

**APPENDIX**

### List of Publications

- 1)\* K. N. Jain, B. Mallik, K. G. Mandal and T. N. Misra  
"Electronic spectra of polyenes : evidence of a low-lying forbidden transition in some linear conjugated polyenes"  
Indian J. Pure and Appl. Phys., **13**, 699 ( 1975 )
- 2) K. N. Jain, B. Mallik and T. N. Misra  
"Electronic spectra of 9-nitroanthracene : solvent effect on  $^1A \leftarrow ^1L_a$  and  $^1A \leftarrow ^1L_b$  transitions!"  
Indian J. Pure and Appl. Phys., **14**, 59, ( 1976 )
- 3)\* K. N. Jain, B. Mallik and T. N. Misra  
"Evidence of a low-lying forbidden transition in methyl bixin"  
Indian J. Pure and Appl. Phys., **15**, 239 ( 1977 )
- 4) K. N. Jain, B. Mallik and T. N. Misra  
"Electronic spectra of 2-nitrofluorene : solvent effect on  $^1A \leftarrow ^1L_a$  transition"  
Indian J. Pure and Appl. Phys., **15**, 267 ( 1977 )
- 5)\* K. N. Jain, B. Mallik and T. N. Misra  
"Charge-transfer spectrum of all trans -  $\beta$  carotene"  
Indian J. Biochem. Biophys., **15**, 233, ( 1978 )
- 6)\* K. N. Jain, B. Mallik and T. N. Misra,  
"Charge transfer complexes of some linear conjugated Polyenes"  
Biochem. J., **180**, 547 ( 1980 )
- 7) K. N. Jain and T. N. Misra  
"On the luminescence of 1,4-dinitronaphthalene" ( communicated to Chem. Phys. Lett. )
- 8) K. N. Jain and T. N. Misra  
"Low-lying energy states in 1,4-dinitronaphthalene" ( communicated to Chem. Phys. )
- 9) K. N. Jain, A. Ghosh, B. Mallik and T. N. Misra  
"Semiconductive properties of organic compounds : gas-adsorption effect on 9-nitroanthracene"  
Indian J. Phys., **52A**, 543 ( 1978 )
- 10) K. N. Jain, A. Ghosh and T. N. Misra  
"Gas-adsorption effect on the semiconductive properties of nitrobenzoic acids"  
Ind. J. Appl. Phys., **19**, 1347 ( 1980 )

- 11) K. M. Jain, A. Ghosh, B. Dalik and T. N. Misra  
"Compensation effect in the electrical conduction process  
in some nitroaromatic semiconductors"  
Jpn. J. Appl. Phys. ( in press, 1981 )
- 12) K. M. Jain, A. Ghosh and T. N. Misra  
"Effect of adsorption of vapours on the electrical  
conductivity of some nitroaromatic semiconductors : adsorption  
and desorption kinetics"  
Proc. Indian Acad. Sci. ( in press, 1981 )
- 13) K. M. Jain, A. Ghosh and T. N. Misra  
"Two stage adsorption and desorption processes in some  
nitroaromatic semiconductor - vapour systems : implication  
in compensation effect in dark conduction process"  
Proc. Indian Acad. Sci. ( in press, 1981 )
- 14) K. M. Jain, A. Ghosh and T. N. Misra  
"On the validity of the compensation effect in some  
nitroaromatic semiconductors" ( communicated to Chem. Phys. Lett.)
- 15) K. M. Jain and T. N. Misra  
"Lowest triplet state in 1,4-Dinitronaphthalene  
Spectrosc. Lett. vol. 14(3) , 00 , 1981

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## Electronic Spectra of 9-Nitroanthracene : Solvent Effect on ${}^1A \rightarrow {}^1L_a$ and ${}^1A \rightarrow {}^1L_b$ Transitions

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Two band systems have been observed in the electronic absorption spectra of 9-nitroanthracene in the near ultraviolet region having origins at 26100 and 23800  $\text{cm}^{-1}$ . These have been assigned as  ${}^1A \rightarrow {}^1L_a$  and  ${}^1A \rightarrow {}^1L_b$  transitions respectively. The emission spectrum of this nitro aromatic compound has also been reported. A good overlapping between the emission spectrum and the  ${}^1A \rightarrow {}^1L_b$  absorption band has been observed. It has been suggested that the low energy excited singlet state is a  $\pi\pi^*$  and not a  $n\pi^*$  state as in some nitro aromatic compounds.  ${}^1A \rightarrow {}^1L_b$  band which is hidden under the intense  ${}^1A \rightarrow {}^1L_a$  band in anthracene, thus, appears in this molecule due to the substitutional perturbation of nitro group. The solvent effect on the  ${}^1A \rightarrow {}^1L_a$  transition energy has been explained in terms of predominant dispersive interaction and weak dipolar interaction in non-polar solvents and in terms of orientation-induction effect and local interaction in polar solvents. The observed change in oscillator strength of  ${}^1A \rightarrow {}^1L_a$  has been explained in terms of intermolecular forces between the solute and the solvent molecules, the translational fluctuations between the induced moments and local interactions. 'Intermolecular force factors' for various solvents have been estimated.

### 1. Introduction

In catacondensed hydrocarbons, as one moves from benzene to higher polyacenes, both  ${}^1L_a$  and  ${}^1L_b$  energy levels of benzene move to lower energy. The lowering in energy of  ${}^1L_a$  is steeper than that of  ${}^1L_b$  and in anthracene the longest wavelength band is due to  ${}^1A \rightarrow {}^1L_a$  transition and  ${}^1A \rightarrow {}^1L_b$  band appears to be hidden under the stronger  ${}^1A \rightarrow {}^1L_a$  transition<sup>1</sup> at 3700 Å.

The nitro group is an important chromophore. In the ground state, each of the two lower bonding and non-bonding orbitals of nitro group is occupied by two electrons and the anti-bonding orbital is vacant. Substitution of nitro group in the anthracene ring is expected to show a strong effect on the  $\pi$ -electronic states of anthracene molecule. It was, therefore, thought worthwhile to study the electronic spectra of 9-nitroanthracene. The effect of various polar and non-polar solvents on the electronic absorption spectra of this molecule has also been investigated.

### 2. Experimental Procedure

The sample of 9-nitroanthracene, a gift from Prof. R. S. Becker, was further purified by repeated recrystallization using purified benzene. Needle-shaped yellow coloured crystals having melting point at 146°C were obtained. Solvents of spectrograde quality were used.

The absorption spectra in various solvents were recorded at room temperature (25°C) on a Perkin-

Elmer 202 recording spectrophotometer and also on a Spectromom. 202 spectrophotometer of Hungarian Optical Co. The emission spectrum was recorded on Aminco Bowman spectrofluorometer.

### 3. Results and Discussion

#### 3.1 Spectra

The absorption spectra of 9-nitroanthracene in various non-polar and polar solvents with the same concentration at room temperature are reproduced in Figs. 1 and 2 respectively. The results of the analysis of the bands are summarized in Tables 1, 2 and 3. In all the solvents, a well defined intense band system at about 26100  $\text{cm}^{-1}$  is observed with vibrational structure. In non-polar solvents, however, few more weak bands appear towards the lower energy side of this band system. In polar solvents, these weak bands lose their structure and a general broad weak absorption band is observed in this spectral region.

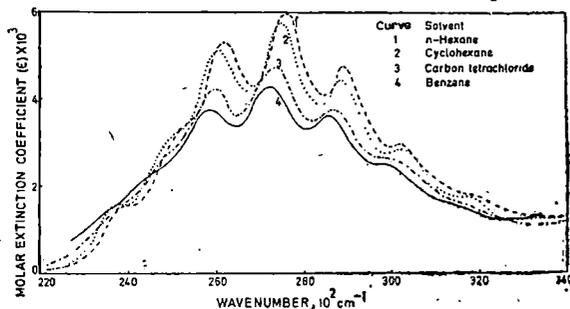


Fig. 1—Electronic spectra of 9-nitroanthracene in various non-polar solvents

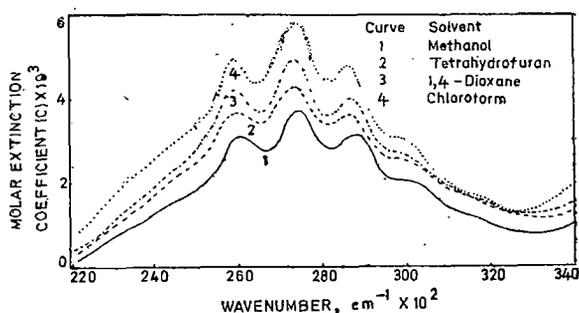


Fig. 2—Electronic spectra of 9-nitroanthracene in various polar solvents

A close examination of the absorption spectra of 9-nitroanthracene in various solvents reveals that the strong band system at about  $26100\text{ cm}^{-1}$  resembles the lowest energy absorption band of anthracene (Fig. 3). The bands on the lower energy side are structurally different from the bands in the intense system and possibly belong to different electronic transitions. This deduction has been further substantiated by the vibrational analysis of the spectra in various solvents.

It has been pointed out by Coggeshall and Pozefsky<sup>2</sup> that in benzene and naphthalene spectra the vibrational spacing involving transitions to a  ${}^1L_a$  state is of the order of  $1400\text{ cm}^{-1}$  and in transitions to a  ${}^1L_b$  state it is of the order of  $1000\text{ cm}^{-1}$ . The  $1400\text{ cm}^{-1}$  vibration is associated with the C—H in-plane bending whereas the  $1000\text{ cm}^{-1}$  vibration is the breathing vibration of the ring.

The analysis of the spectra of 9-nitroanthracene shows that the separation between the bands in the intense system is about  $1400\text{ cm}^{-1}$  which possibly is C—H in-plane bending vibration. This vibration forms a progression in the absorption spectra of anthracene solution at room temperature (Fig. 3). But the separation between the bands *b* and *c* is about  $900\text{ cm}^{-1}$ . This suggests that *b* and *c* belong to two different electronic transitions. The separation between the bands *a* and *b* of the lower energy band system is much less than  $1400\text{ cm}^{-1}$  and is about  $1050\text{ cm}^{-1}$ . It seems that possibly the breathing vibration of the ring forms the progression in the weak low energy band system. We assign this band system to  ${}^1A \rightarrow {}^1L_b$  transition, which has been shifted to red more than the intense  ${}^1A \rightarrow {}^1L_a$  transition and the two band systems have been resolved in this 9-nitroanthracene molecule.

The emission spectrum of 9-nitroanthracene has been investigated. In cyclohexane, emission has been observed. The emission spectrum is reproduced in Fig. 3. A good overlapping between the observed emission and weak low energy absorption spectrum is observed. This observation is interesting in view

of the fact that the luminescence of nitroaromatics is not yet clearly understood. Many nitroaromatic compounds exhibit either fluorescence or phosphorescence and few exhibit both types of emission. The lowest excited singlet and triplet states of nitroaromatic compounds are usually nearly degenerate and both  $\pi\pi^*$  and  $n\pi^*$  states are present in each molecule. A good overlapping between the lowest energy weak absorption and the emission shows that both initiates from the same states which has a  $\pi\pi^*$  character. It has been suggested by Plotnikov<sup>3</sup> that as the size of the aromatic system increases,  $\pi\pi^*$  state moves to a level lower energy than the  $n\pi^*$  state energy level. Intramolecular charge transfer character of the low energy state is also expected to increase with the size of the polynuclear nitroaromatics. This should increase the  ${}^1\pi\pi^* \rightarrow {}^1\pi\pi^0$  transition probability.

Thus, we conclude that the lowest excited singlet state in 9-nitroanthracene molecule is a  $\pi\pi^*$  state and that the system having origin at about  $23800\text{ cm}^{-1}$  belongs to  ${}^1A \rightarrow {}^1L_b$  and the other having origin at about  $26100\text{ cm}^{-1}$  belongs to  ${}^1A \rightarrow {}^1L_a$  transition.

### 3.2. Solvent Effect

**Solvation energy**—The solvent effects on the electronic absorption spectra of 9-nitroanthracene have been studied. The non-polar solvents *n*-hexane, cyclohexane, carbon tetrachloride and benzene and polar solvents methanol (MeOH), tetrahydrofuran (THF), 1, 4-dioxane and chloroform have been used.

In polar solvents, though  ${}^1A \rightarrow {}^1L_a$  transition shows a vibrational structure, in  ${}^1A \rightarrow {}^1L_b$  the vibrational structure is not generally observed. In non-polar solvents the vibrational structure of both  ${}^1A \rightarrow {}^1L_a$  and  ${}^1A \rightarrow {}^1L_b$  transitions are observed. However, the vibrational structure observed in saturated hydrocarbons is appreciably blurred in the solvents like carbon tetrachloride and benzene, possibly due to stronger interaction between the solute and solvent molecules.

The solvent effect on the absorption spectra of a solute is known to be due to dispersive interaction, dipolar interaction and in case of polar solvents also due to the orientation-induction effects of the solvent dipole on the solute molecule.<sup>4,5</sup> In addition, local interaction like bond formation, etc. may also affect the transition energy. Quantitative estimation of the absorption energy could be made for  ${}^1A \rightarrow {}^1L_a$  transition only. For both non-polar and polar solvents, plots of transition energy against the factor  $(n^2 - 1)/(n^2 + 2)$  give good straight lines, where *n* is the refractive index of the solvent used. The linear plot for the polar solvent is, however, on the lower

Table 1—Absorption Bands of 9-Nitroanthracene in Various Non-polar Solvents at Room Temperature

<i>n</i> -Hexane			Cyclohexane			Carbon tetrachloride			Benzene		
Wave-number cm <sup>-1</sup>	Intensity	Tentative assignment	Wave- number cm <sup>-1</sup>	Intensity	Tentative assignment	Wave- number cm <sup>-1</sup>	Intensity	Tentative assignment	Wave- number cm <sup>-1</sup>	Intensity	Tentative assignment
24150	w	0 <sub>1</sub>	24000	w	0 <sub>1</sub>	23900	vw	0 <sub>1</sub>	23700	vw	0 <sub>1</sub>
25200	vw	0 <sub>1</sub> +1050	25000	vw	0 <sub>1</sub> +1050	24950	vvw	0 <sub>1</sub> +1050	24750	vvw	0 <sub>1</sub> +1050
26250	s	0 <sub>2</sub>	26075	s	0 <sub>2</sub>	25975	s	0 <sub>2</sub>	25850	s	0 <sub>2</sub>
27625	vs	0 <sub>2</sub> +1400±25	27475	vs	0 <sub>2</sub> +1400	27375	vs	0 <sub>2</sub> +1400	27250	vs	0 <sub>2</sub> +1400
29000	s	0 <sub>2</sub> +2×1400 ±25	28900	s	0 <sub>2</sub> +2×1400 ±25	28750	s	0 <sub>2</sub> +2×1400 ±25	28650	s	0 <sub>2</sub> +2×1400
30350	w	0 <sub>2</sub> +3×1400 ±25	30275	w	0 <sub>2</sub> +3×1400 ±25	30100	vw	0 <sub>2</sub> +3×1400 ±50	30000	vw	0 <sub>2</sub> +3×1400 ±50

w, weak; v, very; and s, strong

Table 2—Absorption Bands of 9-Nitroanthracene in Various Polar Solvents at Room Temperature

Methanol			Tetrahydrofuran			1, 4-Dioxane			Chloroform		
Wave- number cm <sup>-1</sup>	Intensity	Tentative assignment	Wave- number cm <sup>-1</sup>	Intensity	Tentative assignment	Wave- number cm <sup>-1</sup>	Intensity	Tentative assignment	Wave- number cm <sup>-1</sup>	Intensity	Tentative assignment
Broad and weak absorption in the range 25500 cm <sup>-1</sup> to 22000 cm <sup>-1</sup>			Broad and weak absorption in the range 25300 cm <sup>-1</sup> to 22000 cm <sup>-1</sup>			Broad and weak absorption in the range 25500 cm <sup>-1</sup> to 22500 cm <sup>-1</sup>			Broad and weak absorption in the range 25000 cm <sup>-1</sup> to 22000 cm <sup>-1</sup>		
26100	s	0 <sub>2</sub>	25950	s	0 <sub>2</sub>	25900	s	0 <sub>2</sub>	25875	s	0 <sub>2</sub>
27550	vs	0 <sub>2</sub> +1400	27350	vs	0 <sub>2</sub> +1400	27300	vs	0 <sub>2</sub> +1400	27275 <sup>a</sup>	vs	0 <sub>2</sub> +1400
28925	s	0 <sub>2</sub> +2×1400 ±25	28725	s	0 <sub>2</sub> +2×1400 ±25	28700	s	0 <sub>2</sub> +2×1400	28675	s	0 <sub>2</sub> +2×1400

v, very; and s, strong.

Table 3—Experimental Oscillator Strength Values and the *X*-Factors

Solvent	Oscillator strength	(1+ <i>X</i> ) <i>f</i> <sub>i</sub>	Solvent	Oscillator strength	(1 × <i>X</i> ) <i>f</i> <sub>i</sub>
Non-polar			Polar		
<i>n</i> -Hexane	0.1281	0.1044	Methyl alcohol	0.0801	0.0674
Cyclohexane	0.1221	0.0961	Tetrahydrofuran	0.1078	0.0866
Carbon tetrachloride	0.1130	0.0869	1, 4 Dioxane	0.1141	0.0902
Benzene	0.1070	0.0799	Chloroform	0.1341	0.1042

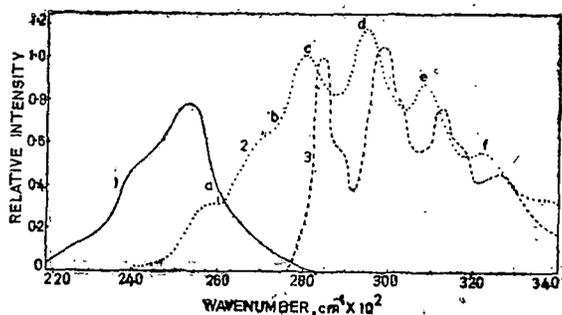


Fig. 3—Emission and absorption spectra in cyclohexane [1, Emission spectrum of 9-nitroanthracene; 2, absorption spectrum of 9-nitroanthracene; and 3, absorption spectrum of anthracene]

energy range and has a different slope than that for non-polar solvents (Fig. 4). A close examination of the expression for solvent shift in the absorption spectra of a solute as discussed by Basu<sup>5</sup> leads to some interesting conclusions. The linear plot in non-polar solvents indicates that the dispersive interaction predominates over the dipolar interaction. For the  ${}^1A \rightarrow {}^1L_a$  transition of medium intensity, this possibly further suggests that the change in the dipole moment on excitation is small in 9-nitroanthracene molecule. The linear plot in polar solvents is not easy to rationalize. It possibly indicates that the difference in dipole moment in the excited and in the ground state is small and also the sum total of orientation induction effect and local interaction is not much dependent on the solvent refractive index. Small refractive index dependence is, however, present giving a different slope of the linear plot. Indeed, 9-nitroanthracene is expected to have strong local interaction with some polar solvents used. It is known<sup>6,7</sup> that 1, 4 dioxane forms a weak N.....O bond in the same way as alcohol forms hydrogen bond. The hydrogen bond is much more stronger than N.....O bond. Tetrahydrofuran is more polar than dioxane and is similar in structure and may form a stronger N.....O bond than dioxane.

**Oscillator strength**—Theoretical studies on the solvent effect on the  $f$ -value of an electronic transition in the solute molecule have been mostly concerned with the local field effect, e. g. Lorentz-Lorenz field by Chako<sup>8</sup> or Böttcher-Onsager field by Schuyer and Bakhsier *et al.*<sup>9</sup> The results are always analyzed in terms of local field contributions and distortions of electronic charge distribution by the surroundings. Chako's correction factor for the spectral intensity change is not sufficient to explain the observed results. Recently, considering long range dispersive forces to be operative, Abdunur<sup>10</sup> has shown that for the conversion of the oscillator strength value in

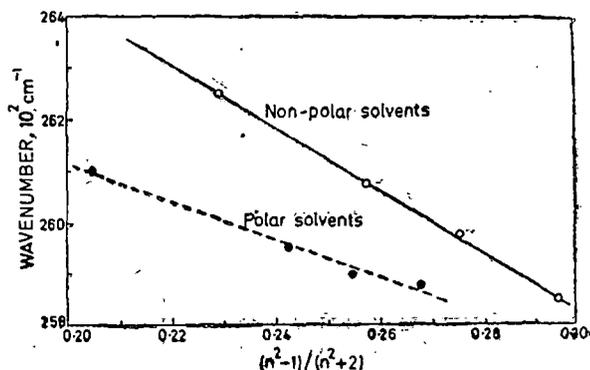


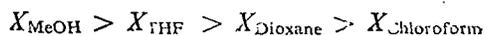
Fig. 4—The plot of transition energy of  ${}^1A \rightarrow {}^1L_a$  band of 9-nitroanthracene against  $(n^2-1)/(n^2+2)$  where  $n$  is the refractive index of the solvent

solution from the corresponding isolated molecular value, Chako's correction factor ( $n$  being the refractive index of the solvent) is of minor importance compared to an additional 'IMF' factor originating from the intermolecular forces between the solute and the solvent molecules and from the translational fluctuations between the induced moments.

Our results for the  $f$ -values in various solvents cannot be explained by Chako's correction factor alone. Expanding the 'IMF' factor to include local interactions between the solute and the solvent molecules as well, the experimental oscillator strength in solution  $f_i$  can be expressed by the empirical relation

$$\frac{1}{\gamma} (1 + X) f_i = f_0$$

where  $1/\gamma$  is the Chako's factor,  $f_i$  is the free molecular oscillator strength and  $X$  is the expanded IMF factor. We have estimated the values of  $(1 + X) f_i$  from the experimentally observed oscillator strengths in solution which are presented in Table 3. With the increase of  $n$ , while in polar solvents the  $f$ -value increases;  $f$ -value decreases in non-polar solvents. In case of non-polar solvents, the dispersive interaction plays a very important role. In going from *n*-hexane to benzene the solute-solvent interaction increases. The  $X$  factor increases with the increase of refractive index. Thus, the observed decrease in  $f$ -value followed by increase in  $X$  factor indicates a negative value for this interaction factor in non-polar solvents. In polar solvents the contribution to the  $X$  factor is not only due to dispersive interaction or dipole interactions but also due to local interactions. As has been pointed out before, local bond formation with 9-nitroanthracene and solvent molecule is possible. Thus, the  $X$  factor in polar solvents will be in the order :



The experimentally observed  $f$ -values increase in the same order indicating a positive value for the  $X$ -factor in polar solvents.

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## 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  $\sigma$  (27°C) and the pre-exponential factor ( $\sigma_0$ ) 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., carbontetrachloride, 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  $\beta m$  is the activation energy associated with the rate of adsorption ( $dm/dt$ ). The factor  $\beta$  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 polyenes 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 ( $\sigma_0$ ) 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 mil 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

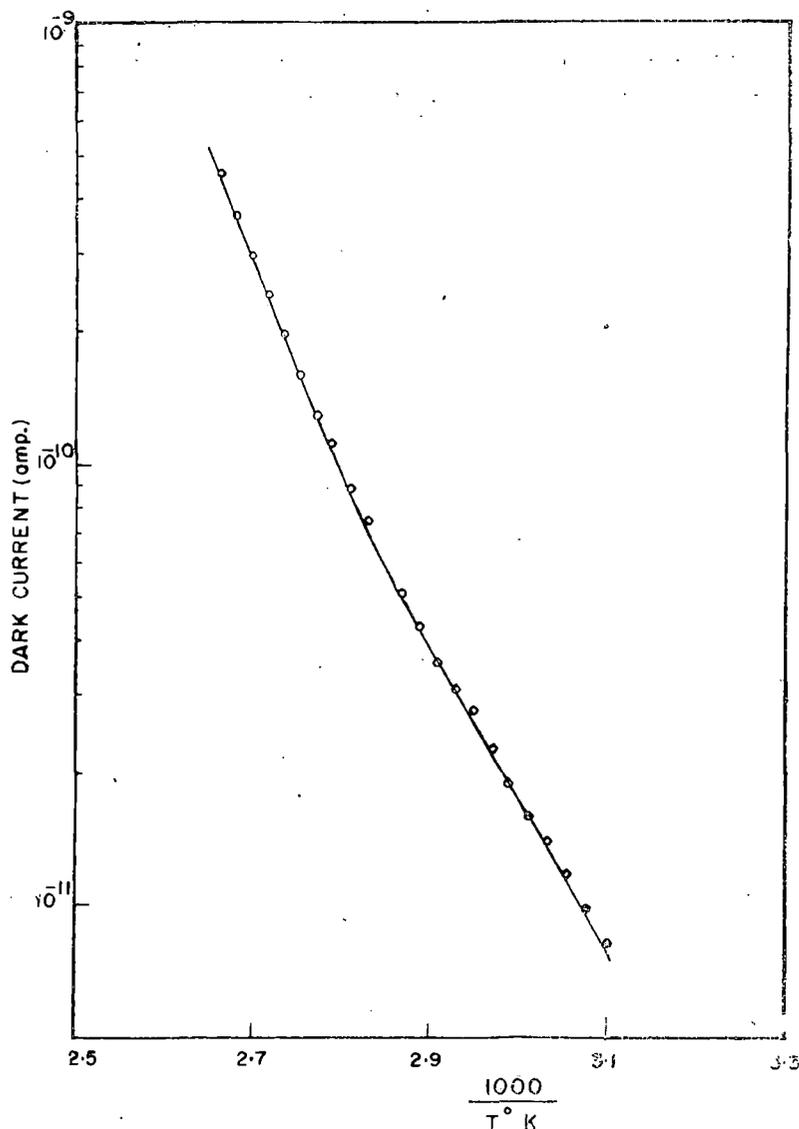


Fig. 1. Conductivity in a 9-nitroanthracene powder cell.

intrinsic region for this semiconductor. The specific conductivity ( $\sigma$ ) at 27°C and the pre-exponential factor ( $\sigma_0$ ) 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.

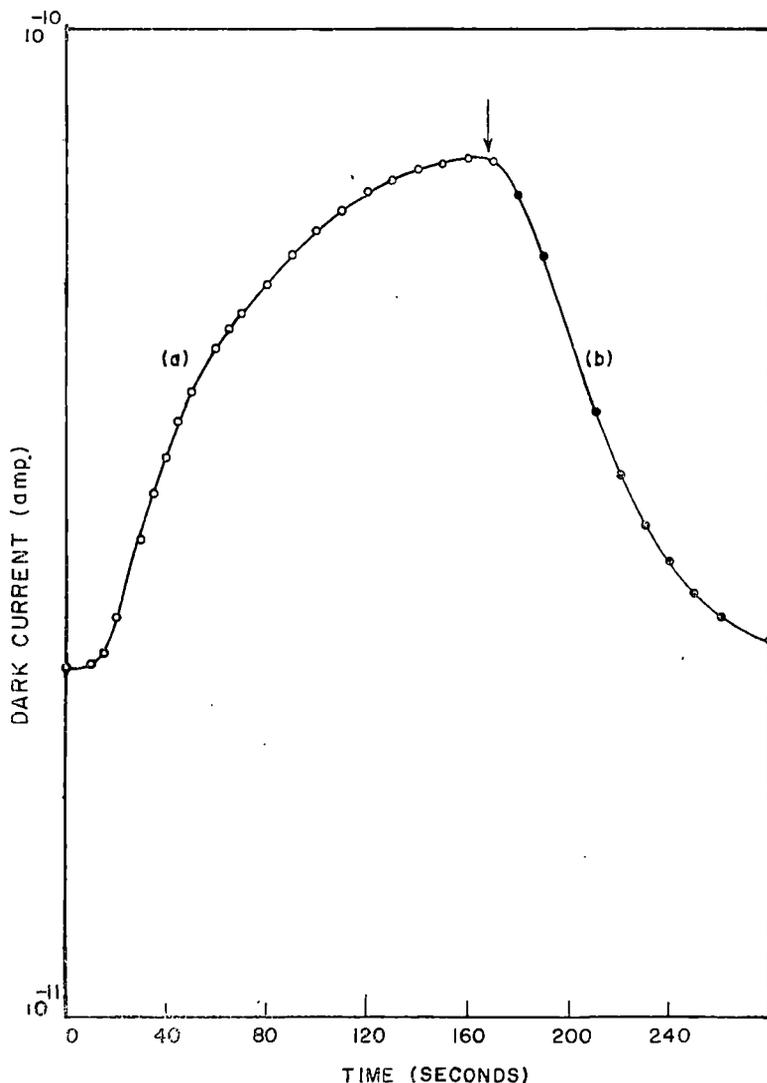


Fig. 2. The change in dark current in a 9-nitroanthracene powder cell with (a) adsorption and (b) desorption of carbon-tetrachloride vapour at 32.4 mm. vapour pressure (sample kept at 27°C).

### 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  $\alpha$  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. Thus we assume that in the initial region

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

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

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

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. When small

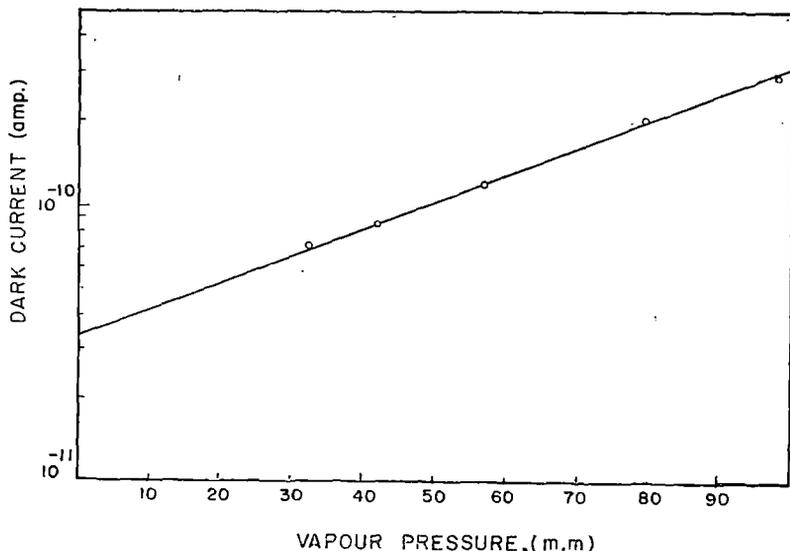


Fig. 3. Change in the dark current of 9-nitroanthracene powder cell as a function of the vapour pressure of carbon-tetrachloride.

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 1 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 1. 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	$3 \times 10$
Benzene	$3 \times 10$
Ethanol	$1.2 \times 10^2$
Iso-Propanol	$9.2 \times 10^2$

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

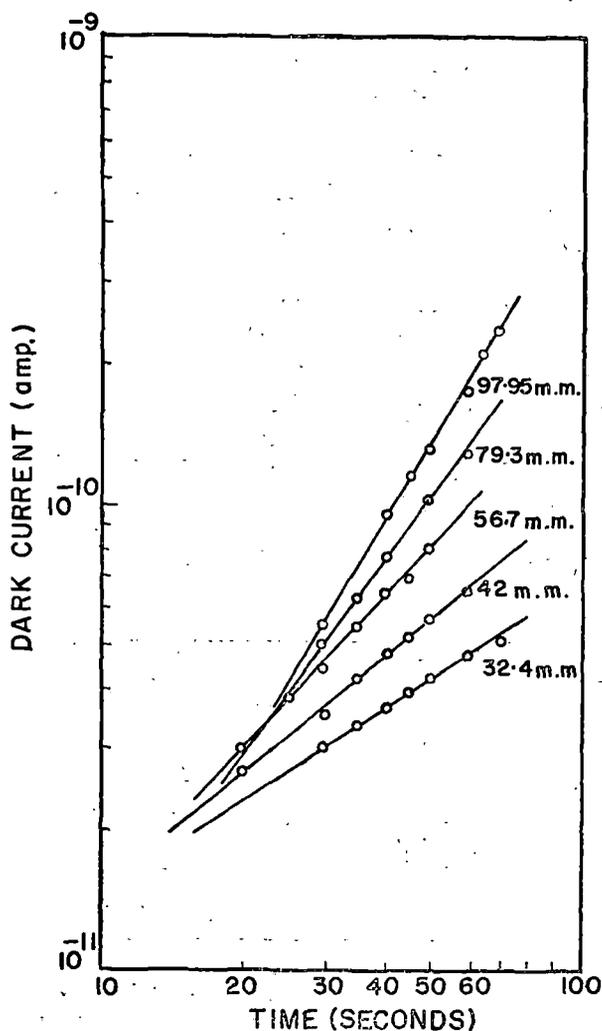


Fig. 4. Adsorption kinetics data plotted according to Roginsky-Zeldovich equation.

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

$$\frac{dm}{dt} = A \exp(-\beta m/kT) \quad \dots (5)$$

where  $\beta$  is a constant.

Integrating (5), we get

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

combining (3a) and (6),

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

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

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

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

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

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  $\alpha$  shows the vapour pressure dependence of  $\beta$ . (Table 2).

Table 2. Vapour pressure dependence of the factor  $\beta'$  for carbon-tetrachloride vapour adsorption kinetics.

Vapour Pressure (mm)	$(\beta/\alpha)$ (ev.)
32.4	$4.074 \times 10^{-2}$
42.0	$3.218 \times 10^{-2}$
56.7	$2.458 \times 10^{-2}$
79.3	$1.907 \times 10^{-2}$
97.95	$1.577 \times 10^{-2}$

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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