

PRESSURE EFFECT ON THE EDA-COMPLEXES FORMED BETWEEN MESITYLENE, HEXAMETHYLBENZENE AND TETRACYANOETHYLENE IN CARBON TETRACHLORIDE

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The intermolecular charge transfer spectra of tetracyanoethylene with mesitylene and hexamethylbenzene have been measured in carbon tetrachloride under high pressures up to 1400 kg/cm² at 25°C. Both the equilibrium constants for the formation of EDA-complexes and their molar absorption coefficients were increased with pressure. The values of the volume change for the formation of the complexes were -7.1 and -14.1 cm³/mole for mesitylene-TCNE and HMB-TCNE complexes, respectively. For mesitylene-TCNE complex, the red shift of the absorption maximum was observed with increasing pressure. On the other hand, HMB-TCNE complex showed the red shift at first and turned to the blue shift with higher pressure.

Introduction

In the previous paper¹⁾ the absorption spectra of benzene-tetracyanoethylene (TCNE) and toluene-TCNE complexes in carbon tetrachloride were measured under high pressures up to 1500 kg/cm²*. The equilibrium constants were increased with pressure, giving $\Delta V = -3.4$ and -4.9 cm³/mole for benzene-TCNE and toluene-TCNE complexes, respectively. And their absorption maxima shifted toward longer wavelength with increasing pressure. It was interpreted that the negative values of ΔV might be due to smaller volumes of the EDA-complexes than the sum of molecular volumes of the components in solution, actually as confirmed in solid state by X-ray diffraction for chloranil-hexamethylbenzene (HMB)²⁾. The red shift might be explained in terms of the increase of the refractive index of the solvent with pressure, based on the relation proposed by Bayliss³⁾.

On the contrary, HMB-TCNE complex in solution was found to show a red shift at first and then turn to a blue shift with increasing pressure^{4,5)}, which could be explained by neither the simple theory of Bayliss nor the shortening of the intermolecular distance⁶⁾.

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* 1 kg/cm² = 0.9807 × 10⁵ Pa

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- 3) N. S. Bayliss, *J. Chem. Phys.*, **18**, 292 (1950)
- 4) J. R. Gott and A. J. Maisch, *ibid.*, **39**, 2229 (1963)
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The present paper deals with the studies of the EDA-complexes formed between TCNE as an acceptor and mesitylene and HMB as a donor.

Experimental

TCNE was purified by the same method described previously¹⁾. Mesitylene was dried over calcium chloride and distilled before use. HMB was recrystallized three times from methanol and dried in vacuum at room temperature at least for a week. Spectrograde carbon tetrachloride was used without further purification. The solutions containing large excess of the donor were prepared so as to give suitable absorbances of the charge transfer bands. The concentrations of the solutions at high pressure were corrected by the Tait equation⁷⁾ for the pure solvent.

All the experimental procedures and apparatus used in the present study are the same as those in the previous paper, except that the sapphire windows were used instead of the quartz windows. All the spectral measurements were carried out only up to 1400 kg/cm² at 25°C, because the solution froze at higher pressure.

Results

Spectra

The typical absorption spectra of mesitylene-TCNE and HMB-TCNE systems in carbon tetrachloride at various pressures are shown in Figs. 1 and 2. The parent molecules, TCNE, mesitylene and HMB have no absorptions in the visible region, and these broad absorption bands having the maximum at 464 and 534 nm for mesitylene-TCNE and HMB-TCNE at 1 atm, respectively, can be attributed to the EDA-complexes. Ewall and Sonnessa⁸⁾ also reported 464 and 535 nm for the same systems at 1 atm. The absorbances of the charge transfer bands were largely increased with increasing pressure. Such a tendency was found also in benzene-TCNE and toluene-TCNE complexes¹⁾. The relative increases of the absorbances at the maxima are shown in Fig. 3. The pressure scarcely caused a broadening or a sharpening but caused the slight shift of the absorption maximum. For mesitylene-TCNE complex, the red shift with increasing pressure was observed; the absorption maxima were 464 nm at 1 atm and 468 nm at 1400 kg/cm². Such a red shift was usually observed for neutral-neutral EDA-complexes in solution^{1,4,5,9)} and also in solid state¹⁰⁻¹²⁾. However, for HMB-TCNE complex, the pressure led to the slight red shift first, but the higher pressure to the blue shift; the absorption maxima were 534 nm at 1 atm, 536 nm at 800 kg/cm² and 534 nm at 1400 kg/cm², respectively. The

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pressure 1400 kg/cm², at which the absorption maximum returned to that at 1 atm, was much lower than those by other workers; about 7000 atm⁴⁾ and 5000 atm⁵⁾ in dichloromethane, and 10 kb in polymer matrix¹²⁾.

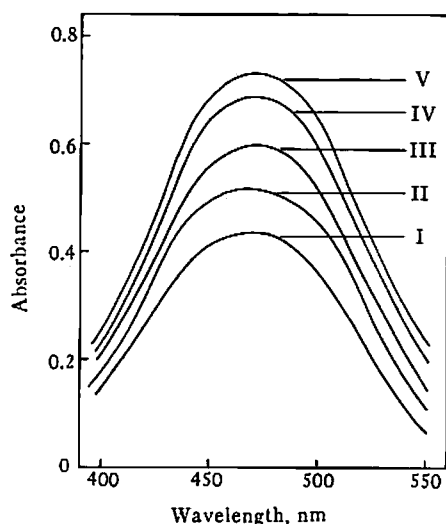


Fig. 1 Absorption spectra of mesitylene-TCNE complex in carbon tetrachloride at various pressures at 25°C. (initial conc., mesitylene: 5.051×10^{-2} mole/l, TCNE: 4.886×10^{-4} mole/l)
I: 1 atm, II: 400 kg/cm², III: 800 kg/cm², IV: 1200 kg/cm², V: 1400 kg/cm²

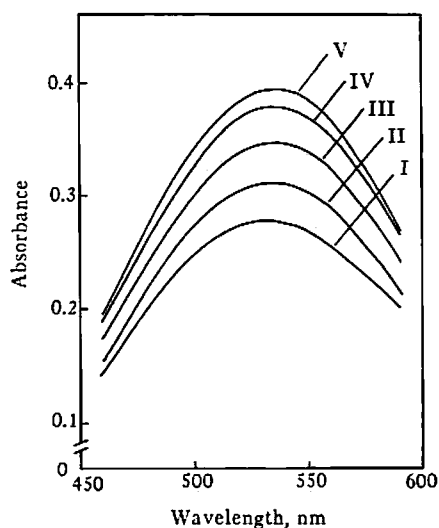


Fig. 2 Absorption spectra of HMB-TCNE complex in carbon tetrachloride at various pressures at 25°C (initial conc., HMB: 1.661×10^{-2} mole/l, TCNE: 0.8096×10^{-4} mole/l)
I: 1 atm, II: 400 kg/cm², III: 800 kg/cm², IV: 1200 kg/cm², V: 1400 kg/cm²

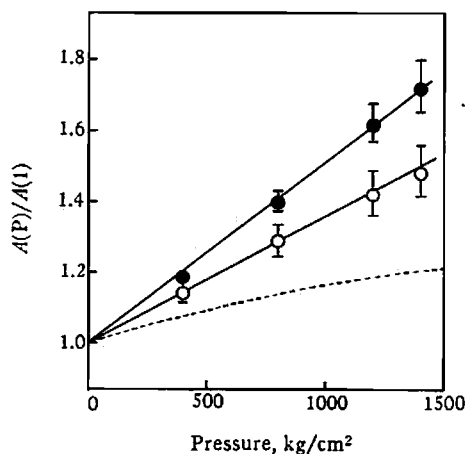


Fig. 3 Increase of the absorbance at absorption maximum as a function of pressure. The dotted line is the square of the relative density of solvent.
●: mesitylene-TCNE, ○: HMB-TCNE

Equilibrium measurement

The formation of these EDA-complexes is reversible.



Since only 1:1 complexes are formed in carbon tetrachloride⁸⁾ and the components of these complexes have no absorption in this region, Scott's equation¹³⁾ can be applied to a series of solutions in which one of the components (the donor in this case) exists in large excess,

$$\frac{[A]_0[D]_0 l}{A} = \frac{1}{\epsilon} [D]_0 + \frac{1}{K\epsilon}, \quad (2)$$

where $[A]_0$ and $[D]_0$ are, respectively, the initial concentrations (molar unit) of the acceptor and donor, and A is the absorbance with the light path length of l cm. Scott's plots for mesitylene-TCNE and HMB-TCNE complexes are shown in Figs. 4 and 5, respectively, where each A is measured at the

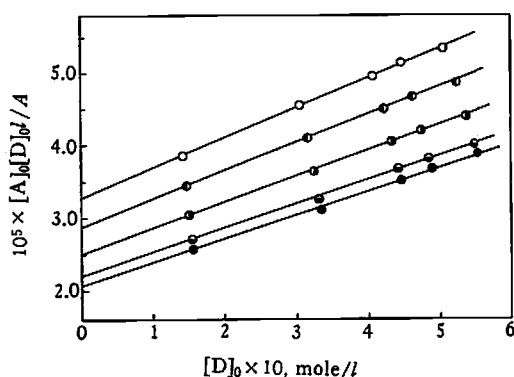


Fig. 4 Scott's plots for mesitylene-TCNE complex in carbon tetrachloride at various pressures at 25°C

○: 1 atm, ◐: 400 kg/cm², ●: 800 kg/cm², ◑: 1200 kg/cm², ●: 1400 kg/cm²

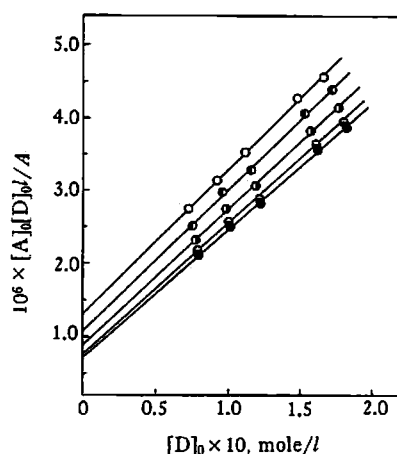


Fig. 5 Scott's plots for HMB-TCNE complex in carbon tetrachloride at various pressures at 25°C

○: 1 atm, ◐: 400 kg/cm², ●: 800 kg/cm², ◑: 1200 kg/cm², ●: 1400 kg/cm²

absorption maximum. The values of the equilibrium constant K and molar absorption coefficient ϵ_{\max} at various pressures were calculated from the slopes and intercepts of Scott's plots. The oscillator strength f were also calculated from the relation,

$$f = 4.319 \times 10^{-9} \times \Delta\nu_{\frac{1}{2}} \times \epsilon_{\max}. \quad (3)$$

where $\Delta\nu_{\frac{1}{2}}$ is the band half-width. Since the change of $\Delta\nu_{\frac{1}{2}}$ with increasing pressure is negligible, the change of f is mainly due to the change of ϵ_{\max} . All the numerical values are listed together in Table 1.

The volume changes ΔV for the complex formation were determined from the slopes of approximately linear plots as shown in Fig. 6. Table 2 shows the observed values of ΔV , including the previous results for benzene-TCNE and toluene-TCNE complexes.

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Table 1 Equilibrium constants and spectroscopic parameters for the EDA-complexes of mesitylene-TCNE and HMB-TCNE in carbon tetrachloride at 25°C

Press. kg/cm ²	mesitylene-TCNE				HMB-TCNE		
	K l. mole ⁻¹	$\epsilon_{\max} \times 10^{-3}$ cm ⁻¹ l. mole ⁻¹	f	λ_{\max} nm	K l. mole ⁻¹	$\epsilon_{\max} \times 10^{-3}$ cm ⁻¹ l. mole ⁻¹	λ_{\max} nm
1	12.8	2.40	0.070	464	140	5.16	534
	8.54 ± 0.340^a	3.057 ± 0.093^a			123 ± 8.8^a	5.14 ± 0.140^a	
400	13.3	2.61	0.077		177	5.20	
800	14.0	2.84	0.084		205	5.42	536
1200	14.9	3.04	0.089		229	5.63	
1400	15.7	3.09	0.093	468	242	5.73	534

a; ref. 8

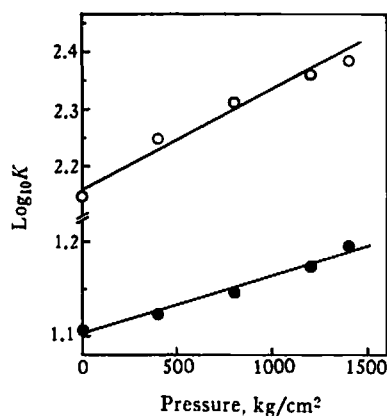


Fig. 6 Pressure effect on the equilibrium constants

●: mesitylene-TCNE,
○: HMB-TCNE

Consideration

As seen in Fig. 3 and Table 1, the enhancement of absorption with pressure can be ascribed not only to the increase of concentrations of solutes caused by compression but also to the increase of K and ϵ_{\max} . Taking into account that K and λ_{\max} are 0.964 l/mole and 385 nm for benzene-TCNE, and 1.92 l/mole and 411 nm for toluene-TCNE complexes¹³, it seems to be concluded that the higher the transition energy $h\nu_{\text{ct}}$ of the EDA-complex, the smaller its equilibrium constant K . The similar trend was reported in a series of aromatic hydrocarbon-TCNE complexes in dichloromethane¹⁴. However, the inverse trend was observed in vinyl ether-TCNE complexes¹⁵. The increase of K with pressure can be interpreted by Mulliken's original description¹⁶ that both the no-bond and dative structures have smaller intermolecular distance than the sum of the van der Waals radii of the component molecules. Actually, it was confirmed in solid state by X-ray diffraction studies². Since the same fact is

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expected in solution, the volume change for the complex formation will be negative, which results in the increase of K with pressure.

As seen in Table 2, the values of ΔV became more negative with the increasing number of substituents of the donor. This tendency seems to be reasonable, since the molecular size of the donor might become larger with the number of substituents.

Table 2 Volume changes for the EDA-complex formations of TCNE and spectral shift induced by pressure in carbon tetrachloride at 25°C

Donor	$-\Delta V$, cm ³ /mole	Spectral shift
Benzene	3.4	red
Toluene	4.9	red
Mesitylene	7.1	red
HMB	14.1	red-blue

Several authors have attempted to account for the influence of solvent on the spectra of neutral-neutral EDA-complexes. Since the excited state of the complex is considerably more polar than the ground state, it has been predicted that increasing solvent polarity should cause a red shift as a consequence of increased stabilization of the polar excited state. This prediction, however, was not in accord with the experimental facts that the spectral shift did not correlate with the dielectric constant as a measure of solvent polarity. McRae¹⁷⁾ derived theoretically the following expression for the frequency shift caused by the dipole interaction, using the solvent perturbation theory;

$$\Delta h\nu \cong (AL+B) \frac{n^2-1}{2n^2+1} - C \left(\frac{D-1}{2D+1} - \frac{n^2-1}{2n^2+1} \right), \quad (3)$$

where $(AL+B)$ and C are constants characteristic of a solute, and n is the refractive index and D the dielectric constant of solvent, and $\Delta\nu$ is the amount of the red shift from vapor phase to solution. Since the second term can be disregarded because $n^2=D$ in nonpolar solvent, McRae's expression should be simplified to a form similar to Bayliss' equation³⁾ derived by using the model of an oscillating point dipole in a continuum medium. Accordingly, the following relation was obtained:

$$\Delta h\nu \propto \frac{n^2-1}{2n^2+1} \quad (4)$$

Actually, Voigt¹⁸⁾ and Aihara *et al.*¹⁹⁾ found a good linear correlation between the spectral shift of EDA-complex and $(n^2-1)/(2n^2+1)$ in various solvents. Furthermore, Ham⁹⁾ has applied this relation to his pressure studies of aromatic hydrocarbon-iodine complexes in *n*-heptane, but his results failed to be extrapolated to the vapor phase. On the other hand, Robertson *et al.*²⁰⁾ derived theoretically the relation, $\Delta\nu \propto \rho$ where ρ is the density of solvent, for non-polar solute in non-polar medium and recognized that this relation held good for some aromatic hydrocarbons in *n*-heptane under high pres-

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20) W. W. Robertson, O. E. Weigang and F. A. Matson, *J. Molecular Spectro.*, **1**, 1 (1957)

sure. According to all the suggestions mentioned above, the pressure should induce only the red shift because both $(n^2-1)/(2n^2+1)$ and ρ are increased with pressure. And the contraction of the donor-acceptor distance of an EDA-complex by pressure also should lead to the red shift, as predicted by Shuler⁶⁾. Thus, the spectral shift of the EDA-complexes except the HMB-TCNE complex might be explained in terms of the change of solvent properties, such as the refractive index and the density of solvent. However, as seen in the present and other studies^{4,5)}, the HMB-TCNE complex showed a slight red shift at first and then a blue shift with increasing pressure in solution. Offen and Abidi²²⁾ discussed the solvent effect on the EDA-complexes as follows: as the energy of the dative structure is reduced, the enhanced mixing with the no-bond structure results in larger splittings of the ground and excited state as seen in Fig. 7, and so the observed shift from non-polar to polar solvent results from

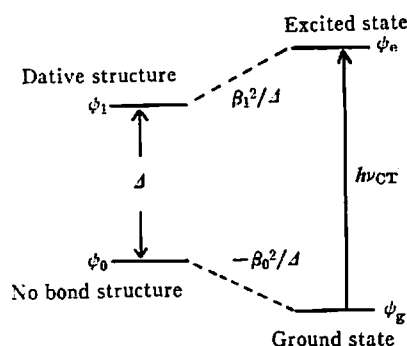


Fig. 7 Charge transfer interaction diagram

$$h\nu_{CT} = \Delta + \frac{\beta_0^2 + \beta_1^2}{\Delta} + \dots$$

$$\beta_0 = W_{01} - W_0 S_{01}$$

$$\beta_1 = W_{01} - W_1 S_{01}$$

$$\Delta = W_1 - W_0$$

$$W_{01} = \int \phi_0 H \phi_1 d\tau$$

$$S_{01} = \int \phi_0 \phi_1 d\tau$$

a balance between the red shift due to the decrease in Δ and the blue shift due to additional splittings $(\beta_0^2/\Delta + \beta_1^2/\Delta)$. Accordingly, it may be concluded that the blue shift occurs when the additional splitting due to the enhanced perturbation is larger than the reduced energy of the dative structure with increasing pressure. For the HMB-TCNE complex, the amount of Δ is smaller than those of other complexes as seen in the transition energy, so that even the small decrease of Δ by pressure might cause the larger splittings compared with those of other complexes. The phenomenon of the change from the red to blue shift of the HMB-TCNE complex may be explained, based on the relative change in Δ and $(\beta_0^2 + \beta_1^2)/\Delta$ with pressure.

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