

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

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**Abstract.** On adsorption of various vapours, the electrical conductivity of nitroaromatic semiconductors 9-nitroanthracene, 1,4-dinitronaphthalene and 1,3,5-trinitrobenzene changes appreciably. This phenomenon has been used as a probe to study the adsorption and desorption processes in these nitroaromatic polycrystals. The adsorption and desorption kinetics have been found to follow the modified Roginsky-Zeldovich relation. Two adsorption processes have been identified. One, a two-stage process, the first 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 nitroaromatic crystallites. In the second process, in addition to the two stages of the first process, a third stage with a comparatively deep potential energy surface is reached by activation over a second potential barrier and strongly bound complexes are finally formed.

**Keywords.** Nitroaromatic semiconductors ; adsorption kinetics ; desorption kinetics ; vapour adsorption effect ; electrical conductivity.

### 1. Introduction

In a series of papers, Mallik *et al* (1979a, 1980a, b) established that the adsorption of vapours of various reagent chemicals on polyene semiconductors enhances the semiconduction current with a concomitant decrease in the activation energy ( $E$ ) in some cases (Mallik *et al* 1979a) and increase in others (Mallik *et al* 1980b). In both cases, true compensation effect (Rosenberg *et al* 1968a; Johnston and Lyons 1970) as indicated by a precise point of intersection of the Arrhenius plots of the logarithm of the specific conductivity of the semiconductor against the inverse of absolute temperature has been observed. The adsorption and desorption kinetics in both the cases have been found to follow the modified Roginsky-Zeldovich relation (Mallik *et al* 1979b; Ghosh *et al* 1980a) and the kinetic data

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analysis has established a two-stage adsorption process in all these cases (Ghosh *et al* 1980a).

Recently we have observed (Ghosh *et al* 1980b) that in nitroaromatic semiconductors, when the semiconduction activation energy  $E$  is varied by adsorption of certain vapours, true compensation effect is observed as in polyenes but on adsorption of certain other vapours the compensation relation is not satisfied. It was, therefore, considered worthwhile to examine if the adsorption and desorption kinetics are different in the two cases. In this paper we examine the kinetics of adsorption and desorption of vapours of some reagent chemicals on some nitroaromatic semiconductors and estimate the activation energies of adsorption and desorption from kinetic data analysis. We show that two distinctly different kinetic processes operate in the two cases.

## 2. Experimental

Commercial 9-nitroanthracene (NA), 1,4-dinitronaphthalene (DNN) and 1,3,5-trinitrobenzene (TNB) were further purified by repeated recrystallisation from the solvents of spectrograde quality. The sandwich cell technique with a conducting glass and a stainless steel electrode was used. The reagent chemicals, ethanol, methanol, ethyl acetate, benzene, carbontetrachloride, *n*-hexane, cyclohexane, methyl cyclohexane, *n*-heptane and toluene used in the gas-adsorption study were of spectrograde quality (E. Merck, B.D.H.) and were used without further purification. To allow various vapours inside the chamber, dry nitrogen gas was passed through a bubbler containing the solvent kept at a desired temperature. Repeated heating and cooling of the sample cell initially in vacuum and finally in dry nitrogen atmosphere ensured desorption of water vapour or any other adsorbed gases. The details of the experimental arrangement and the method of measurement were the same as described earlier (Mallik *et al* 1979a, b).

## 3. Results

### 3.1. *Effect of adsorption of vapours on the semiconduction current of the nitroaromatics*

The effect 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 maintained at a constant temperature and the dry nitrogen carrier gas was passed through the reagent liquid 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 a saturation value is attained with certain vapours showing compensation effect. With certain other vapours, such a saturation value is not reached and only a trend to reach a saturation value is observed. The results of two such different measurements, one for methanol vapour adsorption in DNN and the other for ethyl acetate vapour

adsorption in TNB are shown in figures 1 and 2 respectively. When the chamber is flushed with dry nitrogen gas, the vapour is desorbed from the crystallite surfaces and the current comes back to the initial value in the case of methanol vapour adsorption in DNN. However, in ethyl acetate vapour adsorption in TNB the initial value is not attained even after 60 minutes (figures 1 and 2). Such an adsorption and desorption kinetic curves were also obtained with other vapour-semiconductor pairs. Adsorption and desorption of vapours of ethan 1, methanol ethyl acetate, benzene and carbontetrachloride on and from 9NA, vapours of ethanol, methanol and cyclohexane on and from DNN and of ethanol, methanol, *n*-hexane and cyclohexane on and from TNB show a behaviour as shown in figure 1. Adsorption and desorption curves similar to that shown in figure 2 are obtained for ethyl acetate, benzene, carbontetrachloride and *n*-hexane adsorption on DNN and for ethyl acetate, benzene, carbontetrachloride, toluene, *n*-heptane and methyl cyclohexane adsorption on TNB.

The maximal value of current reached under particular experimental condition, in cases where such saturation value is reached, 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 on the flow rate.

We have tested the sensitivity of a particular nitroaromatic semiconductor for adsorption of different vapours by measuring the saturation current after adsorption of various vapours at a fixed partial pressure with a constant flow rate and a constant sample cell temperature. The sensitivity is measured by the  $\sigma_A/\sigma_V$  values

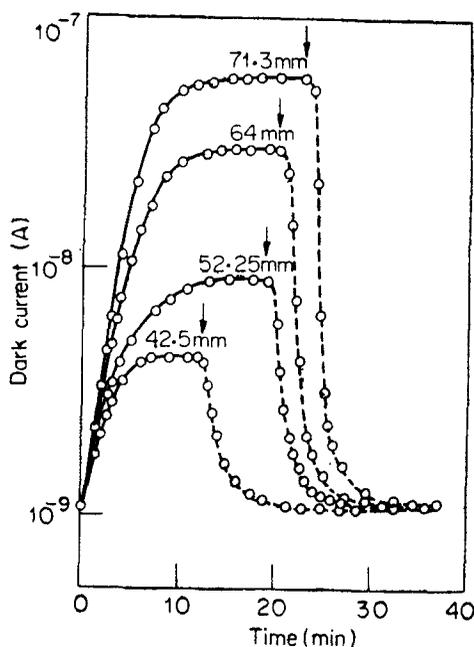


Figure 1. The change in dark current in a 1,4-dinitronaphthalene powder cell kept at 22°C on adsorption and desorption of methanol vapour at different vapour pressures. Arrow indicates the initiation of desorption (note that the saturation is attained in a short time. Solid lines are for adsorption and broken lines for desorption).

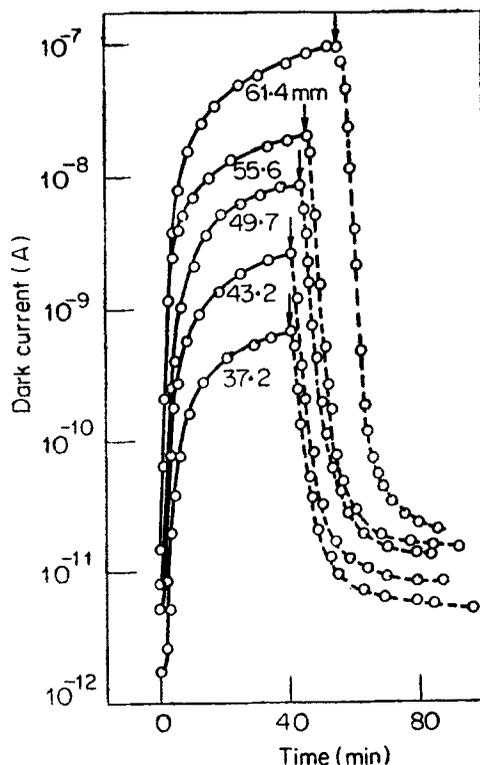


Figure 2. Same as in figure 1 for ethyl acetate vapour adsorption on 1,3,5-trinitrobenzene (the dark current shows a trend to reach a steady value even at a long time).

where  $\sigma_A$  is the specific conductivity at saturation after vapour adsorption and  $\sigma_V$  is that of before adsorption. The results are summarised in table 1. As with polyenes, the sensitivity depends on the chemical nature of the adsorbed molecules.

### 3.2. Vapour pressure dependence of conductivity

The magnitude of the current enhancement at a constant sample cell temperature (22° C) has been studied as a function of the partial pressure of the vapours in the chamber. The partial pressure of the vapour in the chamber was changed by altering the temperature of the reagent chemical through which the carrier gas was passed and fed into the conductivity chamber. The steady-state current was noted for different vapour pressures, and only where such steady state was reached could be studied. The kinetics for the dark current enhancement for different partial pressures of methanol ambient vapour for 1,4-dinitronaphthalene are shown in figure 1. The time required to reach the saturation current increases with increasing vapour pressure as at saturation more vapours get adsorbed at higher pressure (Eley and Leslie 1964). Similar results were obtained also with the other vapour-semiconductor pairs specified in the previous section.

**Table 1.** Rise in the dark current in the powder cells of some nitroaromatic semiconductors at 22°C on adsorption of various vapours at the same pressure ( $p$ ) (for semiconductor-vapour pair where quick saturation has been reached).

Vapour used	$\sigma_A/\sigma_V$		
	9-nitroanthracene $p = 50$ mm	1,4-dinitronaphthalene $p = 50$ mm	1,3,5-trinitrobenzene $p = 60$ mm
<i>n</i> -Hexane	..	..	8.5
Cyclohexane	..	3	10
Carbontetrachloride	3	..	..
Methanol	6	8	$2 \times 10$
Benzene	$3 \times 10$	..	..
Ethyl acetate	$3 \times 10$	..	..
Ethanol	$1.2 \times 10^2$	$3 \times 10^2$	$5 \times 10^5$

#### 4. Discussion and conclusions

##### 4.1. Vapour pressure dependence of conductivity

We have shown (Mallik *et al* 1979b; Ghosh *et al* 1980a) that in polyene semiconductors, the relation between the specific conductivity  $\sigma_A(m_0)$  at equilibrium and the pressure ( $p$ ) of the ambient vapour is given by

$$\sigma_A(m_0) = \sigma_V \exp(aQ_0p), \quad (1)$$

where  $m_0$  is the amount of vapour adsorbed at equilibrium,  $a$  and  $Q_0$  are constants. Figure 3 shows that the relation (1) is satisfied for nitroaromatic semiconductors also if the adsorption kinetics is of the type shown in figure 1. The slopes of these curves ( $aQ_0$ ) is a measure of the strength of interaction between the vapour molecules and the semiconductors. In table 2, we present the  $aQ_0$  values for different vapour-semiconductor pair to gauge the relative strength of interaction.

##### 4.2. Adsorption and desorption 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  $\beta$  are constants at a particular vapour pressure  $p$ ,  $k$  and  $T$  are Boltzmann constant and absolute temperatures respectively. The suitable equation for desorption kinetics is given by (Ghosh *et al* 1980a)

$$-dm/dt = A^* \exp(\beta^* m/kT), \quad (3)$$

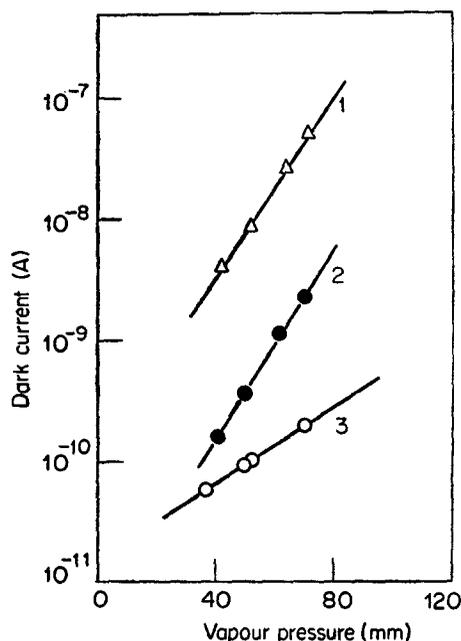


Figure 3. Change in the saturation dark current of (1) 1,4-dinitronaphthalene, (2) 1,3,5-trinitrobenzene and (3) 9-nitroanthracene powder cells at a constant cell temperature of 22° C as a function of the vapour pressure of methanol.

Table 2. Values of  $aQ_0$  for different vapour-semiconductor pair.

Semiconductor	Vapour	$aQ_0$ (mm <sup>-1</sup> )
9-nitroanthracene	Carbontetrachloride	0·022
	Methanol	0·037
	Benzene	0·041
	Ethanol	0·135
1,4-dinitronaphthalene	Methanol	0·087
	Ethanol	0·176
1,3,5-trinitrobenzene	Methanol	0·094
	Ethanol	0·247

$m$  is now the amount of vapour desorbed.  $\beta^* m$  is the activation energy for desorption. In measuring desorption the experiment is so designed that by regulating the dry nitrogen gas flow in the ambient atmosphere the saturation pressure of the gas mixture is much below the saturation limit so that there is no re-adsorption. The relations between  $\sigma_A$ ,  $a$ ,  $\beta$ ,  $\beta^*$  and  $t$  are given by

$$\log \sigma_A = \frac{akT}{\beta} \log (t + t_0) + \text{constant}, \quad (4)$$

for adsorption, and

$$\log \sigma_A = \frac{akT}{\beta^*} \log (t + t'_0) + \text{constant}, \quad (5)$$

for desorption.

Thus from any empirically chosen  $t_0$  or  $t'_0$ , linear plots of  $\log \sigma_A$  versus  $\log (t + t_0)$  for adsorption and  $\log \sigma_A$  versus  $\log (t + t'_0)$  for desorption are suggested. Indeed, Taylor and Thon (1952) suggested that with correctly chosen  $t_0$ , the plot of  $m$  as a function of  $\log (t + t_0)$  should give a straight line.

Such plots for adsorption and desorption of methanol on 1,4-dinitronaphthalene and that of ethyl acetate on 1,3,5-trinitrobenzene are shown in figures 4 and 5 respectively. The time indicated in the abscissa is the time measured from the initiation of adsorption or desorption.

As in polyene semiconductors (Mallik *et al* 1979b; Ghosh *et al* 1980a), in methanol adsorption on DNN also the slopes of the curves at different vapour pressures in the initial region of adsorption and desorption are different. This shows the pressure dependence of  $\beta$  and  $\beta^*$ . The higher the partial vapour pressure, the larger is the slope. We have estimated the values of  $\beta/a (= \beta')$  and  $\beta^*/a (= \beta^*)$  from the slopes. A similar study has been made for other vapour-semiconductor pairs also. In table 3 we show the variation of  $\beta'$  and  $\beta^*$  with vapour pressure for methanol vapour adsorption and desorption on and from DNN. In table 4, the variation of  $\beta'$  and  $\beta^*$  with different vapours at a constant pressure is shown. As expected,  $\beta^*$  is always larger than  $\beta'$  for any particular pressure of a vapour.

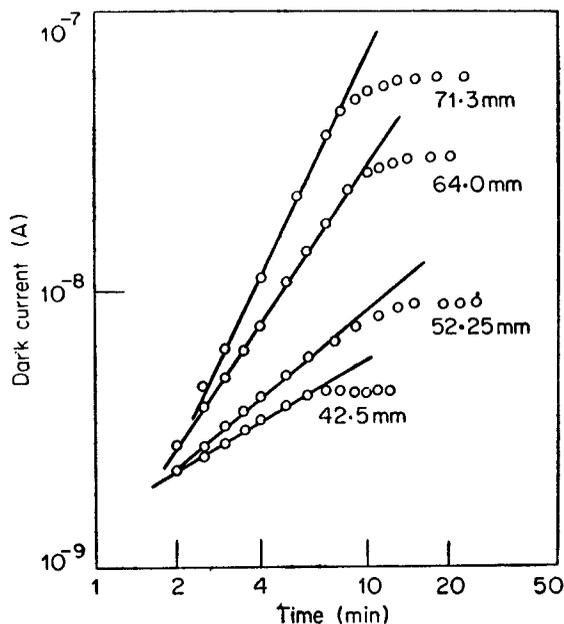


Figure 4 (a). Adsorption kinetics data of figure 1 plotted according to the Roginsky-Zeldovich equation,

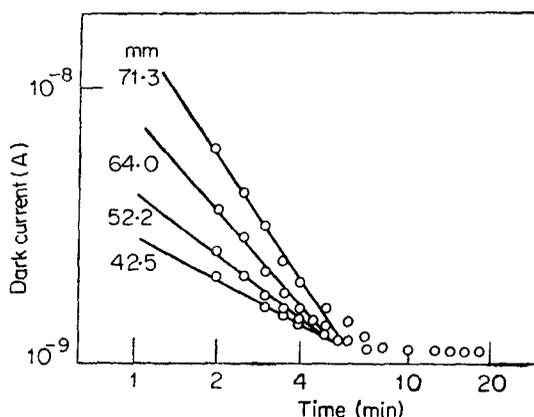


Figure 4(b). Desorption kinetics data of figure 1 plotted according to the Roginsky-Zeldovich equation.

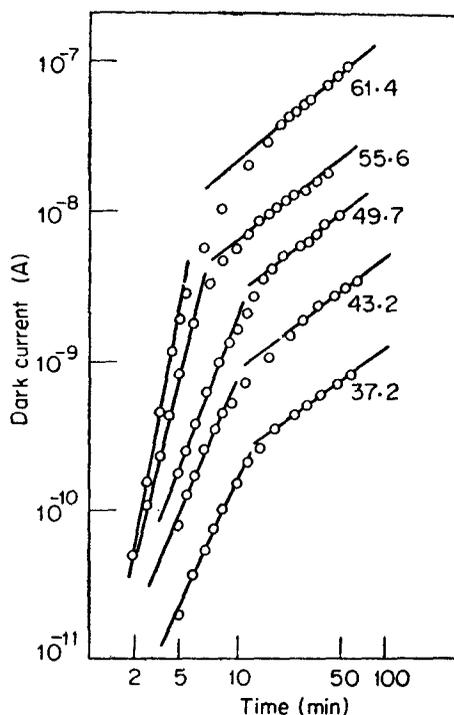


Figure 5(a). Adsorption kinetics data of figure 2 plotted according to the Roginsky-Zeldovich equation.

Figure 5 shows that in the long time region the experimental points in R-Z plots show excellent linearity with a different slope than the one in the short time region. This is different from that observed in figure 4 where the long time region saturation is reached soon after the short time region-linearity is completed. This suggests that R-Z equations

$$dm/dt = \bar{A} \exp(-\bar{\beta}m/kT), \quad (6)$$

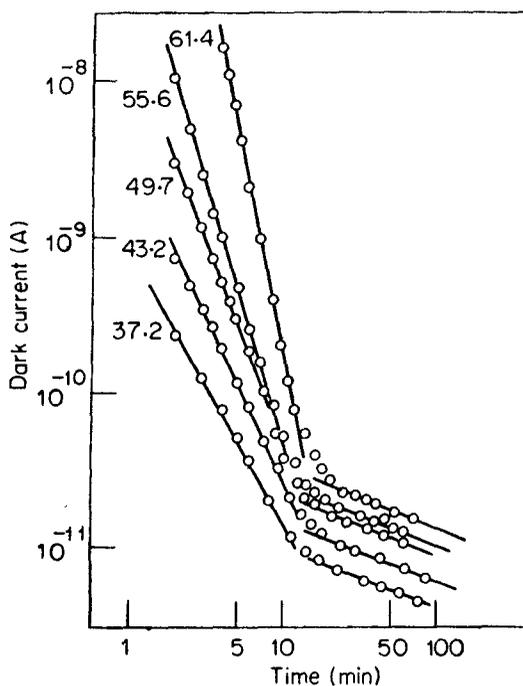


Figure 5(b). Desorption kinetics data of figure 2 plotted according to the Roginsky-Zeldovich equation.

$$\text{and} \quad -dm/dt = \bar{A}^* \exp(\bar{\beta}^* m/kT), \quad (7)$$

with a different activation energy and pre-exponential constant are also applied in the long time region. Such linearity in the R-Z plots in the long time region have been obtained for adsorption and desorption of ethyl acetate, benzene and carbontetrachloride vapour on and from TNB and DNN. We have evaluated the activation energies of adsorption ( $\beta''$ ) and desorption ( $\beta^{*''}$ ) from the slopes of such lines in the long time region. In table 5, we present the values of  $\beta'$ ,  $\beta^{*'}$ ,  $\beta''$  and  $\beta^{*''}$ . It is noted that for any particular pressure of ambient vapour  $\beta^{*'} > \beta'$  and  $\beta^{*''} > \beta''$ .

#### 4.3. Potential energy curves for vapour adsorption process

In the case of adsorption of vapour on polyenes, it has been established that the process is a simple two-stage phenomenon (Ghosh *et al* 1980a). In the first stage, a mobile van der Waals' adsorption on the crystal surface gives a Lennard-Jones potential energy curve which is followed by a rate-determining transition over a potential barrier to the final stage of adsorption forming weakly bound complexes between vapour molecules and polyene crystallites. The barrier is formed by the intersection of the two potential energy curves. Our present results with nitroaromatic semiconductors also suggest such a two-stage process for some vapour-semiconductor pair where the vapour adsorption saturation is quickly reached and the desorption is quick and complete (figure 1). R-Z plots

Table 3. Vapour pressure dependence of the factors  $\beta'$  and  $\beta^{**}$  for 1,4-dinitro-naphthalene on adsorption and desorption of methanol vapour.

Vapour pressure (mm)	$\beta'$ (eV) ( $\times 10^{-2}$ )	$\beta^{**}$ (eV) ( $\times 10^{-2}$ )
42.50	4.3	4.8
52.25	3.1	3.3
64.00	1.7	2.2
71.30	1.2	1.7

Table 4. Vapour pressure dependence of the factors  $\beta'$  and  $\beta^{**}$  for different vapour adsorption and desorption kinetics respectively at a constant pressure of 50 mm.

Semiconductor	Vapour used	$\beta'$ (eV) ( $\times 10^{-2}$ )	$\beta^{**}$ (eV) ( $\times 10^{-2}$ )
9-nitroanthracene	Carbontetrachloride	2.8	3.2
	Methanol	2.2	2.6
	Ethyl acetate	1.7	2.1
	Benzene	1.5	1.8
	Ethano	1.0	1.5
1,4-dinitronaphthalene	Cyclohexane	4.9	6.6
	Methanol	3.8	4.2
	Ethanol	1.0	2.5
1, 3, 5-trinitrobenzene	<i>n</i> -hexane	5.2	5.2
	Cyclohexane	4.9	5.0
	Methanol	4.3	4.5
	Ethanol	0.3	0.8

Table 5. Vapour pressure dependence of the factors  $\beta'$ ,  $\beta''$  and  $\beta^{**}$ ,  $\beta^{***}$  for adsorption and desorption kinetics respectively in ethyl acetate vapour adsorption.

Semiconductor	Vapour pressure (mm)	$\beta'$ (eV) ( $\times 10^{-2}$ )	$\beta''$ (eV) ( $\times 10^{-2}$ )	$\beta^{**}$ (eV) ( $\times 10^{-2}$ )	$\beta^{***}$ (eV) ( $\times 10^{-2}$ )
1,4-dinitronaphthalene	37.0	2.2	6.4	2.4	13.8
	42.1	2.0	6.1	2.0	13.5
	50.0	1.7	5.7	1.7	13.9
	60.8	1.1	5.2	1.1	13.8
1, 3, 5-trinitrobenzene	37.2	1.2	3.4	1.4	6.5
	43.2	1.1	3.3	1.2	6.5
	49.7	1.0	3.2	1.0	6.5
	55.6	0.6	3.2	0.8	6.5
	61.4	0.5	3.0	0.5	6.3

in such cases do not show any measurable slope in the long time region. These are the cases where true compensation effect is observed (Ghosh *et al* 1980b).

In other cases, as in ethyl acetate vapour adsorption on TNB or DNN, an additional stage of adsorption is suggested by the second linear R-Z plot in the long time region. A transition over this second potential barrier occurs and the vapour molecules get strongly bound to the surface molecules of the nitroaromatic crystallites. Our measured  $\beta''$  and  $\beta^{*''}$  are slightly larger than  $\beta'$  and  $\beta^{*'}$ . It is not possible to suggest if this means a higher potential energy barrier in the third-stage adsorption than the second-stage desorption as we have no information about the values of  $a$  and  $a'$  ( $a'$  being the value of  $a$  in second-stage interaction between vapour and the surface-molecules of the semiconductor). The third stage adsorption potential is probably smaller as  $a'$  is expected to have a smaller value. Even if  $a \approx a'$ , the Boltzmann factor for crossing the barrier on the left of the second-stage potential well will be approximately equal to that on the right as the difference in the barrier heights is insignificant. However, considering the fact that the strongly bound complexes are not easily dissociated as are the weakly bound complexes in the two-stage process, it seems that the potential well in the third stage is deep. A model diagram for the three-stage adsorption process is shown in figure 6.

As more vapour molecules get physically adsorbed, 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

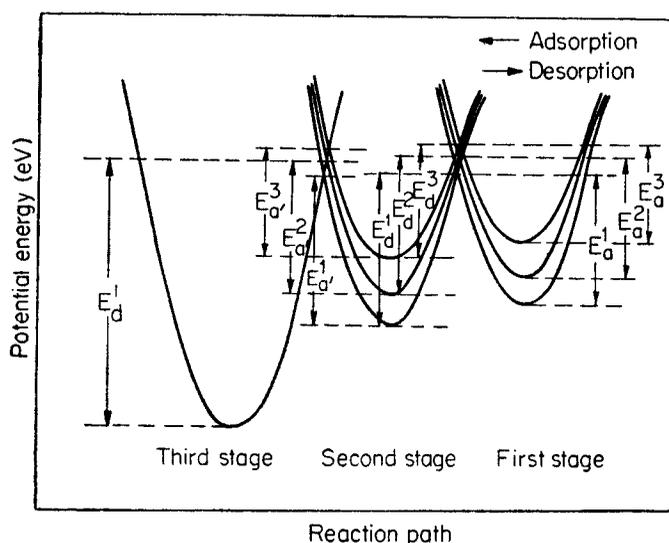


Figure 6. Potential energy curves for three-stage vapour adsorption in nitroaromatic semiconductors, explaining the two-region linearity in the modified Roginsky-Zeldovich plots.  $E_a^1$ ,  $E_a^2$ ,  $E_a^3$  and  $E_{a'}^1$ ,  $E_{a'}^2$ ,  $E_{a'}^3$  are the activation energies of adsorption in the order of increasing pressure in the second and the third stage respectively.  $E_d^1$ ,  $E_d^2$ ,  $E_d^3$  and  $E_d'$  are the activation energies of desorption from these stages.  $E_d'$  does not show any pressure dependence (see table 5).

with increasing pressure. The desorption activation energy from the third stage, as shown in table 5, seems to be independent of vapour pressure. Strongly bound complexes behave more like a chemical species (though the binding energy is very much less) and a certain amount of energy is required to break the bond.  $\beta^{**} m$ , the activation energy for desorption from the third stage should, apart from a small entropy factor, be equal to the binding energy of the vapour-surface molecular complex. We have not been able to estimate the binding energy because our experiments do not provide any numerical value of  $a$  or  $a'$ .

It is interesting to note in this context that Rosenberg *et al* (1968b), in their theory of olfactory transduction mechanism, proposed such a three-stage process of adsorption for odorant molecules in receptor polyenes in the olfactory epithelium. They could not, however, produce any experimental evidence of such a process which we have been able to do here though in a different context.

### Acknowledgements

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