

Temperature effect on the adsorption and desorption processes in retinoic acid crystals: An electrical conductivity study

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Abstract. Using electrical conductivity as a probe, the effect of crystal temperature on the process of adsorption and desorption of some chemical vapours on retinoic acid semiconductor has been investigated. It has been observed that a three-stage adsorption process in a sample at low temperature changes over to a two-stage process at higher temperature. Measures of activation energies of adsorption and desorption at different stages have been estimated from kinetic data analysis by using a modified Roginsky–Zeldovich equation.

Keywords. Adsorption and desorption processes; conductivity of retinoic acid crystal; chemical vapour adsorption; modified Roginsky–Zeldovich equation.

1. Introduction

The effects of adsorption of gases on the conductivity of long chain conjugated polyenes have been studied in the past (Mallik *et al* 1979; Ghosh *et al* 1980; Mitra *et al* 1985) and continue to receive attention (Sircar *et al* 1983; Mitra and Misra 1987). A *p*-type surface exhibits a dark d.c. conductivity that is markedly enhanced after adsorption of electron-acceptor gases and vice versa. The adsorption process found to be operative in polyene crystals is generally two-stage. In some cases, however, a three-stage adsorption process has been identified (Mitra *et al* 1985). In the past, we have studied the enhancement of dark d.c. conductivity as a function of the partial pressure of the chemical vapour in the ambient atmosphere. The adsorption process is also known to be dependent on the sample cell temperature, as the ratio of the mass of the vapour adsorbed and of the absorbent is a function of temperature.

We have now studied the nature of adsorption of various chemical vapours on retinoic acid crystals as a function of a sample cell temperature. It has been observed that a three-stage adsorption process at low sample cell temperature changes over to a two-stage process as the cell temperature is raised. In this paper we report our results. We also report measures of activation energies of adsorption and desorption at different stages as estimated by kinetic data analysis using a modified Roginsky–Zeldovich equation.

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2. Experimental

Highly purified retinoic acid, obtained as a gift from the Hoffmann-La Roche and Co. Ltd., Switzerland, was used without any further purification. We have used the standard sandwich cell technique with a conducting glass and a stainless steel electrode. Spectrograde quality (E Merck/BDH) reagent chemicals, ethyl acetate and ethanol were used. To allow various vapours inside the chamber, nitrogen gas was used as a carrier and was passed at a constant rate of flow through a bubbler containing the solvent kept at the desired temperature to maintain a particular vapour pressure. Repeated heating and cooling of the sample cell, initially in vacuum and finally in a dry nitrogen atmosphere, ensured desorption of water vapour or any other adsorbed gases. The details of the experimental procedure were the same as described earlier (Mallik *et al* 1979).

3. Results and discussion

The change in the dark current in the retinoic acid powder sample kept at fixed temperatures of 296, 300 and 304 K, upon adsorption and desorption of ethanol vapour at a particular pressure (35 mm) is shown in figure 1. As the powder sample adsorbs the vapour from the chamber atmosphere, the current increases and tends to reach a saturation value. The adsorption process in retinoic acid is slow compared to other polyenes (Mallik *et al* 1979). The maximum value of current

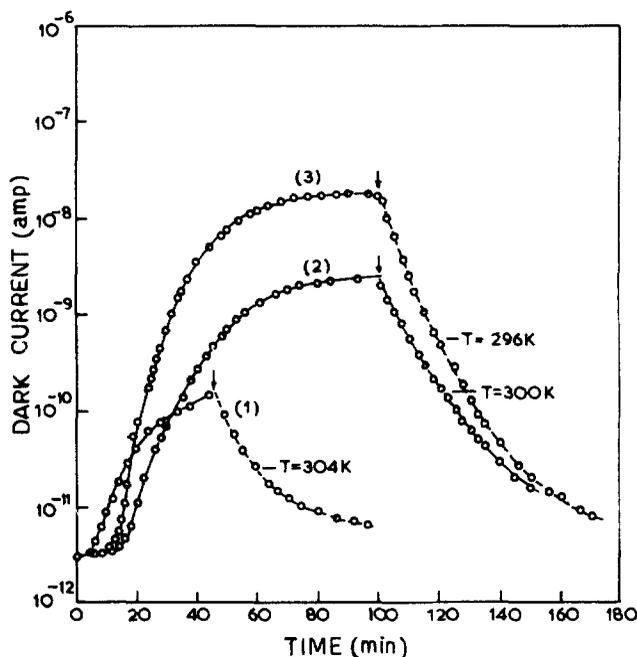


Figure 1. The change in dark current in a retinoic acid powder cell, kept at 296, 300 and 304 K, respectively, on adsorption and desorption of ethanol vapour at 35 mm vapour pressure. The arrows indicate the initiation of desorption. Solid lines are for adsorption and broken lines for desorption.

reached at equilibrium, under a particular experimental conduction, depends on the vapour pressure of the reagent chemical and the sample cell temperature. Here in figure 1, the amount of adsorption is found to increase with the decrease of sample cell temperature. When the chamber is flushed with dry nitrogen gas, the vapour is desorbed from the crystal surface and the current gradually returns to the initial value. Dry nitrogen gas flow in the ambient atmosphere is so regulated that the partial pressure of the gas mixture is kept much below the saturation limit. This ensures that no significant re-adsorption takes place. Adsorption and desorption curves were also obtained with partial vapour pressures of 26, 45 and 55 mm. Similar studies were made for ethyl acetate vapour also. In figure 2 we have shown the adsorption and desorption of ethyl acetate on retinoic acid at different vapour pressures, when the sample cell is kept at a fixed temperature of 304 K. The amount of adsorption is found to increase with the increase of the partial vapour pressure of the reagent chemical.

An exponential dependence of the conductivity on the vapour pressure of the reagent chemical is obtained, which is similar to our previous observations (Mallik *et al* 1972; Ghosh *et al* 1980; Mitra *et al* 1985). Using a modified Roginsky-Zeldovich equation for adsorption and desorption, one can obtain expressions for the specific conductivity σ_A and σ_A^* as a time function during adsorption and desorption respectively as follows (Mallik *et al* 1979; Mitra *et al* 1985)

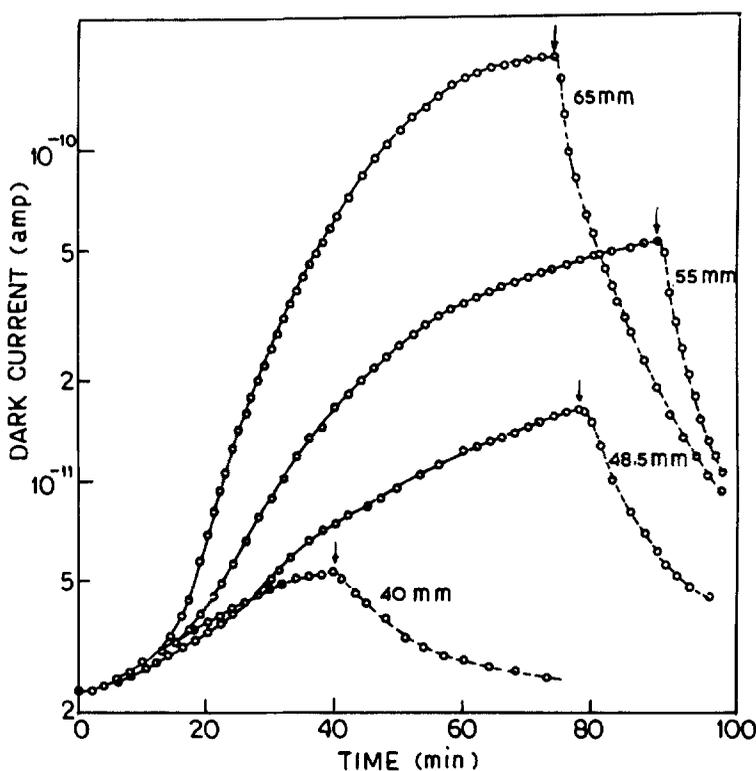


Figure 2. The change in dark current in a retinoic acid powder cell, kept at 304 K, on adsorption and desorption of ethyl acetate vapour at different vapour pressures. The arrows indicate the initiation of desorption. Solid lines are for adsorption and broken lines for desorption.

$$\log \sigma_A = (\alpha KT/\beta) \log(t + t_0) + \text{const}, \quad (1)$$

for adsorption, and

$$\log \sigma_A^* = -(\alpha KT/\beta^*) \log(t + t_0^*) + \text{const}, \quad (2)$$

for desorption, where α and β (β^*) are constants for a pair of semiconductor-vapour molecules and α is a measure of the strength of interaction between them, β/α (or β^*/α) is a measure of activation energy for adsorption (or desorption). Thus from any empirically chosen t_0 and t_0^* , linear plots of $\log \sigma_A$ vs $\log(t + t_0)$ for adsorption and $\log \sigma_A^*$ vs $\log(t + t_0^*)$ for desorption are suggested.

Such plots for adsorption and desorption of ethanol vapour on retinoic acid for a fixed partial vapour pressure (26 mm) but at different sample cell temperatures are shown in figure 3. In figure 4, we show such plots for ethyl acetate vapour adsorption and desorption for a fixed sample cell temperature but for different partial pressures of the reagent chemical. In figure 3, the saturation current decreases with the increase of sample cell temperature, when the pressure is kept constant at 26 mm. From figure 4, we find that the saturation current increases with the increase of partial pressure, at a fixed sample cell temperature. The time indicated in the abscissa is measured from the initiation of the adsorption (or desorption). Segments of straight lines are obtained. In figure 3, for cell temperatures $T = 304$ K and $T = 300$ K, only one straight line segment is obtained in the time region before saturation is reached. On reaching saturation there is no further enhancement of conductivity indicating the zero slope of the second segment, which is similar to our

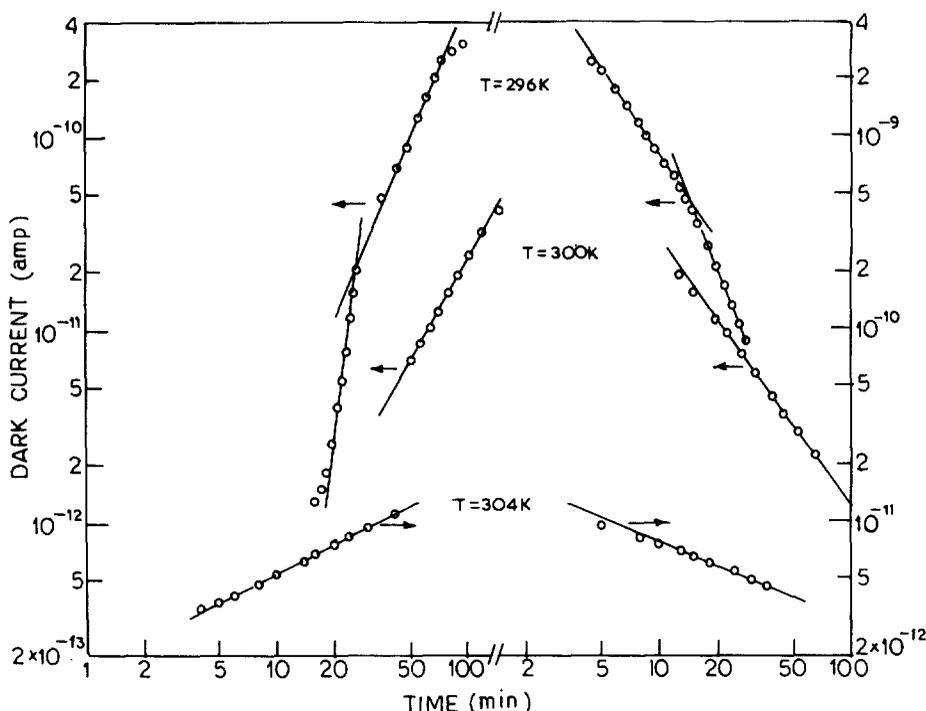


Figure 3. Adsorption and desorption kinetics data plotted according to the modified Roginsky-Zeldovich equation for retinoic acid crystals, at 296, 300 and 304 K, respectively, when ethanol vapour is adsorbed at 26 mm vapour pressure.

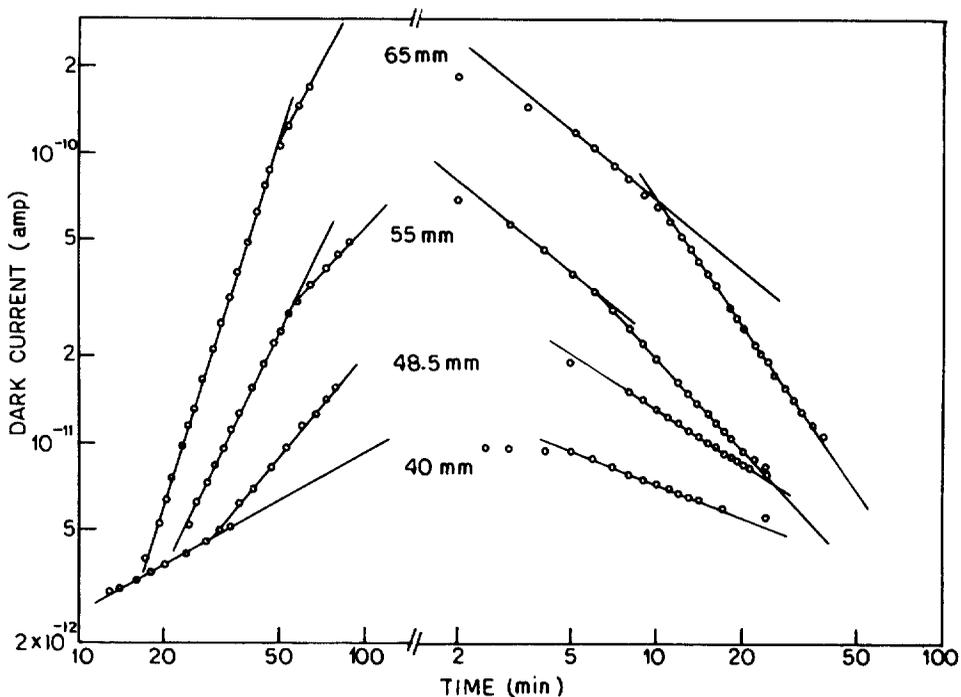


Figure 4. Adsorption and desorption kinetics data plotted according to the modified Roginsky-Zeldovich equation for retinoic acid crystals, kept at 304 K, when ethyl acetate vapour is adsorbed at different vapour pressures.

earlier observations with some other polyenes (Mallik *et al* 1979; Mitra *et al* 1985). However, when the sample cell temperature is lowered to 296 K, two straight line segments are obtained in such plots in two time regions before saturation is reached, suggesting a second activation in the adsorption process, similar to the one we observed in case of lycopene (Mitra *et al* 1985). From figure 4 we find that one line segment occurs in the case of lowest pressure and two slopes are obtained in the case of higher pressure. The modified Roginsky-Zeldovich equations involving two activation energies for adsorption and desorption in two different time domains have been discussed earlier (Mitra *et al* 1985).

Equations (1) and (2) then become

$$\log \sigma_A = (\alpha KT/\beta_1) \log(t + t_0) + (\alpha KT/\beta_2) \log(t + t_0) + \text{const}, \quad (3)$$

for adsorption, and

$$\log \sigma_A^* = -(\alpha KT/\beta_1^*) \log(t + t_0^*) - (\alpha KT/\beta_2^*) \log(t + t_0^*) + \text{const}, \quad (4)$$

for desorption.

The first and the second terms of these equations dominate the short- and long-time regions, respectively. We have estimated the values of

$$\beta_1' (= \beta_1/\alpha), \quad \beta_2' (= \beta_2/\alpha), \quad \beta_1^{*'} (= \beta_1^*/\alpha), \quad \beta_2^{*'} (= \beta_2^*/\alpha)$$

for different samples and temperatures for a fixed partial vapour pressure and at different vapour pressures for a fixed cell temperature, from the slopes of $\log \sigma_A$ vs

log t plots. These are presented in table 1. We find that the second stage of activation appears when the amount of adsorbed vapour is large. From table 1, it is seen that β'_1 , β'_2 and β'_2^* are pressure-dependent. β'_1^* , however, appears to be pressure-independent. It is indeed expected for a strongly bound complex which behaves more like a chemical species. β'_1^*m is the activation energy for desorption from the third stage and apart from a small entropy factor, it should be equal to the binding energy of the complex. This observation has relevance to the theory of olfactory transduction mechanism proposed by Rosenberg *et al* (1968) where adsorption of odorous molecules on polyene receptors in the olfactory epithelium is assumed to initiate the sensory nerve impulse. A receptor cell membrane is always at biological temperature and high concentration of odourant molecules is required to induce odour fatigue through strongly-bound complex formation.

The nature of bonding of the surface molecules of the semi-conducting crystals with the adsorbed vapour molecules is of interest as it is expected to elucidate the conductivity enhancement mechanism on vapour adsorption. In physisorption, the binding energy between the molecules is very small (a few kcal/mol) and is supposed to be due to van der Waal complex formation. Chemisorption, on the other hand, may have binding energy over a wide range and may involve various types of charge transfer complex formation, hydrogen bonding and also new chemical species formation. Besides, many other subtle interactions involving dipole-dipole, ion-dipole and dielectric factors are possible.

Charge transfer complex formation has been widely held responsible for current enhancement in semiconductors on gas adsorption (Laves and Rudyj 1963). As the vapours we have used are good electron donors and the polyenes are known to act both as electron donors and electron acceptors (Platt 1959; Pullman and Pullman 1963) formation of CT complexes between retinoic acid and the adsorbed molecules is possible. The interaction energy of the contact CT complex is small and is of the same order as in van der Waal interaction (Slifkin and Allison 1962; Matsuo and Higuchi 1968). Stable CT complexes have higher binding energy. CT interaction depends on the ionisation potential of the donor [I_D] and the electron affi-

Table 1. Sample cell temperature and vapour pressure dependence of the factors β'_1 , β'_2 and β'_1^* , β'_2^* for adsorption and desorption processes in retinoic acid crystal.

Chemical vapour used	Sample cell temperature/ partial vapour pressure	β'_1 (eV)	β'_2 (eV)	β'_1^* (eV)	β'_2^* (eV)
		($\times 10^{-3}$)			
Ethanol (at partial pressure 26mm)	304 K	51.2	—	—	59.7
	300 K	14.6	—	—	17.7
	296 K	3.3	10.3	16.4	9.7
Ethyl acetate (at partial pressure 40 mm)	304 K	43.5	—	—	65.7
	300 K	6.6	49.8	62.7	37.7
Ethyl acetate	40 mm	43.5	—	—	65.7
	48.5 mm	20.6	—	—	39.1
	55 mm	12.2	22.8	30.5	23.5
	65 mm	7.9	13.0	29.8	17.4

nity [E_A] of the acceptor. The conductivity enhancements on ethanol and ethyl acetate vapour adsorption

$$(\sigma_A/\sigma_v)_{\text{ethanol}} \approx 7 \times 10^4 \text{ and } (\sigma_A/\sigma_v)_{\text{ethyl acetate}} \approx 2 \times 10^2$$

are found to be in the same order as their ionisation potential values. [$I_{D(\text{ethanol})} \approx 10.50 \text{ eV}$ and $I_{D(\text{ethyl acetate})} \approx 10.11 \text{ eV}$]. The second and the third stage of adsorption are likely to represent weakly and strongly bond complexes respectively, though hydrogen bond formation in the final stage cannot be ruled out.

During exposure of the polycrystalline powder sample to the vapours, the vapour molecules may occupy the interspace 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 dielectric constant of the vapour used is expected. The static dielectric constant (Treiber and Koren 1951) of the ethyl acetate is 6.0 and that of ethanol is 24.3 and this indeed is in the same order as the semiconduction current enhancement. However, with our limited experimental data, definite conclusions about the type of complex formation on adsorption cannot be drawn.

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