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Dielectric Studies of Molecular Complexes of *DDT* with Some Compounds of Biological Interest

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The molecular complexation of *DDT* (acceptor) with some compounds of biological interest as donors (e.g. indole, 2-methylindole, 3-methylindole, benzene and naphthalene) have been studied using refractive index, *Guggenheim* and dielectric titration plot methods. The interaction between these donors with solvents (CCl_4 and C_6H_6) have also been observed by calculating μ_{ind} through $\mu_{ind} = \mu_{sol} - \mu_{inert}$. These data have shown that the molecular interaction between polar solutes and non-polar aromatics is governed by dipole-induced dipole electrostatic attraction. The dipole moment obtained due to charge transfer (μ_{DA}) has also been calculated and found that its value increases with the increase in the extent of interaction between donor and acceptor. These data support the charge-transfer complex formation hypothesis for the mode of action of *DDT* on molecular level.

(Keywords: Charge-transfer complexes; DDT; Dipole moments; Equilibrium constants; Indoles; Molecular complexes)

Dielektrizitäts-Untersuchungen an Molekülkomplexen von DDT mit einigen biologisch relevanten Verbindungen

Es wurden Molekülkomplexe von *DDT* (als Acceptor) mit einigen Verbindungen von biologischem Interesse (als Donoren: Indol, 2-Methyl-indol, 3-Methyl-indol, Benzol und Naphthalin) mittels Brechungsindex, *Guggenheim*-Methode und dielektrischer Titration untersucht. Dipolmomentberechnungen ergaben, daß die intermolekulare Wechselwirkung von einer Anziehung induzierter Dipol—Dipol bestimmt wird; es wurde auch der charge-transfer-Anteil des Dipolmoments abgeschätzt. Alle diese Daten unterstützen die Annahme der charge-transfer-Komplexierung von *DDT*.

Introduction

In our previous communication[1], the formation of molecular complexes between *DDT* as acceptor and indole, 2-methylindole, 3-

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methylindole, benzene and naphthalene as donors have been studied in carbon tetrachloride using refractometric and differential refractometric measurements. On the basis of K_1 values[2–6] of these interactions, formation of two types of complexes was observed—one association involving primarily the benzhydryl trichloromethyl grouping of *DDT* with a polar complexing agents and the other interaction of *DDT* aromatic π-electron system with π-electrons of donors in the complexing molecule[7,8]. In order to provide further evidence on these interactions, a dielectric study has been performed in non-aqueous solvents.

Experimental and Data Analysis

The materials used and their purifications are essentially the same as reported earlier[1].

The dielectric constant measurements were carried out at 30 °C at a radio frequency of 1 MHz with the help of Philips RCL bridge model P.P. 9030. The instrument works on a well known principle of heterodyne beat method. The resulting beat frequency is projected on the screen of a cathode ray tube with a 50 cycles per second. A *Lissajous* figure is obtained on the screen. The readings were recorded at the resonance point indicated on the CRT screen by the formation of a single loop pattern.

Refractive indices of solutions were determined at 30 °C with the help of Bausch & Lomb refractometer with an accuracy of ± 0.0002. The dipole moment of solutes and complexes have been calculated by the *Guggenheim* method[9].

Results and Discussion

The dipole moments of the acceptor (*DDT*) and the donors (indole, 2-methylindole, 3-methylindole and naphthalene) have been calculated using refractive index and *Guggenheim* methods; the data are compared in Table 1. From this Table it is evident that 3-methylindole possesses a higher dipole moment than indole and 2-methylindole. This may be due to the effective increase in the electron density at 3-position. This leads the formal negative charge at the nucleus making the molecule more assymmetric than that of indole and 2-methylindole.

It has been noted that *DDT* possesses a different dipole moment in different solvents (Table 1). In cyclohexane, the dipole moment was found to be less than in benzene. This difference in dipole moment may be a result of molecular interaction between solutes and non-polar aromatics (benzene). The significance of this induced dipole moment can be interpreted as follows: Although the aromatics themselves are non-polar, they possess π-electrons which enables them to be easily polarised by neighouring solutes. If the interactions are such that the solute polarizes the aromatics, it results the dipole moment being induced in the latter. The process is then followed by electrostatic attraction between the interacting species. At the same time, the solute experiences the resultant dipole moment of its own and that induced in the aromatic leading to an increase in the dipole moment. In general, it might be considered that the more polar is the solute, the larger is the expected increase in its solution dipole moment, μ_{ind}. Hence it is possible to conclude initially that for these systems the interactions are taking place through dipole-induced dipole mechanism. Thus the dipole moment induced as a result of molecular interaction (μ_{ind}) can be calculated as: $\mu_{ind} = \mu_{sol} - \mu_{inert}$, where μ_{sol} and μ_{inert} are the dipole moments of solute in the interacting solvents (benzene, CCl_4) and inert solvent, respectively.

Table 1. *Dipole moments of donors and acceptor (DDT) in different solvents at 30 °C calculated from refractive index and Guggenheim methods*

Donor/Acceptor	$\mu \times 10^{18}$ e.s.u.							
	Refractive Index Method				*Guggenheim* Method			
	C_6H_{12}	CCl_4	C_6H_6	μ_{ind}	C_6H_{12}	CCl_4	C_6H_6	μ_{ind}
DDT	1.002	1.008	1.20	0.018	1.00	1.005	1.018	0.018
Indole	1.95	1.96	2.00	0.05	1.91	1.950	1.95	0.04
2-Methylindole	2.23	2.21	2.28	0.05	2.20	2.202	2.250	0.05
3-Methylindole	2.25	2.28	2.31	0.06	2.21	2.252	2.292	0.082
Naphthalene	0.00	0.00	0.00		0.00	0.00	0.00	

We have observed that the solutes have higher dipole moments in CCl_4 than in cyclohexane. This increase in dipole moment may again be interpreted due to the molecular interaction between solutes and carbon tetrachloride. Though it is believed that CCl_4 is an inert solvent but it has also been observed that CCl_4 can act as a electron acceptor[12]. In the case of *DDT*—CCl_4 interaction, the π-electron of benzene ring of the *DDT* can act as an electron donor. From Table 1 it is evident that the indoles have higher dipole moments in CCl_4 than in cyclohexane. This again may be interpreted due to the molecular interaction between indoles and CCl_4. It is also observed that in this interaction 3-methylindole has a higher dipole moment than 2-methylindole and indole (Table 1). This may be due to the better donor capability of 3-methylindole than other indoles. Consequently, 3-methylindole forms a stronger complex than other indoles. This is in parallel agreement with our earlier observations that 3-methylindole—*DDT* complex has higher K_1 values than other indoles[1,7].

The dipole moment of molecular complexes of *DDT* with indoles, naphthalene and benzene calculated from the *Guggenheim*[9] and refractive index methods are recorded in Table 2. From this Table it is

Table 2. *Dipole moments (μ) for 1:1 molecular complexes of some donors with DDT in carbon tetrachloride at 30 °C*

	Dipole Moment ($\mu \times 10^{18}$ e.s.u.)				
	DDT—indole	*DDT*—2-Methyl-indole	*DDT*—3-Methyl-indole	*DDT*—Naph-thalene	*DDT*—Benze
Refractive Index Method	3.830	4.200	4.410	1.800	1.38
Guggenheim Method	3.855	4.207	4.457	1.805	1.405
Refractometric Titration Plot	3.880	4.250	4.482	1.823	1.455
μ_{DA}[a]	0.90	1.0	1.2	0.80	0.40
Equilibrium Constant[b] $(K_1)\,l\,mol^{-1}$	0.308	0.330	0.468		

[a] μ_{DA} values have been calculated by using the data obtained from *Guggenheim* method.

[b] Taken from Ref.[7].

evident that an appreciable increase in dipole moments have been observed when *DDT* is mixed with indoles and aromatics in carbon tetrachloride which has been interpreted due to the molecular complexation of donors with *DDT*. This is in good agreement with our previous observations[1,7].

The stoichiometry of above molecular complexes have been determined by using a dielectric titration technique where changes on the dielectric permittivity ($\Delta\varepsilon$) of a solution of one component (*DDT*) on addition of successive amounts of an other component is measured[12]. In the case of the addition of dipolar donor to a non-dipolar acceptor, a complex is produced which has a dipole moment value larger than that of the donor. The addition of a small amount of donor generates an equal amount of complex. The permittivity increases on successive additions of the donor and continues to increase until equal amount of the donor and acceptor are present. This situation is schematically shown by line XY of Fig. 1, which indicates 1:1 stoichiometry of these complexes. Further addition of the donor increases the permittivity by an amount depending on the dipole moment of the donor. A break has been observed in the graph at the donor-acceptor ratio corresponding to the ratio existing in the complex. In practice, the dissociation of the complex causes departure from the line XYZ. The magnitude of this departure depends on the equilibrium constant of the initial portion, XY, of the graph which gives the dipole moment of the complex and the slope of YZ gives the dipole moments of the acceptor. The dipole moment of molecular complexes and acceptor, thus calculated are recorded in Table 2. These data clearly indicate their agreement with the *Guggenheim*[9] and refractive index methods through which the dipole moment of solutes and the complexes have been determined.

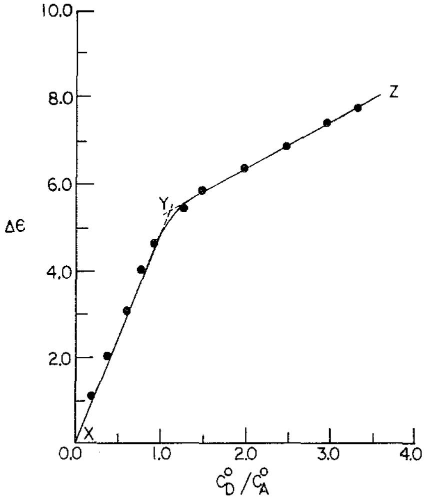

Fig. 1. Dielectric titration plot for the 3-methylindole—*DDT* complex indicating 1:1 stoichiometry in carbon tetrachloride

The dipole moment arising from donor-acceptor interaction, μ_{DA}, has been calculated after due allowance is made for the polarity of the component molecules by using the following equation[12,13],

$$\mu_{DA} = \mu_C - (\mu_A + \mu_D)$$

where μ_C, μ_A and μ_D refer to the dipole moment of overall component molecules, acceptor and donor, respectively. The equilibrium constant, K_1, and μ_{DA} data are listed in Table 2. From this Table it is evident that the order of μ_{DA} thus noted is: 3-methylindole > 2-methylindole > indole > naphthalene > benzene. The similar order of interaction was noted in our NMR[7], and refractometric studies[1].

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