - x)^z]$. The average observed ϵ_x would therefore be

$$\epsilon_x = (1 - x)^z\epsilon_0 + [1 - (1 - x)^z]\epsilon_1 \tag{8}$$

which leads directly to

$$\frac{\epsilon_1 - \epsilon_0}{\epsilon_x - \epsilon_0} = \frac{1}{1 - (1 - x)^z} = f(x,z) \tag{9}$$

Equation 7, case I, is of the same linear form as equation 4, but with the additional two restrictions that the straight line is of unit slope and also passes through the origin. This theoretical line is denoted by I in Figs. 2, 3 and 4. Equation 9, case II, implies that the plot of $(\epsilon_1 - \epsilon_0)/(\epsilon_x - \epsilon_0)$ against $1/x$ should be identical with that of $f(x,z)$ against $1/x$; this plot, labeled II, is shown in Figs. 3 and 4 for the assumed values of $z = 10$ and $z = 6$. (For closest packing of equal spheres one has $z = 12$; the value $z = 10$ is probably reasonable for a liquid, well below its boiling point, where solute and solvent molecules are of about equal size. If the solute is much smaller than the solvent, $z = 6$ is probably a closer approximation.) The relation between $f(x,z)$ and $1/x$ is not linear; but it is almost indistinguishable from linear for $1/x > 3$ (see Figs. 3 and 4).[12] Cases where the perturbing influence of the active solvent is intermediate between our assumed extremes I and II would be expected to give almost linear plots of $(\epsilon_1 - \epsilon_0)/(\epsilon_x - \epsilon_0)$ against $1/x$, and with slopes between the lines I and II in Figs. 2, 3 and 4.

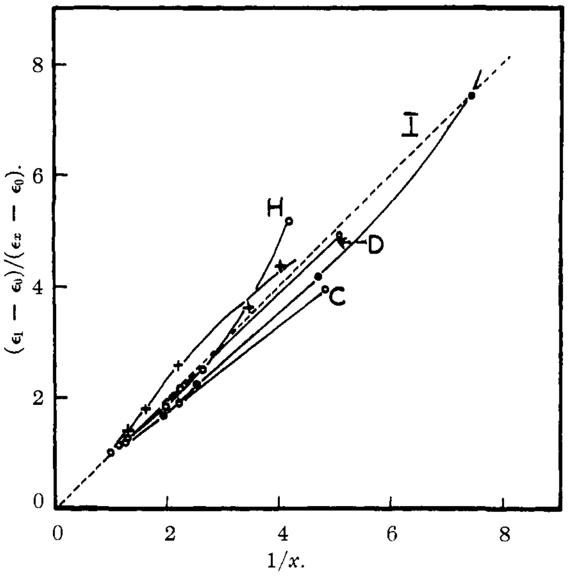

Fig. 2.—Plot to show application of equation 7: I, theoretical line of perturbation hypothesis I; H, D,C, nitromethane in benzene–heptane, benzene–dioxane, and benzene–carbon tetrachloride, respectively: ●, SO_2 in benzene–carbon tetrachloride (ref. 17); ×, oxalyl chloride in benzene–heptane (ref. 18).

Comparison with Experimental Results.—We have plotted $(\epsilon_1 - \epsilon_0)/(\epsilon_x - \epsilon_0)$ against $1/x$ for benzene as the active solvent in Fig. 2 and for toluene and dioxane as active solvents in Fig. 3. Considering Fig. 2, the results in benzene–dioxane mixtures lie almost exactly on the theoretical broken straight line I of equation 7. The benzene–heptane results lie on a curve which in its lower portion coincides with the same line I. The benzene–carbon tetrachloride figures are linear but have a slope slightly less than the required unit gradient of I. Within experimental error and the validity

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[11] A more elaborate derivation, considering as in II the random distribution of active and inactive solvent molecules among an assembly of cages, leads to exactly the same result.

[12] For $1/x$ less than 3 it turns rather abruptly into an almost horizontal line to the point (1,1). For $1/x$ less than unity, the mathematical behavior of $f(x,z)$ is complicated; but in this region $1/x$ and also equations 2, 3, 4, 7 and 9 are physically meaningless.

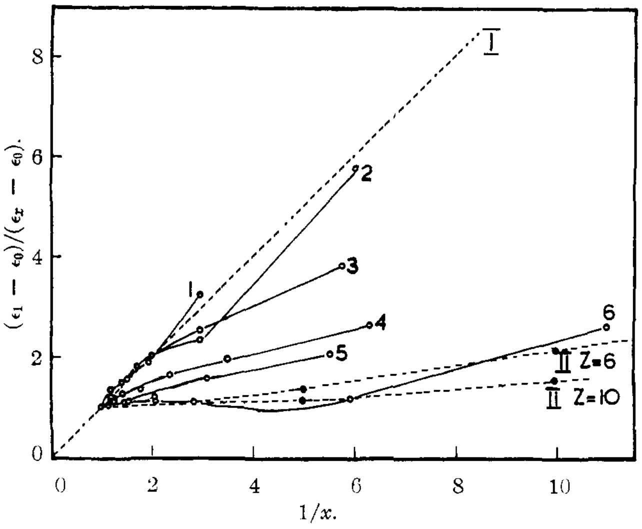

Fig. 3.—Application of equations 7 and 9: I, II, theoretical lines of perturbation hypotheses I and II. Experimental points are for nitromethane in (1) toluene–carbon tetrachloride; (2) dioxane–heptane; (3) toluene–isoöctane; (4) dioxane–methanol; (5) toluene–methanol; (6) dioxane–water.

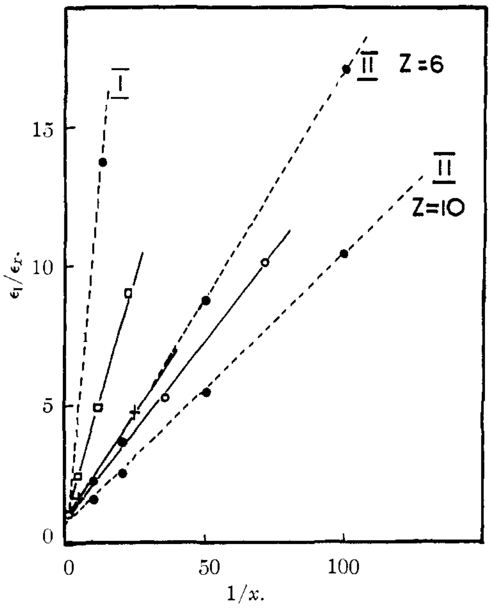

Fig. 4.—Application of equations 7 and 9 to iodine spectra (ref. 4): ●, theoretical points of perturbation hypotheses I and II; □, iodine in benzene–carbon tetrachloride; ×, iodine in mesitylene–heptane; ○, iodine in mesitylene–carbon tetrachloride.

of our assumptions, the results in Fig. 2 conform therefore well to the requirements of physical hypothesis I. Considered in the light of equation 4 for complex formation, strict conformity with line I would represent the limiting case of $K = 0$ and $\epsilon_c = \infty$; all actual cases involving finite values of K and ϵ_c would necessarily have a gradient less than unity. This is not the case with the benzene–heptane results, but by plotting the benzene–dioxane and benzene–carbon tetrachloride results on a larger scale, and taking experimental error into account, we found it possible to obtain straight lines that were consistent with values of K of the order of 0.1 and of ϵ_c of the order of 100.

Thus in Fig. 2 the results in benzene as active solvent are on the whole compatible both with weak 1:1 complex formation and with the assumption of a physical perturbation (I), since it is extremely difficult experimentally to distinguish between an extrapolation precisely to the origin as required by equation 7 and one that is close to the origin as demanded by equations 3 and 4 if ϵ_c is even moderately large. This difficulty, which is associated with the appearance of ϵ_c in the denominator of the constant term in equations 3 and 4, has been noted by Andrews[8] in connection with the determination of ϵ_c from the Benesi–Hildebrand equation 4.

In Fig. 3, curves 1, 2 and 3 with carbon tetrachloride, heptane and isoöctane as inactive solvents depart from linearity but in their lower portions conform well to the physical hypothesis I. Curves 4, 5 and 6 with methanol and water as inactive solvents show greater deviations from I and from linearity. Although they tend toward the curves II, we prefer in terms of the assumption of a physical interaction to regard them as indicative of the expected departure from the ideal or the regular solution when one component is hydroxylic. Even taking experimental error into account, it is difficult to reconcile Fig. 3 with the assumption of complex formation since, to take an example, curves 1 and 5 if smoothed to straight lines obviously extrapolate to widely discordant values of ϵ_c for the toluene–nitromethane complex.

Application to Other Cases.—There are other cases in which physical perturbation has been suggested as an alternative to 1:1 complex formation. Thus Schuler and Schuler[13] find that their results for iodine spectra in alkyl iodides are more compatible with the physical concept. Also the search for the expected infrared spectra of iodine complexes with solvents such as benzene and mesitylene has been rather unsuccessful,[14–16] leading Haller, Jura and Pimentel[16] to state that it is "neither possible nor necessary to differentiate between weak complex formation and strong solvent perturbation." (However we show below that the differentiation is both possible and necessary.) It is therefore pertinent to reconsider in terms of equations 7 and 9 at least some typical cases where the existence of 1:1 complexes has been deduced as a result of conformity with equations 2 and 3. Unfortunately few of the papers in the extensive literature[8,9] provide enough detail to replot the experimental data, but we have been able to select four examples involving a range of apparent K values. In Fig. 2 we have superimposed on our own results the data of Andrews and Keefer[17] for sulfur dioxide in benzene-carbon

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(13) D. E. Schuler and R. H. Schuler, This Journal, **76**, 3092 (1954).

(14) N. S. Ham, A. L. G. Rees and A. Walsh, *Nature*, **169**, 110 (1952); *J. Chem. Phys.*, **20**, 1336 (1952).

(15) D. L. Glusker, H. W. Thompson and R. S. Mulliken, *ibid.*, **21**, 1407 (1953).

(16) W. Haller, G. Jura and G. C. Pimentel, *ibid.*, **22**, 720 (1954).

(17) L. J. Andrews and R. M. Keefer, This Journal, **73**, 4169 (1951).

tetrachloride, and those of Saksena and Kagarise[18] for oxalyl chloride in benzene–heptane, both being cases where weak complex formation has been postulated. It is evident from Fig. 2, firstly, that the data are not strictly linear as required by either equation 4 or 7 and, secondly, that subject to the departures from linearity they fit closely to the physical hypothesis expressed by the theoretical line I of unit slope. In Fig. 4 we have replotted on a different scale the data of Benesi and Hildebrand[4] for iodine in benzene–carbon tetrachloride, mesitylene–heptane and mesitylene–carbon tetrachloride. These are cases where the perturbation of the ultraviolet spectrum of iodine by the active solvents benzene and mesitylene is very much greater than the other perturbations considered hitherto in this paper, and where the K values are correspondingly greater. Thus it is significant that the iodine–mesitylene results are very close to the lines II in Fig. 4 that are predicted by equation 9; that is they are consistent with a strong physical perturbation that reaches its maximum when one mesitylene molecule is in the n.n. cage. It is also to be noted that the theoretical lines II, though not straight, could hardly be distinguished experimentally from straight lines. The iodine–benzene results in Fig. 4 are consistent with a physical perturbation whose dependence on the number of active solvent molecules in the n.n. cage lies between the extremes of our hypotheses I and II.

Interpreted on the basis of 1:1 complexes, the slopes of the experimental lines in Figs. 2, 3 and 4 are related to $1/K$. We believe it to be significant that a high proportion of the 1:1 complexes reported in the literature have values of K that are small and that lie within a narrow range; out of 41 cases we have examined concerning I_2, Cl_2, ICl and SO_2 as solutes, only 8 have K greater (and then not much greater) than the value $K = 7.2$ for iodine–mesitylene. Thus the great majority, if plotted on Fig. 4, would have slopes lying within the limits imposed by our hypotheses I and II.[19] The important consequence is that conformity with equations 2–4 is of itself not sufficient to distinguish between 1:1 complex formation and a physical perturbation in cases where the apparent K is of the order of that for iodine–mesitylene or less.

Distinction between Complex Formation and Physical Perturbation.—There is an important difference between the two concepts which lies in the relation of the solute molecule to the perturbing or active solvent. If 1:1 complexes exist, then even in a pure active solvent there are at any instant two species of solute molecule—those that are "free" or unperturbed, and those that are complexed. If however the perturbation is physical, *every* solute molecule in a pure active solvent undergoes the perturbation. Taking nitromethane in pure benzene as an example, with an apparent $K = 0.1$, complex formation requires that (at any given time) 90% of the dissolved nitromethane molecules are unperturbed, even though each is surrounded by an n.n. cage of solvent benzene molecules. In contrast, the physical hypothesis requires the perturbation of every nitromethane molecule in pure benzene, and in a mixed solvent of every nitromethane that has at least one benzene molecule in the n.n. cage. Expressed in other words, complex formation involves the chemical concept of saturation of the perturbation by one active solvent molecule, and even in this sense is different from our extreme hypothesis II in that it also involves equilibrium between two distinct solute species. A generalized physical perturbation may achieve saturation as in the extreme case II, but it excludes the concept of two distinct solute species in a pure active solvent.

Conclusion

We have shown that the spectrophotometric evidence of itself does not enable a decision to be made between the alternatives of 1:1 complex formation and physical perturbation, provided the interaction is weaker than, or perhaps not much stronger than, that between iodine and mesitylene. Although the evidence for the specifically 1:1 nature of the complexes is largely spectrophotometric, there is a great body of other evidence that has been cited in favor of complex formation in general,[8,9] including the theoretical work of Mulliken[5] and the relations that have been found between complex formation and the electron donor and acceptor properties of solvent and solute.[7,20] It is beyond the scope of this paper to review the evidence in detail; we suggest however that physical perturbation would probably be strong between neighboring electron donors and acceptors although there seems to be no quantitative theory of such an effect, and also that Mulliken[5b] has indicated the extension of his own theory to what he terms n:1 complexes, which in the case of weak interaction might be indistinguishable from what we have called a generalized physical perturbation.

Acknowledgment.—We acknowledge the assistance given by the Research Fund of the University of Western Australia.

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(18) B. D. Saksena and R. E. Kagarise, *J. Chem. Phys.*, **19**, 994 (1951).

(19) A referee has suggested that this statement is invalid in view of the "huge increases" reported by Ham (THIS JOURNAL, **76**, 3875 (1954)) for the K values of iodine complexes at 77°K. We agree with the criticism if Ham's values can be confirmed; but in the meantime we suggest that they should be treated with reserve. They are not experimental values, but have been calculated using the standard equation $d \ln K/dT = \Delta H/RT^2$ with the assumption that ΔH remains constant in the temperature range 298–77°K. Since ΔH is the small difference between the much larger H values of the substances concerned, and since these H values decrease markedly as T decreases, it would be remarkable if the assumption of constant ΔH were true. Quite small changes in ΔH in either direction cause *very large* changes in the calculated K values in *either* direction.

(20) S. H. Hastings, J. L. Franklin, J. C. Schiller and F. A. Matsen, *ibid.*, **75**, 2900 (1953).