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The dielectric properties of metal thiocarboxamide complexes and their molecular complexes with iodine

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ABSTRACT

The dielectric properties of molecular complexes have been formed by Co $(ETH)_2$, Ni $(ETH)_2$, Cu $(ETH)_2$, and Zn $(ETH)_2$ (ETH represents, N-Ethoxycarbonylpyrrole-2-thiocarboxamide) and iodine have been studied in carbon tetrachloride. These studies provide a substantial information on the geometry of these molecular complexes.

Key words: Metal thiocarboxamide, Molecular complex, iodine

INTRODUCTION

In the recent years[1,2] the dielectric properties of molecular complexes have been used to provide information on the molecular charge distribution on complex formation and also life time of complex[3]. The dipole moment of charge transfer complex is particular interest in that it should be directly related to the dative contribution to the ground state of the complex.

Comparison of the dipole moment of the complex with dipole moment of the complex with dipole moment of the component molecules provides information on the charge redistribution on complex formation. Thus it gives a measures of the strength of the interaction between the donor and acceptor molecules. Further, electronic coupling solvent reorganization, and the distance of charge transfer are factors of central significance in the kinetics of nearly all the molecule based electron transfer reactions[4,5]. The magnitude and, therefore, and absolute quantitative influence of each can depend on an enormously wide variety of donor, acceptor and bridge structural and chemical compositional consideration.

Since donor (metal complexes) acceptor (iodine) complexes exhibit a donor-acceptor charge transfer (DACT) in visible to near I.R. region of spectrum[6,7]. The extent of charge transfer associated with DACT processes, a critical factor in characterizing electronic interactions is difficult to obtain quantitatively. For weak coupling between donor and acceptor, the electronic coupling matrix element. H_{ab} can be estimated by using Hush theory[8,9]

$$H_{ab} = (2.06 \times 10^{-2}) \frac{\sqrt{\nu_{max.} \varepsilon_{max.} \overline{\nu}_{1/2}}}{\Delta\mu / e}$$

where $\nu_{max.} \varepsilon_{max} and \nu_{1/2}$ are the peak location extincaiton-coefficeint, and full width at half maximum, respectively, of the absorption. $\Delta\mu$ is the change in dipole moment between the ground and excited state and defines the effective charge transfer distance $\Upsilon_{ab} = \Delta\mu/e$ where ε is the unit of charge.

Electroabsorption spectroscopy can provide quantitative information on the change in dipole moment and polarizability for an electronic transition[10].

EXPERIMETNAL

Materials

Metal thiocarboxamide complexes have been prepared by the procedure elsewhere[11].

Preparation of the solutions

The stock solutions of metal thiocarboxamide complexes were prepared by weighing on an analytical balance and subsequent dilution of the required volume in volumetric flasks in carbon tetrachloride of chloroform. The solutions employedinthe measurements of dipole moment were prepared from the stock solutions by pipetting the calculated volume into 10 ml. volumetric flasks. All the stock solutions were made on the day of different studies for dipole moment.

Measurement of density

The density of the different metal thiocarboxamide complexes were measured by the usual relative density bottle (5 ml) method. The weinghing for all the solutions were made on an analytical balance.

Determination of refractive index

The refractive index, η, of all he metal thiocarboxamide complexes were measured by the help of Abbe's Refractrometer at room temperature.

Determination of dielectric constant

In the present study, we have used the R.C.L bridge for measuring the dielectric constant.

Evaluation of the dipole moment

Matter is polarized by external fields. Molar polarization, P, is related to the relative permittivity, $\in$. of the material by:

$$P = \frac{\in -1}{\in +2}.\frac{M}{d} \qquad ...(1)$$

Where M, is the molar mass and d, the density. Equation (1) is known as the clausius-Mosotti equation[12]. They related the molar polarization to the polarizability, α, of non-polar molecules by

$$P = \frac{\in -1}{\in +2}.\frac{M}{d} = \frac{N}{3\in}.\alpha \qquad ...(2)$$

where N is the Avogadro constant and $\in$ is the permittivity of vacuum.

Equation (2) converse to the Lorenz-Lorentz[13] equation for the molar refraction, R, is given by.

$$R = \frac{n^2-1}{n^2+2}.\frac{M}{d}\frac{N}{3\in}.\alpha \qquad ...(3)$$

where n, is the refractive index. Debye[14] extended the Clausius-Mosottti equation to dipolar systems and deduced.

$$P = \frac{\in -1}{\in +2}.\frac{M}{d} = \frac{N}{3\in}\left(a + \frac{\mu 2}{3KT}\right) \qquad ...(4)$$

The orientation polarization P_0, $N\mu^2/9$ KT (μ is the magnitude of the dipole moment vector) and the distortion polarization

$$P_D = P_E + P_A = N(\alpha_E + \alpha_A) / 3 \in,$$

where α_E and α_A are the electronic and atomic polrizabilties, respectively. The equation (4) εform the basis of most evaluations of molecular dipole moments. However, in dilute solutions and in the absence of molecular interactions (e.g., hydrogen bonding) the Debye[14] and Onasager15 equations yield dipole moments in reasonable agreement with each other.

In the present work the dipole moment was measured by the help of Debye[14] equation which is accurate one particularly for the dilute solutions. In the case of liquids, the poles are very near to each other and neutralize each other due to association. Now, fi the polar substance is dissolved in a non-polar solvent the tendency for dipole interaction to occure is generally relatively small, so that the total polarization can be regarded as equal to the sum of the polarization of the constituents. On this basis, equation (4) can be written as

$$P_{1,2} = \frac{\in_{1,2}-1}{\in_{1,2}+2}.\frac{C_1M_1+C_2M_2}{d_{1,2}} = C_1P_1+C_2P_2 \qquad ...(5)$$

where $P_{1,2}$ is the total polarization of the solution of a non-polar substance1, and a polar compound 2,$\in_{1,2}$ is the dielectric constant of the complex. $d_{1,2}$ is the density of the complex C_1, M_1,

Table - 1: Dielectric data on the interaction of N-Ethoxycarbonxylpyrrole-2-thiocarboxamide (ETH) wiht iodine* in CCl_4 at 22°C

ETH	η	d	Δ	μx10^{18}	μx10^{18}
5.00 × 10^{-1} M	1.4546	1.5829	12.624	2.838	
2.50 × 10^{-1} M	1.4545	1.5828	12.99	2.840	
1.66 × 10^{-1} M	1.4544	1.5827	13.49	2.843	
1.25 × 10^{-1} M	1.4544	1.5826	13.74	2.845	2.844
1.00 × 10^{-1} M	1.4543	1.5826	13.99	2.848	
0.83 × 10^{-1} M	1.4542	1.5825	13.99	2.848	
0.70 × 10^{-1} M	1.4542	1.5825	14.09	2.849	

*The concentration of iodine was constant kept constant at 1 × 10^{-3} M in each case.

Table - 2: Dielectric data on the interaction of Co $(ETH)_2$ wiht iodine* in CCl_4 at 22°C

Co $(ETH)_2$	η	d	Δ	μx10^{18}	μx10^{18}
5.00 × 10^{-3} M	1.4673	1.5851	3.676	2.129	
2.50 × 10^{-3} M	1.4670	1.5849	4.251	2.133	
1.66 × 10^{-3} M	1.4669	1.5848	4.751	2.140	
1.25 × 10^{-3} M	1.4669	1.5848	5.371	2.143	2.141
1.00 × 10^{-3} M	1.4668	1.5847	5.701	2.145	
0.83 × 10^{-3} M	1.4667	1.5847	5.876	2.150	
0.70 × 10^{-3} M	1.4667	1.5847	4.881	2.151	

*The concentration of iodine was kept constant at 1 × 10^{-3} M in each case.

Table - 3: Dielectric data on the interaction of Ni (ETH) wiht iodine* in CCl_4 at 22°C

Ni $(ETH)_2$	η	d	Δ	μx10^{18}	μx10^{18}
5.00 × 10^{-3} M	1.4671	1.5849	3.674	2.127	
2.50 × 10^{-3} M	1.4668	1.5847	4.249	2.131	
1.66 × 10^{-3} M	1.4667	1.5846	4.749	2.138	
1.25 × 10^{-3} M	1.4667	1.5846	5.369	2.141	2.139
1.00 × 10^{-3} M	1.4666	1.5845	5.699	2.143	
0.83 × 10^{-3} M	1.4665	1.5845	5.874	2.148	
0.70 × 10^{-3} M	1.4665	1.5846	4.879	2.149	

*The concentration of iodine was kept constant at 1 × 10^{-3} M in each case.

Table - 4: Dielectric data on the interaction of Cu $(ETH)_2$ wiht iodine* in CCl_4 at 22°C

$Cu(ETH)_2$	η	d	Δ	μx10^{18}	μx10^{18}
5.00 × 10^{-3} M	1.4660	1.5840	3.376	1.54	
2.50 × 10^{-3} M	1.4658	1.5838	3.751	1.55	
1.66 × 10^{-3} M	1.4659	1.5837	4.126	1.56	
1.25 × 10^{-3} M	1.4659	1.5837	4.376	1.57	1.56
1.00 × 10^{-3} M	1.4657	1.5836	4.626	1.57	
0.83 × 10^{-3} M	1.4656	1.5836	4.801	1.58	
0.70 × 10^{-3} M	1.4656	1.5835	4.801	1.58	

*The concentration of iodine was kept constant at 1 × 10^{-3} M in each case.

Table - 5: Dielectric data on the interaction of Zn $(ETH)_2$ wiht iodine* in CCl_4 at 22°C

$Zn(ETH)_2$	η	d	Δ	μx10^{18}	μx10^{18}
5.00 × 10^{-3} M	1.4657	1.5838 ∈	3.374	1.52	
2.50 × 10^{-3} M	1.4655	1.5836	3.749	1.53	
1.66 × 10^{-3} M	1.4656	1.5835	4.124	1.54	
1.25 × 10^{-3} M	1.4656	1.5835	4.374	1.55	1.54
1.00 × 10^{-3} M	1.4654	1.5834	4.624	1.55	
0.83 × 10^{-3} M	1.4653	1.5833	4.799	1.56	
0.70 × 10^{-3} M	1.5653	1.5833	4.799	1.56	

*The concentration of iodine was kept constant at 1 × 10^{-3} M in each case.

Table - 6: Comparison of dipole moment of Metal thiocarboxamie complexes with iodine in CCl_4 at 22°C

M(ETH)2	μ_{donor} ×10^{18}	$M(ETH)_2$-I_2	$\mu_{complex}$ ×10^{18}
ETH	2.628	ETH	2.844
Co $(ETH)_2$	1.324	Co $(ETH)_2$-I_2	2.141
Ni $(ETH)_2$	1.321	Ni $(ETH)_2$-I_2	2.139
Cu $ETH)_2$	1.210	Cu $(ETH)_2$-I_2	1.56
Zn $(ETH)_2$	0.960	Zn $(ETH)_2$-I_2	1.54

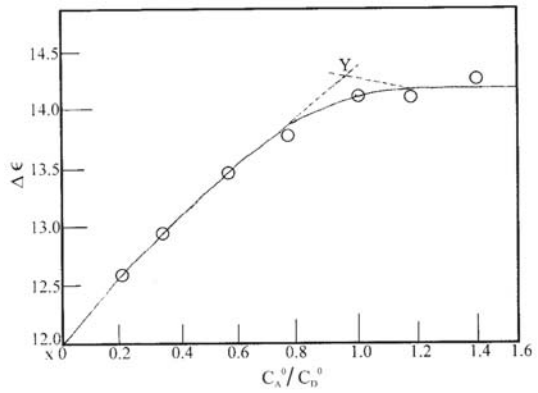

Fig. - 1: Plot of C_A^0 / C_D^0 versus ΔE for the interactionof ETH - iodine in CCl_4.

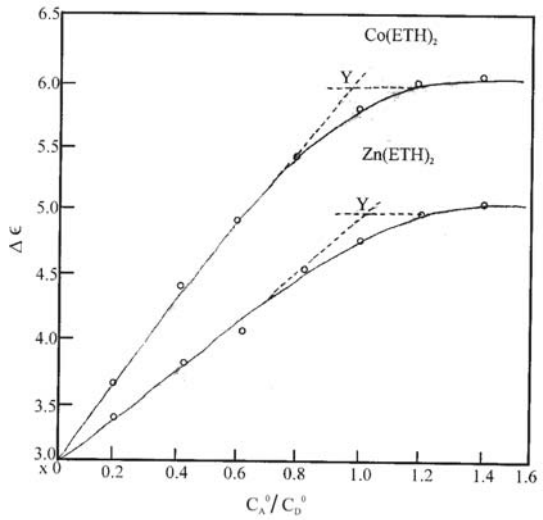

Fig. - 2: Plot of C_A^0 / C_D^0 versus ΔE for the interactionof Co $(ETH)_2$ and Zn $(ETH)_2$ - iodine in CCl_4.

P_1, C_2., M_2, P_2, are molar fraction, molecular weight and total polarization of the solvent and solute respectively.

Since 1, is non-polar. P_1, can be determined by the relation and then P_2 can be

$$P_1 = \frac{\epsilon_1 - 1}{\epsilon_1 + 2} \cdot \frac{M}{d_1} \qquad ...(6)$$

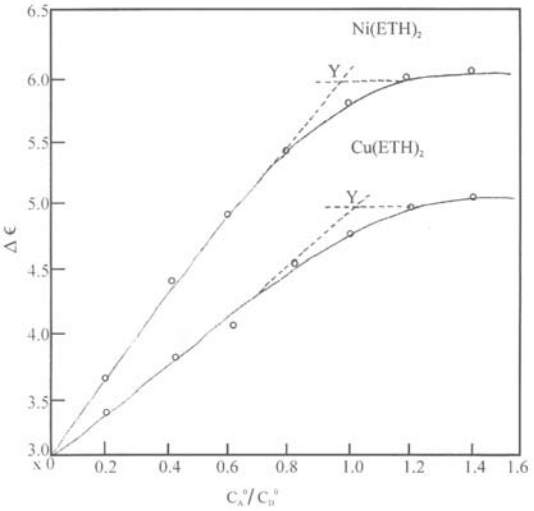

Fig. - 3: Plot of C_A^0 / C_D^0 versus ΔE for the interactionof Ni $(ETH)_2$ and Cu $(ETH)_2$ - iodine in CCl_4.

calculated. When we have determined the total polarization P_2 we can find Pμ (the orientation polarization) by the refraction method, given by

$$\mu = 0.0127 \times 10^{-18} \sqrt{(P\text{-}P_D)}\, T \qquad ...(7)$$

where P, is the total polarization and P_D ($P_E + P_A$), the distortion polarization ($P\text{-}P_D$) being equal to Pμ, the distortion polarization, P_D is determined by

$$P_D = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} \qquad ...(8)$$

where n, is the refractive index of the complex.

RESULTS AND DISCUSSION

The diploma moments of the molecular complexes of iodine with N-Ethoxycarbonylpyrrol-2-thiocarboxamide (ETH), Co (ETH)2, NI (ETH)2, Cu(ETH) and Zn (ETH)2 were obtained from the method given in (e) and have been recorded in Table-5. The dipole moments of pure and charge

transfer complex are compared in Table 6. From this table, it is evident that when ETH or metal thiocarboxamide form molecular complexes with iodine, there is an increase in the dipole moments after complexation. Further, the maximum increase in dipole moment of the complex is observed in the case of ETH complex. This indicate stronger interaction with iodine in this particular case and it follows the following order:

$$ETH > Co(ETH)_2 > Ni(ETH)_2 > Zn(ETH)_2$$

The stoichimetry of above molecular complexes has been determined using dielectric titration technique[16]. Through this technique, the change in the dielectric permittivity, Δ is of a solution of one component (iodine) on the addition of successive amount of the other component (metal thiocarboxamide complexes) has been measured. Now considering the addition of a dipolar donor to a non-dipolar acceptor producing a complex with a dipole moment larger than the dipole moment of the donor. The addition of a small amount of donor generates an equal amount of complex. The permittivity increases on successive addition of the donor and continues to increase until the equivalent quantities of the donor and acceptor are present. This situation is schematically shown by line xy of figure 1 to 3 which indicates the 1:1 stoichiometry of these complexes.

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