

ELECTRICAL PROPERTIES OF IODINE COMPLEXES OF ASPHALTENES

Gustave A. Sill and Teh Fu Yen

Mellon Institute
Pittsburgh, Pennsylvania 15213

INTRODUCTION

Polynuclear aromatic hydrocarbons generally form charge-transfer complexes with halogens. Some of the fused aromatic hydrocarbons, e.g., perylene, violanthrene, yield solid complexes exhibiting extremely good semiconduction (1,2,3) while others, e.g., coronene, show only fair to poor semiconduction (4). A number of charge-transfer complexes of aromatic containing polymers have been investigated for possible differences in electrical properties (5,6,30).

A polymeric dielectric may be converted to a polymeric semiconductor by increasing the aromaticity of the insulator, followed by complex formation with a halogen (7,8). The increase in aromaticity can be effected by radiation--e.g., cyclization of polyethylene and followed by dehydrogenation (7); or by heat--e.g., pyrolysis or graphitization to a pyropolymer (8). The resulting products when treated with iodine exhibit a wide range of interesting electrical properties.

From a structural standpoint asphaltene (9) are considered to consist of two-dimensioned fabrics of condensed aromatic rings, intermingled with short aliphatic chains and fused naphthenic ring systems (10). X-ray diffraction (11,12) and ESR investigations (13) have indicated that these aromatic systems tend to form stacks of graphite-like layers surrounded by a disorganized zig-zag chain structure of saturated carbons. Morphologically they may be considered as a highly associated "multipolymer" (14), the

molecular weight of which can vary from a few thousand (unit or particle weight) to a few million (micelle weight) (15). The aromatic centers, roughly 15Å in diameter, are considered to be pericondensed (23,18). It has been demonstrated that asphaltics can form charge-transfer complexes, due to the presence of such aromatic systems (20).

Most polynuclear aromatic compounds form well defined crystals, the iodine complexes of which are stable and stoichiometric in composition. Asphaltics are mesomorphic (17) owing to the random distribution and isotropic orientation of the structural units, and it is to be anticipated, therefore, that the conduction mechanism will be different from that of the crystalline environment (due to diffusion and phonon processes) (16). Since there is a difference in the conduction mechanism between crystalline and amorphous aromatics, one would like to know whether the mesomorphic nature of asphaltics would retard or inhibit the conductivity, and if so to what extent.

The aims of this research were two-fold. The first was simply to observe where asphaltenes fall in the conductivity range and to determine the extent to which conductivity can be enhanced by iodine complex formation. The second was a more general study of the electrical properties of asphaltics as another approach to a better understanding of their structure. To the authors' best knowledge, there is no published work on the electrical characteristics of these materials. Iodine may be visualized as a tracer or indicator for condensed aromatic systems, even when buried in a matrix of paraffinic or cycloparaffinic material. It was thought, therefore, that iodine complex formation and its effect

on the overall electrical properties of the asphaltene might yield independent information of the size and distribution of the aromatic centers in these multipolymers.

EXPERIMENTAL

Resistance Measurements

A General Radio type 1230A electrometer was used for specimens with resistance less than 10^{12} ohms (ambient temperature), and a Cary model 31 electrometer was used for specimens of higher resistance. In each case a glass vessel equipped with a ball joint and appropriate electrostatic shielding was coupled to the head of the electrometer (Fig. 1). Each specimen (approximately $1 \times 0.5 \times 0.1$ cm) was pelleted with a Beckman KBr press at 7.09×10^3 kg/cm² between two pieces of 52 mesh platinum screen. The pellet was degassed for eight hours and the electrical measurements made in a vacuum of 5×10^{-4} Torr. Using the high resistance leak method, a standard resistor served as calibrating reference (21); data were taken under conditions of both falling and rising temperature, a minimum of 30 minutes being allowed for equilibration at 10° levels. Upon completion of the temperature dependence measurements, the physical dimensions of the specimen block were obtained with a travelling microscope (10X) with an x,y micrometer attachment (0.0001 cm precision).

Preparation of Sample

The asphaltene sample was prepared by our standard procedure (9). Two native asphaltenes were investigated, one from the Boscan crude oil from Venezuela (Sample VY), the other from the Baxterville crude from

Mississippi (Sample GS). Stock solutions in benzene of iodine and of the individual asphaltenes were made up in fixed concentration and samples of varied composition prepared by mixing appropriate quantities of these stock solutions at room temperature and lyophilizing at reduced pressure to yield powdered solids with a homogeneous iodine distribution. These samples were analyzed before and after the electrical measurements for %I by ignition in oxygen, reduction with hydrazine sulfate, and potentiometric titration of the resulting iodide with AgNO_3 using a Beckman model K automatic titrator. Usually there was no observable loss of free iodine during electrical measurements; 10-15% loss of iodine was found after degassing. The iodine values used in the present work are those values obtained after completion of the electrical measurements for the entire specimen.

Treatment of Data

The resistance values along with the corresponding temperature data and dimensions of the specimen were key punched on IBM cards and evaluated on an IBM 7090-1401 digital computer system. Given A, the area of the cross section, and L, the length of the specimen, the resistivity, ρ , can be evaluated from the resistance, R, as follows: $\rho = AR/L$. The temperature dependence of the resistivity is then evaluated by the relationship:

$$\rho_T = \rho_0 \exp (\epsilon/2kT),$$

where k is Boltzman's constant, ϵ is the energy gap in eV and ρ_0 is the resistivity extrapolated to $\frac{1}{T} = 0$. By use of a California Computer Products 30-in. plotter (300 steps; 1/500-in. per step) the temperature dependence data were fitted to straight lines (Fig. 2) as given by the equation

$$\log \rho = \log \rho_0 + \epsilon / (2kT \ln 10)$$

From the digital output, $\rho_{25^\circ\text{C}}$ and ϵ can be obtained. The applied voltage was limited to values under 10 V; in this region Ohm's law was followed.

The temperature range examined was from ambient to 90°C .

There is error involved in any single measurement of resistance, owing to systematic errors in the electrometer; errors also enter in the measurement of the dimensions of the specimen. That the results were not influenced by such systematic errors is evident from the two sets of data for two different preparations of an asphaltene (VY)-iodine complex, as given in Table I. The uncertainties in the per cent iodine and sample size may be judged from the variations in the independent measurements. Despite these variations, the resistivity at 25°C and the energy gap are within ca. 5% of the mean values.

Infrared Analysis

Differential IR spectra were obtained from a scan of an iodine-containing asphaltene versus a reference asphaltene at equal asphaltene concentration in CS_2 (the iodine-containing sample is normalized to 100% asphaltene for purposes of comparison) using a Beckman IR-12 instrument. A control scan of asphaltene in CS_2 solution against itself also was made for each sample.

X-ray Diffraction

A Norelco x-ray diffractometer equipped with a $\text{CuK}\alpha$ radiation source and a geiger tube detector was used to study the asphaltene-iodine system. In order to record the shift of the d-spacing due only to change in mass absorption coefficients, adamantane was added to an asphaltene-iodine complex (24% I) and to the original asphaltene. Strong (111) and (200) reflections due to the adamantane mixed with the VY asphaltene were

found at 5.7 and 4.9Å; for the VY asphaltene-iodine complex shifts were observed to 5.5 and 4.7Å, respectively. The spacing is reproducible to $\pm 0.2\text{\AA}$.

Electron Spin Resonance

ESR spectra were taken with a Varian V-4502 x-brand EPR spectrometer system in conjunction with a 12-inch magnet and a "Fieldial." The relative intensity observed was used as a guide for the spin concentration of the asphaltene (VY)-iodine complexes and native asphaltene (VY) (13).

RESULTS

All asphaltene-iodine samples studied gave repeatable linear relations in the temperature range investigated as shown in Fig. 2. There is no significant deviation from Ohm's law through the range 2.5 to 97 V as indicated by Fig. 3 in the temperature interval 313° to 372°K.

The native asphaltenes (Points 1, Fig. 4) fall generally in the insulator range. Upon the addition of iodine the resistivity falls, a to b, then increases sharply, b to c, and finally drops, c to d, as iodine content rises. Both complexes appear to yield curves of similar shape. The gap energy values for the asphaltene-iodine complexes are plotted versus their iodine contents (Fig. 5). The smallest energy gap measured in each case was $\sim 0.5\text{eV}$, but the absolute minimum is uncertain. These minima (points b) correspond to the sharp transitions of resistivity shown in Fig. 4.

Scanning in the far IR region revealed no C-I stretching frequencies for those iodine complexes for which ρ was determined. However, the differential IR measured in the 700-1200 cm^{-1} did show an additional band at

1080 cm^{-1} (Fig. 6), and freshly prepared asphaltene-iodine complexes in CS_2 also exhibited an enhancement in absorption in the region of 1000 to 1150 cm^{-1} , which is generally ascribed to complex formation.

The x-ray spectrograms in the region $2\theta = 2 - 42^\circ$ of the asphaltene (VI)-iodine system yielded an amorphous pattern with broad halos as shown in Fig. 7. For samples with an iodine content of less than 5 per cent, the 3.5\AA band still appeared as a shoulder. In the meantime a new band was formed at around 8.7\AA . At higher iodine contents ($>10\%$), the 3.5\AA band has apparently disappeared and the 8.7\AA band became clearly visible. There is a general overall decrease of total intensity as %I increases since the iodine itself absorbs an increasingly large fraction of the diffracted x-rays. In the present case, the noise level coupled with the intensity reduction has made the disappearance of the 3.5\AA shoulder difficult to detect.

In general, the ESR spectra obtained from the asphaltene-iodine samples indicated an increase in free radical concentration with increase in iodine content. The increase in relative intensity for an asphaltene (VI)-iodine complex containing 20% I over the corresponding native asphaltene is about 3.8 fold.

DISCUSSION

In all the samples studied, including both native asphaltenes and their iodine adducts, a negative temperature coefficient of resistivity was obtained. The linearity of $\log \rho$ vs. reciprocal T is substantiated by the plots shown in Fig. 2. The resistivity is inversely related to the concentration of the charge carriers (holes and electrons), but the fact that the number of charge-carriers increases exponentially with temperature does not enable a choice to be made between electronic or ionic conduction

mechanisms. However, the voltage dependence for the current at a relatively low electric field is linear, indicating that Ohm's law is valid (Fig. 3). This adherence to Ohm's law supports the belief that the conduction is electronic (19).

The fact that the asphaltene-iodine sample exhibits (Fig. 6) strong enhancement of absorption near 1080 cm^{-1} suggests that an iodine molecule forms a donor-acceptor complex with the aromatic portion of the asphaltenes. It is known that the iodine molecule forms such a charge-transfer complex with benzene and other alkylated benzenes, and that these complexes, in general, exhibit bands from 992 cm^{-1} to 1200 cm^{-1} (24,25). Arguing from analogy, it is plausible that the complex assumes the axial model (model A of Mulliken) while the acceptor molecule is sitting perpendicular to the plane of the aromatics (26). Further, our failure to locate any C-I stretching frequencies in the $400\text{-}600\text{ cm}^{-1}$ region supports the view that iodination of the asphaltene samples did not occur.

Most charge-transfer complexes of iodine with aromatics are crystalline. An exception to this is the violanthrene-iodine system, which x-ray diffraction indicates to be amorphous (2). X-ray results also indicate a low degree of order for the asphaltene-iodine complexes. If the acceptors (I_2) are homogeneously distributed in the host matrix (asphaltene), these systems may be considered analogous to the impurity or valence-controlled semiconductor systems. Disappearance of the 3.5\AA spacing of the (002) band means that the layered structure of asphaltene must have been altered (Fig. 7). The 4.6\AA γ -band, due to the saturated carbon in the structure, did not change in the complexing process.

The new band at 8.7\AA then may be due to the expansion of the aromatic interplanar distance to allow for complexing by the iodine molecule. In the case of the perylene-iodine systems, the spacing found at 10.7\AA was interpreted (5) as the distance between perylene molecules when iodine molecules were sandwiched between the aromatic layers. The present observed value of 8.7\AA can be viewed as the sum of the interplanar distance (5.5\AA) and the iodine length ($4 \times 1.53\text{\AA}$). The picture of these interlinked layers resembles that of an intercalation compound of graphite (Fig. 6).

Referring again to Fig. 4, the room temperature resistivities for the two native asphaltenes are seen to be in the insulator range ($>10^{14}$ Ohm). Upon addition of the iodine, the resistivity decreases about six decades or a million fold. This is essentially the same behavior as that observed for polymeric charge-transfer complexes such as poly(vinylpyridium TCNQ) and its derivatives. These polymeric salts are dependent upon the TCNQ concentration which at best increases the conductivity six decades. Here we have to point out that it is not easy to prepare a polymeric charge-transfer complex with good semiconduction. Slough (5) made a number of polymeric complexes from aromatic-containing polymers, with acceptors such as tetracyanoethylene, chloranil, etc., and found the conductivities of these complexes were not measurably higher than those of the original polymeric donors. These mesomorphic materials may lack the order of the π -systems needed to open a path for charge carriers. More likely, the aromatic systems are too small to form stable charge-transfer complexes.

For pure polynuclear aromatic hydrocarbons, donor-acceptor complexes, especially the iodine complexes (2,3), exhibit increases in conductivity of 12 to 16 decades when compared to the parent hydrocarbon.

The enhancement in conduction by the addition of iodine can be illustrated by comparison of the complexes with a valence controlled semiconductor, a typical example being nickel (II) oxide doped with lithium oxide (22). In Fig. 9 a comparison is made between this system and the aromatic-iodine complexes. The trends in resistivity with the concentration of impurity are quite similar.

Asphaltenes contain fused ring aromatics, the peripheral hydrogens of which are substituted heavily by short chain alkyl groups (23). Owing to the relatively large porportion of methyl groups (20%) and the large average layer diameters ($L_a \sim 15\text{\AA}$), the asphaltic molecule can be viewed as a typical aromatic donor (D); halogens such as iodine can behave as an acceptor (A). Through charge-transfer by overlapping of the molecular orbitals of the two moieties, the dative structure (D^+A^-) should result in which asphaltene is the positive ion.

Fig. 4 clearly indicates that the increase of conductivity follows two different paths, the first a to b, is the path followed for small increments of iodine, terminating at b with fixed composition (VY, 15.5%; GS, 10.0%); the other, c to d, is for higher percentages of iodine. Line bc represents the transition state. The curve cd may be extrapolated to a resistivity value of 5.8×10^6 ohm-cm, corresponding to that for pure I_2 (27). The same results were found (23) for violanthrene-iodine system with a minimum corresponding to a 2:1 iodine-violanthrene molar ratio for the complex. Apparently b in Fig. 4 corresponds to a stoichiometric ratio of

a stable complex where conductivity is at a maximum. It is assumed that for iodine contents less than that corresponding to the minimum the amount is insufficient to form the complex. At bc the resistivity is highly sensitive to the number of iodine molecules. When c is passed, excess iodine acts as an impurity in the stoichiometric complex. The transition at b is also reflected by the energy gap plot in Fig. 5. The same fixed composition (VY, 15.5%; GS, 10.0%) is obtained in either plot. At these minima, the energy gap value is ca. 0.5eV suggesting favorable conditions for conduction.

A number of aromatic-iodine complexes have been reported (2,3) and from their phase diagrams (either temperature or density vs. mole per cent of iodine) the complexes are found to be stoichiometric (29). For example perylene-iodine can have 2:3, or 1:3; pyranthrene-iodine is 1:2; violanthrene-iodine is 1:2; pyrene-iodine is 1:2. In all cases for peri-type aromatics the ratio of I_2 to aromatic is higher than unity. Since the diameter of the aromatic system in asphaltics falls in the range 8-15Å (12), the system would be comparable in size to violanthrene or perylene.

Assuming the composition at the transition (VY, 15.5%; GS, 10.0%) is stoichiometric, then for any given ratio of aromatic and iodine, the molecular weight of the asphaltene can be calculated. We have taken the liberty of calculating this weight for VY and GS asphaltenes based on sample ratios of I_2 :asphaltene of 2:1, 3:2 and 1:1. Since all layers contain the aromatic moieties and the sample is free of wax contamination, the molecular weight obtained is that of the unit sheet weight (weight of an average sheet containing both aromatic and saturated carbon atoms). These

values are listed in Table II. Next, provided aromaticity is also known (f_a for VY, 0.35; for GS, 0.51), the disk weight (weight of aromatic carbon atoms in a single sheet) and the layer diameter also can be approximated. These values are also listed in Table II. Experimental values for the VY and GS asphaltenes from a previous paper (15) are included. It is of interest that the unit weight values obtained from GPC, mass spectrometry, x-ray diffraction and the electron microscopic measurements agree in general magnitude with the weights obtained by the present method. Deviations of the disk weight of GS calculated from resistivity from that obtained by mass spectrometry may be due to the polydispersity of the GS asphaltene (e.g., M_w/M_n for VY is 1.27; for GS, 1.74 (15)).

From Table II, the asphaltene-iodine complexes formed appear to correspond to an I_2 :asphaltene ratio of about 1.5:1. This composition is shown in model A of Fig. 8. Actually aromatic disks of the size present in asphaltenes should be able to accommodate more than one molecule of iodine.

Finally the increase in the free spins, as demonstrated by the EPR spectra, may be indicative of an increase in carrier concentration (2). The nature of these charge carriers will have a strong bearing on the conduction mechanism and will be the subject of a separate investigation.

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- (14) The word "multipolymer" refers to a polymer with a very large number of different building blocks, say ca. 100. Simpler structures can be referred to by more specific terms, as for example, "copolymer" (2 blocks) or "terpolymer" (3 blocks).

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TABLE I

Resistivity and Gap Energy Measurements
 from Asphaltene (VI)-Iodine Complexes

Sample No. ^a	Iodine	A. (cm)	L. (cm)	$\rho_{25^\circ\text{C}} \times 10^{-12}$ (ohm-cm)	ϵ (eV)
23	17.1	1.262 ₈	0.099 ₄	1.75 ₆	1.74 ₂
25	16.8	1.266 ₄	0.103 ₃	1.61 ₄	1.82 ₅
27	17.2	1.259 ₂	0.119 ₂	1.77 ₆	2.00 ₇
24	15.8	1.267 ₅	0.102 ₇	2.15 ₅	1.95 ₀
28	15.7	1.276 ₆	0.051 ₉	2.06 ₃	1.75 ₃
29	15.8	1.147 ₉	0.048 ₀	2.25 ₄	1.81 ₄

(a) Same numbers used in curves of Fig. 4; Sample Nos. 23, 25, and 27 are from one preparation; Sample Nos. 24, 28, and 29 are from another preparation.

TABLE II

Determination of the Molecular Weight and Aromatic Sheet Size
of Native Asphaltenes by Various Physical Methods

Physical Methods	Unit Weight ^a		Disk Weight ^b		Layer Diameter (Å) ^c	
	VY	GS	VY	GS	VY	GS
<u>Resistivity Calculation</u>						
I ₂ :Asphaltene						
2:1	2770 ^d	4570	969 ^e	2330	14.6 ^f	22.6
3:2	2080	3430	727	1750	12.6	19.5
1:1	1380	2290	484	1170	10.3	16.0
GPC (M _n) ^{g,h}	3160	3780	-	-	-	-
<u>Mass Spectrometry^h</u>						
(Mean)	-	-	634	543	-	-
<u>X-ray Diffraction^h</u>						
(L _a)	-	-	-	-	11.9	17.0
<u>Electron Microscope^{h,i}</u>						
(Particle weight)	3440	4030	-	-	-	-

(a) Weight of a single sheet containing both aromatic and saturated carbon atoms (see J. P. Dickie and T. F. Yen, A. C. S., Div. Petroleum Chem., Preprints, Miami meeting, April, 1967).

(b) Weight of aromatic carbon atoms in a single sheet.

(c) Diameter of aromatic cluster; see T. F. Yen, J. G. Erdman, and S. S. Pollack, Anal. Chem., 33, 1587 (1961).

(d) Calculated based on $254t^{-1}R$ (100- t) where R is the ratio of I₂ to asphaltene and t is the %I corresponding to the transition in resistivity and gap energy.

(e) Calculated from $f_a \times$ (unit weight).

(f) $L_a = (2.62 C_A)^{1/2}$, C_A from disk weight without contribution of hydrogens.

(g) From gel permeation chromatography data on the native asphaltene, number average molecular weight.

(h) Experimental data from J. P. Dickie and T. F. Yen, A. C. S., Div. Petroleum Chem., Preprints, Miami meeting, April, 1967.

(i) J. P. Dickie and T. F. Yen, A. C. S., Div. Petroleum Chem., Preprints, 11, 39 (1966).

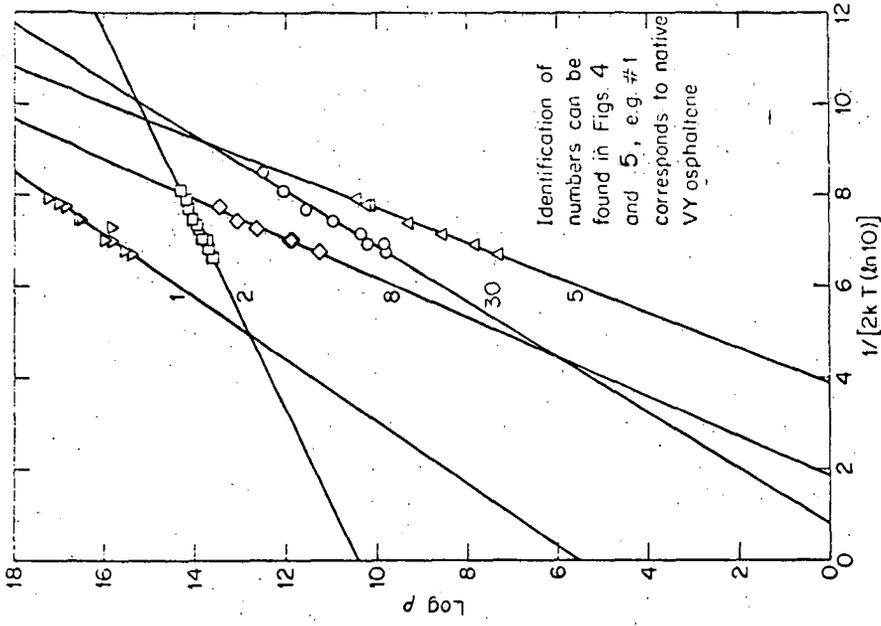


Fig. 2-Temperature Dependence of Resistivity for the Asphaltene-Iodine System.

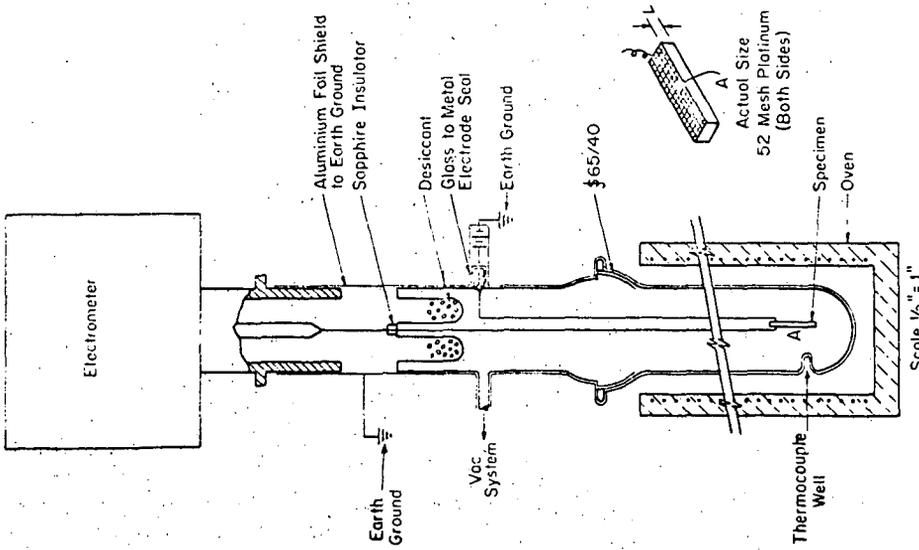


Fig. 1-Apparatus for Resistance Measurement

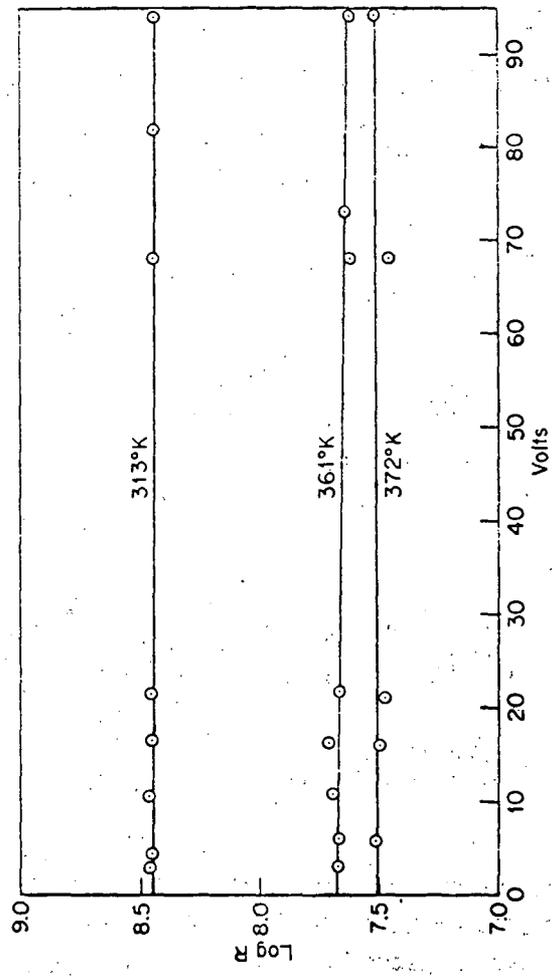


Fig. 3-Voltage Dependence of Resistance for an Asphaltene-Iodine Complex (1% = 11).

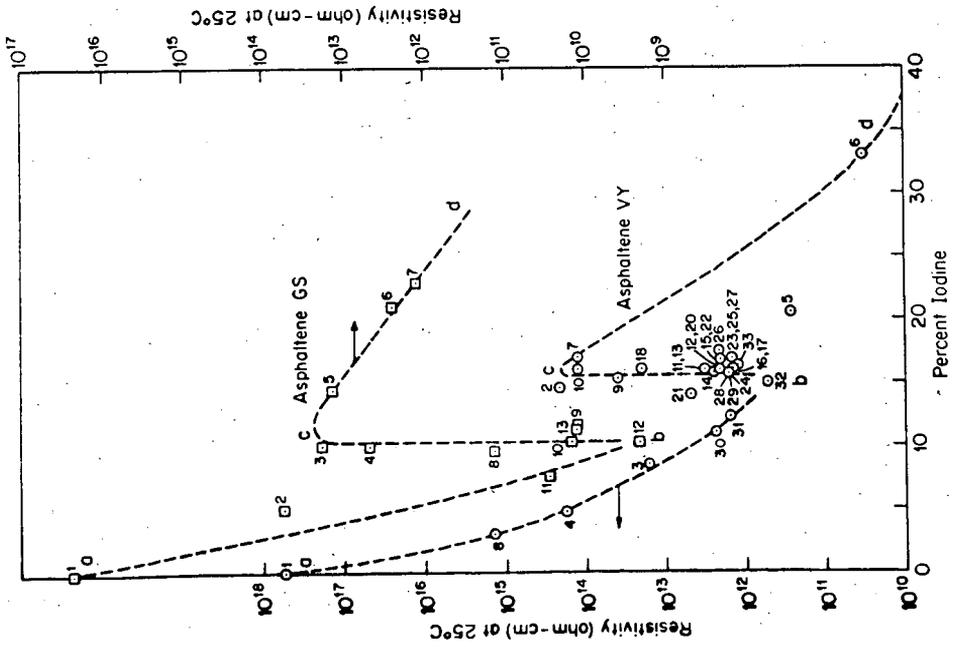


Fig. 4-Resistivity of the Asphaltene-Iodine Complex as a Function of Iodine Content.

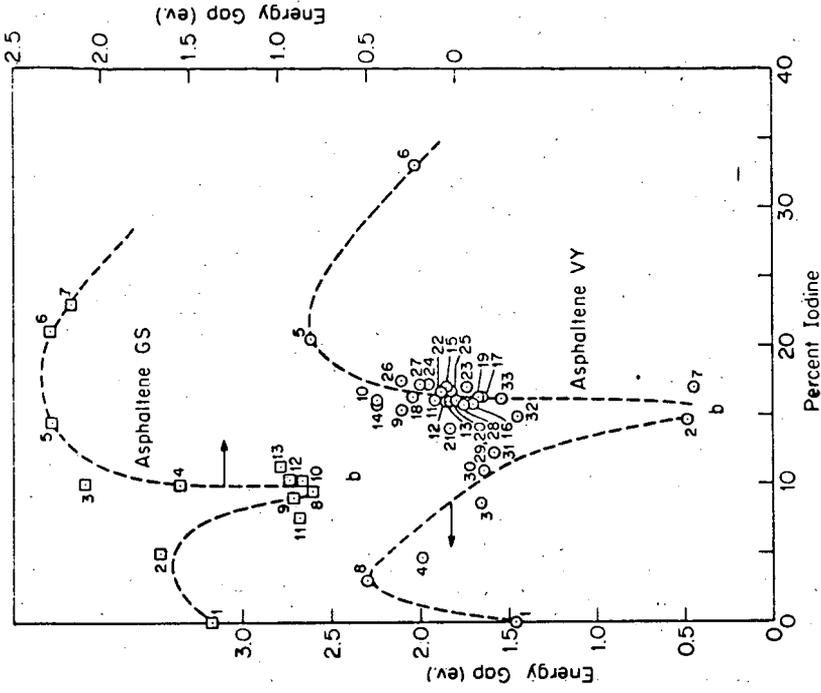


Fig. 5-Gap Energy of the Asphaltene-Iodine Complex as a Function of Iodine Content.

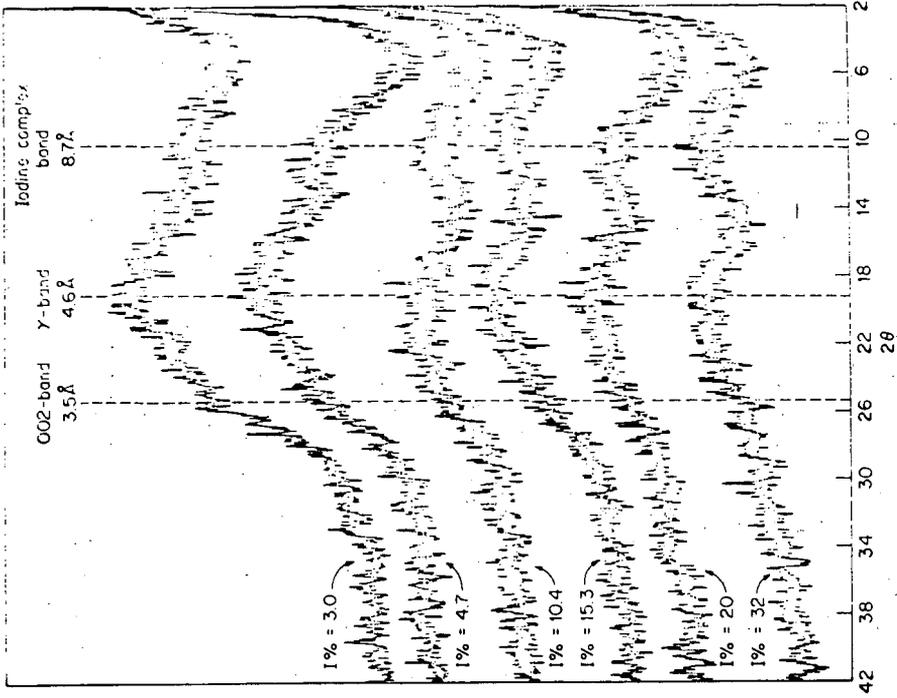


Fig. 7 - X-Ray Patterns of the Asphaltene (VY)-Iodine System

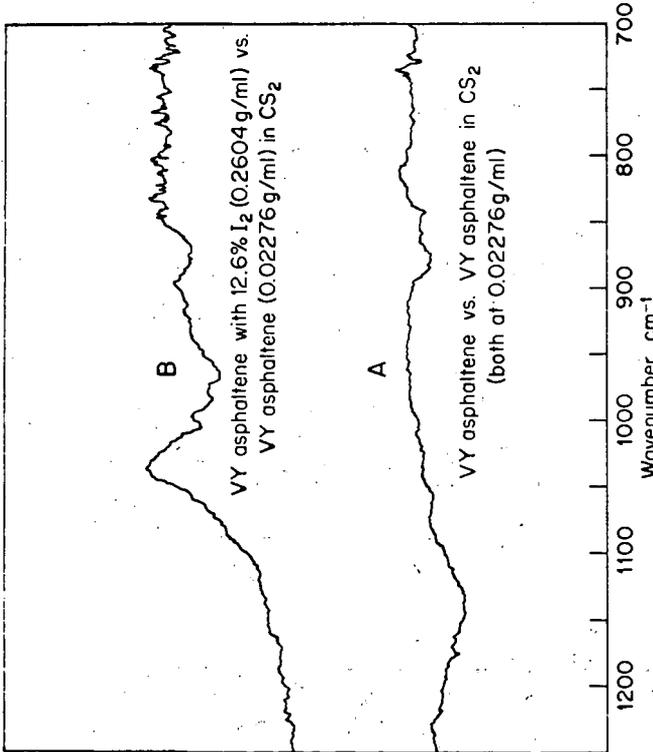


Fig. 6 - Differential Infrared Spectra of Asphaltene-Iodine Complex.

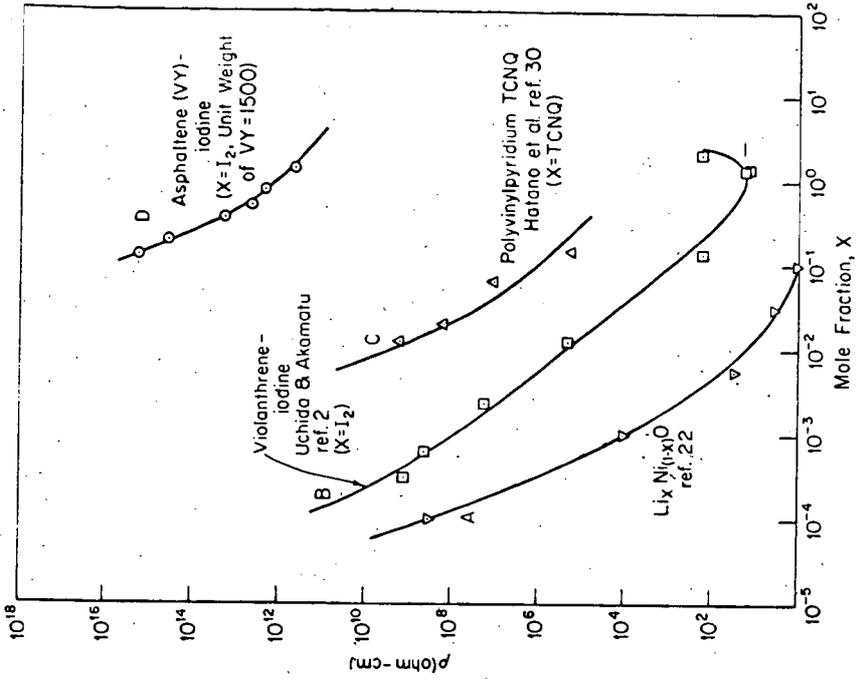


Fig. 9-Aromatic-Iodine Complexes Vs. a Valence Controlled Semiconductor with Resistivity as a Function of Impurity Content.

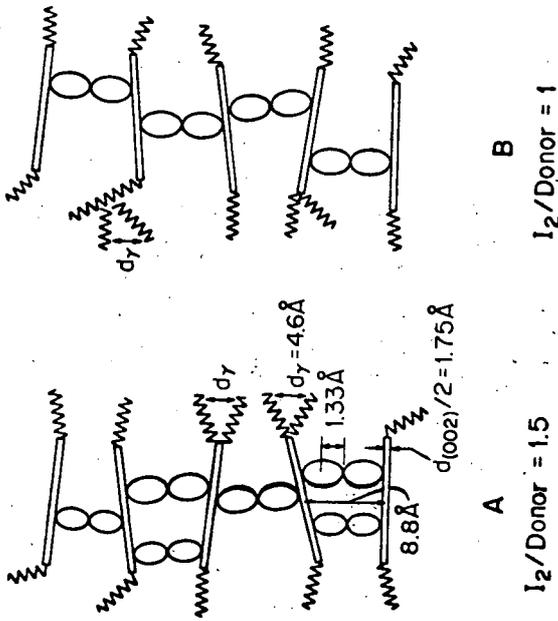


Fig. 8-Proposed Model of Asphaltene-Iodine Complexes
A, 2 Asphaltene $\cdot 3 \text{I}_2$; B, Asphaltene $\cdot \text{I}_2$.

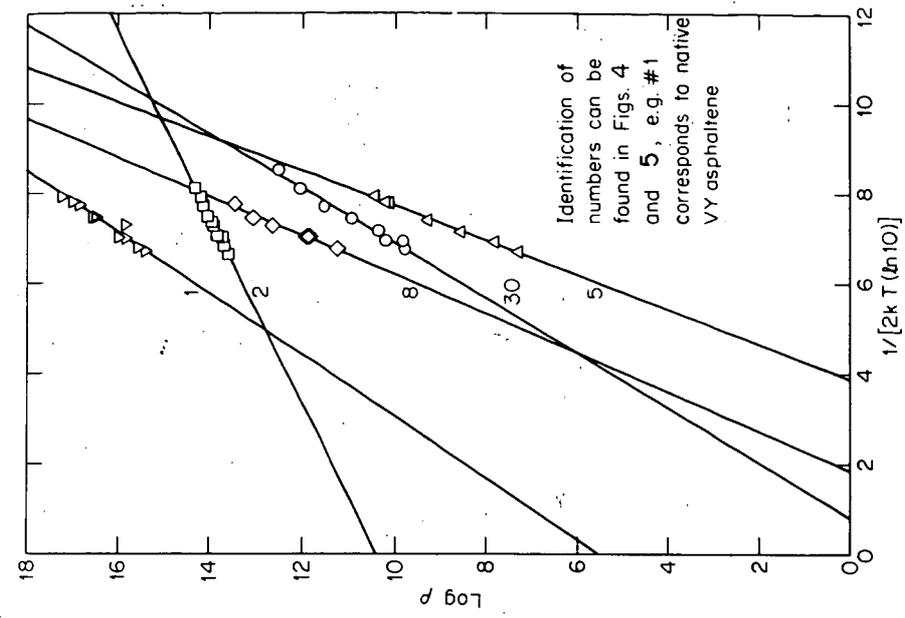


Fig. 2-Temperature Dependence of Resistivity for the Asphaltene-Iodine System.

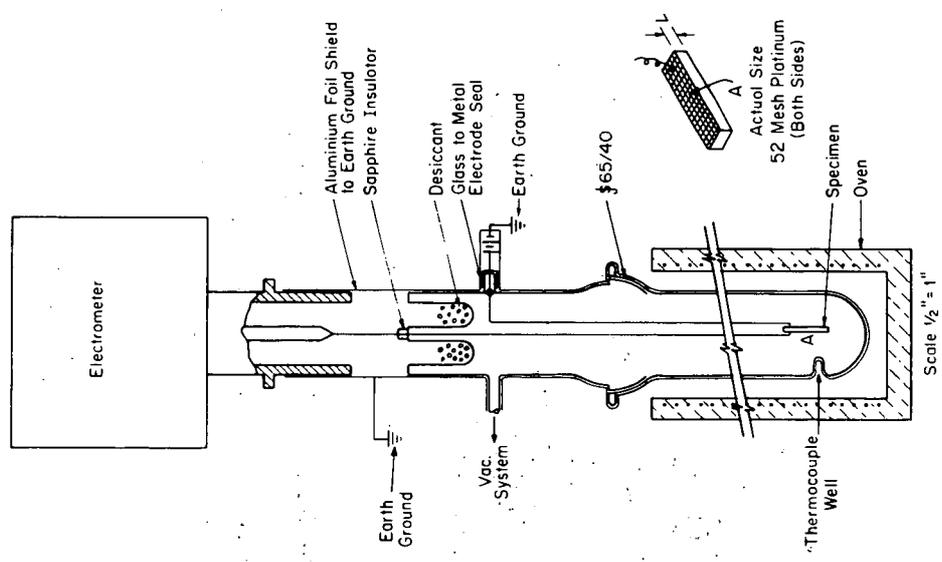


Fig. 1-Apparatus for Resistance Measurement

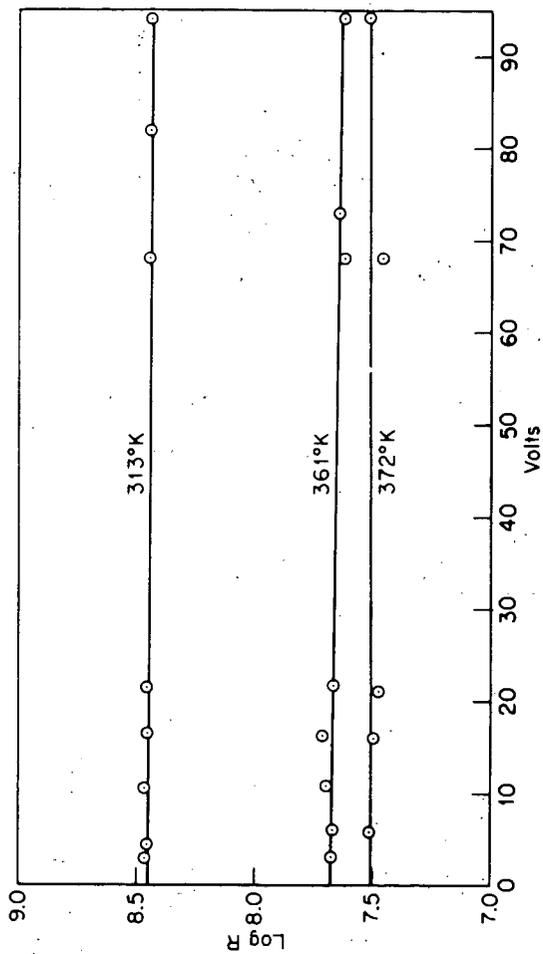


Fig. 3-Voltage Dependence of Resistance for an Asphaltene-Iodine Complex (1% = 11).

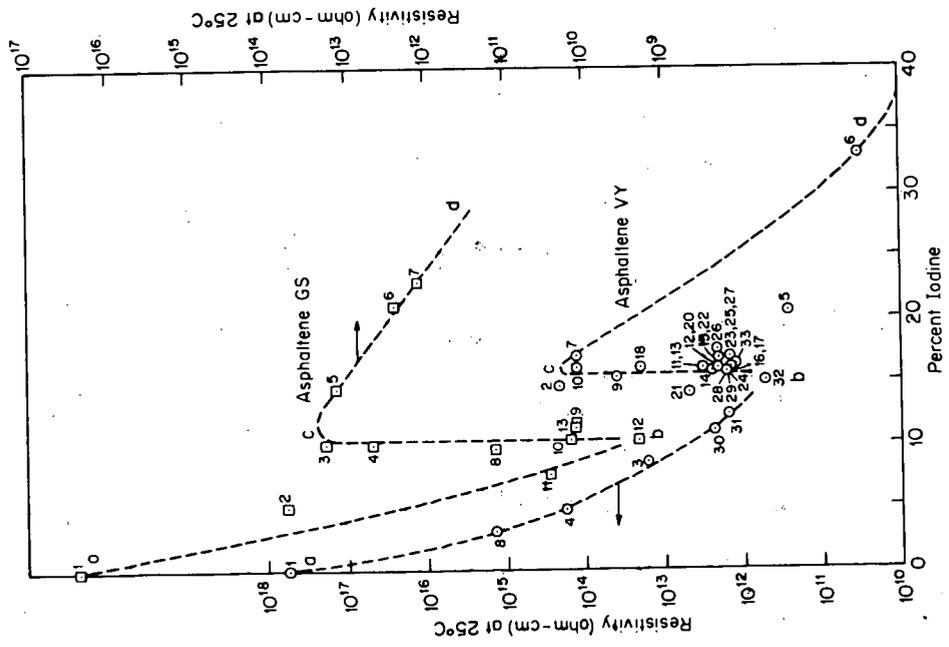


Fig. 4-Resistivity of the Asphaltene-Iodine Complex as a Function of Iodine Content.

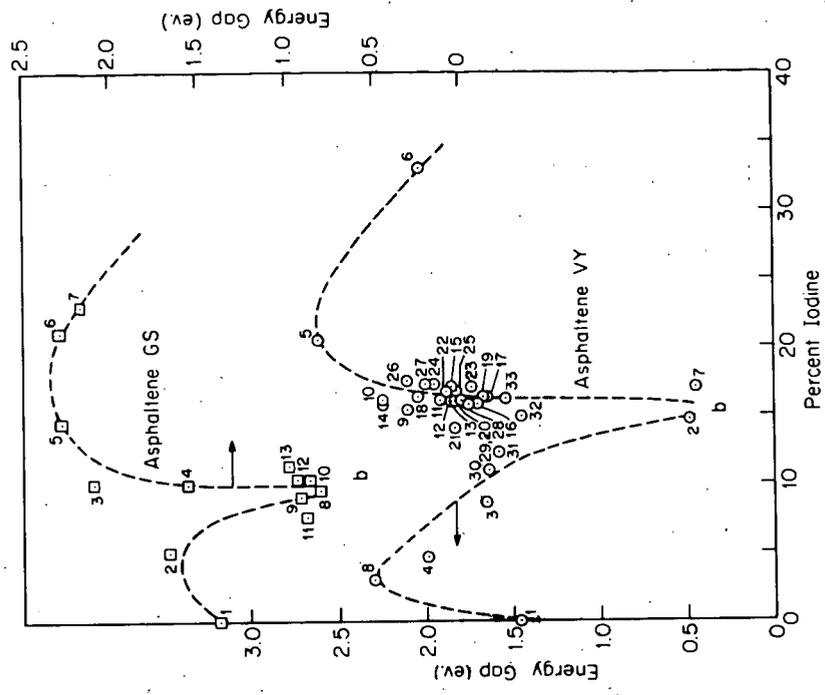


Fig. 5-Gap Energy of the Asphaltene-Iodine Complex as a Function of Iodine Content.

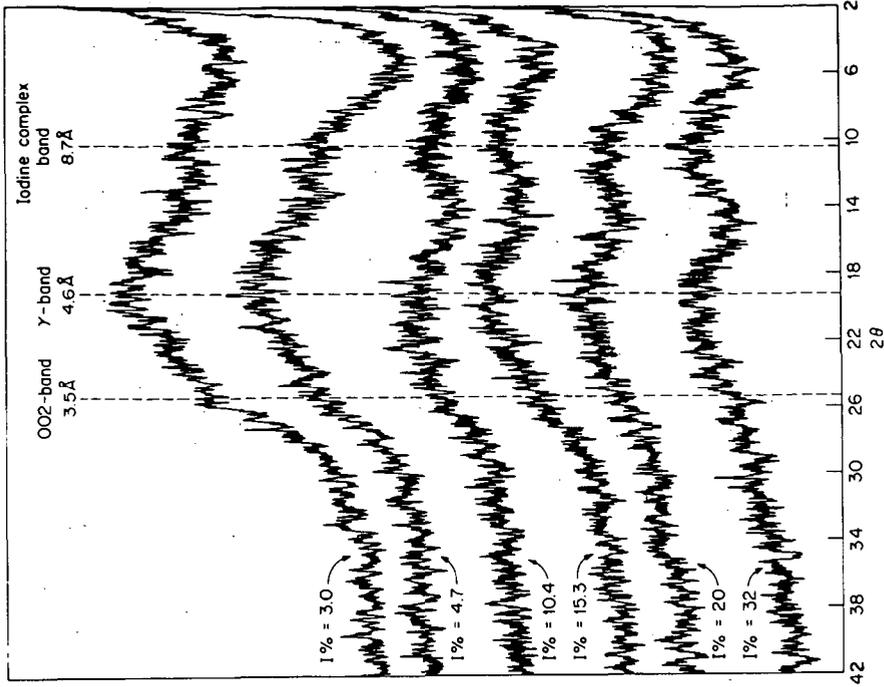


Fig. 7 - X-Ray Patterns of the Asphaltene (VY)-Iodine System

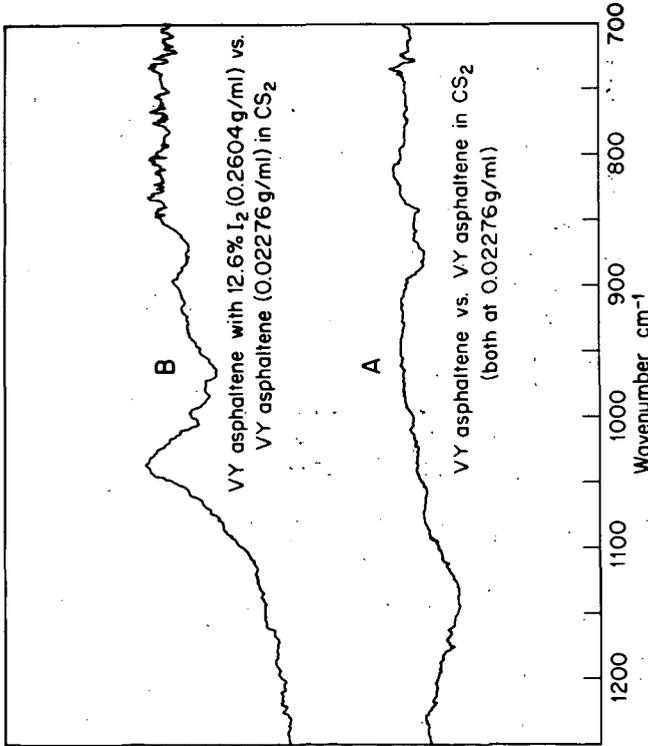


Fig. 6 - Differential Infrared Spectra of Asphaltene-Iodine Complex.

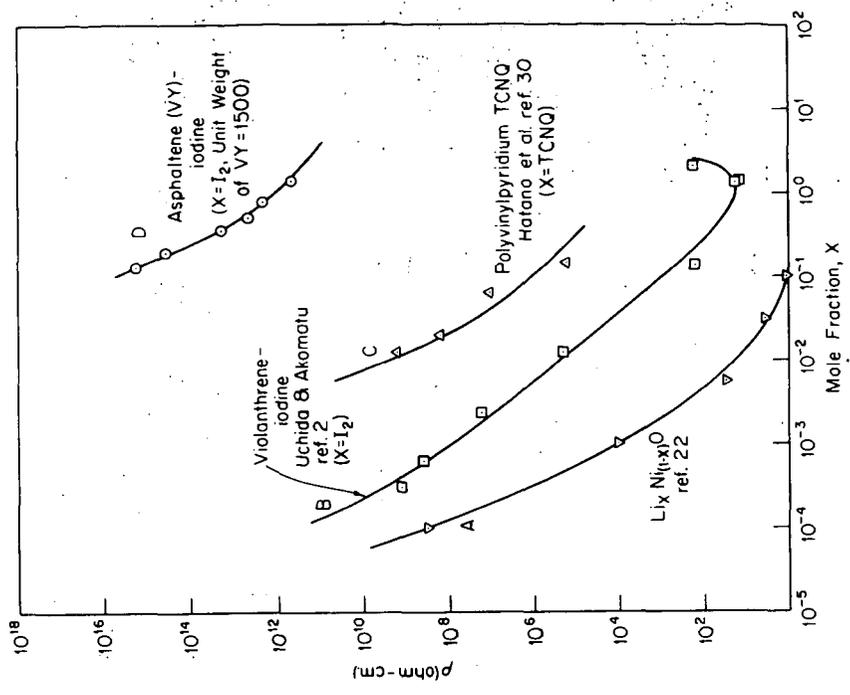


Fig. 9--Aromatic-Iodine Complexes Vs. a Valence Controlled Semi-conductor with Resistivity as a Function of Impurity Content.

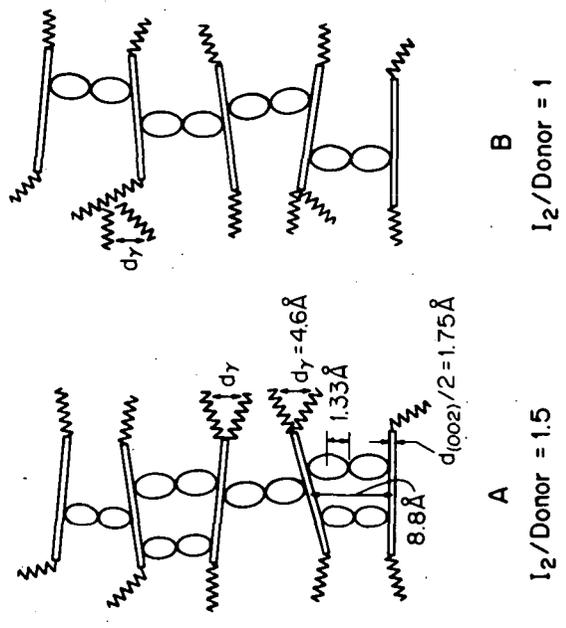


Fig. 8--Proposed Model of Asphaltene-Iodine Complexes
A, 2 Asphaltene $\cdot 3 I_2$; B, Asphaltene $\cdot I_2$.