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Pre-exponential Factor in Semiconducting Vitamin A (Alcohol and Acetate)

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The semiconductive properties of vitamin A (alcohol and acetate) on adsorption of various vapors have been studied. The adsorbed vapors increase the semiconduction currents by several orders of magnitude and decrease the semiconduction activation energies. Such change depends on the chemical nature and also on the amount of vapor adsorbed. Semiconducting vitamin A follows the three-constant equation

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

where the conventional pre-exponential factor σ_0 has been replaced by $\sigma_0' \exp(E/2kT_0)$ (the so called compensation effect). Here T_0 and σ_0' are constants for the substance and T_0 is called the characteristic temperature. Various methods used for evaluating these constants have yielded consistent results with $T_0 \approx 402$ K and $\sigma_0' \approx 2.8 \times 10^{-9}\ \Omega^{-1}$ cm^{-1} for vitamin A alcohol and $T_0 \approx 335$ K and $\sigma_0' \approx 1.5 \times 10^{-10}\ \Omega^{-1}$ cm^{-1} for vitamin A acetate. Excellent correlation obtained between the relevant parameters in semiconducting vitamin A indicates that σ_0 and E are physically related. Various models for conduction mechanism leading to compensation effect have been discussed. The measured activation energies on adsorption of same amount of various vapors show a linear relationship with the ionization potential of the adsorbed molecules suggesting that charge-transfer interaction is responsible for the semiconductivity enhancement.

The electrical conductivity of conjugated π-electronic organic compounds follows the operational definition of a semiconductor

$$\sigma(T) = \sigma_0 \exp(-E/2kT) \tag{1}$$

where $\sigma(T)$ is the specific conductivity at any absolute temperature T, σ_0 is a pre-exponential factor, E the semiconduction activation energy and k is Boltzmann constant ($E/2$ is often written as E', however, we shall use the former throughout this paper). Experimentally, E is obtained from the slope of the linear plot of log $\sigma(T)$ *vs.* $1/T$. Recently, the so called pre-exponential factor σ_0 has been the subject of much discussion[1-6] as experimental evidence accumulated shows that σ_0 contain exponential functions. Gutmann and Lyons[7] showed a linear relationship of the form

$$\log \sigma_0 = \alpha E + \beta \tag{2}$$

holds good for one entire class of organic compounds, α and β being constants. Rosenberg[2,8] *et al.* showed evidence that if E is varied by hydration or complex formation relation (2) is valid for a single organic substance as well and they suggested an expression for the specific conductivity of the form

$$\sigma(T) = \sigma_0' \exp(E/2kT_0) \exp(-E/2kT) \tag{3}$$

thus introducing an additional constant T_0, called characteristic temperature. σ_0' and T_0 for the same compound remain invariant. The linear relationship between the logarithm of the pre-exponential factor and the activation energy is called the compensation effect. σ and E change in such a manner that their effect on σ_0 are mutually compensated. It has been pointed out by Johnston and Lyons[4] that the linear relationship between log σ_0 and E may originate solely from the calculation of these parameters and the compensation effect requires no physical interpretation. However, they have suggested that if σ_0 and E are physically related, one should get a linear relationship between log σ and E yielding the semiconductive parameters in agreement with the values obtained from other sources. From Eq. 3, for any particular temperature T_1, the specific conductivity is given by

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

Thus, the plot of log $\sigma(T_1)$ *vs.* E is expected to be linear with a slope $(1/T_0 - 1/T_1)/2k$ and an intercept of log σ_0'. The value of σ_0' obtained from this plot should also show a good agreement with the values obtained from the log σ_0 *vs.* E and log σ *vs.* $1/T$ plots. In the experiment of Johnston and Lyons[4] the log σ_0 *vs.* E plots were linear, but a very poor correlation between log σ and E was observed[4] in one component crystal of anthracene by changing its purity and doping with tetracene. Some recent theoretical works[9,10] suggest that in biological semiconductors the compensation effect arises due to the dark conduction process. In view of the scanty experimental works available on this effect, it was thought worthwhile to investigate the conduction process in more biological semiconductors. To test the validity of the compensation effect, E is generally varied by various ways and log σ_0 is plotted against E. The adsorption of gases is known[8,11] to change the activation energies of organic semiconductors. Recently, being motivated to examine the hypothesis that vitamin A is involved in olfactory transduction mechanism,[12] we have studied the effect of adsorption of gases on solid vitamin A. Such adsorption changes the activation energy and enhances the conductivity. In this paper we present experimental evidence to indicate that the compensation rule is valid for solid vitamin A and that σ_0 and E are indeed physically related. Further, the formation of donor-acceptor complex between vitamin A and the adsorbed gas molecule is shown to be responsible for the observed activation energy change.

Experimental

High purity vitamin A alcohol and vitamin A acetate were obtained from Hoffmann-La Roche and Co., Ltd., Switzerland. These were used without any further purification. Sandwich cell technique with a conducting glass and/a stainless steel electrode was used. There was a gas inlet and an outlet in the conductivity chamber, made of brass and fashioned with Teflon, for gas adsorption study. The temperature of the sandwich cell could be controlled from outside. Temperature measurements were made using a copper-constantan thermocouple attached at the top of the metal electrode. The semiconduction currents were measured with an electrometer amplifier EA815 of the Electronic Corporation of India Ltd. Vapors of methanol, ethanol, heptane, ethyl acetate, benzene, and toluene were allowed to be adsorbed on the semiconductors. The reagent chemicals of spectrograde (E. Merck, B. D. H.) quality were used without further purification; otherwise repeated fractional distillation was done before use. To pass various vapors inside the chamber, dry nitrogen gas was used as carrier which was passed through a bubbler containing the reagent chemical. The partial pressure of the reagent vapor in the conductivity chamber was kept constant during adsorption at a pressure less than the saturation vapor pressure at the sample cell temperature by carefully adjusting the temperature of the bubbler. The partial pressure of the vapor was the saturation vapor pressure of the reagent chemical at the temperature of the bubbler. The same partial pressure (40 mm) was maintained inside the chamber for various vapors. Under this condition it is a valid assumption that the same amount of various vapors are adsorbed on the semiconductors. Repeated heating and cooling of the sample initially in vacuum and finally in dry nitrogen atmosphere ensured desorption of water vapor or any other adsorbed gases. Temperature (12.5 °C) of the sample cells and the inlet flow were kept constant during adsorption.

To determine the effect of adsorbed vapor on the semiconduction activation energy, the sample was allowed to come to a steady state in the chamber atmosphere containing the vapor with nitrogen. The pressure of the total gas mixture in the chamber was atmospheric pressure. The saturation current, after vapor adsorption was found to be almost constant even after four hours indicating that the conduction in the system is mainly electronic.[13,14] The sample cell was then rapidly cooled to about −40 °C and then the chamber was flushed gently with dry nitrogen gas. Semiconduction current was measured with increasing temperature of the sample cell. The outlet of the chamber was kept open to maintain atmospheric pressure inside the chamber.

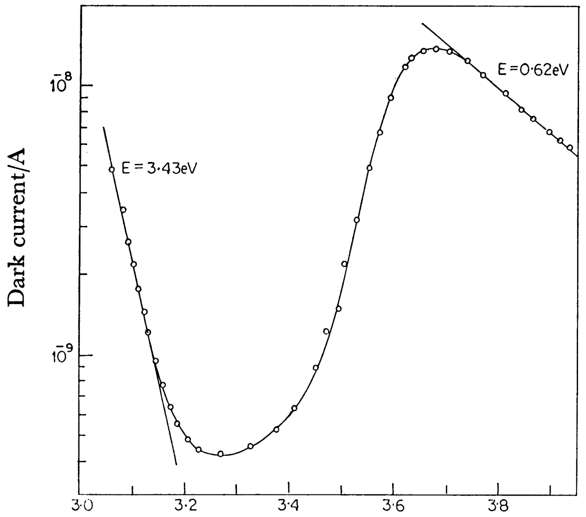

Fig. 1. Semiconductivity in a vitamin A acetate powder cell with desorption of ethyl acetate vapor as the temperature increases.

Results and Discussion

The semiconduction activation energy of crystalline powders of vitamin A (alcohol and acetate) has been measured several times in dry nitrogen atmosphere. The observed values are 2.06 and 3.50 eV (approx.) for the alcohol and acetate respectively. The adsorption of gases enhances the semiconduction current (by several orders of magnitude in some cases) and decreases the activation energy appreciably. The results of one such typical experiment is shown in Fig. 1. The straight line portion in the low temperature region shows the semiconducting properties of vitamin A acetate powder with adsorbed ethyl acetate vapor and the slope of this line gives the activation energy (0.62 eV) of this semiconducting system. The straight line portion in the high temperature region gives the activation energy of vitamin A acetate in nitrogen atmosphere. The observed value (3.43 eV) is slightly lower possibly due to incomplete desorption of adsorbed vapors. The intermediate portion shows the semiconduction behavior

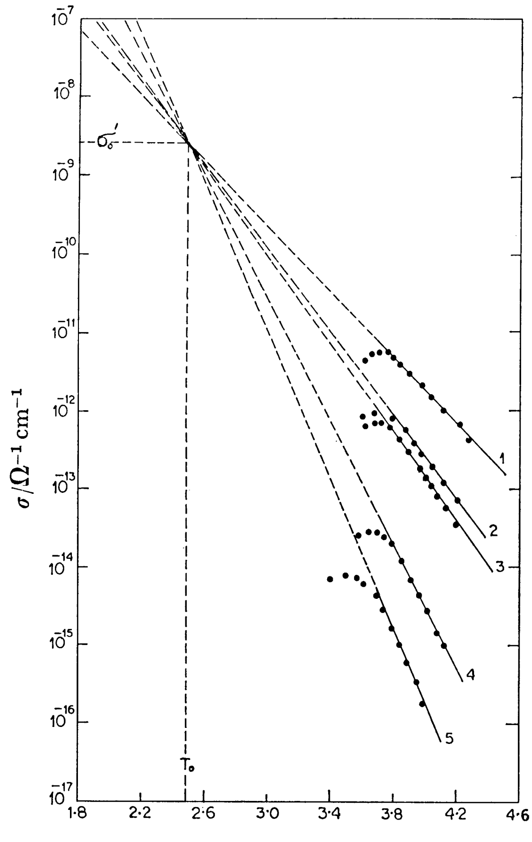

Fig. 2(a). Semiconductivity in vitamin A alcohol powder cell (steady state condition) with the adsorption of same amount of different vapors. Solid lines represent temperature region of measurements, dashed lines are extrapolations. Each line refers to a specific vapor adsorbed state. Vapors are (1) toluene; (2) ethyl acetate; (3) heptane; (4) ethanol; and (5) methanol. To avoid overlapping with (2) the line corresponding to benzene vapor is not shown. The value of $T_0 \approx 402$ K; $\sigma_0' = 2.65 \times 10^{-9}$ Ω^{-1} cm^{-1}.

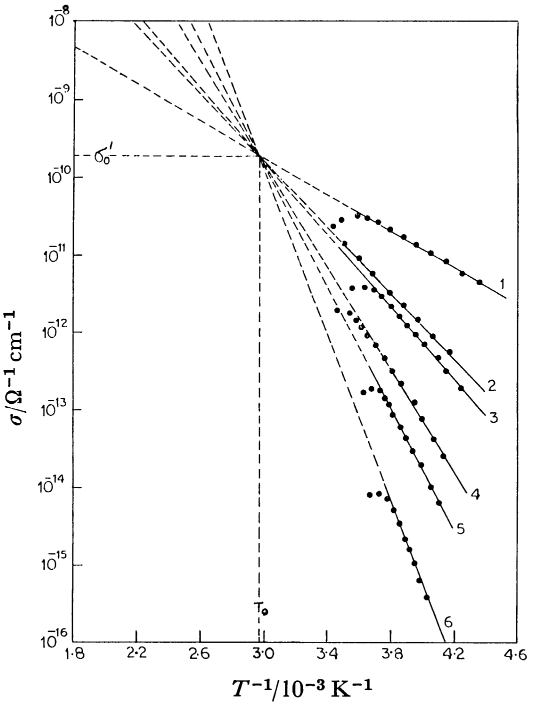

Fig. 2(b). Same as Fig. 2(a) for vitamin A acetate with adsorbed vapors (1) toluene; (2) benzene; (3) ethyl acetate; (4) heptane; (5) ethanol; and (6) methanol. $T_0 \approx 335$ K; $\sigma_0' = 1.8 \times 10^{-10}\ \Omega^{-1}\ \mathrm{cm}^{-1}$.

of the sandwich cell during desorption process. Similar curves were also obtained with other vapors.

The Characteristic Temperature for the Semiconducting Vitamin A. In Figs. 2(a) and 2(b) we show the straight portion in the low temperature region for a number of adsorbed vapors in vitamin A alcohol and acetate respectively. It is observed that with the same amount of vapor adsorbed, the activation energy values are different for different vapors. In this case no single value of σ_0 is found if either $T \rightarrow \infty$ or $E \rightarrow 0$ as is expected from Eq. 1. The extrapolated lines intercept the ordinate at a wide varieties of positions, but they all pass approximately through a single point at a temperature T_0, characteristic of the semiconductor. This is exactly what is expected from Eq. 3. Figs. 2(a) and 2(b) show $T_0 \approx 402$ K for vitamin A alcohol and $T_0 \approx 335$ K for vitamin A acetate. At these characteristic temperatures $\sigma(T_0) = \sigma_0'$ values of vitamin A alcohol and acetate are 2.65×10^{-9} and $1.8 \times 10^{-10}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ respectively. Adsorption of different amount of same vapor also changes the semiconduction activation energy to different extent. The plots of $\log \sigma(T)$ *vs.* $1/T$ for different amount of ethyl acetate vapor adsorbed on vitamin A alcohol and acetate semiconductors are shown in Figs. 3(a) and 3(b). These two sets also give values of T''_0's and σ'_0's [403 and 334 K and 3.1×10^{-9} and $1.65 \times 10^{-10}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ for vitamin A alcohol and acetate respectively] in good agreement with those obtained earlier.

If plotted in alternate fashion as $\log \sigma_0$ *vs.* E, the plots are linear as expected [since $\log \sigma_0 = E/(2kT_0) + \log \sigma_0'$] and are shown in Fig. 4. The value of T_0 obtained from the slopes are 404 and 333 K for vitamin A alcohol and acetate respectively. The σ_0' values obtained from the intercepts of these plots are 2.8×10^{-9} and $1.5 \times 10^{-10}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ for vitamin A alcohol and acetate respectively. Thus the values of T_0 and σ_0' obtained from various plots are consistent and show excellent agreement.

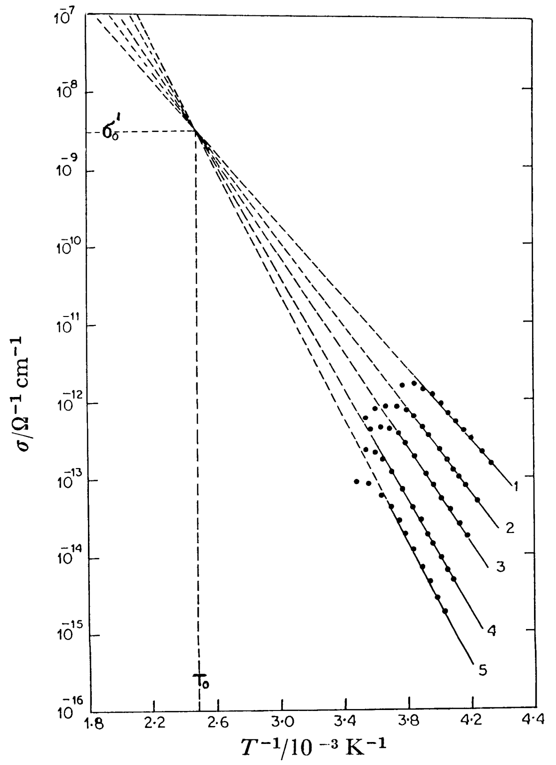

Fig. 3(a). Semiconductivity data for vitamin A alcohol powder cell (steady state condition) with adsorption of different amount of ethyl-acetate vapor. The lines (1) →(5) refer to the states with the decreasing amount of adsorbed vapor. $T_0 \approx 403$ K; $\sigma_0' = 3.1 \times 10^{-9}\ \Omega^{-1}\ \mathrm{cm}^{-1}$.

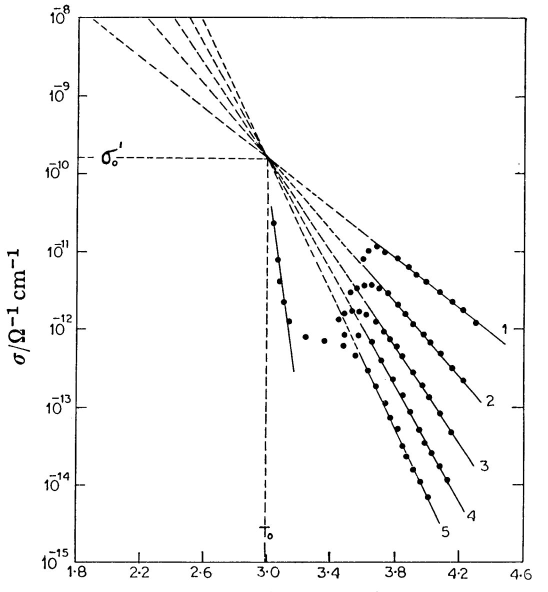

Fig. 3(b). Same as Fig. 3(a) for vitamin A acetate. Here, $T_0 \approx 334$ K; $\sigma_0' = 1.65 \times 10^{-10}\ \Omega^{-1}\ \mathrm{cm}^{-1}$.

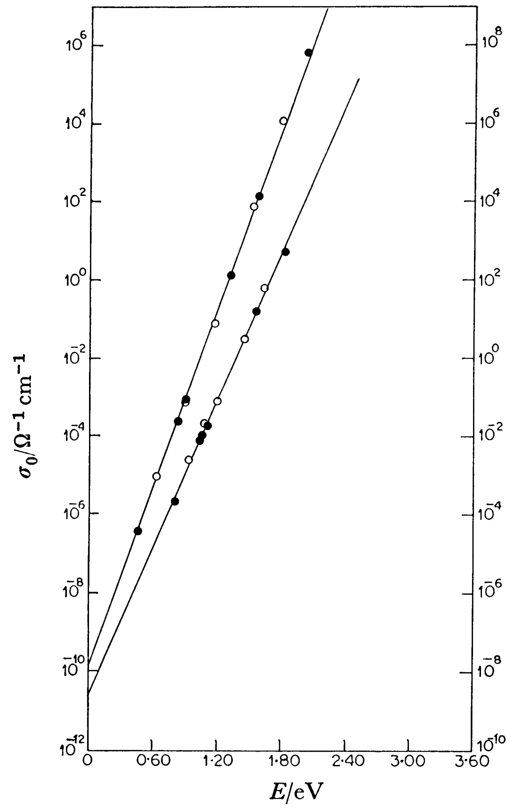

Fig. 4. Plot of the log σ_0 values [from Eq. 1] *vs.* the activation energies for vitamin A (alcohol and acetate) at a constant temperature [$1/T = 3.8 \times 10^{-3}$ K^{-1}] The lower line is for vitamin A alcohol (right scale) and the top line is for vitamin A acetate (left scale). The dark circles refer to different vapors and the open circles to different amounts of same vapor. Slopes and σ_0' values are 14.45 eV^{-1} and 2.8×10^{-9} Ω^{-1} cm^{-1} for vitamin A alcohol and 17.52 eV^{-1} and 1.5×10^{-10} Ω^{-1} cm^{-1} for vitamin A acetate respectively.

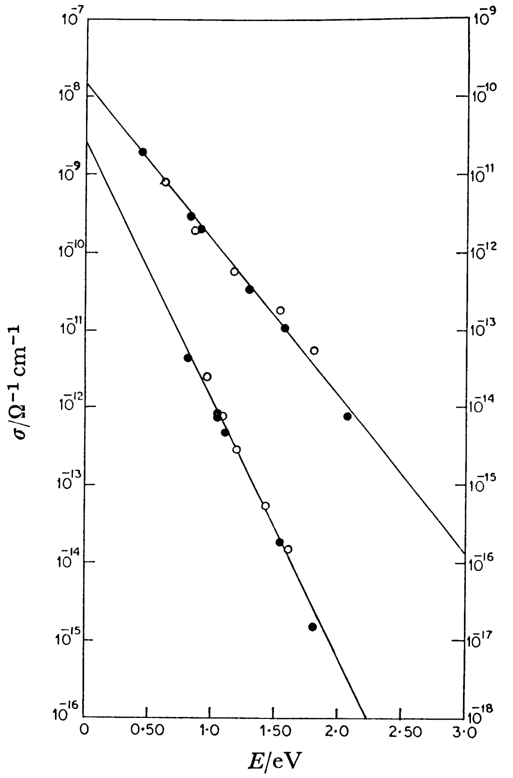

Fig. 5. Plot of the log σ values for vitamin A (alcohol and acetate) *vs.* E at a constant temperature ($1/T_1 = 3.8 \times 10^{-3}$ K^{-1}). The lower line refers to vitamin A alcohol (left scale) and the top line to vitamin A acetate (right scale). The dark circles refer to different vapors and the open circles to different amounts of same vapor. Slopes and σ_0' values are 7.70 eV^{-1} and 2.85×10^{-9} Ω^{-1} cm^{-1} for vitamin A alcohol; 4.55 eV^{-1} and 1.6×10^{-10} Ω^{-1} cm^{-1} for vitamin A acetate respectively.

Using the values of $1/2kT_0 \approx 14.45$ eV^{-1} and $\sigma_0' = 2.8 \times 10^{-9}$ Ω^{-1} cm^{-1} for vitamin A alcohol, $1/2kT_0 = 17.52$ eV^{-1} and $\sigma_0' = 1.5 \times 10^{-10}$ Ω^{-1} cm^{-1} for vitamin A acetate, we calculate the expected σ_0 values and compare these with experimentally measured values as obtained from the intercepts of the log σ *vs.* $1/T$ plots. These are shown in Tables 1 and 2. These data confirm the validity of Eq. 3 for vitamin A semiconductor.

The plots of log σ (T_1) *vs.* E are shown in Fig. 5 for $1/T_1 \approx 3.8 \times 10^{-3}$ K^{-1}. Taking $1/(2kT_0) \approx 14.45$ and 17.52 eV^{-1} from Fig. 4, the expected slopes are 7.73 and 4.66 eV^{-1} for vitamin A alcohol and acetate respectively. The observed slopes in Fig. 5 are 7.70 and

Table 1. Semiconduction parameters for vitamin A (alcohol and acetate) on adsorption of various vapors according to Eq. 3

Vapors adsorbed	Ionization potential[a)]	Vitamin A alcohol (solid state crystalline powder) $(2kT_0)^{-1} = 14.45$ eV^{-1}, $\sigma_0' = 2.8 \times 10^{-9}$ Ω^{-1} cm^{-1}			Vitamin A acetate (solid state crystalline powder) $(2kT_0)^{-1} = 17.52$ eV^{-1}, $\sigma_0' = 1.5 \times 10^{-10}$ Ω^{-1} cm^{-1}		
	eV	$\frac{E}{\mathrm{eV}}$	$\frac{\sigma_0' \exp[E/(2kT_0)]}{\Omega^{-1}\,\mathrm{cm}^{-1}}$	$\frac{\sigma_0}{\Omega^{-1}\,\mathrm{cm}^{-1}}$	$\frac{E}{\mathrm{eV}}$	$\frac{\sigma_0' \exp[E/(2kT_0)]}{\Omega^{-1}\,\mathrm{cm}^{-1}}$	$\frac{\sigma_0}{\Omega^{-1}\,\mathrm{cm}^{-1}}$
Toluene	8.81	0.80	2.93×10^{-4}	4.1×10^{-4}	0.448	3.84×10^{-7}	6.1×10^{-7}
Benzene	9.24	1.04	9.41×10^{-3}	7.98×10^{-3}	0.821	2.65×10^{-4}	3.8×10^{-4}
Ethyl acetate	10.11	1.06	1.26×10^{-2}	1.15×10^{-2}	0.896	9.85×10^{-4}	1.7×10^{-3}
Heptane	10.35	1.10	2.24×10^{-2}	2.6×10^{-2}	1.310	1.39×10^{0}	1.2×10^{0}
Ethanol	10.50	1.55	1.49×10^{1}	1.3×10^{1}	1.570	1.32×10^{2}	7.0×10^{1}
Methanol	10.85	1.82	7.39×10^{2}	1.25×10^{3}	2.070	8.44×10^{5}	8.0×10^{5}

a) Ref. 7, pp. 669—689.

Table 2. Semiconduction parameters for vitamin A (alcohol and acetate) on adsorption of ethyl-acetate vapor of different amounts

Vitamin A alcohol (Solid state crystalline powder) $(2kT_0)^{-1}=14.45$ eV^{-1}; $\sigma_0'=2.8\times 10^{-9}\ \Omega^{-1}\ \mathrm{cm}^{-1}$				Vitamin A acetate (Solid state crystalline powder) $(2kT_0)^{-1}=17.52$ eV^{-1}; $\sigma_0'=1.5\times 10^{-10}\ \Omega^{-1}\ \mathrm{cm}^{-1}$			
Curve No. from Fig. 3(a)	$\frac{E}{\mathrm{eV}}$	$\frac{\sigma_0' \exp[E/(2kT_0)]}{\Omega^{-1}\ \mathrm{cm}^{-1}}$	$\frac{\sigma_0}{\Omega^{-1}\ \mathrm{cm}^{-1}}$	Curve No. from Fig. 3(b)	$\frac{E}{\mathrm{eV}}$	$\frac{\sigma_0' \exp[E/(2kT_0)]}{\Omega^{-1}\ \mathrm{cm}^{-1}}$	$\frac{\sigma_0}{\Omega^{-1}\ \mathrm{cm}^{-1}}$
1	0.94	2.22×10^{-3}	2.0×10^{-3}	1	0.63	9.32×10^{-6}	1.0×10^{-5}
2	1.08	1.68×10^{-2}	2.3×10^{-2}	2	0.89	8.87×10^{-4}	1.7×10^{-3}
3	1.19	8.22×10^{-2}	1.8×10^{-1}	3	1.16	1.00×10^{-1}	1.6×10^{-1}
4	1.43	2.64×10^{0}	3.5×10^{0}	4	1.52	5.51×10^{1}	1.5×10^{1}
5	1.62	4.11×10^{1}	3.0×10^{1}	5	1.80	7.43×10^{3}	1.2×10^{3}

Curve No. 1→5 corresponds to the decreasing amount of adsorbed ethyl acetate vapor.

4.55 eV^{-1} for these two compounds respectively. The agreement is excellent. Also the intercepts give $\sigma_0' \approx 2.85\times 10^{-9}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ for vitamin A alcohol and $\sigma_0' \approx 1.6\times 10^{-10}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ for vitamin A acetate. These values agree well with the values obtained from the log σ_0 *vs.* E and log σ *vs.* $1/T$ plots. Thus the high correlation between the relevant parameters in semiconducting vitamin A powder on adsorption of various vapors indicates that Compensation rule is valid in these biological semiconductors and that σ_0 and E are indeed physically related.

Type of Interaction between the Adsorbed Gas and the Semiconducting Material. It needs to be pointed out that the reason for the semiconduction activation energy change is not quite settled.[8,11)] However, donor-acceptor complex formation has been widely held responsible for the increase of current in some semiconductors[15–17)] due to gas adsorption. As the vapors used in this present investigation are good electron donors and polyenes are known to act both as electron donor and electron acceptor,[18,19)] formation of charge-transfer complexes of vitamin A (alcohol and acetate) with the adsorbed vapors may be possible. It had generally been observed[20,21)] that in solid charge-transfer complexes with a particular acceptor and a number of similar type of donors, the semiconduction activation energy as obtained from relation (1) and the energy ($h\nu_{\mathrm{CT}}$) of the lowest charge-transfer band are linearly related by the expression

$$\begin{aligned} E &= h\nu_{\mathrm{CT}} - \delta \\ &= I_{\mathrm{D}} - E_{\mathrm{A}} + C_1 - \delta \qquad (4) \end{aligned}$$

where, I_{D} is the vertical ionization potential of the donor, E_{A} is the vertical electron affinity of the acceptor, C_1 is a constant[22)] and δ is also another constant of very low value.[20)] In Fig. 6, we show a plot of E *vs.* I_{D}. A linear relationship is obtained as expected from Eq. 4. The slope of the line (0.6) however, is much less than unity. Such a value for the slope is a rather general observation[23,24)] in $h\nu_{\mathrm{CT}}$ *vs.* I_{D} plots. The intercept of this plot is -3.8 eV. The value of $-C_1$ is usually[22,25)] around 3 eV. The electron affinity of anhydro vitamin A which is expected to be close to that of vitamin A (alcohol and acetate) has been reported to be[26)] 0.7 eV. This gives a value of 0.1 eV for δ which is a very reasonable value.[21,23)] This adds further credence to the proposed charge-transfer concept.

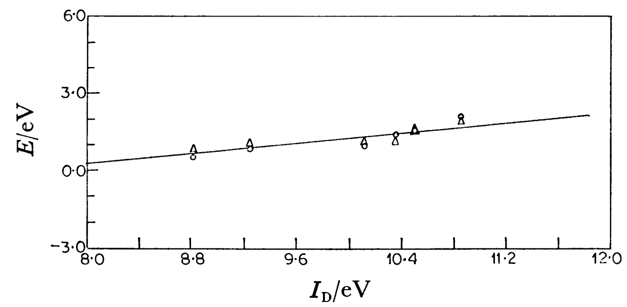

Fig. 6. Semiconductive activation energy (E) *vs.* ionization potential (I_{D}) of the adsorbed vapor molecules.
—△—: Vitamin A alcohol.
—○—: Vitamin A acetate.

There are number of theses about the mechanism of conduction in organic semiconductors leading to compensation effect. The carrier injection model of Green[27)] produces the type of activation energy dependence of the pre-exponential factor as observed experimentally, but does not provide any physical basis for the interpretation of T_0. Significant difference in T_0 values for these two compounds suggests that T_0 is a molecular characteristic of these organic semiconductors. Kemeny and Rosenberg[28)] observed compensation law in tunneling of small polaron through molecular barrier from thermally activated energy levels of molecules. Their model predicts that $T_0=\theta/2$ (where θ is the Debye temperature) and that at $T>T_0$, small polaron tunneling is not possible and compensation effect is not expected to be observed. No experimental study seems to have been reported on the semiconductive behavior of organic compounds at $T>T_0$. Debye temperature for vitamin A alcohol and acetate are not known. It has been reported[29)] that the Debye temperature for a series of crystals of large aromatic molecules lie in the range 100—130 K. It seems that the T_0 values measured are far too high to justify the polaron tunneling model.

An interaction between the electrons and the vibrational motion has been thought[9,10)] to be the mechanism behind compensation effect. A change in the electronic state (due to complex formation) gives rise to an activation entropy because of a change in vibrational frequencies. The variation in both the electronic energy gap

(E_g) and the activation entropy (S) can account for compensation effect if the changes in these parameters are given by

$$E_g = E_{g_0} + nE_{g_1} \text{ and } S = S_0 + nS_1$$

where n is a definite number for each system and E_{g_0}, E_{g_1}, S_0 and S_1 are same for all the systems. In this case the characteristic temperature is given by

$$T_0 = E_{g_1}/(2S_1).$$

Unfortunately due to the fact that the nature of the activated complex is not precisely known, the activation entropy S (hence S_1) is a relatively obscure quantity and any quantitative estimate of T_0 is not possible.

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