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Adsorption-Induced Unusual Changes in the Electrical Conductivity of Some Ferrocene Derivatives

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The effects of adsorption of different organic vapors on the electrical conductivity of some ferrocene derivatives have been studied using the sandwich cell technique. A conductivity peak is observed in the plot of measured current versus temperature for a sandwich cell of powdery material with some adsorbed vapors. The dependence of the intensity of the peak and the temperature at which it appears have been studied as a function of grain size of powdery materials, heating rate, amount of adsorbed vapor, and also the nature of the adsorbed vapors. At the vapor-adsorbed state these materials show very high value of activation energy and the pre exponential factor σ_0 (in the usual semiconduction equation). Results indicate that the adsorption is a physical adsorption. The usual mechanisms for the adsorption-induced change in conductivity and activation energy are not suitable for explaining the observed results. Adsorption induced reversible structural phase transition seems responsible for the anomalous behavior of the adsorption-induced changes in the electrical properties of these materials. The results obtained with different ferrocene derivatives have been compared with that of ferrocene and possible reason for the adsorption induced phase transition is discussed.

Investigations on the effect of adsorption of vapors on the dark conductivity of organic as well as organometallic solid materials have been stimulated in recent years.[1–5] Adsorption or desorption of vapors changes the dark conductivity of these materials significantly. This effect of adsorption induced changes in dark conductivity can be monitored for the detection of various gases/vapors in the environment using these materials in suitable gas detectors.[1–5] The ultimate aim of such research is to find out suitable new materials that can be utilized as gas detectors for detecting specific gases, which has not yet been possible. The effect of adsorption-induced change in conductivity has shown another application also as the change in conductivity of vitamin A (alcohol and acetate) and some other linear conjugated polyenes could be involved in the primary mechanism of olfactory-transduction process.[6–7] Rosenberg et al.[6] have speculated that a week charge-transfer complex formation between vapor molecules and a semiconductor is responsible for the enhancement of conductivity and the change in activation energy in case of some polyenes. The nature of interaction between vapor or gas molecules and the solid surface is a complicated one and it is not yet clearly understood. Systematic studies are required to understand the nature of such interaction.

Recently, the studies on the effect of adsorption of vapors on ferrocene, the first synthesized organometallic compound has become a subject of great interest to us,[8] following the suggestion[9] that adsorption of minute amounts of moisture on this material may have an important role for the inconsistent results reported in the literature[10,11] regarding the pressure dependence of the electrical conductivity. In our earlier communication[8] we have discussed about the adsorption-induced unusual changes in the electrical conductivity of ferrocene. We have studied the adsorption-induced changes in the electrical conductivity of some ferrocene derivatives for eluciding the effect of substituent groups on the adsorption-induced changes. The results of this investigation are presented in this paper.

Experimental

High-purity microcrystalline ferrocenecarboxylic acid (Fc-COOH), ferrocenecarbaldehyde (Fc-CHO), acetylferrocene (Fc-$COCH_3$) in powdered form were obtained from Aldrich Chem. Co., Inc. (U.S.A.) and then were used after purification by repeated crystallization. Reagent chemicals used in this experiment were of spectrograde (E. Merck) or equivalent quality. The usual sandwich cell technique[7,12,13] with a conducting glass and a stainless steel electrode was used and the cell was placed inside a suitably designed conductivity chamber, made of brass and fashioned with teflon. The experimental arrangement for measurement of semiconduction parameters of these ferrocene derivatives with various adsorbed vapors was the same as described in earlier communications.[12,13] The finely powdered and coarsely powdered materials were used as materials of smaller grain size and larger grain size respectively. The grain size of the powdery materials taken for preparing different sample cells was kept same in each experiment. A d.c. voltage of 27 Volts was applied across the electrodes as a bias potential and a teflon spacer of 2 mil (0.005 cm) thickness was used. The conductivity chamber was first evacuated and then filled with dry nitrogen gas and its flow at a constant rate was maintained throughout the experiment. Repeated heating-cooling cycles were performed for each cell to ensure the absence of any kind of adsorbed vapors or moisture in the material before adsorption studies. For adsorption of vapors on the solid materials, dry nitrogen gas at a constant rate was bubbled through a solvent inside a bubbler kept at a fixed temperature to maintain a constant vapor pressure and then it was passed through the conductivity chamber. The cell temperature was kept at 258 K during adsorption and after obtaining saturation current the cell was further cooled down to about 250 K. Then the cell was heated with a constant heating rate of 0.01 K sec^{-1} (otherwise mentioned in the text) and the values of the dark current were noted with temperature. For current measurement an electrometer (model No. EA815) of Electronic Corporation of India Ltd. was used. The temperature measurements were carried out by a Panel meter (model No. 2301) of HIL, India. It is reported that Fc-$COCH_3$ shows structural phase transition[14] near melting point. Therefore, during heat treatment the maximum temperature of the sample cell was kept much below the melting point for Fc-$COCH_3$. Similarly, in case of Fc-CHO, the maximum temperature of the cell was kept below 317K to avoid the structural phase transitions.[15]

Results and Discussion

The effect of adsorption of different vapors on the electrical conductivity (proportional to current) of the ferrocene derivatives as a function of temperature was studied. Such an effect of adsorption of toluene vapors (30 Torr vapor pressure, 1 Torr=133.322 Pa) on Fc-$COCH_3$ is illustrated in Fig. 1 [curve(1)]. At temperatures near 250 K current observed (not shown) was very low ($<10^{-14}$ A). As the temperature increases initially the current rises slowly and then rapidly; and attains a maximum value of 1.37×10^{-9} A at about 282 K. Then the current starts to decrease sharply with increasing temperature and attains a value almost equal to that of the pure sample near the room temperature. Above room temperature the current rises again with increasing temperature similar to the pure sample in nitrogen atmosphere. Thus a conductivity peak is observed at the adsorbed state by plotting the current values against temperature [curve 1, Fig. 1]. It is interesting to note that the conductivity variation [curve (2), Fig. 1; plotted in a magnified scale] in the same temperature range in pure acetylferrocene in dry nitrogen atmosphere does not show any conductivity peak and the variation is usual one as expected for a pure organic semiconductor. However, the above-mentioned conductivity peaks were also observed with different adsorbed vapors on various ferrocene derivatives.

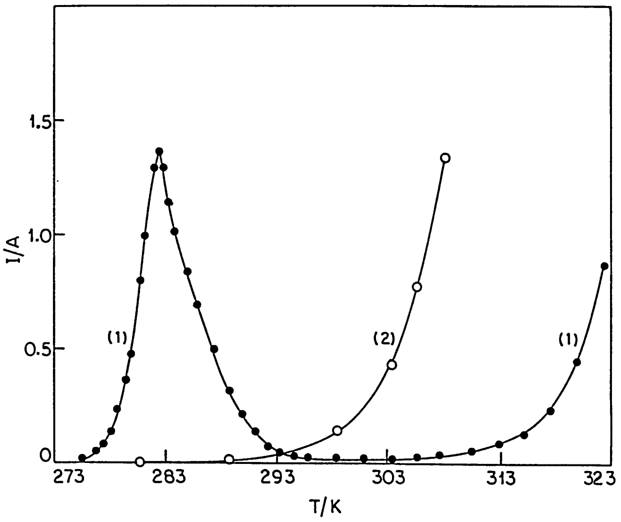

Fig. 1. Variation of dark current (conductivity) as a function of temperature in a powder cell of acetylferrocene:
1) with adsorption of toluene vapor at 30 Torr vapor pressure (left scale$\times10^{-9}$).
2) pure sample in dry nitrogen atmosphere (left scale $\times10^{-11}$).

The effect of adsorption of vapors on the dark conductivity of different ferrocene derivatives were studied under different measurement conditions such as (i) with different grain size of the powdery materials, (ii) change of heating rate, (iii) with different amounts of adsorbed vapors, and (iv) nature of adsorbed vapors. These are described below in detail.

(i) The adsorptive property of a solid surface depends on the grain boundaries of the particles constituting the surface. To investigate such a dependence in case of different polycrystalline ferrocene derivatives, qualitative experiments were performed with two different grain sizes of polycrystalline powders of these materials. The results of such a typical experiment with adsorbed ethanol vapor at 40 Torr vapor pressure on Fc-$COCH_3$ are shown in Fig. 2 for two different grain sizes. The conductivity curve corresponding to bigger grain sizes has shown a higher value of that temperature (T_{max}) at which the conductivity peak appears associated with a slightly lower value of current (I_{max}) corresponding to the conductivity peak compared to that of the smaller grain sizes. The current versus temperature curve corresponding to the former has a larger band width than that of the curve corresponding to the latter one. Dependence of I_{max} and T_{max} on the grain size was observed with other vapors and also with different ferrocene derivatives.

(ii) Similar to ferrocene (Fc-H)[8] in these derivatives also the rate of heating has an influence on the value of I_{max} as well as T_{max}. Figure 3 illustrates two conductivity curves for Fc-$COCH_3$ powders of same grain size on adsorption of ethanol vapor at 40 Torr pressure for

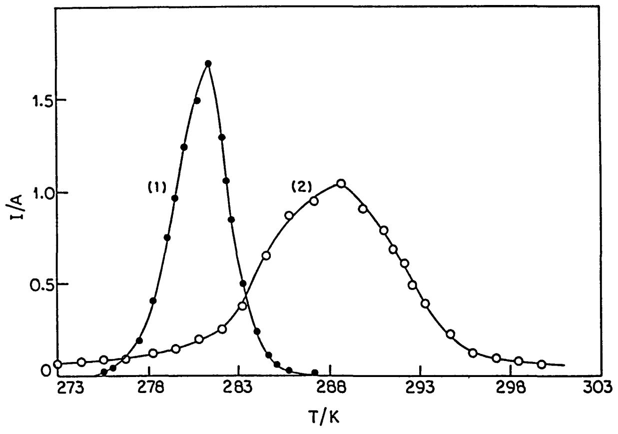

Fig. 2. Variation of dark current as a function of temperature in a powder cell of acetylferrocene with adsorbed ethanol vapor at 40 torr vapor pressure for two different grain sizes: (left scale$\times10^{-9}$)
1) smaller grain size (value of T_{max}=281.3 K),
2) bigger grain size (value of T_{max}=288.6 K).

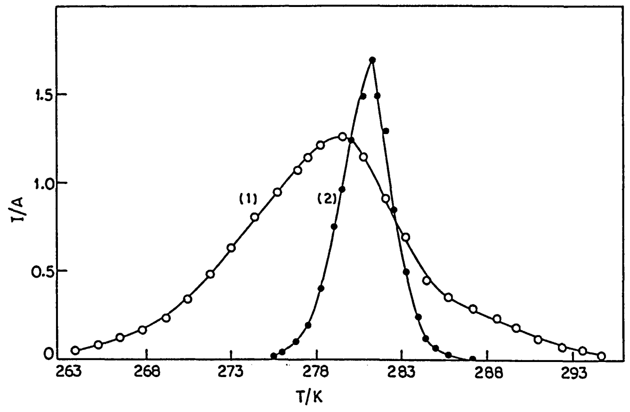

Fig. 3. Variation of dark current as a function of temperature in a powder cell of acetylferrocene with adsorbed ethanol at 40 Torr vapor pressure for two different heating rates: (left scale$\times 10^{-9}$)
1) heating rate: 0.02 K sec^{-1},
2) heating rate: 0.01 K sec^{-1}.

two different heating rates. In case of higher heating rate the conductivity peak appears at lower temperature (i.e., lower value of $T_{\max}$) with a slightly lower value of $I_{\max}$. But the conductivity curve in this case has a higher band width. In poly vinylalcohol, a spontaneous current emission induced by first heating run has been observed.[16] The presence of moisture in the material was thought to be the cause for such a current emission. Though the observed current versus temperature curves in case of poly vinylalcohol were very broad and different in nature from the present case, a shift of $T_{\max}$ towards lower temperature with increasing heating rate was also observed in that case as in the present experiment. The location of the conductivity peaks on the temperature scale depends on the heating rate. This is possibly due to the fact that the materials in the adsorbed state change their properties gradually over a certain temperature interval.

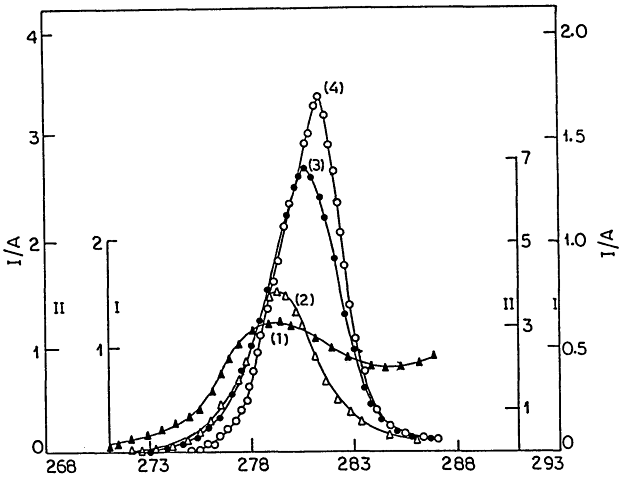

Fig. 4. Variation of dark current as a function of temperature in a powder cell of acetylferrocene with adsorption of ethanol vapor at different vapor pressures:
1) 12 Torr (left scale I$\times 10^{-12}$),
2) 22 Torr (left scale II$\times 10^{-11}$),
3) 30 Torr (right scale II$\times 10^{-11}$),
4) 40 Torr (right scale I$\times 10^{-9}$).

(iii) The dependence of $I_{\max}$ and $T_{\max}$ on the amounts of adsorbed vapors (i.e. on the vapor pressure of the adsorbed vapors) were studied for different ferrocene derivatives under study. Such a dependence is illustrated in Fig. 4 in case of Fc-COCH$_3$, where the values of dark current in a sample cell on adsorption of ethanol vapor at different vapor pressures are plotted as a function of temperature. In general it is observed that the peak value of current ($I_{\max}$) increases with increasing vapor pressure and the temperature ($T_{\max}$) corresponding to this peak value of current shifts a little towards the higher temperature side for larger amount of adsorbed vapors. Similar observations has been reported from the thermal desorption spectroscopic study for oxygen adsorption upon Ge surface.[17]

(iv) To study the effect of different vapors on $I_{\max}$ and $T_{\max}$ in case of a particular material experiments were performed with various vapors e.g. ethanol, methanol, 2-propanol, benzene, toluene, carbon tetrachloride etc. adsorbed at a fixed vapor pressure. (Benzene vapor solidifies at 278 K. But from the quick response of the current due to adsorption of benzene

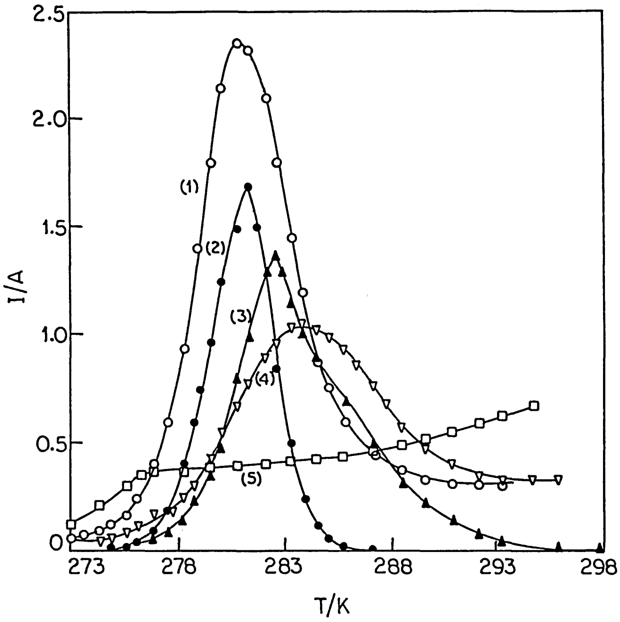

Fig. 5. Variation of dark current as a function of temperature in a powder cell of acetylferrocene with adsorption of different vapors at 40 Torr vapor pressure:
1) Benzene (left scale$\times 10^{-11}$),
2) Ethanol (left scale $\times 10^{-9}$),
3) Toluene* (left scale $\times 10^{-9}$),
4) Methanol (left scale $\times 10^{-11}$),
5) Carbon Tetrachloride (left scale$\times 10^{-12}$).
*Vapor pressure=30 Torr.

vapor upon the cell at 258 K and the similarity in the nature of the current response due to adsorption of other vapors of much lower freezing temperature it appears that the rate of adsorption is faster than the rate of freezing of benzene vapor). Results of such an experiment is shown in Fig. 5 for Fc-COCH$_3$. With the change of vapor, the change in I_{max} as well as T_{max} is evident from this figure (Fig. 5). In case of toluene vapor though the vapor pressure is less than the others, the current enhancement is comparable to (e.g. ethanol) or even higher than some other vapors (e.g. methanol, benzene). On adsorption of carbon tetrachloride vapor no sharp peak was observed. For the appearance of the conductivity peak, a particular vapor is sensitive (the sensitivity, S, may be defined as the ratio of the value of conductivity corresponding to the above-mentioned peak and the value of the conductivity of the pure material without adsorption at the temperature corresponding to the peak) to different ferrocene derivatives to a different extent. This is illustrated in Fig. 6 which shows the variation of dark current with temperature for adsorption of ethanol vapor at 40 Torr vapor pressure on different materials. From this figure the effect of substituent groups on the electrical conductivity is evident. In case of Fc-H adsorbed with ethanol vapor, multiple conductivity peaks have been observed, but no such multiple peaks have been appeared in its derivatives. The effects of adsorption of various vapors on S and T_{max} in case of Fc-H and its different derivatives are summarized in Table 1 (corresponding values for Fc-H is also included for comparison). The following interesting observations may be noted from this table.

(a) For most of the adsorbed vapors the value of T_{max} as well as S in case of Fc-H is higher than the corresponding values for any derivative.

(b) In case of adsorption of different vapors in a particular compound the sequence of vapors for the enhancement of S does not correspond to the same sequence for the increase in T_{max}.

(c) For adsorption of a particular vapor in the different derivatives the increase or decrease in S is accompanied by a simultaneous increase or decrease in T_{max} (except for adsorption of benzene vapor in Fc-CHO).

(d) Either ethanol or 2-propanol shows the maximum value of S in these materials.

(e) In general, methanol shows the minimum value of S for these materials.

The experiments on adsorption of various vapors on various ferrocene derivatives under different measurement conditions indicate that the mechanism behind the appearance of the above mentioned conductivity peaks is expected to have a physical basis.

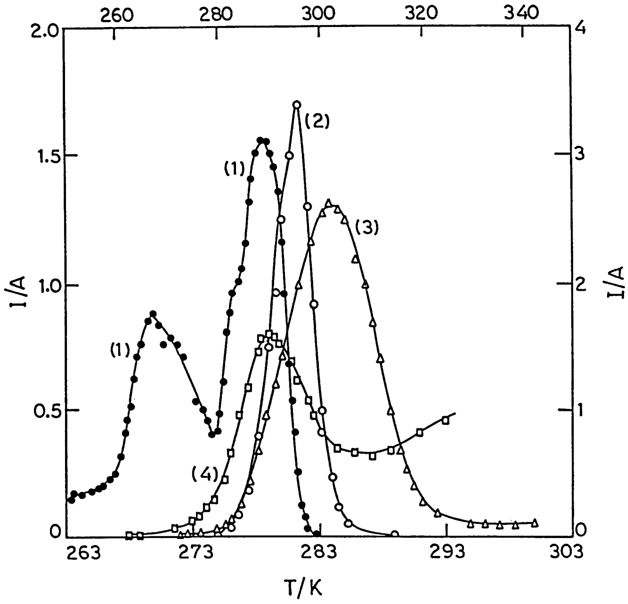

Fig. 6. Variation of dark current as a function of temperature in powder cells of different materials on adsorption of ethanol vapor at 40 Torr vapor pressure:

1) Ferrocene (right scale $\times 10^{-8}$, upper temperature scale),

2) Acetylferrocene (left scale $\times 10^{-9}$),

3) Ferrocenecarbaldehyde (right scale $\times 10^{-9}$),

4) Ferrocenecarboxylic acid (left scale $\times 10^{-11}$).

Table 1. The Values of S and T_{max}(K) for Adsorption of Different Vapors (at 40 Torr Vapor Pressure) on Ferrocene and Some of Its Derivatives at a Cell Temperature of 258 K

Vapors used	Values of ionization potential in eV [18]	Values of electron affinity in eV [19]	Values of dielectric constant at 298 K [12,20]	Different materials studied							
				Fc-H		Fc-COOH		Fc-CHO		Fc-COCH$_3$	
				S	T_{max}	S	T_{max}	S	T_{max}	S	T_{max}
Toluene[a]	8.81	0.820	2.379	4.28×10^4	298.5	5.95×10	280	2.87×10	279	3.42×10^3	282.5
Benzene	9.24	2.46	2.274	8.75×10^3	298	5.59×10^2	283	1.82×10^3	276	6.33×10	281
Ethyl acetate	10.11	—	6.02	6.25×10^2	280	1.07×10^2	279	6.15×10^2	276	—	—
Ethanol	10.5	0.594	24.0	1.5×10^5	289.5	4.76×10	279	5.65×10^3	283	4.52×10^3	281.3
2-Propanol	10.79	0.672	18.3	3.21×10^6	289	6.36×10^2	278	8.16×10^3	281	—	—
Methanol	10.85	0.377	32.63	0.045	298.5	—[b]	—	—	—	2.09×10	283.7
Carbon tetrachloride	—	1.215	2.228	3.2×10^4	295.2	1.2×10^2	280	3.25×10	279.5	1.8×10	276.3

a) Vapor pressure in this case is 30 Torr. b) A hump was observed in this case.

The electrical conductivity in organic as well as organometallic materials, charge-transfer complexes, and adsorption induced conductivity is usually expressed[7,13,21] by the Arrhenious relation

$$\sigma(T)=\sigma_0 \exp(-E/2kT), \qquad (1)$$

where $\sigma(T)$ is the specific conductivity at any absolute temperature T, σ_0 is the pre exponential factor, E is the activation energy, and k is the Boltzmann constant. Experimentally E is obtained from the slope of the linear plot of $\log\sigma(T)$ or $\log I(T)$ versus $1/T$, where $I(T)$ is the current at the temperature T. As a representative curve the variation of log $I(T)$ against reciprocal of temperature for a sample cell of Fc-COCH$_3$ with adsorbed toluene vapor is shown in Fig. 7 [curve(1)]. Usually a plot of $\log\sigma(T)$ or $\log I(T)$ versus $1/T$ gives a straight line in the low temperature region,[13,22] which shows the conduction properties of the solid material with adsorbed vapor. The slope of this line gives the activation energy of the material at the adsorbed state and the straight line at higher temperature region gives the activation energy of the pure material in vacuum or nitrogen atmosphere. Similar to the case of Fc-H,[8] in the present case also two different straight lines (AB and BC in curve 1 of Fig. 7) instead of one line have been observed at the adsorbed state and a transition from one line to another is prominent at the point B. The portion of the curve, DE represents the change in current due to desorption of vapors and the portion EF shows the conduction behavior similar to pure material in nitrogen atmosphere. The value of activation energy evaluated from the line EF is 3.7 eV which is equal to the activation energy of pure material in nitrogen atmosphere and these results show that the adsorption is a physical adsorption. The activation energy values evaluated from the portion AB and BC are 5.05 and 9.75 eV respectively. The value of σ_0 for pure Fc-COCH$_3$ is 1.76×10^{17} $\Omega^{-1}\text{cm}^{-1}$ and for the sample with adsorbed toluene vapor (corresponding to line BC in Fig. 7) at 30 Torr vapor pressure is about 4.48×10^{75} $\Omega^{-1}\text{cm}^{-1}$. Both the values of activation energy and σ_0 at the adsorbed state are anomalously high. Such an appearance of two straight lines is not a typical property for adsorption of a particular vapor only. For most of the vapors studied similar behavior was observed in each material. Figure 8 shows the appearance of such two straight lines in case of ethanol vapor adsorption on various ferrocene derivatives. The appearance of two straight lines possibly indicates that the adsorption is a two stage process.[24] Out of these two lines, the line at higher temperature (Fig. 8) gives the value of activation energy (E) which is in general much higher than the activation energy of the pure material. In Table 2 we

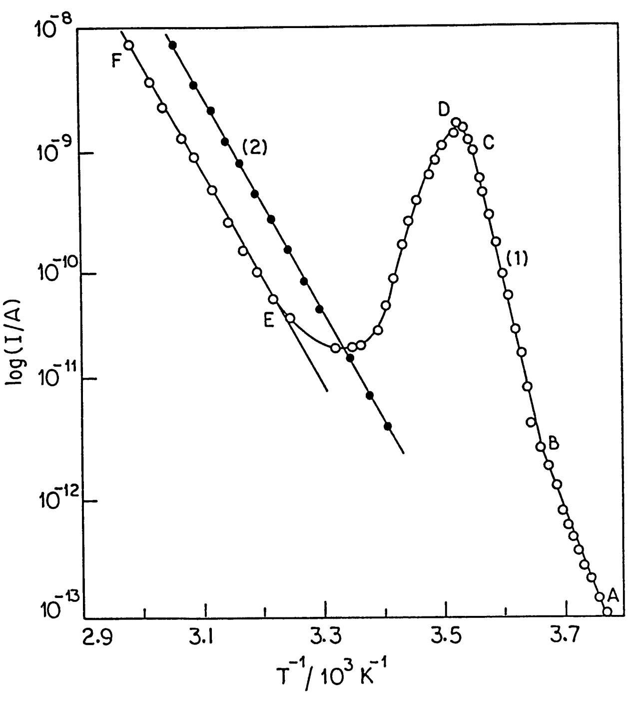

Fig. 7. Plot of logarithm of dark current vs. reciprocal of temperature for a powder cell of acetylferrocene:
1) with adsorption of toluene vapor at 30 Torr vapor pressure,
2) pure sample in dry nitrogen atmosphere.

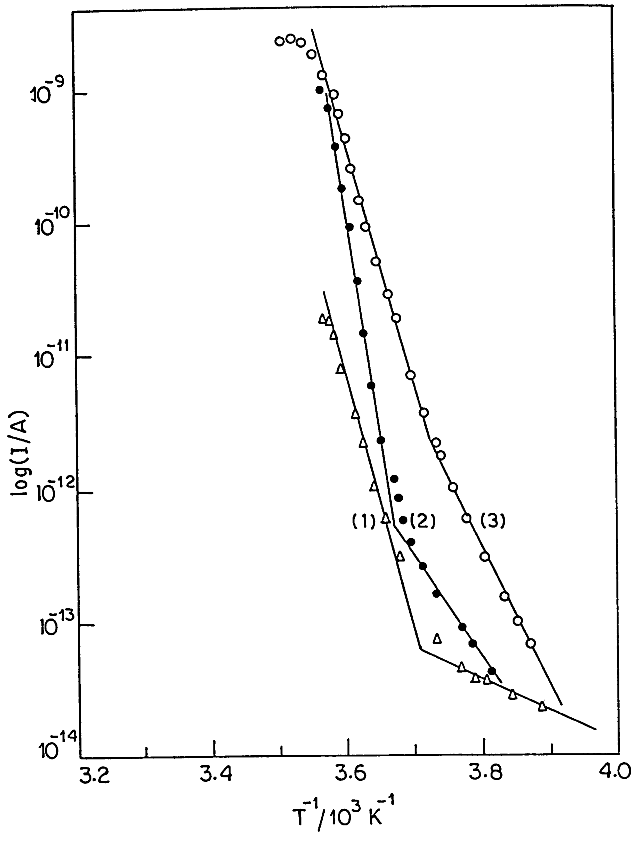

Fig. 8. Plot of logarithm of dark current vs. reciprocal of temperature at the low-temperature region for powder cell of different ferrocene derivatives with adsorption of ethanol vapor at 40 Torr vapor pressure:
1) Ferrocenecarboxylic acid,
2) Acetylferrocene,
3) Ferrocenecarbaldehyde.

Table 2. The Values of E (eV) and Corresponding σ_{O} ($\Omega^{-1}\,\mathrm{cm}^{-1}$) for Adsorption of Different Vapors (at 40 Torr Pressure) on Ferrocene and Some of Its Derivatives at a Cell Temperature of 258 K

Vapors used	Different materials studied							
	Fc-H		Fc-COOH		Fc-CHO		$\mathrm{Fc\text{-}COCH_3}$	
	E	σ_{O}	E	σ_{O}	E	σ_{O}	E	σ_{O}
Carbon tetrachloride	10.37	9.07×10^{75}	4.33	1.99×10^{24}	3.75	5.95×10^{18}	4.3	4.34×10^{23}
Benzene	9.39	1.18×10^{68}	9.75	1.15×10^{74}	5.7	1.03×10^{39}	8.12	6.03×10^{58}
Toluene[a)]	8.16	1.16×10^{58}	7.35	1.26×10^{52}	4.6	1.36×10^{27}	9.75	3.13×10^{75}
Ethyl acetate	7.5	7.87×10^{53}	7.22	1.72×10^{51}	4.75	6.11×10^{29}	—	—
2-Propanol[b)]	—	—	7.3	7.09×10^{52}	5.62	3.97×10^{38}	—	—
Ethanol[b)]	—	—	7.22	2.14×10^{53}	7.1	2.21×10^{51}	15.0	$>10^{99}$
Methanol	2.8	6.95×10^{18}	—	—	3.15	1.11×10^{15}	5.5	5.02×10^{44}

a) Vapor pressure is 30 Torr in this case. b) In case of ferrocene multiple peaks were observed, so these values could not be evaluated.

show the values of E evaluated from these lines along with some other parameters for adsorption of different vapors on these ferrocene derivatives. This table shows that the value of E and σ_{O} are enormously high. These results are certainly unusual.

As the adsorption is a surface phenomenon the observed adsorption-induced change in the electrical conductivity of the solid materials arise mainly due to the change in surface conduction. When adsorption of vapors occurs, an exchange of charges takes place between the adsorbed molecules and the solid materials causing a change in surface electrical conductivity. It needs to be pointed out that depending on the extent of adsorption/absorption of vapors there is a possibility of formation of a solvated surface film (that may form and disappear at different temperatures) producing very high electrical conductivity. The variation of the solvated surface film with changing temperature may be related to the consequent change in conductivity. In fact, in case of the formation of solvated films, usually irreversible change is observed and it is more likely (as we have noticed also) that in a sandwich type of cell configuration due to solvation, the positive and negative electrodes will be short circuited by solvent molecules/dissolved materials. In the present experiment such a situation was carefully avoided by controlling the amount of adsorption (by adjusting the vapor pressure of the adsorbed vapor) and only the reversible adsorption-induced changes were considered. So, the appearance of the observed conductivity peak due to the formation of the solvated surface film can easily be ruled out.

The reason for the change in E in organic/organometallic semiconductors on adsorption of vapors is not yet well understood. The possible mechanism which is quite often considered is the formation of charge-transfer (CT) complexes[6,13)] of adsorbed vapor molecules with the solid surface. Rosenberg et al.[23)] proposed that such change in E on adsorption is associated with a change in effective dielectric constant of the material at the adsorbed state. We have checked the applicability of these theories and found that these theories are not suitable for the explanation of the change in E as well as conductivity.[8)] Again the observed conductivity versus temperature curves look similar to the conventional glow curves (arise due to the thermally stimulated currents or TSC).[24)] On adsorption of vapors, trapping states within the band gap of a semiconductor could be populated by charge carriers and consequently on heating TSC may appear due to detrapping of charge carriers.[25,26)] But the values of trap depth calculated by the usual theory of TSC[24)] are much higher than the activation energy values of the pure materials. So, the theory of TSC can not be considered as the possible mechanism behind the appearance of peak in the observed conductivity versus temperature curve under discussion.

From Eq. 1 it is clear that the increase in σ_{O} is responsible for the increase in conductivity and σ_{O} contains factors depending on temperature. The pre exponential factor σ_{O} of the Eq. 1 can be expressed as[27)]

$$\sigma_{\mathrm{O}} = qN\mu, \tag{2}$$

with

$$N = (N_{\mathrm{A}} \cdot \rho \cdot Z)/M, \tag{3}$$

where q is the charge on the carrier, μ is the mobility, N_{A} is Avogadro's number, M is the molecular weight of the solid material, ρ is the density, and Z is the number of charge carriers available for excitation per molecule. The mobility of charge carriers for most organic and biological semiconductors usually lies[27)] between 10 and 10^{-5} $\mathrm{cm^2\,V^{-1}\,sec^{-1}}$. So a large change in σ_{O} upon adsorption of vapors can not be considered due to the change in the mobility of these charge carriers in the sample in the adsorbed state. Thus the large value of σ_{O} must be associated with a large density of activated charge carriers. In some organic materials an exponential temperature dependence of the charge carrier mobility has been observed.[28)] The reported value of the mobility activation energy (E_{μ}) of a large number of organic materials lies between 0.20 and 0.77 eV.[28)] Therefore, even if the exponential temperature dependence of charge carrier mobility is considered, the anomalously large value of E remains unexplained.

It is known that a phase transition occurs in ferrocene under the influence of changes in external parameters like temperature[29] and pressure.[9] The ferrocene derivatives under investigation exhibit[14,15,30,31] various kinds of structural phase transitions associated with intermolecular interactions. From these observations it appears that a structural phase transition in these ferrocene derivatives due to interaction with various vapors in a suitable temperature range is not unlikely. Phase transition in the adsorption process has been reported in the literature.[32,33] It is reported[34] that as result of phase transition, the activation energy of some organic materials increases by a large amount and such phase transition is indicated by a deviation from the linearity of the $\log \sigma(T)$ or $\log I(T)$ versus $1/T$ plots. It is interesting to note that such a deviation from linearity has also been observed in the present case (Figs. 7 and 8). This adds further credence to the idea of adsorption-induced structural phase transition in these ferrocene derivatives. Such phase transitions depend on the nature of adsorbed vapors and these transitions are reversible on desorption of vapors. We have mentioned earlier that a large change in σ_0 (hence in σ) upon adsorption of vapors must be associated with a large density of activated charge carriers. The reason for such a large value of the density of activated charge carriers occuring upon a phase transition can be explained by concept of conformon,[35-37], which is considered as the activated charge carrier plus the accompanying conformational changes (here due to phase transition) carrying energy and entropy. By conformon concept Kemeny and Goklany[36] has suggested that the effective density of states for the activated charge carriers would be greatly increased due to interaction between the activated carriers and the vibrational degrees of the molecules. A change in the electronic state (as involved in transport) gives rise to an activation entropy ΔS because of a change in the vibrational frequency associated with a conformational change and this would contribute to the pre-factor σ_0. Thus, using proper thermodynamic quantities σ_0 can be written as[38]

$$\sigma_0 = A_1 \exp(\Delta S/2k) \cdot \exp(-\Delta H/2kT), \tag{4}$$

where A_1 is a constant, ΔS is known as activation entropy and ΔH is the activation enthalpy. Hence the process of current emission can be represented by the relation

$$\sigma(T) = A \exp(\Delta S/2k) \cdot \exp(-E^*/2kT), \tag{5}$$

where A is another constant and $E^* = (\Delta H + E_\mu + E)$, which accounts for the large value of activation energy in the present case.

The lattice dynamical nature of Fc-COCH$_3$, Fc-COOH, and some other ferrocene derivatives has been investigated[14,30] by some researchers in the solid state (in the tempearature range from 100 K to nearly melting point of these materials) by comparing their Mössbaur spectra with the crystal structure determined by X-ray diffraction spectroscopy. In these ferrocene derivatives the mean square amplitude of lattice vibration (thermal) of iron atoms measured from Mössbaur spectra has been observed[14,30] to be proportional to the absolute temperature nearly upto room temperature (300 K) indicating that the molecules are in harmonic lattice vibration; but a significant deviation has been found near the phase-transition temperature. From X-ray diffraction and Mössbaur spectroscopic studies Daniel et al.[31] have reported that Fc-CHO shows anomalous behavior near phase transition temperature (317 K). These results indicate a substantial modification in the lattice characteristics of the solid due to phase transition. Such phase transition has been thought[14,30,31] to be associated with a cooperative motion of different neighboring molecules. It has been suggested[14] that the orientational motion of Fc-COCH$_3$ may be hindered by interaction with neighboring molecules, for instance the steric hindrance of –COCH$_3$ groups which probably reduces the thermal motion. Two molecules of Fc-COOH have an intermolecular hydrogen bonding[30] between –COOH groups. In Fc-CHO, the –CHO side group is almost coplaner with the ring to which it is attached,[15] thus allowing conjugation of the π-electron system of the $\rangle$C=O bond and the aromatic cyclopentadienyl ring. As a result of different cooperative interactions, phase transition in different ferrocene derivatives (also in pure ferrocene) occurs at different temperatures. In the temperature range of present experiment the molecules of the pure ferrocene derivatives exhibit harmonic thermal vibration. But possibly due to the presence of adsorbed vapor molecules, the harmonic thermal vibration of the molecules of the ferrocene derivatives is perturbed and due to cooperative interaction such phase transition appears. As mentioned earlier, such adsorption-induced phase transition depends on the nature of the adsorbed vapor and also on the substitution group in a particular ferrocene derivative. In general methanol is less sensitive for the adsorption-induced changes. Though 2-propanol is good sensitive to most of the materials studied (Table 1), it is almost insensitive to Fc-COCH$_3$. Thus, the selectivity in the interaction of vapors with the different derivatives is evident from the observed results. In fact, the cooperative interaction which determines the phase transition is very complicated in nature[31] and it is not possible to correlate the nature of adsorption-induced phase transition with the presence of substituent group in the ferrocene derivatives at the present stage.

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