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Electrical conductivity of aromatic hydrocarbon–iodine charge transfer complexes

Part I *Anthracene–iodine system*

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The electrical conductivity of the anthracene–iodine charge transfer complex has been thoroughly investigated in the temperature range 288–338 K for samples of different molar ratios of anthracene and iodine (1 :1, 1 :1.5, 1 :2, 1 :2.5, 1 :3, 1 :3.5, 1 :4, 1 :4.5, 1 :5, 1 :5.5 and 1 :6). It has been found that the complex having a molar ratio = 1 :5 possesses the highest room-temperature conductivity of $3.18 \times 10^{-2}\ \Omega^{-1}\,\mathrm{cm}^{-1}$. Powder X-ray analysis of these samples has revealed the amorphous nature of these complexes. The occurrence of a phase transition around room temperature has been attributed to the change of the complex from crystalline to amorphous in nature. From the present investigations, it is clearly seen that a weak complex of anthracene–iodine has been formed. Although there is enhancement in the electrical conductivity by the addition of iodine into anthracene, these electrical parameters tend to be affected by undesirable features such as instability at ambient conditions.

1. Introduction

It has already been established that polycyclic aromatic hydrocarbons with halogens form molecular complexes of charge transfer type in the solid state, exhibiting very high electrical conductivity [1–4]. Much work has been done with the iodine complexes of perylene, phenothiazine, violanthrene, etc., but no extensive study has been done with complexes of anthracene, except for a report by Matnishyan *et al.* [5], which deals only with the electrical conductivity. A study of the stability and nature of the complexes of anthracene with iodine was therefore undertaken and their suitability and applicability in energy conversion systems was examined. Efficient all-solid-state batteries with charge transfer complexes (CTCs) as cathodes have already been fabricated [6, 7] and hence the present investigation on anthracene–iodine CTC defines the viability of the complex for use as cathode material in solid-state batteries.

2. Experimental procedure

2.1. Materials

Research-grade chemicals of anthracene, iodine and graphite powder with 99% purity were used for preparing the samples.

2.2. Complex preparation

The formation of charge transfer complexes by direct mixing in the solid state has already been reported [8]. The same procedure was followed by taking appropriate amounts of anthracene and iodine and grinding together thoroughly in an agate mortar and pestle until a fine shiny powder with dark brown colour was obtained. Complexes with molar ratios of (anthracene: iodine) 1:0, 1:1.5, 1:2, 1:2.5, 1:3, 1:3.5 1:4, 1:4.5, 1:5, 1:5.5 and 1:6 were prepared.

2.3. Electrical conductivity measurements

The apparatus employed in the measurement of electrical conductivity is the same as reported by Suthanthiraraj and Radhakrishna [9]. All the samples were pressed into pellets of 13 mm diameter at a pressure of $3\ \mathrm{ton\,cm^{-2}}$ with graphite layers on both faces to act as electrodes. The temperature dependence of electrical conductivity was studied for four samples with molar ratios 1:1, 1:1.5, 1:2 and 1:2.5 using a Keithley electrometer (Model 614) in the temperature range 288–338 K. In order to analyse the stability of the complex, the room-temperature conductivity was measured every day for all the samples until the value reached $10^{-8}\ \Omega^{-1}\,\mathrm{cm}^{-1}$.

2.4. X-ray analysis and ultraviolet and visible spectrophotometric studies

The prepared complexes were examined by powder X-ray diffraction using a Seifert–Guinier X-ray diffractometer with a CuK_α radiation ($\lambda = 0.154\ 18$ nm) and by ultraviolet and visible spectrophotometry using a Carl–Zeiss UV–VIS spectrophotometer.

3. Results and discussion

Powder X-ray diffraction patterns of the freshly prepared samples with molar ratios of 1:1, 1:3 and 1:5

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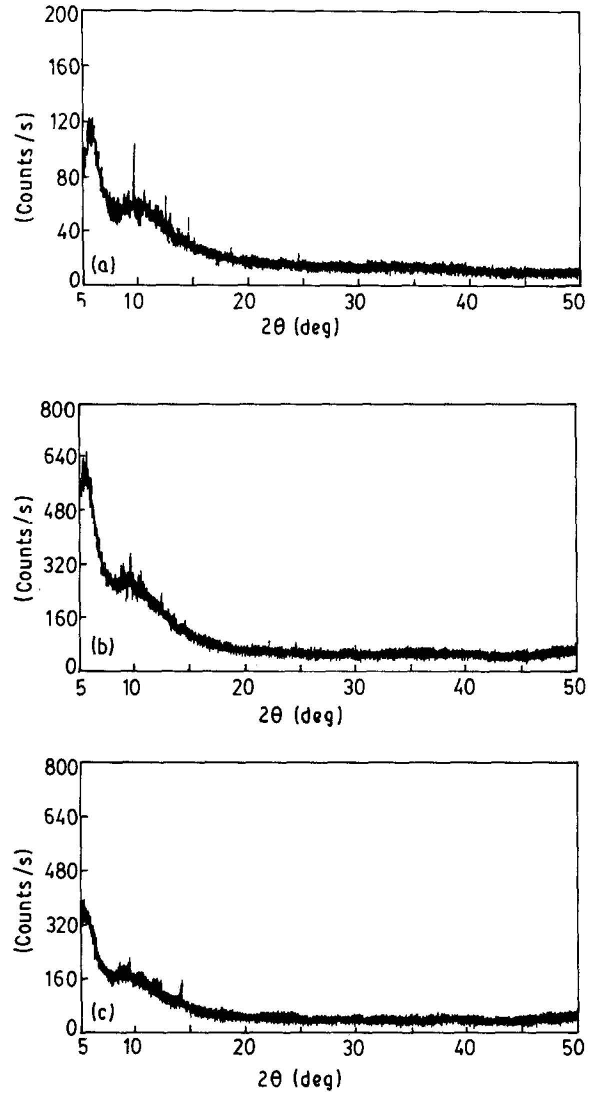

Figure 1 Powder X-ray diffraction patterns of the anthracene–iodine complex with a molar ratio of (a) 1:1, (b) 1:3, and (c) 1:5.

are presented in Fig. 1a–c, respectively. These X-ray patterns exhibit some small peaks around the lower scattering angles indicating that the complex is completely amorphous.

The ultraviolet and visible spectrum of the complexes have two sharp peaks around 356 and 375 nm, indicating the presence of the triiodide ion, I_3^- [10–12], and a stable, broad and featureless band at 504 nm which is a characteristic of the donor–acceptor type complexes. It confirms the formation of CTCs of anthracene with iodine in the present investigation.

The room-temperature electrical conductivity values for all the samples were measured and their dependence on iodine content is shown in Fig. 2. In earlier studies done on other CTCs [13, 14], the conductivity was found to increase with increasing iodine content, and at a particular ratio it reached a maximum and further increase of iodine resulted in a reduction in conductivity. Such a type of variation and dependency of conductivity on iodine content were not noticed in anthracene-iodine complexes. This anomaly may be due to the very weak complex formation between anthracene and iodine. From the stability tests, it was inferred that the complex with 1:5 molar ratio was stable for 6 days while a complex with 1:2.5 composition was stable for 5 days only. The complex with the highest conductivity value of $3.18 \times 10^{-2}\ \Omega^{-1}\,\mathrm{cm}^{-1}$ was also the most stable composition. This indicates that the iodine content is sufficient

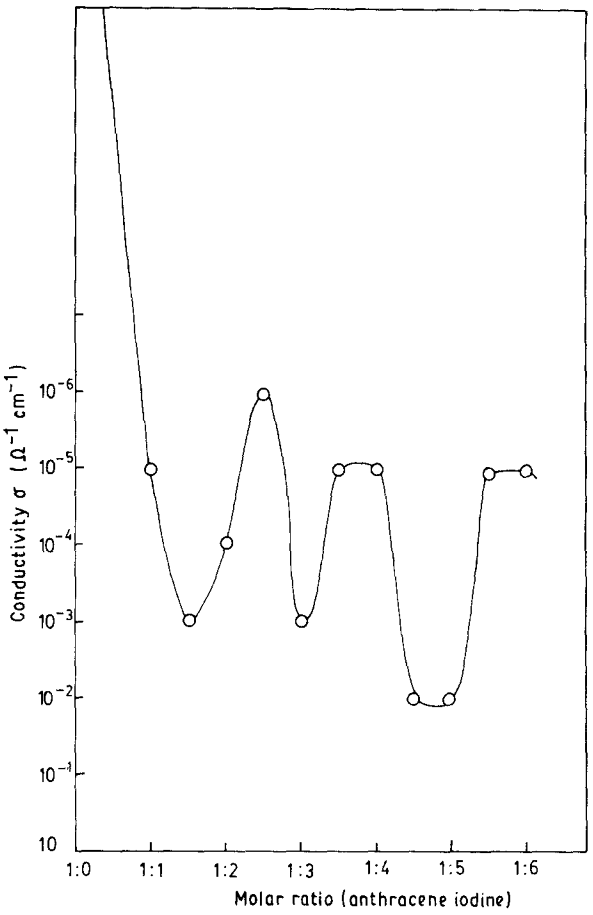

Figure 2 Room-temperature electrical conductivity plotted against the molar ratio in the anthracene–iodine system.

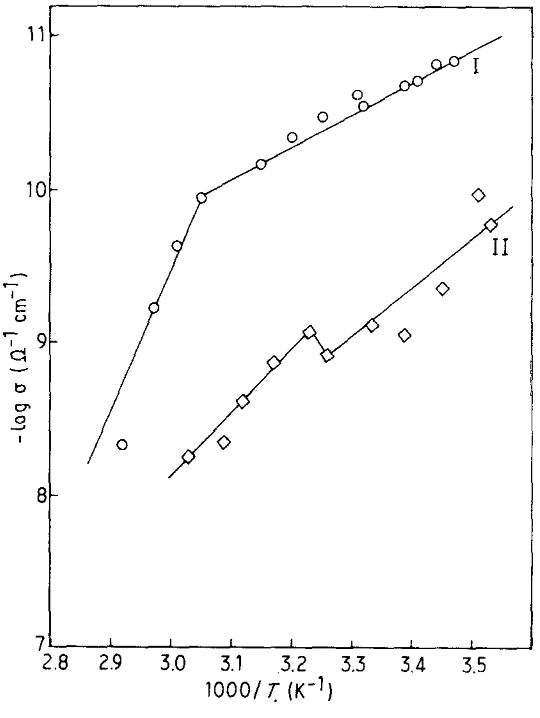

Figure 3 Temperature dependence of electrical conductivity for the anthracene–iodine complex with molar ratios of (○) 1:1 (Sample I) and (◇) 1:1.5 (Sample II).

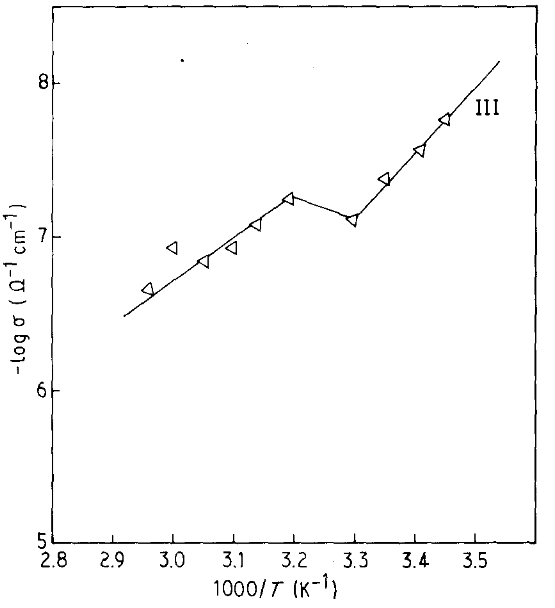

Figure 4 Temperature dependence of electrical conductivity for the anthracene–iodine complex with a molar ratio of 1:2 (Sample III).

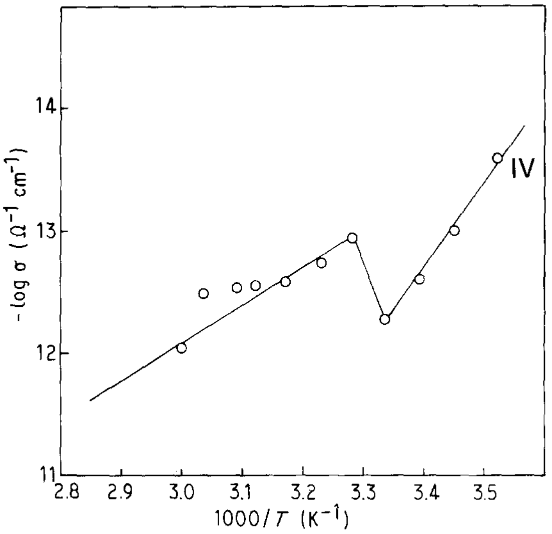

Figure 5 Temperature dependence of electrical conductivity for the anthracene–iodine complex with a molar ratio of 1:2.5 (Sample IV).

in the formation of the adduct with all molecules of anthracene at this molar ratio, 1:5, and in all other samples, iodine molecules were present in some state other than the addition complex [2, 3]; due to this, the complex formation was weak and iodine sublimation was higher, hence the unstable tendency of the complexes. Further, from measurement of electrical conductivity at different temperatures for the samples with molar ratios 1:1, 1:1.5, 1:2 and 1:2.5, a phase transition was observed at around 3–5 °C above room temperature at 305, 307, 308 and 303 K (Figs 3–5), respectively, and this may be due to the complex becoming amorphous from the crystalline nature at this transition temperature.

4. Conclusions

From electrical conductivity studies on charge transfer complexes of anthracene and iodine with different molar ratios, it is concluded that the addition of iodine to anthracene enhances the conductivity from 10^{-12} to $10^{-2}\ \Omega^{-1}\,\mathrm{cm}^{-1}$ and the complex stability studies clearly indicate that only a weak complex could be obtained between anthracene and iodine.

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