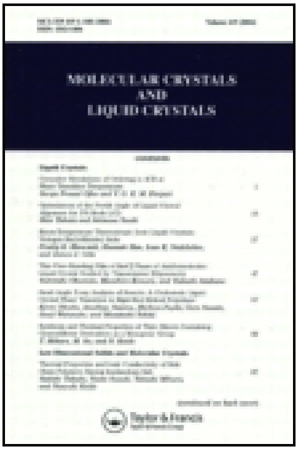

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PREPARATION AND ELECTRICAL CONDUCTION OF OCTADECANOYL FERROCENE ORGANIZED IN LANGMUIR-BLODGETT FILMS

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Octadecanoyl ferrocene has been successfully organized in Langmuir-Blodgett (LB) films. For characterization, electronic absorption spectra of these films have been studied and compared with those in solution. Electrical conductivity of these films has been measured under different experimental conditions. The voltage dependence of current has suggested the existence of a single discrete level-type trap distribution in this organized film. From the temperature dependence of conductivity studies, it appears that the band theory can predict the transport phenomena of these LB films, and the material under study is extrinsic in nature.

Keywords: octadecanoyl ferrocene; LB films; electrical conductivity; optical properties

INTRODUCTION

Applications of ferrocene, the first synthesized organometallic sandwich compound, have been well recognized in various technological fields [1]. Few common applications of ferrocene can be noted here, e.g., it has been used (1) efficiently as a mediator in various electron transfer processes [2], (2) in the development of biosensors [2], (3) for the synthesis of new materials [3] of higher electrical conductivity from poly(vinylidine

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*Corresponding author. Fax: 81-298-61-6303; E-mail: bera-rn@aist.go.jp chloride), (4) for the preparation of the charge transfer compounds with organic solids [4,5], etc. In recent years the studies on the electrical properties of ferrocene and its derivatives using powder sample with sandwich-type cell technique have presented some interesting results [6–8]. So it was thought worthwhile to study the electrical properties of ferrocenes with thin films.

But ferrocene and most of its derivatives are not suitable for preparation of thin films by thermal evaporation using vacuum coating unit. In this context preparation of Langmuir-Blodgett (LB) film from ferrocenes has also been fraught with considerable difficulties, particularly because these materials do not generally form a stable monolayer at air-water interface even when these materials are mixed with long chain fatty acids. This has prompted a number of research groups [9–14] to direct efforts towards developing specially substituted ferrocene derivatives, which could be amenable to form a stable monolayer under pressure at water-air interface. The LB technique offers a valid tool for preparation of molecular architecture in a controlled way—by means of this technique monomolecular layers are subsequently deposited onto substrates of different nature, making it possible to control the structure of a material at the molecular level [15]. In this paper we report the lifting of octadecanoyl ferrocene from water subphase to form LB films and their optical characterization. In addition, results of the electrical properties of the LB films are also reported. Though the preparation of LB films with some different amphiphilic ferrocenes are reported [9–14], the experimental studies of electrical properties of ferrocene derivatives organized in LB films are still significant because of the scarcity of such data, as most of the reported studies have not been associated with the detail electrical measurements in LB films.

EXPERIMENTAL

Octadecanoyl ferrocene (ODFcH), whose molecular structure is shown in the inset of Figure 1, was obtained from Prof. B. C. Ranu, Department of Organic Chemistry, IACS, as a gift and was used after further purification by crystallization. The synthesis and purification of sample can be found in Ranu et al. [16]. A LB alternate layer trough made of poly(tetrafluoroethylene) (Model 4 Joyce Loeble, Newcastle-Upon-Tyne, UK) was used for deposition of the monolayers. A filter paper Whilhelmy plate attached to a microbalance, which in turn was interfaced to a microcomputer, maintained constant pressure with an accuracy of 1 mNm^{-1} over a very long time. Triple distilled water further purified by a milli-Q plus water purification system was used as a subphase. The resistivity of water

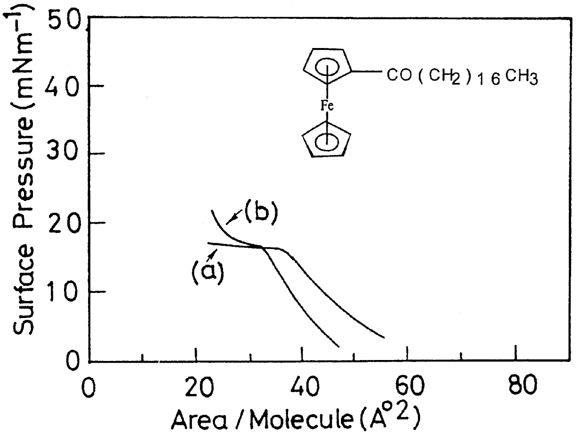

FIGURE 1 Plots of surface pressure versus area per molecule isotherms in the case of (a) octadecanoyl ferrocene and (b) octadecanoyl ferrocene : stearic acid (1:1 molar ratio). Inset shows the molecular structure of octadecanoyl ferrocene.

used was 18.2 MΩ cm. ODFcH was dissolved in spectroscopic-grade chloroform (E. Merck, Mumbai, India) to a concentration of 1 mg ml^{-1} and spread on the clean water surface of the Langmuir trough. Temperature of the trough water was maintained ca. 20°C. After waiting for about 20–30 min (depending on the amount of solution) for the solvent to evaporate, the film was slowly compressed at a rate of 2 cm^2 min^{-1}. The isotherm data of surface pressure versus area per molecule was collected by an IBM PC and analyzed with the software from Joyce Loebl (Newcastle-Upon-Tyne, UK). Y-type deposition of the LB films was achieved by allowing the substrate to dip with a speed of 5 mm min^{-1} with a drying time of about 30 min. The film was transferred on ultra clean solid substrate (glass or quartz) at a constant surface pressure, 14 mNm^{-1}. Transfer ratio was found to be almost equal to unity (0.94 ± 0.04). For surface pressure measurements and lifting of films, freshly prepared sample solution was used. The film was kept inside a desiccator under vacuum for 24 h before any type of measurement.

Electronic absorption spectra of the LB films deposited on quartz slides were recorded with the help of a Shimadzu 210 UV-vis spectrophotometer, and the emission spectra of the LB films were recorded by a Perkin Elmer MPF-44A spectrophotometer. For electrical measurements the substrate with LB films was placed in a specially designed conductivity chamber [6–8] made of brass and fashioned with teflon. Temperature of the chamber was controlled by a proportional temperature controller (model RTE 110, Neslab Inst. Inc., Newington, New Hampshire, USA) and was measured by using a copper-constantan thermocouple with the help of a digital millivoltmeter. The electrical current was recorded by a programmable electrometer (model 617, Keithley Inst. Inc., Cleveland, Ohio, USA). For the measurement of current-voltage (I-V) characteristics, voltage up to 100 volts was applied from the voltage source of the above-mentioned electrometer, and for higher voltages a DC Power Supply (model PS 2500) of Hoefer Scientific Inst. (San Fransisco, California, USA) was used. Before the conductivity measurements, desorption of water vapor or any preadsorbed (if adsorbed during film preparation) vapors from the sample cell was ensured by repeated heating and cooling treatments of the cell, initially in vacuum and finally in dry nitrogen gas atmosphere. All the electrical measurements were performed in dry nitrogen atmosphere. The details of the experimental set-up for electrical measurements can be found elsewhere [6–8]. For the electrical measurements, before deposition of LB films, the end portions of the glass slides were metallized by the thermal evaporation of aluminum with the help of a mask, and after deposition of the LB films electrical contacts were made from the aluminum using silver paste. Electrical measurements (surface conductivity) were done by using two-probe technique; by varying the distance between the electrodes, it has been established that the contact resistances were negligible.

RESULTS AND DISCUSSION

Figure 1 gives the surface pressure versus area per molecule isotherms of (a) pure ODFcH and (b) ODFcH/stearic acid (1:1 molar ratio), which exhibits a relatively better surface pressure versus area per molecule isotherm. The area-time plots (not shown) for both cases are also shown to be very stable, and this is consistent with the good transfer ratio obtained during film deposition.

Figure 2 shows the electronic absorption spectra of the LB films deposited on a quartz substrate along with the absorption spectra in ethanol solution with concentration of the order of 10^{-5} (M). The absorption spectrum of ODFcH in ethanol solution show sharp and distinct peaks at 226, 269, 339, and 455 nm, respectively. The absorption spectrum of pure ODFcH in LB films (27 layers) corresponds to the peaks more or less in the same positions but the peaks are relatively broad compared to the corresponding peaks in solution phase. No electronic emission spectrum has been observed for ODFcH organized in LB films either at room temperature or at liquid nitrogen temperature.

The electrical properties of 51-LB layers of pure ODFcH on plain glass plate have been studied. Figure 3 shows the I-V characteristics at different temperatures. In the lower voltage region the I-V characteristics show good linear behavior with slope close to unity in log-log plot, indicating

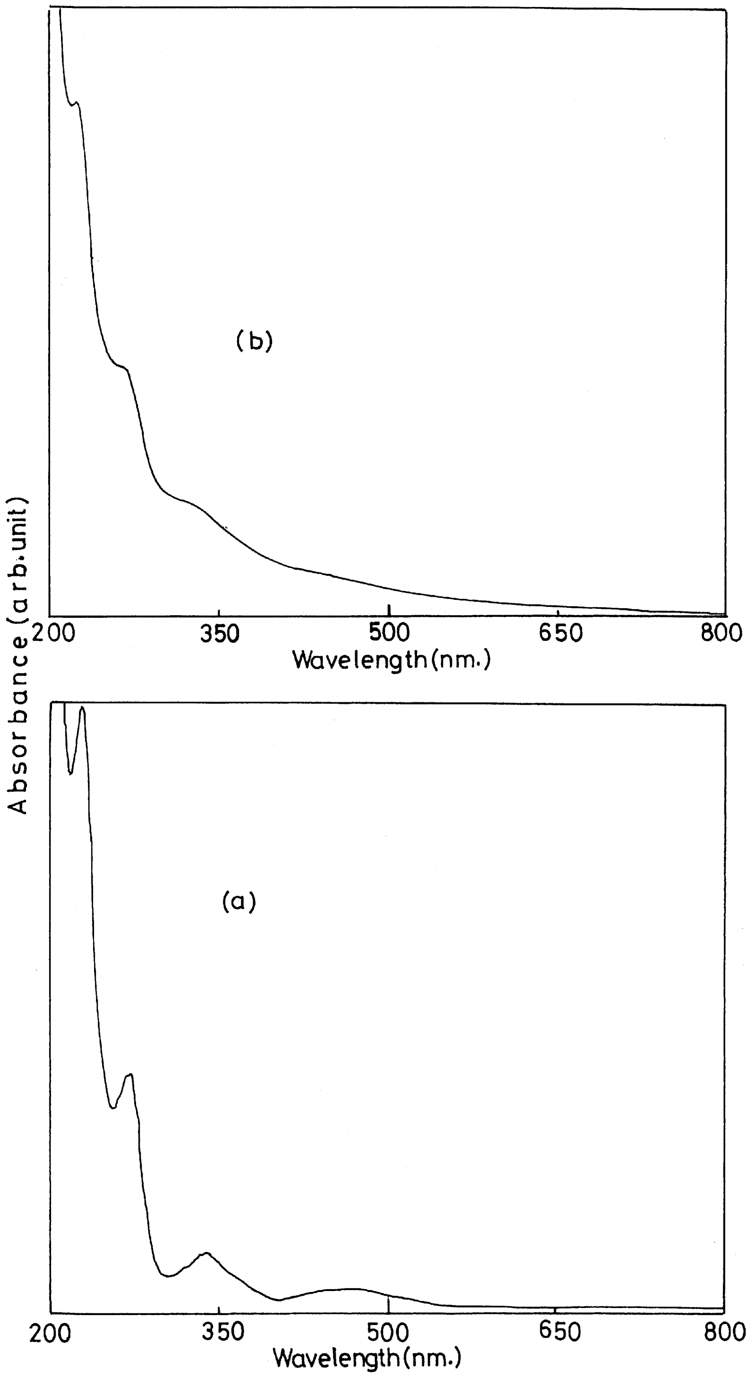

FIGURE 2 Absorption spectra of octadecanoyl ferrocene, (a) in ethanol solution with concentration of the order of 10^{-5} M and (b) in 27 layers of LB films.

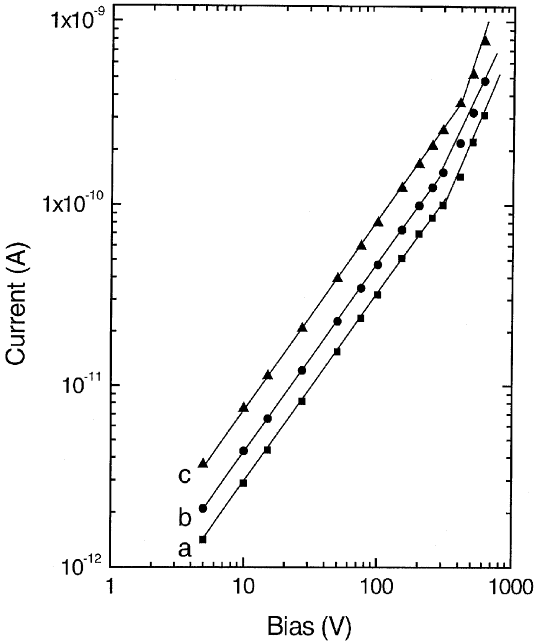

FIGURE 3 Plots of current against bias voltage in the case of LB film (51 layers) of octadecanoyl ferrocene at different temperatures: (a) 295 K, (b) 298 K, and (c) 303 K, respectively.

the Ohmic nature of current in this region. In the higher voltage region, space-charge-limited current (SCLC) has been observed. In SCLC region the currents (I_{SCLC}) are approximately proportional to the square of the applied voltage (V) in these LB films. The range of biases over which this power law has been inferred is not so large because we could not apply much higher voltage in our experimental system. The observed power law ($\mathbf{I}_{SCL} \propto \mathbf{V}^2$) in the SCLC region indicates the single discrete level type of trap distribution [17] in this ferrocene derivative organized in LB films. The single discrete level type of trap distribution has also been observed in the case of some other ferrocene derivatives studied with powder sample using sandwich-type cell technique [18]. The crossover voltage (V_t) at which the current converts from Ohmic to space-charge-limited behavior can be expressed by the relation [19]

$$\mathbf{V}_t \propto \mathbf{L}^2 \tag{1}$$

where **L** is the distance between the electrodes. We also obtained the same relationship for $\mathbf{V}_t$, which adds further support in favor of the SCLC in higher voltage region though the range of bias over which SCLC has been observed is small. At a temperature of 303 K, $\mathbf{V_t}$ was found to be 400 V. With increase of film temperature this value of $\mathbf{V_t}$ shifts slightly towards the higher values for a fixed **L**. The increase in $\mathbf{V_t}$ with temperature as observed in the present experiment is due to the increase of bulk carrier density as proposed by Rose [20]. It may be mentioned here what Nakahara et al. [11] observed, that the logarithmic of electrical current is proportional to the square root of the applied voltage in the case of a long-chain ferrocene derivative (N-n-octadecylferrocenecarboxamide) organized in LB films. But they measured the current in a direction perpendicular to the plane of the film by sandwich-type cell technique, while we measured the surface conductivity of the LB films with different ferrocene derivative.

We have studied the temperature dependence of electrical conductivity. The electrical conductivity in organic as well as organometallic materials and charge-transfer complexes is usually expressed by the Arrhenius relation [21],

$$\sigma = \sigma_0 \exp\left(-\frac{\mathbf{E}}{2\mathbf{kT}}\right) \qquad (2)$$

where σ is the specific conductivity at any absolute temperature **T**, σ_0 is the pre-exponential factor, and **E** is the activation energy. Experimentally **E** is obtained from the slope of the linear plot of log (σ) or log (I) vs. 1/**T** (I is the semiconduction current at temperature **T**). The variation of the logarithm of the current against the reciprocal of the temperature for the LB films of ODFcH is shown in Figure 4. This plot as well as the plots of log (I) against $\mathbf{T}^{-1/2}$, $\mathbf{T}^{-1/3}$, and $\mathbf{T}^{-1/4}$ (not shown) shows linearity. The standard error coefficients for the plots (in the ohmic region) against $\mathbf{T}^{-1}$, $\mathbf{T}^{-1/2}$, $\mathbf{T}^{-1/3}$, and $\mathbf{T}^{-1/4}$ are 0.02788, 0.03167, 0.0357, and 0.03986, respectively. But error coefficient must be minimum for the best fitting. So it is evident that for $\mathbf{T}^{-1}$ plot, the fit is better than any other plot. From our experimental results, it appears that band theory can predict the transport phenomenon in this organized ODFcH film. The activation energy in both Ohmic and SCLC region for this organized film has been calculated from the liner plots of Figure 4. For the present experiment, activation energy for both ohmic and SCLC region are the same and its value is 1.65 eV, indicating the extrinsic nature [19] of the material in thin film. The extrinsic nature has also been observed in the case of ferrocene [18] studied with powder sample. It is interesting to note that the extrinsic nature has not been observed for any other derivatives studied so far in our laboratory [18] such as ferrocene carbaldehyde, acetylferrocene, and ferrocenedicarboxylic acid.

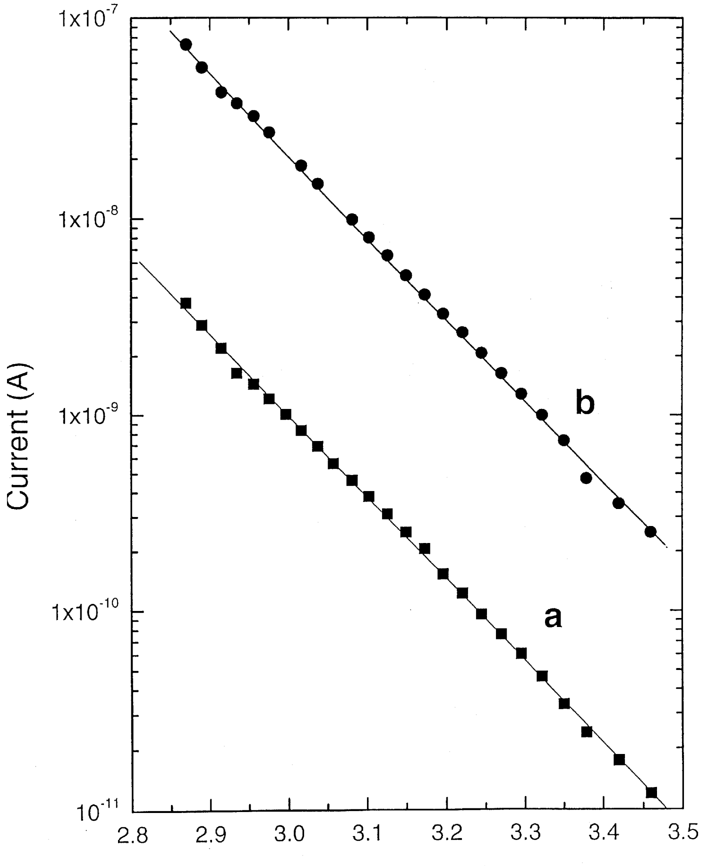

FIGURE 4 Plots of current against reciprocal of temperature in the case of LB films (51 layers) of octadecanoyl ferrocene: (a) 27 V bias and (b) 500 V bias.

CONCLUSIONS

Pure octadecanoyl ferrocene forms stable monolayers at water-air interface under pressure. The material has been successfully organized in LB film. The electronic absorption spectrum of this material in LB film corresponds to the peaks more or less in the identical positions with that of solution. No electronic emission spectrum has been observed of this LB film either at room temperature or at liquid nitrogen temperature. Results of electrical measurements suggest the existence of single discrete level-type trap distribution in this organized ferrocene derivative. Band theory can predict the mechanism of conduction, and the material under study is extrinsic in nature.

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