

Effect of adsorption of vapours on the electrical conductivity of some polyene semiconductors: adsorption and desorption kinetics

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Abstract. The change in semiconductive properties of β -apo-8'-carotenal, astacene and methyl bixin on adsorption of various vapours on the crystallite surfaces has been studied at a constant sample temperature. The adsorption of vapours enhances the semiconductivity of the polyenes appreciably. This enhancement depends on the chemical nature and also on the pressure of the adsorbed vapour. The adsorption and desorption kinetics follow the modified Roginsky-Zeldovich relation. A two stage adsorption process, the first stage of which gives a Lennard-Jones potential energy curve and is followed by a rate-determining transition over a potential energy barrier to the second stage of adsorption forming weakly bound complexes between the vapour molecules and the polyene crystallites, can explain satisfactorily the experimentally observed kinetic data.

Keywords. Organic semiconductors ; vapour adsorption effect ; desorption kinetics ; adsorption kinetics ; electrical conductivity ; polyene semiconductors.

1. Introduction

The effect of adsorption of various vapours and gases on the semiconductive properties of polyenes are of considerable interest as the change in conductivity of these compounds on vapour or gas adsorption could be involved in the primary mechanism of olfactory transduction process (Rosenberg *et al* 1968 ; Misra *et al* 1968). In an earlier paper (Mallik *et al* 1979a) we have reported that the adsorption of vapours of benzene, toluene, ethyl acetate, heptane, ethanol and methanol on vitamin A (alcohol and acetate) enhances the semiconduction current and decreases the semiconduction activation energy appreciably. The adsorption kinetics were observed (Mallik *et al* 1979b) to follow the modified Roginsky-Zeldovich equation which assumes that the rate of adsorption possesses an activation energy which increases linearly with the amount of adsorbed vapour. Recently (Mallik *et al* 1980) we have observed that the adsorption of these vapours on the polycrystals of some other polyenes, namely β -apo-8'-carotenal, astacene and methyl bixin also enhances the specific conductivities of the compounds but unlike that in vitamin A, increases the activation energies. It was, therefore,

considered worthwhile to examine if the similar adsorption kinetics are followed in these polyenes also. In this paper we examine the adsorption and desorption kinetics, and estimate the activation energies of adsorption and desorption from the kinetic data analysis and discuss a possible model for the adsorption process.

2. Experimental

The polyene semiconductors studied are β -apo-8'-carotenal, astacene and methyl bixin. These high quality compounds were obtained from Hoffman and La-Roche Co. Limited, Switzerland, and have been used without further purification. The reagent chemicals, toluene, benzene, ethyl acetate, *n*-heptane, ethanol and methanol used in this experiment were of spectrograde quality (BDH and E Merck). The experimental arrangement is similar to that reported in the earlier communication (Mallik *et al* 1979b).

Results

3.1. Semiconduction of the polyenes and the effect of adsorption of vapours

The effects of adsorption of vapours were studied in the usual manner by applying the sandwich cell technique. The sandwich cell was temperature-cycled and in addition dry nitrogen gas was allowed to pass through the chamber to desorb any vapour or gas adsorbed by the sample prior to the experiment. The cell was then kept at room temperature (25° C) and the carrier gas, dry nitrogen, was passed through the reagent liquid which was kept at a constant temperature to maintain a desired vapour pressure. As the powder sample adsorbs the vapour from the chamber atmosphere, the current increases and finally attains a saturation value. The current enhancement was by several orders of magnitude in some cases. The result of such a measurement for ethyl acetate vapour adsorption in β -apo-8'-carotenal is shown in figure 1. When the chamber is flushed with dry nitrogen gas, the vapour is desorbed from the crystallite surfaces and the current comes back to its initial value. This is shown in curve (b) of figure 1. The arrow indicates the time when desorption starts. Such adsorption and desorption kinetic curves were obtained with other vapours. The other polyenes also show similar adsorption and desorption curves. The maximal value of current reached under particular experimental conditions, depends on the vapour pressure of the reagent liquid at its temperature and also on the temperature of the sample cell; the time to reach this value depends also on the flow rate. To test the sensitivity of a particular polyene semiconductor for adsorption of different vapours, saturation current values were noted after adsorption of various vapours at a fixed partial vapour pressure with a constant flow rate and a constant sample cell temperature (18.5° C). The sensitivity as measured by σ_A/σ_V values where σ_A is the specific conductivity after vapour adsorption and σ_V is that of before adsorption. The results are summarised in table 1. Apparently, the sensitivity depends on the chemical nature of the adsorbed molecules.

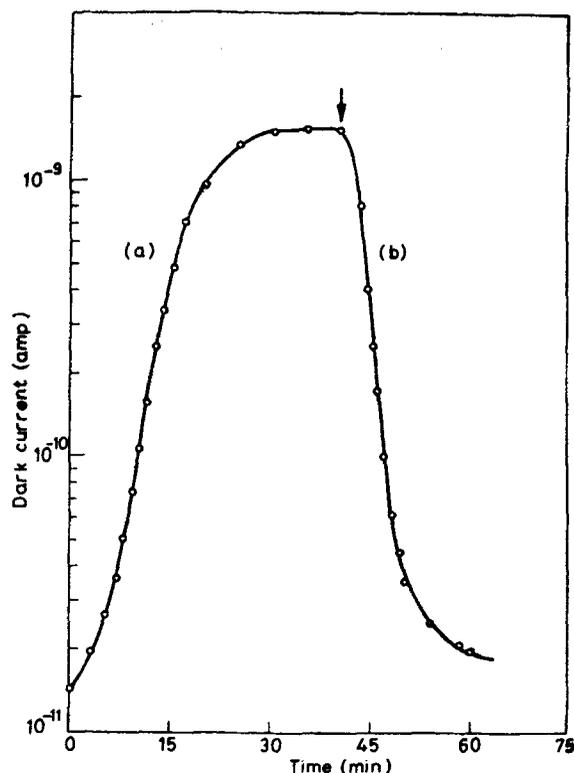


Figure 1. Change in dark current in a β -apo-8'-carotenal powder cell kept at 25° C with (a) adsorption and (b) desorption of ethyl acetate vapour at 59.5 mm pressure.

3.2. Semiconduction as a function of vapour pressure

We have studied the magnitude of the current increase at a constant sample cell temperature (25° C) as a function of the partial pressure of the vapours in the chamber. To change this partial pressure, the temperature of the reagent liquid through which dry nitrogen gas was passed and fed into the conductivity chamber was varied. The steady-state current was noted for different vapour pressures. The kinetics for the dark current enhancement for different partial pressures of ethyl acetate ambient vapour for β -apo-8'-carotenal is shown in figure 2. The time required for reaching the saturation current increases with the increasing vapour pressure as at saturation more vapours get adsorbed at higher pressure (Eley and Leslie 1964). Similar results were obtained with other vapours. The other polyenes also show similar behaviour.

4. Discussion and conclusions

4.1. Dependence of the conductivity on vapour pressure

We have shown (Mallik *et al* 1979b) in vitamin A (alcohol and acetate) that the relation between the specific conductivity $\sigma_A(m_0)$ at equilibrium and the pressure (p) of ambient vapour is given by

$$\sigma_A(m_0) = \sigma_V \exp(aQ_0 p), \quad (1)$$

Table 1. Rise in the dark current in the powder cells of some polyenes at 18.5° C due to adsorption of various vapours at the same pressure (p) for a particular polyene.

Vapour adsorbed	σ_A/σ_V		
	β -apo-8'-carotenal $p = 42$ mm	Astacene $p = 50$ mm	Methyl bixin $p = 60$ mm
Toluene	7.3	1.8	1.5
Benzene	4.2	2.5	3.3
Ethyl acetate	5.0×10^3	1.5×10^3	1.0×10^1
<i>n</i> -Heptane	4.4
Ethanol	5.0×10^3	4.0×10^3	1.0×10^3
Methanol	6.5×10^3	5.0×10^3	3.3×10^1

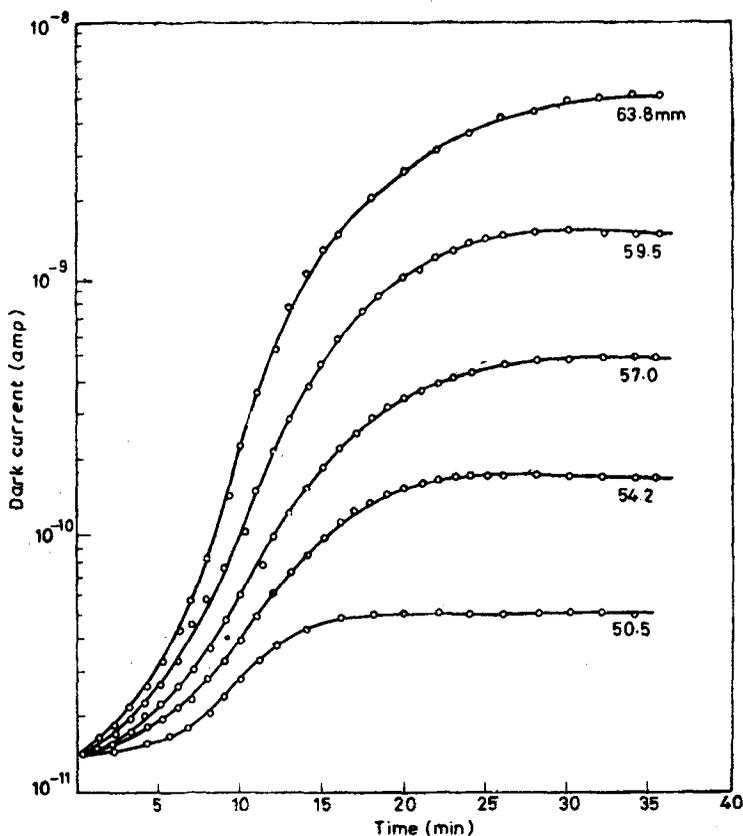


Figure 2. Change in dark current in a β -apo-8'-carotenal powder cell kept at 25° C after adsorption of ethyl acetate vapour at different pressures.

where m_0 is the amount of vapour adsorbed at equilibrium, α and Q_0 are constants. According to equation (1), a plot of $\log \sigma_A (m_0)$ versus the vapour pressure (p) at equilibrium is expected to be linear. In figure 3 we show such plots of logarithm of the saturation currents versus vapour pressure (p) at equilibrium for ethyl acetate adsorption on various polyene semiconductors. Fairly good straight lines are obtained. The slope of these curves (αQ_0) is a measure of the strength of interaction between the vapour molecules and the semiconductors. The values of αQ_0 as obtained from the slopes of the lines in figure 3 are 0.354, 0.089 and 0.078 mm^{-1} for β -apo-8'-carotenal, astacene and methyl bixin respectively.

4.2. Adsorption kinetics

The Roginsky-Zeldovich equation for adsorption kinetics in a modified form is given by (Mallik *et al* 1979b)

$$dm/dt = A \exp(-\beta m/kT), \quad (2)$$

where m is the amount of vapour adsorbed at time t , A and β are constants at a particular vapour pressure, k is the Boltzmann constant and T is the absolute temperature. The relation between σ_A , α , β and t is given by

$$\log \sigma_A = \frac{\alpha k T}{\beta} \log(t + t_0) + \text{constant}. \quad (3)$$

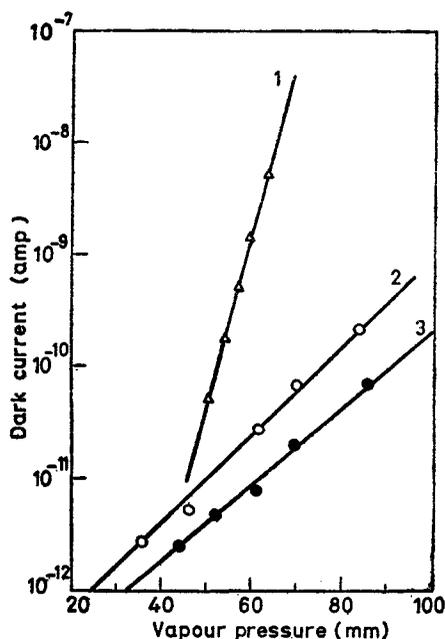


Figure 3. Change in the dark current [$I_A (m_0)$] of β -apo-8'-carotenal, astacene and methyl bixin powder cells kept at 25° C as a function of the vapour pressure of ethyl acetate. The lines 1, 2 and 3 correspond to β -apo-8'-carotenal, astacene and methyl bixin respectively.

Thus, from any empirically chosen t_0 , a linear plot of $\log \sigma_A$ versus $\log (t + t_0)$ is suggested. With correctly chosen t_0 , the plot of m as a function of $\log (t + t_0)$ should give a straight line (Taylor and Thon 1952). Such plots for β -apo-8'-carotenal are shown in figure 4. The time indicated in the abscissa is the time measured from the initiation of adsorption. As in vitamin A (alcohol and acetate), in the initial region different slopes observed at different vapour pressures show the vapour pressure-dependence of β . The higher the partial vapour pressure, the larger is the slope. We have estimated the values of β/α ($= \beta'$) from the slopes to see its pressure dependence. In table 2 variation of β' with vapour pressure for ethyl acetate vapour adsorption on various polyenes is shown.

4.3. Desorption kinetics

Equation (2) is valid for the rate of adsorption. Since desorption is a reverse process of adsorption, equation for the rate of desorption can be written in a similar form with a positive sign in the exponent, i.e., by

$$- dm/dt = A^* \exp (\beta^*m/kT). \quad (4)$$

Here, β^*m is the activation energy for desorption. In the measurement of desorption, the experimental conditions are so arranged that there is no re-adsorption. The plots of logarithm of current versus logarithm of time for desorption of ethyl

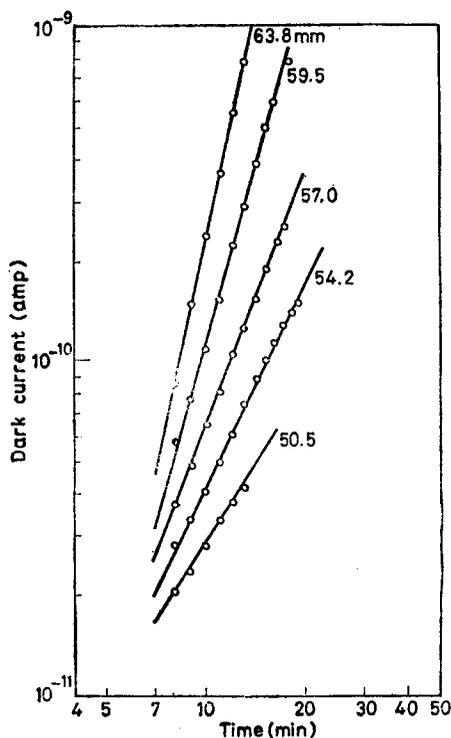


Figure 4. Adsorption kinetics data plotted according to modified Roginsky-Zeldovich equation for β -apo-8'-carotenal,

Table 2. Vapour pressure dependence of the factors β' and β^{*} for vapour adsorption and desorption kinetics respectively in case of ethyl acetate vapour adsorption.

Polyenes	Vapour pressure (mm)	β' (eV) ($\times 10^{-2}$)	β^{*} (eV) ($\times 10^{-2}$)
β -apo-8'-carotenal	50.5	1.629	8.621
	54.2	1.245	1.919
	57.0	0.994	1.322
	59.5	0.718	1.015
	63.8	0.555	0.808
Astacene	35.8	3.973	6.733
	46.0	2.568	4.591
	61.0	1.422	1.720
	70.0	1.168	1.250
	84.0	0.931	0.969
Methyl bixin	44.0	5.714	8.312
	52.0	4.131	5.971
	61.0	2.526	4.322
	70.0	1.638	2.215
	86.0	1.039	1.431
Vitamin A alcohol	31.0	1.202	2.304
	35.0	1.005	1.347
	37.5	0.930	1.492
	43.5	0.759	1.201
	50.5	0.543	0.798
Vitamin A acetate	31.0	0.819	1.431
	35.7	0.753	1.151
	41.7	0.660	1.023
	48.2	0.601	0.802
	55.2	0.518	0.648

acetate vapour for β -apo-8'-carotenal crystallites are shown in figure 5. The time indicated in the abscissa is the time measured from the initiation of desorption. Similar plots have been made for other polyenes also. In table 2 we present the experimental values of β^{*} ($=\beta^{*}/\alpha$) obtained from these plots for ethyl acetate vapour desorption from different polyene crystallites. We have also included the data of vitamin A (alcohol and acetate) to show the generality of the kinetics of vapour adsorption and desorption in all these polyenes. As in β' , β^{*} also decreases with increasing vapour pressure. For any particular pressure of ambient vapour, β^{*} is larger than β .

The Roginsky-Zeldovich equation can be treated in different ways (Stone 1955), A simple two-stage process after Eley and Leslie (1964) as shown in figure 6 seems quite satisfactory to account for the experimental observations. In the first stage a mobile van der Waals' adsorption on the crystal surface gives a Lennard-Jones potential energy curve which is assumed to depend on the fraction of surface coverage. This stage is followed by a rate-determining transition over a potential energy

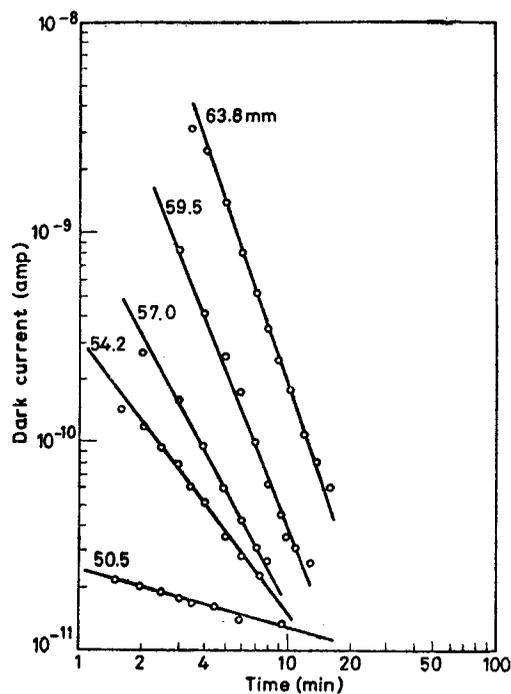


Figure 5. Desorption kinetics data plotted according to modified Roginsky-Zeldovich equation for β -apo-8'-carotenal.

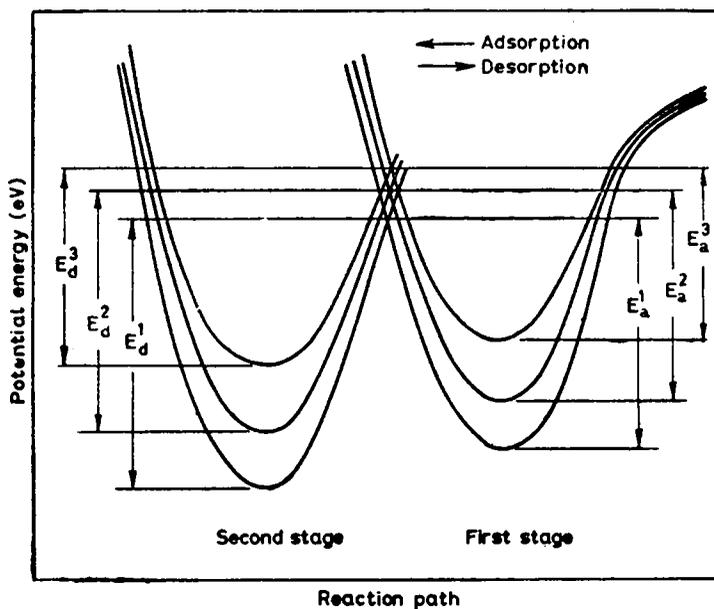


Figure 6. Potential energy curves for vapour adsorption in two stages in polyenes, explaining modified Roginsky-Zeldovich plots. E_d^1 , E_d^2 and E_d^3 are activation energies of desorption in order of increasing pressure. Similarly E_a 's are activation energies for adsorption.

barrier to the final stage of adsorption forming weakly bound complexes between the vapour molecules and the polyene crystallites. The barrier is formed by the intersection of the two potential curves. As more vapour molecules get physically adsorbed (van der Waals), a repulsive interaction between the dipoles will raise the potential energy curve for the first stage thereby lowering the barrier height giving decreasing activation energy of adsorption with increasing vapour pressure. As the surface coverage of the second stage rises, this potential curve also rises resulting in lowering of desorption activation energy with increasing pressure. The rise of the second stage curve is such that the minimum of this curve is always at lower energy than the minimum of the first stage, the energy difference between these two minima decreasing with increasing vapour pressure.

Here β^*m , the activation energy for desorption should, apart from a small entropy factor, be equal to the vapour-surface molecular complex. In table 2, we have shown the experimental value of β^* . Unfortunately neither our experiments give any numerical value of α , nor we have been able to measure m , the amount of vapour adsorbed. Any reliable estimate of the binding energy of various vapours with different polyenes has, therefore, not been possible. In the hydration of proteins, Rosenberg (1964) estimated $\alpha \approx 2.6$. For a similar value of α for these cases of vapour desorption from polyene crystallites, the value of binding energy is $\approx 10^{-2}$ eV per unit of m desorbed. This low value of the binding energy accounts for easy and efficient desorption of these vapours from the polyene crystals.

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