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Effects of mechanical pressure on charge transport in ferrocene in the presence of adsorbed vapours

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The change in the adsorption-induced electrical conductivity of ferrocene as a function of temperature has been studied under moderate pressure. At constant temperature, the logarithm of conductivity has been observed to be proportional to the applied pressure. A drastic change in the electrical conductivity behaviour of ferrocene, at the adsorbed state, as a function of temperature under mechanical pressure has been observed. The results are discussed in the light of different existing theories. Our results suggest that ferrocene in the vapour-adsorbed state undergoes phase transition which is modified by both temperature and pressure, and the effect of such phase transition is reflected in the unusual variation of conductivity with temperature under different pressures.

1. Introduction

The metallocenes have occupied the most privileged position in organometallic research because of their technological usefulness recognized in different fields [1]. Ferrocene, the first synthesized organometallic sandwich compound, is well known for its important electrochemical properties [2–5]. During the past three decades, three reports have been published about the effects of mechanical pressure upon ferrocene. Okamoto *et al.* [6] reported a slight increase in the electrical conductivity of ferrocene with increasing pressure up to 400 MPa and then conductivity decreases even up to a pressure of 3.3 GPa. In contrast, Maksimychev *et al.* [7] found a monotonically decreasing conductivity over the entire pressure range of 100 MPa–3.3 GPa. Karvaly *et al.* [8] reinvestigated the effects of pressure on the electrical conductivity of ferrocene to determine the reason behind the inconsistent results reported in the literature [6, 7]. From their experimental results, evidence was found for a slow continuous phase transition in ferrocene under pressure at room temperature [8]. After release of pressure, the effects of such phase transition in ferrocene were also noticed for several hours. Except for the very initial pressure range, the qualitative shape of the current–pressure characteristics obtained relatively soon after pressure pretreatment, produced the results of Okamoto *et al.* [6]. On the other hand, the current–pressure characteristic curve for precompressed samples which were left to relax before data collection, reproduced results similar to those of Maksimychev *et al.* [7]. Thus, the two different current–pressure characteristic curves reported in the literature were thought [8] to be dependent upon the prehistory of the sample. It was also proposed [8] that adsorption of minute amounts of moisture on ferrocene may cause additional effects on the pressure dependence of conductivity, particularly in the low-pressure region. It appears that the systematic pressure-dependent conductivity studies, in lower pressure regime, may provide new insight into both bulk and surface properties. The use of mechanical pressure to modulate the electrical transport properties has been proved to be the most fruitful technique available. We were interested in investigating the effects of mechanical pressure on the adsorption-induced conductivity of ferrocene and its variation with temperature under carefully controlled conditions. To the best of our knowledge, studies on the adsorption-induced electrical conductivity as a function of temperature under mechanical pressure have not been reported for ferrocene, except a recent brief communication by us [9]. In the present paper, we report the results of our systematic studies on the change in the electrical conductivity of ferrocene in the adsorbed state as a function of temperature under mechanical pressure.

2. Experimental procedure

High-purity microcrystalline ferrocene (in powder form) was obtained from Aldrich Chemical Co. Inc. (Milwaukee, Wisconsin, USA) and subsequently further purified by repeated crystallization. The chemical reagents used were of spectrograde quality and used without further purification. The experiments were performed using a pressure cell (see Fig. 1) placed inside a suitably designed conductivity chamber [10, 11] made of brass and fashioned with Teflon. Dry samples (30 mg) were loaded (indicated by the dots in

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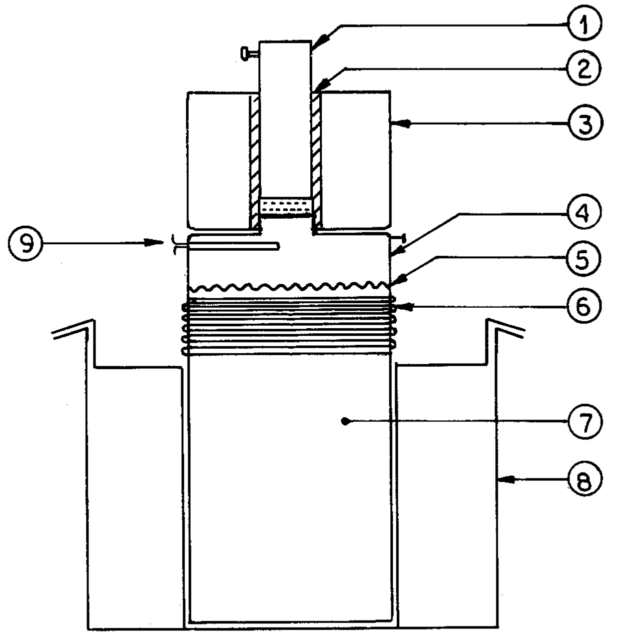

Figure 1 Conductivity-measuring cell under pressure (the dotted area indicates the sample compartment). 1, Pressure-transducing piston; 2, Teflon insulator; 3, cylindrical chamber; 4, base plate; 5, electrical insulation; 6, heating coil; 7, stainless steel rod; 8, temperature bath; 9, thermocouple.

Fig. 1) into the stainless steel pressure cell lined with an appropriate Teflon tubing and placed inside the chamber. The sample was then evenly distributed over the base plate. Teflon insulators were used at every critical place where leakage could have interferred with the measurements. Repeated heating and cooling in a dry nitrogen atmosphere ensured complete desorption of pre-adsorbed gas or vapour, if any. To allow the presence of various vapours inside the chamber, dry nitrogen gas was passed at a constant rate through a bubbler which contained the desired adsorbate chemical kept in a thermostatted bath to obtain a specific vapour pressure. After exposure of the sample at 299 K for ~ 30 min (the usual time for saturated adsorption) to the desired vapour at 5.33 kPa vapour pressure inside the chamber, the adsorption was turned off. The pressure-transducing piston was then introduced in the cylindrical cavity and the pressure cell was cooled to 288 K. The pressure was then applied. After allowing sufficient time (about 1 h) to attain equilibrium, the value of saturated current, I_S, was noted at a steady 40 V d.c. bias, and then the cell was heated slowly (heating rate 0.01 K s^{-1}). The current was also noted with changing temperature. The base plate and the pressure-transducing piston served as electrodes. An external mechanical pressure was created by placing different weights upon a platform, which exerted pressure on the pressure-transducing piston of the pressure cell. This pressure-generating part developed, closely resembles that of the system used by Inokuchi and Akamatu [12]. The pressure cell was placed inside the conductivity chamber, on top of an electrically insulated solid cylindrical stainless steel rod, the bottom of which was immersed inside a closed thermostatted liquid bath. The desired temperature of this liquid bath and thus that of the sample, was controlled by a proportional temperature controller (model RTE-110, Neslab Instruments Inc. USA). The current was measured using an electrometer amplifier (model EA815, Electronic Corporation of India Ltd). The cell temperatures were recorded with a Panel Meter (model 2301, H.I.L., India) using a copper–constantan thermocouple attached to the base plate of the pressure cell. Precautionary measures were taken to avoid any contamination of the sample during loading and measurements.

3. Results and discussion

The effects of mechanical pressure on the dark conductivity, σ, (proportional to current) at 288 K of ferrocene in dry and vapour-adsorbed states are shown in the Fig. 2. In the case of the dry material (curve 1, Fig. 2) the logarithm of dark current increases for the very initial low pressurization, but remains almost independent of further pressurizations. For the material with adsorbed methanol and ethanol vapours (curves 2 and 3, respectively, Fig. 2) the logarithm of conductivity increases slowly with increasing pressurizations. The current enhancement is higher for ethanol adsorption. The pressure dependence of the conductivity of the powdered materials subjected to low compressions is usually determined

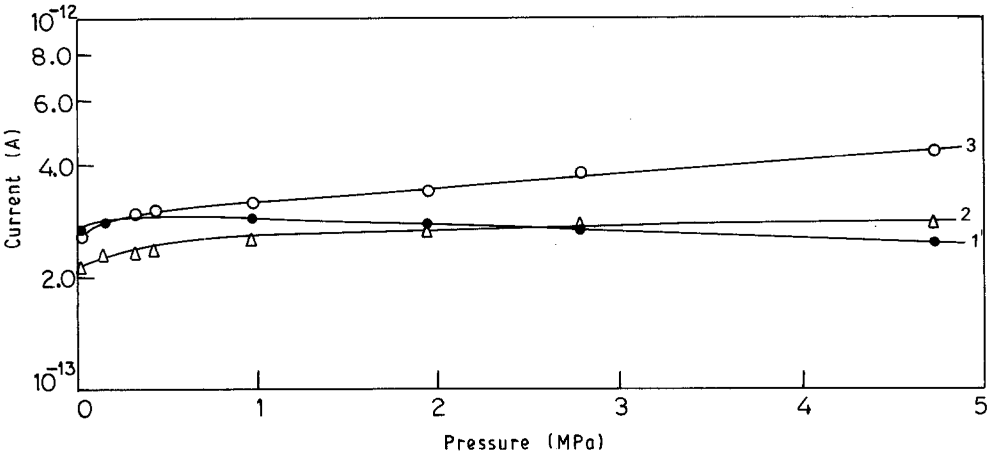

Figure 2 Current–pressure plots at 288 K for ferrocene under different adsorbed conditions: 1 (●) pure and dry material; 2 (△) adsorbed with methanol; 3 (○) adsorbed with ethanol.

by the number and area of the grain-boundary regions connecting the particles [13]. Thus the conductivity of polycrystalline and powdered materials is expected to exhibit qualitatively a characteristic pressure dependence: a considerable increase with increasing pressure at low compression. Data presented here have not been corrected for the pressure-induced change in the sample geometry; primarily in thickness. Measurement of the pressure-induced change in sample thickness is very difficult. To gain some idea about the effects of pressure-induced change in the thickness of the sample cell on the conductivity, σ/d values have been plotted against pressure (Fig. 3), where $\sigma/d = I/AV$, d is the thickness of sample cell, I the current at a particular pressure and temperature, A the area of the sample cell, and V the applied voltage across the electrodes. From Fig. 3 it is seen that σ/d is nearly independent of pressure for dry ferrocene, and for the sample with adsorbed methanol vapour, the σ/d factor increases linearly (slope = 0.0479) with increasing pressure. In the case of ethanol vapour adsorption, two straight-line plots (slopes 0.0672 and 0.2577) are observed from Fig. 3 and in the higher pressure region the enhancement in σ/d is rapid. The value of σ/d depends on the pressure-induced change in the sample thickness, d, and also on the pressure-induced change in conductivity arising from solid–vapour interaction under pressure. It is believed that the current–pressure diagram reflects the fundamental material properties of the powdery materials. The conductivity change due to adsorption for many powdery materials has been well studied [10, 11, 14]. The rise in conductivity under pressure thus appears to be due to compaction and related pressure-induced changes in the contact areas at grain boundaries and the pressure-sensitive conductivity components related to the vapour adsorbed on or bound to ferrocene molecules.

The conductivity of a pure and dry ferrocene cell as a function of temperature (without any mechanical pressure on it) is shown in curve 1, Fig. 4. When a ferrocene cell adsorbed with ethanol vapour was heated without any mechanical pressure applied upon it, the dark conductivity changed with temperature as shown in curve 2, Fig. 4. Here a broad band peak (at 297.25 K) has appeared together with a small hump at the higher temperature side of the plot. With application of 0.16 MPa pressure (curve 3, Fig. 4), a decrease in the conductivity was observed over the entire temperature region, but a conductivity peak appeared at the same temperature, as observed without application of pressure. The hump also appeared with a pronounced nature. Interestingly, another hump or peak appeared with the main peak. With further increase of pressure (0.30 MPa) the conductivity at low temperatures decreased and a conductivity peak appeared of lower height at 298.5 K (curve 4, Fig. 4). Further pressurization of 0.42 MPa (curve 5, Fig. 4) yielded a higher conductivity at the low temperatures, compared to that at 0.30 MPa. A small hump/peak was also observed at 299.6 K with a lower value of peak/hump current. As the pressure was increased to 0.97 MPa, the conductivity at low temperatures again decreased and it was found to become steady around 298.5 K (curve 6, Fig. 4). Further increase in pressure produced higher conductivity at low temperatures and a small peak/hump around 298.5 K was also noticed (curves 7 and 8, Fig. 4). It is interesting to note that the first pressurization caused an enormous change in the conductivity of ferrocene at the adsorbed state, particularly in the lower temperature region. The appearance of new side bands/humps/peaks at low pressures

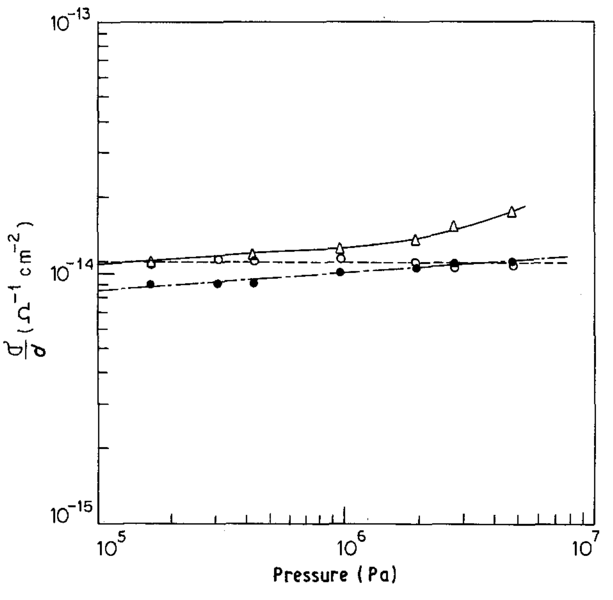

Figure 3 The plots of σ/d versus pressure at 288 K for ferrocene under different adsorbed conditions: (○) pure and dry material; (●) adsorbed with methanol; (△) adsorbed with ethanol.

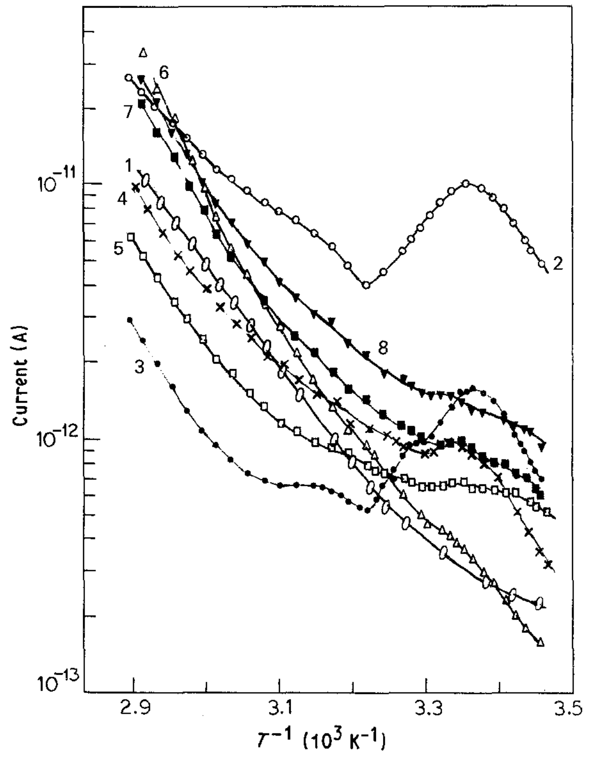

Figure 4 The plots of current versus $10^3/T$ for different ferrocene cells adsorbed with ethanol vapour (at 5.33 kPa vapour pressure) under different applied mechanical pressure. 1 (0) Pure and dry material under no pressure; 2 (○) adsorbed material under no pressure; 3 (●) 0.16 MPa; 4 (×) 0.30 MPa; 5 (□) 0.42 MPa; 6 (△) 0.97 MPa; 7 (■) 1.94 MPa and 8 (▼) 2.77 MPa.

and their disappearance at higher pressures was spectacular. We have reported previously [15] that multiple conductivity peaks appeared on heating a ferrocene sandwich cell in its adsorbed state (under clipping pressure of 0.035 MPa). Although those results were obtained under different experimental conditions compared to the present case, a close relationship exists between the two cases; a conductivity peak appears in both the cases. Here the applied mechanical pressure influences the conductivity–temperature behaviour. The effects of pressure on the intensity, I_{max}, of the above-mentioned conductivity peak and the temperature, T_{max}, at which the peak/-hump appears, is shown in Table I. The value of I_{max} is observed to decrease with increasing pressure up to 0.97 MPa and then I_{max} increases slowly with increasing pressure. The change in T_{max} with pressure is small. In Table I, the pressure dependence of the saturation current, I_S, at 288 K is also presented. Except for a fluctuation at 0.42 MPa, I_S decreases with increasing pressure up to 0.97 MPa, then I_S starts to increase with increasing pressure. The differences in the conductivity–temperature curves for ferrocene in the adsorbed state under pressure is due to pressure-induced modifications. The results are interesting and well reproducible.

The dark conductivity in organic as well as organometallic materials is usually expressed by the Arrhenius relation [11, 14, 16]

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

where $\sigma(T)$ is the specific conductivity at absolute temperature, T, σ_0 the pre-exponential factor, E the semiconduction activation energy, and k the Boltzmann constant. We have estimated the values of E (E_L at lower temperature and E_H at higher temperature) from all the plots in Fig. 4 and these are listed in the Table I. An interesting variation in the E values under different pressures has been obtained and this is shown in Fig. 5. As the heating rate and the method of experiment are the same for all sets of experiments, it appears that the change in E values for ferrocene in the adsorbed state is solely due to the interaction between the adsorbent and adsorbate under different pressures. To study the role of the nature of the adsorbate in this interaction, we have performed similar experiments on ferrocene, with different adsorbed vapours (e.g. iso-propanol, benzene, ethyl acetate and carbontetrachloride, etc.) at the same vapour pressure, under a constant mechanical pressure of 0.16 MPa. The results observed are shown in Fig. 6. It is interesting to note that a conductivity hump is observed in the conductivity–$1/T$ plot for ferrocene with adsorbed ethyl acetate and carbontetrachloride vapours. No conductivity peak/hump has been observed for adsorption of iso-propanol and benzene vapours. Fig. 6 shows that in the case of iso-propanol and benzene vapour, the value of E in the lower temperature region is lower than that of E in the higher temperature region. For the material with adsorbed ethyl acetate and carbontetrachloride vapours, at temperatures lower than the temperature where the hump/peak appears, the value of E could not be evaluated due to a limited number of data points in the linear portion of the curve. At higher temperatures, except for ethanol vapour, in the case of all other vapours the value of activation energy is smaller than the activation energy of pure material (1.35 eV). The calculated values of E_H are presented in Table II, in which values of I_S observed for adsorption of

TABLE I The values of I_S, I_{max}, T_{max}, E_L and E_H for different applied mechanical pressures upon a ferrocene cell with adsorbed ethanol vapour at 5.33 kPa vapour pressure

Pressure (MPa)	I_S (10^{-12} A)	I_{max} (10^{-11} A)	T_{max} (K)	E_L (eV)	E_H (eV)
0	5.3	1.02	297.25	1.65	1.22
0.16	0.76	0.158	297.25	1.89	1.69
0.30	0.24	0.10	298.50	1.88	1.73
0.42	0.555	0.071	299.60	0.76	1.61
0.97	0.18	0.042	298.50[a]	1.35	2.28
1.94	0.52	0.10	298.50[a]	0.70	2.05
2.77	0.765	0.15	298.50[a]	0.50	1.93

[a] Instead of the main peak, a hump appeared in these cases around this temperature.

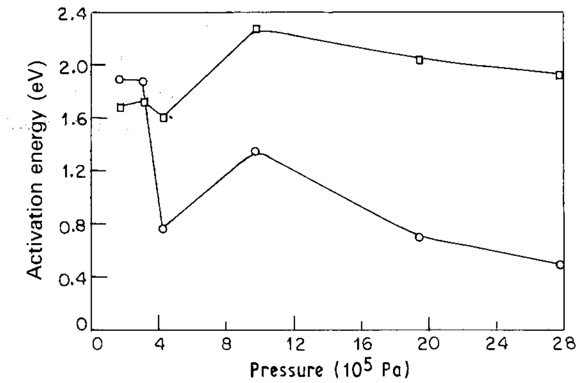

Figure 5 The plots of (○) E_L and (□) E_H versus pressure for ferrocene with adsorbed ethanol vapour at 5.33 kPa.

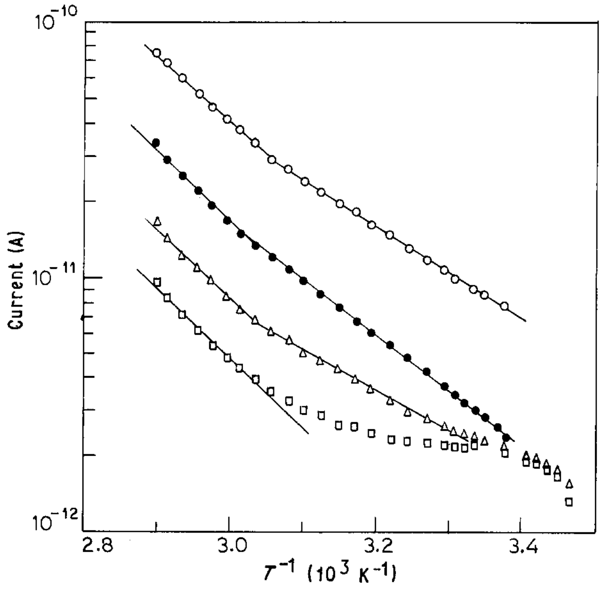

Figure 6 The plots of current versus $10^3/T$ for different ferrocene cells under the same pressure of 0.16 MPa, adsorbed with different vapours at 5.33 kPa vapour pressure. (○) iso-propanol; (●) benzene; (△) ethyl acetate, and (□) carbontetrachloride.

TABLE II The values of I_S and E_H for adsorption of different vapours (at 5.33 kPa vapour pressure) on ferrocene under applied mechanical pressure of 0.16 MPa

Vapours used	Ionization potential (eV) [17]	Electron affinity (eV) [18]	Dielectric constant at 298 K [10, 19]	I_S (10^{-12} A)	E_H (eV)
Benzene	9.24	2.46	2.274	1.75	1.05
Ethyl acetate	10.11	–	6.02	1.45	1.09
Ethanol	10.5	0.594	24.30	0.76	1.69
Iso-propanol	10.79	0.672	18.3	1.70	1.10
Methanol	10.85	0.377	32.63	1.20	–
Carbon tetrachloride	–	1.215	2.228	5.80	0.99

different vapours are also shown together with the values of ionization potential, electron affinity and dielectric constant of the vapours used. The E_H values evaluated characterize the dependence of the adsorbent–adsorbate complex system upon the nature of the adsorbates under constant pressurization.

The effect of pressure on the conductivity of semiconducting powdered materials have been reported by several authors [8, 20–24]. The conductivity of organic materials generally increases with increasing pressure, but this trend is reversed in some materials at higher pressures, leading to a steady decrease in conductivity [20]. The theory of Pohl *et al.* [21] and Boon's random field model [22] predicted that the logarithm of conductivity should be proportional to the square root of the applied pressure. However, Boon [22] has mentioned that for materials of lower dielectric constant, the logarithm of conductivity may be proportional to the applied pressure, as has been observed by him in the case of some amorphous organic semiconductors up to 200 kbar. Thus our observation (Fig. 2) of a linear relationship (except for the initial portion) of logarithm of conductivity with applied pressure agrees with Boon's prediction [22] for a pressure-dependence of conductivity in the case of materials with lower dielectric constant. The formation of charge-transfer (CT) complexes [25] may be one possible reason behind the observed results. It is known that the energy of the lowest charge-transfer absorption band decreases gradually with initial increasing pressure and ultimately it attains almost a saturation value against further increasing pressure [26]. Again, as the semiconduction activation energy of a solid CT complex is linearly related [11] to the energy of the lowest charge-transfer absorption band of the solid CT complex, in favour of formation of CT complexes, a similar change in semiconduction activation energy with pressure is expected. However, our results (Fig. 5) do not agree with this prediction. Again, in the case of the formation of CT complexes under a particular pressure, the current enhancement (i.e. saturation current, I_S) should show a linear relationship with ionization potential or the electron affinity of the vapours used [10]. Our results (Table II) do not show such a relationship, which excludes the possibility of formation of CT complexes. If the conductivity change in ferrocene with adsorbed vapours and under moderate pressure is due to physical mixing of vapours with solid molecules, a relationship between I_S and dielectric constant of the vapours used is expected. Rosenberg [27] proposed that enhancement in electrical conductivity with a simultaneous decrease in activation energy of hydrated proteins are associated with the increase in effective dielectric constant of the material in the adsorbed state. Such a relationship has not been found to exist between the saturation current value, I_S, after pressurization (and also activation energy) in the adsorbed state and the dielectric constant of the corresponding vapours used (Fig. 7 and Table II).

The activation energy, E, in Equation 1 can be written as [24]

$$E = I_P - E_A - 2P \qquad (2)$$

where, in the case of intrinsic conduction, I_P and E_A are the ionization energy and electron affinity of a molecule in the gas phase; P is the polarization energy of a crystal by a single charge on one molecule [24]. Batley and Lyons [24] have pointed that Equations 1 and 2 are also valid for the extrinsic conduction, provided that carriers of one species are free to move independently of those of the other types. Then I_P and E_A require different but analogous interpretations [24]. The decrease in the volume at high pressure will produce an increase in the polarization energy, P, and hence a decrease in E. Thus the E values obtained from the slopes of the conductivity–$1/T$ plots under pressure (Fig. 4) in the high-temperature region (shown in Table I) should have a linear relationship with pressure applied. But no such relationship has been observed, as is evident from Fig. 5.

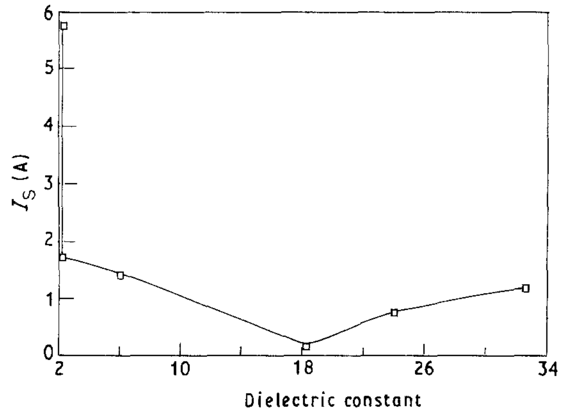

Figure 7 The plots of I_S versus dielectric constant of the vapours used, for ferrocene under the same pressure (0.16 MPa).

At high pressures, on contact of adsorbate vapour molecules with the adsorbent, one may expect a highly specific surface phenomenon [28]. It has been reported that antiprismatic arrangement and the rotational disorder of the cyclopentadienyl rings, as well as the disordered crystal structure, may provide favourable conditions for ferrocene molecules to accommodate themselves to a variety of structures under pressure [29–31]. It is also reported that a phase transition occurs in ferrocene under the influence of external parameters such as temperature [32] and pressure [8]. An adsorption-induced reversible structural phase transition in ferrocene at suitable temperatures has also been established recently [15]. Thus on the basis of this evidence we suggest that ferrocene in the vapour-adsorbed state undergoes a phase transition, which is modified by both temperature and pressure, and this is manifested in the unusual variation of conductivity with temperature under different values of pressure. The externally applied mechanical pressure influences the binding properties of the adsorbed vapour molecules and their physical state. The molecular properties of the adsorbates occupying the strategically important positions along the charge transport routes in the ferrocene molecular matrix is a function of both pressure and temperature, and may be changed under pressure due to phase transition in ferrocene affecting the conductivity drastically. At higher pressures the decrease in the conductivity in the vapour-adsorbed state in the low-temperature region is possibly due to the reorientation of the adsorbed vapour molecules along the charge transport routes.

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