

Charge Transfer Complexes Between Some Polar Solvents and π -Acceptors

NADIA M. GHOBRIAL

*Department of Chemistry, University College for Women
Ain-Shams University, Heliopolis, 11757, Cairo, Egypt*

The charge-transfer complexes formed by a number of π -acceptors with dimethylsulphoxide, dimethylformamide and tetrahydrofuran have been measured in methylene chloride at 25°C. Transition energies of these complexes as well as ionization potentials of the π -donors have been determined. All CT complexes studied have a 1 : 1 stoichiometry. Solvent effect on the electronic transition of the CT have been presented and discussed.

INTRODUCTION

Solvent effect studies on the position of the 1-propanamine-3-triethoxysilyl : chloranil complex bands, in organic solvents of different dielectric constants, have shown that the transition energies decrease as the polarity of the solvent increases¹. However, complexation in oxygen-containing solvents such as dimethylsulphoxide (DMSO) exhibits no correlation between the polarity of the solvent and the energy of the charge-transfer transition. We proposed that this might be due to the formation of complexes with these solvents. According to Slifkin², there is an interaction between chloranil and polar solvents DMSO, tetrahydrofuran (THF), and dimethylformamide (DMF), probably the formation of a 1 : 1 charge-transfer complex. The objective of the present study is to determine the stoichiometry of the charge-transfer (CT) complexes between DMSO, THF and DMF with chloranil (CHL), 2,3-dichloro 5,6-dicyanobenzoquinone (DDQ) and iodine (I₂) in methylene chloride. In addition, we wish to apply the tool of CT complexation to estimate the ionization potentials of the three organic solvents.

EXPERIMENTAL

The purification of DMSO has been described as earlier³, other organic solvents used were purified according to standard methods⁴. CHL (Merk) was crystallized from benzene; DDQ (Aldrich) was crystallized from benzene : chloroform (2 : 3).

For the purpose of determining the stoichiometry utilizing the conventional Job's continuous variation method⁵, stock solutions (10⁻² M) of donor and acceptors were prepared. The electronic spectra of the complexes were measured in 3 ml stoppered silica cells after mixing the donor and acceptor solutions at 25°C using a Perkin-Elmer spectrophotometer model λ_4 . All measurements were made immediately after mixing

the two components. The electronic spectra of all molecular complexes formed were recorded within the wavelength range 200–750 nm, using methylene chloride as a solvent.

RESULTS AND DISCUSSION

It was observed that spectra of the π -acceptors DDQ, CHL and I_2 in the polar solvents DMSO (I), DMF (II) and THF (III) are not very different from that of the acceptor in an inert solvent⁶. However, by studying the difference spectra between polar solvent + π -acceptor versus π -acceptor solution of the same concentration (Fig. 1) the electronic spectra of (I), (II)

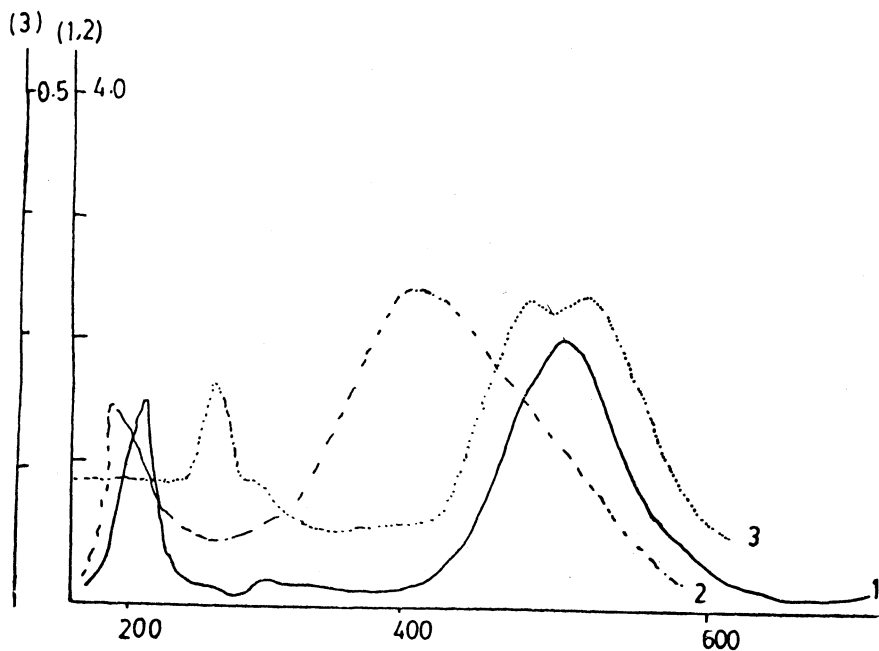


Fig. 1. Absorption spectra

0.1 M iodine in methylene chloride ——— 1
 0.1 M dimethylsulphoxide in methylene chloride - - - - - 2
 0.1M iodine vs. 0.1 M iodine + 0.1 M dimethylsulphoxide in methylene chloride 3

and (III) with various electron acceptors under investigation in methylene chloride solution show extra absorption band(s) not due to either component alone. These bands have been attributed to the formation of donor-acceptor molecular complexes in these solutions. The values for the positions of absorption maxima, molar extinction coefficients, transition energies of the molecular complexes of the electron donors (I), (II) and (III) with the different electron acceptors are listed in Table 1.

TABLE I

MAXIMUM ABSORPTION WAVELENGTH λ_{\max} (nm), MOLAR EXTINCTION COEFFICIENT ϵ_{\max} ($\text{mol}^{-1} \text{cm}^{-2}$) AND TRANSITION ENERGIES E (k cal mol^{-1}) OF THE CHARGE-TRANSFER COMPLEXES FORMED BETWEEN POLAR ORGANIC SOLVENTS (DMSO, DMF AND THF) AND π -ACCEPTORS IN METHYLENE CHLORIDE AT 25°C AS WELL AS THE IONIZATION POTENTIALS i.p. (e.v.) OF THE DONORS

Electron Donors	Acceptor	λ_{\max}	ϵ_{\max}	Transition Energy	i.p.
DMSO	DDQ	368	46.0	77.7	9.89
	CHL	377	16.0	75.9	9.82
	I ₂	276	28.0	103.6	9.82
DMF	DDQ	426	32.0	67.1	9.30
	CHL	372	12.2	76.9	9.10
	I ₂	307	9.4	93.1	9.06
THF	DDQ	440	24.0	65.0	9.20
	CHL	387	10.0	73.9	8.95
	I ₂	314	11.0	91.1	8.90

The ionization potential (i.p.) values listed in Table 1 were calculated from the energies of the charge-transfer bands applying the following empirical equations^{7,8} which were used in substituted benzene and polynuclear hydrocarbons as donors :

$$(A) \text{ i.p. (e.v.)} = 5.00 + 1.53 \cdot 10^{-4} \cdot \bar{\nu}_{\text{CHL}} (\text{cm}^{-1})$$

$$(B) \text{ i.p. (e.v.)} = 5.76 + 1.52 \cdot 10^{-4} \cdot \bar{\nu}_{\text{DDQ}} (\text{cm}^{-1})$$

$$(C) \text{ i.p. (e.v.)} = 2.90 + 1.89 \cdot 10^{-4} \cdot \bar{\nu}_{\text{I}_2} (\text{cm}^{-1})$$

where, $\bar{\nu}$ is the wavenumber corresponding to the charge-transfer band. These equations have also been used in estimation of i.p. of heterocyclic compounds⁹. This method provides a simple means of estimating ionization potentials which may be difficult to determine by other methods, such as Rydberg series, photoionization and electron impact, because of practical details such as the low vapour pressure of some of these substances⁸.

A 1 : 1 composition of the complexes between acceptors and donors is observed, by employing the Job's continuous variation method¹² (Fig. 2, 3 and 4), except in the case of the complex between DMSO and DDQ (Fig. 2). The absorption maxima at 0.4 indicates that the ratio of D : A is

2 : 1. DDQ relatively higher electron affinity (1.9 e.v.)⁷ might account for the 2 : 1 D : A ratio.

Solvent effect studies on the position of CHL-DMSO complex bands, in organic solvents of different dielectric constants, have shown that the transition energy generally increases with the polarity of the solvent

"DDQ MOL. FRA. vs DONOR ABS"

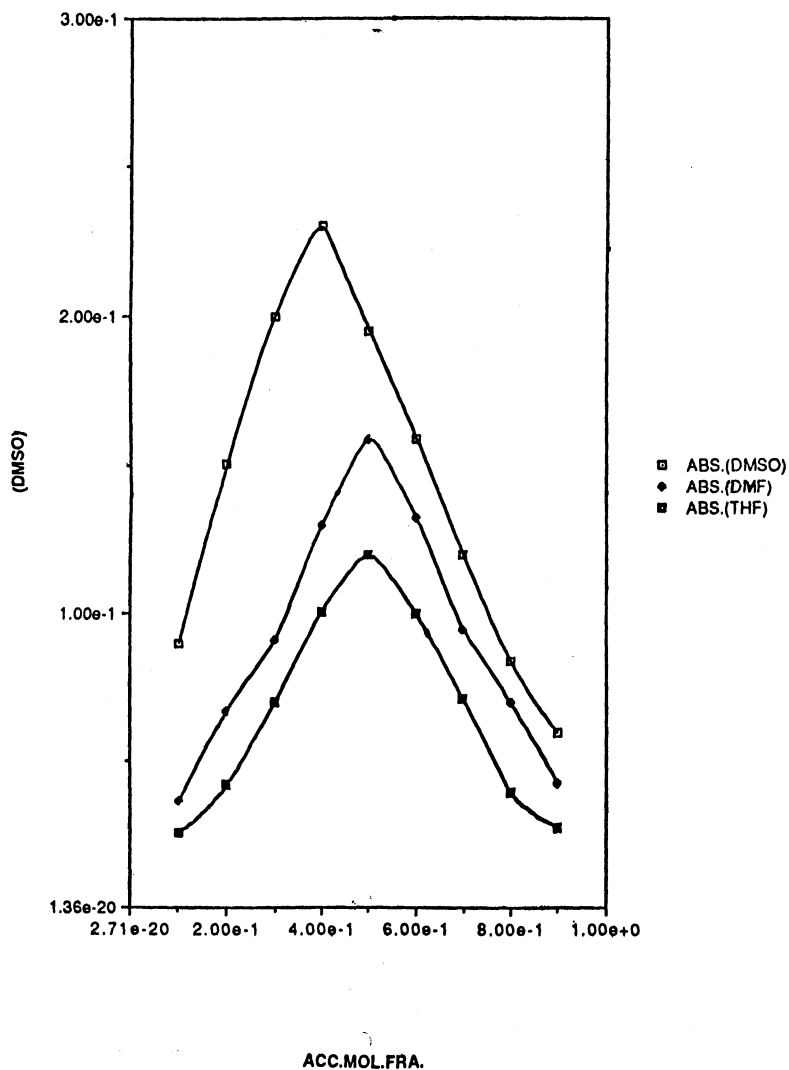


Fig. 2

"IODENE MOL.FRA. vs DONOR ABS."

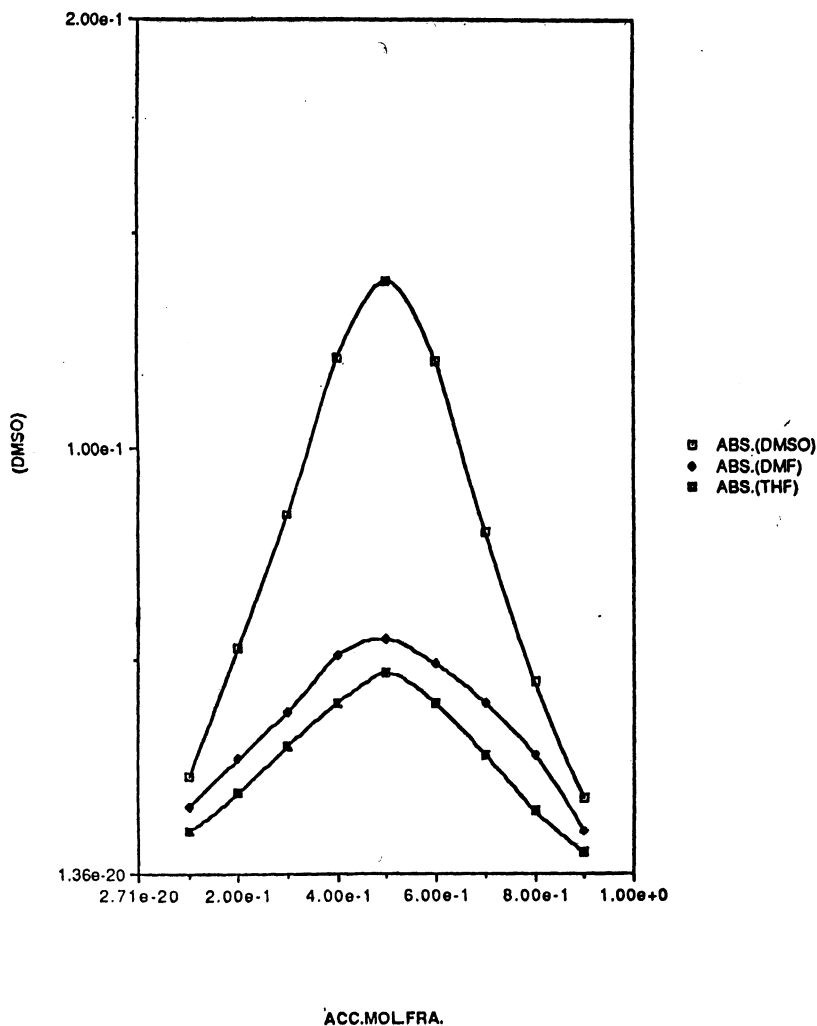


Fig. 3

(Table 2). A similar increase in transition energies with the polarity of the solvent has been reported by Kosower¹⁰. The decrease of the energy of the transition as the polarity of the solvent increases might be due to the high stabilization of the excited state in which the charge is probably more separated than in the ground state.

"CHL. MOL. FRA. vs. DONOR ABS."

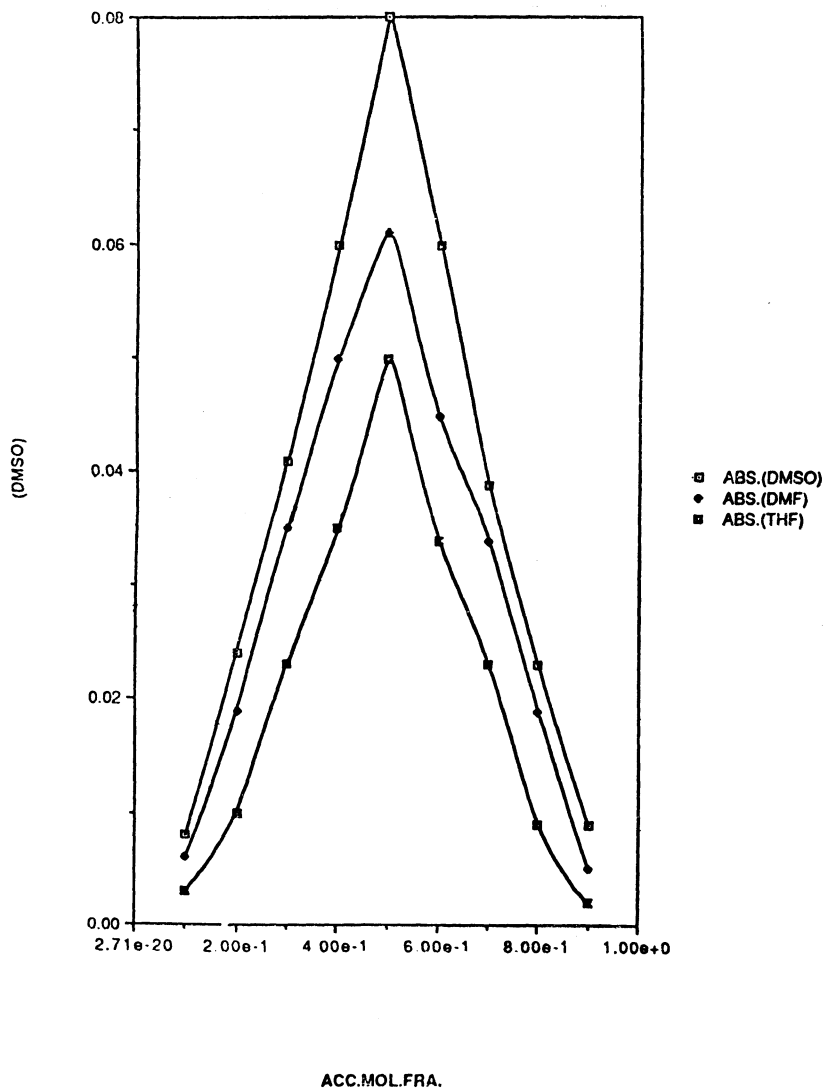


Fig. 4

In the case of oxygenated solvents no correlation appears between polarity of the solvent and the energy of the transition.

The stability of the CT complexes is proportional to the electron affinity of the electron acceptor compounds and on the ionization

TABLE 2

EFFECT OF SOLVENT ON POSITION OF THE MAXIMUM ABSORPTION WAVELENGTH BAND OF CHL-DMSO COMPLEX IN DIFFERENT ORGANIC SOLVENTS AT 25°C

Solvent	λ_{\max}	ϵ_{\max}	Transition Energy	Dielectric Constant at 25°C
Ethyl acetate	405	6.6	70.6	6.0
Chloroform	400	15.3	71.5	4.8
Methylene chloride	377	16.0	76.0	9.1
Benzene	408	12.0	70.1	2.3
Cyclohexane	415	8.0	68.9	2.0
Acetone	375.5	4.5	76.3	21.0
Acetonitrile	325	11.6	88.0	37.5

potential of the electron donor components and increases with the following order:



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