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 $\alpha$-\omega-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\textsubscript{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 II\textsubscript{1} and II\textsubscript{2} 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 II\textsubscript{1} and II\textsubscript{2} 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 II\textsubscript{1} and II\textsubscript{2} 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 \( \sigma_{\text{A}}(m_0) \) at equilibrium and the partial vapour pressure \( p \) is related by

\[
\sigma_{\text{A}}(m_0) = \sigma_0 \exp(\alpha Q_0 p)
\]

where \( m_0 \) is the amount of vapour adsorbed at equilibrium; and \( \alpha, Q_0 \) are constants. Thus a plot of \( \log \sigma_{\text{A}}(m_0) \) 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

\[
\log \sigma_{\text{A}}(m) = \frac{\alpha kT}{\beta} \log (t + t_0) + \text{constant},
\]