APPENDIX

LIST OF PUBLICATIONS AND REPRINTS

LIST OF PUBLICATIONS

1. B. Mallik, K.M. Jain, K.G. Mandal and T.N. Misra, "Electronic Spectra of Polyenes : Evidence of a low-lying forbidden transition in some linear conjugated polyenes",

   Ind. J. Pure Appl. Phys., 13, 699 (1975).

2. B. Mallik, K.M. Jain, K.G. Mandal and T.N. Misra, " On the evidence of a low-lying forbidden π -electronic state in Methyl bixin "

   Ind. J. Pure Appl. Phys., 15, 229 (1977).

3. B. Mallik, K.M. Jain and T.N. Misra, " Charge-transfer complexes of all-trans- β -carotene".

   Ind. J. Biochem. Biophys., 15, 233 (1978).

4. B. Mallik and T.N. Misra, " Charge-transfer complexes of some polyenes".

   Ind. J. Biochem. Biophys., (communicated)

5. B. Mallik, A. Ghosh and T.N. Misra, "Semiconductive properties of biologically important compounds : Gas adsorption effect on vitamin A (alcohol and acetate).

   Proc. Indian Acad. Sci. A, 88A, 25 (1979).

6. B. Mallik, A. Ghosh and T.N. Misra, " Compensation effect in semiconducting vitamin A (alcohol and acetate) "

   Jpn. J. Appl. Phys., 18, 331 (1979).

7. B. Mallik, A. Ghosh and T.N. Misra, " Pre-exponential factor in semiconducting vitamin A (alcohol and acetate)"

Bull. Chem. Soc. Jap., 52, 0000 (1979).

8. B. Mallik, A. Ghosh and T.N. Misra, " Compensation effect in some polyene semiconductors "

Bull. Chem. Soc. Jap., (communicated).

9.* B. Mallik, K.M. Jain and T.N. Misra, "Electronic spectra of 9 -Nitro anthracene : Solvent effect on $^1A \longrightarrow {}^1L_a$ and $^1A \longrightarrow {}^1L_b$ transitions "

Ind. J. Pure Appl. Phys., 14, 53 (1976).

10.* B. Mallik, K.M. Jain and T.N. Misra, " Electronic absorption spectra of 2-Nitrofluorene : Solvent effect on $^1A \longrightarrow {}^1L_a$ transition ".

Ind. J. Pure Appl. Phys., 15, 267 (1977).

11.* B. Mallik, G.B. Talapatra and T.N. Misra, " Host crystal field effect on the electronic absorption spectra of tetracene guest in mixed crystals.

Ind. J. Phys., 53A, 00 (1979).

12.* B. Mallik, K.M. Jain, Alpana Ghosh and T.N. Misra, "Semiconductive properties of organic compounds : Gas adsorption effect on 9-nitroanthracene ".

Ind. J. Phys., 52A, 543 (1978).

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* Not included in this thesis.

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Semiconductive properties of biologically important compounds: Gas adsorption effect on vitamin A (alcohol and acetate)

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Abstract. The change in semiconductive properties of vitamin A (alcohol and acetate) after adsorption of various vapours on its crystallite surface has been studied at a constant sample temperature. A rapid enhancement in the semiconductivity has been observed. The rise in conductivity has been found to be exponential with increasing vapour pressure of the adsorbed gas. It has been suggested that charge transfer (CT) interaction may be responsible for such conductivity change. The adsorption process being efficiently reversible this CT complex is weakly bound.

The biological implication of these observations is discussed.

Keywords. Organic semiconductors; gas adsorption effect; gas adsorption kinetics; semiconductive study.

1. Introduction

The biological importance of vitamin A and other conjugated long chain polyenes is well known. These are known to have an important role in the primary mechanism of olfactory transduction (Misra *et al* 1968; Rosenberg *et al* 1968). The carotenoids present in the olfactory organ can form weakly-bound reversible complexes with adsorbed odourous gas molecules which increase the conductivity of the olfactory membrane leading to the electrical event of olfaction. Selectivity of smell comes from the interaction of the odourous molecules with one or the other carotenoid present in the olfactory epithelium. It has been shown that all-trans β-carotene is a poor receptor for the methyl acetate molecules but vitamin A alcohol responds very well with these molecules and the conduction properties of vitamin A change significantly on adsorption of the acetate molecules. The limited experiment done earlier with vitamin A alcohol showed the effect of adsorption of methyl acetate molecules only. We have now systematically studied the effect of adsorption of various gases on the semiconductive properties of vitamin A (alcohol and acetate) and have examined the kinetics of such adsorption. In this paper we present our results.

2. Experimental

The sample of vitamin A (alcohol and acetate) was obtained from Hoffman La-Roche, Bombay. We have used these compounds without further purification. Organic solvents used in this investigation were of high purity. The experimental set-up is shown in figure 1. The fine powder of the compounds was pressed in a sandwich cell between a conducting glass and a stainless steel electrode. The separation between the electrodes was maintained by a 2 mil. thick teflon spacer. A d.c. voltage of 22·5 V was applied across the cell which was placed on a thermal bar platform in a suitably designed conductivity chamber made of brass and fashioned with teflon. The temperature of the sandwich cell could be controlled from outside. There was a gas inlet and an outlet in the chamber for gas adsorption study. Temperature measurements were made by using a copper-constantan thermocouple attached at the top of the metal electrode and a millivolt potentiometer. All the conductivity measurements were made in dry nitrogen/vacuum atmosphere with an electrometer amplifier EA 815 of the Electronic Corporation of India Limited. To pass various vapours inside the chamber, dry nitrogen was used as a carrier which was passed through the bubbler containing the solvent kept at a required temperature to maintain a fixed partial vapour pressure less than the saturation vapour pressure at sample cell temperature. The pressure inside the conductivity chamber was kept constant by carefully controlling the inlet and the outlet flow. The sample cell was maintained at a constant temperature throughout each set of experiment.

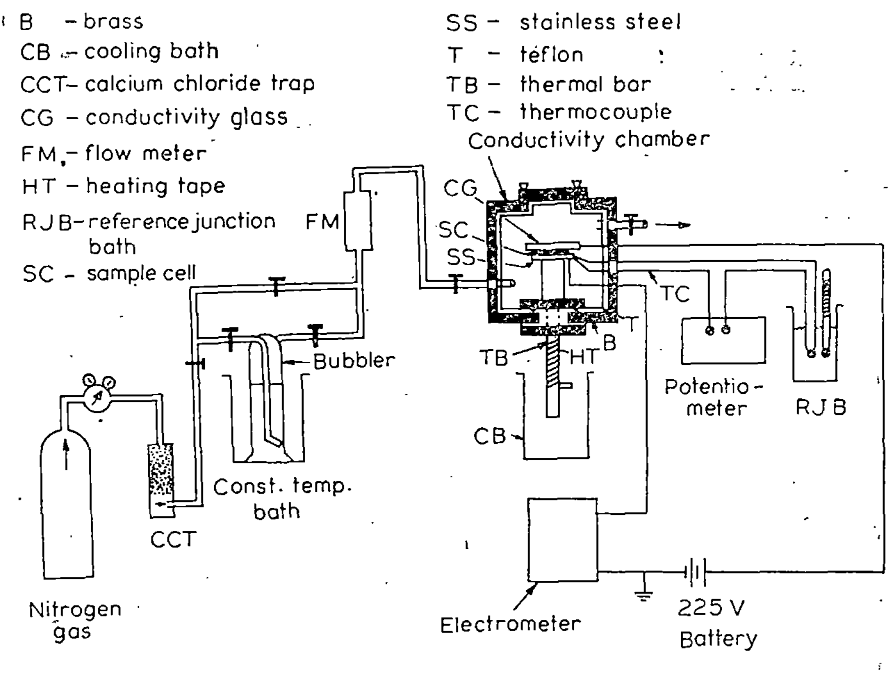

Figure 1. A schematic diagram of the apparatus used to test the effects of the adsorbed gases on the conductivity of vitamin A (alcohol and acetate).

3. Results

On adsorption of vapours on the crystallite surface of the compounds studied a rapid enhancement in the conductivity is observed. The adsorption process is fast and almost completely reversible. The initial value of the dark current is reached quickly simply by flushing the chamber with dry nitrogen (figure 2). Adsorption and desorption behaviour with vitamin A acetate is similar. The rise in the conductivity depends on the vapour pressure (figure 3). Different vapours at the same vapour pressure show different extents of enhancement of conductivity. The results are presented in table 1.

4. Discussion and conclusions

4.1. *Dependence of the conductivity on vapour pressure*

The rise in conductivity was studied at a constant temperature (25° C) as a function of partial pressure of ethyl acetate. The total gas mixture inside the chamber was at atmospheric pressure and the partial pressure of the vapour was the vapour pressure of the solvent used at the temperature of the experiment. For low amount

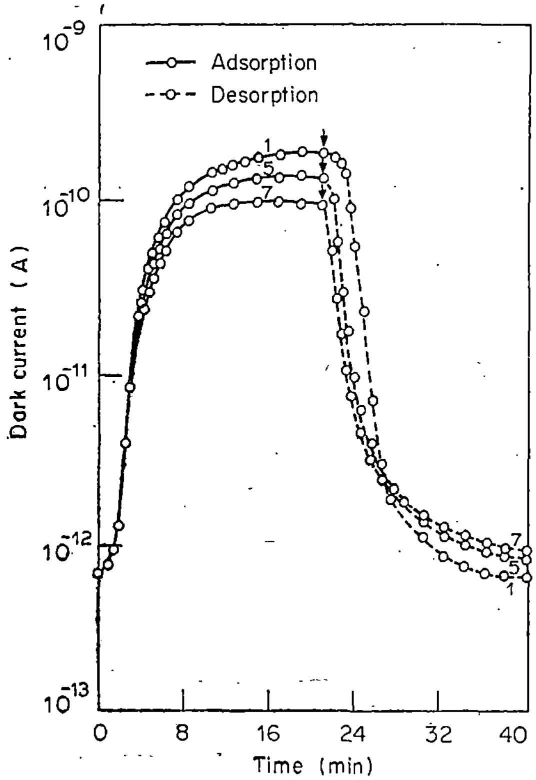

Figure 2. The change in dark current in a vitamin A alcohol powder cell kept at 25° C with repeated injection of ethyl acetate vapour (40·0 mm).

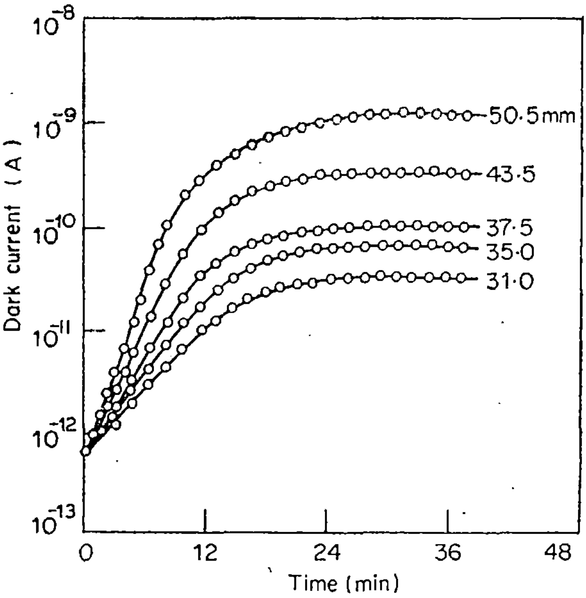

Figure 3. The change in dark current after adsorption of ethyl acetate vapour at different vapour pressure on vitamin A alcohol.

of vapour adsorption the conductivity after adsorption $\sigma_A (m)$ follows the relation (Misra *et al* 1968)

$$\sigma_A (m) = \sigma_V \exp (am) \tag{1}$$

where σ_V is the conductivity before adsorption of any vapour.

a is a constant and m is the amount of the vapour adsorbed. m depends on the partial pressure (p) of the reagent chemical. In the initial period, m depends also on the time of exposure. After some time, however, an equilibrium is established. Thus we assume that in the initial region

$$m (t) = Q (t) \cdot p \tag{2a}$$

Table 1. Rise in the dark current in vitamin A (alcohol and acetate) powder cells at 12·5° C due to adsorption of various vapours at the same pressure of 40 mm

Vapour	Dielectric constant at 25° C	Ionisation potential (eV)	σ_A / σ_V	
			Vitamin A (alcohol)	Vitamin A (acetate)
Toluene	2·38	8·81	$2{\cdot}3 \times 10^4$	$5{\cdot}0 \times 10^4$
Benzene	2·28 (20° C)	9·24	$6{\cdot}7 \times 10^3$	$1{\cdot}7 \times 10^4$
Ethylacetate	6·00	10·11	$6{\cdot}5 \times 10^3$	$1{\cdot}3 \times 10^4$
n-heptane	1·93 (20° C)	10·35	$4{\cdot}0 \times 10^3$	$3{\cdot}8 \times 10^3$
Ethanol	24·30	10·50	$3{\cdot}0 \times 10^2$	$2{\cdot}0 \times 10^3$
Methanol	32·60	10·85	$4{\cdot}5 \times 10$	$3{\cdot}2 \times 10^2$

where $Q(t)$ is a function of time. At equilibrium,

$$m_0 = Q_0 \cdot p \tag{2b}$$

where Q_0 now becomes independent of time. This is expected from Langmuir's adsorption isotherm, when a small fraction of the surface is covered by gas molecules. Hence,

$$\sigma_A \{m(t)\} = \sigma_V \exp\{a \cdot Q(t) \cdot p\} \tag{3a}$$

and at equilibrium

$$\sigma_A(m_0) = \sigma_V \exp(a \cdot Q_0 \cdot p). \tag{3b}$$

A plot of $\log \sigma_A(m_0)$ *versus* vapour pressure (p) at equilibrium is expected to be linear. Our experimental result in figure 4 shows a good agreement with this.

4.2. *Change in conductivity in different vapours*

When the powdered semiconductor is exposed to some vapour, the vapour molecules may enter the inter-space between the crystallites and form a dielectric medium different from the original one. If the conductivity change on adsorption of vapours is due to such physical mixing, a relationship between the conductivity enhancement and the dielectric constant of the vapours used is expected. But our experimental results for the conductivity rise at the same vapour pressure for different vapours (table 1) do not suggest this. The static dielectric constant (Treiber and Koren 1951) of the vapours used are in the order n-heptane < benzene < toluene < ethyl-acetate < ethanol < methanol which is not in agreement with the semiconduction current enhancemment (table 1). It has been reported (Pullman and Pullman 1963; Platt 1959; Mairanovsky *et al* 1975) that polyenes can act both as electron acceptors and electron donors. The adsorbed molecules may form a weak (D^+A^-) charge transfer complex with vitamin A

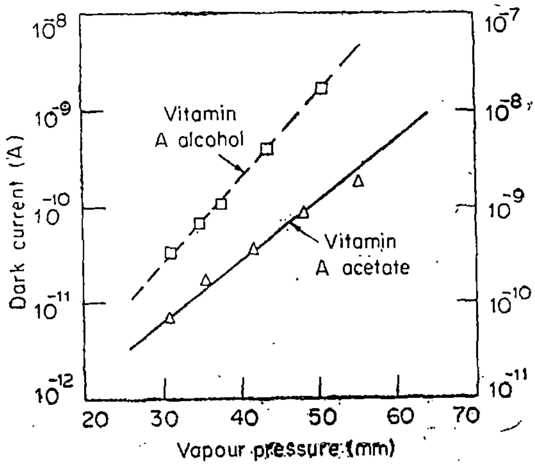

Figure 4. Change in the dark current of vitamin A (alcohol and acetate) powder cell as a function of the vapour pressure of ethyl acetate.

resulting in a change in the conductivity. In such a case, the current enhancement should show a relationship with the ionisation potential or the electron affinity of the reagent molecules. The reagent molecules used are generally electron donors (Foster 1969). Table 1 shows that in general as the ionisation potential (Gutmann and Lyons 1967; Lorquet 1965) of the vapour molecules decreases, semiconduction current enhances. These results show that the enhancement of conductivity is possibly due to the formation of donor-acceptor ($D^+ A^-$) complexes of these compounds with the vapour molecules adsorbed. The fact that the conductivity change is efficiently reversible shows that any C-T complexes formed are weakly bound.

4.3. *Kinetics*

The adsorption kinetics follows Roginsky-Zeldovich equation in a modified form (Rosenberg *et al* 1968; Eley and Leslie 1964). It was assumed that there is an activation energy associated with the adsorption rate, which increases linearly with the amount of adsorbed gas. Thus, the rate of adsorption (dm/dt) will be

$$dm/dt = A\exp(-\beta m/kT), \tag{4}$$

where β is a constant. Integrating (4), we get

$$m(t) = \frac{kT}{\beta}\log(t + t_0) + \text{constant} \tag{5}$$

From (1) and (5) we get,

$$\log\sigma_A = \frac{akT}{\beta}\log(t + t_0) + \text{constant.} \tag{6}$$

Thus, a linear plot of log σ_A *versus* log $(t + t_0)$ is suggested from (6) and our experimental results in figure 5 are in good agreement with this. In the initial region, different slopes observed at different vapour pressures show the vapour pressure-dependence of β (since a is pressure-independent). The higher the partial vapour pressure, the larger is the slope. This justifies the assumption made in expression (2) and shows an inverse relationship between p and β (table 2).

Table 2. Vapour pressure dependence of the factor $\beta' = (\beta/a)$ for ethyl acetate vapour adsorption kinetics.

Vitamin A (alcohol)		Vitamin A (acetate)	
Vapour pressure (mm)	β' (eV)	Vapour pressure (mm)	β' (eV)
31·0	$1{\cdot}202 \times 10^{-2}$	31·0	$0{\cdot}819 \times 10^{-2}$
35·0	$1{\cdot}005 \times 10^{-2}$	35·7	$0{\cdot}753 \times 10^{-2}$
37·5	$0{\cdot}930 \times 10^{-2}$	41·7	$0{\cdot}660 \times 10^{-2}$
43·5	$0{\cdot}759 \times 10^{-2}$	48·2	$0{\cdot}601 \times 10^{-2}$
50·5	$0{\cdot}643 \times 10^{-2}$	55·2	$0{\cdot}518 \times 10^{-2}$

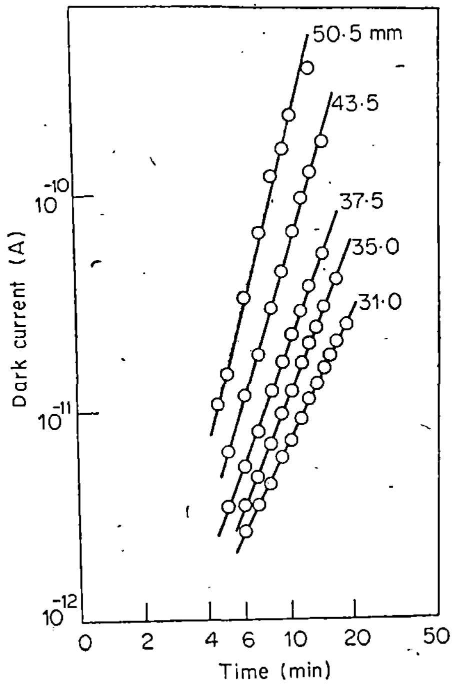

Figure 5. Adsorption kinetics data plotted according to Roginsky-Zeldovich equation for vitamin A alcohol.

The change in conductivity of β-carotene with repeated injection of odourous gas molecules in the chamber was found to decrease with the number of repetition of the exposure. This was related to fatigue effect in olfaction (Rosenberg *et al* 1968). In the present investigation, we have studied the change in conductivity of vitamin A with injection of ethyl acetate vapour in the chamber and have observed similar effect. This is shown in figure 2. However, our observed change is not large enough in comparison with that of β-carotene (Rosenberg *et al* 1968). This is possibly due to the fact that the present experiment was performed at a low vapour pressure and also at higher temperature of the sample. From the desorption curves in figure 2 it is observed that after a number of exposures to ethyl acetate vapour, a longer time is required to bring the current back to the original value on nitrogen flushing. This may be due to the fact that for long and repeated exposures strongly bound complexes are formed and such complexes unlike the weakly-bound CT type complexes, do not affect the conductivity change significantly.

Acknowledgements

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References

Eley D D and Leslie R B 1964 *Advances in Chemical Physics* (New York: Interscience Publishers) **7** 238

Foster R 1969 *Organic Charge-Transfer Complexes* (London and New York: Academic Press) p 396

Gutmann F and Lyons L E 1967 *Organic Semiconductors* (New York : John Wiley) p 669

Lorquet J C 1965 *Mol. Phys.* **9** 101

Misra T N, Rosenberg B and Switzer R 1968 *J. Chem. Phys.* **48** 2096

Mairanovsky V G, Engovatov A A, Ioffe N T and Samokhvalov G I J 1975 *Electroanal. Chem.* **66** 123

Pullman B and Pullman A 1963 *Quantum Biochemistry* (New York : Interscience Publishers) p 440

Platt J R 1959 *Science* **129** 372

Rosenberg B, Misra T N and Switzer R 1968 *Nature London* **217** 423

Treiber S and Koren M 1951 *Nat. Bur. Stand. Circ.* p 514

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Electronic Spectra of Polyenes : Evidence of a Low-lying Forbidden Transition in some Linear Conjugated Polyenes

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Electronic absorption and emission spectra of *all-trans* vitamin A alcohol, *all-trans* vitamin A acetate, β-apo-8′-carotenal and astacene have been investigated. The effects of different solvents on the absorption and emission bands of these polyenes are appreciably different. This indicates that different excited states are involved in absorption and emission. Effect of adsorption of certain gases on the crystallite surface of β-apo-8′ carotenal and astacene has been discussed. On adsorption of certain gases, a new band appears on the low-energy side of the strongly allowed ^1B_u state. It has been concluded that in these long-chain polyenes there exists a low-lying-forbidden ^1A_g state below the strongly allowed ^1B_u state.

1. Introduction

IN RECENT YEARS, interest in the electronic spectra of linear conjugated polyenes[1-5] has been revived. Little experimental work has been done in this class of molecules in comparison to the effort expended in aromatic molecules. The strongly allowed transition in the visible and near UV region of the spectrum in the linear polyenes has been known so far to be the lowest excited singlet state, ^1B_u. The absorption and emission spectra of these molecules show very little or no overlap[3,6]. Some workers have tried to explain it on the basis of "Franck-Condon forbiddenness".

It has been shown by Schulten and Karplus[4] that when double excited configurational interaction is taken into account, a singlet (^1A_g) state appears below the strongly allowed ^1B_u state in some polyenes like butadiene, hexatriene and octatetraene. Hudson and Kohler[5] have presented some experimental evidence that there exists a low-lying forbidden state below the well-defined lowest π-electron state in α, ω-diphenyl octatetraene. Recently, Mandal and Misra[7] have shown that adsorption of certain gas molecules on the solid film makes this transition allowed. We have extended such investigations to some more polyenes. In addition, the effect of different solvents on absorption and emission spectra of these polyenes has been studied, and the results are presented in this paper.

2. Experimental Procedure

The polyenes employed in the present study are *all-trans* vitamin A alcohol, *all-trans* vitamin A acetate, β-apo-8′-carotenal and astacene. Compounds of high quality obtained from Hoffman-La Roche Co., Switzerland were used without further purification. Solvents used in this investigation were of the spectro-grade quality. The absorption spectra were recorded by a Perkin-Elmer recording Spectrophotometer-202 and Spectromom-202. The emission spectra were recorded by Aminoco Bowman spectrophoto fluorometer.

Thin films of polycrystals of the polyenes were made on the quartz surface by gently rubbing the material. Solid films thus made were exposed to vapours of various solvents. The exposure was made by holding the films for about 5 min over a beaker containing the chemicals. The films were thus exposed at the saturated vapour pressure of various chemicals at room temperature (25°C).

3. Results

In the polyenes studied, a very broad absorption band is generally observed. The absorption spectrum of β-apo-8′-carotenal in non-polar solvents, however, consists of three vibronic bands with the central one most intense. This structure represents an upper state fundamental of about 1000 cm^{-1}. In common polar solvents, this vibrational structure is completely lost and only a very broad absorption band is observed. It has been observed that the absorption bands are strongly solvent-dependent. In all the polyenes studied, the emission spectra do not show any vibrational structure and no mirror image relationship is observed with the intense absorption band. The room temperature absorption and emission spectra of different polyenes in ethyl acetate are shown in Fig. 1. Though the absorption and emission spectra of β-apo-8′-carotenal show some overlap, such overlaps very small for astacene and in case of *all-trans* Vitamin A (alcohol and acetate) practically no overlap is observed.

The effect of different solvents on the absorption and emission spectra of *all-trans* vitamin A alcohol is

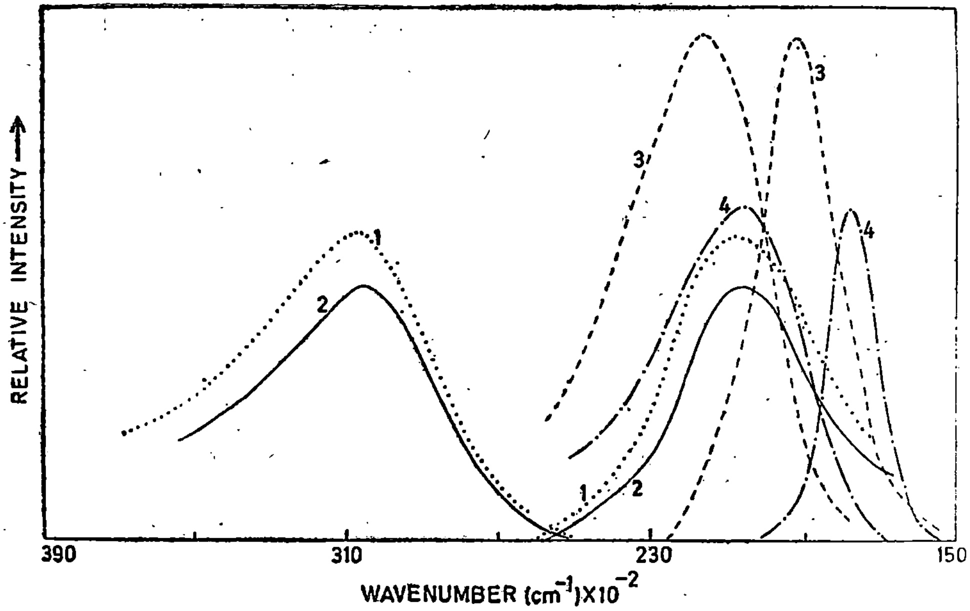

Fig. 1—Absorption and emission spectra of different polyenes in ethyl acetate at room temperature, [1, All-*trans* vitamin A alcohol; 2, all-*trans* vitamin A acetate; 3, β-apo-8′-carotenal; and 4, astacene]

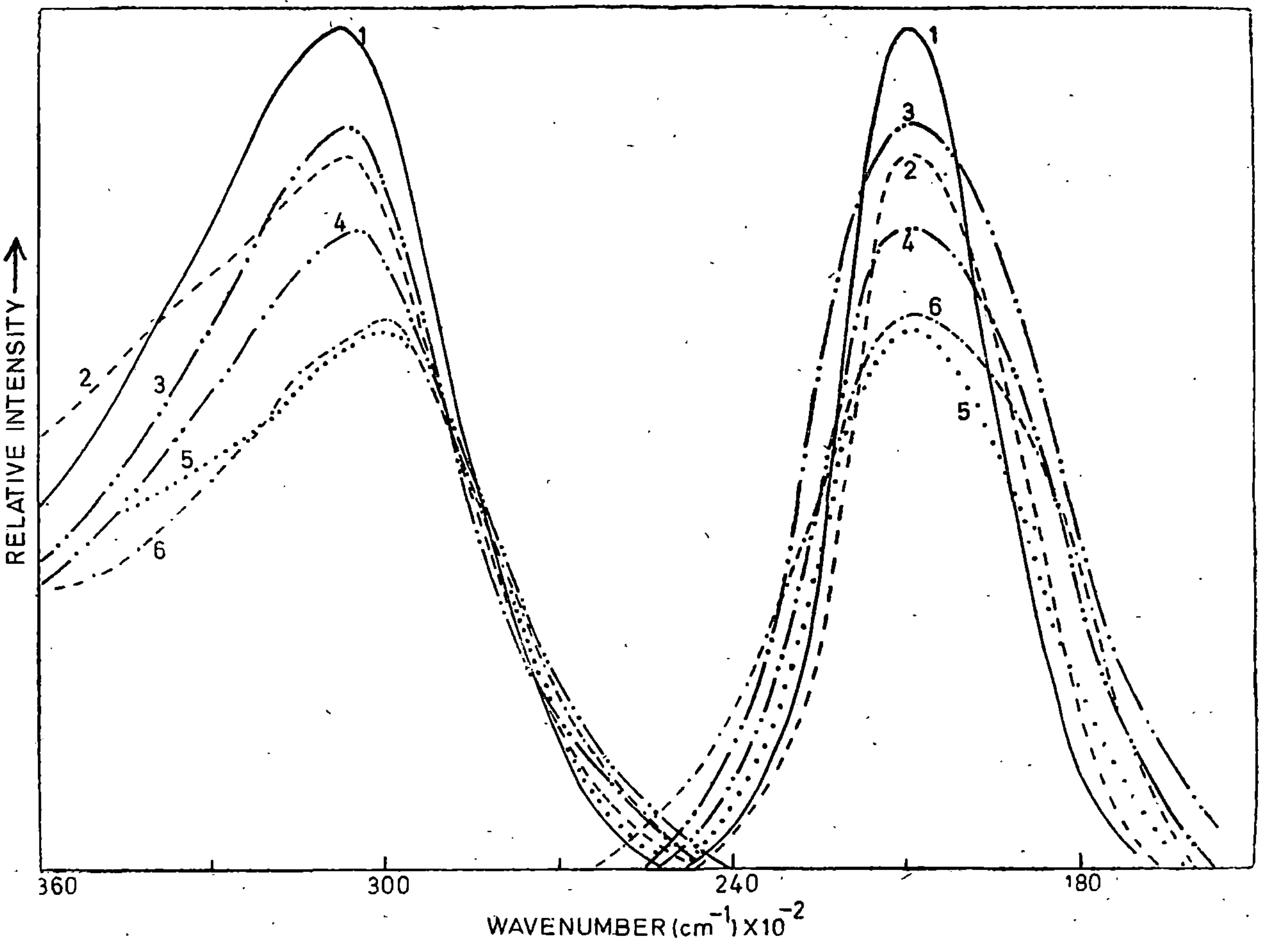

Fig. 2—Absorption and emission spectra of all-*trans* vitamin A alcohol in different solvents at room temperature [1, Methanol; 2, ethanol; 3, ethyl acetate; 4, 1, 4-dioxane; 5, carbon tetrachloride; and 6, benzene]

shown in Fig. 2. The absorption spectra show large solvent shift, but for emission spectra such shift is small.

The room temperature absorption spectra of β-apo-8′-carotenal and astacene in the solid state and after vapour adsorption are shown in Figs. 3 (a) and (b) respectively. To see the effect of the adsorption of gases on the solid film, various vapours were used. With all the vapours studied, the effect is similar except, that with certain of these the effect is more pronounced than with others. Pyridine vapour adsorption on β-apo-8′-carotenal affects the absorption spectra intensely whereas aniline vapour shows a strong effect on astacene spectrum.

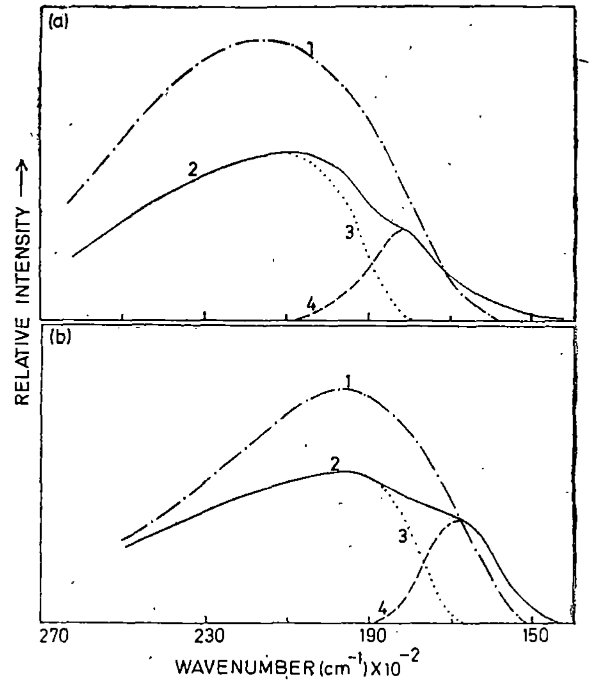

Fig. 3—(a): Absorption spectra of β-apo-8′-carotenal [1, Absorption spectrum for the solid film; and 2, absorption spectrum for the solid film after pyridine vapour adsorption. Resolution of the total adsorption; spectrum for the solid film after pyridine vapour adsorption ; 3, band of the solid film; and 4, new band]

(b) : Absorption spectra of astacene [1, Absorption spectrum for the solid film; and 2, absorption spectrum for the solid film after aniline vapour adsorption. Resolution of the total absorption spectrum for the solid film after aniline vapour adsorption: 3, band of the solid film; and 4, new band]

The absorption spectrum of β-apo-8′-carotenal in the solid state, as shown in Fig. 3 (a), is a broad band. After exposure to various vapours, the solid state spectrum shows a marked change in which a new band appears at about ~~16660~~ 18200 cm^{-1}. The other band remains unchanged.

The absorption spectrum of astacene in the solid state is also a broad band. When solid film of this polyene is exposed to different vapours, a new band appears at about ~~18200~~ 16660 cm^{-1} along with the band observed before vapour adsorption.

4. Discussion

For strong absorption band of linear polyenes, the solvent shift[8] can be expressed in the form

$$\Delta\bar{\nu} = k.f. \frac{n^2-1}{n^2+2}$$

where k is a parameter which is constant for a given molecule, f is the oscillator strength for a particular transition and n is the refractive index of the solvent. The absorption band of the polyenes under investigation shows a large red shift with the increase of the refractive index of the solvents. But in case of emission, this shift is very small compared to that for absorption. In Table 1, values of ν_{max} for the absorption and emission of some polyenes in various solvents are given. Our experimental results show that in all the polyenes studied, the plot of $\bar{\nu}_{max}$ for both absorption and emission against $(n^2-1)/(n^2+2)$ is a straight line. In Fig. 4, such plots are shown. The slope of the plot for absorption (which is a measure of the oscillator strength involved) is about seven times larger than that for emission. This difference in

Table 1—Solvent Effect on the Absorption and Emission Bands of Some Polyenes
($\bar{\nu}_{max}$ in cm^{-1})

		Vit. A alcohol		Vit. A acetate		β-apo-8′-carotenal		Astacene	
Solvent	$(n^2-1)/(n^2+2)$	$(\bar{\nu}_{max})_E$	$(\bar{\nu}_{max})_A$	$(\bar{\nu}_{max})_E$	$(\bar{\nu}_{max})_A$	$(\bar{\nu}_{max})_E$	$(\bar{\nu}_{max})_A$	$(\bar{\nu}_{max})_E$	$(\bar{\nu}_{max})_A$
Methanol	0·203	21008	30864	20833	30614	—	—	—	—
Acetone	0·219	—	—	—	—	19157	21880	18018	20746
Ethanol	0·221	20964	30769	20833	30581	—	—	—	—
Ethyl acetate	0·227	20942	30722	20730	30534	19157	21739	17857	20661
n-Hexane	0·228	—	—	—	—	19011	21790	—	—
1, 4-Dioxane	0·254	20942	30534	20790	30487	19083	21459	17921	20408
Cyclohexane	0·257	—	—	—	—	19120	21500	—	—
Carbon tetrachloride	0·275	20964	30303	20876	30030	19047	21270	17889	20242
Benzene	0·294	20920	30303	20790	30030	19083	21220	17889	20202

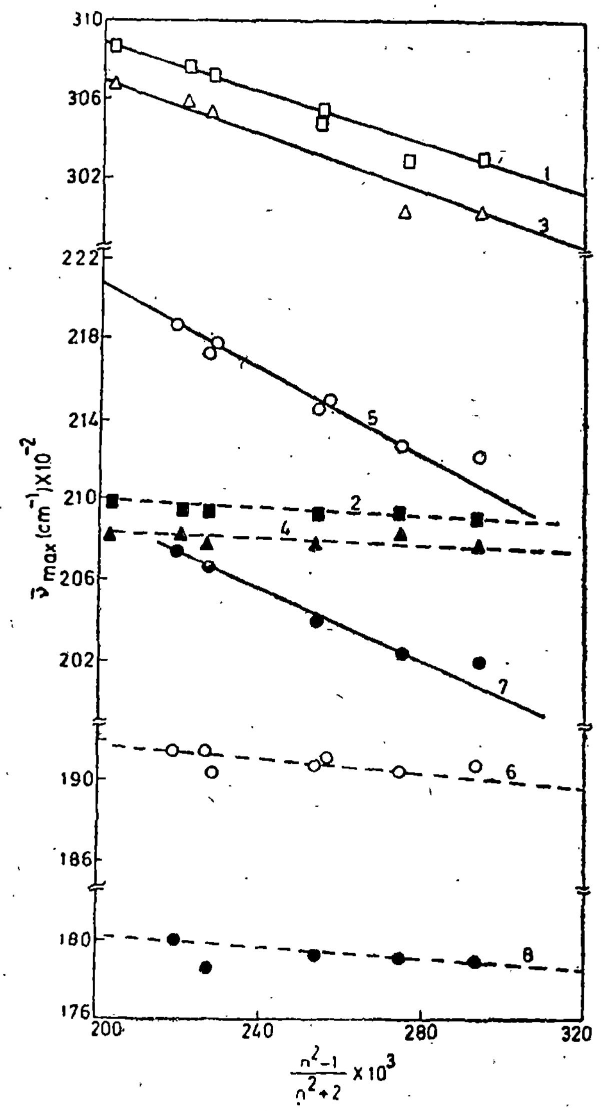

Fig. 4—Plots of $\bar{\nu}_{max}$ against $(n^2-1)/(n^2+2)$ for the lowest energy absorption band and the highest energy emission band of the polyenes studied

Polyene	Curve	
	Absorption	Emission
All-*trans* vitamin alcohol	1	2
All-*trans* vitamin acetate	3	4
Apo-8′-carotenal	5	6
Astacene	7	8

solvent behaviour and the small overlap of the absorption and emission bands indicate that the absorbing and emitting states of these polyenes are different. The existence of a low-lying π-electronic state below the strongly allowed ^1B_u state in these polyenes is thus indicated by such solvent behaviour.

We have observed that when certain vapours are absorbed on the surface of crystals, a new band appears in β-apo-8′-carotenal and astacene. There is a large overlap between the new band and the usually observed intense band. In order to get the longest wavelength band contour out of the total spectrum we have resolved qualitatively the whole spectrum into two parts—one corresponding to the new band and the other to the solid film spectrum before vapour adsorption. The resolved spectra are shown in Figs. 3 (a) and 3 (b).

We have studied the emission spectra of the polyenes in solution only. These emission bands in case of Vitamin A (alcohol and acetate) show good overlap and mirror image relationship with the new band[7]. In β-apo-8′-carotenal and astacene, the emission bands are slightly on the high energy side of the new band in the crystal film. In view of the fact that free molecular electronic energy states are generally lowered in the state of aggregation, the emission of these crystal film polyenes is expected to be on the lower energy side of that in solution, and one can then reasonably expect to get good overlap between the new absorption bands and the emission bands of these polyenes in the crystalline state. Unfortunately, the emission from the crystalline film of these polyenes could not be recorded. We conclude that the new absorption band which appears as a result of adsorption of gas molecules on the solid film of polyenes, corresponds to transition to the lowest excited state which is possibly a ^1A_g state. The adsorbed gas molecules introduce the perturbation required for the enhancement of the low-lying forbidden transition.

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References

1. Misra, T. N. & Rosenberg, B., *J. chem. Phys.*, **48** (1968), 5734.
2. Mandal, Krishnagopal & Misra, T. N., *Indian J. pure. appl. Phys.*, **10** (1972), 86.
3. Thomson, A. J., *J. chem. Phys.*, **51** (1969), 4106.
4. Schulten, K. & Karplus, M., *Chem. Phys. Lett.*, **14** (1972), 305.
5. Hudson, B. S. & Kohler, B. E., *Chem. Phys. Lett.*, **14** (1972), 299.
6. Cherry, R. J. & Chapman, D., *Trans. Faraday Soc.*, **64** (1968), 2304.
7. Mandal, Krishnagopal & Misra, T. N., *Chem. Phys. Lett.*, **27** (1974), 57.
8. Basu, S., *Advances in quantum chemistry*, Vol. 1, edited by P. O. Lowdin (Academic Press, Inc. New York), 1964, 145.

On the Evidence of a Low-lying Forbidden Π-Electronic State in Methylbixin

Electronic absorption and emission spectra of methylbixin have been studied. The solvent behaviour of absorption and emission bands is different. A large solvent shift appears in absorption whereas in emission such shift is very small. No mirror image relation between absorption and emission spectra exists. It has been suggested that in this polyene there exists a low-lying forbidden Π-electronic state (^1A_g) below the strongly allowed ^1B_u state.

According to semi-empirical and *a priori* calculations[1] the excited electronic states of linear polyenes are ^1B_u, ^1A_g, ^1A_g, and ^1B_u in order of increasing energy. The lowest singlet-singlet transition of polyenes is $^1A_g - ^1B_u$ and is strongly allowed. There is experimental evidence that there is no or little overlap between the origins of absorption and emission.[2,3] Attempts have been made[3] to explain it in terms of Franck-Condon forbiddenness. A recent theoretical work[4] has shown that inclusion of double-excitation configuration interaction for the excited states in addition to single-excitation configuration in semi-empirical and *a priori* calculations lowers significantly the lower ^1A_g state in the energy so that a forbidden ^1A_g state appears below the strongly allowed ^1B_u state. Recent experimental investigations[6,7] of polyenes have shown that there exists a low-lying forbidden Π-electronic state (^1A_g) below the well-studied lowest Π-electronic state ^1B_u. It is, therefore, expected that in polyenes the energy of absorption to ^1B_u state and of emission from ^1A_g state will show different solvent effects. In this note, we present our results on the effect of different solvents on the absorption and emission spectra of methylbixin.

The compound under investigation is obtained from Hoffman-La Roche Co., Switzerland and used without further purification. Solvents used are of spectrograde quality. The absorption and emission spectra are recorded at room temperature by Spectromom-202 spectrophotometer and Aminco Bowman spectrofluorometer, respectively.

The absorption and emission spectra of this polyene in benzene are shown in Fig. 1. It is observed that the absorption spectrum consists of three vibronic bands with the central one most intense. This structure is the upper state fundamental of about 1000 cm^{-1}. Due to the solvent-solute interaction this structure becomes blurred in some solvents. The effect of different solvents on the spectra results in a shift of the position of the band. It is found that the absorption and emission spectra shift differently when the solvent is changed. Also the absorption spectrum is much more solvent-dependent than the emission spectrum, the latter does not resemble the former and no mirror image relation between absorption and emission exists.

The absorption band of the polyene shifts more towards red with the increase of the refractive index of the solvents whereas this shift is comparatively very small in emission. This solvent shift is expressed in the form[8,9]

$$\Delta\bar{\nu} = k\,f(n^2-1)/(n^2+2)$$

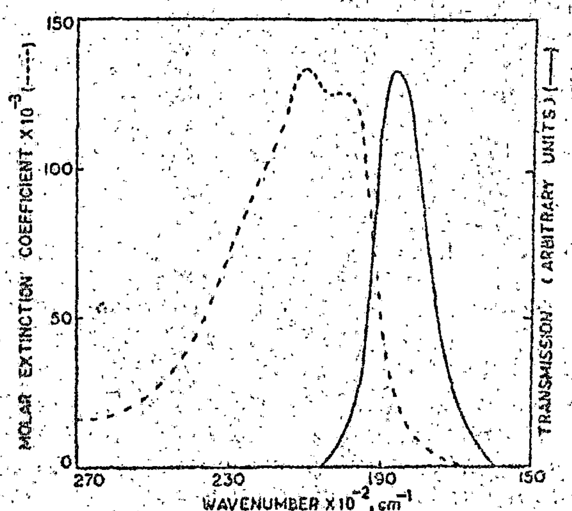

Fig. 1—Absorption (– – –) and emission (——) spectra of *methylbixin in benzene*

Table 1—Solvent Effect on the Absorption and Emission Bands of Methylbixin

Solvent	$\frac{n^2-1}{n^2+2}$	Transition Energy Emission (in cm^{-1})	Transition Energy Absorption (in cm^{-1})
Acetone	0·2195	18796	21645
Ethanol	0·2217	18761	21598
Ethyl acetate	0·2272	18726	21505
1, 4-Dioxane	0·2546	18691	21220
Cyclohexane	0.2578	18796	21186
Carbon tetrachloride	0·2754	18726	20920
Benzene	0·2946	18691	20920

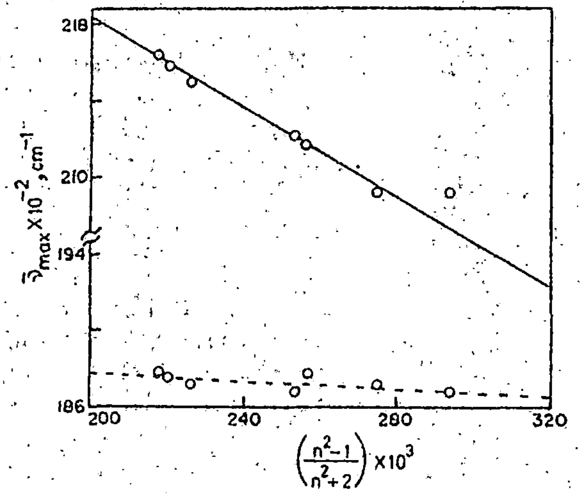

Fig. 2—Plot of $\bar{\nu}_{max}$ versus $(n^2-1)/(n^2+2)$ for absorption (———) and emission (– – –)

Here k is a parameter constant for a given molecule, f the oscillator strength for a particular transition and n the refractive index of the solvent. The positions ($\bar{\nu}_{max}$) of the lowest energy absorption and the highest energy emission bands in different solvents are shown in Table 1. Our experimental results show that the plot of $\bar{\nu}_{max}$ versus the solvent polarizability $(n^2-1)/(n^2+2)$ for both absorption and emission is a straight line as shown in Fig. 2. The slope of this plot gives a measure of the oscillator strength of the electronic transition and it is found that the oscillator strength for the transition involved in absorption is much greater than that for emission. This difference in solvent behaviour and the absence of mirror image relationship between absorption and emission lead to the suggestion that the electronic states involved in absorption and emission are different. Thus the solvent behaviour of absorption and emission indicates the presence of a low-lying forbidden Π-electronic state below the strongly allowed ^1B_u state in this polyene.

The authors are thankful to the University Grants Commission, New Delhi, for financial assistance.

References

1. Suzuki H, *Electronic absorption spectra and geometry of organic molecules* (Academic Press, New York), 1967.
2. Cherry R J & Chapman D, *Trans. Faraday Soc.*, 64 (1968), 2304.
3. Thomson A J, *J. chem. Phys.*, 51 (1969), 4106.
4. Schulten K & Karplus M, *Chem. Phys. Lett.*, 14 (1972), 305.
5. Hudson B S & Kohler B E, *Chem. Phys. Lett.*, 14 (1972), 299.
6. Mandal Krishnagopal & Misra T N, *Chem. Phys. Lett.*, 27 (1974), 57.
7. Mallik B, Jain K M, Mandal K G & Mishra T N, *Indian J. pure appl. Phys.*, 13 (1975), 699.
8. Basu S, *Advances in quantum chemistry*, Vol. 1, edited by P O Lowdin (Academic Press, New York), 1964, 145.
9. Hudson B S & Kohler B E, *J. chem. Phys.*, 59 (1973), 4984.

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Charge-transfer Complexes of *all-trans*-β-Carotene

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On adsorption of some electron acceptor molecules on the solid films of *all-trans*-β-carotene, a new absorption band appears on the longer wavelength side of the spectrum in addition the original bands of *all-trans*-β-carotene. The position of this new band is dependent on the electron effinity (E_A) of the acceptor molecules. A linear relationship between the of ν_{max} the new band and E_A has abee observed. The ionization potential of *all-trans*-β-carotene has been estimated from the intercept of this plot. The value 5.44 ev obtained agrees satisfactorily with the experimental value. It has been concluded that *all-trans*-β-carotene behaves as an electron donor and forms charge-transfer complexes with suitable electron acceptors.

THE observation that β-carotene may form charge-transfer (CT) complexes was made by Platt[1] who suggested that donor-carotene-acceptor trimolecular complex could be involved in the primary photosynthesis process. In a mixture of β-carotene and iodine in $ClCH_2Cl$ solution Lupinski[2] observed a new absorption band at 10000 Å proposed as charge-transfer band of β-carotene....I^+ complex.

Ebrey[3], on the other hand, believed that the band observed by Lupinski, instead of being a charge-transfer band of donor-acceptor type, was a band of β-carotene shifted to longer wavelength due to charge-transfer effect, thus suggesting that β-carotene-I^+. complex has several resonance structures for the β-carotene ground state that would equalise bond length and cause its shifting to longer wavelength.

Significant change in semiconduction current and activation energy of β-carotene powder cell on adsorption of certain gases and vapours on the crystalline surface has been attributed to possible CT complex formation between β-carotene and the adsorbed vapour molecules[4]. We have studied spectroscopically the effect of adsorption of acceptor vapours on the solid film of β-carotene to see if CT complexes are really formed in the solid state. The results of such studies are presented in this paper.

The sample of *all-trans*-β-carotene of high quality has been obtained from Hoffman-La-Roche Co, Switzerland. We have used this compound without further purification. Thin films of polycrystals of this polyene have been made on the quartz surface by gently rubbing the material on it. The solid films thus made have been exposed to nitric acid, iodine, bromine and iodine monochloride vapours. These chemicals are of high quality. The absorption spectra at room temperature (28°C) were recorded immediately after exposing the solid films to vapours. Spectromom-202 spectrophotometer of Hungarian Optical Works was used.

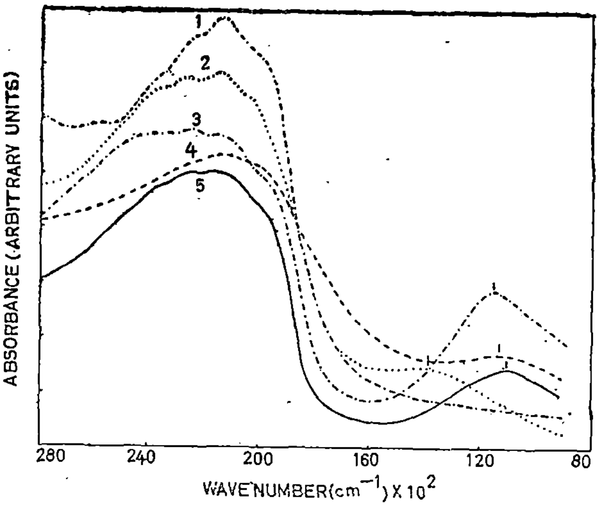

Fig. 1—Electronic absorption spectra of *all-trans*-β-carotene solid film after adsorption of different electron acceptor vapours. [(1), all-trans-β-carotene solid film; (2), nitric acid vapour adsorption; (3), iodine vapour adsorption; (4), bromine vapour adsorption; (5), iodine monochloride vapour adsorption]. (The position ν_{max} of the new bands is indicated by a vertical mark)]

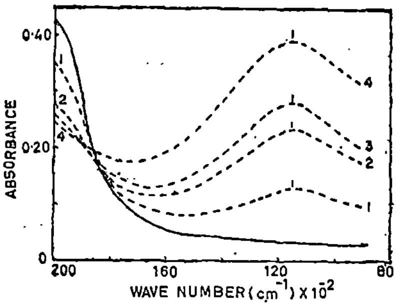

Fig. 2—Enhancement of the intensity of the new band with the amount of adsorbed acceptor molecules. [(—), no adsorption; (....), on adsorption of I_2 vapour; (1-4), in order of increasing amount of acceptor molecules)]

The room temperature absorption spectrum of all-trans-β-carotene in the solid state and the spectra after adsorption of different acceptor vapours are shown in Fig. 1. In the latter case, a new band appeas on the longer wavelength side of the spectra in addition to the original bands of β-carotene solid film. With the increasing amount of acceptor molecules adsorbed on the film surface, the intensity of this new band increases as is usually observed in the case of a charge-transfer band (Fig. 2). The position of this new band is found to be dependent on the acceptor vapours used and shows large red shift with increasing electron affinity of the acceptor molecules. Only acceptors fairly volatile at ordinary temperature are suitable for such experiment. As number of such acceptors are very limited, only a few acceptors could be used. The position of the new band appearing due to the adsorption of different acceptor vapours on the solid film of all-trans-β-carotene are summarized in Table 1.

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Table 1—Position (ν_{max}) of the New Band Appearing on Adsorption of Different Acceptor Vapours on the Solid Film of *all-trans*-β-Carotene

Acceptor used	E_A (ev)	Ref.	ν_{max} (cm^{-1})
Nitric acid	1.83	5	13900
Iodine	2.4	6	11550
Bromine	2.6	6	11300
ICl	2.7	6	11100

The Mulliken theory for charge-transfer complex formation leads to the equation[5].

$$h\nu_{CT} = I_D^V - E_A^V + C_1 + \frac{C_2}{I_D^V - E_A^V + C_1} \quad (1)$$

where $h\nu_{CT}$ is the energy of the lowest energy intermolecular CT band, I_D^V is the vertical ionization potential of the donor, E_A^V is the vertical electron affinity of the acceptor and C_1 and C_2 are constants. The last term is often small, so that its variation can be neglected, giving the equation

$$h\nu_{CT} = I_D^V - E_A^V + C_1 \quad ..(2)$$

Thus for a particular donor, a plot of $h\nu_{CT}$ against E_A^V should be linear. Unfortunately, reliable values of vertical electron affinities are very scare. The vertical electron affinity of nitric acid is not avaiable in the literature. Recently, Chen and Wentworth have emphasised that the correlation of $h\nu_{CT}$ with the absolute electron affinities (E_A) of acceptors is consistent with the usual linear equations and their associated assumptions. The adiabatic electron affinities of I_2, Br_2 and ICl, estimated theoretically by Person[6], were 2.4 ± 0.3, 2.6 ± 0.3 and 2.7 ± 0.3 ev respectively, agreeing satisfactorily with the experimental absolute values measured by Hughes *et al.*[7] We have, therefore, used these adiabatic electron affinity values as the absolute values. The value of E_A for nitric acid has been taken from Chen and Wentworth's table[5].

A plot of ν_{max} (cm^{-1}) of the new band against E_A gives a linear curve (Figs. 3). The ionization potenial of β-carotene can be estimated from this ν_{max} versus E_A plot. The intercept of this curve gives $I_D + C_1 = 2.44$ ev. In typical donor-acceptor CT complexes, $-C_1$ is usually around 3 ev[5,8]. This gives a value of the ionization potential of β-carotene as 5.44 ev. The experimental[9,10] value of the ionization potential of β-carotene is 5.5 ev. This agreement leads credence to the above linear plot and also to the CT concept for this complex. From Eq. 2, one expects a slope of unity for ν_{CT} *versus* E_A^V plot. Fig. 3 gives a slope of 0.44. This low value of slope could be due to that the electron affinity values used for the plot being absolute rather than vertical.

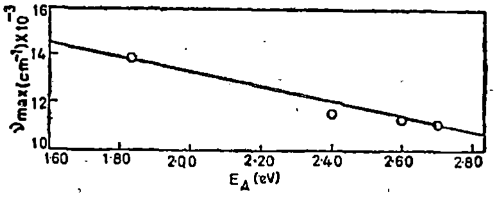

Fig. 3— Plot of ν_{max} (cm^{-1}) against E_A

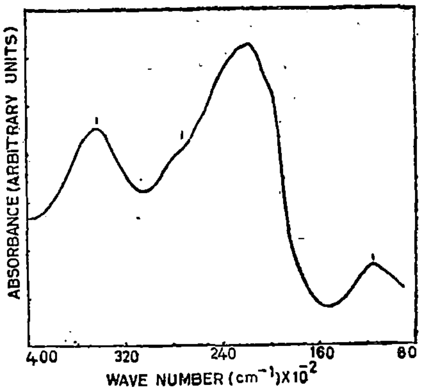

Fig. 4—Electronic absorption spectrum of *all-trans*-β-carotene solid film after adsorption of I_2 vapour. [The position of the new bands is indicated by a vertical mark]

Further, Eq. 2 is only approximate and there is no reason to expect that the last term in Eq. 1 is negligible for all the pairs of donors and acceptors. Indeed, such deviation of slope from unity is a general observation in these types of experiments[11,12].

The room-temperature absorption spectrum of *all-trans*-β-carotene in the region 40000—9000 cm^{-1} after adsorption of I_2 vapour is shown in Fig. 4. From the spectrum, it is observed that in addition to the new band in the longer wavelength side another weak new band is also observed at about 27200 cm^{-1}. This band is possibly the absorption band of I_3^- ion. The other absorption band of this molecular ion expected at about 33900 cm^{-1} has possibly been merged with the original band of *all-trans*-β-carotene at 35400 cm^{-1}. In the case of I_2, possibly through the reaction

$$\beta\text{-carotene} + 2I_2 \rightleftharpoons (\beta\text{-carotene I})^+ + I_3^-$$

β-carotene forms CT complex with iodine. The observed new band on the longer wavelength side arises from the transition between the complex in its ground state (β-carotene.... I^+) and the excited state of the complex (β-carotene$^+$.... I)

Contrary to that suggested by Ebrey, our results indicate that at least in the solid state single resonance structure

$$C = C - (C = C)_n - C = C. \ldots . I^+$$

is quite stable and usual donor-acceptor complexes are formed.

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References

1. Platt J. R. (1959) *Science* **129**, 372.
2. Lupinski J. H. (1963) *J. phys. Chem.* **67**, 2725.
3. Ebrey, T. G. (1967) *J. phys. Chem.* **71**, 1963.
4. Rosenberg, B., Misra, T. N. & Switzer, R. (1968) *Nature* **217** 423.
5. Chen, E. C. M. & Wentworth, W. E. (1975) *J. chem. Phys.* **63**, 3183.
6. Perion, W. B. (1963) *J. chem. Phys.* **38**, 109.
7. Hughes, B. M., Lifshitz, C. & Tiernan, T. O. (1973) *J. chem. Phys.* **59** (6), 3162.
8. Farragher, A. L. & Page, F. M. (1967) *Trans. Faraday. Soc.* **63**, 2369.
9. Vilesov, F. I. (1960) *Dokl. Akad. Nauk. SSSR, Ser. Fiz.* **132**, 632.
10. Vilesov, F. I. & Terenin, A. N. (1960) *Dokl. Akad. Nauk. SSSR, Ser. Fiz.* **133**, 1059.
11. McConnel, H., Ham, J. S. & Platt, J. R. (1953) *J. chem. Phys.* **21**, 66.
12. Foster, R. (1960) *Tetrahedron* **10**, 96.

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Compensation Effect in Semiconducting Vitamin A (alcohol and acetate)

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Inorganic semiconductor the compensation rule, a linear relationship between the logarithm of the pre-exponential factor in the expression for specific conductivity and the semiconduction activation energy, has been a subject of great interest in the recent years.[1-4] The pre-exponential factor σ_0 is generally assumed to be a constant in the equation

$$\sigma(T)=\sigma_0 \exp(-E/2kT), \qquad (1)$$

where, $\sigma(T)$ is the specific conductivity at any absolute temperature T, E is the semiconduction activation energy and k is the Boltzmann constant. But experimental evidence shows that σ_0 contains exponential functions.[5] To study the compensation rule in a semiconductor E is generally varied by different ways and $\log \sigma_0$ is plotted against E. Recently, Masui *et al.*[1] have reported that this compensation rule is valid for uniaxially drawn low density polyethylene. Experimental results of Sawa *et al.*[2] show that in case of high energy irradiated polyethylene with different radiation doses also this rule is valid. However, adsorption of gases is known to change the semiconduction activation energies of many organic semiconductors.[6,7] Such change depends on the chemical nature and also on the amount of vapour adsorbed. We have used this method of varying the activation energy of semiconducting Vitamin A by adsorbing various vapours and different amounts of the same vapour on the crystallite surface. In this note we present our experimental results and show that the compensation rule is valid for semiconduction is solid Vitamin A (alcohol and acetate).

The samples of Vitamin A alcohol and acetate powder were obtained from Hoffmann-La Roche & Co. Ltd., Switzerland. The experimental procedure for the measurement of semiconduction activation energy of these compounds on vapour adsorption is similar to that of Misra *et al.*[7] The finely powdered compounds pressed in a sandwich cell between a conducting glass and a stainless steel electrode was maintained at a moderate pressure by spring clips. The separation between the electrodes was maintained by a 2 mil thick teflon spacer. A d.c. voltage of 22.5 volts from a dry battery pack was applied across the cell which was placed on a thermal bar platform in a suitably designed conductivity chamber made of brass and fashioned with teflon. There was an inlet and a outlet for gas in the chamber. The temperature of the cell which could be controlled from outside was measured by a copper constantan thermocouple attached to the metal electrode. The dark current was measured with Electrometer Amplifier EA815 of Electronic Corporation of India Limited. Chemicals used in this experiment were of spectrograde (E. Merck, B.D.H.) or equivalent quality. The semiconduction activation energy of Vitamin A (alcohol and acetate) with toluene (1), benzene (2), ethyl acetate (3), n-heptane (4), ethanol (5) and methanol (6) vapour and also with different amounts of ethyl acetate vapour adsorption have been determined from the Arrhenious plots of eq. (1).

At a constant temperature T_1, log [for $(1/T_1)=3.80\times10^{-3}\ \mathrm{K}^{-1}$] is plotted against the measured values of activation energy (E). Linear plots as shown in Fig. 1 are obtained. The observed slopes in Fig. 1 are 7.70 and 4.55 eV^{-1} for Vitamin A alcohol and acetate respectively. The expected slope according to eq. (1) is 22.18 eV^{-1} for both the compounds. These low values of the observed slopes indicate that eq. (1) is not valid in these cases. To test the validity of the compensation rule $\log \sigma_0$ is plotted against E. The plots are linear (Fig. 2). Rosenberg *et al.*[4] have suggested the following equation for the specific conductivity which takes account of the compensation effect

$$\sigma=\sigma_0' \exp(E/2kT_0) \exp(-E/2kT) \qquad (2)$$

So that

$$\sigma_0=\sigma_0' \exp(E/2kT_0), \qquad (3)$$

where T_0 is the characteristic temperature of the semiconducting material. σ_0' and T_0 for the same compound remain invariant. The

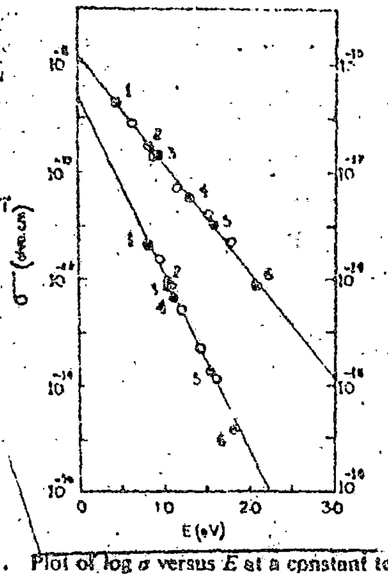

Fig. 1. Plot of log σ versus E at a constant temperature $[(1/T_1)=3.80\times10^{-3}\ \mathrm{K}^{-1}]$ for Vitamin A (alcohol and acetate).
Vitamin A alcohol: lower line (left scale);
Vitamin A acetate: top line (right scale).
—●— different vapours (the numbers indicate the specific vapour as stated in the text).
—○— different amounts of ethyl acetate vapour (activation energy decreases with the increasing amount of the vapour adsorbed).

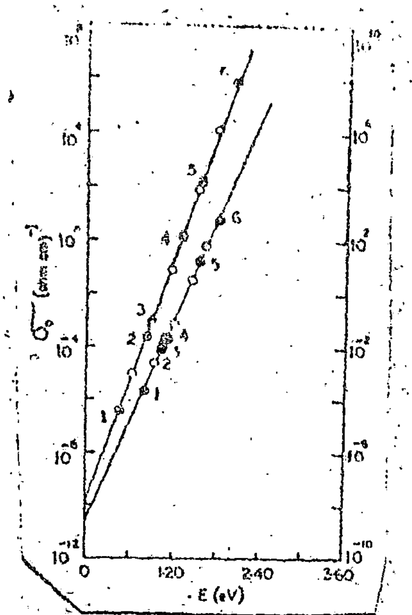

Fig. 2. Plot of the log σ_0 values versus E [from eq. (1)] for Vitamin A (alcohol and acetate) at a constant temperature $[(1/T_1)=3.80\times10^{-3}\ \mathrm{K}^{-1}]$.
Vitamin A alcohol: lower line (right scale);
Vitamin A acetate: top line (left scale).
The closed and open circles indicate same as in Fig. 1.

value of the slope i.e. $(2kT_0)^{-1}$ obtained from Fig. 2 is 14.45 and 17.52 eV^{-1} for Vitamin A alcohol and acetate respectively.

From eq. (2) it is seen that for any particular temperature T_1 the specific conductivity is expressed by

$$\log \sigma(T_1)=\log \sigma_0'+\left[\frac{1}{T_0}-\frac{1}{T_1}\right]\frac{E}{2k} \qquad (4)$$

giving a slope equal to $[(1/T_0)-(1/T_1)](1/2k)$ and an intercecept of log σ_0' for the linear plot log $\sigma(T_1)$ vs E. The calculated slopes with $(2kT_0)^{-1}$ as obtained from Fig. 2 are 7.73 and 4.66 eV^{-1} for Vitamin A alcohol and acetate respectively. The experimentally observed slopes (Fig. 1) are in excellent agreement with this. The value of σ_0' obtained from Fig. 2 [2.80×10^{-9} and 1.50×10^{-10} $(\Omega\cdot\mathrm{cm})^{-1}$ for Vitamin A alcohol and acetate respectively] and Fig. 1 [2.85×10^{-9} and 1.60×10^{-10} $(\Omega\cdot\mathrm{cm})^{-1}$ for Vitamin A alcohol and acetate respectively] agree satisfactorily. Thus our results confirm the validity of the compensation rule in solid Vitamin A semiconductor.

We thank the Council of Scientific and Industrial Research, India for a Senior Research Fellowship (to B.M.) and Prof. G. S. Kastha for his kind interest in this problem. Thanks are also due to M/s. Hoffmann-La Roche & Co., Switzerland for a kind gift of the Vitamin A samples.

References

1) M. Masui, H. Nagasaka and K. Yahagi: Jpn. J. Appl. Phys. 16 (1977) 117.
2) G. Sawa, K. Kitagawa and M. Ieda: Jpn. J. Appl. Phys. 11 (1972) 416.
3) D. D. Eley, A. S. Fawcett and M. R. Willis: Trans. Faraday Soc. 64 (1968) 1513.
4) B. Rosenberg, B. Bhowmik, H. C. Harder and E. Postow: J. Chem. Phys. 49 (1968) 4108.
5) F. Gutmann and L. E. Lyons: *Organic Semiconductors* (Wiley, New York, 1967) p. 428.
6) B. Rosenberg: J. Chem. Phys. 36 (1962) 816.
7) T. N. Misra, B. Rosenberg and R. Switzer: J. Chem. Phys. 48 (1968) 2096.

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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 $\sigma_0' \approx 2.8\times10^{-9}\,\Omega^{-1}\,\mathrm{cm}^{-1}$ for vitamin A alcohol and $T_0 \approx 335$ K and $\sigma_0' \approx 1.5\times10^{-10}\,\Omega^{-1}\,\mathrm{cm}^{-1}$ 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

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

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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 und 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.

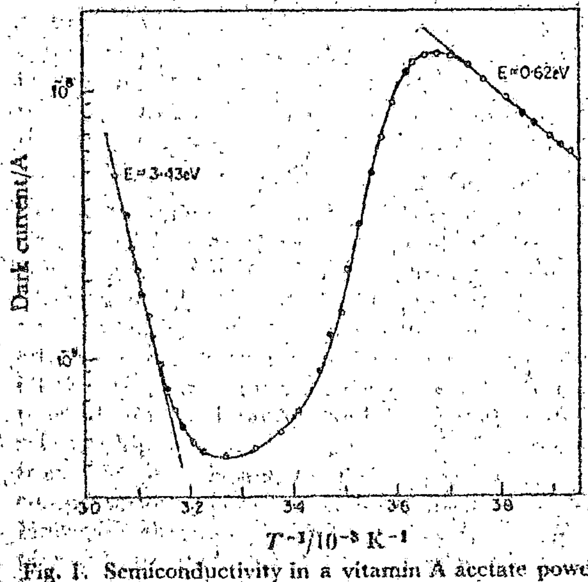

Fig. 1. Semiconductivity in a vitamin A acetate powder cell with desorption of ethyl acetate vapor as the temperature increases.

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

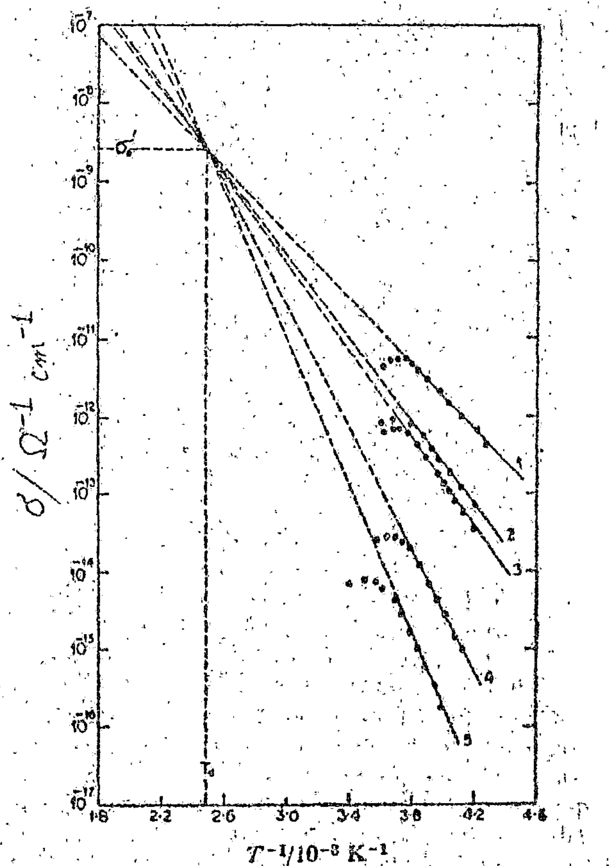

Fig. 2(a). Semiconductivity in vitamin A alcohol powder cell (steady state condition) with the adsorption of same amount of different vapors. Solid lines represent temperature region of measurements, dashed lines are extrapolations. Each line refers to a specific vapor adsorbed state. Vapors are (1) 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_d=402 K; σ_0'=2.65×10^{-9} Ω^{-1} cm^{-1}.

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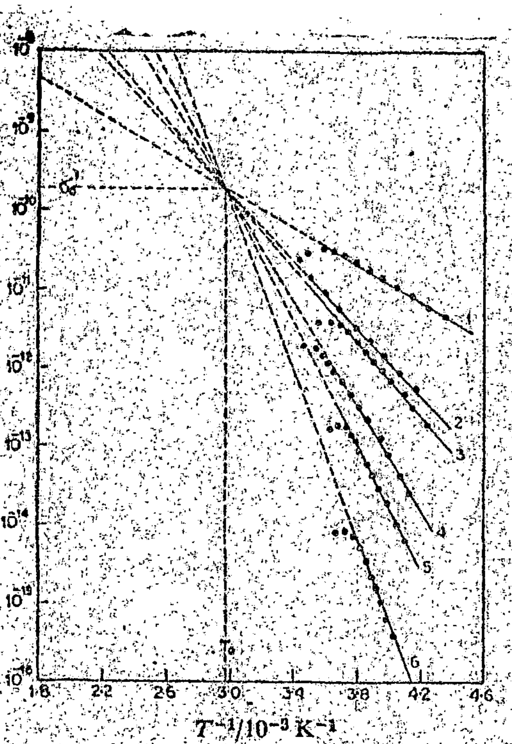

Fig. 2(b). Same as Fig. 2(a) for vitamin A acetate with adsorbed vapors (1) toluene; (2) benzene; (3) ethyl acetate; (4) heptane; (5) ethanol; and (6) methanol. $T_0 \approx 335$ K; $\sigma_0' = 1.8 \times 10^{-10}\ \Omega^{-1}\ \text{cm}^{-1}$.

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 $1.8 \times 10^{-10}\ \Omega^{-1}\ \text{cm}^{-1}$ 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 $1.65 \times 10^{-10}\ \Omega^{-1}\ \text{cm}^{-1}$ for vitamin A alcohol and acetate respectively] in good agreement with those obtained earlier.

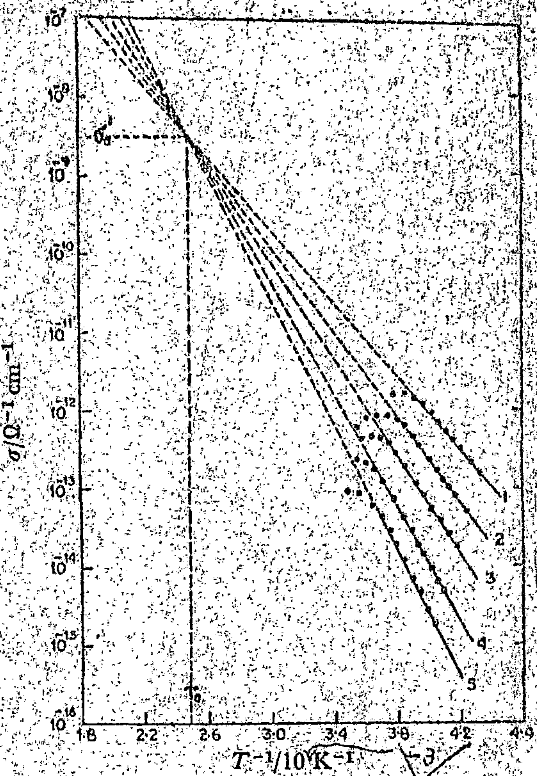

Fig. 3(a). Semiconductivity data for vitamin A alcohol powder cell (steady state condition) with adsorption of different amount of ethyl-acetate vapor. The lines (1) →(5) refer to the states with the decreasing amount of adsorbed vapor. $T_0 \approx 403$ K; $\sigma_0' = 3.1 \times 10^{-9}\ \Omega^{-1}\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

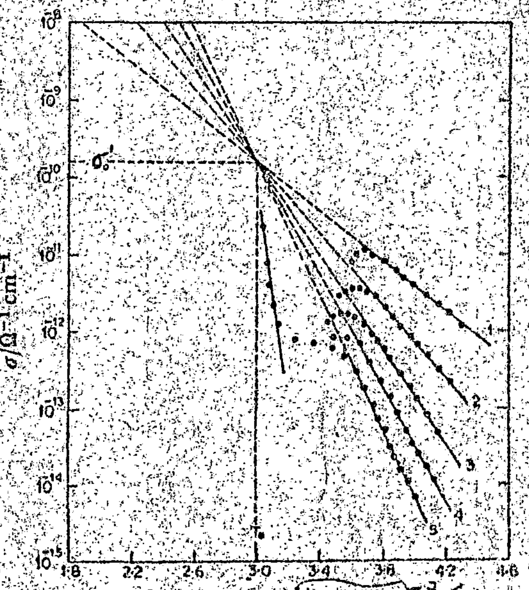

Fig. 3(b). Same as Fig. 3(a) for vitamin A acetate Here, $T_0 \approx 334$ K; $\sigma_0' = 1.65 \times 10^{-10}\ \Omega^{-1}\ \text{cm}^{-1}$.

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 $1.5 \times 10^{-10}\ \Omega^{-1}\ \text{cm}^{-1}$ 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.

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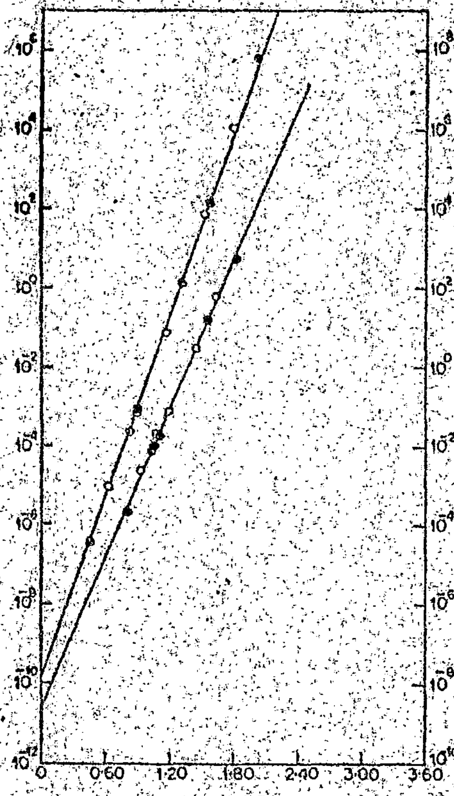

Fig. 4. Plot of the log σ_0 values [from Eq. 1] *vs.* the activation energies for vitamin A (alcohol and acetate) at a constant temperature [$1/T=3.8\times10^{-3}$ K^{-1}]. The lower line is for vitamin A alcohol (right scale) and the top line is for vitamin A acetate (left scale). The dark circles refer 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.

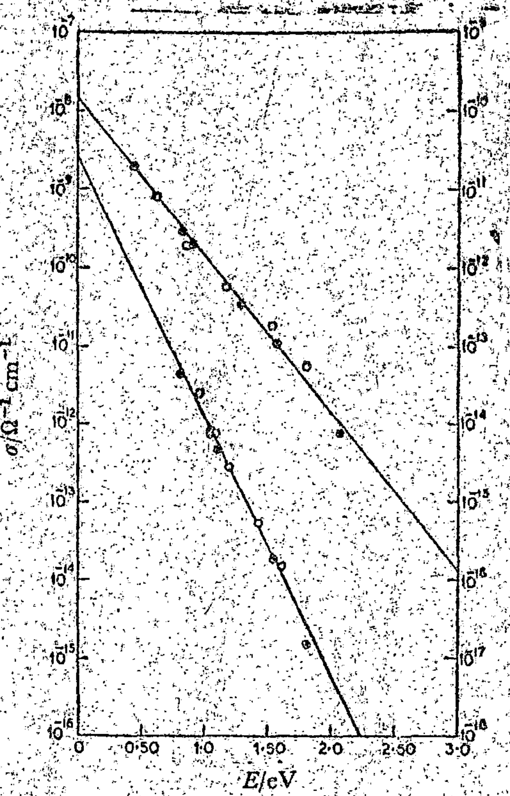

Fig. 5. Plot of the log σ values for vitamin A (alcohol and acetate) *vs.* E at a constant temperature ($1/T_1=3.8\times10^{-3}$ K^{-1}). The lower line refers to vitamin A alcohol (left scale) and the top line to vitamin A acetate (right scale). The dark circles refer to different vapors and the open 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.

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Using the values of $1/2kT_0\approx14.45$ eV^{-1} and $\sigma_0'=2.8\times10^{-9}$ Ω^{-1} cm^{-1} for vitamin A alcohol, $1/2kT_0=17.52$ eV^{-1} and $\sigma_0'=1.5\times10^{-10}$ 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 $1/T_1\approx3.8\times10^{-3}$ K^{-1}. Taking $1/(2kT_0)\approx14.45$ 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}, $\sigma_0'=2.8\times10^{-9}$ Ω^{-1} cm^{-1}			Vitamin A acetate (solid state crystalline powder) $(2kT_0)^{-1}=17.52$ eV^{-1}, $\sigma_0'=1.5\times10^{-10}$ Ω^{-1} cm^{-1}		
	eV	$\frac{E}{\text{eV}}$	$\frac{\sigma_0'\exp[E/(2kT_0)]}{\Omega^{-1}\,\text{cm}^{-1}}$	$\frac{\sigma_0}{\Omega^{-1}\,\text{cm}^{-1}}$	$\frac{E}{\text{eV}}$	$\frac{\sigma_0'\exp[E/(2kT_0)]}{\Omega^{-1}\,\text{cm}^{-1}}$	$\frac{\sigma_0}{\Omega^{-1}\,\text{cm}^{-1}}$
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}	1.31	1.39×10^{0}	1.2×10^{0}
Ethanol	10.50	1.55	1.49×10^{1}	1.3×10^{1}	1.57	1.32×10^{2}	7.0×10^{1}
Methanol	10.85	1.82	7.39×10^{2}	1.25×10^{3}	2.07	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) $(2kT_0)^{-1}=14.45\ \mathrm{eV}^{-1}$; $\rho_0'=2.8\times10^{-9}\ \Omega^{-1}\ \mathrm{cm}^{-1}$				Vitamin A acetate (Solid state crystalline powder) $(2kT_0)^{-1}=17.52\ \mathrm{eV}^{-1}$; $\sigma_0'=1.5\times10^{-10}\ \Omega^{-1}\ \mathrm{cm}^{-1}$			
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	$9.32\times10^{-}$ 6	$1.0\times10^{-}$ 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 $\sigma_0' \approx 2.85\times10^{-9}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ for vitamin A alcohol and $\sigma_0' \approx 1.6\times10^{-10}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ for vitamin A acetate. These values agree well with the values obtained from the $\log \sigma_0$ *vs.* E and $\log \sigma$ *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.[30] 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[22,26] 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.[21,22] This adds further credence to the proposed charge-transfer concept.

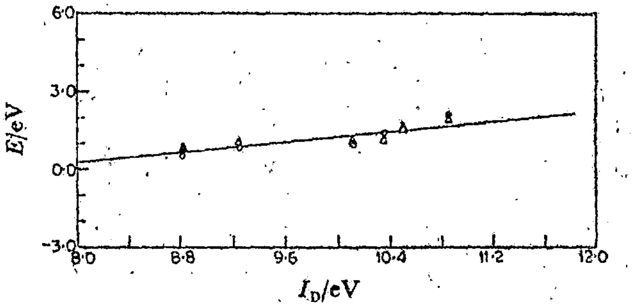

Fig. 6. Semiconductive activation energy (E) *vs.* ionization potential (I_{D}) of the adsorbed vapor molecules.

—○—: Vitamin A alcohol.
—△—: Vitamin A acetate.

n-Data ar changed.

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 lies 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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References

1) D. D. Eley, *J. Polym. Sci., Part C*, **17**, 73 (1967).
2) B. Rosenberg, B. Bhowmik, H. C. Harder, and E. Postow, *J. Chem. Phys.*, **49**, 4108 (1968).
3) D. D. Eley, A. S. Fawcett, and M. R. Wills, *Trans. Faraday Soc.*, **64**, 1513 (1968).
4) G. R. Johnston and L. E. Lyons, *Aust. J. Chem.*, **23**, 2187 (1970).
5) Ulbert, *Aust. J. Chem.*, **23**, 1347 (1970).
6) M. Masui, H. Nagasaka, and K. Yahagi, *Jpn. J. Appl. Phys.*, **16**, 177 (1977).
7) F. Gutmann and L. E. Lyons, "Organic Semiconductors," John-Wiley, New York (1967), pp. 428—435.
8) B. Rosenberg, *J. Chem. Phys.*, **36**, 816 (1962).
9) G. Kemeny and I. M. Goklany, *J. Theor. Biol.*, **40**, 107 (1973).
10) T. A. Kaplan and S. D. Mahanti, *J. Chem. Phys.*, **62**, 100 (1975).
11) T. N. Misra, B. Rosenberg, and R. Switzer, *J. Chem. Phys.*, **48**, 2096 (1968).
12) B. Rosenberg, T. N. Misra, and R. Switzer, *Nature*, **217**, 423 (1968).
13) B. Rosenberg, *Nature*, **193**, 304 (1962).
14) B. Rosenberg, "Physical Processes in Radiation Biology," Academic Press (1969), p. 119.
15) M. M. Labes and O. N. Rudyj, *J. Am. Chem. Soc.*, **85**, 2055 (1963).
16) P. J. Reucroft, O. N. Rudyj, and M. M. Labes, *J. Am. Chem. Soc.*, **85**, 2059 (1963).
17) P. J. Reucroft, O. N. Rudyj, R. E. Salomon, and M. M. Labes, *J. Phys. Chem.*, **69**, 779 (1962).
18) B. Pullman A. Pullman, "Quantum Biochemistry," Interscience New York (1963), p. 440.
19) J. R. Platt, *Science*, **129**, 372 (1959).
20) H. Kuroda, K. Yoshihara, and M. Akamatu, *Bull. Chem. Soc. Jpn.* **35**, 1604 (1962).
21) H. Kuroda, M. Kobayashi, M. Kinoshita, and S. Takemoto, *J. Chem. Phys.*, **36**, 457 (1962).
22) E. C. M. Chen and W. E. Wentworth, *J. Chem. Phys.*, **63**, 3183 (1975).
23) H. McConnel, J. S. Ham, and J. R. Platt, *J. Chem. Phys.*, **21**, 66 (1953).
24) R. Foster, *Tetrahedron*, **10**, 96 (1960).
25) A. L. Farragher and F. M. Page, *Trans. Faraday Soc.*, **63**, 2369 (1967).
26) V. G. Mairanovaky, A. A. Engovatov, N. T. Ioffe, and G. I. Samokhvalov, *J. Electroanal. Chem.*, **66**, 123 (1975).
27) M. E. Green, *J. Chem. Phys.*, **51**, 3279 (1969).
28) G. Kemeny and B. Rosenberg, *J. Chem. Phys.*, **53**, 3549 (1970).
29) E. I. Mukhtarov, A. A. Pichurin, and A. I. Kitaigorodskii, *Sov. Phys. Solid State (U.S.A.)*, **17**, 1871 (1975).