

Effect of adsorption of vapours on the electrical conductivity of a series of pyrenyl polyenes: adsorption and desorption kinetics

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Abstract. This paper deals with the change in electrical conductivity in a series of pyrenyl polyenes of the type $R-(CH=CH)_n-R$ (where R stands for the pyrenyl group and $n = 1-4$) on adsorption of various vapours. Appreciable change in the conductivity is observed. The adsorption and desorption kinetics follow a modified Roginsky-Zeldovitch equation. The results show that in all these vapour-semiconductor systems, adsorption is a two-stage process.

Keywords. Pyrenyl polyenes; polyene semiconductors; adsorption kinetics.

1. Introduction

In an earlier study on some nitroaromatic semiconductors it was shown (Ghosh *et al* 1981a, b; Jain *et al* 1981) that the compensation effect observed in the electrical conduction in some polyenes is related to the kinetics of sorption, when the activation energy is changed by the adsorption of various gases. On adsorption of certain vapours a true compensation effect is observed while for others, the compensation relation is not satisfied. When the gases form weak complexes with the semiconducting material in a two-stage adsorption process, a compensation relation is observed whereas in a three-stage adsorption process resulting in a strong complex formation, the relation is not satisfied. Further, in our study on naphthyl polyenes (Sircar *et al* 1982) of the type $R-(CH=CH)_n-R$, where R stands for the naphthyl group and $n = 1-6$, we have found that the compensation temperature T_0 is distinctly different for compounds with an odd or an even number of double bonds. Even in a two-stage adsorption process, we have observed two distinct kinetic processes associated with ambient vapour pressure dependence for compounds with an odd or an even number of double bonds (Sircar *et al* 1983). Recently our study was extended to a series of pyrenyl polyenes and we have observed different compensation behaviour for odd and even double bonded compounds (Sircar *et al* 1984). Therefore it was considered worthwhile to probe into the kinetic behaviour of adsorption in these polyenes. The results of our investigations are reported in this paper.

2. Experimental

The samples under study were highly pure α - ω -di-2 pyrenyl polyenes, which were obtained from Prof. M Nakagawa of the Osaka University, Japan. The samples were

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used without further purification. We have followed their convention (Nakasuji *et al* 1972) of denoting these samples as II_n and have employed the usual sandwich cell technique with a conducting glass and a stainless steel electrode. The reagents used *e.g.* ethyl acetate, methanol, ethanol were of spectrograde quality and were used without additional purification. To pass the vapours into the chamber, dry nitrogen gas was used as a carrier which was passed through a bubbler containing the reagent maintained at a fixed partial vapour pressure. Spacing between experimental pressures was chosen to ensure a fairly good difference in the saturation current values between any two sets of experiments. The sample cell temperature 265 K was chosen such that it was not much below the room temperature (to facilitate maintenance at a constant value) but at the same time a fairly good amount of vapour was adsorbed to enhance the semiconduction current appreciably. Repeated heating and cooling of the sample in vacuum and in the ambient nitrogen atmosphere ensures desorption of any residual adsorbed gas or water vapour. The details of experimental arrangements were described earlier (Mallik *et al* 1979).

3. Results and Discussion

We have studied the magnitude of current increase at a constant sample cell temperature as a function of partial vapour pressure of the chemical reagent. The steady state current was noted for different partial vapour pressures. In figure 1 adsorption kinetics of II₁ and II₂ are seen, showing the dark current increase at different pressures of ethyl acetate vapour. The rate of flow and the length of the flow line to the chamber control, the initial time region in the adsorption process, and the difference of adsorption kinetics in II₁ and II₂ in the short time region, is possibly of no significance. When the chamber is flushed with dry nitrogen gas, the vapours start to desorb and the desorption kinetics for ethyl acetate vapour on II₁ and II₂ is shown in figure 2. Similar observations were made for methanol and ethanol vapours also. The amount of current enhancement, however, was different for different vapour adsorbed for the same partial pressure in the chamber.

From figure 1 we have obtained an exponential dependence of conductivity on the vapour pressure of the reagent. This is similar to our previous observations on naphthyl and other polyenes (Sircar *et al* 1983; Ghosh *et al* 1980). The specific conductivity $\sigma_A(m_0)$ at equilibrium and the partial vapour pressure (p) is related by

$$\sigma_A(m_0) = \sigma_v \exp(\alpha Q_0 p) \quad (1)$$

where m_0 is the amount of vapour adsorbed at equilibrium; and α , Q_0 are constants. Thus a plot of $\log \sigma_A(m_0)$ vs the vapour pressure p is expected to be linear and this is what we have observed in the case of pyrenyl polyenes (figure 3). The slope of these curves is a measure of the amount of enhancement of dark conductivity on vapour adsorption.

In the earlier papers we have mentioned that the Roginsky-Zeldovitch equation in a modified form is given by

$$\log \sigma_A(m) = \frac{\alpha kT}{\beta} \log(t + t_0) + \text{constant},$$

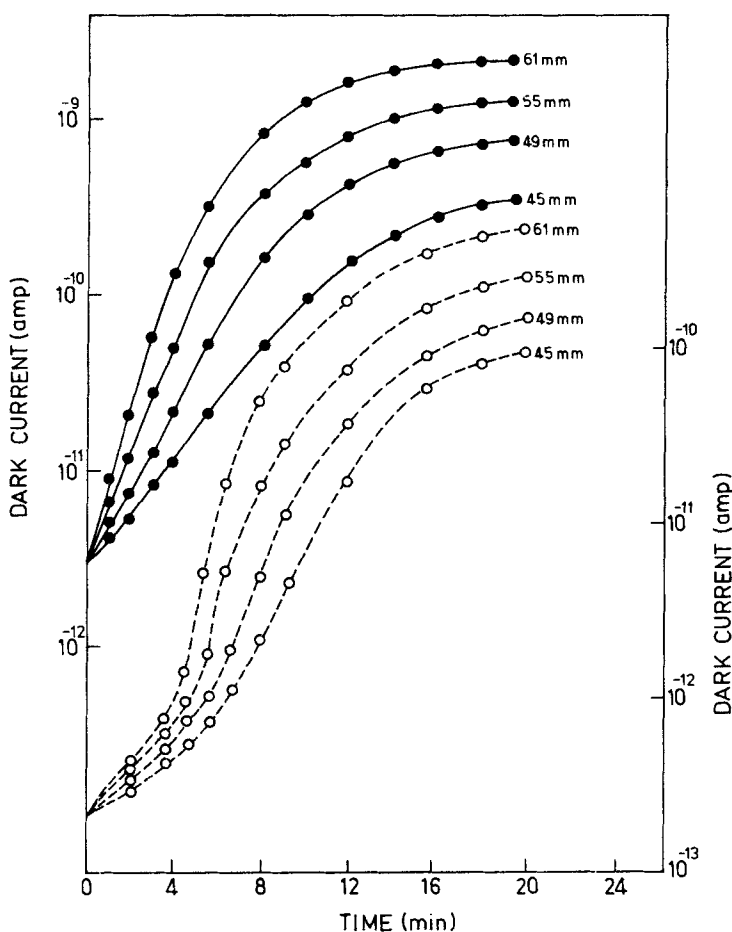


Figure 1. Change in dark current in II₁ and II₂ powder cells kept at 265 K on adsorption of ethyl acetate vapour at different pressures. Broken line and right scale for II₁ and solid line and left scale for II₂.

for adsorption and

$$\log \sigma'_A(m) = -\frac{\alpha kT}{\beta^*} \log(t + t'_0) + \text{constant},$$

for desorption, where, $\sigma_A(m)$ and $\sigma'_A(m)$ are conductivities at time $(t + t_0)$ and $(t + t'_0)$ respectively, α , β , β^* are constants at a particular vapour pressure. βm and $\beta^* m$ are activation energies for adsorption and desorption respectively. The $R-Z$ plot of compound II₁ is shown in figure 4 for adsorption and desorption respectively. The time indicated in the abscissa is measured from the initiation of adsorption or desorption. The adsorption observed in the initial time region is influenced more by the flow rate and the length of the flow line leading to the chamber and does not reflect the true adsorption process in a specific ambient atmosphere. The data points in this time slot were excluded for the $R-Z$ plot. After saturation is reached and dynamical equilibrium

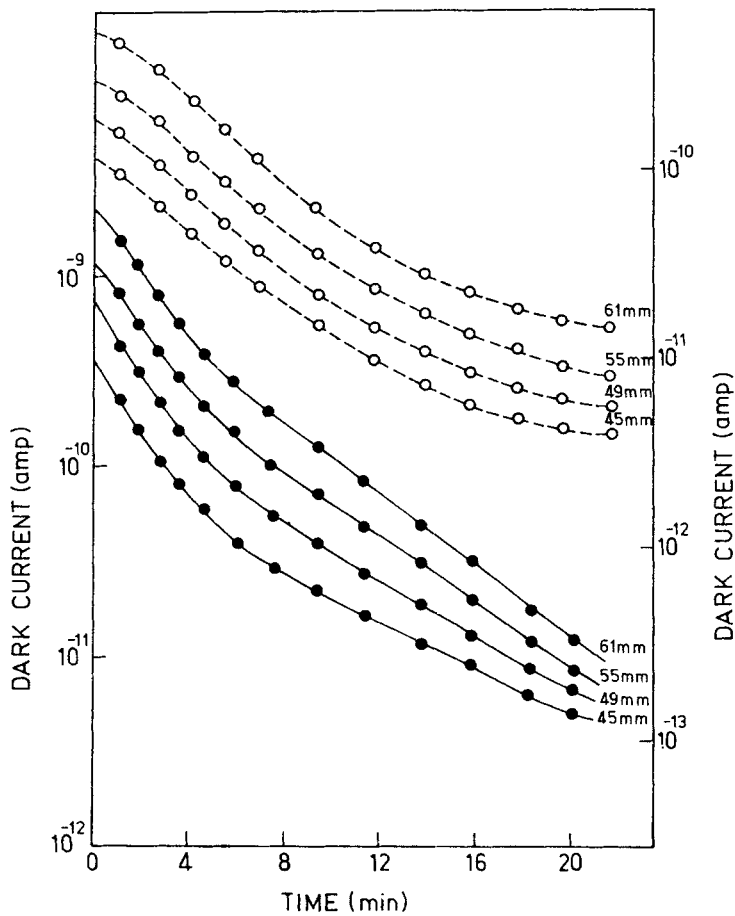


Figure 2. Change in dark current in II_1 and II_2 powder cells kept at 265 K during desorption of ethyl acetate vapour at different pressures. Broken line and right scale for II_1 and solid line and left scale for II_2 .

is established in the adsorption process, the R - Z plot in a two-stage adsorption process becomes parallel to the log time axis (Jain *et al* 1981). As our intention is to derive the activation energy values for the adsorption process, only the intermediate time region is used. Similar plots for II_2 compound for adsorption and desorption are shown in figure 5.

In the case of II_1 , different slopes observed at different vapour pressures indicate the vapour pressure dependence of β and β^* , whereas for II_2 the R - Z plots being almost parallel suggests that β and β^* are almost independent of ambient partial pressure. In II_3 also the β and β^* are almost independent of p whereas in II_4 these parameters are strongly pressure-dependent. In table 1 the values of β' and β^{*} for different pyrenyl polyenes are shown. Here

$$\beta' = \beta/\alpha; \beta^{*'} = \beta^*/\alpha.$$

A simple two-stage adsorption process (Ghosh *et al* 1980) in the first stage of which a

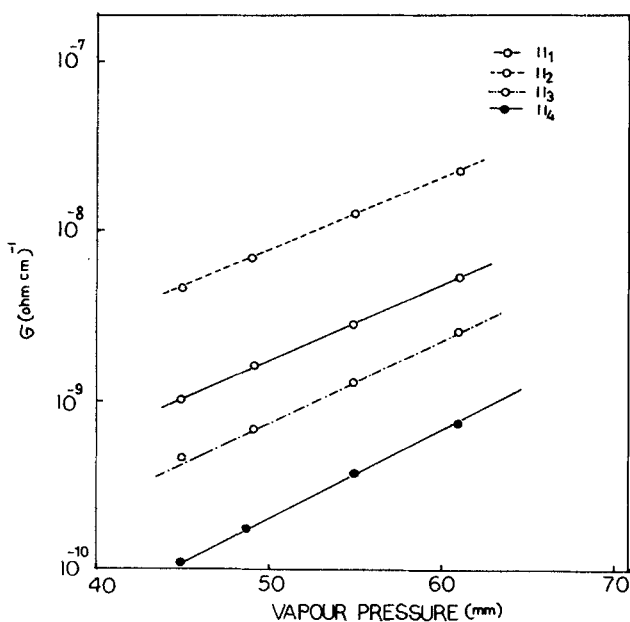


Figure 3. Change in dark conductivity as a function of vapour pressure of ethyl acetate for compounds II₁-II₄ kept at 265 K.

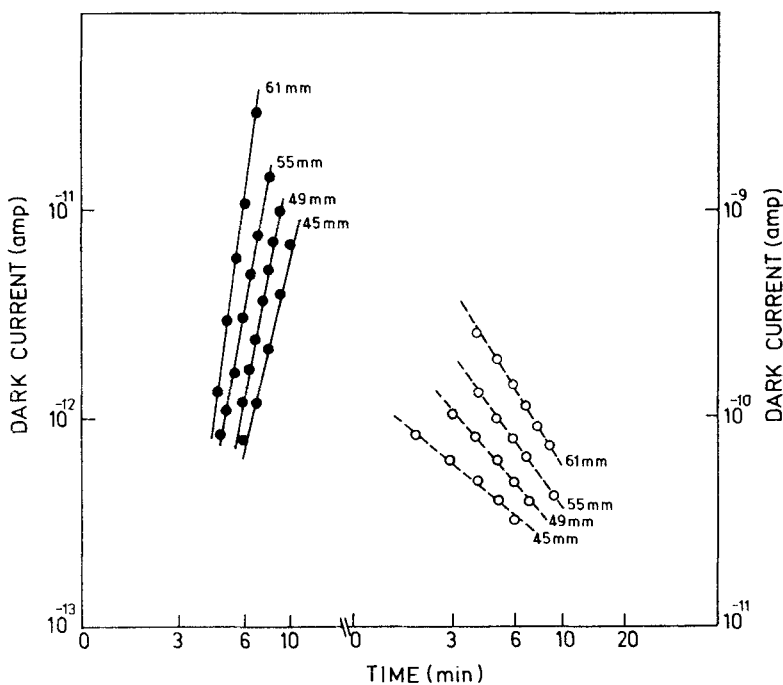


Figure 4. Adsorption and desorption kinetics data plotted according to the modified Roginsky-Zeldovich equation for II₁. Solid line and left scale for adsorption and broken line and right scale for desorption.

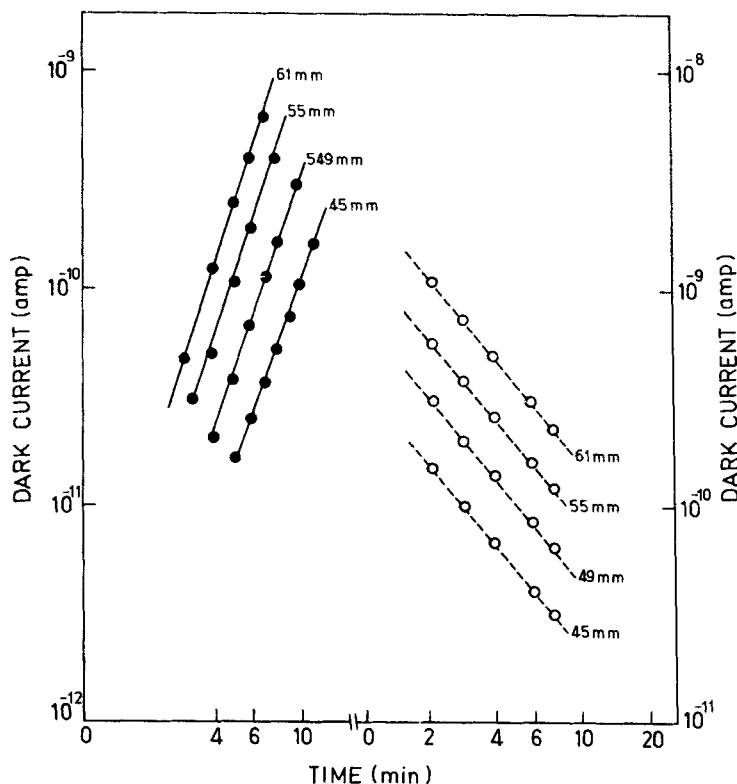


Figure 5. Adsorption and desorption kinetics data plotted according to the modified Roginsky-Zeldovich equation for I_2 . Solid line and left scale for adsorption and broken line and right scale for desorption.

Table 1. Vapour pressure dependences of β' and $\beta^{*'}$ for compounds II_1 – II_4 for ethyl acetate vapour adsorption (Sample cell temperature 265 K).

Pyrenyl polyenes	Vapour Pressure* (mm)	$\beta' \times 10^{-2}$ (eV)	$\beta^{*'} \times 10^{-2}$ (eV)
II_1	45	0.565	2.75
	49	0.455	1.88
	55	0.412	1.59
	61	0.317	1.34
II_2		0.285	1.85
II_3		1.16	4.52
II_4	45	1.93	3.23
	49	1.33	3.83
	55	1.02	4.97
	61	0.829	6.18

* In II_2 and II_3 , β' and $\beta^{*'}$ are observed to be pressure independent.

mobile van der Waals adsorption of the molecule on the crystal surface gives rise to a Lennard-Jones potential energy curve, is followed by a rate-determining transition over the potential barrier to the final stage of adsorption forming a weakly bound complex, satisfactorily accounting for our observed kinetics. The potential barrier is formed by the intersection of the potential curves. In some cases, as in II₁ and II₄, the depth of the potential well decreases with increasing pressure whereas in II₂ and II₃ it is pressure-independent.

These results suggest that the compensation effect observed in pyrenyl polyenes is not related to the dependence of the potential barrier for adsorption and desorption on the ambient partial pressure of the vapour. Finite compensation temperature T_0 in the pyrenyl polyenes, as in the naphthyl polyenes, is observed only in compounds having an even number of double bonds. Thermodynamic parameters like entropy, free energy etc are known to be different for odd and even numbers of double bonds. Indeed T_0 is thought to be related to the change in activation energy and entropy (Kaplan *et al* 1975).

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