

Semiconductive properties of organic compounds : gas adsorption effect on 9-nitroanthracene

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The conductivity of powdered 9-nitroanthracene in a sandwich cell has been studied. Conductivity of this organic compound follows the operational semiconductivity relation

$$\sigma(T) = \sigma_0 \exp(-E/2kT)$$

The intrinsic value of the activation energy (E) is found to be 2 eV both in vacuum and in dry nitrogen atmosphere. The specific conductivity σ (27°C) and the pre-exponential factor (σ_0) are $0.9031 \times 10^{-15} \Omega^{-1} \text{cm}^{-1}$ and $75.11 \Omega^{-1} \text{cm}^{-1}$ respectively. Effect of the adsorption of various vapours e.g., carbon tetrachloride, benzene, ethyl acetate, methanol, ethanol and iso-propanol has been studied at a constant vapour pressure. The change in conduction current shows a distinct inverse relationship with the ionization energies of the adsorbed gases. This suggests that charge-transfer interaction may be responsible for such change. The rise in conductivity is exponential with increasing vapour pressure. The adsorption kinetics observed is fast and efficiently reversible which follows the modified Roginsky-Zeldovich equation

$$\frac{dm}{dt} = A \exp(-\beta m/kT)$$

where A is a constant and βm is the activation energy associated with the rate of adsorption (dm/dt). The factor β has been found to have inverse dependence upon vapour pressure.

1. INTRODUCTION

Semiconductive properties of organic crystals on adsorption of gases on the crystallite surfaces in a sandwich cell depend on the nature and strength of interaction between the adsorbed gas molecules and the semiconductor. This results in change in semiconduction current and the activation energy of the semiconductor. Both organic and inorganic semiconductors are very much sensitive to the ambient atmosphere (Gutmann & Lyons 1967). It has been speculated by Rosenberg *et al* that a weak charge-transfer complex formation between vapour molecule and the semiconductor is responsible for the enhancement in the conductivity and lowering in the activation energy in case of polycenes and other compounds (Misra *et al* 1968, Rosenberg *et al* 1968). Attempts have also been made

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to explain such change of conduction current on gas adsorption in terms of physical mixing of original unperturbed semiconductor and the perturbed (due to gas adsorption) compound at the surface, resulting in so called compensation effect (Ulbert 1970). A three constant conductivity equation involving change in the pre-exponential factor (σ_0) has also been proposed (Rosenberg *et al* 1968)

We have undertaken a programme on the systematic investigations of the conductive properties of various organic compounds in a sandwich cell on gas adsorption at different vapour pressures using nitrogen as carrier gas. In this paper we present our results on the conductive properties of 9-nitroanthracene, adsorption and desorption kinetics and vapour pressure dependence of the semiconduction current in various ambient atmospheres.

2 EXPERIMENTAL PROCEDURE

Commercial 9-nitroanthracene was further purified by repeated recrystallization using purified benzene. Needle-shaped yellow coloured crystals having melting point at 146°C were obtained. Solvents of high purity were used to study gas adsorption phenomenon. The compound in the form of fine powder was pressed in a sandwich cell between a conducting glass and a stainless steel electrode. Separation between the electrodes was maintained by 3 ml thick teflon spacers. A d.c. voltage of 22.5 volts was applied across the cell which was placed on a thermal bar platform in a suitably designed conductivity chamber made of brass and fashioned with teflon. The temperature of the sandwich cell could be controlled from outside. Gas inlet and outlet were also provided for gas adsorption study. Temperature measurements were made using a copper-constantan thermocouple, attached at the top of the metal electrode and a millivolt potentiometer. All the conductivity measurements were made in dry nitrogen atmosphere/vacuum with an electrometer amplifier EA 814 of Electronics Corporation of India Limited. To pass various vapours inside the chamber, nitrogen was used as a carrier gas which was passed through the bubbler kept at constant temperature. Repeated heating and cooling of the sample in nitrogen atmosphere ensured desorption of adsorbed water, oxygen or any other gas molecules prior to the experimental run. Temperature of the sample was maintained constant at 27°C during adsorption studies at different vapour pressures.

3. RESULTS

3.1 Conductivity of 9-nitroanthracene powder

The conductivity of powdered 9-nitroanthracene studied in a sandwich cell in the temperature range of 30°C to 103°C in dry nitrogen atmosphere follows the operational conductivity relation for semiconductors.

$$\sigma = \sigma_0 \exp(-E/2kT) \quad \dots (1)$$

as shown in Fig. 1. In high temperature region, a higher value of activation energy (about 2 eV) is observed than that of low temperature region which is about 1.4 eV. Thus, the high temperature region might be attributed to the

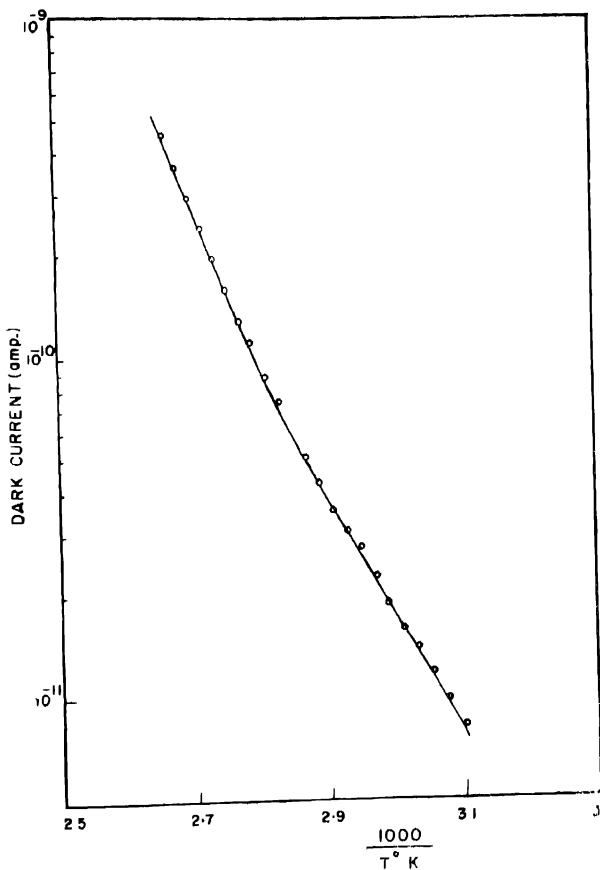


Fig. 1. Conductivity in a 9-nitroanthracene powder cell.

intrinsic region for this semiconductor. The specific conductivity (σ) at 27°C and the pre-exponential factor (σ_0) were found to be of the order of $0.9031 \times 10^{-15} \Omega^{-1}\text{cm}^{-1}$ and $75.11 \Omega^{-1}\text{cm}^{-1}$ respectively.

3.2 Gas Adsorption Effect

The adsorption of various vapours, e.g., carbon-tetrachloride, benzene, ethyl acetate, methanol, ethanol and iso-propanol have been observed to have a pronounced effect on the enhancement in the conductivity as shown in table 1. The adsorption process is fast and efficiently reversible. The initial value of dark current is reached quickly simply by flushing the chamber with dry nitrogen. This is shown in Fig. 2.

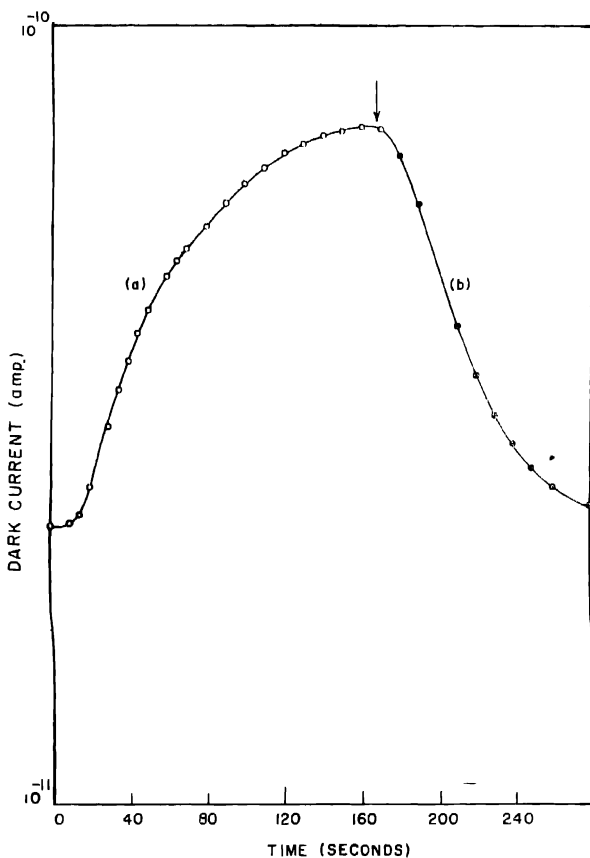


Fig. 2. The change in dark current in a 9-nitroanthracene powder cell with (a) adsorption and (b) desorption of carbon-tetrachloride vapour at 32.4 mm vapour pressure (sample kept at 27°)

3.3 Vapour Pressure Dependence

Measurements were made on the conductivity rise at constant temperature as a function of partial vapour pressure of carbon-tetrachloride inside the chamber. The total gas mixture inside the chamber was at atmospheric pressure and the partial vapour pressure was the vapour pressure of the chemical used. At constant flow and constant vapour pressure the conductivity after adsorption $\sigma_A(m)$ follows the relation (Misra *et al* 1968)

$$\sigma_A(m) = \sigma_V \exp(\alpha m) \quad \dots (2)$$

where α is a constant and m is the amount of the vapour adsorbed. m depends on the partial vapour pressure of the chemical and in the initial period, also on the time of exposure. After sometime, however, an equilibrium is established

$$m(t) = Q(b) p \dots \dots (3)$$

$Q(t)$ is a function of time. At equilibrium

$$m_0 = Q_0 p \quad \dots (3)$$

where Q_0 is another constant. So, at equilibrium

$$\sigma_A(m_0) = \sigma_V \exp(\alpha Q_0 p) \quad \dots (4)$$

A plot of $\log \sigma_A(m_0)$ versus vapour pressure (p) is expected to be linear. Our experimental result in Fig. 3 shows a good agreement with this.

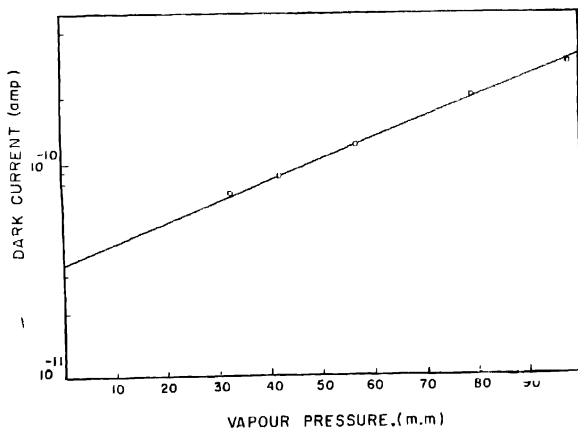


Fig. 3 Change in the dark current of 9-nitroanthracene powder cell as a function vapour pressure of carbon-tetrachloride.

fraction of the surface is covered by gas molecules equation (3) is expanded from Langmuir's adsorption isotherm.

4. DISCUSSION

4.1 Change in Semiconduction current

When the powdered semiconductor is exposed to some vapour, then the molecules at the surface will be influenced much causing change in the conductivity. If the resulting conductivity change is due to physical mixing of the original semiconductor and the perturbed semiconductor due to gas adsorption then, a relationship between the conductivity enhancement and the dielectric constant of the chemical used is expected. But our experimental results for conductivity rise at the same vapour pressure as shown in table I do not suggest this. The static dielectric constants are in the order carbon-tetrachloride < benzene < ethyl acetate < iso-propanol < ethanol < methanol which is not in agreement with the semiconduction current enhancement. 9-nitroanthracene is an electron acceptor because of the presence of nitro-group chromophore. The adsorbed molecule having electron donating nature may form a weak (D^+A^-) charge-transfer complex causing change in the conductivity. Carbon-tetrachloride and benzene both have approximately the same value of static dielectric constant, but the conductivity enhancement in benzene is about ten times than that of carbon-tetrachloride, possibly due to the more electron donating nature of benzene than carbon-tetrachloride. Indeed the enhancement of conductivity shows a distinct inverse relationship with the ionisation energies of the adsorbed gases.

Table I Rise in the dark current in a 9-nitroanthracene powder cell due to adsorption of various vapours at the same vapour pressure of 50 mm.

Vapour	Measured factor for current rise [$\sigma(\text{steady state})/\sigma(\text{initial})$]
Carbon-tetrachloride	3
Methanol	6
Ethyl Acetate	3×10^{-2}
Benzene	3×10
Ethanol	1.2×10^2
Iso-Propanol	9.2×10^2

4.2 *Kinetics*

The change in dark current in a 9-nitroanthracene powder cell with adsorption and desorption of carbon-tetrachloride vapour at 32.4 mm vapour pressure is shown in Fig 2. Adsorption kinetics follows Roginsky-Zeldovich equation in a modified form (Misra *et al* 1968, Eley *et al* 1964). It was assumed that there is an activation energy associated with the adsorption rate, which increases

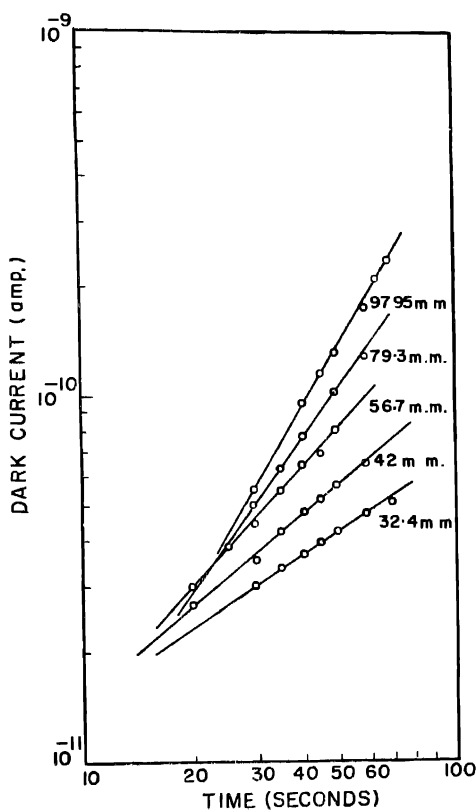


Fig. 1. Adsorption kinetics data plotted according to Roginsky-Zeldovich equation

linearly with the amount of adsorbed gas. Thus, the rate of adsorption (dm/dt) will be

$$dm = A \exp(-\beta m/kT) \quad (5)$$

where β is a constant.

Integrating (5), we get

$$m(t) = \frac{kT}{\beta} \log(t + t_0) + \text{constant} \quad (6)$$

combining (3a) and (6),

$$p = \frac{kT}{\beta Q(t)} \log(t + t_0) + \text{constant} \quad (7)$$

Now, expression (2) can be re-written as

$$\log \sigma_A = \alpha Q(t) p + \text{constant} \quad (8)$$

Substitution for p from (7) in (8) results in

$$\log \sigma_A = \frac{\alpha kT}{\beta} \log(t + t_0) + \text{constant} \quad (9)$$

A linear plot of $\log \sigma_A$ versus $\log(t + t_0)$ is suggested and our experimental results in Fig. 4 are in good agreement. Different slopes observed at different vapour pressures for the same value of α shows the vapour pressure dependence of β . (Table 2)

Table 2 Vapour pressure dependence of the factor β' for carbon-tetrachloride vapour adsorption kinetics

Vapour Pressure (mm)	(β/α) (ev.)
32.4	4.074×10^{-2}
42.0	3.218×10^{-2}
56.7	2.458×10^{-2}
79.3	1.907×10^{-2}
97.95	1.577×10^{-2}

Our experimental results indicate that the activation energy associated with the rate of adsorption is not linearly increasing with the amount of the adsorbed vapour.

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