Compensation Effect in the Electrical Conduction Process in Some Nucleic Acid Base Complexes with Acriflavine Dye

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The validity of the compensation rule is studied for nucleic acid bases, adenine, cytosine, and uracil complexes with acriflavine dye. The value of the semiconduction activation energy of a complex varies with dye concentration. It is shown that at low dye concentration, these semiconducting complexes follow the three parameter equation $\sigma(T)=\sigma_0'\exp(E/2kT_0)\exp(-E/2kT)$, where σ_0' and T_0 are constant for a particular base, other notations have their usual meaning. Consistent values for σ_0' and T_0 have been obtained by using various methods of evaluation. These results suggest that compensation effect has a physical origin.

In some earlier communications we have demonstrated the validity of the compensation rule in the electrical conduction process in some polyene[1,2] and nitro aromatic[3] semiconductors. The variation in the semiconduction activation energy was obtained by adsorbing various chemical vapors on the crystallite surfaces in a polycrystalline sandwich cell configuration. It has been shown that these organic semiconductors follow the three constant equation

$$\sigma(T) = \sigma_0' \exp(E/2kT_0)\exp(-E/2kT), \quad (1)$$

where $\sigma(T)$ is the specific conductivity at TK, E is the semiconduction activation energy and k is the Boltzmann constant. The parameters σ_0' and T_0 are constants for a particular semiconductor.

The activation energy of a semiconductor may be varied by other methods also e.g. hydration, doping of impurity, complex formation, physical mixing etc. The interaction of acridine dyes with DNA and nucleic acid bases is of considerable biological significance. Such interaction is involved in frame shift mutation, antibacterial activities and photodynamic action. The spectroscopic studies confirm the complex formation between flavins and the purine and pyrimidine bases.[4] The binding of the dye molecules with the bases are believed to bring about the biological effects. For interaction with DNA two modes of interaction are suggested depending upon the DNA/Dye ratio.[4] For complex formation with nucleic acid base, the site of attack in a base depend on the electronic properties of the dye.[5] However, the modes of binding of nucleic acid bases with dyes also depend on dye concentration.[6] We have studied the semiconductive properties of the complexes of acriflavine dye with nucleic acid bases, adenine, cytosine, and uracil at various dye concentrations. In this paper we show that in the low dye concentration range ($\lesssim 10^{-1}$ mol mol^{-1}), these semiconducting complexes show compensation effect.

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Experimental

The purine and pyrimidine bases used in the present study are adenine, cytosine, and uracil. These were obtained from Sigma Chemical Company, U. K., Acriflavine, a mixture of 2,8- and 3,6-diamino-10-methylacridinium chloride and 2,8- and 3,6-diaminoacridine was also obtained from the same commercial source. The bases and the dye were extensively purified by repeated crystallization from distilled water and methanol respectively and finally dried under vacuum before use. For preparing the complexes, acriflavine dye and the bases were taken in required proportions and dissolved in distilled water and then evaporated in vacuum. The finely powdered sample pressed in a sandwich cell between a conducting glass and a stainless steel electrode was maintained at moderate pressure by clips. The separation between the electrodes was maintained by a three mil thick teflon spacer. The cell was placed in a suitably designed conductivity chamber. A d.-c. voltage of 27 volts from a dry battery pack was applied across the cell. Dark conductivity was measured in both nitrogen atmosphere and vacuum using an Electrometer amplifier EA 815 of ECIL, India. The thermo emf was measured by a digital panel meter model HIL 2301, India. The experimental procedure for the measurement of activation energy was similar to that described earlier.[1]

Results and Discussion

The semiconduction activation energies of the crystalline powders of pure adenine, crytosine, uracil bases, and various base-dye complexes were measured several times in dry nitrogen atmosphere and also in vacuum (10^{-3} Torr (1 Torr=133.322 Pa)). All measurements gave consistent values. Almost the same values were obtained in dry nitrogen and in vacuum. The activation energies of pure adenine, cytosine, uracil, and acriflavine are 2.10, 2.12, 2.15, and 2.25 eV, respectively. The room temperature (30 °C) specific conductivities of the bases and also of the dye is typically of the order of 10^{-16}—10^{-18} Ω^{-1} cm^{-1}.

The current voltage characteristics of all the pure samples and the complexes are observed to be ohmic in the low voltage region (36 V) of our studies. In

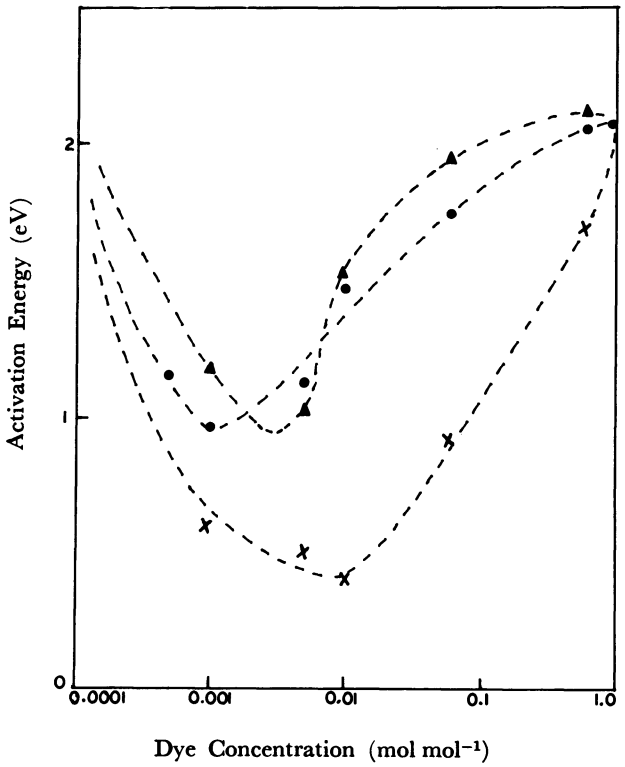

Fig. 1. Dye concentration dependence of semiconduction activation energy of various nucleic acid base-dye complexes. The lines are only for visual guide. Acriflavine complexes with i) Cytosine —×—. ii) Uracil —▲—. iii) Adenine —●—.

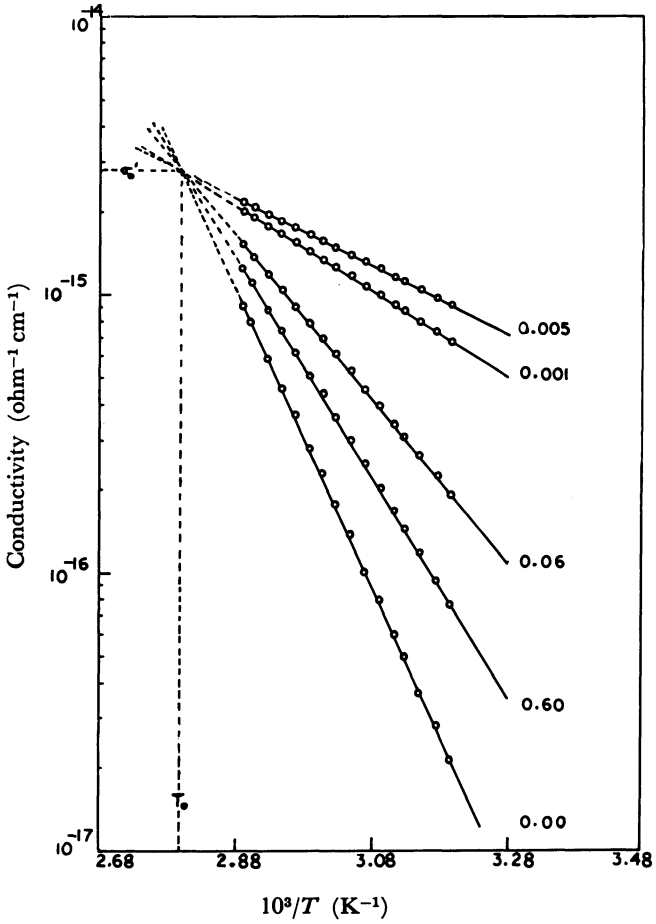

Fig. 2. $\log \sigma(T)$ vs. $1/T$ plot for cytosine-acriflavine dye complexes of different dye concentrations. The dye concentrations in mol mol^{-1} are shown in the diagram.

Fig. 1, we show the dye concentration dependence of activation energy for various complexes. As the dye concentration in a complex decreases from 1 mol mol^{-1} semiconduction activation energy decreases and reaches a minimum value at a certain dye concentration below which it starts increasing again and approaches the activation energy value of pure purine or pyrimidine base. For cytosine-acriflavine complex the minimum activation energy value obtained is 0.40 eV at 10^{-2} mol mol^{-1} dye concentration. For uracil-acriflavine and adenine-acriflavine complexes the minimum E value measured are 1.02 eV at 3×10^{-3} mol mol^{-1} dye concentration and 0.96 eV at 10^{-3} mol mol^{-1} dye concentration, respectively.

The binding of metal cations to nucleic acid bases and its relationship with electrostatic molecular potential of the bases have been discussed by Pullman and Pullman.[7] Their calculated electrostatic interaction energy is large for cytosine whereas it is small and is about the same magnitude for adenine and uracil. It is interesting to note that the change in semiconduction activation energy of our base-dye complexes also show a similar order.

In Fig. 2, we show the log σ (T) vs. $1/T$ plot for cytosine-acriflavine complexes of different dye concentration. It is seen that the extrapolated lines in these plots for complexes with different dye concentration intersect the ordinate at a wide variety of positions, but they all pass approximately through a single point at a temperature T_0. This result is in conformity with expression (1). At the characteristic temperature T_0, the value of $\sigma(T_0)$ gives the σ_0' value. For cytosine-acriflavine complexes, T_0=357 K and $\sigma_0'=2.8\times10^{-15}\,\Omega^{-1}\,\mathrm{cm}^{-1}$. In Figs. 3 and 4, we have shown similar log σ (T) vs. $1/T$ plot for uracil-acriflavine and adenine-acriflavine complexes. In these complexes, also the extrapolated lines pass through a single point. However in these complexes, the point of intersection is in the low temperature side of the working temperature region. From expression (1) we get that at any experimental temperature T_1K,

$$\sigma(T_1) = \sigma_0' \exp\left(\frac{1}{T_0} - \frac{1}{T_1}\right)\frac{E}{2k}.$$

The $\sigma(T_1)$ will show different behavior with variation of E depending on if $T_1>T_0$ or $T_1>T_0$. This is exactly what we see in the three complexes. In cytosine-acriflavine complex $\sigma(T_1)$ increases with

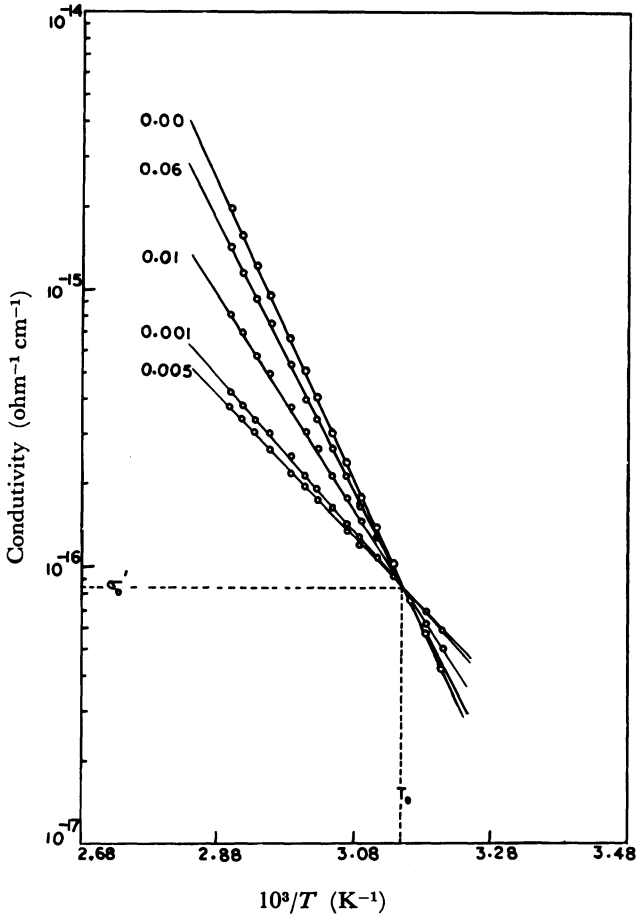

Fig. 3. $\log \sigma(T)$ vs. $1/T$ plot for uracil-acriflavine dye complexes of different dye concentrations. The dye concentrations in mol mol^{-1} are shown in the diagram.

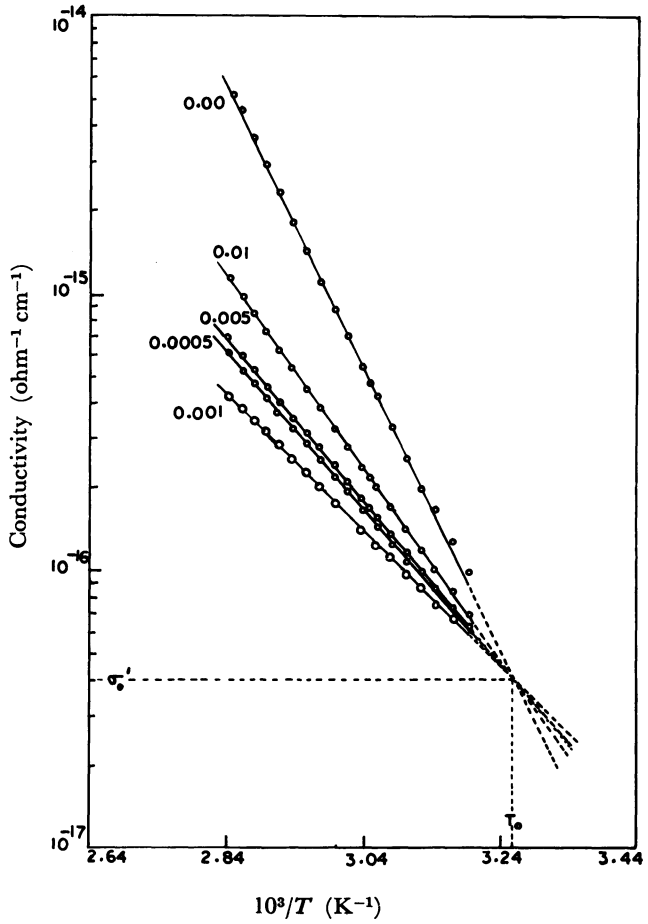

Fig. 4. $\log \sigma(T)$ vs. $1/T$ plot for adenine-acriflavine dye complexes of different dye concentrations. The dye concentrations in mol mol^{-1} are shown in the diagram.

decreasing E whereas in adenine-acriflavine and uracil-acriflavine complexes inverse behavior is observed. Inspite our measurement being limited by the electrometer sensitivity, we have been able to measure $\sigma(T)$ on both sides of T_0 in case of uracil-acriflavine complexes. To our knowledge, this is the first experimental demonstration of different behavior of change of $\sigma(T)$ with variation of E on two sides of a specific temperature in an organic semiconductor thus showing the physical significance of compensation temperature T_0.

It is now clear from experiments that the compensation temperature T_0 of a semiconductor plays an important role in dark conduction process. Acriflavine complexes with the three nucleic acid bases cytosine, adenine, and uracil have three distinct T_0 values. This result confirms our earlier observation with some polyenes[1,2] and some nitro aromatics[3] that T_0 is a molecular property.

"True" compensation effect is thought to arise from the existence of a linear relationship between the activation energy and the activation entropy of the system. It has been pointed out by Johnston and Lyons[6] that if a true linear free energy relation (LFER) does hold for dark conduction indicating a physical relationship between σ_0 and E, $\log(T_1)$ vs. E must also be linear where T_1 is a specific temperature. In Fig. 5, we show such plots for cytosine-acriflavine, adenine-acriflavine, and uracil-acriflavine complexes. T_0 and σ_0' are obtainable from the slopes and intercepts of these plots. These parameters can also be evaluated from plots made in alternate fashion as $\log \sigma_0$ vs. E since $\log \sigma_0 = \log \sigma_0' + E/2kT_0'$ σ_0 and E being experimentally measured. In Fig. 6, we show such plots for three different complexes. The plots are linear as expected from expression (1) and T_0 and σ_0' are obtained from the slopes and the intercepts respectively of these plots. In Table 1, we compare the values of T_0 and σ_0' for the complexes obtained by various methods of evaluation. The agreement is quite satisfactory. These results confirm that σ_0 and E are physically related and that T_0 has a physical origin. That we have observed compensation effect only in complexes of low dye concentra-

Table 1. Comparison of T_0 and σ_0' of Nucleic Acid-Base Acriflavine Dye Complexes Obtained by Various Methods of Calculation

Base	Different Parameter	Nucleic acid base/Dye ratio						
		1 : 0.00	1 : 0.0005	1 : 0.001	1 : 0.005	1 : 0.01	1 : 0.06	1 : 0.60
Cytosine	E / eV	2.12	—	0.60	0.50	—	0.92	1.70
	σ_T / ohm^{-1} cm^{-1}	8.70×10^{-18}	—	4.10×10^{-16}	6.10×10^{-16}	—	7.20×10^{-17}	2.00×10^{-17}
	σ_0 / ohm^{-1} cm^{-1}	3.87×10^{0}	—	5.40×10^{-11}	1.08×10^{-11}	—	7.50×10^{-9}	4.80×10^{-13}
	σ_0' / ohm^{-1} cm^{-1} from Fig. 2.	←			2.80×10^{-15}			→
	σ_0' / ohm^{-1} cm^{-1} from Fig. 6.	←			4.00×10^{-15}			→
	T_0/K from Fig. 2.	←			357.10			→
	T_0/K from Fig. 6.	←			344.00			→
Uracil	E / eV	2.15	—	1.25	1.02	1.53	1.90	—
	σ_T / ohm^{-1} cm^{-1}	2.50×10^{-18}	—	1.85×10^{-17}	2.15×10^{-17}	1.07×10^{-17}	3.30×10^{-18}	—
	σ_0 / ohm^{-1} cm^{-1}	1.58×10^{1}	—	8.50×10^{-7}	1.30×10^{-8}	1.70×10^{0}	1.57×10^{-1}	—
	σ_0' / ohm^{-1} cm^{-1} from Fig. 3.	←			8.40×10^{-17}			→
	σ_0' / ohm^{-1} cm^{-1} from Fig. 6.	←			6.80×10^{-17}			→
	T_0/K from Fig. 3.	←			317.50			→
	T_0/K from Fig. 6.	←			302.00			→
Adenine	E / eV	2.10	1.10	0.96	1.18	1.46	—	—
	σ_T / ohm^{-1} cm^{-1}	1.60×10^{-17}	2.30×10^{-17}	2.55×10^{-17}	2.40×10^{-17}	2.00×10^{-17}		
	σ_0 / ohm^{-1} cm^{-1}	1.12×10^{1}	1.4×10^{-7}	3.90×10^{-9}	1.56×10^{-6}	5.00×10^{-5}		
	σ_0' / ohm^{-1} cm^{-1} from Fig. 4.	←			4.00×10^{-17}			→
	σ_0' / ohm^{-1} cm^{-1} from Fig. 6.	←			2.20×10^{-17}			→
	T_0/K from Fig. 4.	←			306.40			→
	T_0/K from Fig. 6.	←			290.80			→

tion may imply that the nature of complex formation and hence the dye-base interaction at high and low dye concentrations is different.

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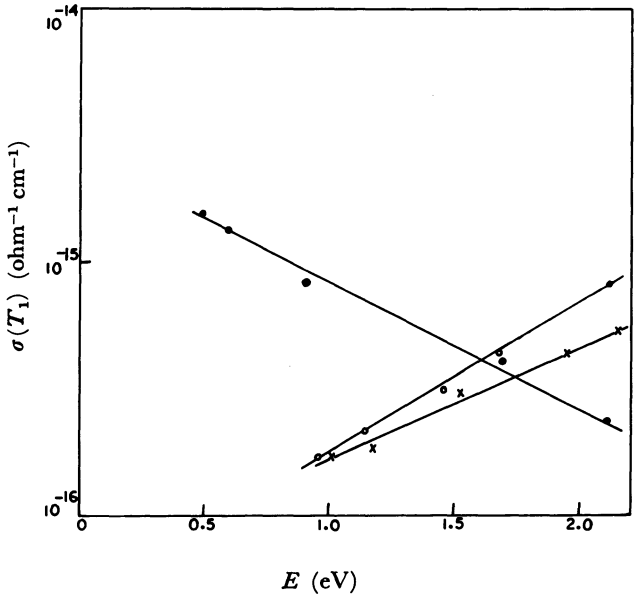

Fig. 5. Plot of log $\sigma(T_1)$ value at a constant temperture T_1(332.9 K) vs. E for a base-dye complexes, σ (T_1) and E change with dye concentration. (1) —●— for cytosine-acriflavine complex, (2) —×— for uracil-acriflavine complex, and (3) —○— for adenine-acriflavine complex.

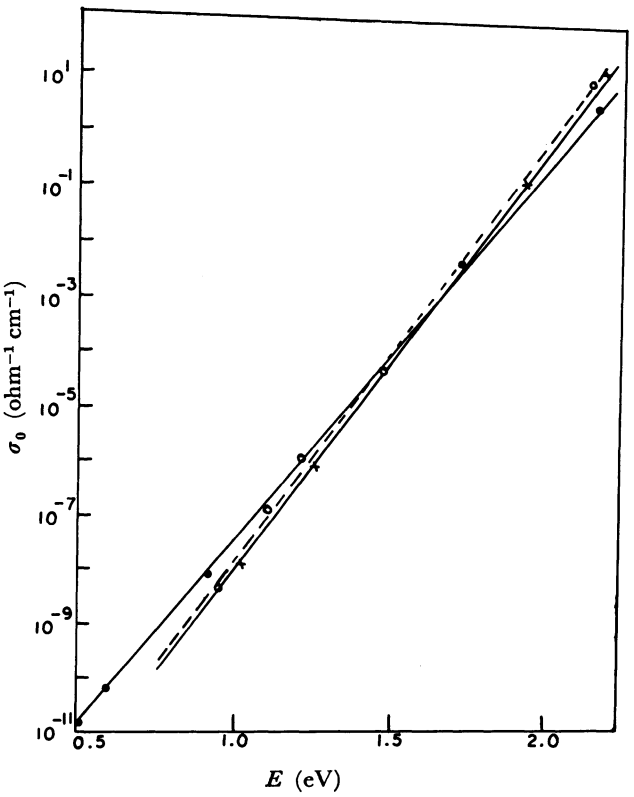

Fig. 6. Plot of log σ_0 value vs. E for base-dye complex as σ_0 and E change with dye concentration. (1) —●— for cytosine-acriflavine complex (2) —×— for uracil-acriflavine complex (3) —○— for adenine-acriflavine complex.

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