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Thermodynamic stability and electrical conductivity of halogen complexes of organic solids

Degraff, Darnel, Ph.D.

City University of New York, 1987

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THERMODYNAMIC STABILITY AND ELECTRICAL CONDUCTIVITY OF HALOGEN COMPLEXES OF ORGANIC SOLIDS

BY

DARNEL DEGRAFF

A dissertation submitted to the Graduate Faculty
in Chemistry in partial fulfillment of the requirements
for the degree of Doctor of Philosophy
The City University of New York

1987

This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

9/23/87
Date

Seymour Aronson
Chairman of Examining Committee

9/28/87
Date

Executive Officer

Supervisory Committee

The City University of New York

ABSTRACT

THERMODYNAMIC STABILITY AND ELECTRICAL CONDUCTIVITY OF HALOGEN COMPLEXES OF ORGANIC SOLIDS

by

DARNEL DEGRAFF

ADVISOR: PROFESSOR SEYMOUR ARONSON

By means of a solid state electrochemical technique, we have measured the Gibbs free energy of formation for a number of charge-transfer complexes of nitrogen-bearing polymers and polycyclic compounds with molecular iodine or bromine. The polymers studied are: aniline black(AB), paracyanogen(Pcy), 2-polyvinylpyridine(PVP), cyclized-polyacrylonitrile(C-PAN), and polyquinoxaline. The polycyclic compounds comprise anthracene, phenazine, phenothiazine, phenanthridine, 1,10-phenanthroline, thianthrene, 7,8-benzoquinoline, indazole, benzotriazole, benzothiodiazole, benzimidazole, and phenanthrene.

The Emf data were obtained using solid state electrochemical cells of the type:

$$(-)Pt/Ag/AgI/I_2(P)/Pt(+)$$

where $I_2(P)$ represents either pure solid iodine or the iodine complexed with the organic solid, P. The results indicate that chemical bonding between iodine and the organic solids is weak. Bonding with bromine is stronger.

The electrical conductivities of these complexes were also measured using the Van der Pauw four-probe technique. The conductivities were found to be in the semiconducting range of 10^{-7} to 10^{-2} $(\text{ohm cm})^{-1}$ with a strong dependence on the halogen content.

Electrochemical experiments were performed which demonstrate that conduction in these systems is primarily electronic.

ACKNOWLEDGMENTS

I enthusiastically express my thanks and my gratitude to my mentor, Professor Seymour Aronson for his guidance, his unlimited patience and his benevolence.

I offer my heartfelt thanks to my family for their support and encouragement, especially to my dear mother, Marie Therese Degraff, for being my inspiration.

I present my sincere thanks to Professor Fitzgerald B. Bramwell who, through his confidence in me, opened the door of opportunity.

My special thanks to my thesis committee, Professors Richard Pizer and Henry Teoh. Prof. Teoh skillfully constructed the apparatus I used for the conductivity measurements.

Also, I would like to thank all the members of the Chemistry Faculty, my colleagues and friends, especially Gardy Cadet, for helping me with the computers, Georgine Francis, Wilner Alceus and Webert Dorestant for moral support.

DARNEL DEGRAFF

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CHAPTER 1

INTRODUCTION

Since 1950, when Mulliken[1] suggested that the intense characteristic absorption in the near ultra-violet of a solution of iodine in benzene may be due to intermolecular charge transfer between a donor(benzene) and an acceptor(iodine), interest in the subject of molecular complexes has greatly increased. Most of the studies done in this area have been in solution[2,3]. It was not until recently that scientists began to show interest in molecular complex formation in the solid state.

One of the most interesting and technologically[4] promising properties of solid organic charge transfer complexes is the ability to sustain electrical conduction. Possible applications for organic conductors are well known. These include, to name a few, usage as cathodes in solid-state pacemaker power cells, photovoltaic devices and pressure transducers. Despite some practical problems, conducting organic complexes have persistently been viewed as potential replacements for materials in short supply[5]. It is however important to point out that despite the rapid pace of experimental developments in the field of organic semiconductors, complete theoretical understanding regarding transport properties and prediction of new conducting systems is lacking.

In our investigation of organic complex systems, our effort was geared toward discovering new organic molecules and polymers capable of forming complexes with iodine or bromine and evaluating their thermodynamic stability and electrical conductivity.

CHAPTER 2

EXPERIMENTAL METHODS

2.1 Chemicals

Anthracene, phenazine, phenothiazine, phenanthridine, 1,2,4,5-tetraminobenzene tetrahydrochloride, 2,5-dihydroxybenzoquinone, thianthrene, 1,10-phenanthroline, 7,8-benzoquinoline, indazole, benzotriazole, phenanthrene, benzimidazole, and benzothiodiazole were purchased in the highest commercial grades available from Aldrich Chemical Co. of Milwawkee, Wisconsin.

Laboratory grade resublimed iodine and silver iodide were obtained from Fisher Scientific Company in Fair Lawn, New Jersey; and bromine from J.T. Baker Chemical Co. in Phillipsburg, NJ. Silver powder and silver bromide were purchased in high purity from Johnson Matthey Inc. Seabrook, New Hampshire. Sp-1 grade graphite powder was obtained from The National Carbon Co.(Union Carbide).

Aniline black (AB) was synthesized by the oxidation of aniline hydrochloride in aqueous $KClO_3$[6]. 15 grams of aniline hydrochloride was dissolved in 100 ml of water and added slowly to 100 ml of a hot aqueous solution of 1M $KClO_3$ containing 100 mg of $CuCl_2$. The mixture was stirred at the boiling temperature for 90 minutes. The crude material was filtered and washed several times with hot water. After drying at 105°C, the product was extracted with benzene in a

Soxhlet's apparatus for 48 to 60 hours. The black residue was dried in vacuum at room temperature for a minimum of 24 hours.

Paracyanogen (Pcy) was prepared by the polymerization of mercuric cyanide in vacuum. About 5 grams of $Hg(CN)_2$ was placed in a bottle-shaped glass tube. At first, as in reference (7), the tube was evacuated, sealed and heated to 440°C. But unfortunately, after a couple of hours, the tube shattered. This explosion was probably due to pressure built up from insufficient evacuation and/or the vapor pressure of mercury which formed as a product. To avoid this problem, we heated the system under pumping vacuum for 24 hours. The mercury metal was collected in a dry ice-acetone trap. A dark-brown, fluffy product was recovered from the reaction tube.

Polyquinoxaline was prepared in accord with reference (8) as follow: to a polyphosphoric acid solution prepared from 31 grams of phosphorus pentoxide and 35 grams of phosphoric acid was added 0.5776 grams of 1,2,4,5-tetraminobenzene tetrahydrochloride dissolved in 5 grams of phosphoric acid. The temperature of the mixture was raised to 140°C to allow complete displacement of HCl. When the evolution of gas ceased, 0.2803 grams of 2,5-dihydroxy-p-benzoquinone dissolved in 5 grams of phosphoric acid was added to the reaction mixture. The temperature of the reaction mixture was raised to 180°C and the reaction allowed to proceed for 6 hours. At the conclusion of the reaction, the cooled reaction mixture was added slowly to 500 ml of water. The finely divided black precipitate was washed twice with 50 ml of water, three times with 50 ml portions of a 15% ammonium carbonate solution and finally twice with 50 ml of water. The polymer was dried at 180°C in vacuum over phosphorus pentoxide.

2-polyvinylpyridine (2-PVP) and cyclized-polyacrylonitrile (c-PAN) were available from previous work in our laboratory[5].

2.2 I_2 or Br_2 Vapor Absorption

Since the feasibility of this work is based on the ability of the organic solids to react with the halogen, preliminary experiments were conducted to see whether the organic substances are capable of absorbing iodine or bromine. We used the apparatus depicted in Figure (1) below. A weighed sample of the substance of interest is placed in a vial above a sufficient amount of solid iodine. The system is evacuated and left in an oven for 48 hours at 90°C. The only contact between the two substances occurs through the iodine vapor. The amount of iodine absorbed by the organic solid is calculated by weight difference.

Specific I_2 to organic substance mole ratios were prepared by mixing appropriate amounts of the halogen and organic substance in an evacuated and sealed glass tube. The sample mixture was annealed at 90°C for 48 hours.

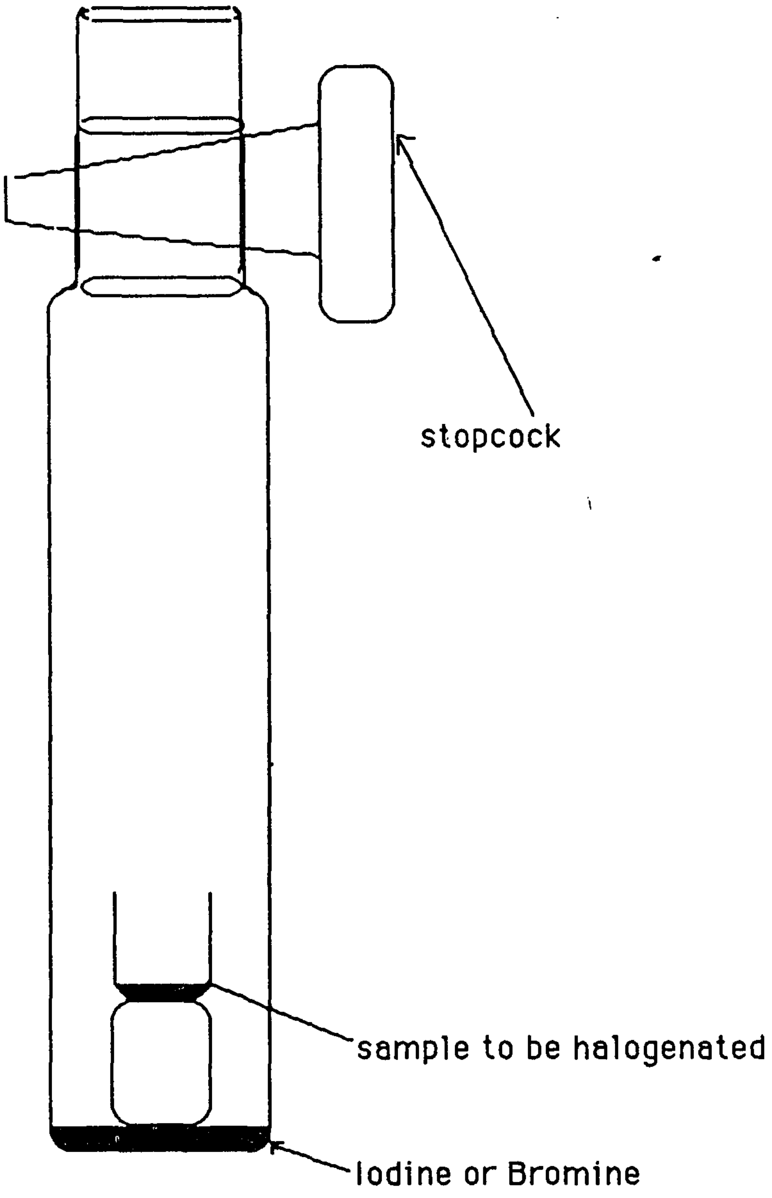


Figure 1. Apparatus used for I_2 or Br_2 vapor absorption.

The apparatus in Figure (1) was also used for bromine absorption but at room temperature, since the vapor pressure of bromine is sufficiently high at that temperature. To obtained specific bromine to organic substance mole ratios, the reaction was stopped at calculated time intervals and the sample mixture was weighed. Those substances which either did not take up iodine or formed mushy or liquid solutions were not useful and, therefore, were not further investigated. These were 7,8-benzoquinoline, indazole, phenanthrene and benzothiodiazole.

2.3 Apparatus

The infrared spectra were obtained on potassium bromide pellets using a Perkin-Elmer model 267 infrared spectrometer.

Electrical conductivity measurements on the iodine complexes were made by the four probe Van der Pauw technique[10,11]. Samples were pressed at 18,000 atm. pressure using a 30 ton pellet press Model M-30. The pellets were in the form of discs of uniform thickness, 0.1 cm, and 1.3 cm in diameter. The conductivity apparatus used is shown in Figure (2). The pellet is symetrically placed under the four thin platinum-coated copper probes, where contact is made at the periphery. Currents ranging from 0.1 to 50 microamperes were passed through points (a)-(b) using a power supply Model 5005T from Power Designs Inc., Westbury, NY. The corresponding voltages were measured at (c)-(d) with a Keithley Model 160 digital multimeter. An additional Keithley multimeter (A) was put in the circuit to measure the current at (A). The conductivity σ, was calculated by the following relationship,

$$\sigma = (\ln 2/t\pi)(I/V) \qquad (1)$$

where V and I are the measured voltage and current respectively, and t is the pellet thickness.

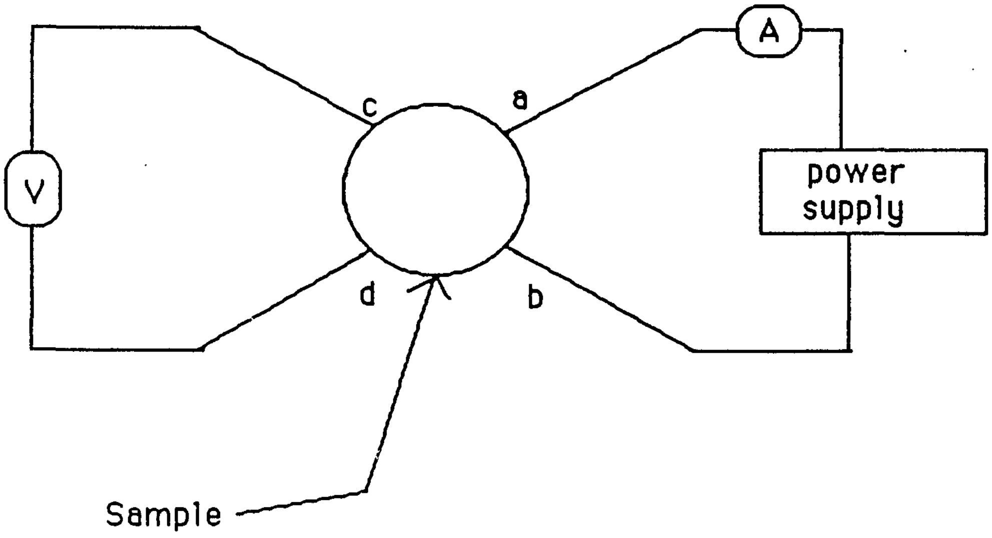


Figure 2. A sketch of the apparatus used for conductivity measurements of the I_2 complexes.

The conductivity of the bromine complexes was calculated from equation (2) below by measuring the resistance, R, of rod-shaped pellets, pressed in a Parr pellet press, 0.25 cm in diameter, using a Keithley Model 160 digital multimeter and the apparatus shown in Figure (3).

$$\sigma = (L/A)(1/R) \qquad (2)$$

L and A are the length and cross-sectional area of the pellet, respectively.

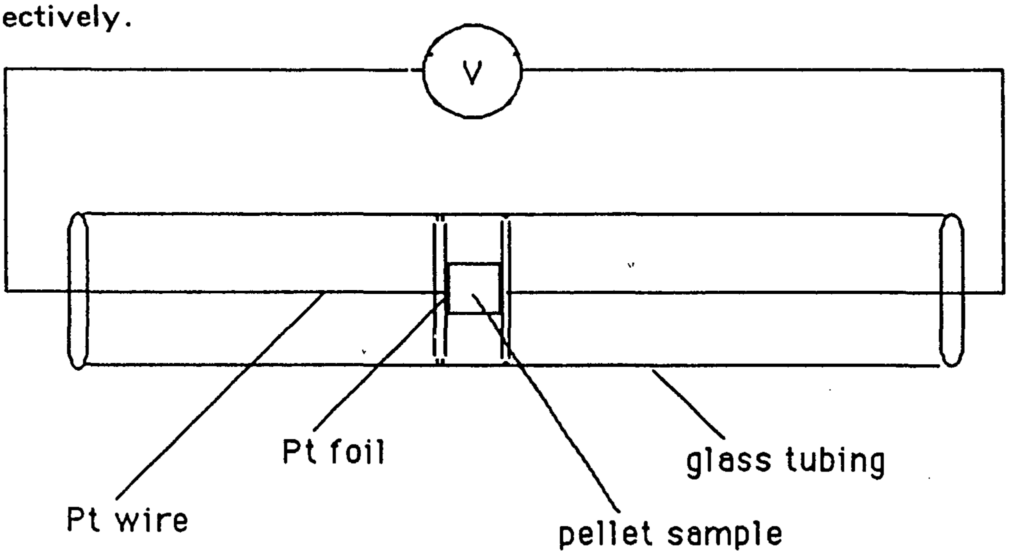


Figure 3. A schetch of the apparatus used to measure the conductivity of the Br_2 complexes.

The experimental facilities available did not permit the application of the Van der Pauw method for the conductivity measurements of the complexes of bromine. At the high pressure required for producing suitable pellets, bromine was released significantly, changing the bromine content of the pellets.

For the Emf measurements, the cell was prepared as follows: using a Parr pellet press, a layer of the appropriate electrolyte was compressed on top of an already pressed silver powder disc in a cylinder of 0.6 cm in bore diameter and finally the complex, uniformly mixed with graphite, was compressed on top of the electrolyte layer. Graphite in the cathode serves as an inert electrically conducting medium. However, the bromine complexes were not mixed with graphite due to possible reaction of the two[12]. Figure (4), below, shows a schematic of the cell used for the Emf measurements made at room temperature with a Keithley 160 digital multimeter. Readings on a given sample were continued for about 20 minutes until a steady value was reached. It was noted that for the systems with limited iodine solubility, i.e. those which formed two-phase regions, an equilibrium Emf value was quickly reached within the first two minutes of the measurement and remained steady. However, those systems which formed a continuum of solid solutions showed larger Emf fluctuations and thus took longer before a steady Emf value was reached. The Emf values were reproducible within ±10 mv for different batches of samples of the same composition.

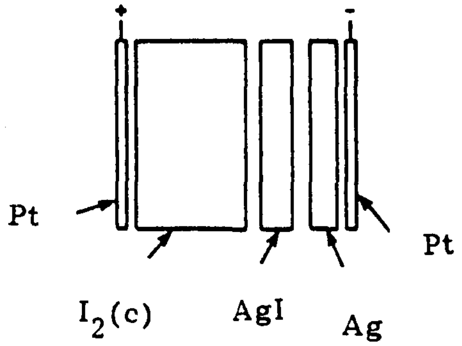


Figure 4. Cell for electrochemical measurements on solid samples

2.4 Analysis and Characterization

Elemental analysis of aniline black was performed by the Swarzkoff Microanalytical Laboratory of Woodside, NY. The composition was found to correspond to the monomeric formula $C_{12}H_8N_{1.8}$.

Infrared analysis of a powder sample of aniline black in KBr showed the following absorption peaks at 1595, 1500, 1300, 1150, and 800 cm^{-1}. These values are in good agreement with those obtained by Langer[6] who proposed the structure shown in Figure (5). The IR spectrum of aniline black is shown in Appendix A.

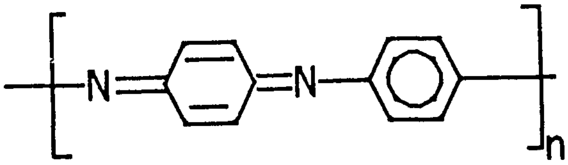


Figure 5. Structure of aniline black

The IR spectrum of paracyanogen (Appendix A) showed one broad absorption peak centered at 1540 cm^{-1}. This absorption frequency is consistent with a completely conjugated double bond system having the structure[7] shown in Figure (6).

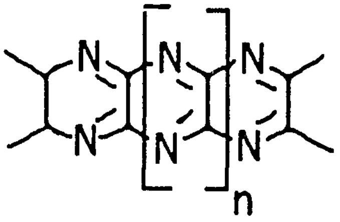


Figure 6. Structure of paracyanogen

The polymer, polyquinoxaline (PQX), was hard and brittle. Thus, we were unable to make the KBr-pellet samples necessary for the IR analysis. The structure[8] of PQX is shown in Figure (7).

As Pcy and PQX were found to absorb only negligible amounts of iodine or bromine, they were no longer of interest to us. We therefore omitted the analysis of their elemental compositions.

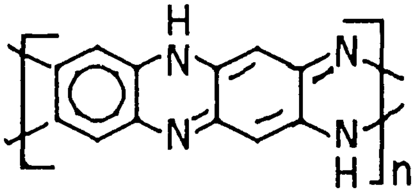


Figure 7. Structure of polyquinoxaline

CHAPTER 3

THERMODYNAMIC STABILITY

3.1 Iodine Complexes

Emf data on the iodine complexes and pure iodine were obtained at room temperature on electrochemical solid state cells of the type:

$$(-)\mathrm{Pt/Ag/AgI/P(I_2)_\alpha/Pt}(+) \qquad (1)$$

$$(-)\mathrm{Pt/Ag/AgI/I_2(s)/Pt}(+) \qquad (2)$$

$I_2(s)$ in (2) refers to pure solid iodine and $P(I_2)_\alpha$ in (1) represents iodine complexed in varying amount, α, with the organic solid, P, under study. We assume electrochemical reversibility and the following cell reactions:

$$2\mathrm{Ag} + (1/\delta)\mathrm{P(I_2)}_\alpha = 2\mathrm{AgI} + (1/\delta)\mathrm{P(I_2)}_{\alpha-\delta} \qquad (1a)$$

$$2\mathrm{Ag} + \mathrm{I_2(s)} = 2\mathrm{AgI} \qquad (2a)$$

where reactions (1a) and (2a) correspond to cells (1) and (2) respectively. Subtraction of equation (1a) from (2a) gives:

$$I_2(s) + (1/\delta)P(I_2)_{\alpha-\delta} = (1/\delta)P(I_2)_{\alpha} \qquad (3)$$

where δ is infinitesimally small, and the concentration change is, therefore, negligible.

According to equation (3), a mole of pure solid iodine with molar free energy G^0 is transferred to an iodine complex solution to form a mole of complex with an iodine partial molar free energy G. Thus , on the basis of standard thermodynamic relationships, it follows that the relative partial molar free energy of iodine, $G - G^0$, can be expressed as,

$$G - G^0 = nF(E-E^0) = RT\ln(a/a^0) \qquad (4)$$

where the term on the left is the difference between the partial molar free energy of iodine in the complex and in pure, solid iodine. F is Faraday's number; n is the number of electrons transferred, 2; E^0 and E are the Emf's of the cell with pure iodine and complexed iodine respectively; a^0 and a are the thermodynamic activities of iodine in pure iodine and in the complex, respectively.

The Emf data obtained for the I_2-complex systems studied are plotted as a function of the mole ratio of molecular iodine to the organic molecule or monomeric unit. The graphs are shown in Figures 8 to 15

Inspection of these Emf curves reveals the common feature of increasing Emf with increasing iodine concentration until a plateau is reached. The experimental Emf value at the plateau is equal, within experimental limits, to that expected theoretically for the formation of silver iodide from pure solid silver and iodine using a cell of type (2).

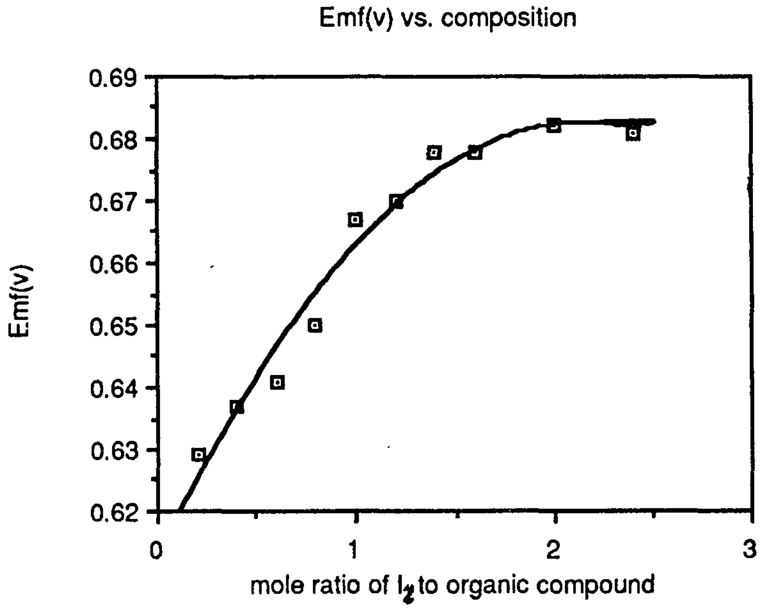


Figure 8. Emf curve for anthracene-I_2

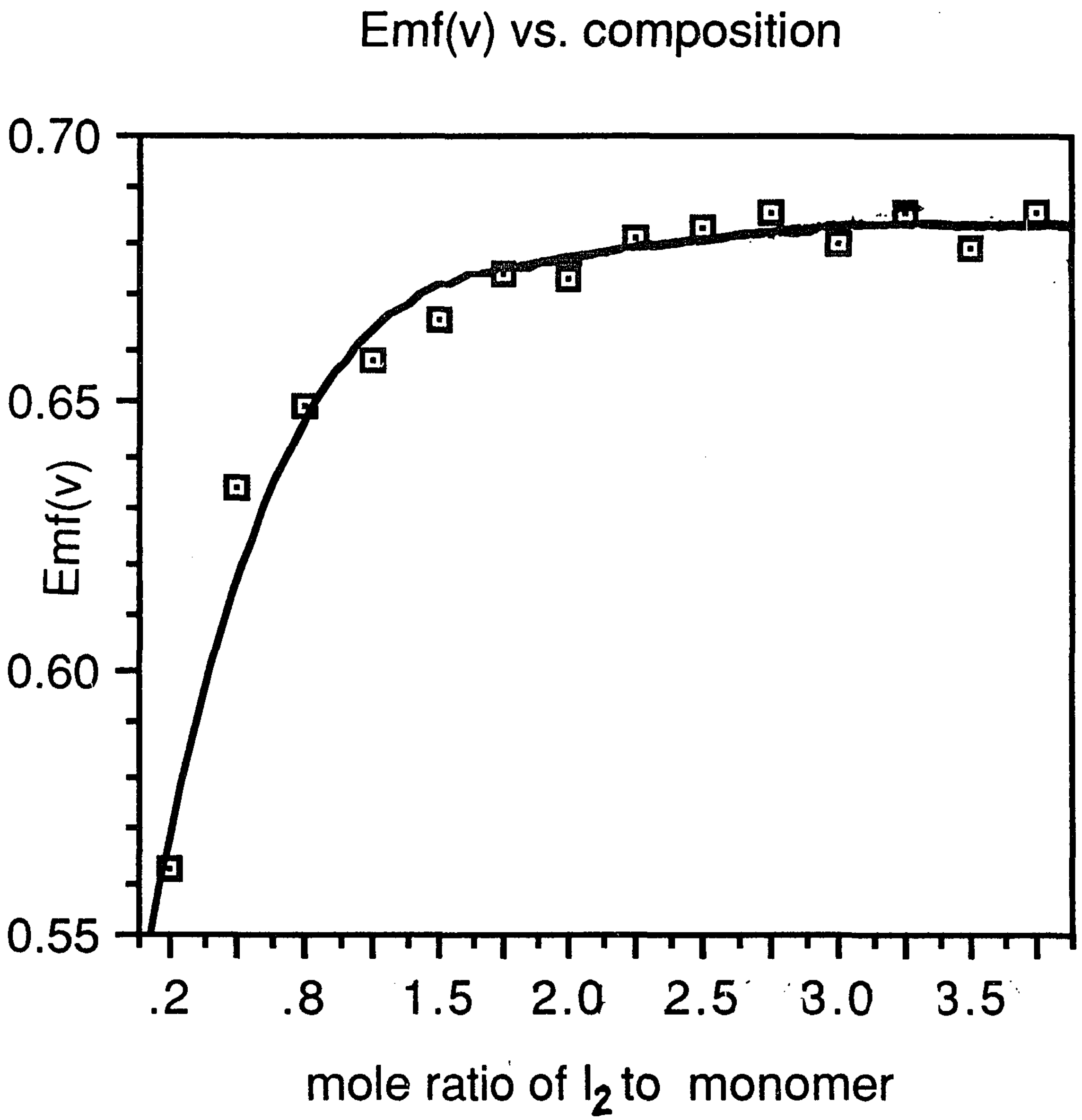


Figure 9. Emf curve for aniline black-I_2

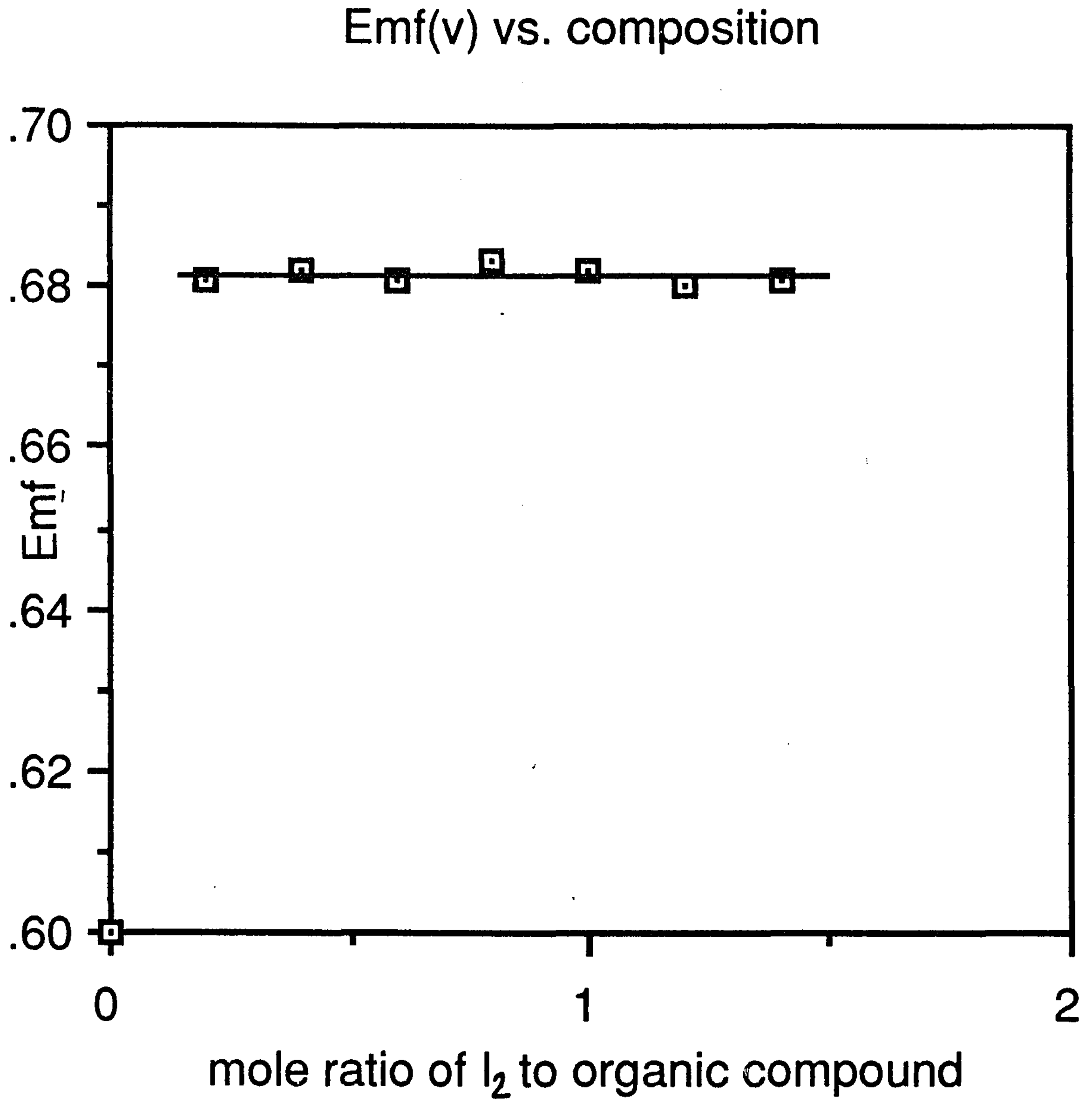


Figure 10. Emf curve for thianthrene-I_2

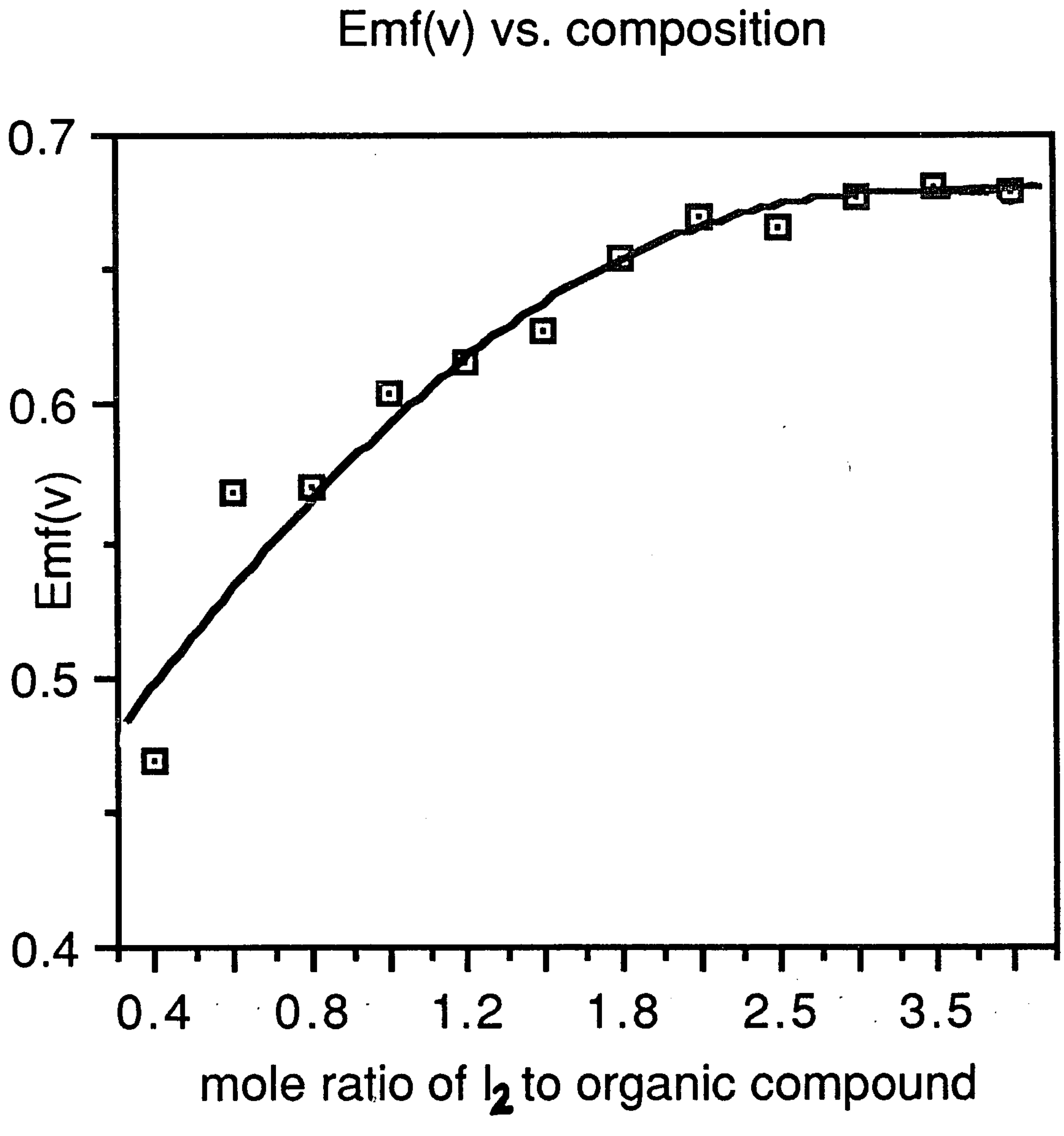


Figure 11. Emf curve for 1,10-phenanthroline-I_2

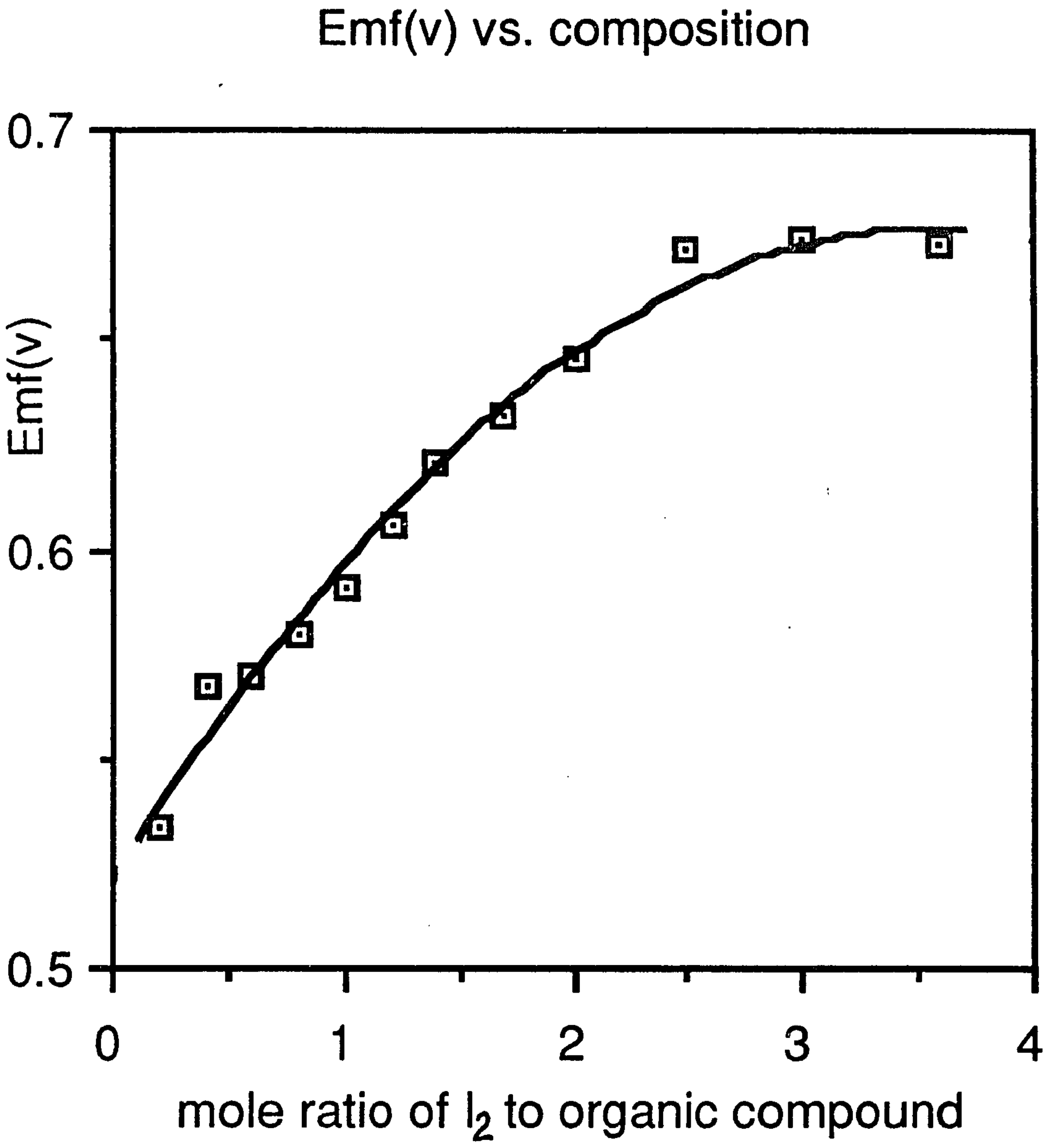


Figure 12. Emf curve for phenanthridine-I_2

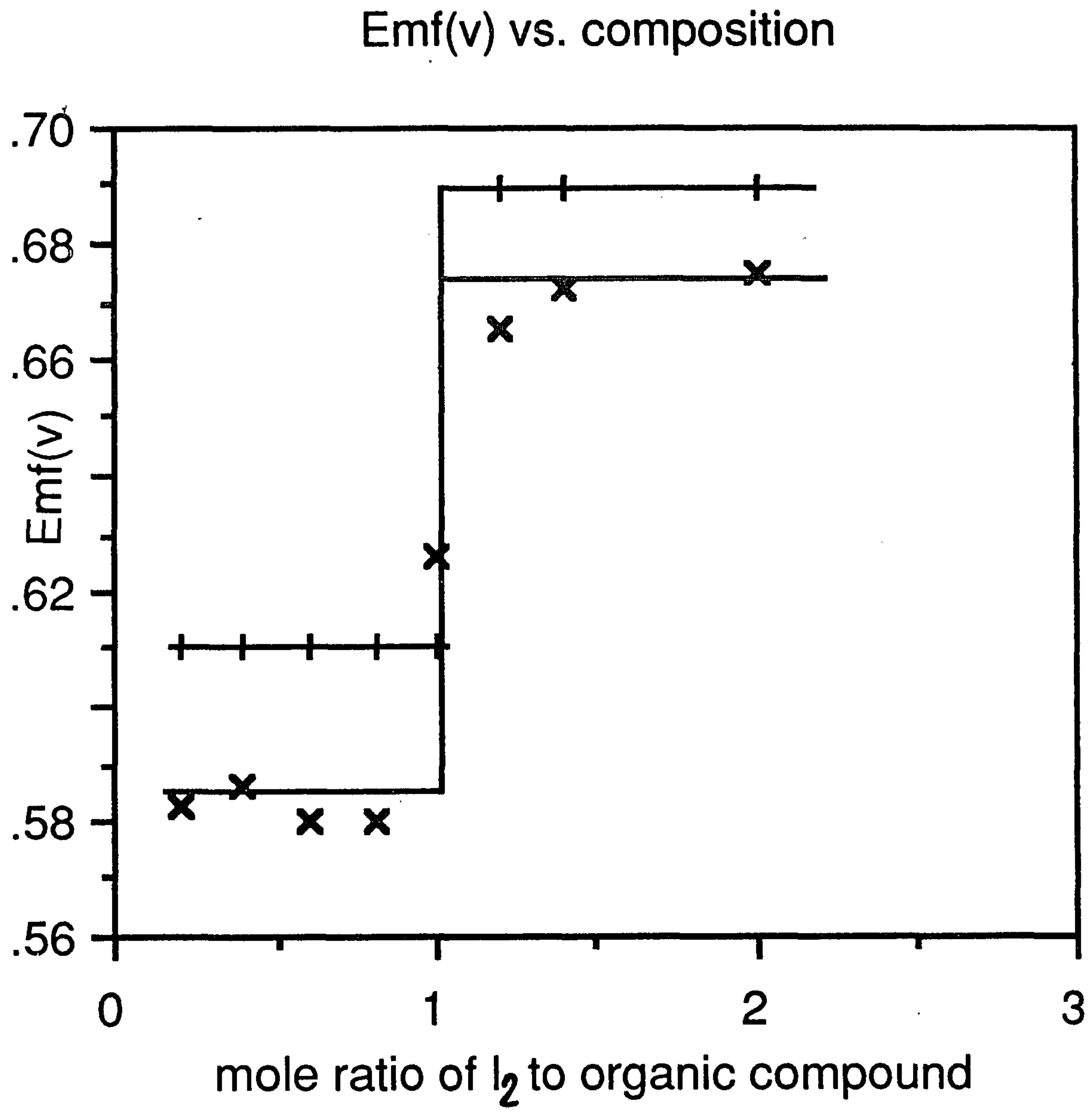


Figure 13. Emf curve for phenazine-I_2
+, Reference 15; x, this work.

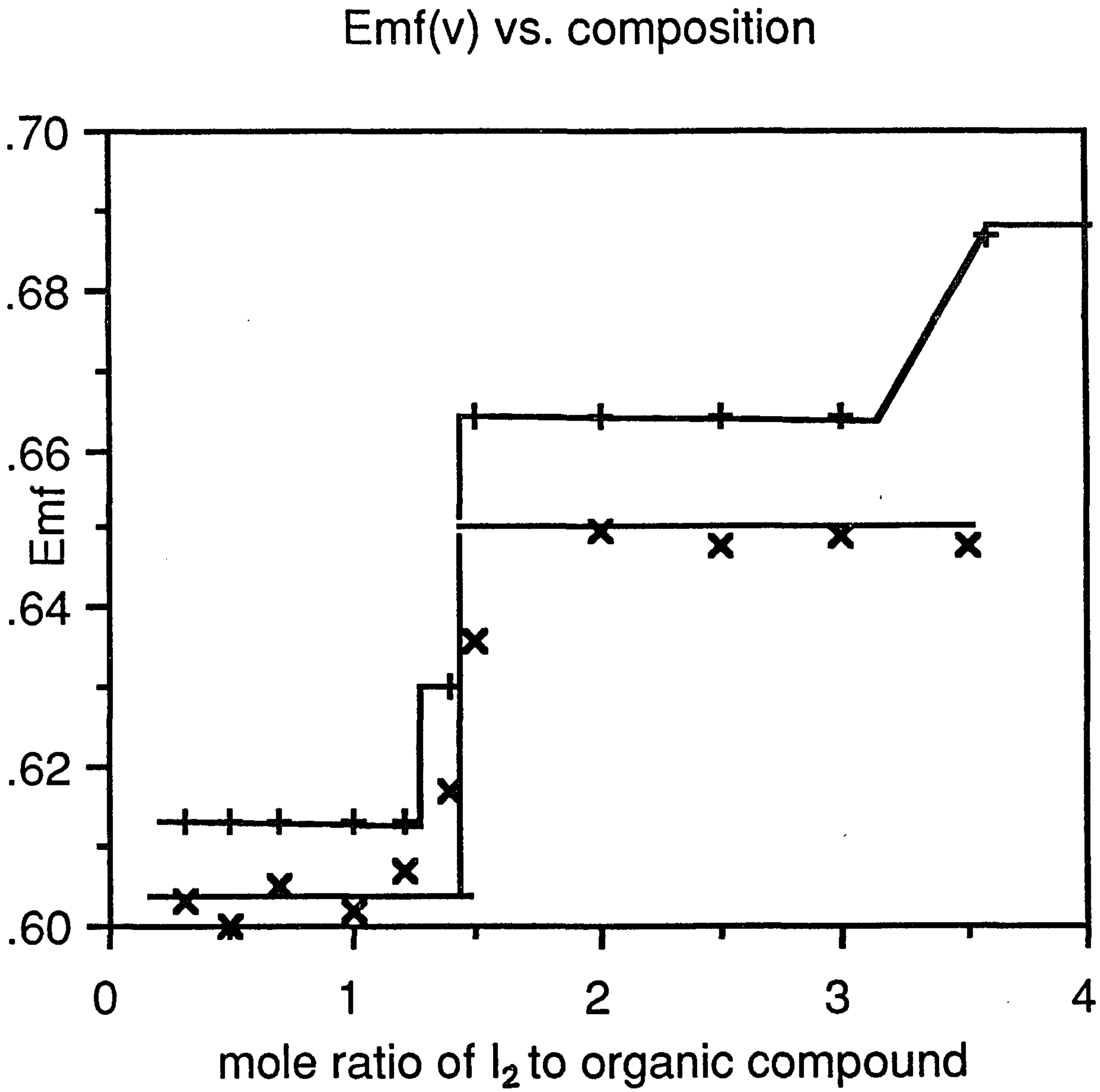


Figure 14. Emf curve for phenothiazine-I_2

+, Reference 14; x, this work.

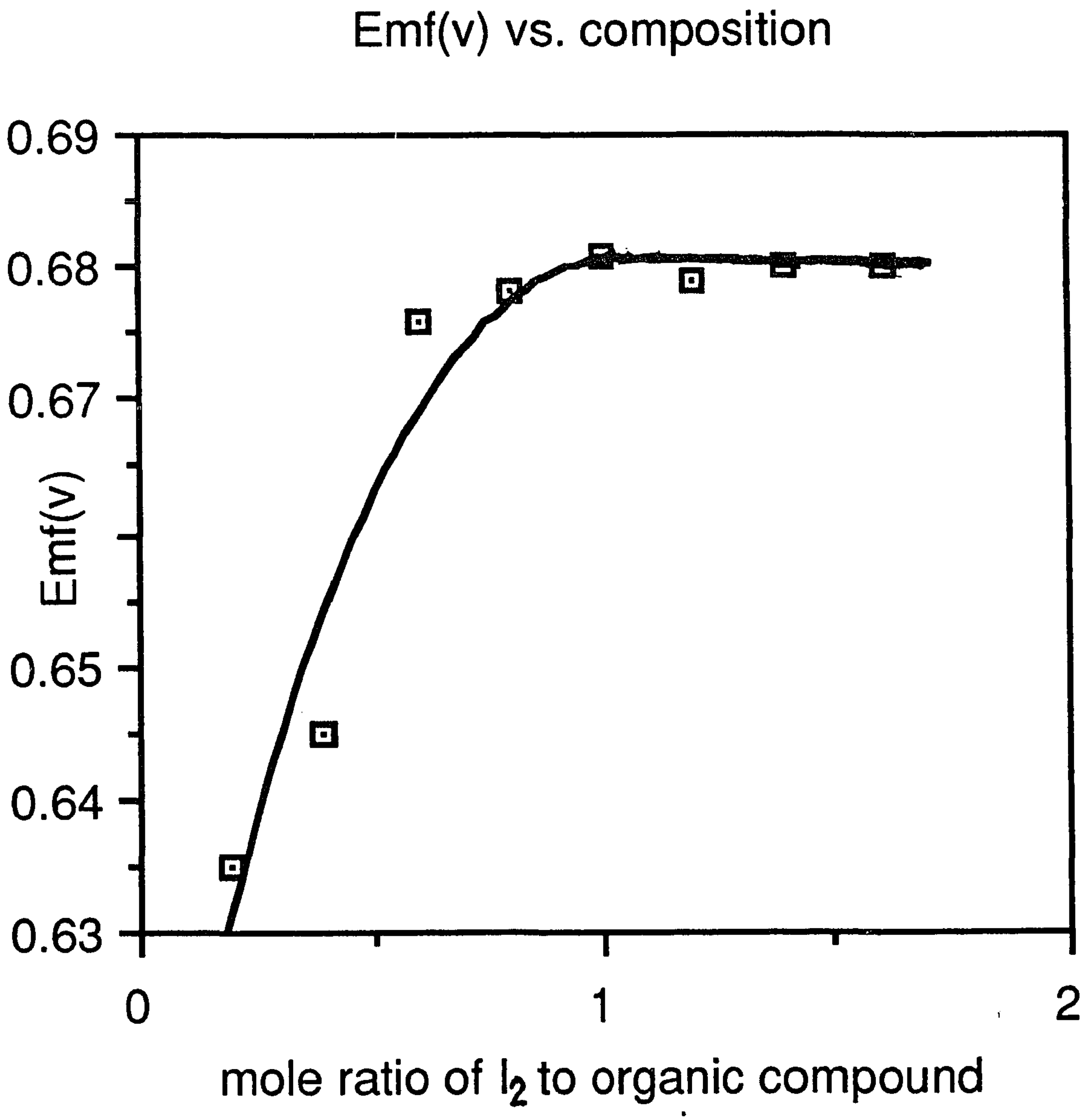


Figure 15. Emf curve for benzotriazole-I_2

Table (1), below, compares the mole ratios of iodine or bromine to the organic unit at which the Emf curves plateau, with the maximum mole ratios obtained from halogen vapor uptake at 90°C.

Table 1. Comparison between the maximum halogen vapor uptake of the compounds and the composition at which the Emf curve levels off.

Substance	I_2/M, at 90°C	I_2/M, Emf curve
aniline black	2.6	2.5
phenanthroline	4.0	3.5
phenanthridine	2.8	3.0
anthracene	2.3	2.0
benzotriazole	2.6	1.0
phenazine	1.2	1.0
phenothiazine	8.5	----
		Br_2/M, at 25°C
aniline black	2.7	1.0
C-PAN	1.0	1.2

The agreement is sufficiently good to warrant the conclusion that pure iodine is present at mole ratios higher than the saturation composition. In the case of benzotriazole-I_2 and aniline black-Br_2, the thermodynamic activity of the complexed halogen slowly approaches that of the pure halogen over a wide composition range.

To calculate the relative integral free energies , ΔG, of the complexes, we solved the following expression[13] by numerical integration,

$$\Delta G = (1-X')/X' \int_{0}^{X'} (G-G^{0})/(1-X)^{2} dX \qquad (6)$$

X is the mole fraction of iodine complexed with the organic substance; X' is the mole fraction of iodine at the composition where the thermodynamic activity of iodine in the complex approaches that of pure iodine. Since the integration must start at $X = 0$, the Emf data were extrapolated to a mole ratio of iodine to organic species of 0.

In the case of phenothiazine-I_2 and phenazine-I_2, the Emf versus iodine composition curves show more than one plateau. In light of the phase rule, each plateau corresponds to an heterogenous system composed of two solid phases. The first plateau represents a mixture of an organic complex, $P(I_2)_\alpha$ with a constant composition, α, and pure solid organic compound, P. For phenothiazine, the next plateau is a mixture of organic complexes $P(I_2)_\beta$ and $P(I_2)_\alpha$ where β is larger than α. The highest plateau consists of organic complex, $P(I_2)_\gamma$ of maximum composition, γ, and pure solid iodine.

Note the peculiar case of thianthrene in Figure (10). The Emf value as a function of composition is almost constant. The themodynamic interpretation of this behavior, based upon electrical conductivity results to be discussed later, is that iodine is almost as active at all compositions in the complex as in pure solid iodine.

Since in each heterogenous region the activity of iodine in the system is a constant, equation (6) becomes,

$$\Delta G = nF(E-E^0) \qquad (7)$$

where n was defined in equation (4).

By applying equations (6) or (7), appropriately, to the graphs in Figures (8-15), free energies of formation of the iodine complexes were calculated. The results are presented in Table (2), along with results obtained by other investigators.

Table 2. Free energies of formation of iodine complexes, at 25°C.

Reaction#	$-\Delta G$(kcal/mole I_2)	
	This work*	Other
AB + $2.5I_2$ = $AB(I_2)_{2.5}$	1.6	
Phe. + $3.5I_2$ = $Phe(I_2)_{3.5}$	2.9	
Phen. + $3I_2$ = $Phen(I_2)_3$	2.6	
Anth. + $2I_2$ = $Anth(I_2)_2$	1.0	
Benzt. + I_2 = $Benzt(I_2)$	1.1	
Phenz. + I_2 = $Phenz(I_2)$	4.1	3.58[14]
Phet. + $1.5I_2$ = $Phet(I_2)_{1.5}$	3.6	3.22[15]
benzimidazole(I_2)	>0**	
thianthrene(I_2)	0	

---

* Estimated limits of error, ±0.5kcal/mol I_2

** Emf data were scattered. However, the results indicate that a stable complex is formed.

\# AB: aniline black

Phe: 1,10-phenanthroline

Phen: phenanthridine

Anth: anthracene

Benzt: benzotriazole

Phenz: phenazine

Phet: phenothiazine

3.2 Bromine Complexes

The Emf data on the bromine complexes were obtained using electrochemical cells similar to type (2) above, except now the solid electrolyte is silver bromide. Graphite was not mixed with the cathode material as it known to react with bromine[12].

The Emf data for aniline black (AB), and cyclized-polyacrylonitrile (C-PAN), plotted against the mole ratio of Br_2 to monomeric unit are shown in Figures (16) and (17). The free energies of formation were calculated using equation (6) and the corresponding Emf curves in Figures (16) and (17). The results are given in Table (3).

Table 3. Free energies of formation of Br_2 complexes of aniline black and cyclized-polyacrylonitrile.

Reaction	$-\Delta G$(kcal/mol Br_2)*
$AB + Br_2 = AB(Br_2)$	19
$CPAN + 1.2Br_2 = CPAN(Br_2)_{1.2}$	11

*Estimated limits of error, ±1kcal/mol Br_2

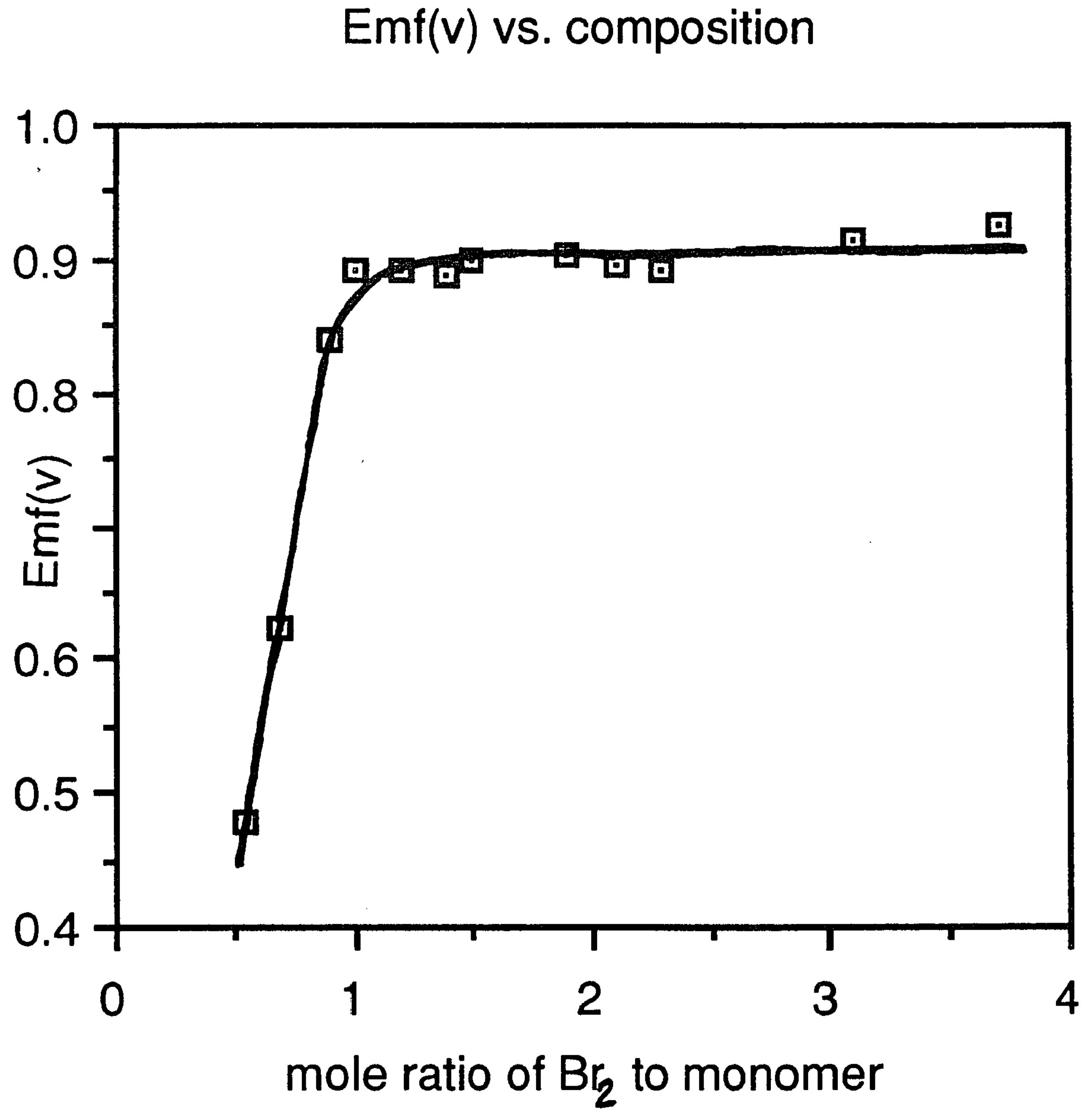


Figure 16. Emf curve for aniline black-Br_2

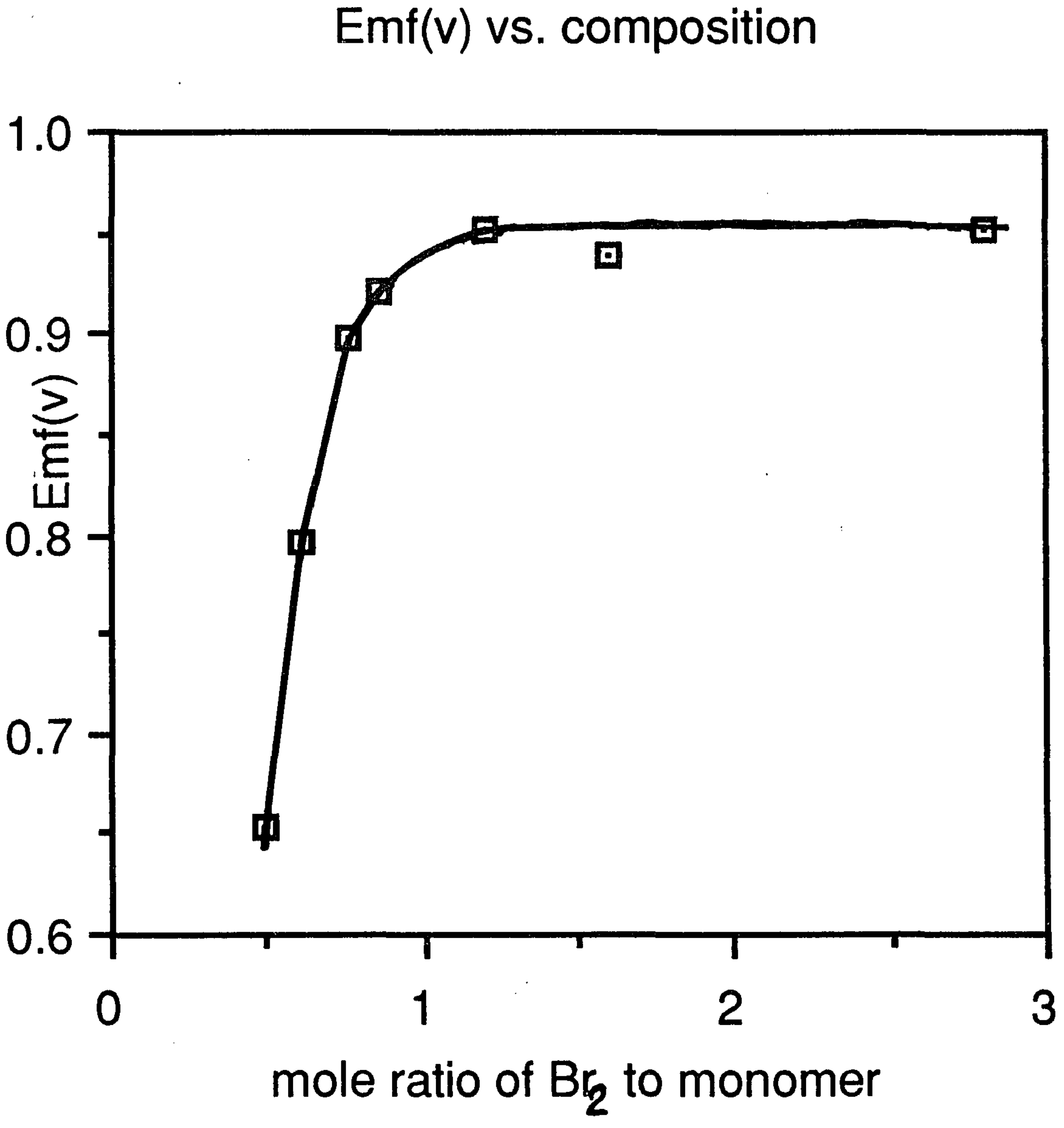


Figure 17. Emf curve for cyclized-polyacrylonitrile-Br_2

3.3 Theory of Charge Transfer Interaction

In view of Mulliken's[16] quantum mechanical treatment of charge transfer complexes between a donor, D and acceptor, A, the ground state of the complex, DA, can be described by the wave function, Y, given by,

$$Y = aY_0(A{:}D) + bY_1(A^-{:}D^+) \qquad (8)$$

Y_0 denotes a no-bond structure, in which the two molecular species interact with ordinary intermolecular forces, such as the Van Der Waals type, and Y_1, a dative or charge-transfer structure in which an electron is transferred from the donor to the acceptor. a and b are normalization constants whose relative magnitudes define the extent of charge transfer. If b is very large, the second term on the right of equation (8) prevails and complexation is stronger. Mulliken's theory considers the complex as a resonance hybrid between the non-bonded and the charge-transfer structures. It has been determined[4] from the experimental value of the dipole moment of the benzene-I_2 complex that the ratio $a^2/b^2 >> 1$; i.e. the contribution of the charge-transfer structure amounts to only a small percentage in the ground state. Nevertheless, the small but non-zero contribution of the charge-transfer structure stabilizes the complex.

There is conclusive evidence that the strength and stability of donor acceptor interaction are dependent on the extent of charge transfer[4].

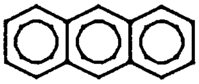
Table (4), below, lists the structures of the organic molecules and the Gibbs free energies of the iodine complexes of the anthracene analogs, for a 1:1 mole ratio, as determined in this work.

The electrochemical technique used to obtain free enery data is not sufficiently sensitive for obtaining precise values of the temperature dependence of the Emf. For this reason, only free energy values and not entropy and enthalpy values are presented. We will compare free energy values of different complexes at the same I_2 to organic substance mole ratio, 1:1, to minimize entropy differences. It has been shown that the entropy values of iodine charge-transfer complexes are very similar[14,15,17]. In the following discussion, we assume that the free energy values are proportional to the enthalpy values which are a measure of the strength of bonding between donor and acceptor.

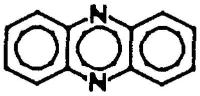
Table 4. Comparison of the free energies of formation for a 1:1 mole ratio of the iodine complexes of a series of anthracene analogs.

Material	Structure	$-\Delta G$(kcal/mol I_2)
anthracene	I	1.9
phenazine	II	4.1
phenothiazine	III	3.6
thianthrene	IV	0

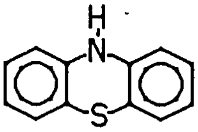
I



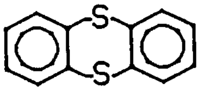
II



III



IV



A comparison of the free energies of the I_2 complexes of anthracene and phenazine immediately suggests that the donor (organic) acceptor (I_2) interaction is stronger in phenazine-I_2 than in anthracene-I_2.

The key structural difference here is the presence of nitrogen in the heterocyclic center ring of phenazine. Nitrogen atoms in these systems are known to act as electron donors[2]. Since the strength of complex formation depends on the extent of charge density donation, the enhanced thermodynamic stability of phenazine-I_2 over anthracene-I_2 may be attributable to the presence of nitrogen, acting as a Lewis base.

As we proceed from phenazine to thianthrene in Table (4), we note a steady decrease in free energy (all comparisons of the magnitude of the free energy refer to the absolute values), though not too marked in the case of phenothiazine. This decrease in stability indicates that sulfur in the central ring somehow disfavors complexation.

In general, the extent of charge transfer in a complex depends on the ionization potential and the electron affinity of the donor and acceptor respectively[18,19]. On the basis of the ionization potential of the donor atoms in the heterocyclic ring alone, we would expect thianthrene and phenothiazine to form stronger complexes than phenazine with iodine. However, this was not the case.

Another consideration may be the fact that π-electron conjugation is disrupted in the central ring of phenothiazine and thianthrene. Complete delocalization of π-electrons leads to a lower ionization potential of the molecule as a whole[5] and, hence, to a larger transfer of charge and a stronger donor acceptor interaction. In such a case, it may be inappropriate to speak of the ionization potential of just an atom in the molecule.

It would be interesting to study the possible I_2-complexes of a molecule like 9,10-dihydroanthracene, in Figure (18), so as to ascertain the effect of the absence of aromaticity in the central ring on the magnitude of the Gibbs free energy.

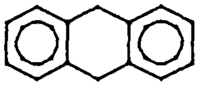


Figure 18. The structure of 9,10-dihydroanthracene.

In Table (5), below, it is observed that the free energy of formation of the 1,10-phenanthroline-I_2 complex is significantly larger than that of phenanthridine-I_2. Since 1,10-phenanthroline contains one nitrogen more than phenanthridine, this result is consistent with the fact that nitrogen acts as an electron donor in these systems.

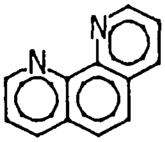
When benzothiadiazole (Table 5) is exposed to I_2 vapor at either 50° or 90°C for 48 hours, it does not take up a significant amount of iodine. For practical purposes, benzothiadiazole does not react with I_2. From this observation we assume that the Gibbs free energy of the complex would be equal to or greater than zero.

The analog of benzothiodiazole, benzotriazole, which does not contain sulfur, has a measurable free energy value of -1.1 kcal/mole I_2. This experimental finding again suggests that the presence of sulfur and/or the absence of aromaticity are factors which influence thermodynamic stability of the complex.

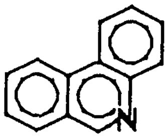
Table 5. Free energy of formation for a 1:1 mole ratio of complexes of phenanthrolines and benzo-azoles

Material	Structure	$-\Delta G$(kcal/mol I_2)
phenanthroline	V	7.6
phenanthridine	VI	5.1
benzimidazole	VII	>0
benzotriazole	VIII	1.1
benzothiadiazole	IX	≤ 0

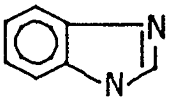
V



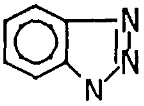
VI



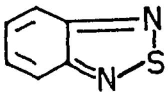
VII



VIII



IX



The data gathered for the organic compounds discussed so far seem to imply that nitrogen-bearing systems form stronger complexes with iodine than do the homopolynuclear aromatic and sulfur-containing compounds. Indeed, the free energy data obtained on the iodine complexes of a number of homonuclear aromatic hydrocarbons ranging from pyrene to ovalene[17] offer some support for this idea.

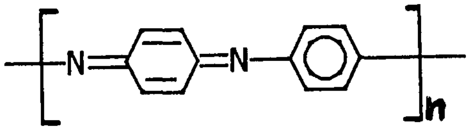
3.4 Polymeric complexes

Table (6) shows the free energies of formation of the iodine complexes of polymeric systems.

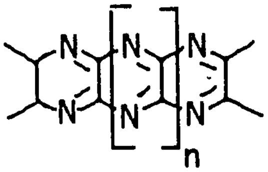
Table 6. Free energies of formation of nitrogen-bearing polymer iodine complexes for a 1:1 mole ratio.

Material	Structure	-ΔG(kcal/mol I_2)
aniline black	X	3.2
paracyanogen	XI	----
polyquinoxaline	XII	----
C-PAN	XIII	2.0[9]
polyvinylpyridine	XIV	4[9]

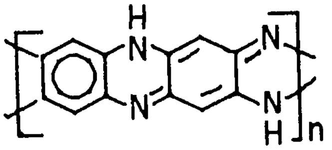
X



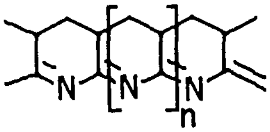
XI



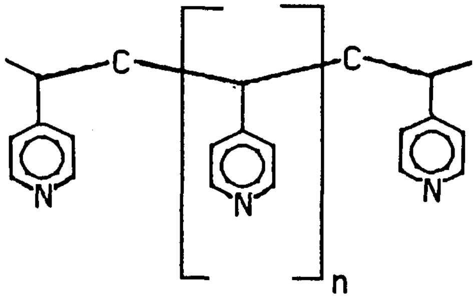
XII



XIII



XIV



At this point, one wonders whether the presence of nitrogen in general guarantees complexation. According to the data obtained on the nitrogen-bearing polymeric systems in Tables (6) and (7), the answer is, apparently, no. Besides containing nitrogen, all of these polymers are π-conjugated. Yet among them are paracyogen and polyquinoxaline which form complexes with neither iodine nor bromine. It may very well be argued that the relatively high degree of chaos known to exist in polymeric system due to possible chain folding, twisting and knotting interferes with the necessary orientations and thus the insertion of the acceptor between the polymer chains. Undoubtedly, these systems require further investigation.

It is worth noting in Tables (6) and (7) that the free energies of the bromine complexes of aniline black and cyclized-polyacrylonitrile are much larger than their iodine counterparts. These results are not surprising considering the higher reactivity of bromine. In fact, in its reaction with aromatic hydrocarbons, bromine has been known to engage in substitution reactions on the rings[12]. Differences in electron affinities between I_2 and Br_2 and in molecular sizes, which can minimize steric factors, may lead to stronger bonding interaction between donor and acceptor molecules.

Table 7. Free energies of formation of the bromine complexes of polymeric systems for a 1:1 mole ratio.

Material	$-\Delta G$(kcal/mol Br_2)
aniline black	19
C-PAN	11
polyquinoxaline	NR*
paracyanogen	NR

---

* NR: no reaction.

CHAPTER 4

ELECTRICAL CONDUCTIVITY

4.1 Iodine Complexes

Electrical conductivities of the iodine complexes were measured at room temperature, using the four-probe Van Der Paw technique[20]. The data obtained are shown graphically in Figures (19) to (26). The logarithm of the conductivities are plotted against moles of iodine per mole of organic molecule or monomer unit. The data represented by the lower curve in Figure (21) were obtained from the literature[21] and are shown for comparison.

A strong dependence of conductivity on iodine content is observed from these curves. Notice that the conductivity passes through a maximum. It is interesting to point out that for some of these systems, the iodine composition at which the conductivity is a maximum is approximately equal to the iodine composition at which the corresponding Emf curves plateau. Since the conductivity is observed to decrease with increasing iodine content beyond the maximum, it can be argued that at that point we are dealing with a two-phase system consisting of a mixture of the complex with pure solid iodine which is an insulator. In other words, the decrease in conductivity beyond the maximum probably resulted from the dispersion of small conducting complex domains within a nonconducting iodine matrix.

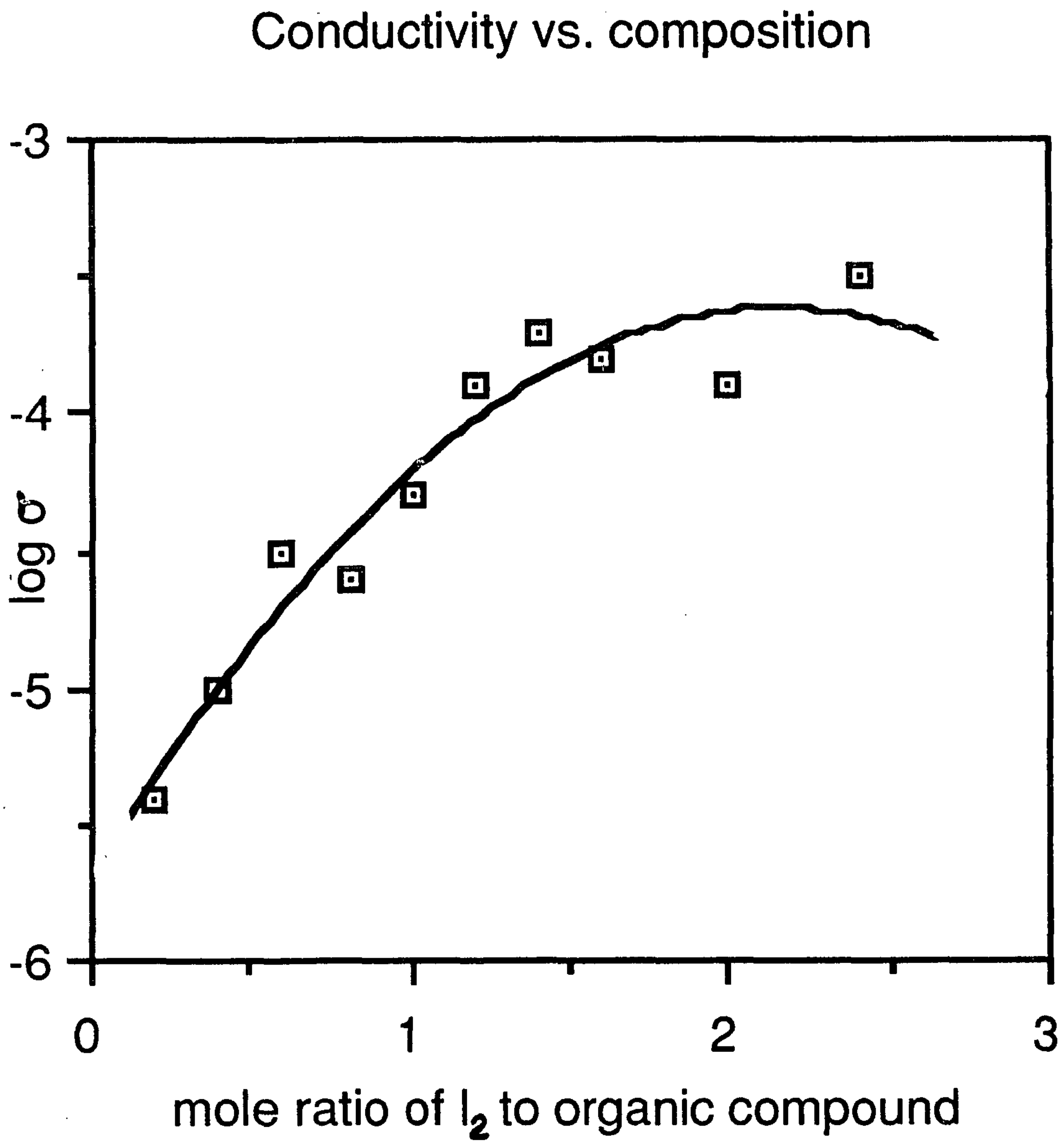


Figure 19. Conductivity curve for anthracene-I_2

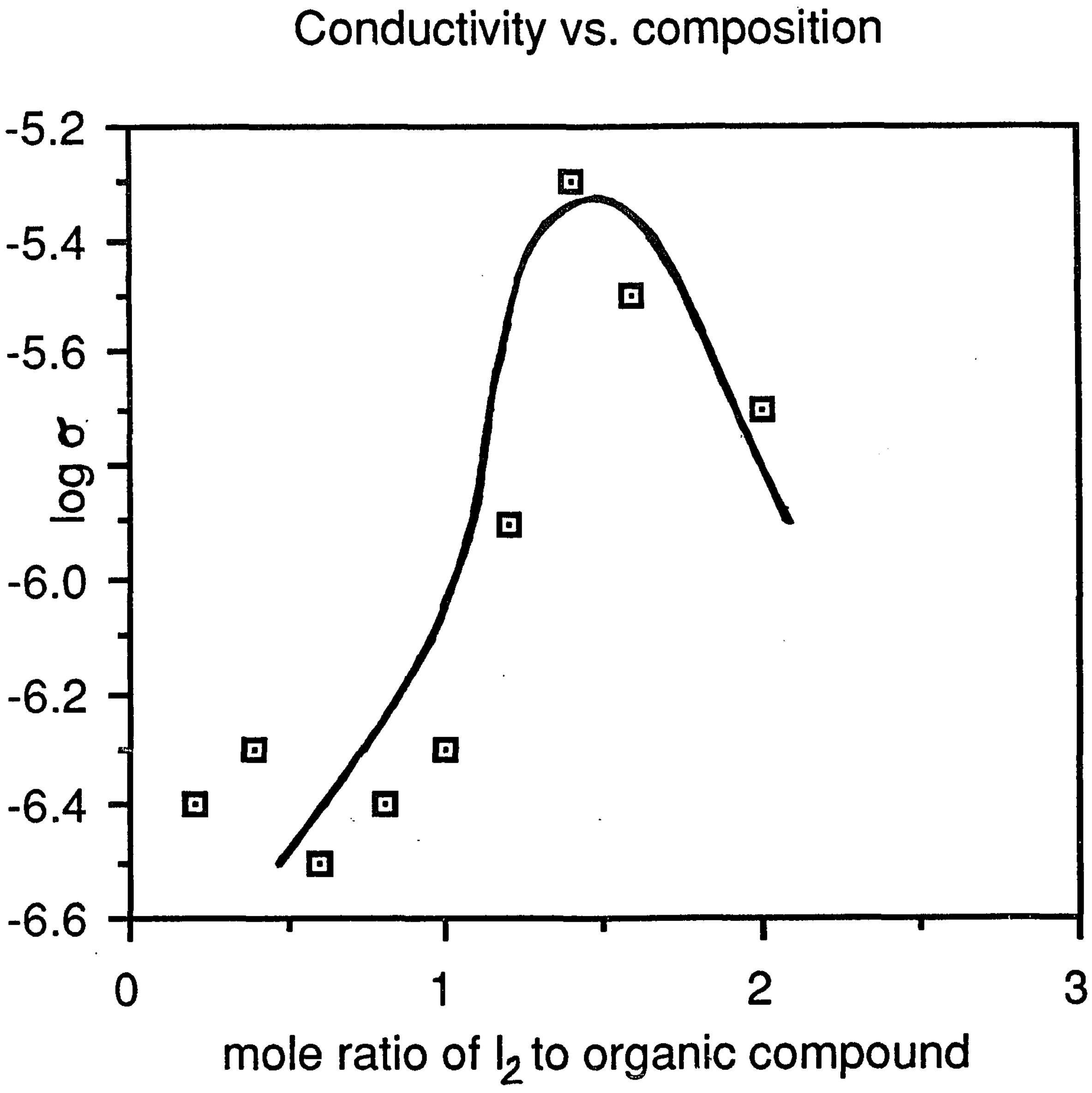


Figure 20. Conductivity curve for phenazine-I_2

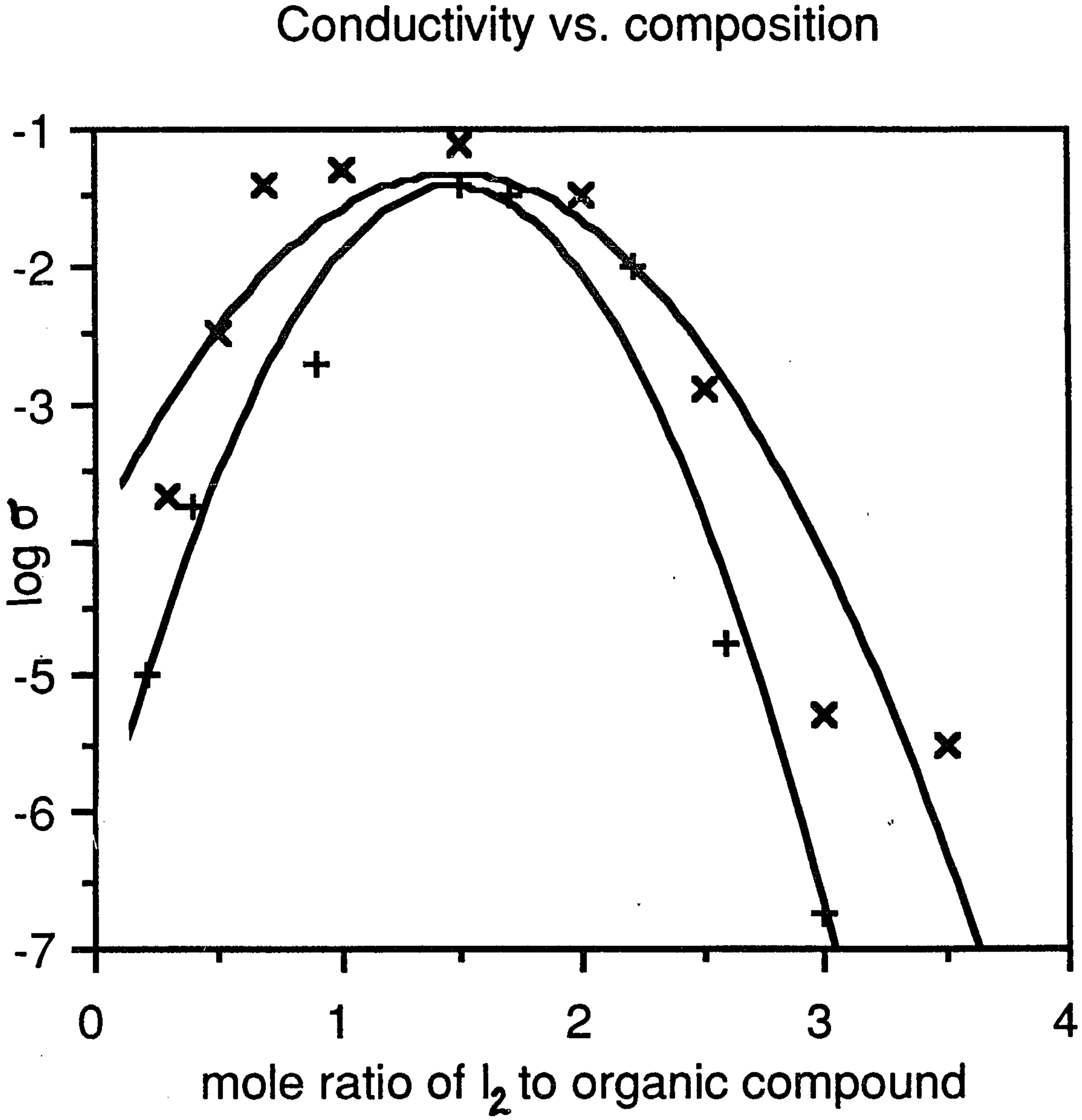


Figure 21. Conductivity curve for phenothiazine-I_2
+, Reference 21; x, this work.

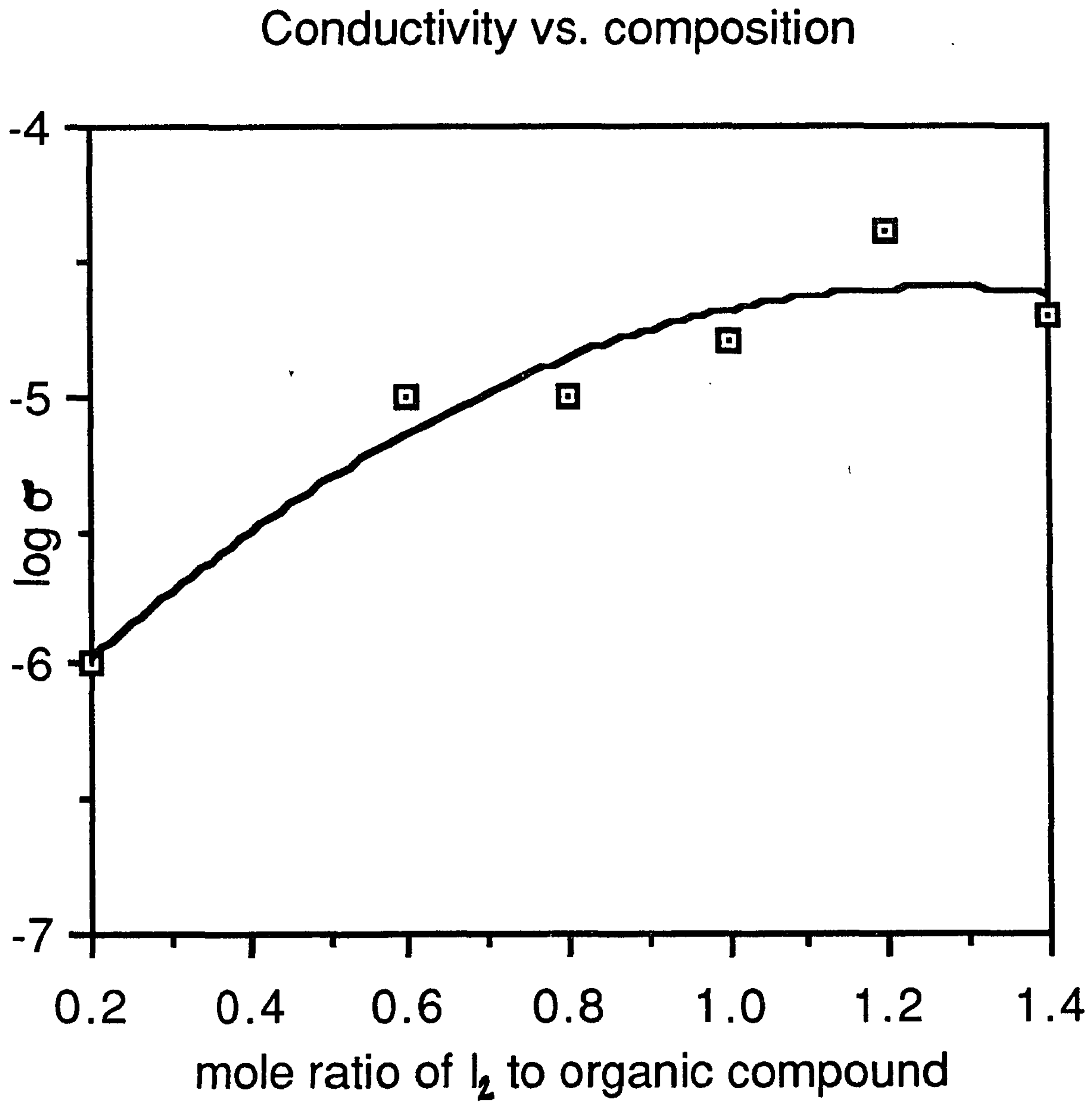


Figure 22. Conductivity curve for thianthrene-I_2

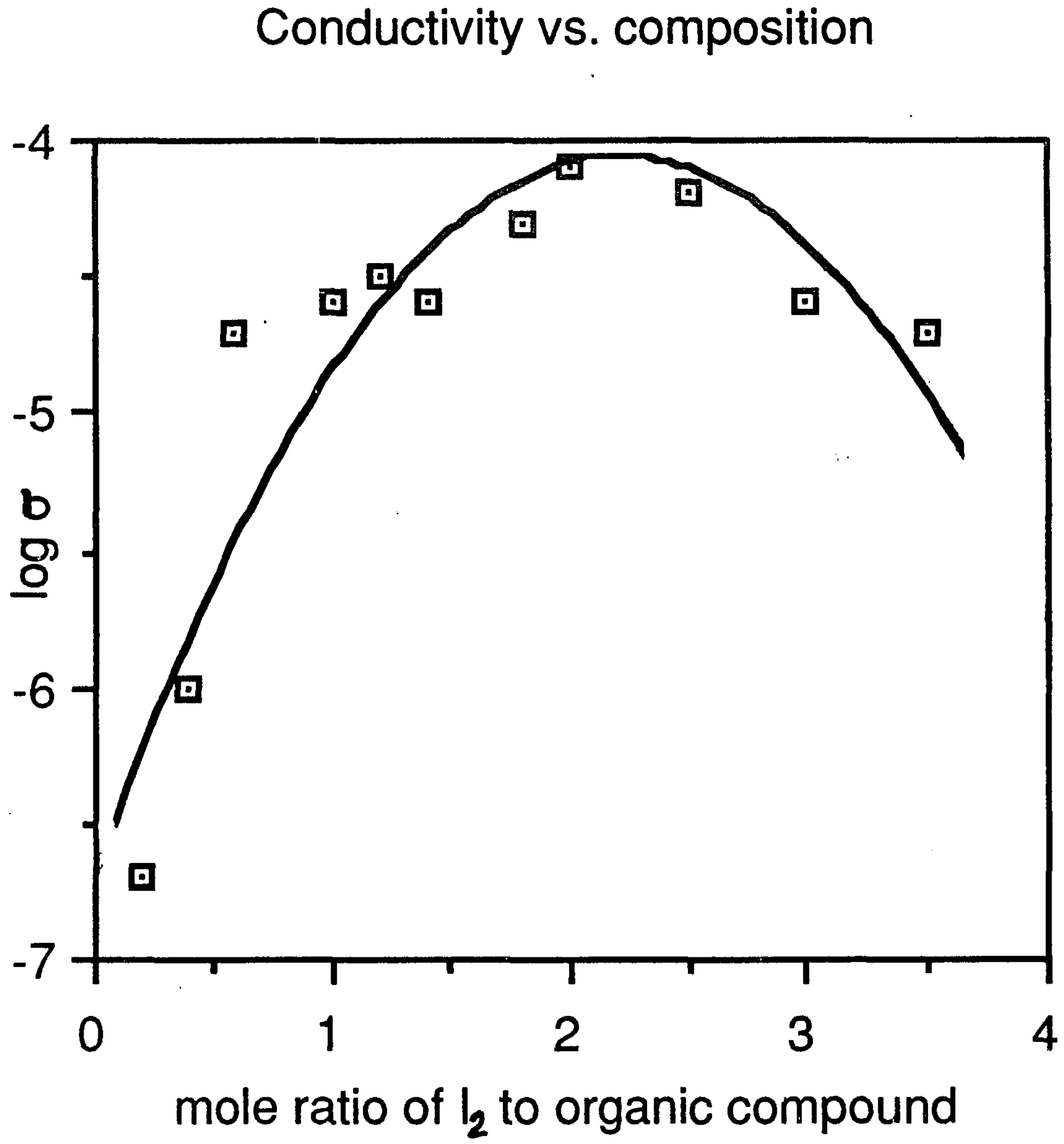


Figure 23. Conductivity curve for 1,10-phenanthroline-I_2

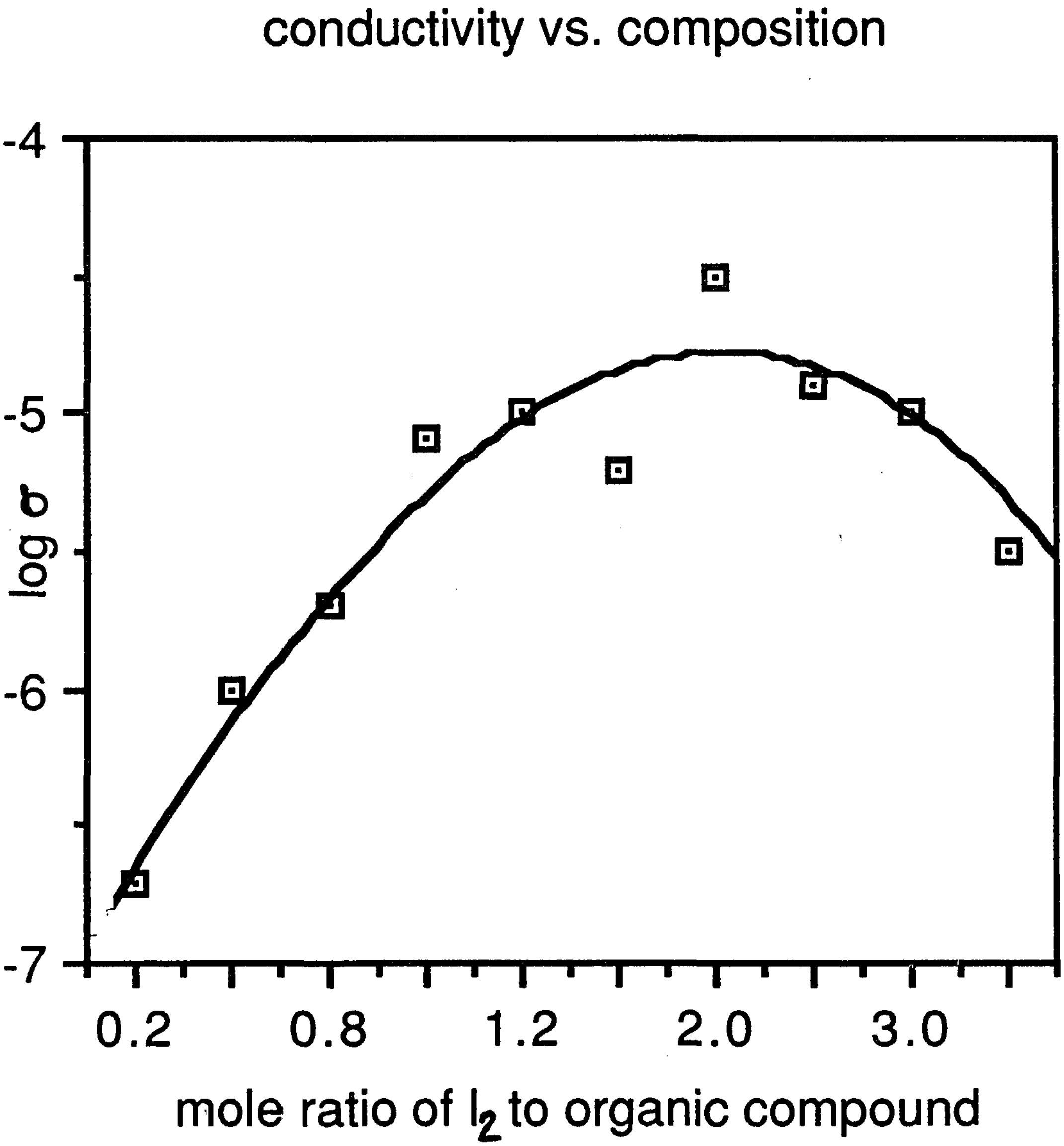


Figure 24. Conductivity curve for phenanthridine-I_2

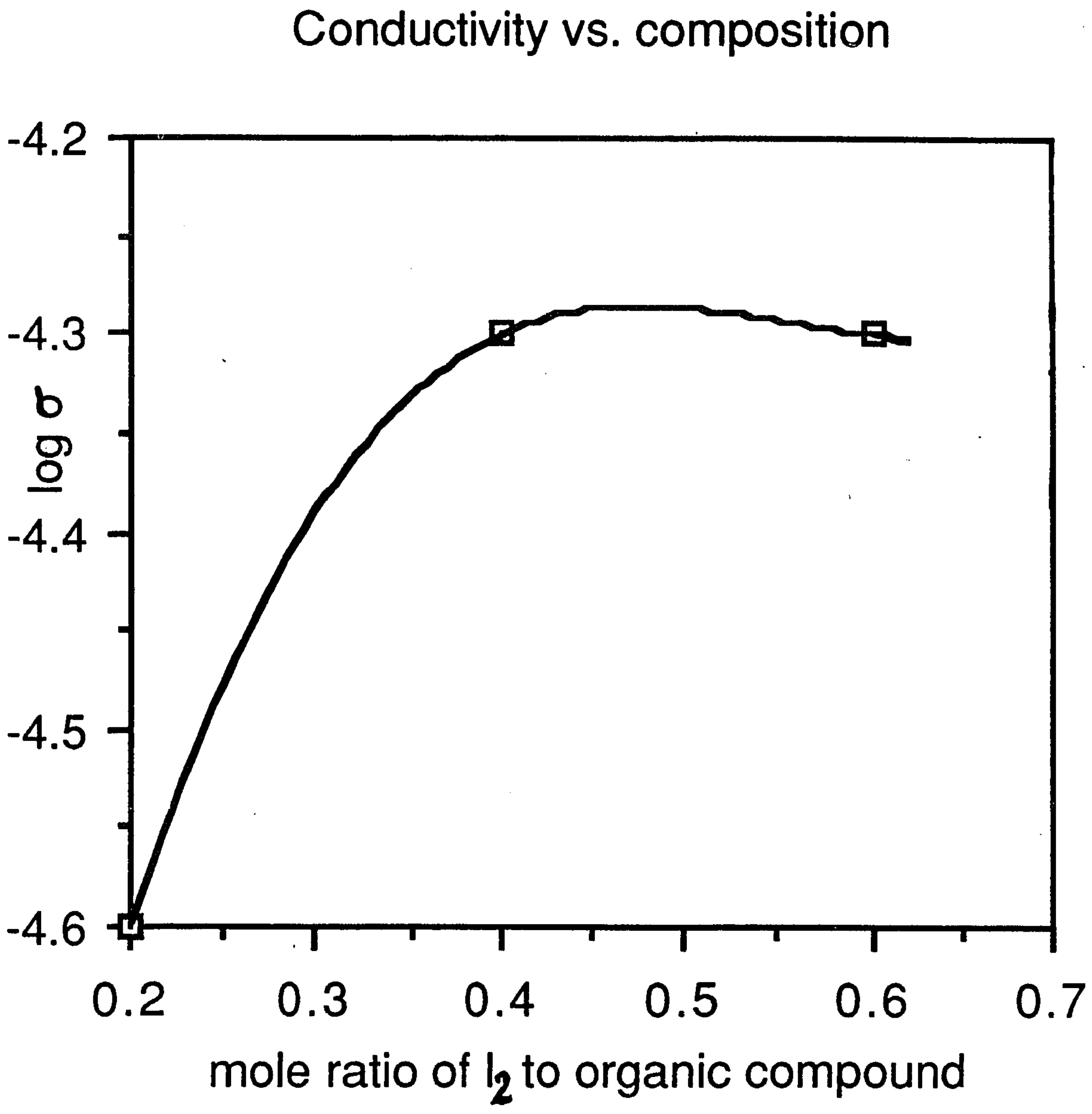


Figure 25. Conductivity curve for benzotriazole-I_2

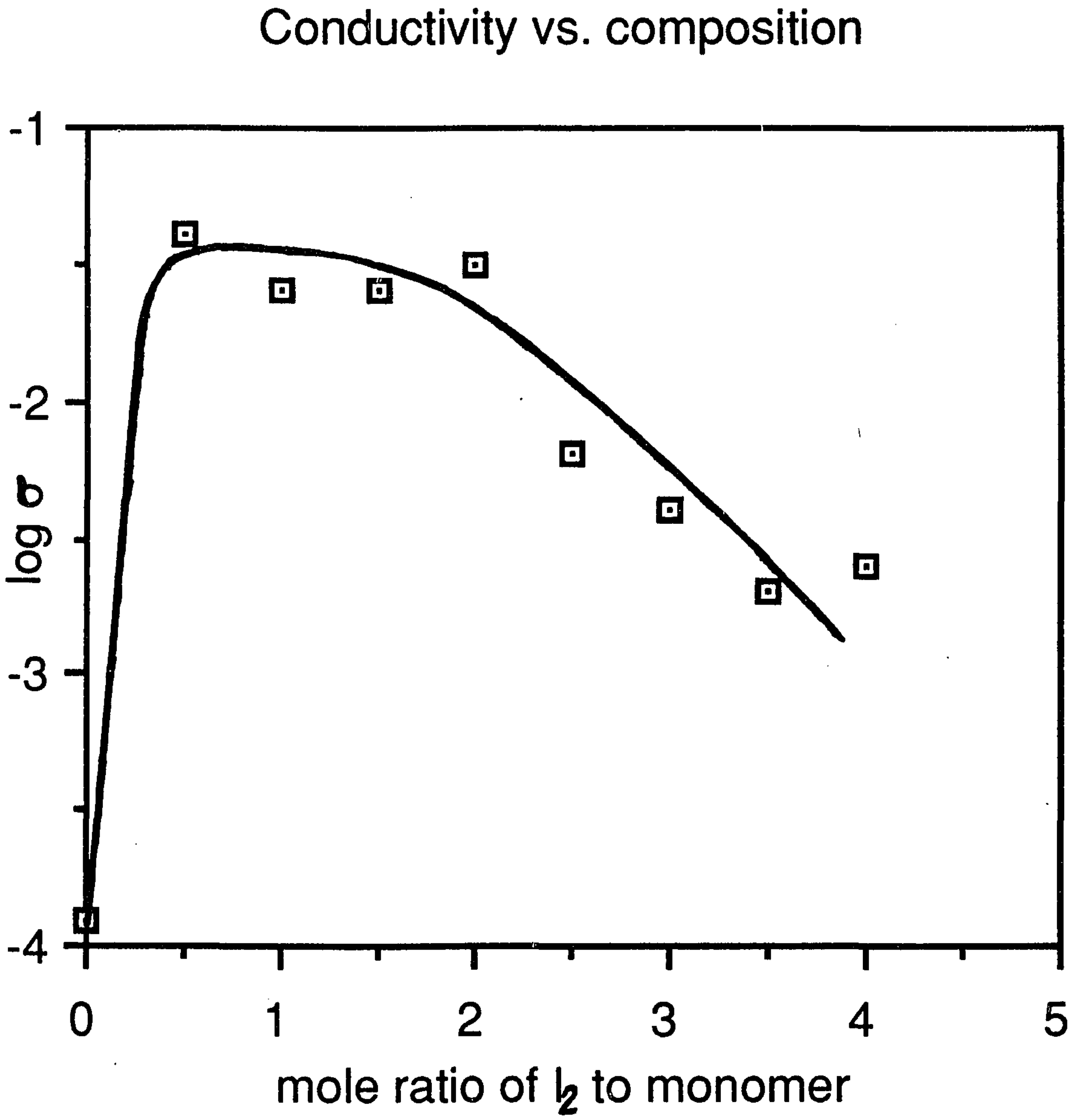


Figure 26. Conductivity curve for aniline black-I_2

4.2 Bromine Complexes

The electrical conductivities of the bromine complexes of aniline black (AB), cyclized-polyacrylonitrile (C-PAN), and 2-polyvinylpyridine were measured at room temperature by the methode described in Chapter (2) Section (3). Figures (27) and (28) depict the variation in conductivity of AB and C-PAN with bromine content, respectively.

The conductivity behavior is similar to that of the iodine systems, except that the curve, unexpectedly, passed through a minimum in the case of AB. This behavior is rather unusual and requires futher study.

The conductivity data for the 2-PVP-Br_2 system were very scattered and, therefore, not adequate for presentation. However, the maximum conductivity that was measured is listed in Table (8).

Table (8) sumarizes the room temperature conductivity of the iodine and bromine complexes of the systems studied, along with some comparative literature values. As noted previously, the conductivity of these complexes is a function of the halogen content and goes through a maximum. Listed here, are the maximum conductivities and, in brackets, the compositions at which they occur. These conductivity values were reproducible within ±25% for different batch of samples of the same composition.

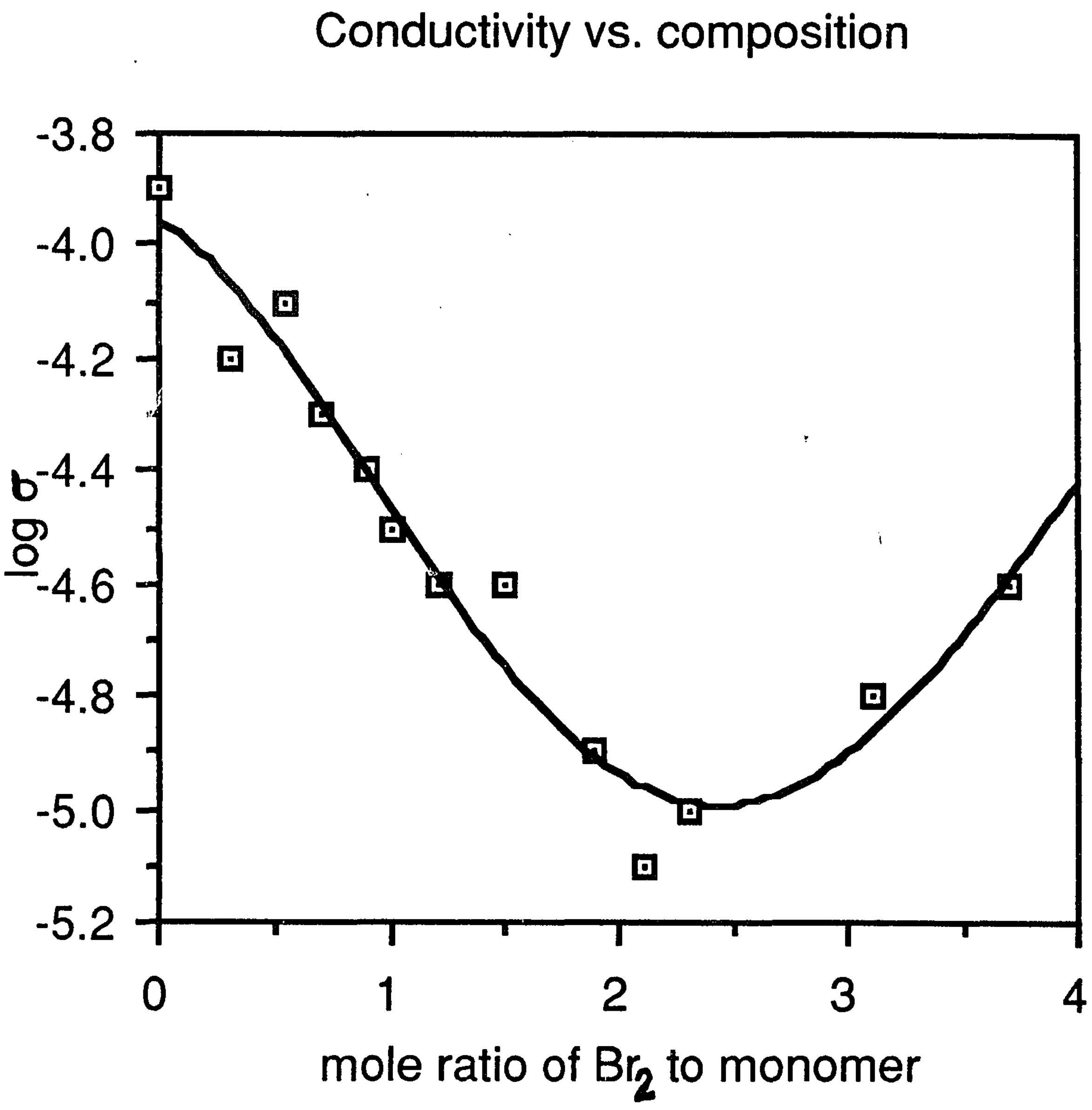


Figure 27. Conductivity curve for aniline black-Br_2

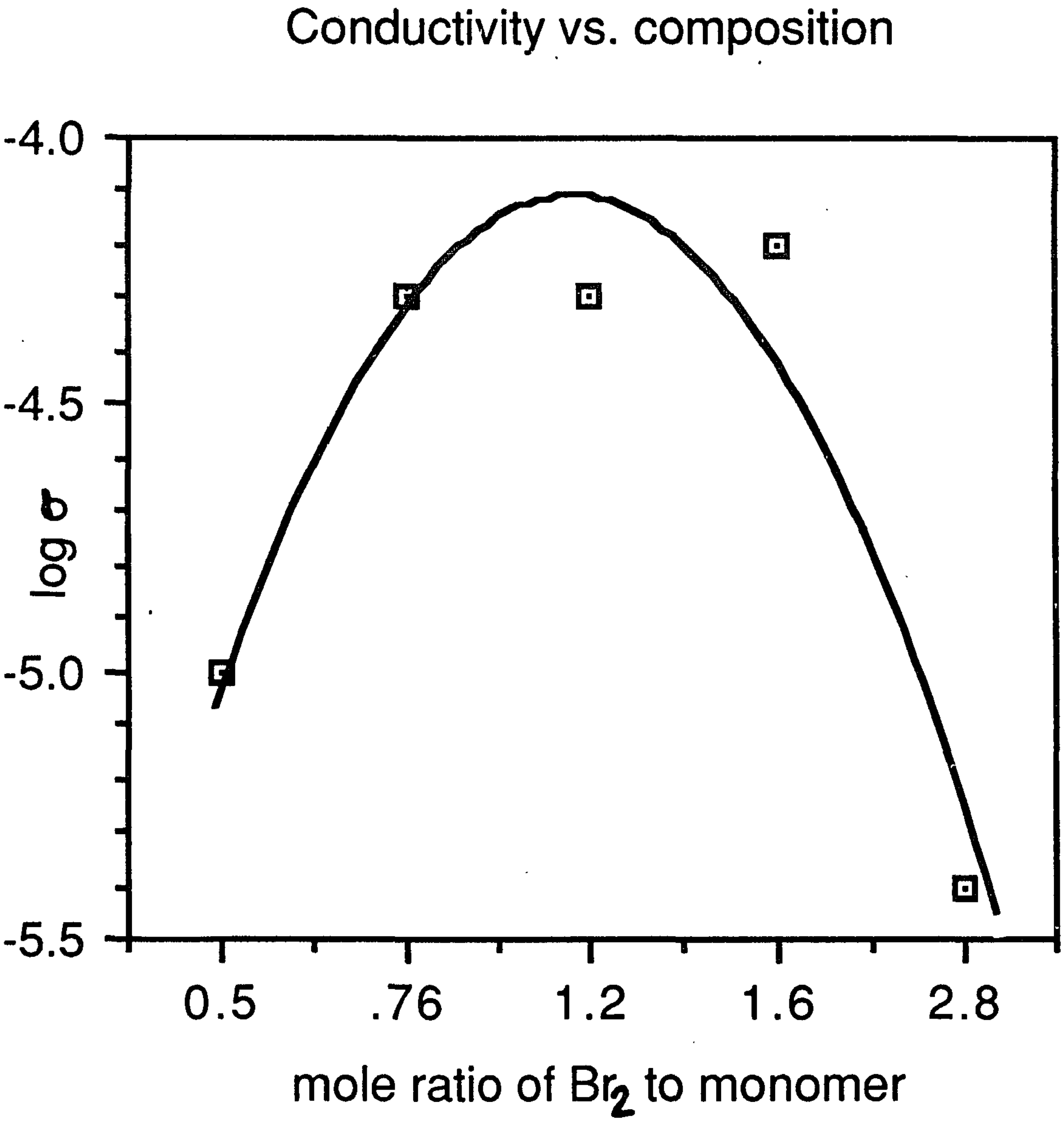


Figure 28. Conductivity curve for cyclized-polyacrylonitrile-Br_2

Table 8. Electrical conductivity of iodine and bromine complexes of organic compounds and polymers.

Material	$\sigma[I_2](\mathrm{ohm.cm})^{-1})$	$\sigma[Br_2](\mathrm{ohm.cm})^{-1}$
anthracene	3.0×10^{-4}. [2.4]	
phenazine	5.0×10^{-6}[1.4]	
phenothiazine	8.4×10^{-2}[1.5]	
phenothiazine	$(4\times10^{-2}[1.5])^{21}$	
thianthrene	4.2×10^{-5}[1.2]	
phenanthroline	7.5×10^{-5}[2.0]	
phenanthridine	3.2×10^{-5}[2.0]	
7,8-benzoquinoline	----	
indazole	----	
benzotriazole	5.0×10^{-5}[0.6]	
benzimidazole	1.0×10^{-5}[1.0]	
benzothiadiazole	----	
aniline black	3.5×10^{-2}[2.0]	7.9×10^{-5}[2.3]*
aniline black	3.0×10^{-4}[0.0]	
polyquinoxaline	----	----
C-PAN	$(1\times10^{-3}[1.0])^{9}$	5.3×10^{-5}[1.2]
2-PVP	$(2.3\times10^{-3}[2.3])^{9}$	4.8×10^{-5}[1.9]
paracyanogen	----	----

* This value corresponds to a conductivity minimum.

It is worth noting that of all the material listed in Table (8), only aniline black is a conductor in its uncomplexed form. Langer[6] reported a conductivity value of $2\text{x}10^{-3}(\text{ohm cm})^{-1}$ for the pure polymer and was able to obtain ESR data indicative of a relatively high free spin density.

Another observation is that the conductivities of the bromine complexes are about two orders of magnitude lower than those of the corresponding iodine complexes for the polymers aniline black, 2-polyvinylpyridine and cyclized-polyacrylonitrile. Figure 29, below, compares the conductivity behavior of the systems c-PAN-Br_2 and c-PAN-I_2. This difference in conductivity is, apparently, not due to different techniques of measurement, since the conductivity values of samples of aniline black, measured with both techniques, only disagree by a maximum of 50%. The difference in conductivity between the I_2 and Br_2 complexes of these polymers may be a consequence of the physico-chemical nature of the complex materials.

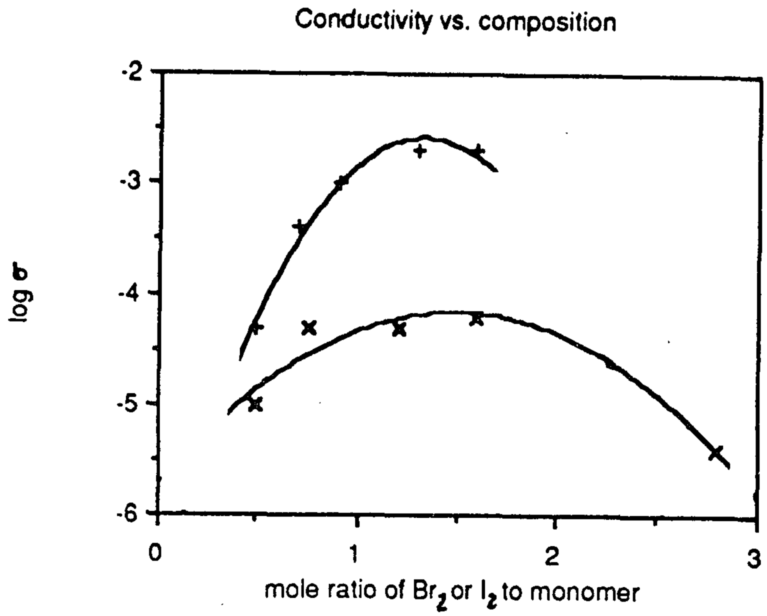


Figure 29. Comparison of conductivity of c-PAN-Br_2, x; and c-PAN-I_2, +, Ref. 9.

4.3 Band Theory of solids.

In an effort to better understand the implications of the above conductivity data, it is necessary to put them in theoretical perspective.

The basic idea of the band theory[22] of solids consists of the formation of restricted ranges of allowed energy states called bands. In the familiar molecular orbital theory, when two atoms are brought together to form a molecule, the atomic energy levels split into a lower bonding orbital and a higher antibonding orbital. When a large number of atoms or molecules are brought together to form a crystalline solid, the electronic states mix so as to form bands. The highest filled band is called the valence band and the lowest empty band, the conduction band.

A band can be partially or completely filled. If the valence band is only partially populated, as in Figure (29), there will exist closely lying empty states above the Fermi level* to which electrons can be promoted. Such an incompletely filled band is a necessary condition for metallic-type conduction in a solid. If the highest occupied band is entirely filled, the material will either be an insulator or have semiconducting property depending on the separation between the valence and the conduction band. This separation is often called the energy gap, Eg. A large Eg is characteristic of insulators, since it would require a relatively large quantity of energy to promote electrons into states within the conduction band.

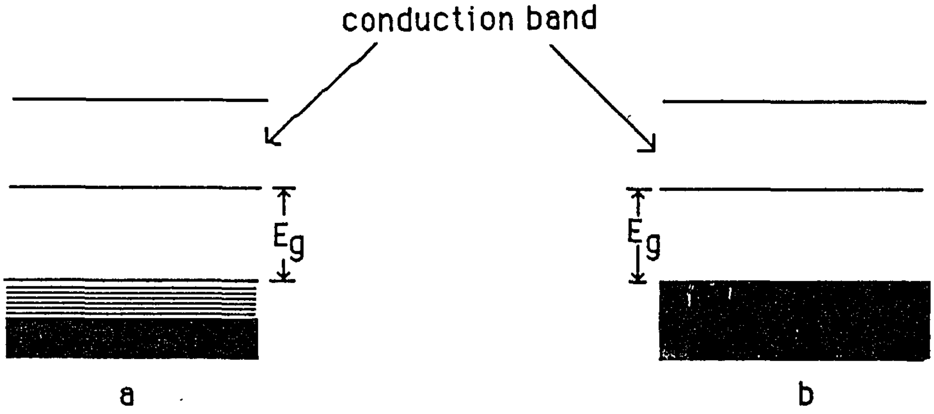


Figure 30. (a) valence band partly filled, (b) valence band completely filled. * The Fermi level is the energy of the highest occupied state within a band, at absolute zero.

Most organic π donors as well as inorganic sigma acceptors like I_2 are insulators because they form completely filled valence bands in their crystalline solids. However, in many cases[18], when the organic material is complexed with electron acceptors, like iodine, the resulting system has semiconducting properties.

An important structural feature for efficient charge transport in organic complex systems is the presence of equally spaced atoms in the case of a polymer chain or equal interplanar distances in stacks of planar polynuclear aromatic molecules, not all in the same oxidation state[18]. In other words, charge migration will not take place in the absence of mixed-valence interactions.

On the basis of the band theory, as it applies to charge transfer processes, there occurs an interaction between the completely filled valence band of the donor and the empty conduction band of the acceptor as their electronic states are brought together in complex formation. As a result, electron density is transferred from donor to acceptor, thereby creating partially filled bands, necessary to support conduction. Depending on the extent of charge transfer, mixed-valence states can be formed, and charge migration can occur.

The extent of charge transfer in organic iodine complexes, as determined from ESR analysis, is relatively small[10]. The small free electron density per iodine atom is consistent with weak donor acceptor interaction, as the Gibbs free energy of complex formation indicates.

It is, therefore, clear that semiconductivity in solid organic complexes arises as a result of electron density transfer from donor to acceptor to form mixed-valence states which facilitates charge migration.

The delocalization of charges can occur along the organic stack and/or possibly along the associated polyiodine chain. The prevalent conduction pathway depends upon proper interplanar distances in the organic stacks and proper iodine bond distances along the polyiodine chain[18]. A detailed knowledge of the crystal structure of a given complex is needed to be able to discriminate between these possibilities.

4.4 Thermodynamic Stability and Conductivity

The values of the Gibbs free energies and conductivities of the halogen complexes studied indicate that higher conductivity is associated with lower binding energy. For example, the Gibbs free energy of formation of anthracene-I_2 is four times lower than that of phenazine-I_2 but the former is one hundred times more conducting. Another illustration involves thianthrene-I_2 and phenazine-I_2. Thianthrene binds very weakly to iodine with a Gibbs free energy of formation of approximately 0 kcal/mole I_2. The resulting complex has a conductivity about ten times higher than that of phenazine-I_2, whose free energy was measured as -4.1kcal/mol I_2.

It is important to point out that the zero free energy value obtained for thianthrene-I_2 only means that the chemical potential of I_2 in thianthrene-I_2 is very nearly equal to that of pure solid iodine, as evidenced by the corresponding Emf data. Some authors[15] have interpreted these Emf data as indicative of no complex formation. This interpretation is not consistent with the relatively high conductivity observed. Both thianthrene and pure solid iodine are electrical insulators. The fact that their interaction produces an electrical conductor strongly suggests that complex formation occurs.

We noted earlier that the conductivities of the bromine polymeric complexes are about one thousand times lower than those of their iodine counterparts. The free energies of the bromine complexes are very much higher than those of the corresponding iodine complexes. These results further indicate that high thermodynamic stability is associated with low conductivity.

As a general conclusion it appears that the nitrogen-bearing systems form stronger iodine complexes than the homopolynuclear aromatics and the sulfur-containing compounds, while the latter form better conductors.

4.5 Conduction Mechanism

The results of ESR studies of a number of charge transfer complexes of organic solids with iodine have been consistent with an electronic conduction mechanism[21,23].

In an attempt to determine whether conduction is ionic or electronic in the organic complexes studied in this work, we have devised the following electrochemical experiment: The electrochemical cell(3) was constructed by combination of cells (1) and (2), the Emf's of which were previously determined as E_1 and E_2, respectively.

$$Pt/Ag/AgI/P(I_2)_\alpha \qquad (1)$$

$$Pt/Ag/AgI/P(I_2)_\beta \qquad (2)$$

$$(+)Pt/Ag/AgI/P(I_2)_\alpha/P(I_2)_\beta/AgI/Ag/Pt(-) \qquad (3)$$

$P(I_2)_\alpha$ and $P(I_2)_\beta$ denotes organic complexes of iodine content α and β.

Consider a virtual electrolysis resulting from the passage of 2 moles of electrons through cell(3). Analysis of the transport processes in the cell leads to the following expression,

$$(t_{el}/\delta)P(I_2)_\alpha + (t_{el}/\delta)P(I_2)_\beta = (t_{el}/\delta)P(I_2)_{\alpha-\delta} + (t_{el}/\delta)P(I_2)_{\beta+\delta}$$

where t_{el} is the electron transport number and δ is the change in iodine content. If t_{el} is unity, a mole of I_2 is transferred from $P(I_2)_\alpha$ to $P(I_2)_\beta$ and the corresponding free energy is given by,

$$\Delta G = -2FE_{el}$$

where $E_{el} = E_2 - E_1$, for $\beta > \alpha$.

If $t_{el} = 0$, no iodine is transferred and the Emf is zero since no free energy change occurs. In this case, we are merely transporting AgI from the right side to the left side of the cell. Thus, the magnitude of the observed Emf will depend on the ratio of electronic to ionic transport in the organic complex. It readily follows that the experimental voltage measured for cell(3), E_{exp}, is related to E_{el}, which would be observed if t_{el} equaled one, by the following expression,

$$E_{exp}/E_{el} = t_{el} \qquad (A)$$

We have used this technique on the I_2 complexes of aniline black, cyclized-polyacrylonitrile and 2-polyvinylpyridine. The results are presented in Table (9).

Table 9. Comparison of the experimental voltage, E_{exp}, and the calculated voltage E_{el}, for the I_2 complexes of AB, C-PAN and 2-PVP.

	comp.	E^*(v)	E_{el}	E_{exp}
AB-I_2				
	2.6	.684	10mv	11.0mv
	1.7	.674		
C-PAN-I_2				
	0.5	.648	40mv	42.0mv
	0.9	.688		
2-PVP-I_2				
	1.4	.648	25mv	26.1mv
	2.0	.673		

---

* voltages of individual cells (1) or (2).

The fact that the value of E_{exp} is very close to the value of E_{el} in each case is good evidence that conduction in these complexes is primarily electronic. The fact that E_{exp} is slightly higher than E_{el} must be due to experimental error since t_{el} in equation (A) cannot be greater than one.

APPENDIX A

Infrared spectra of paracyanogen and aniline black

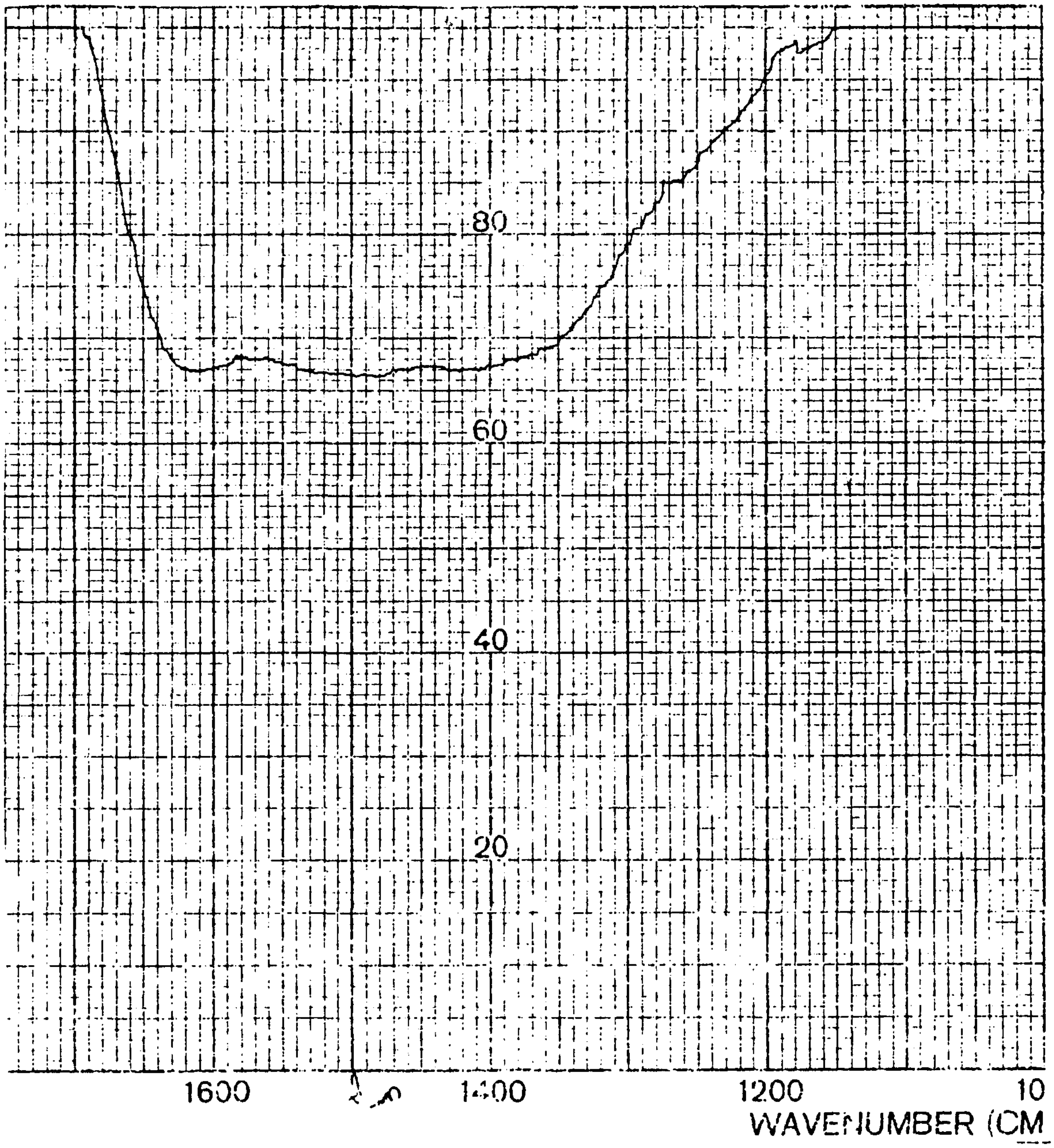


Figure 31. Infrared spectrum of paracyanogen

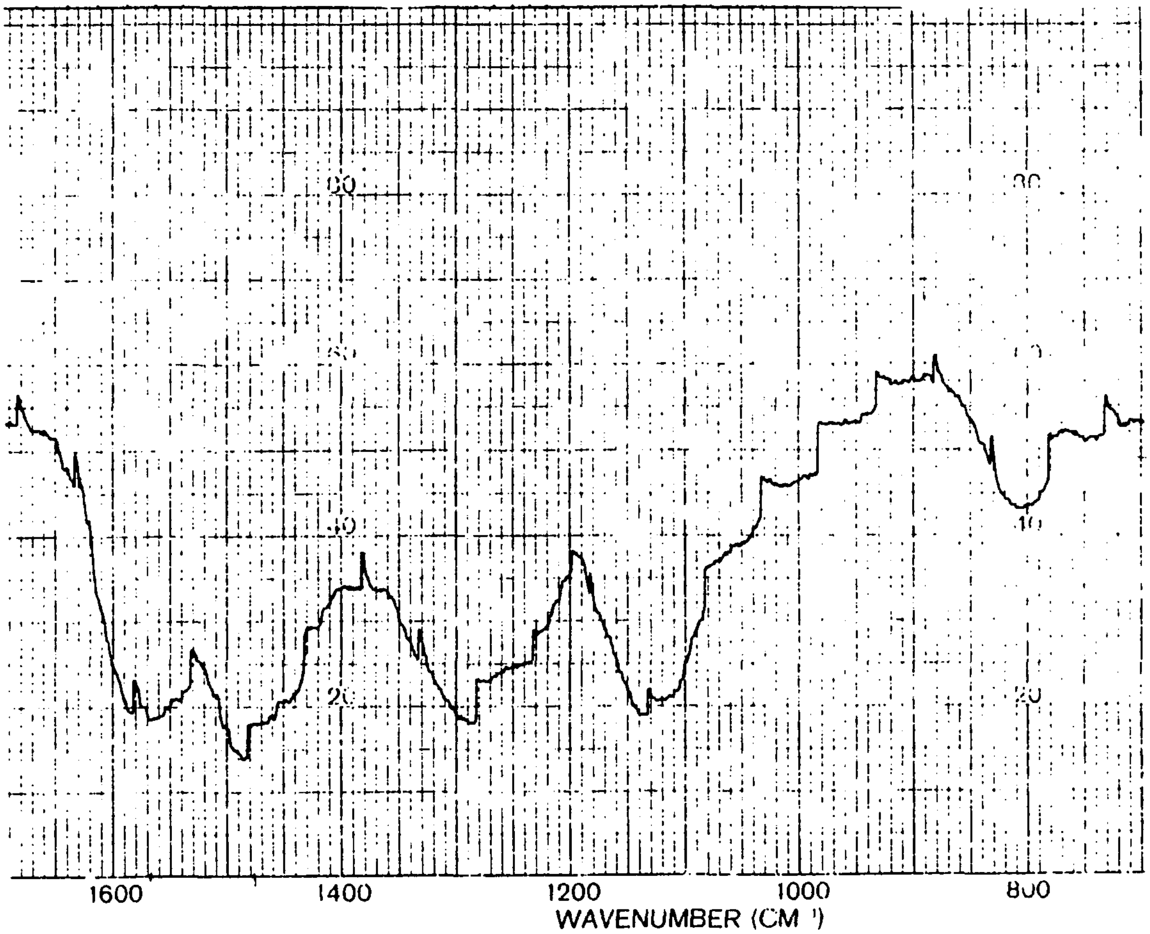


Figure 32. Infrared spectrum of aniline black

APPENDIX B

Emf and conductivity data

Table 10. Emf and conductivity data on aniline black-I_2

Comp.*	Emf(v)	$\sigma(\text{ohm.cm})^{-1}$
0.0	----	$1.3\text{x}10^{-4}$
0.20	.562	-----
0.50	.634	$4.0\text{x}10^{-2}$
0.80	.649	-----
1.0	.658	$2.4\text{x}10^{-2}$
1.5	.666	$2.8\text{x}10^{-2}$
1.7	.674	-----
2.0	.673	$3.5\text{x}10^{-2}$
2.2	.681	-----
2.5	.683	$5.9\text{x}10^{-3}$
2.6	.686	-----
3.0	.680	$4.0\text{x}10^{-3}$
3.2	.686	-----
3.5	.679	$2.2\text{x}10^{-3}$
3.8	.686	-----
4.0	----	$2.4\text{x}10^{-3}$

---

* mole ratio of I_2 to monomer.

----- broken pellet.

Table 11. Emf and conductivity data on aniline black-Br_2

Comp.*	Emf(v)	σ(ohm.cm)$^{-1}$
0.0	-----	1.3x10^{-4}
0.25	.113	----
0.30	.251	7.1x10^{-5}
0.55	.479	8.6x10^{-5}
0.70	.624	5.3x10^{-5}
0.90	.841	4.3x10^{-5}
1.0	.892	3.3x10^{-5}
1.2	.892	2.7x10^{-5}
1.4	.888	5.9x10^{-6}
1.5	.901	2.5x10^{-5}
1.9	.903	1.2x10^{-5}
2.1	.897	8.8x10^{-6}
2.3	.893	9.5x10^{-6}
3.1	.913	1.4x10^{-5}
3.7	.924	2.3x10^{-5}

---

* mole ratio of I_2 to monomer

Table 12. Emf and conductivity data on anthracene-I_2

Comp.*	Emf(v)	$\sigma(\text{ohm.cm})^{-1}$
0.0	----	----
0.20	.629	3.5×10^{-6}
0.40	.637	1.0×10^{-5}
0.60	.641	2.9×10^{-5}
0.80	.650	2.5×10^{-5}
1.0	.667	5.0×10^{-5}
1.2	.670	1.3×10^{-4}
1.4	.678	2.0×10^{-4}
1.6	.678	1.4×10^{-4}
2.0	.682	1.2×10^{-4}
2.4	.681	3.0×10^{-4}

* mole ratio of I_2 to compound.

Table 13. Emf and conductivity data on thianthrene-I_2

Comp.*	Emf(v)	$\sigma(\text{ohm.cm})^{-1}$
0.0	----	----
0.20	.681	1.0×10^{-6}
0.40	.682	----
0.60	.681	1.0×10^{-5}
0.80	.683	1.0×10^{-5}
1.0	.682	1.5×10^{-5}
1.2	.680	4.0×10^{-5}
1.4	.681	2.0×10^{-5}

---

* mole ratio of I_2 to compound.

Table 14. Emf and conductivity data on phenazine-I_2

Comp.*	Emf(v)	$\sigma(\text{ohm.cm})^{-1}$
0.20	.583	$4.0\text{x}10^{-7}$
0.40	.586	$5.0\text{x}10^{-7}$
0.60	.580	$3.0\text{x}10^{-7}$
0.80	.580	$4.2\text{x}10^{-7}$
1.0	.626	$5.3\text{x}10^{-7}$
1.2	.665	$1.2\text{x}10^{-6}$
1.4	.672	$5.0\text{x}10^{-6}$
1.6	-----	$3.1\text{x}10^{-6}$
2.0	.675	$2.0\text{x}10^{-6}$

Table 15. Emf and conductivity data on 2-PVP-Br_2

Comp.	Emf(v)	$\sigma(\text{ohm.cm})^{-1}$
0.23	.00352	$8.6\text{x}10^{-8}$
0.43	.00260	$3.6\text{x}10^{-8}$
0.63	.269	$6.7\text{x}10^{-9}$
0.87	.461	$3.0\text{x}10^{-7}$
1.1	.802	$1.6\text{x}10^{-7}$
1.5	.825	$9.1\text{x}10^{-6}$
1.9	.952	$4.8\text{x}10^{-5}$

* mole ratio of halogen to monomer

Table 16. Emf and conductivity data on phenothiazine-I_2

Comp.*	Emf(v)	$\sigma(\text{ohm.cm})^{-1}$
0.30	.603	2.0×10^{-4}
0.50	.600	3.0×10^{-3}
0.70	.605	4.4×10^{-2}
1.0	.602	5.2×10^{-2}
1.2	.607	-----
1.4	.617	-----
1.5	.636	8.4×10^{-2}
2.0	.650	3.4×10^{-2}
2.5	.648	1.2×10^{-3}
3.0	.649	5.5×10^{-6}
3.5	.648	3.2×10^{-6}
8.5	.680	----

Table 17. Emf and conductivity data on 1,10-phenanthroline-I_2

Comp.*	Emf(v)	$\sigma(\text{ohm.cm})^{-1}$
0.20	.098	2.0×10^{-7}
0.40	.469	9.0×10^{-7}
0.60	.569	2.0×10^{-5}
0.80	.570	-----
1.0	.605	2.5×10^{-5}
1.2	.616	4.5×10^{-5}
1.4	.628	2.5×10^{-5}
1.8	.654	5.0×10^{-5}
2.0	.669	7.5×10^{-5}
2.5	.666	5.7×10^{-5}
3.0	.677	2.5×10^{-5}
3.5	.680	2.0×10^{-5}
3.8	.679	----

* mole ratio of I_2 to compound.

Table 18. Emf and conductivity data on phenanthridine-I_2

Comp.*	Emf(V)	$\sigma(\text{ohm.cm})^{-1}$
0.20	.533	2.0×10^{-7}
0.40	.567	2.0×10^{-7}
0.60	.570	1.0×10^{-6}
0.80	.580	2.0×10^{-6}
1.0	.591	7.0×10^{-6}
1.2	.605	1.0×10^{-5}
1.4	.620	6.3×10^{-6}
1.7	.632	-------
2.0	.645	3.2×10^{-5}
2.5	.672	1.3×10^{-5}
3.0	.674	1.0×10^{-5}
3.6	.673	3.1×10^{-6}

---

* mole ratio of I_2 to compound.

Table 19. Emf data and conductivity data on c-PAN-Br_2

Comp.*	Emf(v)	$\sigma(\text{ohm.cm})^{-1}$
0.22	.00187	------
0.30	.00650	------
0.50	.653	1.1×10^{-5}
0.61	.795	-----
0.76	.899	5.0×10^{-5}
0.86	.920	-----
1.2	.951	5.3×10^{-5}
1.6	.939	7.1×10^{-5}
2.8	.952	3.9×10^{-6}

Table 20. Emf and conductivity data on benzotriazole-I_2

Comp.*	Emf(v)	$\sigma(\text{ohm.cm})^{-1}$
0.20	.635	2.8×10^{-5}
0.40	.645	5.1×10^{-5}
0.60	.676	5.4×10^{-5}
0.80	.678	-----**
1.0	.681	-----
1.2	.679	-----
1.4	.680	-----
1.6	.680	-----
2.0	----	-----

* mole ratio of halogen to monomer

** substance is mushy.

Table 21. Emf and conductivity data on benzimidazole-I_2

Comp.*	Emf(v)	$\sigma(\mathrm{ohm.cm})^{-1}$
0.20	.078	-----
0.40	.074	1.0×10^{-6}
0.60	.151	4.0×10^{-6}
0.80	.610	8.6×10^{-6}
1.0	.637	1.0×10^{-5}
1.2	.647	-----
1.4	.615	6.5×10^{-6}
1.6	.646	----
1.8	.670	----
2.0	.683	----
2.2	.682	----

* mole ratio of I_2 to compound.

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