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The Spectra of Iodine Solutions. II. The Effects of High Pressures upon Iodine Complexes[1]

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Absorption spectra of dilute solutions of iodine and aromatic molecules in *n*-heptane have been studied at 2000 atmospheres pressure. Shifts of about 4 mμ to longer wave lengths are observed for the charge-transfer peak in the near ultraviolet at high pressures. These shifts are attributed to the effect of an increase in the index of refraction resulting from compression of the solvent. Data taken for these iodine–aromatic complexes in non-polar solvents at atmospheric pressure support this hypothesis. These data indicate a large effect of solvent on the charge-transfer peak position. Several attempts to find the charge-transfer absorption in the vapor phase were unsuccessful. Observed increases in the absorption of the charge-transfer bands are attributed to an increased concentration of the complex, due to a shift in equilibrium in solutions at high pressures.

Introduction

This paper reports a study of iodine solutions at high pressures which was undertaken in an effort to learn more about molecular complexes in general and, specifically, more about the iodine–aromatic complexes.

The effect of high pressures upon solution spectra is generally quite small except in those cases where some type of association or complex formation takes place. Earlier studies by Wick have disclosed only a small effect of pressure on the spectra of aqueous solutions of rare earth salts in the visible region[3]; and Collins found no effect upon the harmonics of infrared bands of water and toluene even up to 5000 and 8000 atmospheres.[4] Gibson and Loeffler studied the visible and near ultraviolet absorption spectra of a number of mixtures of aromatic amines with nitro and nitroso compounds under changes in pressure and temperature.[5] Although both components showed little pressure effect by themselves, the mixtures showed a large increase in absorption at high pressures at some wave lengths in the near ultraviolet where both components individually were transparent. This is the wave length region where donor–acceptor complexes have their charge-transfer (CT) absorption.[6] In order to explore further the effect of pressure in cases where complex formation seems probable, various iodine solutions, which are much better understood theoretically than the nitroaromatic complexes, were studied under pressure.

Experimental

In Fig. 1 is shown the design of the high pressure bomb used for the present study. It is identical with the design of the bomb used by Jacobs in a study of alkali-halide crystal color centers under pressure.[7] This design is adapted for spectroscopic studies in conjunction with a Beckman DU spectrophotometer. It has a sample volume $^1/_2''$ in diameter and $1''$ long, enclosed in a steel casing. This volume held, in the present study, a cell containing the solutions being studied. The piston, shown in Fig. 1 as a piston intensifier, was used in the present study solely as a fluid separator to keep the pump fluid (DC-200 silicone oil) from mixing with the heptane around the cell. A Bourdon type pressure gage (Crosby Co.) was used to register the pressure up to the limit used in these experiments, which was 30,000 lb./sq. in. or 2000 atmospheres.

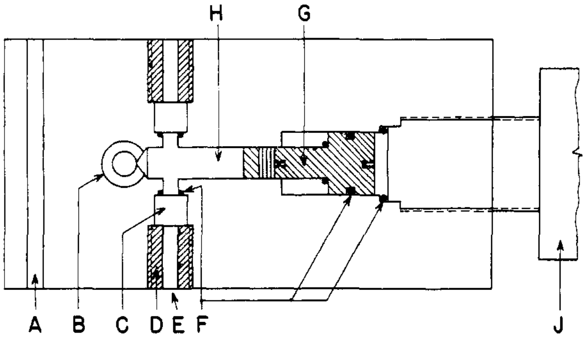

Fig. 1.—Schematic drawing of pressure bomb taken from ref. 7: A, reference hole; B, gage plug hole; C, synthetic sapphire window; D, window plugs; E, observation hole; F, O-rings; G, piston intensifier; H, sample region; J, portion of pump.

Two principal problems arise in any spectrophotometric study of solutions at high pressures. First, the bomb must have windows which transmit the desired radiation and can withstand the high pressures. This was solved by using cylindrical windows of artificial sapphire $^1/_2''$ in diameter and $^1/_2''$ long, sealed with neoprene "O" rings.[7] These unoriented crystals, from Linde Air Products Co., did not break in the pressure range used.

The ultraviolet limit of the spectral studies was set by the transparency of the sapphire windows which had a weak absorption beginning at 270 mμ and which increased rapidly at 230 mμ. Since some thin samples of sapphire are known to transmit to 150 mμ,[8] the observed absorption may have been due to impurities in the artificial sapphires. If more transparent sapphires could be obtained, it would be possible to extend the usable spectral range for high pressure measurements down to the limit of the Beckman spectrophotometer (about 210 mμ).

The second principal problem is to keep the solutions in the light path free from absorbing substances that come from materials used in the construction of the bomb. If an internal cell is used, this problem reduces to the problems of keeping the pressure fluid as clean as possible, of reducing the light path through the pressure fluid as much as possible, and of designing a suitable cell. The pressure fluid, heptane, was discolored very rapidly at first by the neoprene "O" rings, but this discoloration was largely eliminated by presoaking the rings in heptane at atmospheric pressure for several days, after which little further discoloration took place. The light path through the pressure fluid was reduced by inserting two polished quartz slugs between the cell and the bomb windows so that the light passed through less than 0.5 mm. of the heptane pressure fluid surrounding the cell. Thus, the effect of any discoloration of the heptane

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[3] F. G. Wick, *Proc. Am. Acad. Arts Sci.*, **58**, 555 (1923).

[4] J. R. Collins, *Phys. Rev.*, **36**, 305 (1930).

[5] R. E. Gibson and O. H. Loeffler, THIS JOURNAL, **62**, 1324 (1940).

[6] J. Landauer and H. McConnell, *ibid.*, **74**, 1221 (1952).

[7] I. Jacobs, *Phys. Rev.*, **93**, 933 (1954).

[8] H. B. Klevens and J. R. Platt, THIS JOURNAL, **69**, 3055 (1947).

pressure fluid by the gaskets, or by the silicone oil leaking around the fluid separator, was greatly reduced.

The cell shown in Fig. 2 consisted of a piece of 12 mm. Pyrex tubing, sealed at one end and held in a brass holder. The tubing had part of two sides ground off and two quartz windows were cemented into place by araldite cement. The holder consisted of two brass pieces held together by two bronze strips. A threaded hole in the top brass piece served in placing the cell in the bomb and in extracting it from the bomb. A screw in the bottom piece of the holder pressed the glass tubing and the Teflon cover fitting over the open end of it against the top holder piece to seal the cell.

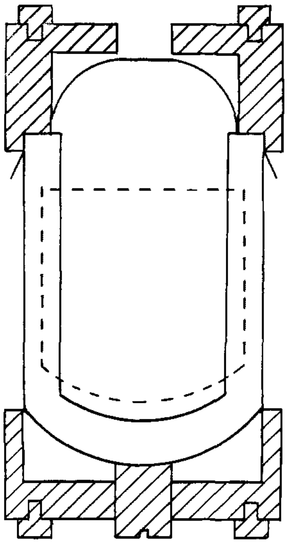

Fig. 2.—Cross section of cell to go into high pressure bomb. Shaded area is brass. Dashed line indicates the position of one of the quartz windows. Bronze strips, attached to the screws on the upper and lower portions of the cell, holding the Teflon cap onto the glass tubing, are not shown.

There is a change in volume upon compression of about 16% for hydrocarbon solutions at 2000 atmospheres so that some allowance must be made for this in any cell design. Previous workers had used either no cell at all (the solutions filled the entire sample volume)[3,4] or else, a mercury seal was used to take up the change in volume.[9] Neither of these possibilities is feasible with iodine solutions because of the chemical reactivity of iodine.

The large change in volume upon compression was taken up by the flexible bulge in the Teflon cover sheet in the present cell. This bulge was shaped from Teflon sheet (0.002" thick) by heating the Teflon to its softening temperature and pressing it into a mold. It was sufficiently flexible so that, as the solution inside the cell was compressed, the bulge would collapse, thus transmitting the pressure into the cell. Although Teflon is a rather difficult material to handle, it was the only material found suitable for a flexible cap which was chemically inert to heptane, aromatic hydrocarbons and iodine.

Unfortunately, the Teflon was difficult to seal well, and occasionally the solution leaked slightly around the edge. To prevent such leaks, liquid porcelain was painted over the edge of the membrane extending from under the brass top. When the porcelain dried, it prevented these small leaks, yet was not in direct contact with the solution being studied.

The choices of solvents and concentrations for solution studies are severely limited by high pressures. Many of the normal solvents are completely unsuitable for use under pressures because they freeze. For example, CCl_4 freezes at 25° at about 800 atmospheres.[10] Also, solubilities decrease rapidly under pressure so that two solvents which are completely miscible at room temperature, such as *n*-heptane and benzene, develop two separate phases over a considerable concentration range at pressures as low as 1000 atmospheres. This necessitated the use of dilute aromatic solutions in heptane with sufficient iodine concentration to bring the optical density of the CT absorption into the range of the spectrophotometer. This procedure seemed to solve the problem, and, in the cases reported here, no evidence of freezing or signs of instability, such as a striated appearance, were noted.

Results at High Pressures

Figures 3 and 4 show optical densities at 1 and 2000 atmospheres pressure of the iodine solutions in heptane containing benzene and mesitylene, respectively. The absorption near 290 mμ in the solution containing benzene and near 333 mμ in the solution containing mesitylene are the CT absorptions of the iodine complexes.[11] The effect of pressure upon this absorption is to increase its in-

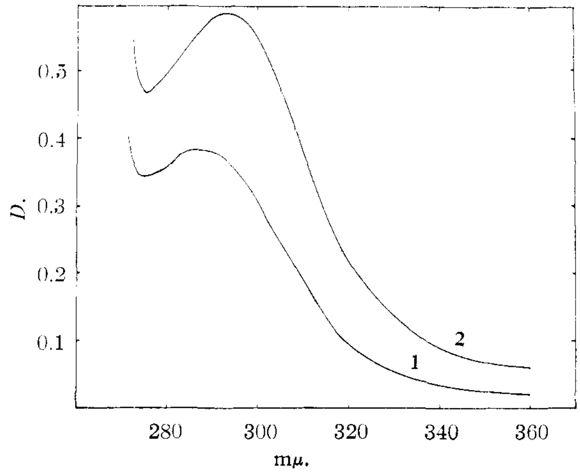

Fig. 3.—The charge-transfer band of the benzene–iodine complex at atmospheric pressure and at high pressures. The background absorption of the solvent and cell were subtracted but not that of the donor and acceptor. The path length of the cell was 0.61 cm. Solvent was *n*-heptane. Concentrations were: $C_I = 1.2 \times 10^{-3}$ mole/l., $C_B = 1.6 \times 10^{-1}$ mole/l. Curve 1 is at atmospheric pressure and curve 2 is at 2000 atmospheres. (The absorption at high pressures is not corrected for the contraction of the solvent.)

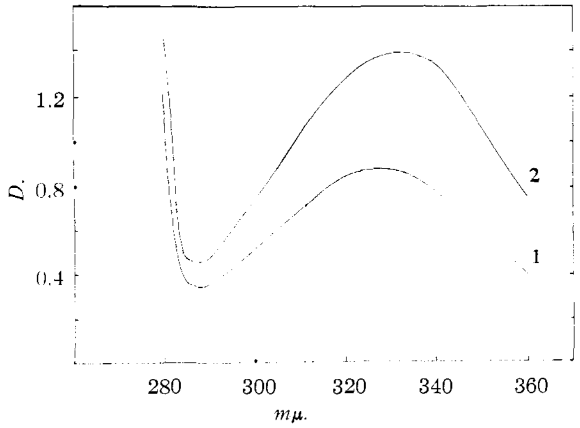

Fig. 4.—The same as Fig. 3 but for the mesitylene–iodine complex. Concentrations were: $C_I = 2.4 \times 10^{-3}$ mole/l.; $C_M = 9.8 \times 10^{-2}$ mole/l.

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[9] R. E. Gibson and J. F. Kincaid, THIS JOURNAL, **60**, 511 (1938).

[10] P. W. Bridgman, "Physics of High Pressures," G. Bell and Sons, London, 1949.

[11] (a) H. A. Benesi and J. H. Hildebrand, THIS JOURNAL, **71**, 2703 (1949); (b) R. S. Mulliken, *ibid.*, **74**, 811 (1952).

tensity, and to shift it slightly to longer wave lengths. The peak positions of the CT band at 1 and 2000 atmospheres pressure are given in Table I along with the ratio of the optical densities at the peak.

TABLE I

THE WAVE LENGTHS OF THE CHARGE-TRANSFER MAXIMA AT ATMOSPHERIC PRESSURE AND 2000 ATMOSPHERES AND THE CHANGE IN OPTICAL DENSITY AT THE CT PEAK FOR IODINE COMPLEXES WITH BENZENE, TOLUENE AND MESITYLENE

The effective change in volume, ΔV, upon complexing in solution is also given. This is calculated from the ratio of optical densities under the assumption that the molar extinction coefficient of the complex remains unchanged.

Donor	Concn., mole/l.	K^a	$\lambda_{\max}$ at 1 atm., mμ	$\lambda_{\max.}$ at 2000 atm., mμ	D_{2000}/D_1	ΔV, cc./mole
Bz	0.160	0.15	288	293	1.51	−1.5
Tol	.264	.16	327	331	1.53	−1.7
Mes	.098	.82	372	375	1.69	−3.3

[a] From L. J. Andrews and R. M. Keefer, THIS JOURNAL, **74**, 4500 (1952), in liter/mole units.

The visible absorption of iodine alone in *n*-heptane with $\epsilon_{\max}$ 910 at 520 mμ exhibits no pressure effect other than an increase in intensity due to the increased concentration of iodine in the light path at high pressures, resulting from compression of the solution. In the solutions containing iodine complexes under pressure, the visible band broadens on the blue side as a result of more iodine being driven into the complex. The presence of large quantities of uncomplexed iodine remaining in the solutions, however, prevents any estimate being given for the shift produced by pressure in the visible band of iodine complexes, since the visible bands of complexed and uncomplexed iodine overlap considerably.

Discussion of Frequency Shift

The frequency shift of the CT band under pressure is of the same order of magnitude as the shifts between iodine solutions in different inert solvents at atmospheric pressures,[12] and may be understood as an index of refraction effect. The effect of the solvent upon electronic transitions is a very complicated interaction and has not been satisfactorily treated theoretically. Bayliss[13] has attempted to explain the influence of non-polar solvents on electronic transitions.

One model Bayliss uses is an oscillating point dipole at the center of a spherical cavity of radius a in an infinite dielectric. The interaction energy is $-\mu R/2$, where μ is the dipole moment and R is the reaction field given by

$$R = \frac{2\mu}{a^3} \times \frac{n^2 - 1}{2n^2 + 1}$$

where n is the index of refraction for the wave length of the absorbed light. This results in a formula giving the frequency shift for going from the vapor phase to a solution

$$\Delta\sigma \sim 10^{10}\frac{f}{\sigma a^3} \times \frac{n^2 - 1}{2n^2 + 1}$$

where f is the oscillator strength of the transition.

Figure 5 shows the position in kilokaysers[14] of the CT band for the iodine complexes of benzene, mesitylene and hexaethylbenzene in heptane and other inert solvents at 1 atmosphere, and in heptane at 2000 atmospheres pressure, plotted against the quantity $(n^2 - 1)/(2n^2 + 1)$ for the solvent. Although the index of refraction at the CT wave length should be used, this is not known in all cases. The value of n for the sodium-D lines was used which makes only a small difference in the relative values of $(n^2 - 1)/(2n^2 + 1)$ for different solvents.[13,15] In order to estimate the index of refraction of heptane at high pressures, the empirical relation

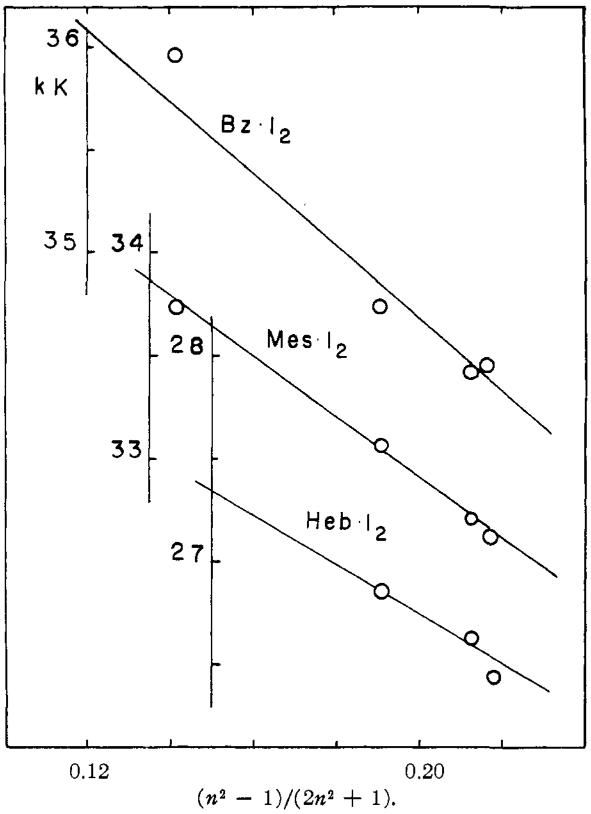

Fig. 5.—Position of the CT maximum of the iodine complexes of benzene, mesitylene, and hexaethylbenzene *vs.* $(n^2 - 1)/(2n^2 + 1)$, where n is the index of refraction of the solvent. The different solvents used were, from left to right, perfluoroheptane, *n*-heptane, CCl_4 and *n*-heptane at 2000 atmospheres pressure. Ordinates in kilo·kaysers.

$$\rho \propto \frac{n^2 - 1}{n^2 + 0.4}$$

which is found to be valid in the case of benzene at high pressures, was used.[9] The density, ρ, increases by a factor 1.16 for heptane between atmospheric

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[12] An unusual example of the shift of the CT band in different solvents is given by C. Reid and R. S. Mulliken, THIS JOURNAL, **76**, 3869 (1954), who found the CT band of the pyridine–iodine complex at 235 mμ in heptane solvent and at 245 mμ in pyridine, which is well within the absorption region of the pyridine.

[13] N. S. Bayliss, *J. Chem. Phys.*, **18**, 292 (1950). (In this paper, Bayliss attempts to explain the CT bands of halogen solutions as perturbed N–V transitions of the halogen. See ref. 19 for evidence against this application of the dielectric shift theory.)

[14] Kilokayser (formerly 10^3 cm.$^{-1}$). See "Transactions of the Joint Commission for Spectroscopy," *J. Opt. Soc. Am.*, **43**, 410 (1953).

[15] N. D. Coggeshall and A. Pozefsky, *J. Chem. Phys.*, **19**, 980 (1951)

pressure and 2000 atmospheres (at 27°) as interpolated from a table given by Bridgman.[10] This gave an estimate of n_D 1.482, at this pressure. Using the theoretical proportionality (Clausius–Mosotti)

$$\rho \propto \frac{n^2 - 1}{n^2 + 2}$$

a slightly different value, n_D 1.478, would be predicted, but the difference is too small to show in Fig. 5. The line shown in Fig. 5 is a straight line as predicted by the theory. It extrapolates to a vapor position of 265 mμ for the CT band of the benzene complex.

There are reasons, however, to question the validity of the Bayliss formula. Experiments show that it definitely does not apply to polar solvents,[16] and even in non-polar solvents it is not very satisfactory.[16b] One of the best test cases of the Bayliss theory is the absorption of mercury atoms in solution. A transition of an atom in solution more closely approaches the assumptions of a point dipole in a spherical cavity in a dielectric than do molecular transitions, and the sharpness of the atomic spectral lines permits accurate measurements of wave length shifts. The three non-polar solvents tested fall on a straight line when the shift is plotted against $(n^2 - 1)/(2n^2 + 1)$, but this line fails to extrapolate to the correct vapor position.[16b] Similar failures to extrapolate correctly to the position for the vapor phase have been observed also for molecular spectral shifts, even though the points for non-polar solvents fall on a straight line.[13]

The partial success of the theory indicates that the index of refraction (or something related to it such as the polarizability) is probably correlated with the wave length shifts of strong electronic transitions in different solvents. The failure of the theory to extrapolate correctly to the vapor phase indicates either that the shift has a different dependence on the index of refraction than given by Bayliss, or else that the index of refraction effect is superimposed upon other effects.

It is possible that pressure compresses the complex so that the average intermolecular distance is reduced at high pressures. Shuler[17] has used a rather crude free-electron model to describe complexes, and has predicted a red shift in the CT spectra due to a decrease in the intermolecular distance at high pressures. This change in intermolecular distance seems to be small since the changes in the spectrum with pressure are of the same order of magnitude as the changes in different solvents where the intermolecular distance of the complex almost certainly remains unchanged. He uses data for a small red shift of the benzene 260 mμ bands in isoöctane at high pressure as evidence for benzene–benzene complexes. This, however, cannot be considered as evidence for complexes in solution since shifts of comparable magnitude occur in various solvents at atmospheric pressure.[18]

Vapor Phase Studies

It has been assumed in previous theoretical calculations of the position of the CT band that it would be at approximately the same position in the vapor phase as in solution.[11b,19] Figure 5 indicates that the effect of the solvent may amount to 4000 kayser, although the extrapolation to the vapor phase, as mentioned above, is quite unreliable.

The presence of CT absorption in the vapor phase has never been clearly demonstrated although the very large collision diameters of iodine with pyridine and ether[20] suggest that complexes do occur to some extent in the vapor phase. Several unsuccessful attempts were made in the present study to find a suitable pair of molecules for vapor phase studies. Bromine was chosen as an acceptor since it has a much higher vapor pressure than iodine, and since quite high vapor pressures should be needed to get an appreciable concentration of complex in the vapor phase because of the small size of the equilibrium constant. Unfortunately, several of the donors that had high vapor pressures (ether, cyclohexene) reacted too readily, and even benzene reacted with bromine in ultraviolet light to form a scum on the windows. These attempts to find the CT absorption in the vapor phase were finally abandoned.

Intensity Changes under Pressure

The increase in optical density at the CT peak of the complex as given in Table I is partly due to the fact that the compression of the solvent increases the concentration of the components in the light path. For a molecule in solution, this would produce a 16% increase in absorption. For a complex which depends upon the concentration of two components, the increase would be about 34% if the equilibrium constant

$$K = \frac{C_{AD}}{C_A C_D}$$

where C_{AD}, C_A and C_D are the molar concentrations, remains unchanged. Actually, the large compression of the solvent probably affects the complex in much the same way as does a change from one inert solvent to another. A different inert solvent is thought to produce only small changes in the molar extinction coefficient of the complex, but to cause large changes in the equilibrium constant.[21]

These changes in equilibrium constant with different solvents are understandable when one uses the true thermodynamic equilibrium constant, including the activity coefficients of the various species present. The activity coefficient, γ_1, of a solute can be estimated by the formula[9]

$$\log \gamma_1 = \frac{V_1 \phi_s^2(\delta_1 - \delta_s)^2}{4.575T}$$

where V_1 is its molar volume and δ_1 is its solubility parameter. The ϕ_s is the volume fraction of the solvent and δ_s is its solubility parameter. For *ideal* solutions, the activity coefficient is unity, but for the class of *regular* solutions, which includes iodine solutions in inert solvents, it may be very large (over 1000 for iodine in perfluoroheptane). The activity

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(16) (a) R. Schnurmann and W. F. Maddams, *J. Chem. Phys.*, **19**, 1430 (1951); (b) M. K. Phibbs, *ibid.*, **18**, 1679 (1950).

(17) K. E. Shuler, *ibid.*, **20**, 1865 (1952); **21**, 765 (1953).

(18) K. Lauer and R. Oda, *Ber.*, **69**, 851 (1936).

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

(20) W. Luck, *Z. Elektrochem.*, **56**, 870 (1952).

(21) T. M. Cromwell and R. L. Scott, THIS JOURNAL, **72**, 3825 (1950).

coefficient of the iodine complex is about equal to the product of those of the iodine and donor at atmospheric pressures,[10a] so that the measured equilibrium constant is of the same order of magnitude as the true thermodynamic one. But changes in the inert solvent (or possibly increases in the pressure) can readily upset this partial cancellation so as to produce moderate changes in K.

Another factor that can change the equilibrium constant at high pressures is that the volume of the complex is probably slightly smaller than the sum of the molecular volume of the components, so that this would produce an increase in the equilibrium constant at high pressures.[22] There is a general thermodynamic relation which connects the effective change in volume upon complexing to the change in equilibrium constant

$$\left(\frac{\partial F}{\partial P}\right)_{\mathrm{T}} = RT\left(\frac{\partial \ln K}{\partial P}\right)_{\mathrm{T}} =$$

This effective change in volume, ΔV, includes, besides the change in volume that would take place in the vapor phase upon complexing, the effect of pressure upon the solubilities of the initial and final solutions, *i.e.*, the changes in the activity coefficients with pressure. Table I gives the resulting changes in effective volume computed from the observed changes in optical density assuming the extinction coefficient of the complex remains unchanged. These volumes are comparable in magnitude to the difference of the molar volumes of mixing of iodine with toluene (3.3 cc./mole) and heptane (5.4 cc./mole),[23] which are obtained by using an extrapolated molar volume of liquid iodine from high temperatures. Note that the volume of mixing is positive in toluene even though iodine forms complexes with it, and the complex probably has a smaller molecular volume than the sum of the molecular volumes of the components.

A positive change in volume upon mixing of some of the aromatic amines and nitro compounds[24] and an increase in absorption with pressure led Gibson and Loeffler to discard the idea of complexes in solution.[5] They reasoned that a positive change in volume upon mixing meant that pressure should destroy complexes in solution. This idea has been questioned by Weiss,[22] on the grounds that the macroscopic positive change in volume upon mixing probably has nothing to do with the molecular change in volume upon complexing, but has to do with something else, possibly the polar nature of the solvents. Thus, it seems possible that the change in volume upon complexing is negative even though the volume upon mixing is positive.

Conclusion

We see that the iodine complexes are favorable experimental material for pressure studies because their CT bands are much sharper and more separated from the component absorption regions than in the systems studied by Gibson and Loeffler where the CT peak is very broad and extends into the region where the components absorb.[5] Figures 3 and 4 show that the increased absorption produced by pressure at the longer wave lengths of the CT maxima of aromatic–iodine complexes, which corresponds to the spectral region studied by Gibson and Loeffler in the aromatic amine–nitro complexes, results from both a shift in position of the peak of the CT band and an increase in its intensity. It seems likely that the large increases in absorption with pressure which Gibson and Loeffler observed are due to similar causes.

In summary, it appears that high pressure produces little change in the complex itself, but changes the nature of the solvent, which in turn affects the spectrum partly by an index of refraction effect and partly by changing the concentration of the complex in solution.

I wish to express my gratitude to Prof. A. W. Lawson and the High Pressure Laboratory for the use of the high pressure bomb and to Dr. I. S. Jacobs who spent much time instructing me in its operation. I wish to thank Prof. R. S. Mulliken for sponsoring this work and Prof. C. Reid and Prof. J. R. Platt for much assistance and encouragement.

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[22] J. Weiss, *J. Chem. Soc.*, 245 (1942).

[23] H. M. Dawson, *ibid.*, **97**, 1041 (1910).

[24] R. E. Gibson and O. H. Loeffler, THIS JOURNAL, **61**, 2877 (1939).