

Spectroscopic Studies of Charge Transfer Complexes

IX. Dimethyl Sulphoxide and Iodine *

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The charge transfer complex between dimethyl sulphoxide and iodine has been studied spectroscopically in the visible and ultraviolet regions. For dilute dimethyl sulphoxide solutions in carbon tetrachloride the complex is of the 1:1 type. Spectral characteristics and thermodynamic functions have been obtained under these conditions: $-\Delta H = 3.7 \pm 0.3$ kcal/mole, $-\Delta G_{25} = 1.43 \pm 0.05$ kcal/mole and $-\Delta S = 7.6 \pm 0.5$ e.u.

When dissolved in polar solvents, the charge transfer peak is shifted towards longer wave lengths. At higher dimethyl sulphoxide concentrations in carbon tetrachloride, the charge transfer band is shifted to longer and the blue shifted iodine band is shifted towards shorter wave lengths. These changes are discussed in terms of a dielectric effect and an association effect. When iodine is dissolved in dimethyl sulphoxide solutions exceeding approx. 3 M, the spectroscopic and electrical conductance data suggest the existence of triiodide ions, probably initiated by an impurity.

Dimethyl sulphoxide (DMSO) has become increasingly important as a solvent for organic and inorganic compounds. It is highly associated in the liquid state¹ as well as in mixtures with benzene² and water.³ Moreover, DMSO forms intermolecular hydrogen bonds to water⁴ and phenols⁵ and with many solvents^{6,7} and this effect undoubtedly aids the miscibility of these compounds.

Electron diffraction data⁸ showed that DMSO has a pyramidal structure and this geometry has been verified by vibrational analysis.^{9,10} The high inversion barrier of the sulphoxides has been demonstrated by the stabilities of the optical isomers, first reported by Harrison and co-workers,¹¹ but inversion has recently been observed.¹² DMSO has a dipole moment of 3.9 D.¹³ The S—O bond has a bond moment probably close to 3.0 D¹⁴ in the sulphoxides and the sulphones, and it is at least partially a double bond.¹⁵

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Because sulphur as well as oxygen have lone pair electrons, the sulphoxides may coordinate from both atoms. Extensive work in the last years on the ligand properties of the sulphoxides¹⁶ to inorganic Lewis acids shows that the sulphoxides generally coordinate through the oxygen atom. The complexes between five sulphoxides and iodine cyanide have been reported¹⁷ as well as the infrared data for the corresponding iodine and iodine monochloride complexes. In each system the complex bond was formed from the oxygen to the iodine atom. In the present study the complex formation between DMSO and iodine in solution has been studied spectroscopically in the visible and the ultraviolet regions. In forthcoming papers the corresponding data will be reported for some other aliphatic and aromatic sulphoxides.

EXPERIMENTAL

DMSO from Fluka AG was dried with barium oxide for several days. The product was distilled three times in a Vigreux column *in vacuo* and each time only a small middle fraction was used. After fractional crystallization the final product had a melting point of 18.4°C. Great precautions were made to exclude water vapour from the hygroscopic DMSO during the handling and storage. Iodine, reagent grade from Merck was sublimed twice with barium oxide. Carbon tetrachloride, Merck, *Uvasole* for ultraviolet spectroscopy, was shaken with anhydrous calcium chloride and distilled over calcium chloride in a Vigreux column. Heptane, ethanol, methanol and chloroform, Merck, *Uvasole* and acetonitrile, Merck, analytical grade, were used as solvents without further purifications.

The ultraviolet and visible spectra were recorded with a Beckman DK-1 recording spectrophotometer equipped with a thermostated cell holder. As a check the visible spectroscopic data were determined independently on a Zeiss PMQ II spectrophotometer. Matched pairs of silica cells of path lengths 1 cm and 5 cm were employed for the ultraviolet and the visible regions, respectively.

The specific conductances were measured with a Philips measuring bridge PR 9500 using an AC signal of 50 c/s. Philips cells having electrodes of platinized platinum were employed and the temperature kept at 20°C.

RESULTS

Ultraviolet region. DMSO has a strong ultraviolet absorption around 210 $m\mu$ when dissolved in heptane but only a low intensity absorption tail in the region 260–300 $m\mu$. Iodine, in concentrations above 3×10^{-4} M in carbon tetrachloride has a broad absorption band at 280 $m\mu$ which does not follow Beer's law and has been assigned as I_2-I_2 charge transfer absorption.¹⁸ The mixed solutions of DMSO-iodine in carbon tetrachloride has an ultraviolet absorption band around 270 $m\mu$ which is apparent from Fig. 1. This is undoubtedly the DMSO-iodine charge transfer (CT) band superposed on the DMSO absorption. The DMSO absorption was subtracted by having an equal concentration of the sulphoxide in the reference cell. It was observed that for increasing DMSO concentration the CT peak was displaced toward longer wave lengths. Thus, when the DMSO concentrations in carbon tetrachloride varied from 3×10^{-5} M to the pure liquid (approx. 14.1 M), the absorption peak was displaced from 272 to 296.5 $m\mu$ as listed in Table 1. For DMSO concentrations below 0.1 M the CT -peak position was fairly constant.

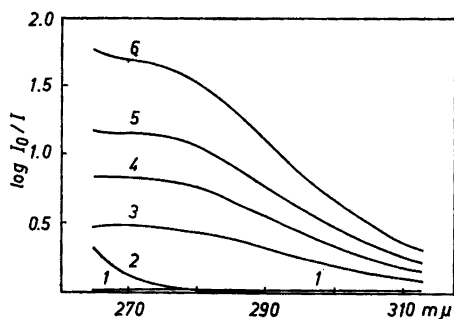


Fig. 1. Ultraviolet absorption spectra of dimethyl sulphoxide and iodine in carbon tetrachloride at 20°C for 1 cm cell. The concentrations (M) are: (1) DMSO zero, I_2 4.115×10^{-4} ; (2) DMSO 0.03795, I_2 zero; (3) DMSO 0.00759, I_2 4.115×10^{-4} ; (4) DMSO 0.01518, I_2 4.115×10^{-4} ; (5) DMSO 0.02277, I_2 4.115×10^{-4} and (6) DMSO 0.03795, I_2 4.115×10^{-4} .

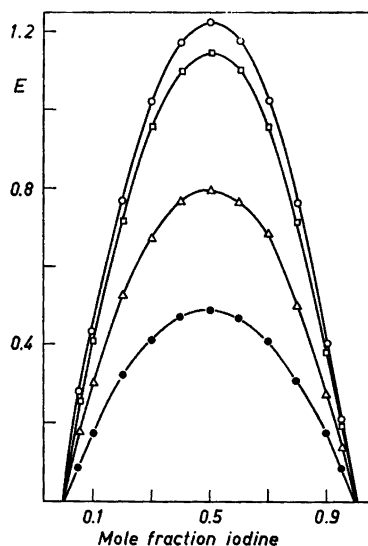


Fig. 2. Method of continuous variation of the dimethyl sulphoxide-iodine system in carbon tetrachloride at 20°C. The absorbance of the solution minus the calculated component absorbance at the following wave lengths: (O) 272 $m\mu$, (\square) 280 $m\mu$, (Δ) 290 $m\mu$ (\bullet) 300 $m\mu$ is plotted versus the mole fraction of iodine. The total concentration of DMSO plus iodine was 0.006032 M.

The DMSO-iodine complex was further studied in different solvents. The positions and half intensity widths of the *CT*-peak recorded in different solvents are listed in Table 2. As expected¹⁹ the *CT*-peak is red shifted in polar solvents. However, no monotonic relationship between the dielectric constant of the solvents and the *CT*-peak position was observed.

Table 1. Spectral data for the ultraviolet absorption band of the DMSO- I_2 system in CCl_4 at different DMSO concentrations.

Conc. DMSO M	Absorpt. peak $m\mu$	$\bar{\nu}_{\max} - \bar{\nu}_L^a$ $10^{-3} \times \text{cm}^{-1}$	Conc. DMSO M	Absorpt. peak $m\mu$	$\bar{\nu}_{\max} - \bar{\nu}_L^a$ $10^{-3} \times \text{cm}^{-1}$
3×10^{-5}	272.0	3.01	0.501	278.0	3.25
0.013	272.1	3.02	1.250	282.0	3.51
0.063	272.5	3.04	2.513	286.2	3.48
0.125	273.9	3.09	4.621	290.0	2.42
0.134	274.4	3.12	7.214	296.3	1.93
0.251	275.0	3.19	14.1	296.5	2.14

^a See footnote a, Table 2, for meaning of the symbols.

Table 2. Spectral data for the ultraviolet absorption band of the DMSO-I₂ complex in different solvents at 20°C.

Solvent	Dielectr. const.	Absorpt. peak $m\mu$	$\bar{\nu}_S - \bar{\nu}_{\max}^a$ $10^{-3} \times \text{cm}^{-1}$	$\bar{\nu}_{\max} - \bar{\nu}_L^a$ $10^{-3} \times \text{cm}^{-1}$
Heptane ^b	1.9	269	3.62	2.98
Carbon tetrachloride ^c	2.2	272		3.02
Chloroform ^c	5.5	288		2.57
Ethanol ^c	24.3	290	2.30	2.21
Methanol ^c	33.1	291	2.13	2.11
Acetonitrile ^c	38.8	288	2.63	2.28
Water ^c	80.0	285	3.02	2.48

^a The symbols have the following meaning: $\bar{\nu}_{\max}$ = wave number at absorption maximum. $\bar{\nu}_S$ and $\bar{\nu}_L$ are wave numbers at the short and the long wave length side, respectively, for which $\epsilon = \frac{1}{2} \epsilon_{\max}$.

^b [DMSO] $\sim 1 \times 10^{-3}$ M. [I₂] $\sim 1 \times 10^{-3}$ M.

^c [DMSO] $\sim 1 \times 10^{-2}$ M. [I₂] $\sim 1 \times 10^{-3}$ M.

In order to determine the stoichiometry¹⁹ of the iodine complex the method of continuous variation²⁰ was employed. The sum of the DMSO and iodine concentrations in carbon tetrachloride was kept constant at 0.006032 M. When $E = E_{\text{obs}} - \epsilon_{\text{DMSO}} \times [\text{DMSO}] - \epsilon_{\text{I}_2} \times [\text{I}_2]$ is plotted against the mole fractions of DMSO at different wave lengths, the curves in Fig. 2 were obtained. E_{obs} is the observed optical density, ϵ_{DMSO} and ϵ_{I_2} are the molar extinction coefficients, and [DMSO] and [I₂] are the concentrations of DMSO and iodine, respectively. Distinct maxima were obtained for [DMSO] = [I₂] pointing to a 1:1 complex. The symmetrical shape of the curves seems to exclude any significant amount of higher complexes, at least for this concentration range.

Carbon tetrachloride was selected as the solvent for the quantitative studies because of the complete miscibility with DMSO. Heptane, being more "inert" and transparent in a much wider ultraviolet region, would have been advantageous as a solvent. It could not be used, however, because it dissolves very small amounts of DMSO.

A series of DMSO-iodine solutions was recorded in the ultraviolet region at 10, 25, and 40°C. The iodine concentration was kept at 3.215×10^{-4} M and the DMSO concentrations varied from 0.00759 to 0.0759 M. The absorption spectra did not change significantly with time under these conditions, in contrast to observations made for high iodine concentrations.¹⁷ In this concentration range the Scott modification²¹ of the Benesi-Hildebrand equation²² was well satisfied and was used to determine the molecular formation constant. Benesi-Hildebrand-Scott plots were constructed at 272, 280, 285, and 290 $m\mu$ by the least squares method after correcting for the overlapping DMSO absorption. The formation constants and molecular extinction coefficients obtained at different temperatures after correcting for the solvent expansion are listed in Table 3. The thermodynamic functions were calculated by standard procedure.

Because carbon tetrachloride is only transparent above 260 $m\mu$, the low wave length side of the *CT* band could not be observed in this solvent. How-

Table 3. Formation constants, extinction coefficients and thermodynamic functions for the DMSO-I₂ complex in CCl₄ obtained from the CT band.^a

Temp. °C	272 mμ		280 mμ		285 mμ		290 mμ	
	K_c M ⁻¹	ϵ M ⁻¹ cm ⁻¹	K_c M ⁻¹	ϵ M ⁻¹ cm ⁻¹	K_c M ⁻¹	ϵ M ⁻¹ cm ⁻¹	K_c M ⁻¹	ϵ M ⁻¹ cm ⁻¹
10	15.7	10.100	15.3	9.400	15.4	8.300	15.0	6.600
25	11.2	10.000	11.4	9.300	11.0	8.200	10.7	6.500
40	8.4	9.800	8.2	9.200	8.2	8.100	8.0	6.400
$-\Delta H^b$	3.57		3.63		3.67		3.63	
$-\Delta G_{25}^c$	1.44		1.43		1.42		1.41	
$-\Delta S^d$	7.15		7.52		7.55		7.45	
Mean value	$-\Delta H^b = 3.6 \pm 0.3$;			$-\Delta G_{25}^c = 1.43 \pm 0.05$;			$-\Delta S^d = 7.4 \pm 0.5$	

^a The values were calculated from absorption data of 9 different DMSO-I₂ solutions.

[I₂] = 3.215×10^{-4} M, [DMSO] varied from 0.00759 M to 0.0759 M, using 1 cm cells.

^b ΔH is in units of kcal/mole.

^c ΔG_{25} is in units of kcal/mole.

^d ΔS is in units of e.u.

ever, when DMSO and iodine are dissolved in heptane the CT band is wider on the short wave length side, and the empirical relationship suggested by Briegleb²³ for π -complexes may be approximately valid: $\Delta\bar{\nu}_{\frac{1}{2}}/2(\bar{\nu}_{\max} - \bar{\nu}_L) \sim 1.2$ where $\Delta\bar{\nu}_{\frac{1}{2}}$ is the half intensity width, $\bar{\nu}_{\max}$ the wave number at the absorption maximum, and $\bar{\nu}_L$ the wave number at the long wave length side for which $\epsilon = \frac{1}{2}\epsilon_{\max}$. The oscillator strength f was calculated from the formula:²⁴

$$f_{CT} = 4.32 \times 10^{-9} \int \epsilon d\bar{\nu} \sim 4.32 (\pi/2) \epsilon_{\max} \Delta\bar{\nu}_{\frac{1}{2}} \times 10^{-9} \\ \sim 4.32 \pi 1.2 (\bar{\nu}_{\max} - \bar{\nu}_L) \epsilon_{\max} \times 10^{-9} \sim 0.5$$

Other series of DMSO-iodine solutions were recorded at 25°C with iodine concentration at 1.4×10^{-4} M and the DMSO concentrations varying from 0.01 M to 0.4 M. Considerable discrepancies were found for the K_c and ϵ values obtained at different wave lengths under these conditions. The K_c values calculated from the absorption data at 270 and 275 mμ agreed reasonably well with those listed in Table 3, but in the region 280–300 mμ lower values for K_c were obtained. This trend would be expected from the band displacement at higher DMSO concentration (Table 1) resulting in variations of ϵ with the DMSO concentration. Finally, it appears from Table 3 that the ϵ values in the region 270–290 mμ diminish somewhat at higher temperatures. This effect can also be expected because the CT-peak was found to be slightly "blue shifted" at higher temperatures.

*Visible region.** When DMSO was added to a solution of iodine in carbon tetrachloride the visible absorption band at $517\text{ m}\mu$ was displaced towards higher frequencies. The new peak was assigned as the blue shifted (*BS*) iodine band. It overlapped partly the free iodine band as shown in Fig. 3 and was situated

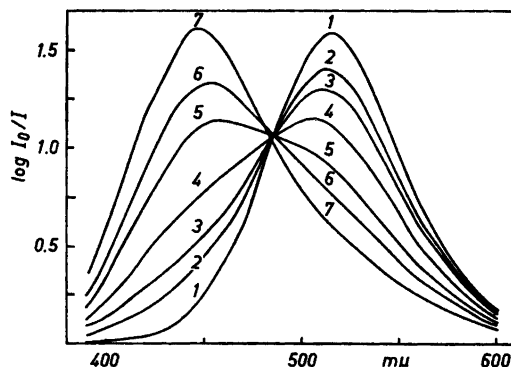


Fig. 3. Visible absorption spectra of dimethyl sulphoxide and iodine ($1.703 \times 10^{-3}\text{ M}$) in carbon tetrachloride at 25°C for 1 cm cell. The concentrations (M) of DMSO are: (1) zero; (2) 0.00904; (3) 0.01507; (4) 0.03015; (5) 0.06030; (6) 0.09044 and (7) 0.1547.

at $446\text{ m}\mu$ for DMSO concentrations lower than approx. 0.12 M. An isosbestic point was observed at $485\text{ m}\mu$. For DMSO concentrations exceeding 0.12 M, however, the absorption curves passed under the isosbestic point, as previously reported for other iodine complexes²⁵ at high donor concentrations. The data listed in Table 4 show that for DMSO concentrations above 4 M a new band appeared around $365\text{ m}\mu$ and the *BS* band was further displaced toward higher frequencies.

Table 4. Visible absorption bands of the DMSO— I_2 system in CCl_4 at different DMSO concentrations.

Conc. DMSO M	Absorpt. peak $\text{m}\mu$	Conc. DMSO M	Absorpt. peak $\text{m}\mu$
0.05	446	1.12	437
0.11	446	1.85	435
0.18	445	2.79	434
0.29	444	4.68	434 365
0.56	441	6.50	434 365
0.78	438	14.1	434 365

* Note added in proof. While this manuscript was in press, Drago *et al.* (Drago, R. S., Wayland, B. and Carlson, R. L. *J. Am. Chem. Soc.* 85 (1963) 3125) published data on the DMSO and tetramethylene sulphoxide complexes with iodine; as observed in the visible spectroscopic region. For the DMSO— I_2 system they reported $K_c(25^\circ) = 11.6 \pm 1.0\text{ M}^{-1}$ and $\Delta H = -4.4 \pm 0.3\text{ kcal/mole}$.

Table 5. Formation constants, extinction coefficients and thermodynamic functions for the DMSO-I₂ complex in CCl₄ obtained from the BS band.^a

Temp °C	435 mμ		440 mμ		445 mμ	
	K_c M ⁻¹	ϵ M ⁻¹ cm ⁻¹	K_c M ⁻¹	ϵ M ⁻¹ cm ⁻¹	K_c M ⁻¹	ϵ M ⁻¹ cm ⁻¹
15	13.9	1495	13.9	1590	14.5	1620
25	10.7	1490	11.2	1590	11.8	1620
35	8.6	1480	8.8	1570	9.2	1610
45	7.3	1460	7.5	1550	7.6	1610
$-\Delta H^b$	3.83		3.80		3.73	
$-\Delta G_{25}^c$	1.41		1.42		1.45	
$-\Delta S^d$	8.12		7.99		7.65	
Mean values	$-\Delta H^b = 3.8 \pm 0.4,$		$-\Delta G_{25}^c = 1.43 \pm 0.05,$		$-\Delta S^d = 7.9 \pm 0.7$	

^a The values were calculated from absorption data of 7 different DMSO-I₂ solutions.

[I₂] = 2.643 × 10⁻⁴ M, [DMSO] varied from 0.00742 M to 0.0742 M, using 5 cm cells.

^b ΔH is in units of kcal/mole.

^c ΔG_{25} is in units of kcal/mole.

^d ΔS is in units of e.u.

A series of DMSO-iodine solutions was studied in the visible region at different temperatures. An absorption cell of path length 5 cm was used, the iodine concentration was 2.643 × 10⁻⁴ M and the DMSO concentration varied from 0.00742 M to 0.0742 M. The formation constants, molecular extinction coefficients and thermodynamic functions calculated from the absorption data by the BHS equation are listed in Table 5. They agreed satisfactorily with those listed in Table 3. Since the CT band has a much higher intensity than the BS band, and the interference from the component absorption is smaller in the ultraviolet region, the values listed in Table 3 are probably somewhat more reliable than those in Table 5. If the former are given the weight 2 and the latter the weight 1, the following values are obtained: $-\Delta H = 3.7 \pm 0.3$ kcal/mole, $-\Delta G_{25} = 1.43 \pm 0.05$ kcal/mole and $-\Delta S = 7.6 \pm 0.5$ e.u. When K_c and ϵ were calculated from the visible absorption data at different wave lengths obtained at higher DMSO concentrations (0.05–0.5 M) large variations were observed. This is expected from the displacements of the blue shifted (BS) band with higher DMSO concentrations.

Conductance measurements. The absorption bands at 295 and 365 mμ are characteristic of the triiodide ion.²⁶ In order to verify the existence of this ion in the DMSO-iodine system, some conductance measurements of concentrated DMSO-iodine solutions were carried out. The data revealed that the DMSO-iodine solutions in carbon tetrachloride had specific conductance in the region 10⁻⁶ ohm⁻¹ cm⁻¹ for high DMSO concentrations, indicating the existence of ionic species. Furthermore, a slight increase in the conductance with time was detected, but after approximately 2 minutes no further variation was observed for several hours.

Three series of solutions were measured having constant iodine concentrations and DMSO concentrations varying from 1 M to 6 M. The iodine concentrations were 0.6×10^{-3} M, 1.2×10^{-3} M, and 2.4×10^{-3} M for the three series, respectively. It was found that the conductance was largely independent of the iodine concentrations, but increased linearly with the DMSO concentrations, as apparent from Fig. 4.

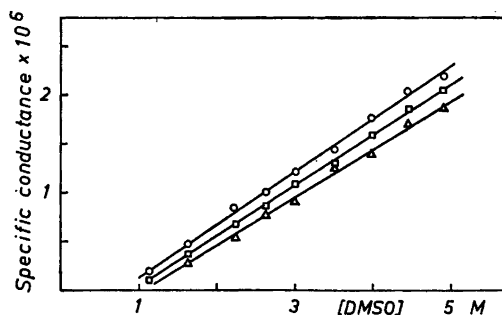


Fig. 4. Plots of the electrical conductance of concentrated dimethyl sulphoxide — iodine solutions in carbon tetrachloride at 20°C versus the DMSO concentrations. Symbols denote the following iodine concentrations; (O) 2.4×10^{-3} M, (□) 1.2×10^{-3} and (Δ) 0.6×10^{-3} M.

DISCUSSION

The observations made in the ultraviolet, visible and infrared¹⁷ regions can be explained in terms of a (n, σ) charge transfer complex between DMSO and iodine. Thus, the blue shifted transition of iodine ($\pi_g \rightarrow \sigma_u$) situated at 446 m μ indicates a fairly strong interaction. The ultraviolet absorption band at 272 m μ suggests an ionization potential of approx. 9.6 eV for DMSO, employing the relationships of McConnell *et al.*²⁷ or Hastings *et al.*²⁸ However, no ionization potentials of DMSO has been found in the literature.

The infrared data¹⁷ demonstrate that DMSO is bonded from the oxygen atom to the three acceptors iodine, iodine cyanide and iodine monochloride. Thus, the 1072 cm⁻¹ band assigned as the S=O stretching vibration¹⁰ is displaced to lower wave number in each of these complexes. This is in agreement with the results reported¹⁶ for the boron halide and most of the metal halide complexes. The infrared band at 683 cm⁻¹ assigned as the antisymmetrical C—S stretching vibration,¹⁰ is displaced to higher wave numbers on complex formation to iodine,¹⁷ supporting the conclusion of a complex bond to the oxygen.

Compared with the results reported for the basicities of X=O compounds to iodine, the sulphoxides are evidently stronger donors than the ketones²⁹ and the aldehydes³⁰ but weaker than the phosphine oxides.³¹ Similar results have been reported by Lindqvist and Zackrisson³² from calorimetric studies of the complex formation to the acceptors antimon pentachloride and tin tetrachloride. They listed DMSO as a stronger donor toward antimon pentachloride than diethyl sulphide. The present results, however, show that DMSO

is a weaker donor toward iodine than dimethyl sulphide,³³ diethyl sulphide^{34,34} and the cyclic, saturated sulphides.³⁶ In the X=O compounds, the electronegativity of X as well as the existence of lone pair electrons on X are important for the availability of the oxygen lone pair electrons for donation. Moreover, the infrared data on the sulphoxide-iodine cyanide complexes¹⁷ as well as work to be reported on other sulphoxide-iodine systems clearly demonstrates that the donor strengths depend upon the inductive effects of the sulphoxide substituents. Thus, the aromatic sulphoxides are the weaker donors because of the electronegative character of the phenyl groups. Similar conclusions can be drawn for the sulphides according to recent data reported for the thioanisoles.³⁷

The high boiling point and entropy of vapourization (Trouton constant) and the variation of the index of refraction with temperature strongly point to an association of DMSO in the liquid state.¹ The extensive studies of Lindberg *et al.*^{2,3} on the thermodynamic properties of DMSO in different solvents confirm that the compound associates in benzene and water solutions. They have proposed the following structure for the dimer



which can be extended to trimers and polymers. Studies of the S=O stretching band intensities when DMSO was dissolved in carbon disulphide showed that Beer's law was obeyed for concentrations smaller than approx. 0.1 M,¹⁷ indicating monomeric molecules. In the quantitative studies the DMSO concentrations were kept below 0.08 M to prevent self association.

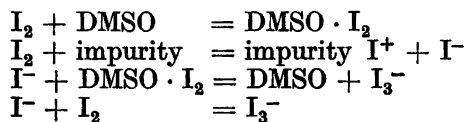
The data listed in Table 2 reveal that the *CT*-band was red shifted in solvents of higher dielectric constants. This effect would be expected because solvent interaction should reduce the energy of the highly polar dative (excited) state, resulting in a lower transitional energy $h \times \nu_{CT}$. However, it appears from Table 2 that there is no monotonic relationship between the dielectric constant and ν_{CT} . It appears that the strong hydrogen bonding solvents: water, methanol and ethanol have deviating effects, which might be caused by specific solute-solvent interactions.

Tables 1 and 4 reveal that the *CT* band as well as the *BS* band is displaced for DMSO concentrations in carbon tetrachloride exceeding approx. 0.1 M. It should be noted that at least for DMSO concentrations below 4 M the displacements of the *CT* band cannot be explained as a superposition of the 272 $m\mu$ band and the 296 $m\mu$ triiodide band. The data in Table 4 demonstrate by the absence of the triiodide band at 365 $m\mu$ that no observable amount of the triiodide ion is present under these conditions. It seems reasonable to assume that these displacements are partly caused by the increasing dielectric constant $D(\text{DMSO}) = 45$ in concentrated sulphoxide solutions in agreement with reported work on other polar donors.²⁵

The association of the DMSO molecules may also contribute to the band displacements. At higher DMSO concentrations the dimers or higher aggregates form complexes with iodine. Assuming structure (I), the lone pair electrons on

the free oxygen should be more available for donation to iodine because of the additional electron density on the sulphur, contributed from the bonded oxygen. The dimer and the polymers may thus have a *CT* band at longer wave length than the monomer.

According to Popov and co-workers²⁶ the trihalide ion has absorption bands at 365 and 295 μ when dissolved in ethylene chloride. It therefore seems reasonable to assign the absorption bands in the highly concentrated DMSO-iodine solutions to the existence of the trihalide ion, superposed on the complex absorption. When these DMSO-iodine solutions are diluted with carbon tetrachloride, however, the bands at 295 and 365 disappear, and the *CT* and *BS* bands appear at the wave lengths corresponding to the DMSO concentration in Tables 1 and 4. The formation of the triiodide ion at high DMSO concentrations is accordingly a reversible reaction. The conductance measurements confirmed that ionic species were present under these conditions, and the specific conductance was approximately proportional to the DMSO concentration in the concentration range studied. It therefore seems reasonable to assume that in spite of the careful purification, the triiodide ions are formed by an impurity present in the concentrated DMSO solutions. The following scheme may be postulated:



The reactions are evidently reversible, the complex $\text{DMSO} \cdot \text{I}_2$ being reformed on dilution with carbon tetrachloride. More work under extremely purified conditions would be necessary to clarify the origin of the spectral changes occurring in very concentrated DMSO solutions.

For DMSO solutions in the concentration region 0.6–2.0 M the *CT* band was somewhat blue shifted with higher temperatures. This may be caused by the lower DMSO self association at higher temperatures. The erroneous formation constants obtained at high DMSO concentrations from the *CT* as well as the *BS* bands can easily be explained from the band displacements and the chemical reactions forming the triiodide ion. However, for DMSO concentrations below 0.08 M, reproducible and constant values for K_c were obtained at each temperature. Moreover, the thermodynamic functions calculated from the *CT* and *BS* bands were in satisfactory agreement.

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REFERENCES

1. Schläfer, H. L. and Schaffernicht, W. *Angew. Chem.* **72** (1960) 618.
2. Lindberg, J. J., Kenttämaa, J. and Nissema, A. *Suomen Kemistilehti* **B 34** (1961) 98, 156.
3. Lindberg, J. J. and Kenttämaa, J. *Suomen Kemistilehti* **B 33** (1960) 32, 98, 104.
4. Cowie, J. M. G. and Toporowski, P. M. *Can. J. Chem.* **39** (1961) 2240.
5. Gramstad, T. *Spectrochim. Acta* **19** (1963) 829.

6. Biscarini, P. and Ghersetti, S. *Gazz. Chim. Ital.* **92** (1962) 61.
7. Bellamy, L. J., Conduit, C. P., Pace, R. J. and Williams, R. L. *Trans. Faraday Soc.* **55** (1959) 1677.
8. Bastiansen, O. and Viervoll, H. *Acta Chem. Scand.* **2** (1948) 702.
9. Salonen, A. K. *Ann. Acad. Sci. Fennicæ* **67** (1961) 5.
10. Horrocks, W. D. and Cotton, F. A. *Spectrochim. Acta* **17** (1961) 134.
11. Harrison, P. W. B., Kenyon, J. and Phillips, H. *J. Chem. Soc.* **1926** 2079.
12. Johnson, C. R. *J. Am. Chem. Soc.* **85** (1963) 1020.
13. Cotton, F. A. and Francis, R. *J. Am. Chem. Soc.* **82** (1960) 2988.
14. Cumper, C. W. N. and Vogel, A. I. *J. Chem. Soc.* **1959** 3521.
15. Moffitt, W. *Proc. Roy. Soc. (London)* **A 200** (1950) 509.
16. See references 1–5 in the preceding paper (Ref.¹⁷).
17. Augdahl, E. and Klæboe, P. *Acta Chem. Scand.* **18** (1964) 18.
18. de Maine, P. A. D. *J. Chem. Phys.* **24** (1956) 1091.
19. Brieleb, G. *Elektronen-Donator-Acceptor-Komplexe*. Springer Verlag, Berlin 1961, p. 37.
20. Job, P. *Ann. Chim.* [10] **9** (1928) 113.
21. Scott, R. L. *Rec. Trav. Chim.* **75** (1956) 787.
22. Benesi, H. A. and Hildebrand, J. H. *J. Am. Chem. Soc.* **71** (1949) 2703.
23. Ref. 19, p. 47.
24. Ref. 19, p. 61.
25. Drago, R. S., Carlson, R. L., Rose, N. J. and Wenz, D. A. *J. Am. Chem. Soc.* **83** (1961) 3572.
26. Buckles, R. E., Yuk, J. P. and Popov, A. I. *J. Am. Chem. Soc.* **74** (1952) 4379.
27. Hastings, S. H., Franklin, J. L., Schiller, J. C. and Matsen, F. A. *J. Am. Chem. Soc.* **75** (1953) 2900.
28. McConnel, H., Ham, J. S. and Platt, J. R. *J. Chem. Phys.* **21** (1953) 66.
29. Yamada, H. and Kozima, K. *J. Am. Chem. Soc.* **82** (1960) 1543.
30. Augdahl, E. and Klæboe, P. *Acta Chem. Scand.* **16** (1962) 1637.
31. Gramstad, T. and Snaprud, S. I. *Acta Chem. Scand.* **16** (1962) 999.
32. Lindqvist, I. and Zackrisson, M. *Acta Chem. Scand.* **14** (1960) 453.
33. Tideswell, N. W. and McCullough, J. D. *J. Am. Chem. Soc.* **79** (1957) 1031.
34. Tsubomura, H. and Lang, R. P. *J. Am. Chem. Soc.* **83** (1961) 2085.
35. Good, M., Major, A., Nag-Chaudhuri, J. and McGlynn, S. P. *J. Am. Chem. Soc.* **83** (1961) 4329.
36. Tamres, M. and Searles, S. *J. Phys. Chem.* **66** (1962) 1099.
37. Veen, J. van der and Stevens, W. *Rec. Trav. Chim.* **82** (1963) 287.

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