

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 semi-conductivity 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.

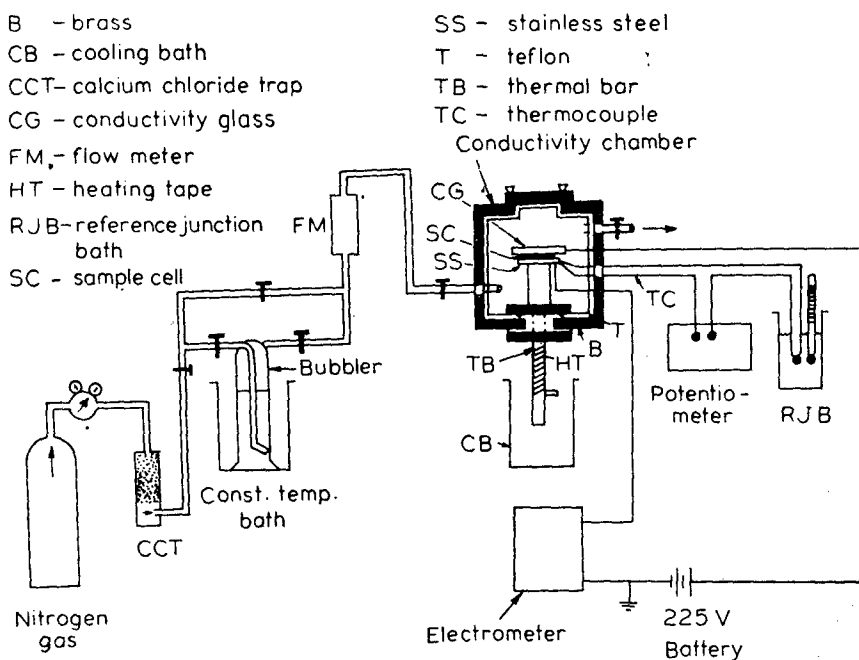


Figure 1. A schematic diagram of the apparatus used to test the effects of the adsorbed gases on the conductivity of vitamin A (alcohol and acetate).

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

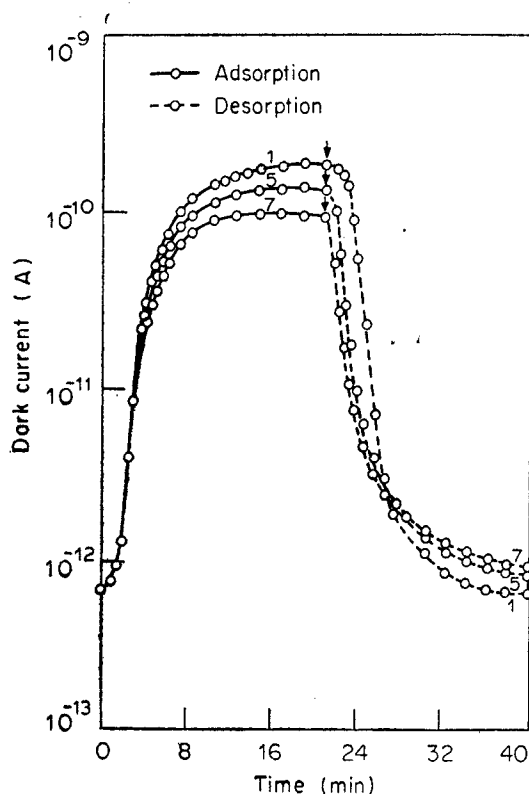


Figure 2. The change in dark current in a vitamin A alcohol powder cell kept at 25° C with repeated injection of ethyl acetate vapour (40.0 mm).

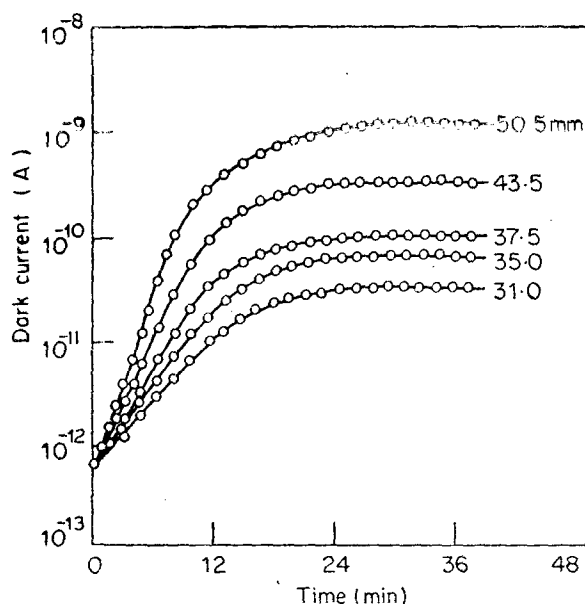


Figure 3. The change in dark current after adsorption of ethyl acetate vapour at different vapour pressure on vitamin A alcohol.

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

$$\sigma_A(m) = \sigma_V \exp(am) \quad (1)$$

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

$$m(t) = Q(t) \cdot p \quad (2a)$$

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	2.33	8.81	2.3×10^4	5.0×10^4
Benzene	2.28 (20° C)	9.24	6.7×10^3	1.7×10^4
Ethylacetate	6.00	10.11	6.5×10^3	1.3×10^4
<i>n</i> -heptane	1.93 (20° C)	10.35	4.0×10^3	3.8×10^3
Ethanol	24.30	10.50	3.0×10^2	2.0×10^3
Methanol	32.60	10.85	4.5×10	3.2×10^2

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

$$m_0 = Q_0 \cdot p \quad (2b)$$

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,

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

and at equilibrium

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

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 enhancement (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

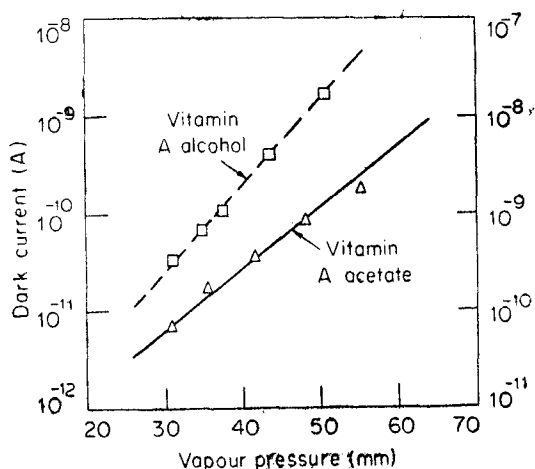


Figure 4. Change in the dark current of vitamin A (alcohol and acetate) powder cell as a function of the vapour pressure of ethyl acetate.

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

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

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

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

From (1) and (5) we get,

$$\log \sigma_A = \frac{\alpha kT}{\beta} \log(t + t_0) + \text{constant}. \quad (6)$$

Thus, a linear plot of $\log \sigma_A$ 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 α 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 $\beta' = (\beta/\alpha)$ for ethyl acetate vapour adsorption kinetics.

Vitamin A (alcohol)		Vitamin A (acetate)	
Vapour pressure (mm)	β' (eV)	Vapour pressure (mm)	β' (eV)
31.0	1.202×10^{-2}	31.0	0.819×10^{-2}
35.0	1.005×10^{-2}	35.7	0.753×10^{-2}
37.5	0.930×10^{-2}	41.7	0.660×10^{-2}
43.5	0.759×10^{-2}	48.2	0.601×10^{-2}
50.5	0.643×10^{-2}	55.2	0.518×10^{-2}

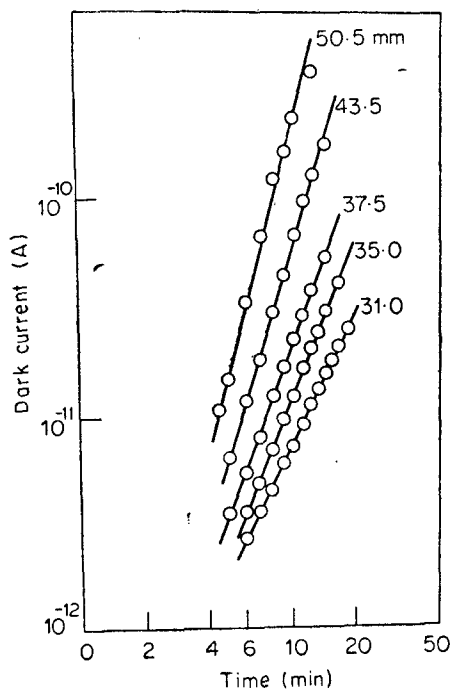


Figure 5. Adsorption kinetics data plotted according to Roginsky-Zeldovich equation for vitamin A alcohol.

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.

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