

Two-stage adsorption and desorption processes in some nitroaromatic semiconductor-vapour systems : implications in compensation effect in dark conduction process

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Abstract. Adsorption and desorption of *n*-hexane, cyclohexane, CCl₄, C₆H₆, ethylacetate, methanol and ethanol vapours on the crystallite surfaces of 2-nitrofluorene and three isomeric nitrobenzoic acid semiconductors have been investigated using electrical conductivity as a probe. Kinetic analysis data show that in all these vapour-semiconductor systems, the adsorption is a two-stage process. Existence of any relationship between the adsorption process and the compensation effect in dark conduction process has been examined. The compensation effect is generally observed in cases where the change in semiconduction activation energy is caused by a two-stage adsorption process.

Keywords. Nitroaromatic semiconductor ; adsorption kinetics ; desorption kinetics ; compensation effect.

1. Introduction

In an earlier paper we identified two different processes in adsorption and desorption kinetics of some nitro-aromatic semiconductor-vapour systems (Ghosh *et al* 1981). 9-Nitroanthracene follows a two-stage adsorption process in all the vapours studied while 1,4-dinitronaphthalene and trinitrobenzene follow a three-stage process in some cases of vapour adsorption. It was further noted that there may exist a relationship between the adsorption process involved and the validity of the compensation rule when semiconduction activation energy is changed by vapour adsorption. It was, therefore, thought worthwhile to extend the investigations on adsorption and desorption kinetics in some more nitroaromatic semiconductors to see if compensation effect in dark conduction process is generally observed in cases where the adsorption is a two-stage process. In this paper, we present the results on adsorption and desorption kinetic analysis of 2-nitrofluorene (NF), *o*-nitrobenzoic acid (*o*-NBA), *m*-NBA and *p*-NBA semiconductor vapour

systems and show that indeed in these cases adsorption is a two-stage process and the compensation rule is generally valid in these cases.

2. Experimental

Commercial NF, *o*-NBA, *m*-NBA and *p*-NBA were purified by repeated recrystallisation from the solvents of spectrograde quality, the reagent chemicals used for vapour adsorption were of spectrograde quality (BDH and E. Merck). The experimental arrangement and details of the procedure are as already reported (Mallik *et al* 1979a).

3. Results

For conductivity measurement sandwich cell technique was applied as usual. The results on the rise in dark current of the nitroaromatic semiconductors at 25° C when used in powder form in sandwich cells due to adsorption of various vapours at 50 τ vapour pressure are summarised in table 1. The maximal value of the current reached at equilibrium, under particular experimental conditions, depends on the vapour pressure of the reagent chemical and the temperature of the sample cell. The time to reach this maximal equilibrium value also depends on the flow rate. The adsorption process observed is fast and when the chamber was flushed with dry nitrogen, the vapour desorbs and the original value is regained.

4. Discussion

4.1. Vapour pressure dependence on conductivity

Similar to what was reported earlier (Ghosh *et al* 1980b, 1981; Mallik *et al* 1979a), we have obtained an exponential dependence of the conductivity upon the vapour pressure of the reagent chemical in the conductivity chamber. The

Table 1. Rise in the dark current due to adsorption of various vapours at the same vapour pressure of 50 τ .

Vapour	σ_A/σ_V			
	NF	<i>o</i> -NBA	<i>m</i> -NBA	<i>p</i> -NBA
<i>n</i> -Hexane	0.25×10	0.15×10	0.2×10	0.2×10
Cyclohexane	0.3×10	0.2×10	0.25×10	0.27×10
Carbontetrachloride	0.4×10	4	3	2
Benzene	0.1×10^2	4.3×10	8	2.5
Ethyl-acetate	0.14×10^2	1×10^4	1.3×10^2	9
Methanol	0.49×10^2	2.5×10^2	2.4×10^2	9
Ethanol	1.2×10^2	1×10^4	3.7×10^2	6.8×10^2

exponential dependence suggests a linear plot of $\log I_A(m_0)$ vs the vapour pressure. $I_A(m_0)$ is the equilibrium dark current after adsorption. In figure 1, we have shown such a linear plot for the ethyl-acetate vapour adsorption on the nitroaromatic semiconductors. The slope is the measure of strength of interaction between the vapour molecules and the semiconductors. The values of the slopes obtained are $0.0598, 0.1794, 0.1472$ and $0.0943 \tau^{-1}$ for NF, ONBA, *m*-NBA and *p*-NBA respectively.

4.2. Adsorption and desorption kinetics

The Roginsky-Zeldovich (R-Z) equation in a modified form is given by

$$\log \sigma_A(m) = \frac{akT}{\beta} \log (t + t_0) + \text{const.} \tag{1}$$

for adsorption and

$$\log \sigma'_A(m) = -\frac{akT}{\beta^*} \log (t + t'_0) + \text{const.} \tag{2}$$

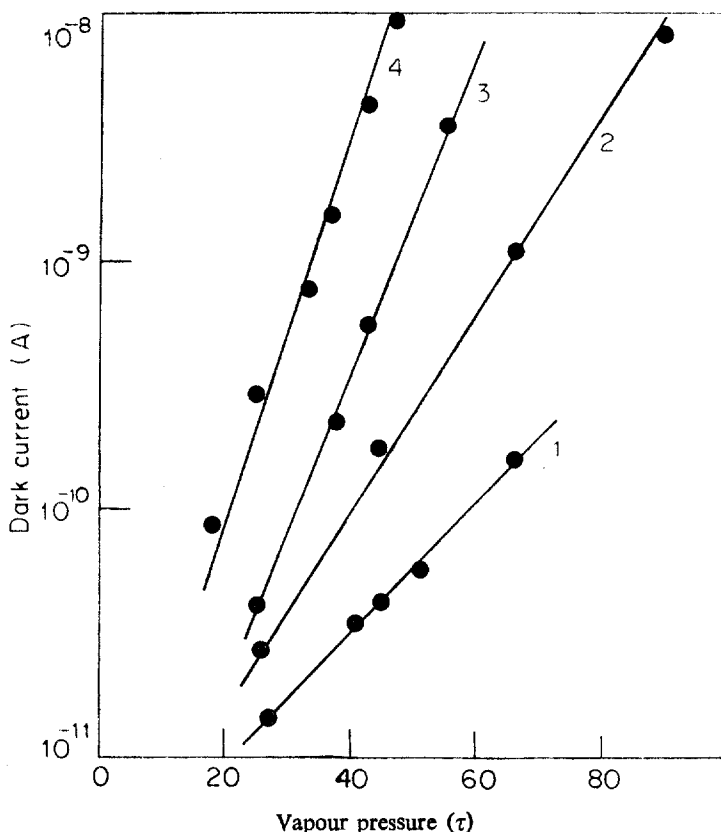


Figure 1. The change in dark current as a function of vapour pressure of ethyl-acetate. 1. 2-nitrofluorene ; 2. *p*-nitrobenzoic acid ; 3. *m*-nitrobenzoic acid and 4. *o*-nitrobenzoic acid.

for desorption where $\sigma_A(m)$ is the conductivity at time $(t + t_0)$, m is the amount adsorbed at time $(t + t_0)$, a and β are the constants at a particular vapour pressure P , k and T are Boltzmann constant and absolute temperature of the cell respectively. βm and $\beta^* m$ are the activation energies for adsorption and desorption respectively. Thus, for any empirically chosen t_0 and t'_0 , linear plots of $\log \sigma_A(m)$ versus $\log(t + t_0)$ and $\log \sigma'_A(m)$ versus $\log(t + t'_0)$ for adsorption and 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 an R-Z plot for adsorption and desorption of some vapours at a constant vapour pressure on NF is shown in figures 2 and 3 respectively. Similar behaviour is observed when the kinetic studies were made by changing the vapour pressure of the chemical vapours in the chamber.

Like other nitroaromatic semiconductors and polyenes (Ghosh *et al* 1980b, 1981) in the initial region of adsorption and desorption different slopes are obtained at different vapour pressures showing vapour pressure dependence of β and β^* . We have estimated the values of β/a ($=\beta'$) and β^*/a ($=\beta^{*}$) at different vapour pressures from the slopes which are presented in table 2. β^{*} is always larger than β' for any particular pressure of the vapour as expected.

Examination of figures 2 and 3 shows that in the long time region saturation is reached soon after the short time region linearity is completed unlike to those observed in 1,4-dinitronaphthalene and trinitrobenzene (Ghosh *et al* 1981) due to ethyl acetate vapour adsorption where the long time region indicates the involvement of a three-stage adsorption and desorption process. Thus, like polyenes and some other nitroaromatic semiconductor vapour systems, the adsorption and desorption are quick again suggesting a simple two-stage process. In the first

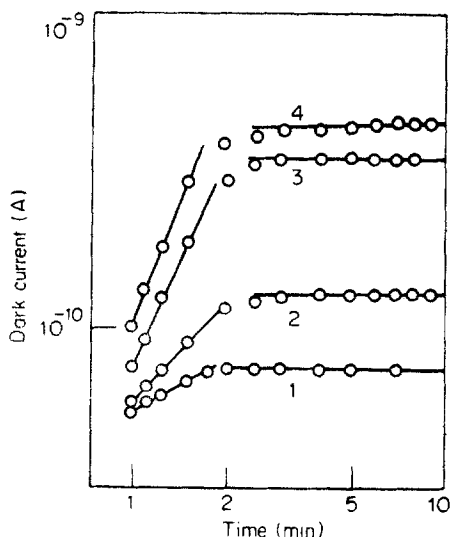


Figure 2. R-Z plot of the kinetic data for adsorption of various vapours on 2-nitrofluorene cell. 1. *n*-hexane; 2. carbontetrachloride; 3. benzene and 4. ethyl acetate.

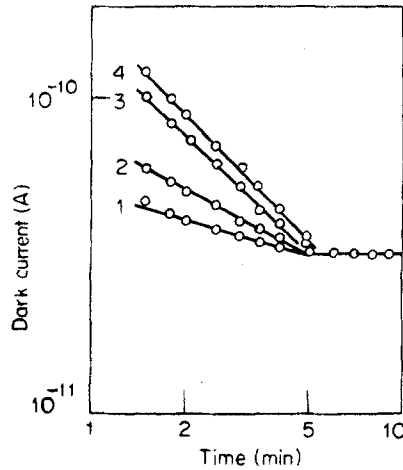


Figure 3. R-Z plot of the kinetic data for desorption of various vapours on 2-nitrofluorene cell. 1. *n*-hexane; 2. carbontetrachloride; 3. benzene and 4. ethyl acetate.

Table 2. Vapour pressure dependence of the factors β' and β^{*} for adsorption and desorption kinetics respectively in case of ethyl-acetate vapour adsorption (sample cell was kept at 25°C).

NF			<i>o</i> -NBA			<i>m</i> -NBA			<i>p</i> -NBA		
VP (τ)	$\beta' \times 10^2$	$\beta^{*} \times 10^3$	VP (τ)	$\beta' \times 10^2$	$\beta^{*} \times 10^2$	VP (τ)	$\beta' \times 10^2$	$\beta^{*} \times 10^2$	VP (τ)	$\beta' \times 10^2$	$\beta^{*} \times 10^3$
27	9.19	11.82	18.2	1.26	2.47	15.7	2.22	2.32	25.5	1.51	2.59
41	5.26	7.72	25.3	0.93	2.25	25.3	1.18	1.78	44.5	0.86	2.04
45	4.36	5.81	33.2	0.79	1.65	37.8	0.67	1.46	66	0.59	1.52
51	2.43	2.74	47	0.56	1.55	55.5	0.26	1.30	90	0.38	1.24
66	1.76	2.08									

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. The two-stage process seems to be the characteristic feature of quick adsorption and efficient desorption phenomenon.

4.3. Implications in compensation effect in dark conduction process

It is interesting to note in this context that Mallik *et al* (1979b, 1980) and Ghosh *et al* (1980a) have recently observed that in the case of polyenes and nitroaromatic semiconductors the compensation effect in dark conduction process is valid if the

vapour-semiconductor systems follow a two-stage adsorption process (Ghosh *et al* 1980a, b, 1981). This suggests that the compensation effect in the present work should be valid in these cases. A compensation effect is always characterised by a point of intersection of the linear plots of $\log \sigma(T)$ versus $1/T$. This point is known as the compensation temperature. Such a point of intersection is shown in figure 4 for 2-nitrofluorene cell. Here the measurements were made with adsorption of various chemical vapours at the same vapour pressure. Thus, we conclude that the compensation effect in dark conduction process is generally observed if the semiconduction activation energy is changed by chemical vapour or gas adsorption and if the adsorption is a two-stage process resulting in a very weakly bound complex formation between the vapour and the semiconductor molecules.

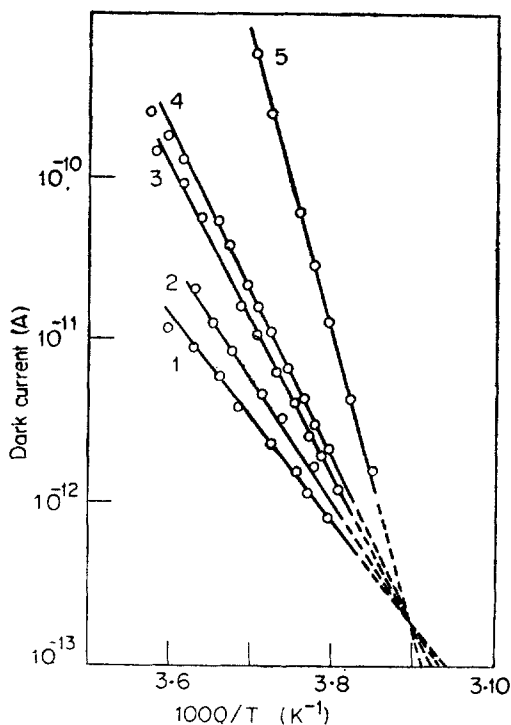


Figure 4. Semiconductivity data for 2-nitrofluorene with the adsorption of various vapours at the same vapour pressure of 50τ (Solid lines represent the temperature region of measurements and broken lines are extrapolations). 1. *n*-hexane ($E = 2.54$ eV) 2. carbontetrachloride ($E = 3.26$ eV); 3. benzene ($E = 3.72$ eV); 4. ethylacetate ($E = 4.0$ eV); 5. ethanol ($E = 7.2$ eV).

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References

- Ghosh A, Jain K M, Mallik B and Misra T N 1980a *Jpn. J. Appl. Phys* (in press)
Ghosh A, Mallik B and Misra T N 1980b *Proc. Indian Acad. Sci. (Chem. Sci.)* **89** 209
Ghosh A, Jain K M and Misra T N 1981 *Proc. Indian Acad. Sci. (Chem. Sci.)* (In Press)
Mallik B, Ghosh A and Misra T N 1979a *Proc. Indian Acad. Sci. (Chem. Sci.)* **88** 25
Mallik B, Ghosh A and Misra T N 1979b *Bull. Chem. Soc. Jpn.* **52** 2091
Mallik B, Ghosh A and Misra T N 1980 *Phys. Status Solidi* (in press)
Taylor H A and Thon N 1952 *J. Am. Chem. Soc.* **74** 4169