ELECTRONIC CONDUCTION IN H_2O DOPED SOLID METHYLENE BLUE

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Abstract : Traces of water as an impurity is found to increase the electronic conductivity of the charge transfer solid methylene blue. It is found that hydrogen bonded and free molecules of water decrease the thermal activation energy of charge carriers in different ways. Theoretical arguments based on the small polaron theory are given to explain the mechanism of conduction.

1. Introduction

Experimental and theoretical investigations on electrical transport in molecular solids, especially charge transfer (CT) complexes have attracted much attention.[4,5,7,8] In general the neutral CT solids are insulators or poor semiconductors while ionic CT complexes show much enhanced semiconduction.[2] The mechanism of conduction in these materials is quite involved and often arise from a band structure or hopping of the charge carriers between localized donor-acceptor sites.[1,3,9] When the mobilities are small the latter mode charge transport is explained satisfactorily by the small polaron theory.[1,3,9]

In this note we report our observations on enhancement of electrical conductivity of methylene blue (organic CT complex) by water molecules present as an impurity. A simple qualitative argument based on the small polaron theory is presented to explain how bonded and free water molecules could reduce the energy needed for the thermal activation of charge carriers.

2. Experimental

Methylene blue (BDH and Aldrich brands) are purified by recrystallization from the alcoholic solution. The purified compound dried in vacuo melts sharply at 463.4 K. Anhydrous samples when exposed to the humid atmosphere readily absorb moisture. Data on thermal gravimetric analysis is indicated in Figure 1. It is seen that in addition to water that is lost continously, the material can also hold $\sim$ 14.5% bonded water corresponding to a hydration number of 3.
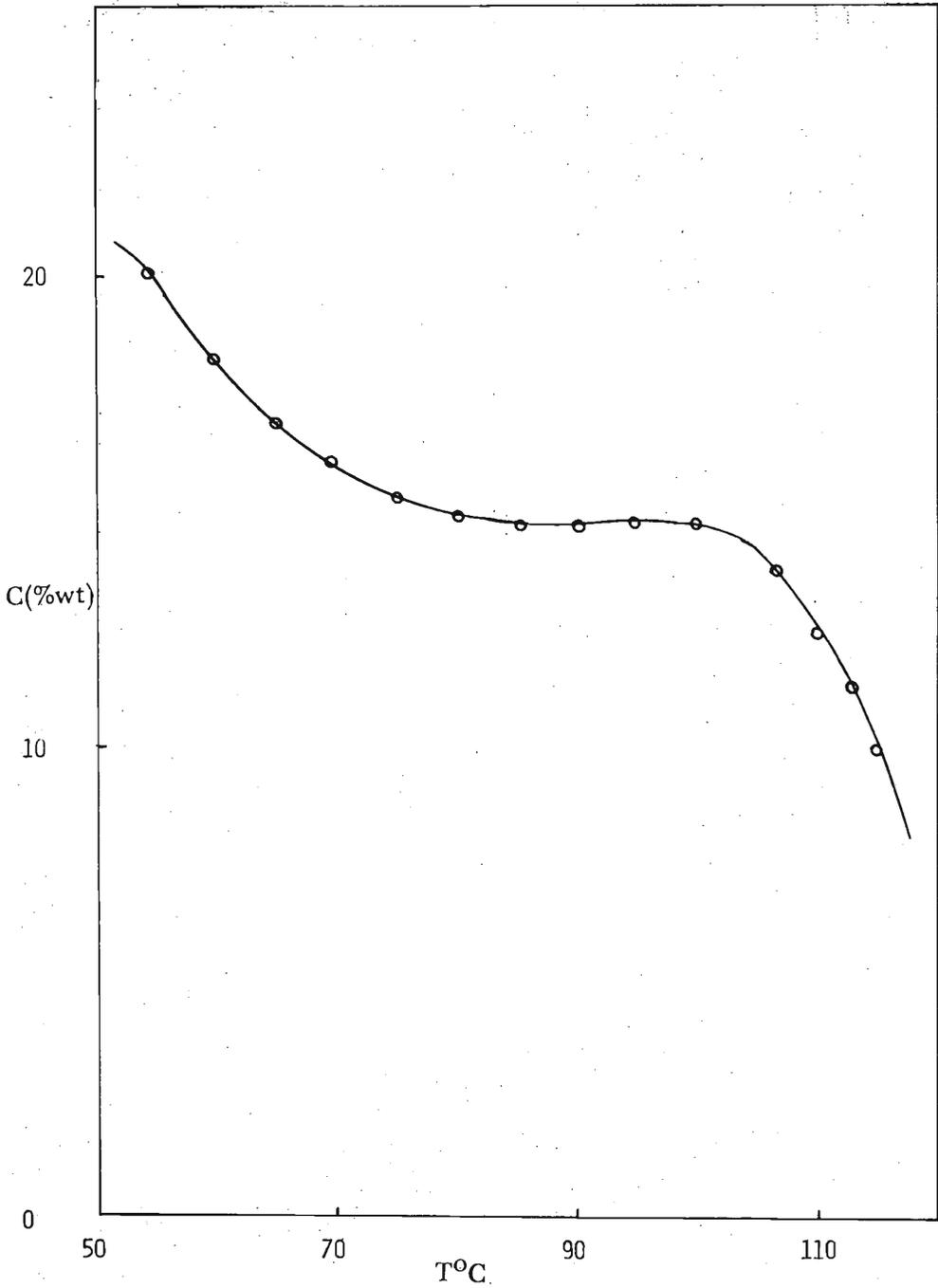
Figure 1. Thermal gravimetric analysis data of a sample of moisture absorbed methylene blue giving the percentage of water (C%) when heated at a constant rate 2 K min^{-1}.

Varying amounts of moisture are introduced by exposing weighed quantities of the material into the humid atmosphere in desiccators containing water. The samples for conductivity measurements are made by pressing the powder between stainless electrodes in pyrex tubes (diameter ~ 0.4 cm, pellet length ~ 0.3 cm). Ends of the tube are sealed with epoxy resin, they are immersed in a thermostatic oil bath and d.c. conductivities at different temperatures are determined using a resistance meter. D.C. current voltage characteristics are tested and found to be linear at all temperatures < m.p, provided the concentration c of absorbed water does not exceed $\sim 10\%$ by weight. Compound containing more than the above quantity of water shows nonlinear and time varying I–V characteristics, at temperatures below $\sim$ 383K. This can be attributed to ionic conduction as electrolytic effects are also seen under these conditions. However when the water content is << 10%, conduction is almost entirely electronic, this can be proved by passing large currents through thin discs of the pressed material, when V.I characteristics remain linear and time invariant. Also polarization effects are not seen when blocking electrodes were used.

Although it is difficult to prepare sizable single crystals, few careful measurements show that there are no significant differences in the conductivity properties of compressed pellets and single crystals. Four terminal and two terminal measurements with compressed pellets give the same results indicating that the surface effects are negligible.

Table 1.   Conductivity and activation energies $E_1(T < T_c)$, $E_2(T > T_c)$ for methylene blue at different levels of doping with H_2O.

C (% wt)	$\sigma_{30}/M^{-1}m^{-1}$	E_1/eV	E_2/eV
0	6.9×10^{-11}	—	1.50
0.2	2.8×10^{-7}	0.69	1.45
1	1.4×10^{-6}	0.66	1.20
3	4.6×10^{-6}	0.61	0.92
5	4.5×10^{-4}	0.55	0.54
10	4.5×10^{-3}	0.42	—

3. Results

The room temperature 303 K conductivity of anhydrous methylene blue is $\sim 10^{-8}$ Ω^{-1} m^{-1}. Traces of moisture increase the conductivity by several orders of magnitude (Table 1). The plot of $\ln \sigma$ vs T^{-1} at different concentrations C of water is shown in Figure 2. It is seen that at lower values of C the data fit into two straight line portions with a sudden change of the slope at $T_c \simeq 383$ K. As C increases further (C > 10%) the abrupt change tends to become continous. The region of continous change of slope is associated with ionic conductivity and at still higher values of C (>20%) ionic conduction is detectable even at room temperature.

It is also found that the values of thermal activation energy E corresponding to the straight line portions $T < T_c$ and $T > T_c$ in the plots $\ln \sigma$ vs T^{-1} decrease linearly with C as long as C does not exceed $\sim$ 10% (Figure 3).

4. Theory and Discussion

As mentioned in the introduction the electrical transport in most low mobility molecular solids is due to hopping of the charge carriers between localized sites. In methylene blue (structural formula given in Figure 4) Cl^- would act as a electron donor and S^+ with an unpaired electron an acceptor. If I = ionization energy of the donor, A = electron affinity of the acceptor. Thermal activation energy of hopping conduction can be written in the form,[6]

$$E = -\left(\frac{Ne^2}{8\pi\epsilon_o r}\right) (1 - \epsilon^{-1})$$

where N = Avogarodo constant, e = electronic charge
ϵ_o = permittivity in vacums, r = radius of the polarization cavitiy,
ϵ = static dielectric constant.

The last term in (1) gives the polarization energy (r = radius of the polarization cavity, ϵ = static dielectric constant). As the dipole moment of the water molecules is very high and they diffuse easily through the solid, the polarization cloud around the hopping electron would consist mainly of water molecules. It is seen from (1) that the high dielectric constant of water increases the polarization energy reducing I.

Again I and A could also be changed by H_2O molecules. The high dielectric constant of H_2O will reduce I and it is reasonable to suppose that bonded H_2O is more effective in decreasing I. The thermal energy kT_c ($\sim$ 0.03 eV) is of the same order of magnitude as that of a hydrogen bond and the sudden increase in E at $T > T_c$ may be interpreted as resulting from breaking of these bonds.
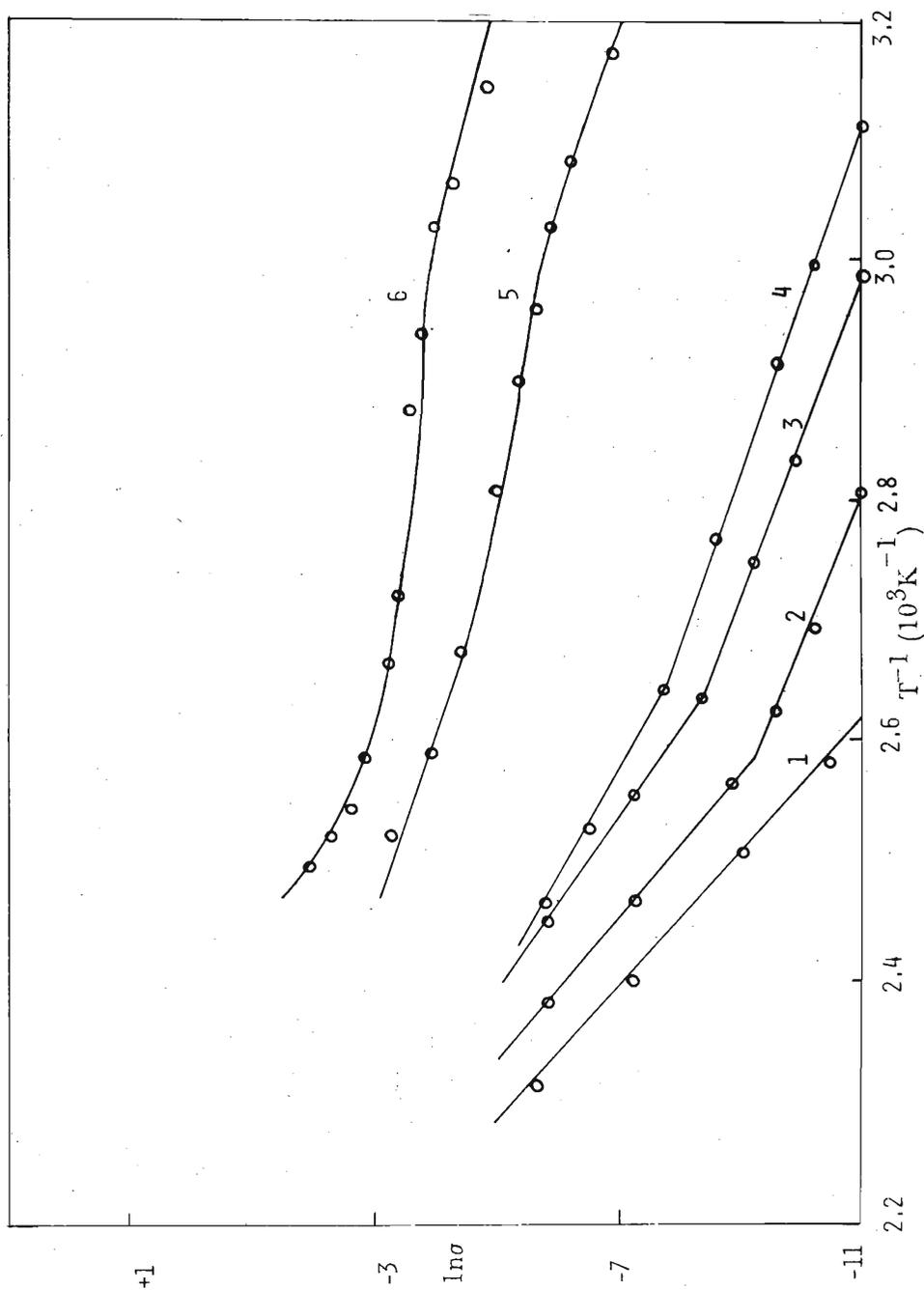
Figure 2.   Plot of $\ln \sigma$ vs T^{-1} (σ in Ω^{-1} m^{-1}). The Percentage of H$_2$O by weight
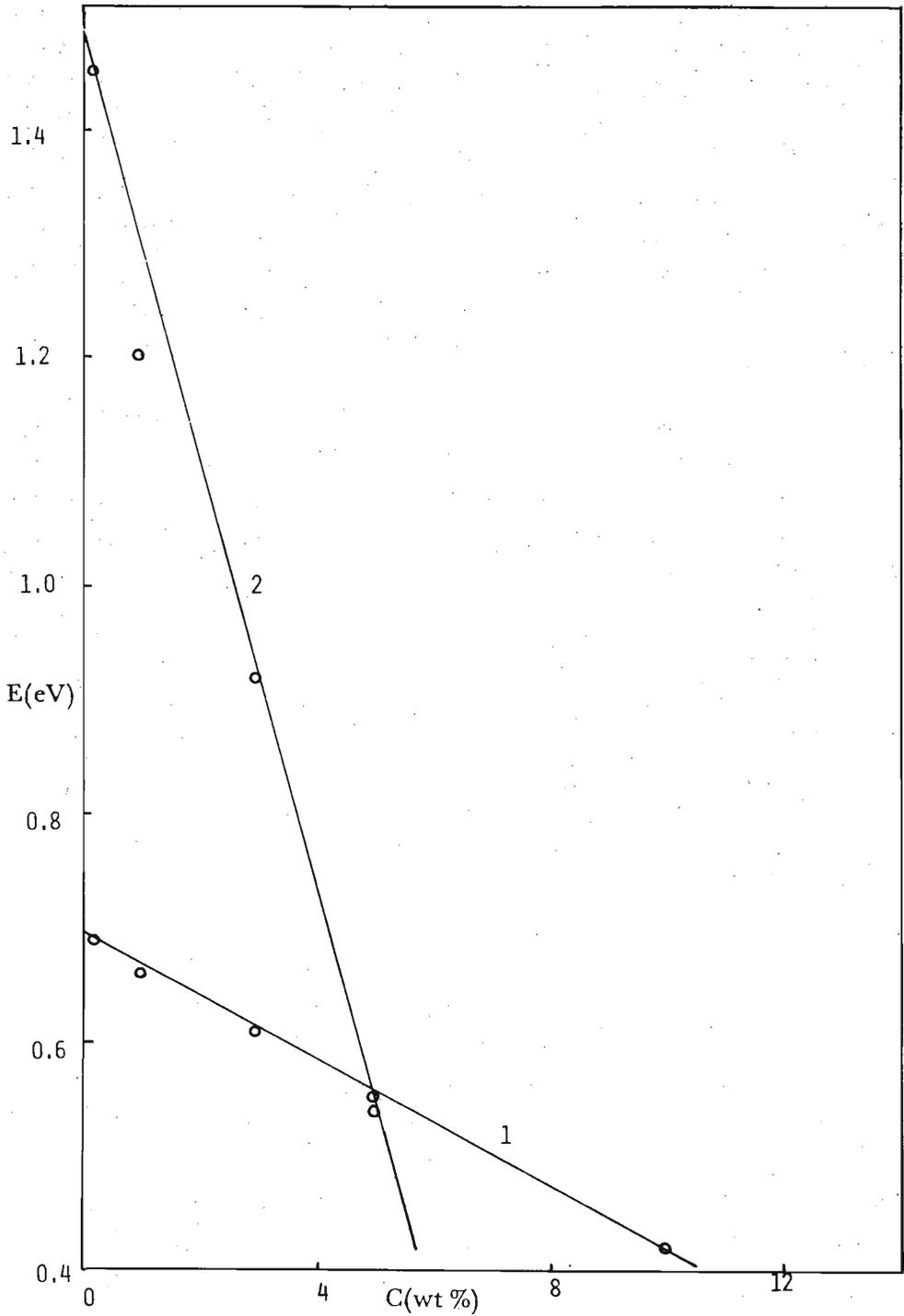(i) 0% (2) 0.2% (3) 1% (4) 3% (5) 5% (6) 10%

Figure 3.   Plot of activation energy E vs concentration of H_2O (% by wt (1) $T < T_c$
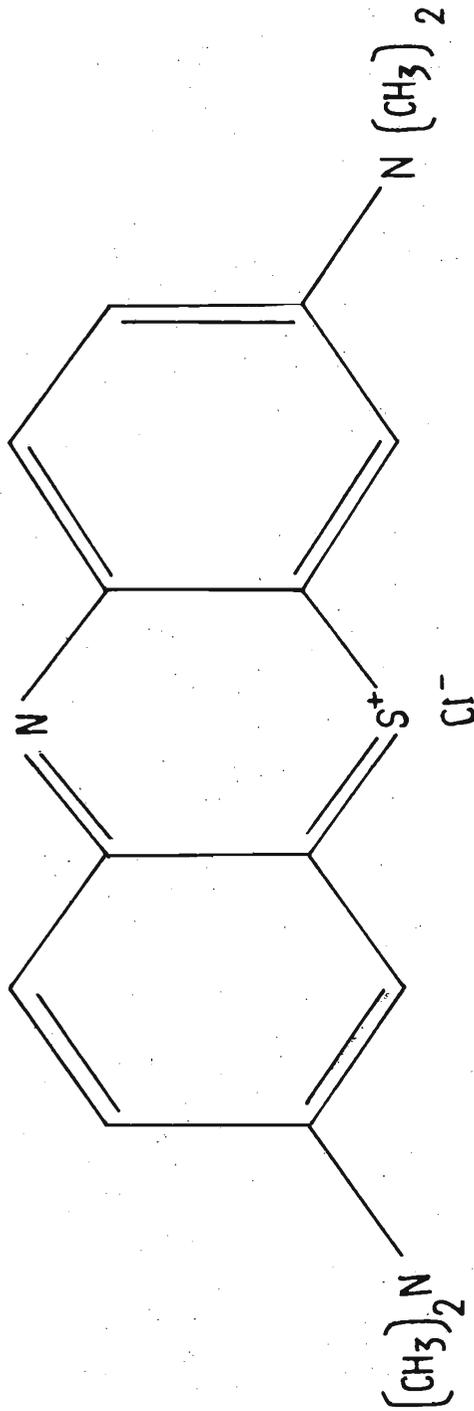(2) $T > T_c$

Figure 4.   Structural Formula of methylene blue.

Several other molecular solids exhibit water activated electronic conduction.[10] Methylene blue is particularly interesting because, the effect of the hydrogen bonded water molecules in reducing the thermal activation energy is clearly manifested as a conductivity transition.

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